Comparative Biodiesel Synthesis using Biowaste-based Catalysts

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Certification Page

This is to certify that Isaac Sewanu **BANKOLE** with matriculation number **LCU/PG/1779** carried out this research work titled “Comparative Biodiesel Synthesis using Biowaste-based Catalysts in Southwest Nigeria” in the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo state, for the award of Master Degree (MSc) in Industrial Chemistry and that this has not been previously submitted.

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Dedication

This research work is dedicated to God Almighty and to all Chemistry Educators

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Abstract

Over the last three decades, effort of chemists has been geared towards the search for an ecofriendly fuel as an alternative to fossil fuel. The search light has been beamed at plant seed oil and waste. This study compared the biodiesel synthesis from *Chrysophyllum albidum* using biowaste -based catalysts of African star apple shell and cow bone. The seeds were collected, washed, dried and cracked. The mesocarp (cotyledon) was separated from the shells, cut into pieces, sundried and was mechanically powered. The powder was Soxhlet extracted for oil using mixture of methanol and n-hexane in ratio 50:50mL as solvent. Four catalysts used were pristine African star apple (ASA) seed shell, carbonized waste Cow bone, sulphonated ASA shell and sulphonated cow bone characterized with XRD and FTIR while GC-Ms was used for characterization of the biodiesel. The result shows that the percentage oil extracted from the African star apple seeds with the mixture of n-hexane and chloroform in a ratio 50:50mL was 28.88%. The percentage biodiesel yield using pristine African star apple shell catalyst was 72.90 % while using carbonized cow bone catalyst was 74.60% as the highest catalyst dose of 1g. The biodiesel yield with 1g catalyst dose of sulphonated African star apple shell catalyst was 75.50% while using sulphonated cow bone catalyst was 78.40%. The study concluded that the sulphonated Cow bone catalyst was more effective for the production of biodiesel and that the African star apple seed oil yield is not sufficient for the feedstock of commercial production of biodiesel but can be used for other industrial purposes.

Keywords: African Star Apple, Biowaste, Cow bone, African Star Apple Shell, Biodiesel

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Abbreviation		**Meaning**
ASA	-	African Star Apple
ASASC	-	African Star Apple-Shell Sulphonated Catalyst
ASASO	-	African Star Apple Seed Oil
CBSC	-	Cow Bone Sulphonated Catalyst
CASAS	-	Carbonized Africa Star Apple Shell
CCB (Pristine)	-	Carbonized Animal Bone

Chapter One

Introduction

1.1 Background to the Study

Over the last centuries, fossil-derived fuel has been the bedrock of the global economy and their exploration/exploitation has largely propelled substantial advancement in the human civilization and socioeconomic development. Howbeit, the grievous environmental consequences derived from the use of fossil fuels cannot be over emphasized. For example, the ever-increasing human population and industrialization has necessitated the over dependence of these fuels as the major source of energy, thereby releasing toxic gases like oxides of nitrogen (NOx), sulphur (SOx), carbon COx and particulate matter ($PM_{2.5}$ and PM_{10}) which depletes the ozone layer and an aftermath effect of global warming and climate change. Moreover, the transport of fossil fuels via pipelines in underground systems is often associated with oil spillage which pollute the terrestrial land and aquatic bodies. Notwithstanding, the current increase in the price of crude oil in the world market is an energy insecurity and economic threat to both the developing and underdeveloped economies. Also, the perceived shortage of the product in the next 50 years is another serious concern. Therefore, the quest for green energy sources as sustainable alternative fuels is on the rise[1,2].

Recent progress in scientific innovations holds that biofuels i.e. biomass-derived fuels obtained from algae material, plant- or animal waste is a promising energy source to replace the fossil fuels[3]. Typically, biodiesel, a renewable, biodegradable fuel containing long-chain fatty acids, especially from the alkyl ester group are obtained domestically from vegetable oils, animal fats, or waste materials via a process known as transesterification[4].

Reports have shown that edible oils such as muster oil, sunflower oil, palm oil, *Jatropha curcas*, just to mention a few, have been successfully employed in biodiesel production. But due to the rising challenge of food security across the globe, oils that are suitable for human consumption have been receiving less attention[5,6,7]. Hence, the search for renewable eco-friendly, non-toxic and low carbon emitting biomass-materials that will not threaten human existence is sort for.

An alternative is to shift attention to the use of non-edible seed oil that would provide a sustainable approach[8,9]. African star apple (*Chrysophyllum albidum*) seed oil is an emerging competitor as a promising feedstock for biodiesel production[10,11].

African star apple (*Chrysophyllum albidum*), popularly called "*Udara*" by the Igbos and "*Agbalumo*" by Yoruba natives (the two large ethnic groups from the Southern part of Nigeria). It is a forest tree that belongs to the family of Sapotaceae which comprises more than 500 species. The tree is evergreen with a projecting height up to 40 m high, while the fruit may contain about five non-edible seeds. The dark brown coat when broken, contain white or cream coloured cotyledons. However, the indiscriminate dumping of the seeds after consumption has posed severe environmental challenge of waste disposal, thereby creating breeding ground for harmful organism. This could be minimized if these seeds can be utilized by possible conversion of the waste to wealth without affecting the environment and also serve as industrial feedstock[12,13].

In the biodiesel production process, a catalyst is essential to inhibit the rate of a chemical reaction rate without being consumed by the chemical reaction. Catalysts can be grouped into three: heterogeneous-, homogeneous-, and enzyme catalysts[14,15,16]. Heterogeneous catalysts exist in distinct phase from the reactants and products. They exist in solid state and are not easily soluble in alcohols when used in the production of biodiesel, but can be easily separated from the final product, as well as being reused. In addition, the recovery is easy by filtration and can be reused thereby reducing the cost of catalyst consumption. However, it is constrained by diffusion when a catalyst, alcohol, and oil triple phase system is present during the production of biodiesel[17,18]. Interestingly, researchers have become more interested in the use of heterogeneous acid catalysts produced from biomass waste for the generation of biodiesel in recent years[19,20]. Sulphonated carbon–based catalyst (SCBC) has also been used due to several advantages which include thermal and chemical stability, environmentally-friendly, easy recoverability and simple production schematics[21,22,23]. This implies that activated carbon obtained by thermal treatment of biomass residue is a viable alternative for SCBC due to its large surface area and enhanced porous structure.

The use of sulphonated activated carbon (SAC) in the biodiesel production has also been studied using various agricultural materials like oil palm trunk, but few studies on African star apple (ASA) were available in literature from this part of the world. This process involves the addition of functional sulphonic acid (–SO_3H) groups across the surface of the carbon material and this can be used in the process of esterification and transesterification reactions simultaneously[24,25,26]. In the AC sulphonation process, the –SO_3H groups are attached to the resultant SCBS thereby increasing the total acid density since the total acid density measures the efficiency of the catalytic activity in the esterification process[27,28,29].

Direct sulphonation with fuming sulphuric acid, H_2SO_4, are common ways of generating sulphonated catalyst because they are readily available and are very cheap[30,31]. The effectiveness of using para-toluenesulphonic acid (PTSA) and H_2SO_4 (direct sulphonation) as sulphonated biomass-derived catalysts has been examined. The results showed that direct sulphonation has higher catalytic activity than that of PTSA[32,33]. Based on the aforementioned, direct sulphonation with concentrated sulphuric acid resulted in a higher total acid density in activated carbon, although fuming H_2SO_4 possessed better catalytic performances.

Therefore, the aim of this study is to convert ASA shell waste and cow bone to energy sources with no negative impact on the environment and explore their industrial application. Specifically, the objective is to prepare, characterize and utilize cow bone (animal) and ASA shell sulphonated biowaste catalysts in the biodiesel production.

1.2 Statement of the Problem

Fossil fuels are extremely toxic to different aspects of the environment. Thus, biofuel has been proposed and extensively investigated as potential alternative energy sources. Biodiesel is a biodegradable and more eco-friendly fuel resulting in lower environmental impact if unknowingly discharge to the ecosystem. As a proposed and promising machine and automation fuel, there are several reports on the health and environmental effect of emissions from biodiesel[34,35,36]. Biodiesel has been reported as a promising alternative renewable fuel composed of monoalkylester of fatty acid obtained from either the transesterification of triglycerides or free fatty acids (FFA) with short chain alcohols using a basic or acidic catalyst[37]. The reaction is characterized by side reactions which include triglycerides hydrolysis and saponification which reduces the catalyst efficiency and increase the cost of purification[38,39]. Because of these reactions, feedstock with high FFAs and moisture cannot be transesterified directly via a basic catalyst. Recently, the utilization of environmental-friendly solid catalysts using naturally-sourced materials as catalyst supports have been proposed and researched upon[40,41]. In particular, materials, for example, wastes from plants and animals, were identified as catalyst sources as a result of their efficiencies, availability and low-cost[2].

The homogenous acid catalyst such as H_2SO_4 or HCl do not show measurable susceptibility to FFAs but are sensitive to moisture and difficult to recycle, as well as the need to operate at high temperature, giving rise to serious environmental and corrosion problem[42,43]. More so, other issues including separation of catalyst-product mix, corrosion of equipment, large volume water usage for washing, and contamination of water associated with homogeneous catalyzed reaction are another sets of serious concern[44,45,46]. In the recent field of green chemistry, solid acid catalysts have attracted intense focus for environmentally-friendly catalytic reaction due to the merit of facile separation, pollution-free, and recyclability.

However, other solid acid catalysts such as Amberlyst-15 are costly with lower performance possibly due to the lower acid density and strength when compared with the traditional mineral acids including HCl, H_2SO_4, HNO_3, just to mention a few [47,48].

1.3 Justification of the Study

The development of solid acid catalyst, which may eventually replace sulphuric acid as the catalyst in the production of biodiesel, was sparked by the discovery of sugar catalyst as a carbon-based catalyst. One of the advantages of carbon-based solid catalysts (CBSCs) is that it can be produced from renewable carbon precursor that are inexpensive. Therefore, there is the need to explore other sources of renewable carbon precursors that can serve as a catalyst in the production of biodiesel[49].

Literature shows that larger number of CBSCs from carbon precursor were researched into in the catalytic synthesis of biodiesel[50]. But in developing countries such as Nigeria, only few studies have been attempted in the development of CBSCs from carbon precursors for the production of biodiesel. Larger amount of waste biomass is being produced from agricultural source annually and these waste materials are used as low value energy resources, some are burnt in the field, and in most cases thrown away. The utilization and management of these wastes is a great challenge. Some researchers have used this agricultural waste to produce biomass carbon catalyst by sulphonation with clear textual properties, abundant porous structure and high catalytic activity[25]. The use of biomass carbon catalyst will create a new road map of utilization and management of agricultural wastes. It is worthy of note that biomass carbon-based catalysts have gained attention in the last decade. For example, rice straw, empty palm fruit bunch, cocoa pod husk, plantain peel and waste potato peel have been employed as raw feedstock for the production of carbon-based catalyst[37,41,50]. However, using agricultural waste such as African star apple seed shell and animal bone has not received much attention. More so, there is need to extensively explore biomass from agricultural wastes that can serve as potential raw materials for solid catalyst production. Developing carbon based solid catalyst from agricultural waste product that can be utilized as catalyst for the production of biodiesel using feedstock like waste African star apple seed oil that are readily accessible in developing nation as Nigeria, will greatly reduce the over dependency on petrol fuel (fossil fuel) alongside with the environmental hazards associated with its usage and make available an alternative source of energy which is green and environmentally safe.

1.4 Aim and Objectives of the Study

This work is aimed at synthesizing environmentally friendly biodiesel from African star apple (*Chrysophyllum albidum)* seed oil as an alternative to the conventional fossil diesel fuel. The specific objectives of this project are to:

i) prepare biochar and sulphonated biochar with concentrated H_2SO_4 from solid bio-mass waste of cow (animal) bone and African star apple seed shell;

ii) characterize the sulphonated ASA shell and cow bone (biowaste char) catalysts via instrumentation such as Fourier Transmission Infrared (FTIR) and X-ray diffraction (XRD);

iii) determine the physiochemical properties of oils from ASA and the biodiesel produced;

iv) analyze biodiesel produced from African star apple seed oil using the sulphonated and non-sulphonated (pristine) cow and ASA (biomass) waste char catalysts using Gas Chromatographic-Mass Spectrometer (GC-MS); and

v) determination of the recyclability of the as-prepared catalyst.

1.5 Scope of the Study

Biodiesel is gradually been accepted as an environmentally friendly alternative diesel fuel. It has been estimated in the coming future that the increasing global consumption of energy with increasing population may lead to increase of the fuel price[23,47,51,52]. In order to sustain the eco-friendliness status of biodiesel, there is need to utilize affordable feedstock to increase the efficiency of the production process, as well as develop affordable catalysts to perform the task. That will not pose environmental threats. Hence, this study will cover the development of carbon based sulphonated solid acid catalyst from African star apple shell and cow bone chars. The synthesized sulphonated solid acid catalyst will then be employed for the transesterification via catalysis of ASA (feedstock) to biodiesel. Also, the most effective catalysts, effects of reaction conditions such as temperature, time and catalyst dosage on the yield of biodiesel from African Star Apple will be investigated.

1.6 Limitation to the Study

This study is limited by non-availability of some equipment that could have been used to unravel more potential of the samples studied in this work. It was also constraint by time and hence limits the parameters to be examined. In addition, this work is limited by financial factor. With all these limitations, the work opens up several ways by which the biowastes in our environment could be of great benefits to chemists in Nigeria and beyond.

1.7 Operational Definition of Terms

The following terms abbreviations were operationally defined in this study as follows:

ASA is the acronym for African Star Apple

ASASC means African Star Apple-Shell Sulphonated Catalyst

ASASO   means African Star Apple Seed Oil

CBSC means Cow Bone Sulphonated Catalyst

CASAS mean carbonized Africa Star Apple Shell

CCB (Pristine) mean carbonized Animal Bone

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Chapter Two

Literature Review

2.1 Conceptual Studies on the Concepts

The variables in this study include biodiesel, catalyst and biowaste catalysts. This section presents the logically and sequentially explanation of the variables in order to show the relationship that exists among these variables. Hence, the variables were examined under the following sub-headings:

i. Global policy and Government incentives on biodiesel
ii. Techniques for Biodiesel production
iii. The concept of Catalysts
iv. Carbon materials as catalysts supports.

2.1.1 Global Policy and Government Incentives on Biodiesel

Presently, different energy policies which reflect environmental issues have been the concern of most researchers and this include developing technologies that are environmentally friendly. In addition to these, policies on the increase in energy security and clean energy supplies have been enacted [1].

With this, there is a steady increase in biofuel consumption and decline in the use of fossil fuel in recent times, though the earlier directives were not met, hence government has to give more incentives during economic crisis to achieve a sustainable biodiesel industry. Such incentives may include crop plantation in abandoned and fallowed agricultural lands, subsidising and discounting soil fertilizers as well as financial aids to local farmers. In Nigeria, the government was particularly not keen on the exploitation of biodiesel development until recently when she indicated interest by the establishment of a policy on biofuel called Nigerian Biofuel Policy. This was gazette as Nigerian Biofuel Policy and Incentives recently[2].

2.1.2 Techniques for Production of Biodiesel

Traditionally, biodiesel is produced by transesterification of refined vegetable oil or waste cooking oil. The process rate is enhanced by a catalyst. Biodiesel may also be produced by the esterification reaction of free fatty acids (FFAs) and alcohol in the presence of a catalyst. In addition to the above processes, biodiesel, can be produced by direct use and blending, pyrolysis thermal cracking and micro-emulsion[3,4,5,6].

2.1.2.1 Transesterification

Transesterification is a process in which a short chain alcohol reacts with oleaginous feedstock (triglycerides, TGs) to produce biodiesel in the presence of a homogeneous or heterogeneous catalyst. This reaction is usually reversible. The triglycerides (TGs) are converted into fatty acid methyl ester (FAMEs), which is the biodiesel (Scheme 1), and producing glycerol as bye product[7,8,9,10].

Catalytic transesterification using methanol is the common method utililised for biodiesel production because methanol is very cheap and accessible. Though the reaction is expected to be reversible, the glycerol formed is immiscible with the product in the backward reaction, hence the backward reaction does not take place and in some cases negligible leading to two phase system [10,11,12]. The expression is as shown below.

$$\text{Triglycerides} + \text{Alcohol} \xrightleftharpoons{\text{Catalyst}} \text{Esters} + \text{Glycerol}$$

Figure 2.1: Catalytic transesterification

Source[9]

Catalyst is used in the process to increase the reaction rate and quantity of the final product. The amount and types of catalyst are determined by the amount of FFAs present in the feedstock. For transesterification reaction, the catalysts often utilized are both homogeneous and heterogenous catalysts. More often, homogeneous alkaline catalyst such as sodium hydroxide NaOH, potassium hydroxide KOH, sodium methoxide CH_3ONa and potassium methoxide CH_3OK are more often used in producing biodiesel. High quality feedstock with a maximum FFA content of 3wt.% is required for the transesterification process using these catalysts; anything beyond this will prevent the reaction from occurring. As a result, anhydrous feedstocks must be employed in alkali-catalyzed transesterification. The presence of water leads to hydrolysis of the oils to FFAs and the FFAs reacts with alkaline catalyst to produce soap. The formation of soap did not only deactivate the catalyst but also causes difficulties in the purification of biodiesel. In addition, for an optimum process, the reaction temperature should be between 50 – 60 °C. Furthermore, the temperature of the reaction should be less than that of the methanol so as to prevent the loss of the alcohol due to vaporization. At the end of the process, the biodiesel and glycerol produced separate out into two distinct layers. The upper layer, the less dense biodiesel and the lower layer is the densest, the glycerol. The cost of refined feedstocks gulps over 70 % of the overall cost of biodiesel production. Due to this reason and many more, several other low-quality feedstocks are been explored such as edible and non-edible oils, as the price of low-quality feedstock is less than refined oil feedstocks. However, the low-quality feedstocks have higher FFAs and water content, thereby making processing to biodiesel challenging [13,14,15,16]. To overcome these difficulties, alkali-catalyzed transesterification is carried out after using acid catalyzed transesterification to reduce the quantity of FFAs, suggesting that using a two-step transesterification process could result in significant biodiesel conversion.

2.1.2.1 Transesterification Mechanism

Transesterification reaction proceeds in three steps, the first is the formation of diglycerides from triglycerides, followed by the formation of monoglycerides and then fatty acid methyl esters, FAMEs, while propane-1,2,3-triol (glycerol) is a by-product of the reaction [12,17,18,19]. Diglycerides and monoglycerides are the intermediate of the process [20].

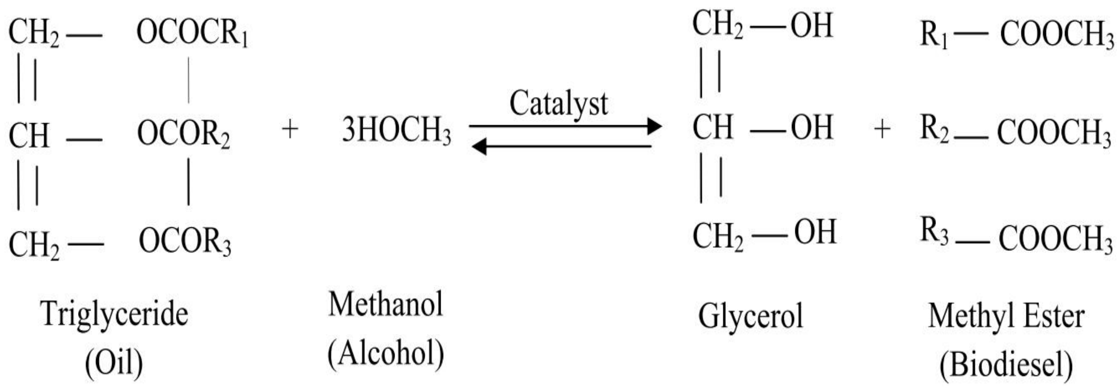

Figure 2.2: Transesterification Reaction of a Triglycerides and Methanol

Source[7]

2.2 Feedstocks for Biodiesel Production

Most biodiesel feedstocks are renewable, but its competition with food source is a major concern. Edible vegetable oils as a feedstock for biodiesel production tends to competes with food supply, hence non-edible oils have been approved for their potential for production of sustainable biodiesel and ecological benefit. There is a need to use non-edible oils like jatropha, castor, rubber seed, and sea mango in order to lessen the dependence on edible oil to create biodiesel. The procedure and quality of the biodiesel produced from these types of oil are equivalent to those produced from edible oils [21,22,23]. Biodiesel from algae is also gaining increasing attention due to its higher yield, facile manufacture, and lack of land conflict with food cultivation. This is in addition that algae produce more oil per acre more comparably to traditional oil crops [24,25]. Nevertheless, there are a number of obstacles to the commercial manufacture of biodiesel obtained from algae and these include high production cost for efficient large-scale bioreactors, insufficient algal cultivation, volatile market prices, and inadequate support from government [26,27,28].

Waste vegetable oils, greases and animal fats as feedstocks, have been reportedly utilized for biodiesel manufacture. When these oils are used, they can be converted into biodiesel production instead of disposing them as waste, however, collection infrastructure and logistics are the major challenges encountered when feedstock like waste cooking oil and grease are us.

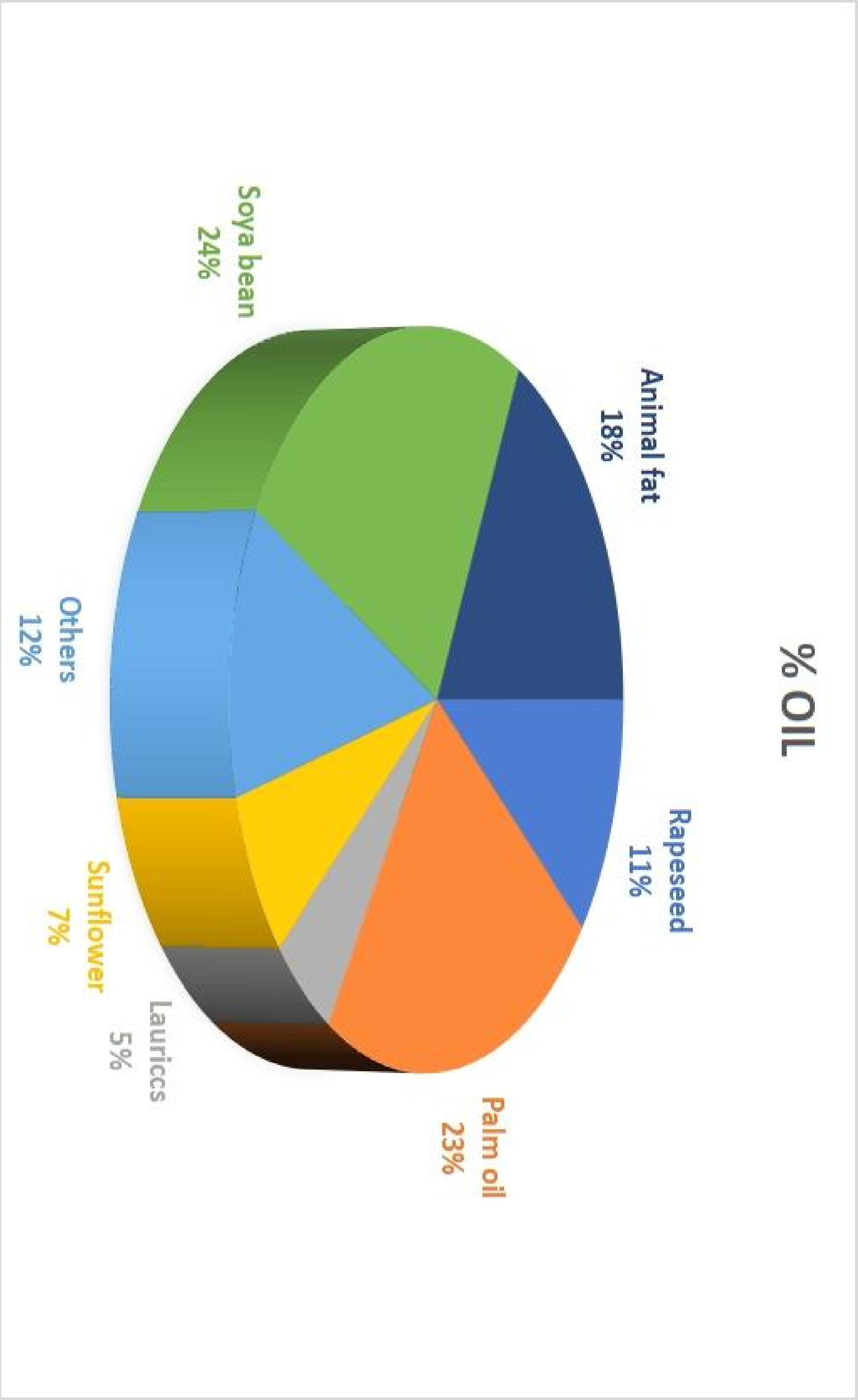

Figure 2.3: Production of Biodiesel from Different Feedstocks

Source[21]

2.2.1 Catalyst

Catalysts used in the production of biodiesel are of three types namely: enzyme (biocatalyst), alkalis/base and acid catalyst. The acid and alkalis/base catalysts are further classified into heterogeneous and homogenous catalysts [29,30]. In most biodiesel production, the base and acid catalyst are the most commonly used catalyst; enzyme catalysts are usually too expensive and have longer reaction times.

2.2.1.1 Enzymes Catalysts (Biocatalyst)

In recent times, the utilization of enzymes as a catalyst has received greater attention as it has been a solution to myriads of challenges associated with man and his environment, especially those associated with conventional homogenous catalytic process. Enzyme catalysis do not generate by-products, in addition to the ease of product recovery, mild reaction conditions, and reusability. Contrary to alkaline catalyst, enzyme catalyst produces high purity biodiesel even from poor grade feedstocks like cooking oil without forming soap. The employment of enzymes as a catalyst is most suited for usage in raw materials embedded with high amounts of free fatty acids (FFAs), including waste oils, beef, and port suet, as the presence of water and FFAs in feedstocks has resulted to associated challenges in the traditional transesterification process. This is because the enzymatic catalysts combine with FFAs converting it to alkyl esters [31,32,33]. As a result, the manufacture of biodiesel by enzyme catalysis has demonstrated a great potential to becoming both an environmentally-benign process as well as a promising substitute for the chemical process [34,35,36,37,38,39,40,41,42,43]. However, the production of biodiesel via enzymes catalysis has some drawbacks, particularly when used on an industrial scale, because to the expensive cost of enzymes, low reaction rates, their tendency to deactivate, their limited usage, and the need for recycling [44].

2.2.1.2 Homogeneous Catalyst

Catalysts that are in the same phase as the reactant and product are termed homogenous catalyst. They are very soluble in alcohols during the transesterification of oils and fat in the biodiesel production, which is usually conducted at a moderate temperature and atmospheric pressure [45]. However, utilizing homogenous catalysts has some demerits such that the catalyst cannot be recycled and reuse and its separation from the product stream is necessary (biodiesel and glycerol). The homogeneous catalysts employed in the production of biodiesel are categorized into two types namely: homogenous base/alkaline catalyst and homogenous acidic catalyst[46,47].

2.2.1.3 Homogenous Base Catalyst

Biodiesel can be synthesized through transesterification by using homogenous alkaline catalyst as it is very cheap and can result into product formation at low temperature in record time. Sodium- (NaOH) and potassium hydroxide (KOH), sodium- ($NaOCH_3$) and potassium methoxide ($KOCH_3$), just to mention a few are the commonly used homogenous base catalysts. Commercially, KOH and NaOH are employed as these are not only affordable but readily available, while the alkoxides are hygroscopic in nature hence very difficult to handle in addition to their expensive price. The overall FFAs concentration associated with the feedstock should not exceed 0.5 wt.%, though, as this is the standard restriction for the use of homogeneous base catalyst, as high level of FFAs lead to soap formation and pose separation problem thereby hindering the production of fuel-grade biodiesel [10,45,48].

2.2.1.4 Homogeneous Acid Catalyst

In the esterification of free fatty acids (FFAs), homogenous acid catalysts are comparably enhanced in performance than base catalysts, however are less effective in the transesterification of triglycerides [10,49,50]. They are often used to lower FFAs in low quality feedstock like waste cooking oil as well as animals' fats before complete transesterification with alkali catalyst. Compared to reactions catalyzed by the same quantity of base catalyst, transesterification reactions catalyzed by acids are 4000 times slower in reaction. Additionally, it requires higher pressure and temperature conditions. When transesterifying feedstocks with a high concentration of FFAs, for example, spent cooking oils, homogenous acid catalyst can be employed because there is no formation of soap unlike when a base catalyst is used. It also has low sensitivity to moisture [10,49,50]. On the contrary, they are corrosive in nature and require special expensive equipment and process. The use of hydrochloric, sulphuric, phosphoric and organic sulphuric acids in the transesterification of different triglycerides have been extensively studied.

2.2.1.5 Heterogeneous Catalysts

Heterogeneous catalysts are the opposite of homogenous catalyst. The reactants are in a different phase than the heterogeneous catalysts. When acting on substrates in a liquid or gaseous reaction mixture, most of the heterogeneous catalysts are solids. Depending on how the adsorption occurs, a variety of processes for surface reactions are known [51]. Meanwhile, heterogeneous catalysts have a number of merits such as thermal stability, goo cyclability, and low production cost [52].

The overall surface area of a solid has a significant impact on the rate of a reaction; the greater the surface area for a given mass of catalyst particles, the smaller the particle size and can easily be separated from the final product, in addition the fact that they can be recycled when the reaction is completed [53]. Furthermore, heterogeneous catalyst is considered to be environmental benign, while the procedure lowers the filtration process for biodiesel filtration, hence energy-saving and waste minimisation [54]. Heterogeneous catalyst used in biodiesel production are classified into two types namely heterogeneous alkaline/base catalyst and heterogeneous acidic catalyst.

2.3 Heterogeneous Alkaline/Base Catalyst

Several researches have been conducted on heterogeneous catalyst in the production of biodiesel with the aim of solving the associated issues of using homogenous catalyst [55]. Solid basic catalysts offer a number of benefits, including increased activity, prolonged catalytic life, and mild reaction conditions. Quite a large number of previously reported literatures on heterogeneous base catalyst used low temperature (less than 65 °C), with the reaction rate being higher compared to its acid catalyst counterpart which needs more vigorous conditions like higher temperature[56]. Base catalyst that can be used for transesterification reactions for biodiesel production includes base zeolites, basic metal oxides, supported basic catalyst, alkali earth alkoxides catalyst and waste derive catalyst [55,56].

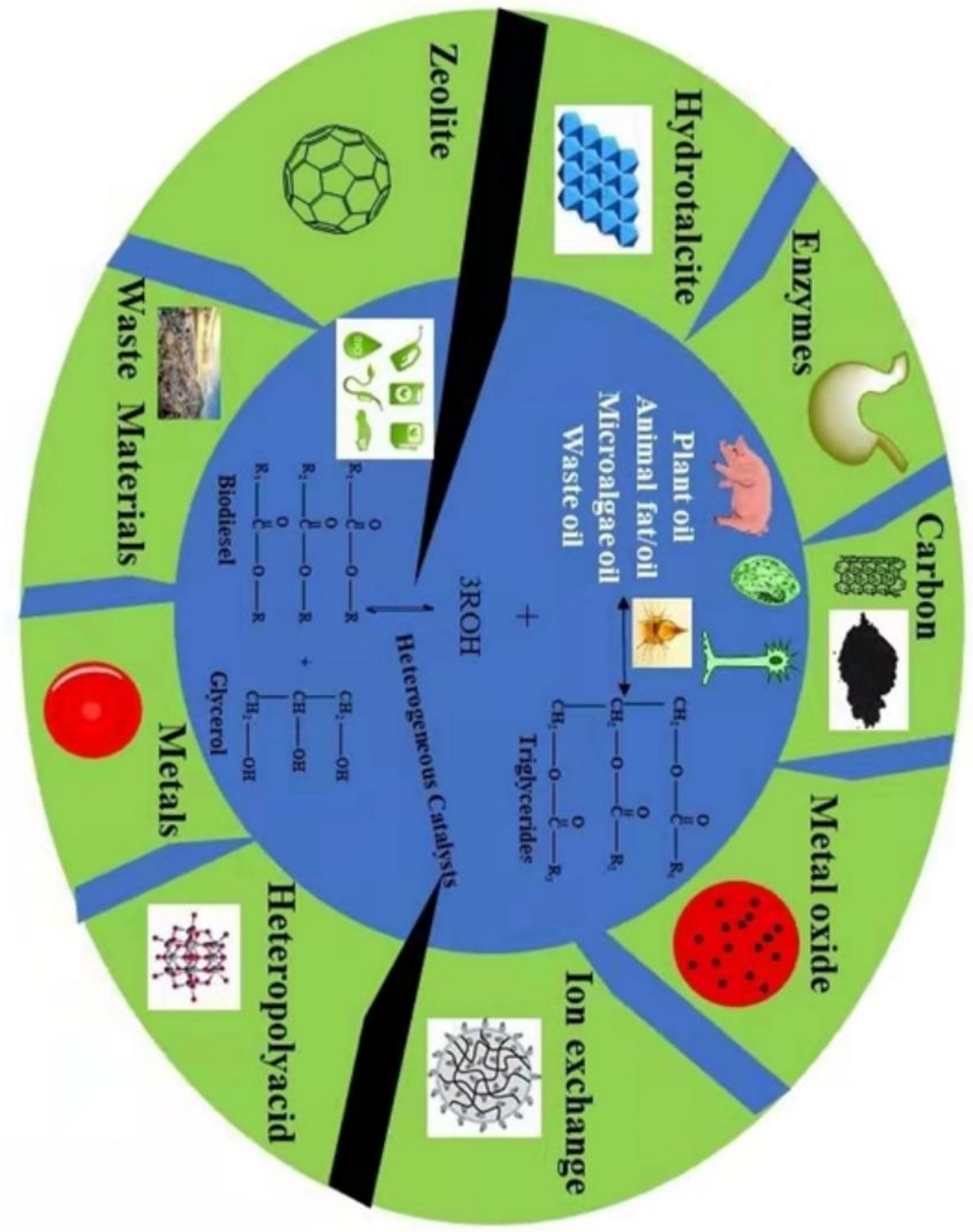

Figure 2.4: Different Types of Heterogeneous Catalysts for the Transesterification of Biodiesel.

Source[56]

2.3.1 Base Zeolites

The basicity or acidity of zeolites, which are flexible and adaptable catalytic materials, can be adjusted by appropriate doping. Alkali-ion-exchanged zeolites, for example, exhibit strong basicity while certain zeolites exhibit acidic characteristics. The basicity increases due to the occlusion of alkali metal oxide clusters which can be produced by the impregnated alkalis undergoing degradation, as well as the increasing electropositivity of the exchanged cation[57].

2.3.2 Basic Metal Oxides

In the transesterification of triglycerides, metals oxides can act a solid base catalyst. Lewis acid-containing cations and Bronsted-base anions are the constituents of metal oxides (MOs), which are used in the production of biodiesel. Examples are magnesium oxides MgO, calcium oxide CaO) and mixed metal oxides (A-B-O type metal oxides); where A is an alkaline-earth metal, alkaline metal or rare earth metal and B is a transition metal[58]. The basicity of the oxides is directly dependent on the rate of reaction. By comparing some MOs (MgO, CeO_2, La_2O_3 and ZnO), La_2O_3 was found to be the most basic, in the order of $La_2O_3>MgO>CeO_2>ZnO$[47]. Amongst the alkaline earth metals oxide catalyst, the order of activity is BaO>SrO>CaO>MgO. Calcium oxide is the most often utilised MO catalyst for the production of biodiesel because it is cheap, possessing a relatively high basic strength and exudes less environmental impact. Mixed metal oxides such as CaMgO and CaZnO have been synthesized in order to increase the basic strength of single oxides, eve as the utilisation of CaO-MgO as a catalyst for biodiesel manufacture was revealed to possess higher catalytic activity compared to CaO[59]. Furthermore, the catalytic activity of CaMgO and CaZnO have been compared with CaO, MgO and ZnO for the conversion of *Jatropha curcas* oil (JCO) to biodiesel. It was observed that CaO gave a slightly higher conversion but CaMgO and

CaZnO maintained their activities after sixth recycle usage while the activity of CaO reduced after fourth cycle[60].

2.3.3 Waste-Derived Catalysts

Bio-based and industrial materials which are often regarded as wastes and discarded can be utilized to produce economical catalysts. Due to the high calcium content in these wastes, they could be used for the syntheses of environmentally friendly heterogenous catalysts. Examples of these wastes include egg shell snail shell, etc. which are commonly found. For example, egg shell comprises mainly of 98.2 % calcium carbonate ($CaCO_3$), 0.9 % of magnesium carbonate ($MgCO_3$) and 0.9 % of phosphate[61].

Waste shells, such as egg, oyster, mollusk shrimp from which catalyst can be synthesized, are found in abundance around us. Catalysts derived from wastes possess green potential in energy efficiency and have been synthesized from waste chicken egg shell, River snail shell and oyster shells, just to mention a few [62,63].

2.2.4 Non-biomass Waste Catalyst

Non-biomass waste materials derived from industrial processes has also found significant application as active catalyst for the biodiesel production from several oils with optimized efficiency and reusability. These materials contain remarkable number of mineral elements like calcium compounds (CaO and $CaCO_3$) with good active sites. Recent reports have shown that the non-biomass waste materials after undergoing calcination could afford over 90 % natural calcium-rich compounds having similar properties as those of commercial $CaCO_3$[62]. For example, waste glass collected from container glasses, remelted, and used to produce new glass are somewhat difficult to eliminate, and not all of them finds suitability for the making new glasses. However, the team of Foroutan showed that using a discontinuous mode, 2 % waste glass catalysts successfully transesterified chicken fat oil to produce 97.74 % biodiesel within 120 min at 65 °C and 15:1 alcohol: oil ratio[64]. Waste materials obtained from concrete, mortar, and cement was employed for the conversion of non-edible Karanja oil in a single-neck glass reactor[65]. At optimum conditions of 30:1, 60°C and 180 min reaction time, 30, 35 and 2.5 wt. % of the respective waste catalysts successfully produced 32, 37.5 and 76 % biodiesel respectively. Meanwhile, the modification of waste egg shell with cobalt nitrate tranesterified Algal lipid from *Scenedesmus quadricauda*in a two-neck flask with 98 % conversion rate[66]**.** The modified catalyst could undergo three successive reruns with an efficiency of 86 % biodiesel conversion after the third run. More also, the combination of waste egg shell and peat clay catalyst converted spent cooking oil to 91 % biodiesel; while 99.2 % biodiesel was produced from the combination of lignite coal fly ash and chicken egg shell catalyst and sunflower oils[68]. Furthermore, 100 % biodiesel conversion have been obtained with fly ash catalyst and waste frying oil in a 360 min reaction time at 59°C and 11.2 wt.% catalyst concentration; as well as with strontium oxide, SrO modified with egg shell for Jatropha oil conversion with 89.8 min in a two-neck round bottom flask reactor set at 65°C and 4.77 wt.% of the catalyst material. Additionally, limescale was used as catalyst on waste cooking oil and soy bean dregs oil**.** The optimum yield of these waste catalyst was 93.41 % biodiesel in 15 min at 61.7 °C and 92.6 % in 180 min at 75°C respectively[69].

2.4 Heterogeneous Acid Catalysts

Regardless of how effective homogeneous acid catalysts are, they could result to contamination issues which require effective separation and product purification process which ultimately can increase the cost of production. A number of the advantages of heterogeneous acid catalyst include insensitivity to free fatty acids (FFAs), ability to concurrently undergo esterification-transesterification, elimination of the washing phase, facile separation process of the catalyst from product, ability to recycle and reuse as well as reduction of corrosion problems. Moreover, the ability of heterogeneous acid catalyst to inhibit the solvation of the catalytic sites from the water impact assists in reducing catalyst deactivation and product contamination[70,71].

2.5 Solid Sulphonated Carbon Catalysts

With the development of green chemistry, the need to develop solid acid catalyst, which has attracted tremendous attention for green catalytic procedure due to the increasing environmental issues has pushed the research for recyclable strong solid acids to replace conventional toxic and corrosive acids catalysts such sulphuric acids. Additionally, they are easier to separate, with less corrosion and toxicity issues than other reported catalysts for the generation of biodiesel[72]. There are numerous heterogeneous solid acid catalysts for the production of biodiesel in literatures, such as sulphated zirconia, ion exchange resins and inorganic-oxide solid acids[70]. However, all of these catalysts are either too expensive or have insufficient catalytic activity and effective acid sites[70,72].

Sulphonated carbon materials have attracted greater attention due to their cheap price, high stability and catalytic activities. The carbon-based materials can be obtained from biomass wastes such as agricultural/forestry wastes, micro algae and macro-fungi resides[70,71,73].

2.5.1 Bio-Char-Based Solid Acid Catalyst

Agricultural wastes can be turned into biochar, a by-product from biomass by several pyrolytic process, which is one of the promising thermochemical methods of producing bio-oil, biochar and combustible gases which is of great benefit. The fast pyrolysis process typically yields ~75 wt.% bio-oil, 10-20 wt.% non-condensable gases and 15-25 wt.% biochar as by-products[74]. The biochar-based catalyst is produced via the addition of sulphuric acid to biochar material under inert gas, and support[75,76,77].

2.6 Methods of Preparing Carbon-Based Sulphonated Catalysts

There are several carbon materials that have been developed and utilized in the preparation of CBSC. The methods employed in preparing carbon based sulphonated catalyst that shows high catalytic activity and stability is very important. During the preparation, various carbon-based feedstocks such as biomass, sulphonating agents and operation conditions could be adopted[74,78].

2.6.1 Direct Incomplete Sulphuric Acid Carbonization

CBSC can be prepared from naphthalene by direct incomplete sulphuric acid carbonization of carbon material[72,79]. The synthesized CBSC showed high catalytic activities in esterification and hydrolysis reaction. CBSC synthesized from low polycyclic aromatic hydrocarbons such as naphthalene, anthracene etc. as raw material showed leaching of $-SO_3H$ groups at high temperature. A CBSC obtained from direct incomplete sulphuric acid carbonization of lignin-derived material, demonstrated excellent catalytic activity during acidified soybean soap stock esterification reaction with methanol[80].

2.6.2 Sulphonation of Biomass Carbonization Product

Carbonized biomass or goods made from biomass can be used to produce biochar. Hydrothermal- and flash carbonization, gasification, pyrolysis, just to mention a few, are some of the carbonization techniques., etc. Pyrolysis is usually conducted around 250-650 °C, while the temperature condition of hydrothermal carbonization is low and the hydrochar obtained possesses more surface oxygen-based groups. Sulphonation of hydrochar has also been developed. Carbonization at high temperature gives rise to a rigid char on the material that will not be favorable for the preparation of $–SO_3H$ group during sulphonation process, leading to low acid density. The sulphonating agents used are concentrated tetraoxosulphate

(VI) acid and fuming tetraoxosulphate (VI) acid, but CBSC prepared with fuming teteraoxosulphate (VI) acid gave higher catalytic activity[73,76,78,80].

2.6.3 Synthesis of CBSC by Other Sulphonating Sources

Carbon-based materials like graphenes and carbon nanotubes are rigid and difficult to sulphonate by concentrated/fuming sulphuric acid. The rigid materials can be sulphonated by special sulphonating agents such as 4-benzenediazoniumsulphate, P-styrenesulphonic acid and chlorosulphonic acid. One of the advantages of using 4-benzenediazonium sulphonate and P-styrene sulphonic acid results from the fact that the temperature for the sulphonation process is very low, such that the initial skeleton composition of the carbon feedstock is maintained. P-toluenesulphonic acid and hydroxyethylsulponic acid have also been used to carry out the sulphonation of CBSC materials. This method has gained popularity in recent times due to the low reaction temperature (< 200 °C), facile synthetic method and separation process, compared the tradition concentrated tetraoxosulphate (VI) acid. However, these sulphonating materials are very expensive and would drive up the preparation cost of CBSC [81].

2.6.4 Synthesis of Resin/Polyvinyl chloride (PVC) Derived CBSC

One good source of polymeric carbon is resinol when carbonized resin is sulphonated, it would result in special polymeric structured CBSC. CBSC have been prepared from phenolic resin, which exhibited enhanced recycle times compared to the carbon resin catalyst and increased concentration attached sulphonyl group than other sulphonated carbon frame work catalyst. Polyvinyl chloride (PVC) is another feedstock to produce CBSC, as the derived CBSC accelerate the diffusion of reactions as well as assists in the reaction of the sulphonyl groups bonded to the carbon skeleton, which would thereafter enhance catalytic performance when compared to the traditional CBSC[48,82].

2.7 Carbon-based Materials as Catalyst Supports

Supported catalysts possess some inherent properties including mechanical strength, pore distribution and thermochemical stability. The supports may act as a stabilizing agent to inhibit the agglomeration of lower melting points materials[80,83]. Advantageously, residual biomass can be converted into carbon materials, which is a desirable quality for lowering a biomass conversion process's purported "carbon footprint"[84].

2.8 Properties Affecting the Role of a Catalyst Support

2.8.1 Surface Area and Porosity

High surface area and a well-developed porosity are very important for achieving a high dispersion of the active phase in the catalyst (*dispersion* is the friction of metal atoms that are on the surface of the support in relation to the total metal loading). Carbon materials, especially activated carbon, exhibit surface areas much higher than those of other conventional catalyst supports. However, a great part of this surface area may be contained in narrow micropores, in which case it may be unavailable to reactants[74,85].

2.8.2 Surface Chemical Properties

Using the appropriate thermal or chemical post-treatments, the nature and concentration of the surface functional groups can be manipulated. Numerous surface functional groups in the carbon material are produced by the presence of heteroatoms, such as -O-, -N-, and -S attached to the edges of the graphene layers. These components are either already present in the initial material or bind chemically during preparation.

Heteroatoms addition to the carbon structure enables control of the electronic properties through the addition of electron acceptors or donors, which can strengthen π-bonding, resulting in improved stability and rate of electron transfer, and consequently, improved the catalyst' performance during the processes[86].

2.8.3 Inertness

Although various types of active phase-support interaction may be induced by the presence of heteroatoms on the carbon surface, it is evident that this rarely occurs than in other frequent catalytic supports, such as metal oxides. For example, when citronellal (3,7-dimethyl-6-octen-1-al) was hydrogenated on RuSi/C, the surface area and support type were investigated on product dispersion. On the supported Ru catalyst, it was reported that the isomerization of citronellal occurs on the surface of the support, as the products distribution was found to depend strongly on the surface area and on the nature of the support[75]. Since there is little contact between the carbon surface and the metals, the carbon surface's comparatively low reactivity or inertness is also very helpful in the creation of bimetallic catalysts. The primary advantage of using carbon as a catalyst support is that its surface is relatively inert, facilitating interactions between active phases or between active phases and promoter[47].

2.9 Application of Carbon-Based Sulphonated Catalysts

2.9.1 Catalytic Hydrolysis

CBSC bearing –SO_3H, −COOH, and –OH groups are efficient catalyst for the hydrolysis of crystalline pure cellulose. The enhanced catalytic activity for the hydrolysis of cellulose hydrolysis is due to the β-1,4-glucan, expansive water surface area and the sulphonyl groups having the tolerability to hydration in the carbonaceous material. The extent of the cellulose hydrolysis increases with the increasing reaction temperature but temperature exceeding

100 °C would cause cellulose surface rupture, thereby inhibit effective hydrolysis[48,49,50]. Also, activated carbon based sulphonated catalyst (ACBSC) exhibited enhanced activity and selectivity for the glucose production from cellulose, yielding a product selectivity of about 90 C% of glucose. Additionally, CBSC has been used in the catalytic hydrolysis of hemicellulose to produce xylose and glucose, dehydration of xylose to produce furfural and hydroxymethylfurfural from fructose [11,15,52].

2.10 Review of Empirical Studies

In recent times, solid acid catalyst used in the production of biodiesel has been found to be very common, and has attracted much attention due to their low cost of production, high catalytic activity and environmental-benign. The empirical studies were examined under the following sub-headings.

2.10.1 Empirical Studies on Non-edible Seed Oils

Several studies have been carried out and many still ongoing with non-edible seed oils for the production of biodiesel. Non-edible seed oils were explored due to paradigm shift from the conventional diesel oils based on fact that conventional diesel is not environmentally friendly. Non-edible seed oils that have been studied to include but not limited to *Jatropha carcus*, neem oil, rubber seed oil and avocado seed oil. In the study, a highly active CaO catalyst (CaO-H) for the transesterification of Jatropha oil with methanol to produce biodiesel was effectively prepared using eggshell waste using a hydration process. The catalyst was found to improve the basicity and active surface area on the multilayer flake-like particles produced by the hydration process. The maximum content of methyl ester of 99.71% was attained with the catalyst at optimum condition (7 mmol/g of SrO, 65 °C, 89.8 min, 27.6:1 MeOH: Oil ratio, catalyst dosage of 4.77 wt%). Addition of SrO at the optimum boosts the basicity, catalytic activity, and reaction rate[87]. Thereafter, the catalytic activity steadily decreased due to decreased basic strength as a result of the loss of its active metals. Also, Murumuru kernel shells waste was carbonized with concentrated sulphuric acid under different sulphonation conditions to obtain sulphonated biochar as heterogeneous acid catalyst, which was thereafter used for the esterification of fatty acids [74]. A conversion of 97.2 % was achieved under optimum esterification reaction conditions (5 wt.% catalyst, 10:1 molar ratio of methanol to oleic acid, 1.5 h and 90 °C). The catalyst was further reported to have maintained a 66.3 % conversion efficiency after fourth cycle use. In another study, hone oil methyl esters (HOME) production from crude hone seed oil (HSO) using a novel catalyst synthesized from a blend of cocoa pod husk and plantain peel was investigated, using a two-step esterification-transesterification method. For the esterification reaction, the crude HSO was pretreated with H_2SO_4 to reduce its high acid value to an acceptable limit of 1.68 ± 0.57 g KOH/g oil at optimal conditions, to give a maximum HOME yield of 98.98 ± 0.04 wt% in 150 min and 15:1 MeOH: pretreated HSO molar ratio [75]. Furthermore, *Azadirachta indica* (Neem) is a common plant in Asia and Africa, that produces seed. The seed is non-edible from where oil was extracted to explore the possibility of conversion to biodiesel using calcined ash obtained from banana peels blended with Li-CaO/$Fe_2(SO_4)_3$ as catalyst for the transesterification reaction resulting into a 99.8 % yield at optimal conditions (8:1 MeOH: Oil ratio, 1.7:1.3 wt.% of calcined banana peels ash:Li-CaO/$Fe_2(SO_4)_3$ catalysts in 53 min[88,89,90].

In a study, seven microalgae species called *Nitzschia* sp., *Nannochloropsis* sp., *Botryococcus braunii*, *Neochloris oleoabundans*, *Schizochytrium* sp., *Chlorella vulgaris L.*, and *Chlorella variabiilis L.* were dried by four drying methods: spray, convective, vacuum, and microwave. Biodiesel was produced from dried microalgae via transesterification[91]. 1.5 g of NaOH was used as catalyst and 200 ml of methanol as alcohol into 400 ml of vegetable oil from microalgae. Biodiesel production by the transesterification method consisted of four steps:

mixing alcohol and catalyst, reaction, separation, and methyl esters washing. In the initial step, NaOH was dissolved in methanol with a hotplate magnetic stirrer (Daihan, MSH-20D, South Korea) at 60 °C. In the second stage, reaction, a vegetable oil obtained from microalgae was heated in a controlled environment using a hotplate magnetic stirrer capable of precise temperature control at 60 °C ±1 NaOH was added to the heated oil. The step was continued for 24 h in a closed environment both to prevent evaporation of the alcohol and to obtain higher quality biodiesel[92]. In the third stage, which was separation, glycerin, and biodiesel, the two main products obtained at the end of the reaction stage, were separated using a centrifuge device (Nüve, NF200, Turkey) rotating at 5000 min^{-1}. In the same step, separated methanol in both biodiesel and glycerin was removed using a rotary evaporator at 50 °C and 50 kPa to allow reuse. Also, the salt in the glycerin obtained was separated by washing[93]. The water was remaining in the glycerin after washing was evaporated with the help of a hotplate magnetic stirrer to obtain glycerin of 80–88% purity. In the last stage, which was the methyl ester washing; the methyl esters in the biodiesel were removed by washing them slowly with hot water several times. The water particles remaining in the washed biodiesel were evaporated by heating at 110 °C for 6 h with the help of a hotplate magnetic stirrer.

The vegetable oil yield was the maximum in spray and vacuum dried Schizochytrium with 35.50 and 34.53%, respectively. Similarly, the highest biodiesel yield with 100% was obtained in Schizochytrium dried by spray technique. However, the cloud point of −1.77 °C was the lowest in *Botryococcus braunii* samples dehydrated by microwave drying. The highest pour point with − 10.13 °C was obtained in microwave dried *Chlorella variabilis* samples, but the maximum freezing point was found in the microwave and convective dried samples of *Chlorella variabilis* with −13.60 and −13.70 °C, respectively. The lowest water content was measured in biodiesel samples from *Botryococcus braunii*, *Chlorella vulgaris*, and *Chlorella variabilis* dried by microwave technique. However, the best results regarding calorific value were found in Schizochytrium samples dried by spray and vacuum. The viscosity with 6.08 $mm^2\ s^{-1}$ and density with 0.90 $g\ cm^{-3}$ of *Botryococcus braunii* dried by the microwave method were at the maximum. Interestingly, two species commonly used in biodiesel production, *Chlorella vulgaris* and *Chlorella variabilis*, could not meet the expectations regarding quality parameters. Also, Schizochytrium and Nitzschia were determined as the most suitable microalgae species for the quality standards for biodiesel production. Compared to the others, the most successful results were obtained in the biodiesel produced from Schizochytrium dried spray drying.

In another study, heterogeneous catalysts, named SPS (sodium potassium silicates), were synthesized with an alternative silica (MPI silica) obtained from beach sand[94]. The MPI was modified with NaOH and KOH producing silicate-based catalyst for biodiesel synthesis from waste cooking oil (WCO). The obtained catalyst was characterized by XRD, CO_2-TPD, the Hammett basicity test, XRF, FESEM, EDX, FTIR and TG/DTG. Biodiesel was synthesized in three consecutive stages: (i) previous filtration of the WCO in a separating funnel to remove impurities; (ii) transesterification reaction at 70 °C with methanol and catalyst in a reflux reactor; and (iii) purification with adaptations. The time, catalyst concentration and molar ratio parameters were varied for synthesis optimization. The results confirmed the presence of K_2O/Na_2O oxides and their silicates, the main active sites responsible for the catalytic action. CO_2-TPD and the Hammett basicity data suggested the presence of weak, medium and strong basic sites. Biodiesel yield was about 92% and the SPS catalyst was reused for five cycles. The biodiesel conversion by NMR 1H was about 93.89%. The DTG deconvolution revealed the decomposition of four typical biodiesel compounds ($R^2 = 0.9987$). The method applied for the WCO biodiesel production using SPS catalyst represents an environmentally friendly process, based on low-cost material and reuse of waste biomass.

In a research, response surface methodology involving central composite design was applied to optimize reaction parameters of biodiesel production from Tra (*Pangasius hypophthalmus*) and Basa (*Pangasius bocourti*) catfish oil during the microwave-assisted single-step transesterification process[95]. Catfish oil (0.025 mol, based on an average molecular mass of 850 g/mole) was dissolved in an appropriate amount of co- solvent (acetone and isopropanol) and transferred to a 100 mL round bottom flask with mechanical stirring method (MS) or 100 mL sealed reactor (Teflon vessel) with microwave-assisted method (MW). The desired amount of potassium hydroxide was then separately dissolved in methanol and added to the round bottom flask or Teflon vessel. The resulting reaction mixture was subsequently heated with vigorous stirring (600 rpm) in a water bath at the desired temperature (MS) or with high stirring and irradiated using the power of 300 W by CEM Discover (MW). Second-order polynomial models of the microwave-assisted method with acetone (MW-A) and isopropanol (MW-I) co-solvent were used to predict the biodiesel yield and the coefficient of determination (R^2) was found to be at 0.9926, and 0.9891, respectively. The results demonstrated that isopropanol had similar effects to acetone on transesterification yields. The optimum biodiesel yield was calculated as 99.05% (MW-A) and 98.96% (MW-I) from the models with the following reaction conditions: methanol-to-oil molar ratio of 5.60 (MW-A) and 5.66 (MW-I), KOH concentration of 1.04 wt% (MW-A) and 1.00 wt% (MW-I), the reaction temperature of 53.20 °C (MW-A) and 53.59 °C (MW-I), the reaction time of 94.43 s (MW-A) and 93.27 s (MW-I), and co-solvent of 24.20 wt% (MW-A) and 22.73 wt% (MW-I). The results of biodiesel yield under optimal conditions have proved that the regression models agreed with the experimental data. Furthermore, the properties of catfish oil biodiesel produced under the optimum conditions were characterized and found to agree with the EN 14214 standard specifications.

A study investigates the SCO yield (and biodiesel characteristics) obtained from sugarcane bagasse hydrolysate through various pretreatment techniques[96]. The pretreatment with 4% v/v H_2SO_4 at 25 min of ultra-sonication provided the best depolymerisation results (based on the glucose concentration). *Yarrowia lipolytica* was inoculated into the hydrolysates, allowed to grow at 25 °C, pH of 6.5 and rapid mixing for six days yielded biomass of 16.39 g/l. Biodiesel was extracted from the biomass via in-situ and ex-situ transesterification.

In-situ direct transesterification, the dried crude biomass was treated with chemical processing without any lipid extraction. Biomass was taken in the range of 2.5 % w/v of methanol in a round bottom flask, and 3 g of K_2CO_3 was added to the sample. The sample filled flask was kept in a water bath along with the reflux set up. The water bath is heated to a temperature of 55 °C for 2 h. At this temperature, some amount of methanol gets vaporized and escapes upward into the condenser column. This vapour is condensed and returns to the solution. The reaction was allowed to take place for about 90 min, and then the solution was allowed to cool down to room temperature. Hexane was added in the ratio of (5:3) into the solution, and then it is rapidly mixed with the help of a magnetic stirrer at 700 rpm for about 30 min. The mixture was transferred into the separating funnel and kept untouched for about 2 h. The layer separation was clearly observed, the top layer contains hexane along with biodiesel, and the bottom layer contains methanol, catalyst and biomass. The top layer containing hexane and biodiesel was separated employing heating above the boiling point of hexane using a thermo-mixer. Then the water-soluble contents were removed by reacting with an equal volume of 0.9 N sodium sulphate solution to separate the biodiesel.

In the ex-situ transesterification process, lipid was extracted (first step), and subsequent lipid transesterification (second step) was carried out. Lipids were extracted from the biomass by adopting Hara and Radin method with minor modification. The team utilized ratio of hexane: isopropanol at 3:2, whereas, in this study, it was modified to a 5:3 ratio to homogenize the mixture and produce a higher yield of lipid extraction. The carbohydrates and proteins were separated from lipids using hydrophilic and hydrophobic solvents. 1 g of dried biomass mixed with 20 ml of hexane: isopropanol solution (5:3) was then poured into 50 ml of the conical flask. The biomass was later subjected to bead milling with the glass beads for 150 min in a magnetic stirrer at 200 rpm and subsequently speeding up to 700 rpm for a period of 30 min. Finally, the lipid components were separated by centrifugation at 8000 rpm for 10 min. The separation of distinct layers was observed in the centrifuge tube. The bottom and top layers contain protein and lipid, respectively. The top layer containing lipids was separated by pipette and dried in a hot air oven at 105 °C for 12 h. An ethanol emulsion test is conducted to confirm the presence of lipids in the given sample. Ethanol interacts with any lipid suspended in water and forms a cloudy appearance, whereas, absence of lipids leads to a clear solution. The lipid samples were tested with this conventional method as a preliminary assessment before being subjected to the analysis of the characteristic functional groups via attenuated total reflectance via Fourier transform infrared spectroscopy (FTIR) scan from 4000 cm- to 700 cm^{-1}.

In-situ transesterification carried out with the catalyst K_2CO_3 yields 80% biodiesel. In comparison, 63% were achieved with ex-situ transesterification, where lipid extraction was carried out as a first step and transesterified further in the presence of catalyst KOH to obtain biodiesel. The obtained fatty acid methyl esters (FAME) were subjected to FTIR analysis, and the observed physicochemical properties were within the international standards.

2.10.2 Empirical Studies on African Star Apple Seed Oil

Studies on African star apple (ASA) seed oil are very scanty in the literature. However, few of the studies were reviewed. Recently, a team of researchers conducted a prospecting research of de-oiled seed cakes of African star apple (ASA) and silk cotton (SCS) as a source of bio-oil using slow pyrolysis. For the ASA seedcake, the optimum yield of 72% was achieved in comparison to 68% yield for SCS at 400 °C[97,98,99]. Also reported was the yield reduction of the bio-char yield from 38% to 28% with increasing temperature (300 °C to 450 °C). This is attributed to the extensive primary decomposition of the biomass samples. Furthermore, the GC-MS analysis showed that ASA bio-oil has acids (25.15%), phenolics (18.35%), and hydrocarbons (18.58%) as the major compounds., while the SCS bio-oil contain N-containing compounds (38.17%), carboxylic acid (23.79%), and phenolic (16.57%) as dominant compounds, respectively[100, 101].

2.11 Impacts and Benefits of Biodiesel

Replacing fossil fuels with biofuels has the potential to generate a number of benefits. In contrast to fossil fuels, which are exhaustible resources, biofuels are produced from renewable feedstocks[102]. Moreover, academic studies using other economic models have also found that biodiesel can lead to reductions in greenhouse gas emissions relative to conventional fuels[103]. Biofuels help to protect and create jobs i.e. an emerging biodiesel industry could offer new jobs that would help to support rural communities and farm households and provide the kind of economic stimulus many agriculturally dependent areas have been seeking[104,105]. Other derived benefits include greater energy security, lowered impact on the environment, savings from foreign exchange, and socioeconomic issues related to the rural sector. For these reasons, the share of biodiesel in the automotive fuel market is expected to grow rapidly in the coming years, thereby serving as environment-supported energy carriers for all countries[106,107].

Endnotes

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Chapter Three

Methodology

3.1 Materials

All chemicals used were of analytical grade and purchased from a reputable chemical shop in Lagos and Abeokuta in Ogun State.

3.1.1 Concentrated Tetraoxosulphate (VI) Acid

3.1.2 Methanol

3.1.3 Sodium Hydroxide (NaOH)

3.1.4 Hydrochloric acid (HCl)

3.1.5 Potassium Hydroxide (KOH)

3.1.6 Sodium Thiosulphate ($Na_2S_2O_3$)

3.1.7 Potassium Iodide (KI)

3.1.8 Starch Solution

3.1.9 Oil Feedstock (African Star Apple Seed Oil)

3.1.10 African Star Apple Seed Shell

3.1.11 Animal Bone (Cow Bone)

3.2 Equipment

The equipment used in the study is as listed.

pH meter, Orion Digital Ion Analyzer Model 601/A

Muffle Furnace

Fourier Transform-Infrared Spectrophotometer, Brucker IFS113v

X-ray Diffraction (XRD)

Gas Chromatography/Mass spectrometry, Agilent 7880 coupled with Mass Spectrometry of Model Agilent 5975.

3.3 Methods

3. 3.1 Preparation of Carbon-based Catalyst and Cow Bone-based Catalyst

Two different biochar was obtained from the biomass - African star apple shell and cow bone. The materials were washed with fresh water separately, followed by with distilled water and allowed to air dry overnight. The carbonization was carried out in a muffle furnace at temperature of 900°C for 4 h. After carbonization, the biochar was ground into powder in a mortar and pestle and sieved using a sieve of mesh size 150mm. The samples were thereafter stored in a plastic container until further use. The sample derived from ASA shell was labelled CASASC (Carbonized African Star Apple shell catalyst) while the sample derived from the cow bone was labelled CCBC (Carbonized Cow Bone catalyst). These catalysts were classified as carbon – based catalysts that is pristine.

3.3.2 Preparation of Sulphonated Catalyst

The biomass powder (ASA shell and animal cow bone) was dried in an oven at 110 °C for 5 h. 10 g of the dried powder was mixed with 50 g of H_2SO_4 in a beaker on a hot plate at 100 °C for 1 h to in-situ incomplete sulphuric carbonization separately. The mixture was cooled for 24 h, the reaction mixture was diluted, filtered and washed repeatedly with hot diluted water until the excess H_2SO_4 was removed. This was confirmed with a pH meter. The resultant plant and animal sulphonated substance (catalyst) were then oven-dried at 120 °C for 2 h. The samples were cooled thereafter and stored in a plastic container until further use. The sample derived from ASA shell was labelled ASASC (African Star Apple shell-based sulphonated catalyst) while the sample derived from the cow bone was labelled CBSC (Cow bone-based sulphonated catalyst).

3.3.3 Characterization of the Catalyst

The two different samples of cow (animal) bone (prepared via carbonization at 900 °C and further sulphonation process) were characterized using X-Ray Diffraction (XRD) to determine the crystallography and size of the pristine and sulphonated cow bone and African star apple shell. The XRD analysis of the sample was conducted on a diffractometer model ADX-2700 serial 26710, in the 2θ range of 5–70°. In all, there were four catalysts in two different groups used in the project. These were the pristine (non-sulphonated ASA shell and Animal cow bone) and the sulphonated catalysts (ASA shell and animal cow bone).

3.3.4 pH Determination

The pH of the carbon-based catalysts was determined by immersing 2.0 g of the samples each in 20 mL of deionized water and stirred for about 15 min. The pH was measured with an Orion digital ion analyzer model 601/A (Orion Research, Inc., Cambridge, MA).

3.3.5 Bulk Density Determination

The bulk density of a powder is the ratio of the mass of an untapped powder sample and its volume as well as the inter particulate void volume. The bulk density is expressed in grams per millilitre (g/mL), grams per cubic centimetre (g/cm^3) or kilogram per cubic metre (1 g/mL = 1000 kg/m^3) because the measurements are made using cylinders. In this study, the bulk density was determined by a trapping method as adopted at the 46th WHO Expert Committee on Specifications for pharmaceutical preparations [1]. A known amount of the biochar sample was added to10 mL measuring cylinder, which was thereafter continuously tapped until the volume remains unchanged and the bulk density is determined as shown in equation 3.1 different weights (3 g and 5 g) were used for the biochar samples and the average of the bulk density was calculated.

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{Weight of dry sample}}{\text{Volume of packed dry sample}} \qquad \text{Equation 3.1}$$

3.3.6 Determination of Total Acidity (TA)

The total acidity of the carbon-based sulphonated catalysts was determined by titration following the method reported in the literatures[2]. In this study, 100 mL of 0.1 M HCl solution was added to 0.5 g sulphonated carbon in a beaker, after which it was stirred for 4 h. The solution was then back titrated with standard 0.1 HCl solution using phenolphthalein indicator. The volume of the acid used was recorded when the color changed from pink to colorless. The TA (N_{total}) of the sulphonated carbon was calculated using Equation 3.2.

$$N_{total\ (mEq/g)} = (V_{NaOH} \times 0.1M\ NaOH) - (V_{HCl} \times 0.1M\ NaOH) \qquad \text{Equation 3.2}$$

Where V_{NaOH} = volume of NaOH used (ml) initially per gram of the sulphonated carbon

M = molarity of NaOH

V_{HCl} = Volume of HCl used (ml)

3.4 Fourier Transform - Infrared Spectrophotometer (FT-IR) Characterization

The use of FTIR is to determine the functional groups present in the extracted oil.

3.4.1 Catalyst Recyclability Test

By recovering African star apple shell (ASA shell) and cow bone (Animal) based sulphonated catalyst and the pristine version, the carbon-based and animal-based catalysts were retrieved from reaction through filtration and washing with dichloromethane, and then reusing them, after which the recyclability of the four prepared catalysts was investigated. All of the reaction parameters in the test, including the volume-to-weight ratio of methanol to palmitic acid, temperature, time, and catalyst loading, were conducted at optimal conditions.

3.4.2 Preparation of Oil Feedstock

The oil feed stock in this study is obtained from African star apple seed (cotyledon). Ripen African Star Apple fruits were freshly harvested from the tree on a farm located in the Idoye Village, Ado-Odo/Ota Local Government Area of Ogun State, Nigeria. The seeds were firstly air-dried at ambient temperature (29 °C) for seven (7) days, after which they were cracked and the cotyledon seed removed. This was followed by another air-drying for 5 days and then oven-drying at 100 °C for 24 h. The dried cotyledon was ground using electric blender into fine particle size and stored in an air tight container. Thereafter, 36.95 g milled sample was placed in a thimble before the addition of *n*-hexane-chloroform mixture (50:50 mL) into the round bottom flask fitted with a reflux condenser and heated at 65 °C for 6 h. The liquid condensate obtained via this process was then made to drip into a thimble containing the milled material. The solvent was subsequently recovered from the extract using a water bath, leaving the extracted oil behind. Thereafter, the oil residue was exposed to air to allow the solvent to evaporate, after which the oil extracted was then characterized.

Figure 3.1: Image of African Star Apple and associated cotyledon seeds and edible flesh

Source: Fieldwork, 2023

3.5 Preparation of Biodiesel

The transesterification reaction of oil feedstock was performed in a 500 mL capacity beaker using the procedure previously reported and performed using the African star apple seed oil and the four prepared catalysts namely the carbonized ASA shell catalyst, carbonized cow bone catalyst, sulphonated ASA shell catalyst and sulphonated cow bone catalyst were used one after the other under three different reaction conditions (temperature, solid catalyst dosage and time)[3]. The biodiesel yield of the reactions was then determined according to the Equation 3.3[4].

$$\%\ \text{yield of biodiesel} = \frac{\text{weight of biodiesel produced}}{\text{weight of oil used for biodiesel}} \times 100 \quad \text{...Equation 3.3}$$

In transesterification, triglycerides (fats) contained in oils (feedstocks) react with alcohol to produce biodiesel (fatty acid alkyl esters (FAAE) and glycerol. Transesterification, otherwise called alcoholysis is a process of exchanging one alcohol for another, which is similar to the hydrolysis reaction, except that alcohol is used in place of water in this reaction. It is a series of reversible, step-by-step reactions that transform triglycerides into products. In the first phase, triglycerides react with alcohol to create diglycerides, which are then transformed into monoglycerides and glycerol, each of which produces an alkyl ester[4]. Figure 3.2 illustrates the processes involved in the production of the biodiesel.

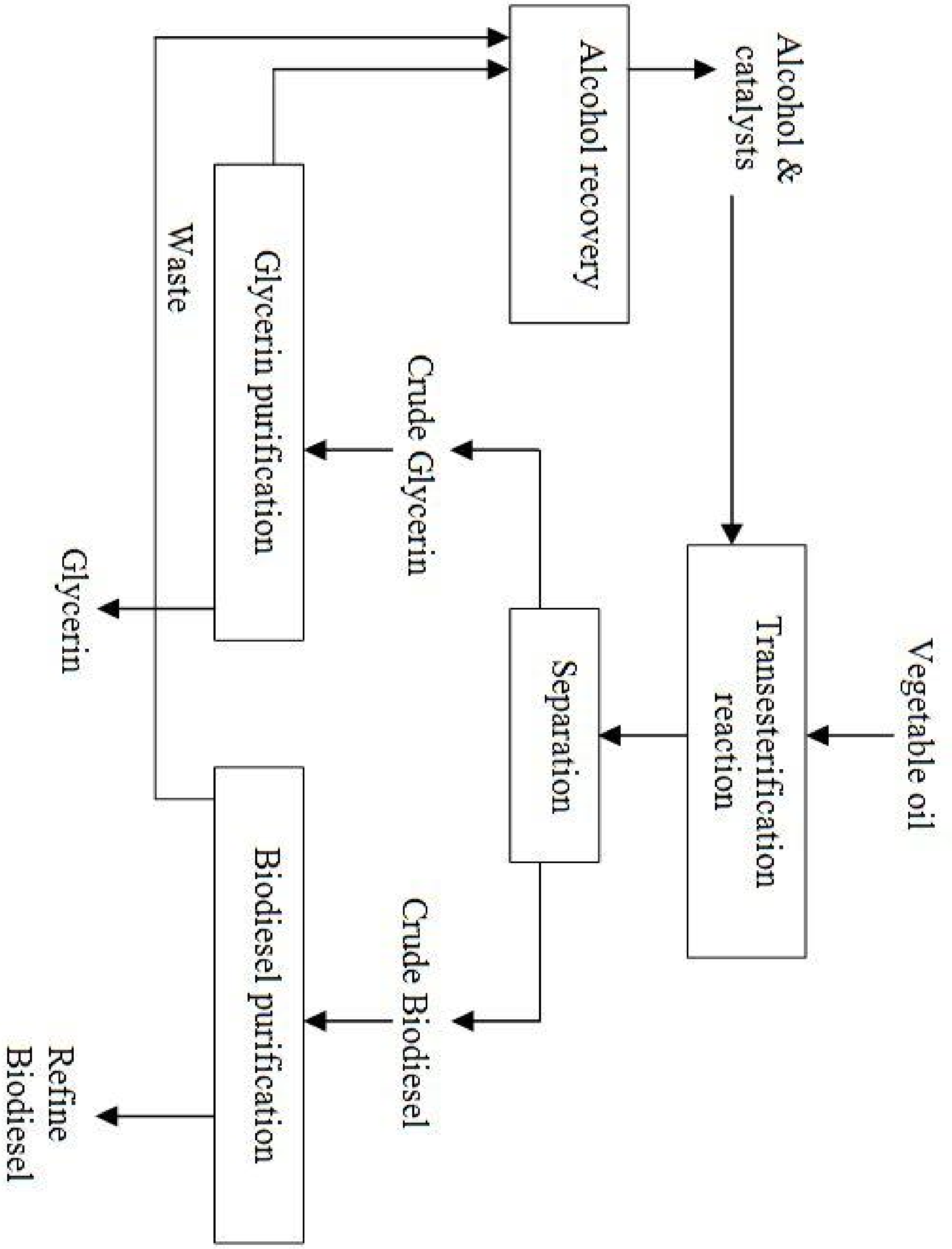

Figure 3.2: Flow chart for the production of biodiesel from African Star Apple Seed. Source: Fieldwork, 2023

3.6 Temperature Effect on Biodiesel Yield

A mixture of extracted African star apple oil and methanol at a ratio of 1:4 was charged into a 500 mL conical flask covered with aluminum foil. To the mixture was added 0.5 g of the prepared catalyst and heated at 60 °C on a magnetic stirrer for 1 h. After 1 h, the reaction mixture was filtered using a Whatman 42 filter paper (125 mm diameter) and centrifuged to separate the catalyst. The mixture was then transferred to a separating funnel and allowed to stand for 8 h to for the glycerol to be separated from the biodiesel phase. The bottomed layer (glycerol) was drained out, leaving the upper layer (the biodiesel) to be collected carefully and washed with hot deionized water. The synthesized biodiesel was then stored in an air tight bottle for further studies. The above procedure was repeated with three other catalysts to determine the optimum temperature, with catalyst dosage of 0.5 g at a constant time of 1 h while the reaction temperature was varied in five experiments at temperature of 30, 40, 50, 60 and 70 °C.

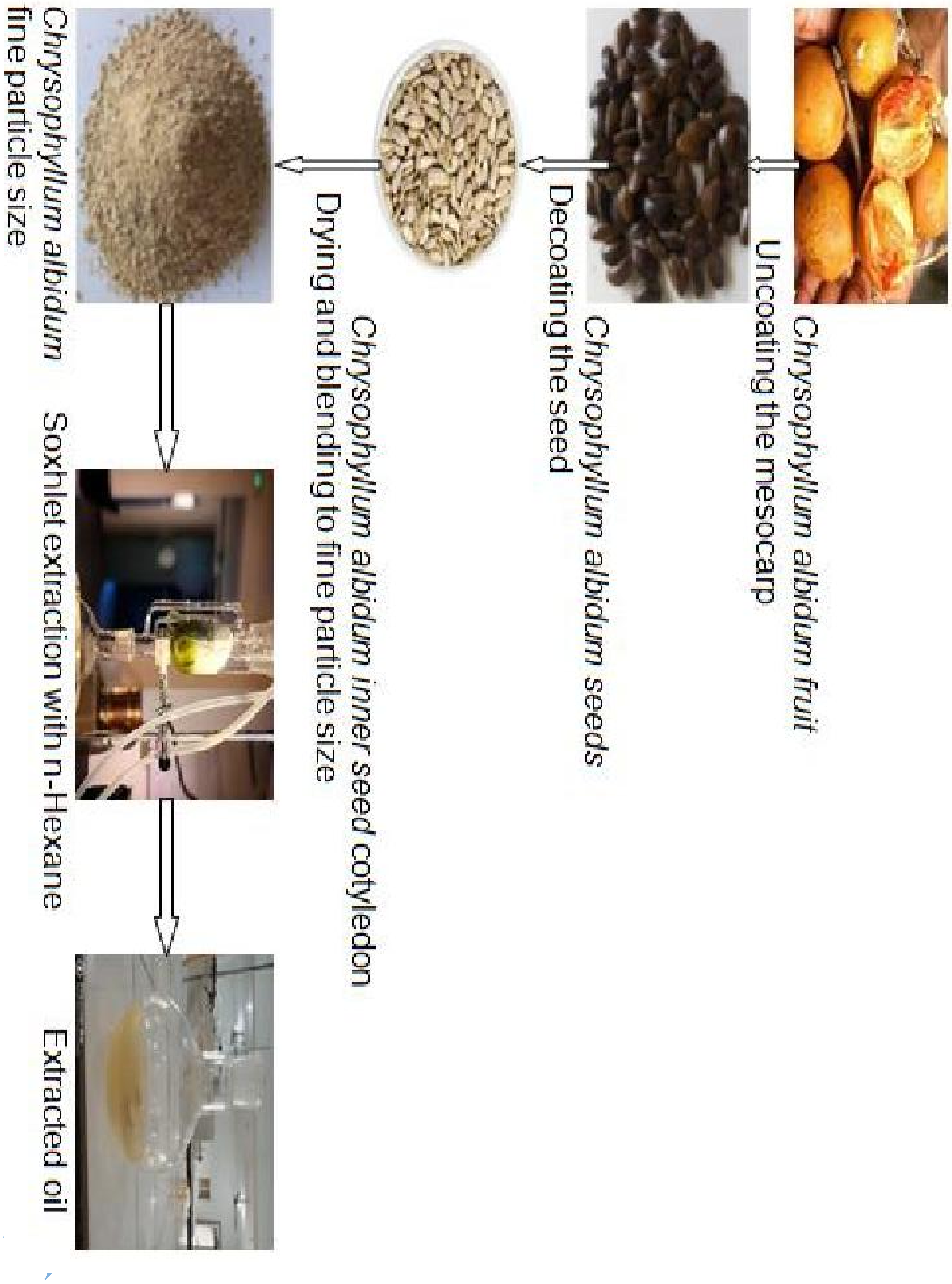

Figure 3.3: Diagrammatic sequence of the processes of extraction of oil from African Star Apple

Source: Fieldwork, 2023

3.7 Effect of Solid Acid Dosage on Biodiesel Yield

The effect of catalyst dosage was determined using the procedure described in Section 4.3.3 and 4.3.4 and various amount of solid acid catalysts prepared (0.5, 1, 1.5, 2 and 2.5 g) was used at 60 °C for a duration of 1 h.

3.8 Effect of Time on Biodiesel Yield

In order to study the effect of time on the biodiesel preparation process, the same procedure used for (a) were employed but the optimized catalyst weight obtained from (b) and reaction temperature obtained from (a) were maintained whilst the reactions were carried at different times of 1, 2 ,3, 4 and 5 h to obtain optimum yield.

3.9 GC Analysis of the Biodiesel Produced

The composition of the biodiesels produced were analyzed using gas chromatography-mass spectroscopy (GC-MS-QP2010 plus Shimadzu, Japan). The mobile phase is helium and the stationary phase is the column of model HP5MS Agilent technologies of length 30 m, internal diameter 0.320 mm and the thickness is 0.25 mm. The GC was operated at 60 °C held for 2 min at 200 °C/min to the temperature of 260 °C and the injector temperature was 260 °C, while the mode of analysis was spitless and the volume of sample used was 1 µL.

3.10 Physiochemical Properties of Biodiesels

The products quality was determined on the properties of the biodiesels such as colour, odour, state of oil, percentage yield, density, viscosity, acid value, saponification, and iodine value and the values compared with ASTM standards[5].

3.10.1 Viscosity

The resistance of the biodiesels was analyzed to determine the flow behavior of the oils at 40°C. The test was carried out using Ostwald method. The viscometer and thermostat were set into a beaker with water and clamped vertically. It was filled with distilled water to a volume to fill the viscometer and heated at 40°C. The samples (biodiesels) were poured in the viscometer through arm 1 till it reaches to the mark II as shown in Figure 2.6 using a pipette filler. The samples were applied using pipette filter so that it flows through the fine capillary tube to fill it to mark IV as shown in the Figure 3.4[4]. Then, the pipette filler attached to arm 2 was removed and the upper meniscus of the sample was observed. When the meniscus aligned with the mark III, the stopwatch was stopped. The total time for each sample was noted. The blank was done using distilled water. The Equation 3.4 below was used in the calculation.

$$\eta_1/\eta 2 = t_1 d_1/t_2 d_2 \qquad \text{Equation 3.4}$$

Where $\eta 1$ =viscosity of liquid 1, $\eta 2$ =viscosity of liquid 2

t_1 = flow time of liquid, t_2 = flow time of liquid 2

d_1= density of liquid d_2= density of liquid 1

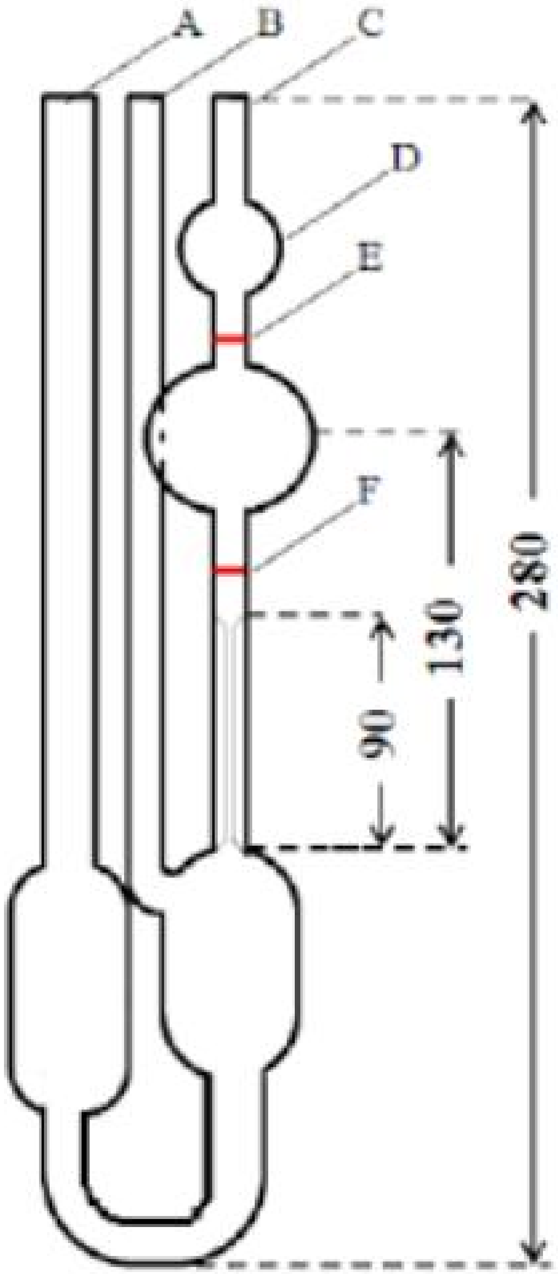

Figure 3.4: Ubelhoder Viscometer

Source[4]

3.10.2 Density

The densities of the biodiesels were determined using a specific gravity bottle according ASTM D792 standard at 23 °C[5]. At first, mass of an empty 50 mL specific gravity bottle (m_1) is filled to the brim with as-obtained biodiesel to obtain (m_2) as adopted for the estimation of the density using equation:

Density = $(m_1 - m_2)/v$ Equation 3.5

Where m_1 = mass of empty specific gravity bottle with the lid on it (kg)

m_2 = mass of specific gravity bottle filled with the biodiesel (kg)

v = volume of the bottle for specific gravity (50 mL)

3.10.3 Saponification Value

Saponification value which measures the molecular weight of the triglyceride and is used to characterized the oil property. Low saponification value implies high molecular weight and high saponification value indicates low molecular weight of the triglyceride[6]. The saponification value is defined as the number of milligrams of KOH required for saponifying 1g of fat under the conditions specified. About 2 g each of biodiesels were used to test the saponification value using standard method[7]. The weighed biodiesel was transferred into a flask containing measured KOH and was connected to air condenser and then boiled for 30 min. Then the mixture was cooled and 3 drops of phenolphthalein was added as an indicator. The mixture was then titrated with against standard 0.5 M HCl until the pink color disappeared. In the same way the blank was titrated in the absence of biodiesel. The saponification value was determined using Equation 3.6.

$$\text{Saponification value} = \frac{(\text{Blank} - \text{titre})}{\text{weight of biodiesel (g)}} \times 28.06 \qquad \text{Equation 3.6}$$

3.10.4 Iodine Value

Iodine value is used to determine fatty acids unsaturation, reported in grams as the percentage of iodine absorbed (% iodine absorbed) per gram of sample. The iodine value of the biodiesel samples was determined by Wijs method[7,8]. In this study, 0.5 g of the biodiesel sample was used to test the unsaturation of the compounds. 15 mL of carbon tetrachloride was added to dissolve the biodiesel after which a 25 mL Wijs reagent was added. A stopper was then inverted and the content of the flask was shaken gently. The flask was then placed in the dark for 5 min. Thereafter, 20 mL of 10 % aqueous potassium iodide and 150 mL of distilled water was added using a measuring cylinder. The content was titrated with 0.1 M sodium thiosulphate solution until the yellow color almost disappeared. A few drops of starch indicator were added and the titration continued by adding sodium thiosulphate drop-wise until blue coloration disappeared after vigorous shaking. The process was repeated with blank under the same conditions. The iodine value (IV) was calculated using Equation 3.7.

$$IV = 12.69 \times T \times (V_1 - V_2) / m \qquad \text{Equation 3. 7}$$

Where V_1 = volume of sodium thiosulphate used for the blank,

V_2 = volume of sodium thiosulphate used for the test portion,

T = molarity of sodium thiosulphate used,

m = Mass in gram of the test portion.

3.10.5 Acid Value

The acid value of the biodiesel samples prepared was determined by AOCS 5a-40 [9]. It is the amount in milligrams of KOH required to neutralize the free fatty acids in 1 g of sample. 5 g biodiesel product sample weighed into an Erlenmeyer flask, followed by the addition of 50 mL of neutralized solvent (1:1 diethyl ether/EtOH), after which it was heated at 40°C. The obtained sample was then titrated against standard KOH to give permanent pink colour, according to Equation 3.8.

$$(AV) = 56.1 \times v \times M/W_s \qquad \text{Equation 3.8}$$

Where W_s = weight of sample (biodiesel),

V= volume of potassium hydroxide solution titrated,

M = molarity of potassium hydroxide.

Endnotes

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Chapter Four

Results and Discussion of Findings

This chapter presents the results of the analysis performed in other to realize the stated objectives of this study. This was presented under the following sub-topics:

i. Catalyst characterization

ii. Oil characterization

iii. Recyclability of the catalysts

4.1 Characterization of the Catalyst

4.1.1 Physiochemical Properties of Catalysts

The result of the physiochemical properties of the four catalysts are highlighted in Table 4.1

Table 4.1: Physiochemical Properties of the Catalysts

Samples	Type	Crystalline size(nm)	pH	Bulk density
African Star Apple Shell	Pristine	98.8	3.35	
African Star Apple Shell	Sulphonated	98.79	7.00	0.68
Cow Bone	Pristine	80.57	3.46	0.46
Cow Bone	Sulphonated	80.32	7.00	

Source: Fieldwork, 2023

4.1.2 XRD of the Pristine and Sulphonated ABP, ASP, ABS, and ASS

The characterization of the four catalysts (African star apple shell pristine (ASP) and Animal (Cow) bone pristine (ABP) and the African star apple shell - sulphonated (ABS) and Animal (Cow) bone sulphonated (ABS) catalysts were performed using X-ray diffraction (XRD) in other to confirm the crystalline or amorphous nature of the catalysts and Fourier Transform Infrared (FT-IR) was carried out to validate the functional groups. The results are shown in Figures 4.1 and 4.2, respectively.

4.1.3 FTIR Analysis of the Catalyst

The FITR spectra analysis of the carbonized and sulphonated African star apple shell and cow bones (Animal) was carried out to determine the presence of sulphonic functional group using Perkin Elmer1725x spectrometer. The results were as shown in Figures 4.3, 4.4 and 4.5, and Tables 4.2a, 4.2b, 4.3a and 4.3b.

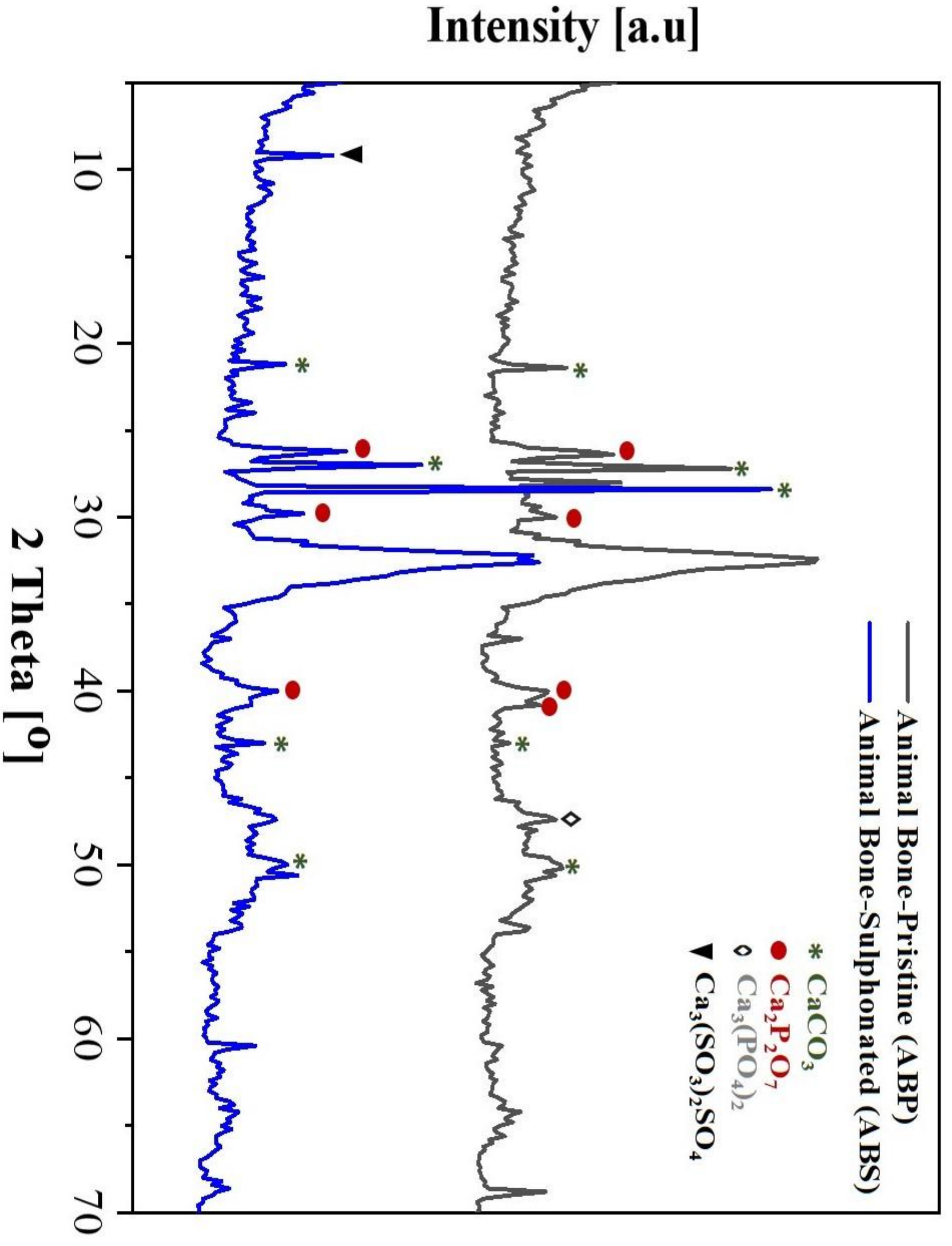


Figure 4.1: Spectra of Animal (Cow) bone pristine (ABP) and Animal bone sulphonated (ABS)

Source: Fieldwork, 2023

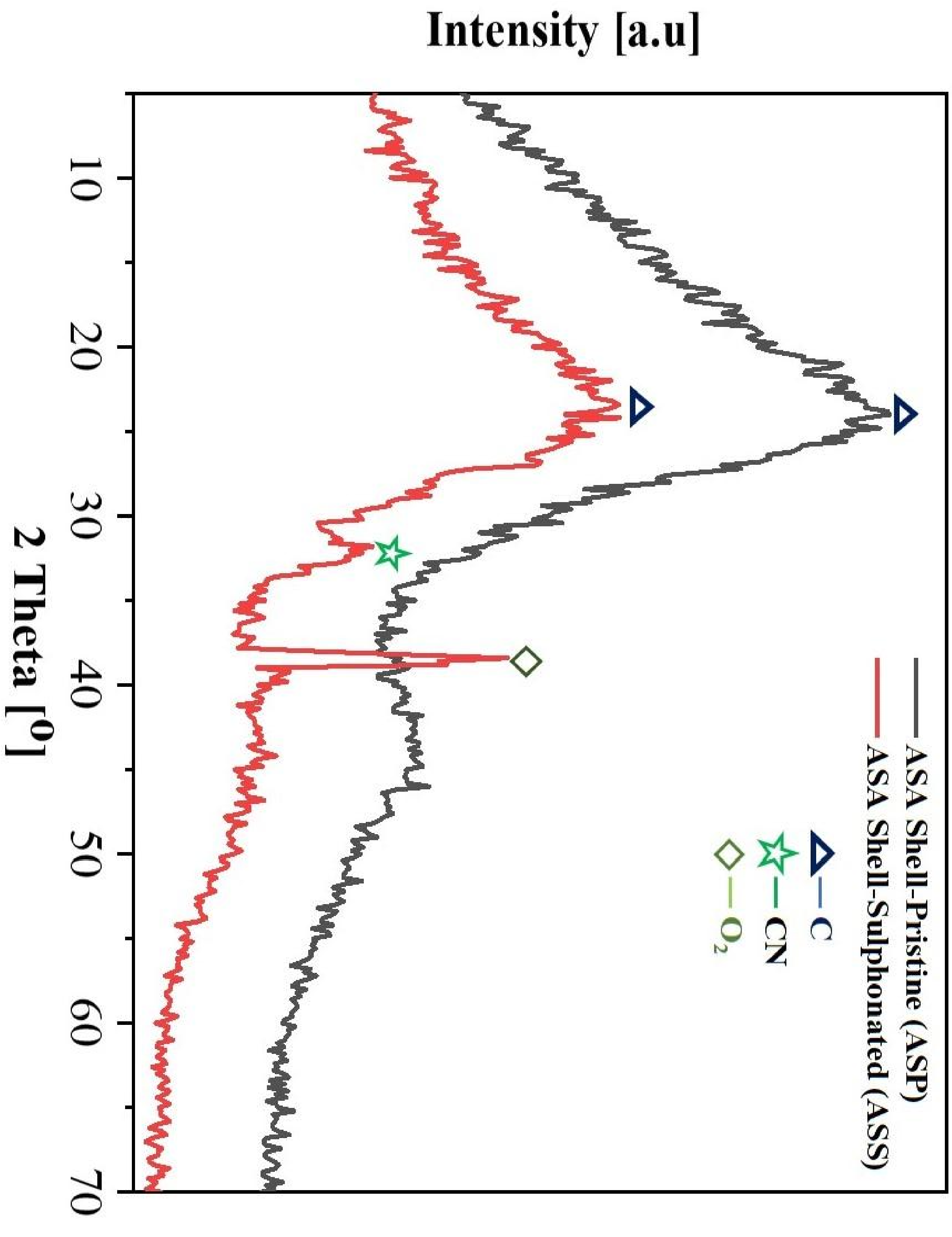
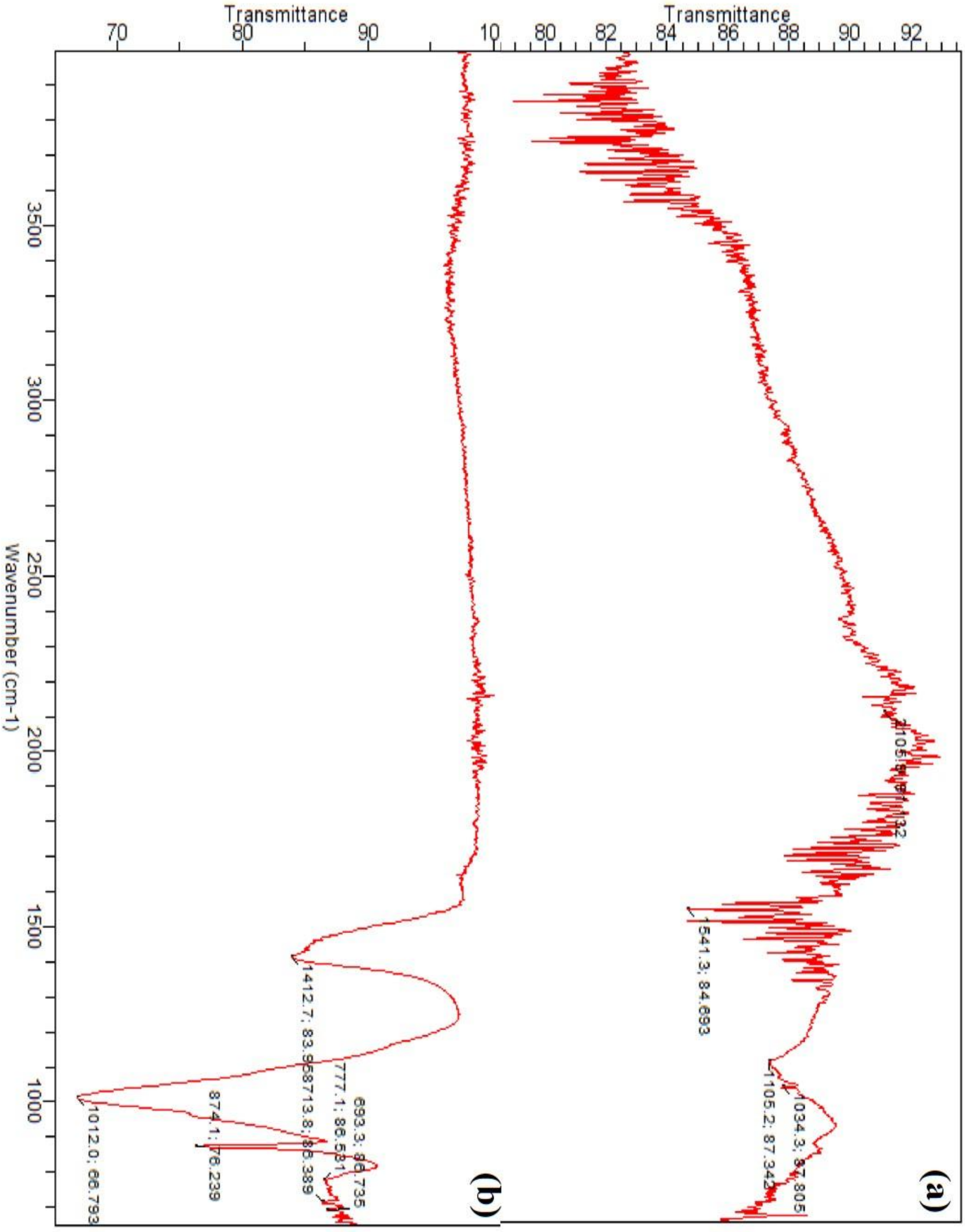


Figure 4.2: Spectra of ASA Shell-Pristine (ASP) and ASA Shell-Sulphonated (ASS)

Source: Field work, 2023.



4.3: FT-IR spectra of carbonized cow bone (a) pristine (b) sulphonated.

Source: Fieldwork, 2023

Table 4.2a: FT-IR Spectra of Carbonized Cow Bone Pristine

Serial no	Vibration	Frequency (cm^{-1})
1	O-C-H, P-O asymmetrical bend stretch	1034.3
2	Amide N=H, C-N, O-Ca-O	1104.2
3	Aromatic C=H	1541.3
4	C=C conjugated	2105.9

Source: Fieldwork, 2023

Table 4.2b: FT-IR Spectra of Cow Bone Sulphonated.

Serial no	Vibration	Frequency (cm^{-1})
1	O=C=O	693.33
2	Ca – O	713.8
3	O=S-H	1012.0
4	-C=O inorganic carbonate	1412.7

Source: Fieldwork, 2023

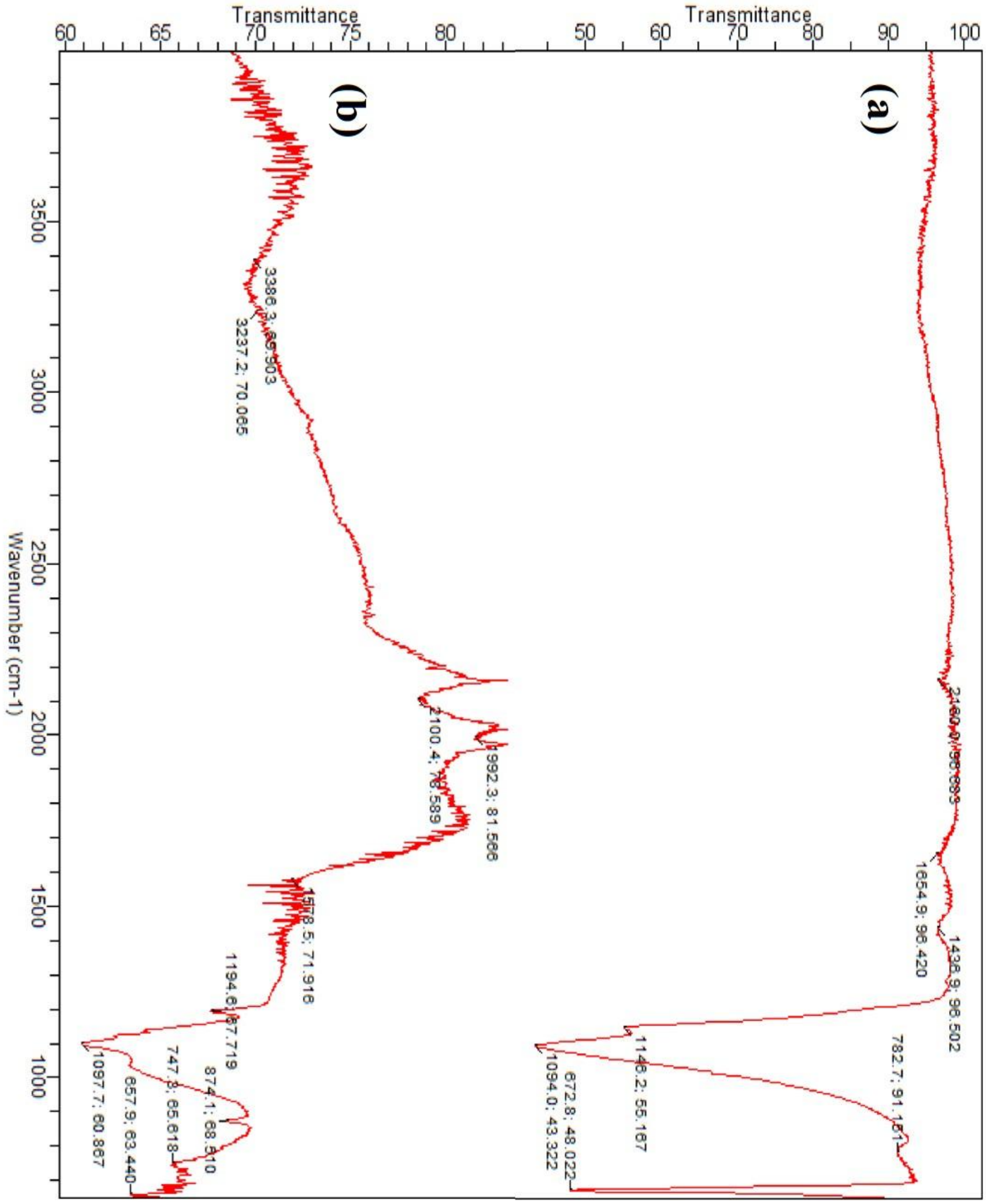


Figure 4.4: FT-IR Spectra of African Star Apple Shell ASA: (a) Pristine; (b) Sulphonated.

Source: Fieldwork, 2023

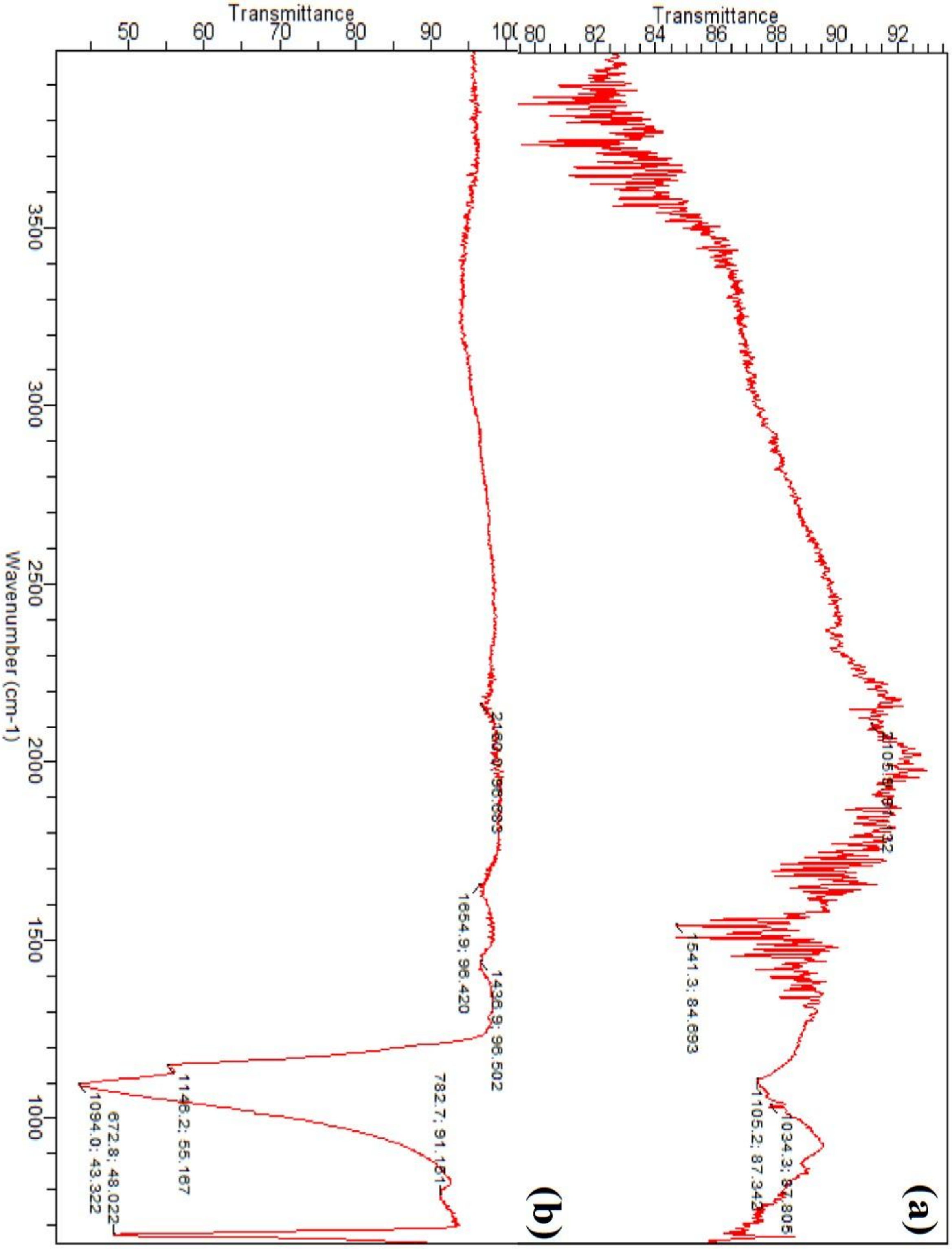


Figure 4.5: FI-TR Spectra (a) Cow Bone-Pristine; (b) Sulphonated

Source: Fieldwork, 2023

Table 4.3a: FT-IR Spectra of African Star Apple Shell ASA Pristine

Serial no	Vibration	Frequency (cm^{-1})
1	Aromatic C-H bend	672.8
2	C-H	782.7
3	C-O, C-H stretching	1094.0
4	N=H, C-O-C	1146.2
5	C-O-H bend	1436.9
6	=S-O-H, C=O	1654.9
7	=C-O-H	2160.0

Source: Fieldwork, 2023

Table 4.3b FT-IR Spectra of African Star Apple Shell (ASA) Sulphonated

Serial no	Vibration	Frequency (cm^{-1})
1	C–H bend	651.9
2	= C- H	747.3
3	S–O stretch	874.1
4	C–C stretch	1194.6
5	Aromatic C= C	1578.5
6	C=C conjugated	2100.4
7	O–H	3237.2
8	C–O –H	3386.3

Source: Fieldwork, 2023

4.2 Oil characterization

4.2.1 Physiochemical Properties of the Extracted Oil

The physiochemical properties of the oil extracted from the African star apple seeds with n-hexane and chloroform in a ratio 50:50ml is presented in Table 4.4

Table 4.4: Physiochemical Properties (Characterization) of the Extracted African Star Apple Seeds Oil

Physiochemical Property	Reported Values
Odour	Pleasant
Colour	Honey -like
State at room temperature(28 °C)	Liquid
Oil content (%)	28.88%
Specific gravity	0.96
Acid value (mg KOH/g)	16.80
Iodine value (mg/100g)	47.60
Saponification value (mg KOH/g)	220.40
Viscosity	3.30

Source: Fieldwork, 2023

4.2.2.1 GC-MS Analysis of African Star Apple Seed Oil

The GC-MS analysis is reported in Figure 4.6

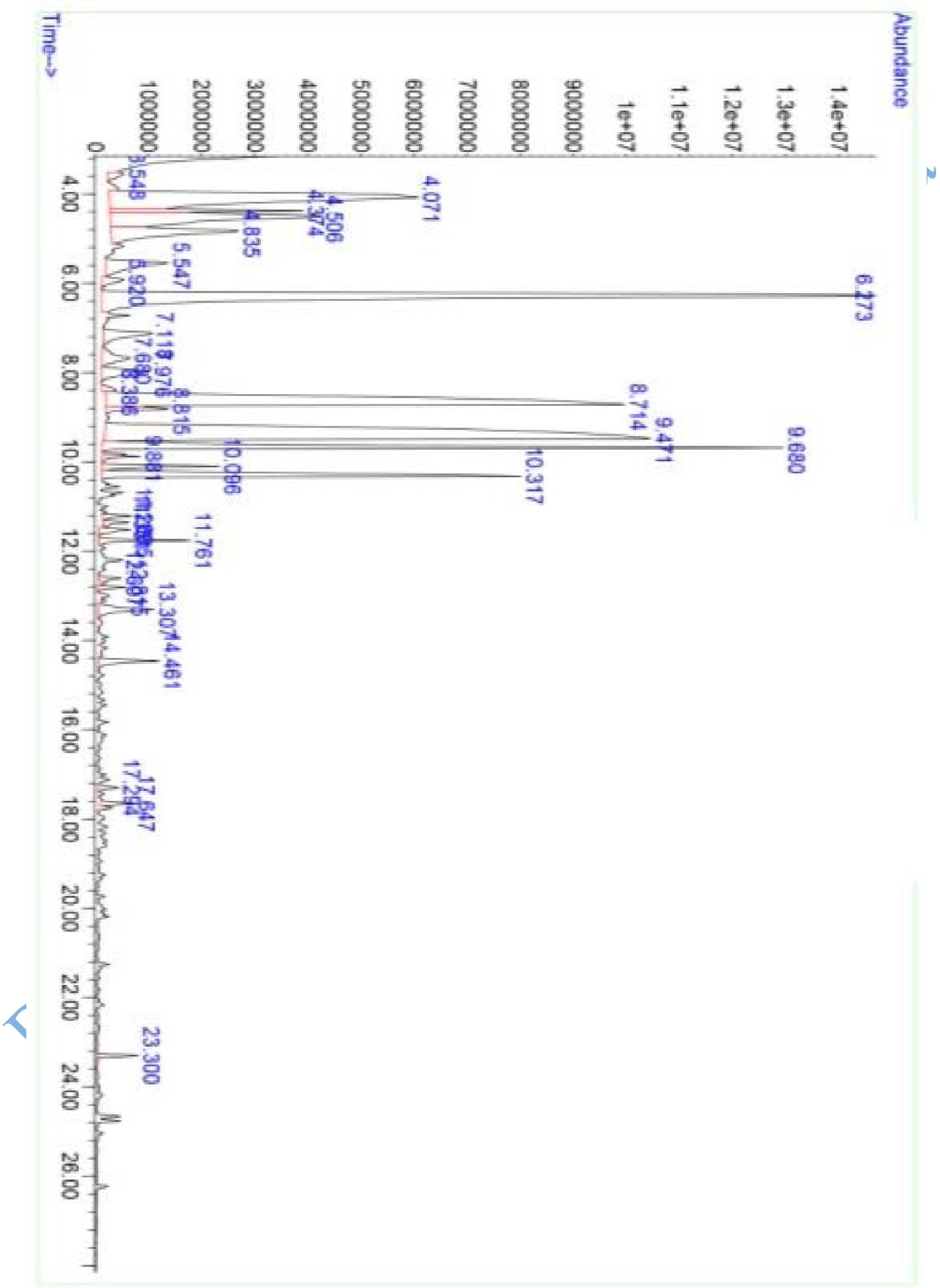


Figure 4.6: Chromatogram of African Star Apple Seed Oil using ASA Shell Catalyst

Source: Fieldwork, 2023

4.2.2.2 GC-MS of Biodiesel using Animal (Cow) Bone Catalyst

The result of the biodiesel from African star apple seed oil using cow bone catalysts is presented in Table 4.5.

Table 4.5: GC-MS Analysis of Biodiesel from ASA Seed Oil Using Cow Bone Catalysts

Retention Time	Name of Compound	Area %	MW
7.679	Methyltrans-3-chloropropenoate	12	119.989
9.667	p-Nitrophenyl hexanoate		12237.1
8.809	Hexan-3-yl 2-methylbutanoate	50	186.162
11.767	Methyl 2-(trimethylsilyl) ethyl malonate	17	218.097

Source: Fieldwork, 2023

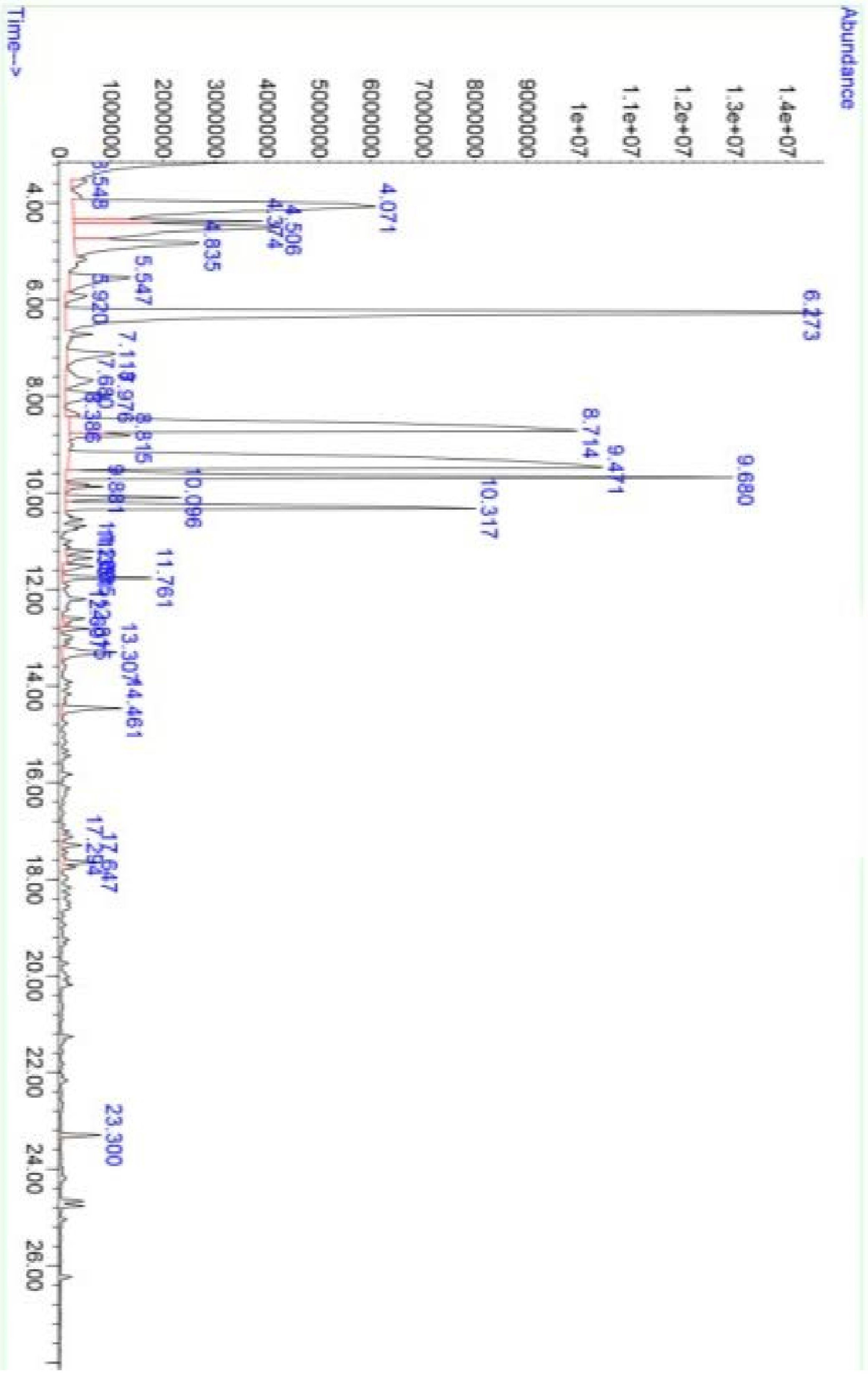


Figure 4.7: Chromatogram of Biodiesel from ASA Seed Oil Using Cow Bone Catalyst

Source: Fieldwork, 2023

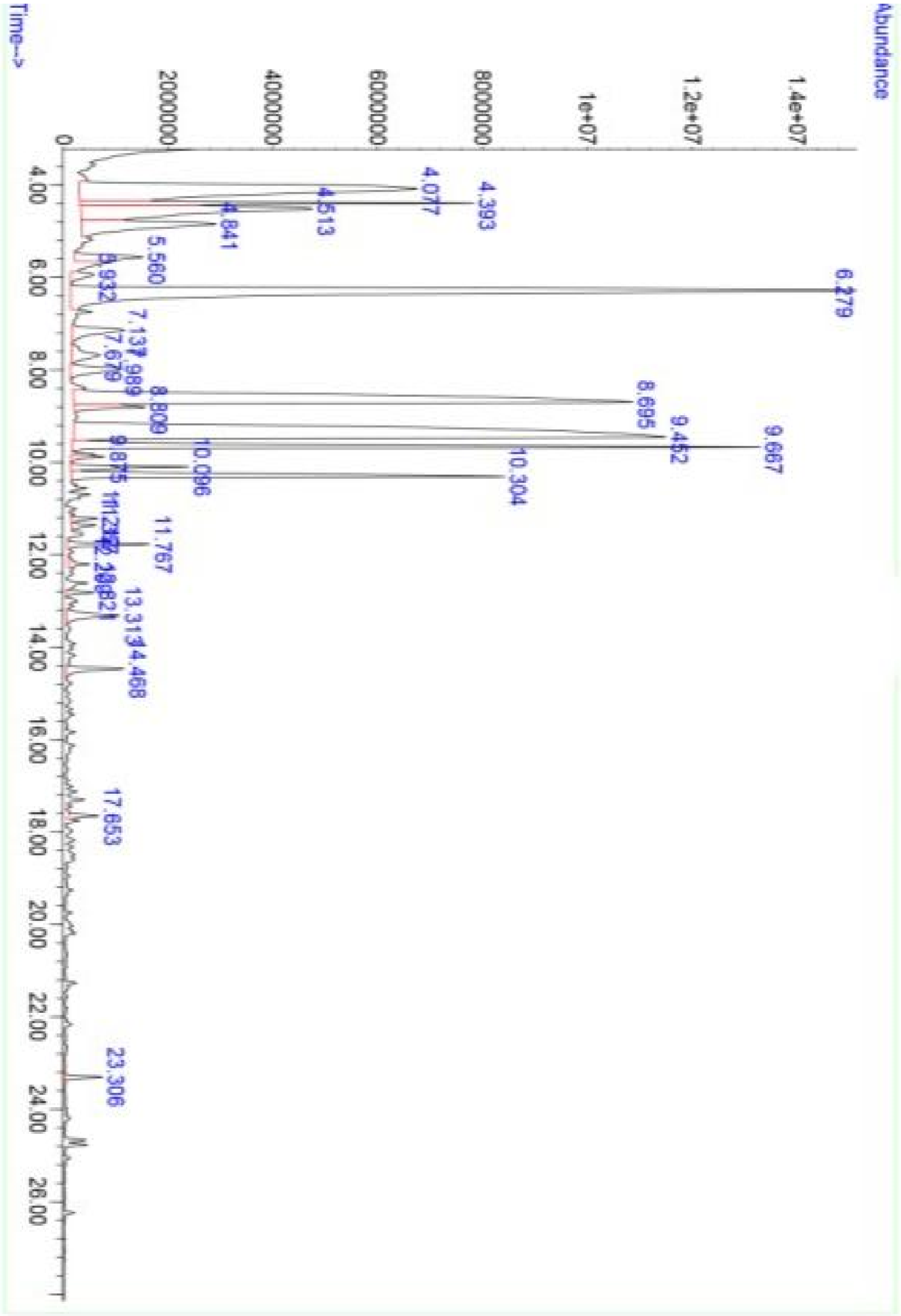


Figure 4.8: Chromatogram of Biodiesel from ASA Seed Oil Using ASA Shell Catalyst

Source: Fieldwork, 2023

The result of the biodiesel from African star apple seed oil using African star apple shell catalyst was presented in Table 4.6

Table 4.6: GC- MS Analysis of Biodiesel from ASA Seed Oil Using African Star Apple Shell Catalyst

Retention Time	Name of Compound	Area %	MW
7.68	Methyl trans-3-chloropropenoate	12	119.989
8.809	Hexan-3-yl 2-methylbutanoate	50	186.162
11.767	Methyl trans-3-chloropropenoate	17	218.097

Source: Fieldwork, 2023

4.3 Catalytic Performance

The catalytic performance of the catalyst used in this study was studied. The process conditions of temperature, time and catalytic dosage was reported in Tables 4.7, 4.8 and 4.9 and Figures 4.9, 4.10, and 4.11 respectively.

4.3.1 Effect of Temperature on Biodiesel Yield using ASA Shell Pristine

Table 4.7: Effect of Temperature on Biodiesel Yield Using ASA Shell Pristine

Temperature (˚C)	Biodiesel Yield (%)
30	32.4
40	39.8
50	56.1
60	71.2
70	32.9

Source: Fieldwork, 2023

4.3.1.1 Effect of Temperature on Biodiesel Yield using ASA Shell Sulphonated

Table 4.8: Effect of temperature on biodiesel yield using ASA shell sulphonated

Temperature (˚C)	Biodiesel Yield (%)
30	44.3
40	47.5
50	60.3
60	74.6
70	42.5

Source: Fieldwork, 2023

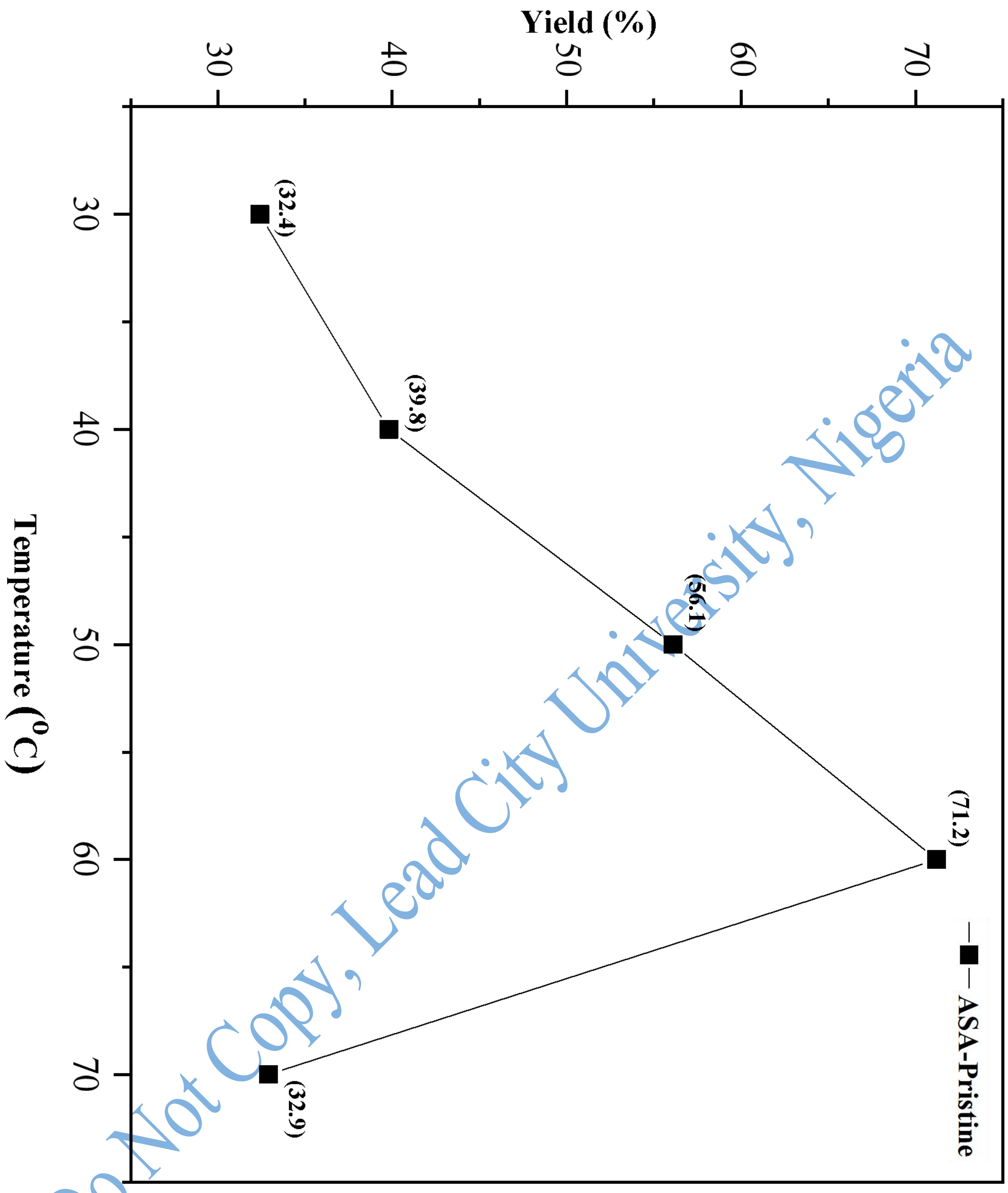


Figure 4.9: Temperature effect on biodiesel yield using 1g of pristine ASA seed oil in 1 h^1.

Source: Fieldwork, 2023

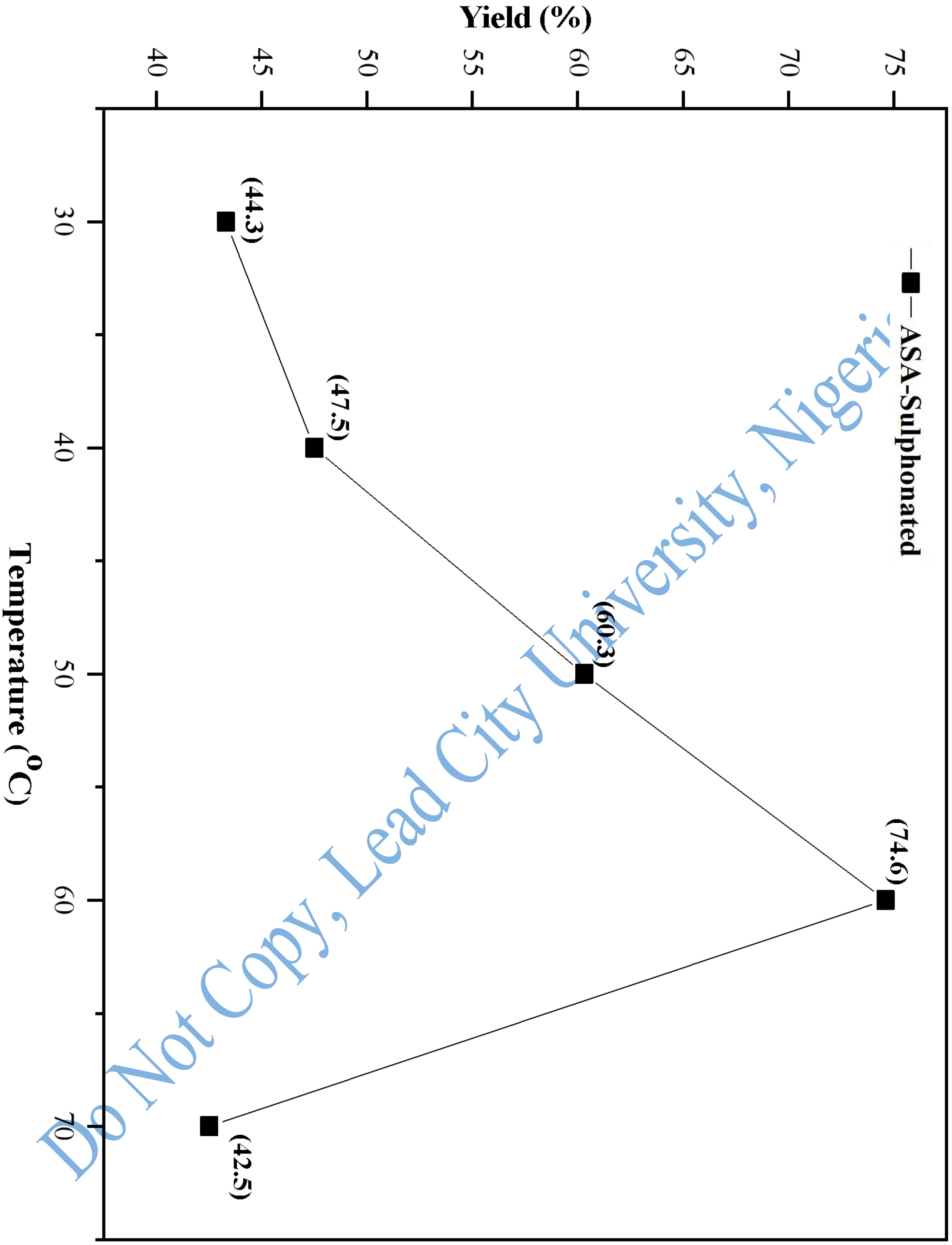


Figure 4.10: Temperature effect on biodiesel yield using 1g of sulphonated ASA seed catalyst in 1 h^2

Source: Fieldwork, 2023

4.3.2 Effect of Temperature on Biodiesel Yield using Pristine Cow Bone

The effect of temperature on biodiesel yield using pristine cow bone catalyst was reported in Table 4.9 and Figure 4.11

Table 4.9: Effect of Temperature on Biodiesel Yield Using Pristine Cow Bone

Temperature (˚C)	Biodiesel Yield (%)
30	41.6
40	49.6
50	61.8
60	73.1
70	28.8

Source: Fieldwork, 2023

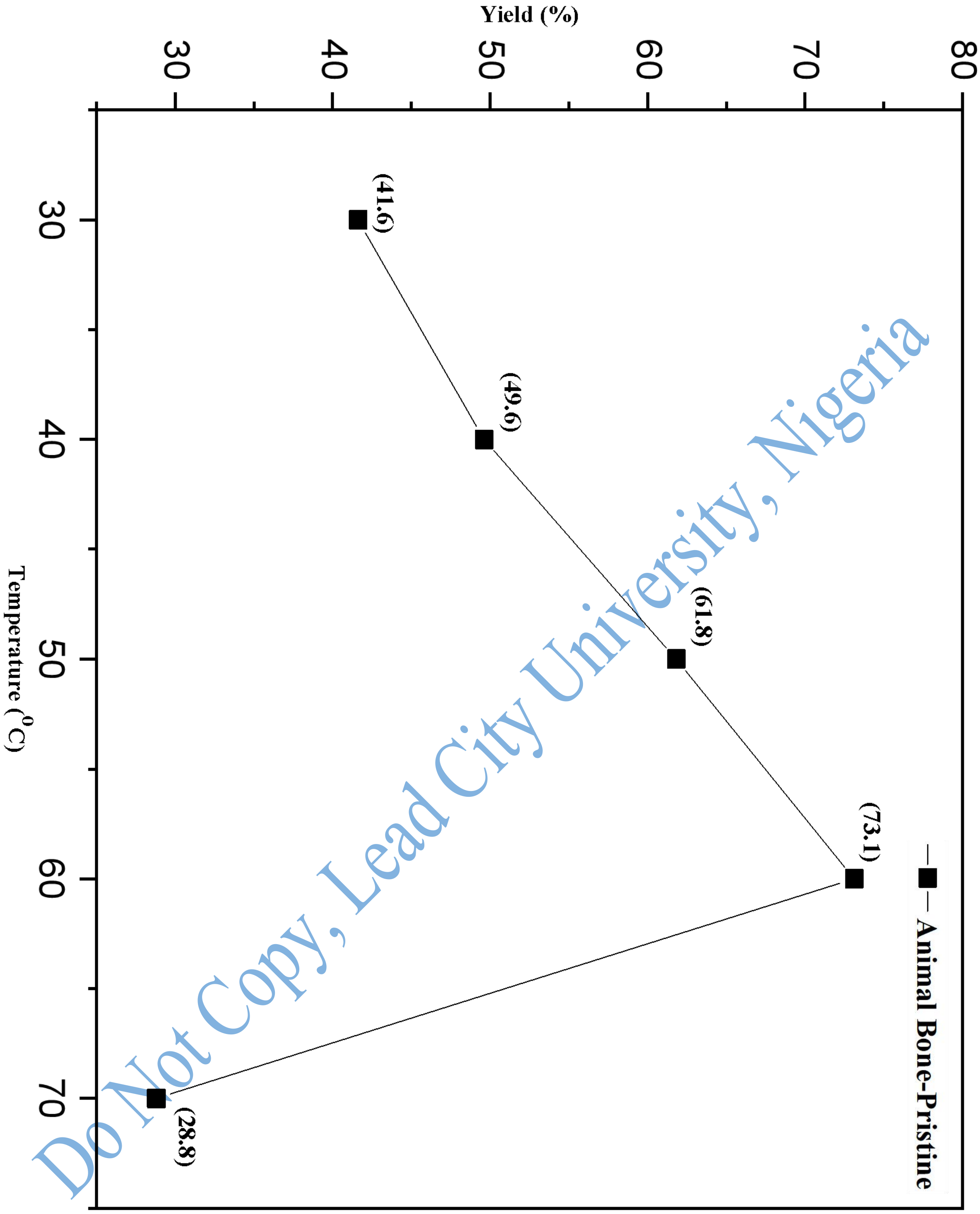


Figure 4.11: Temperature effect on biodiesel Yield using 1g of pristine cow bone in 1 h^3

Source: Fieldwork, 2023

4.3.2.1 Effect of Temperature on Biodiesel Yield using Pristine Cow Bone

The effect of temperature on biodiesel yield using pristine cow bone catalyst was reported in Table 4.10 and Figure 4.12

Table 4.10 Effect of Temperature on Biodiesel Yield using Cow Bone Sulphonated

Temperature (°C)	Biodiesel Yield (%)
30	48.5
40	49.6
50	68.2
60	**75.8**
70	33.6

Source: Fieldwork, 2023

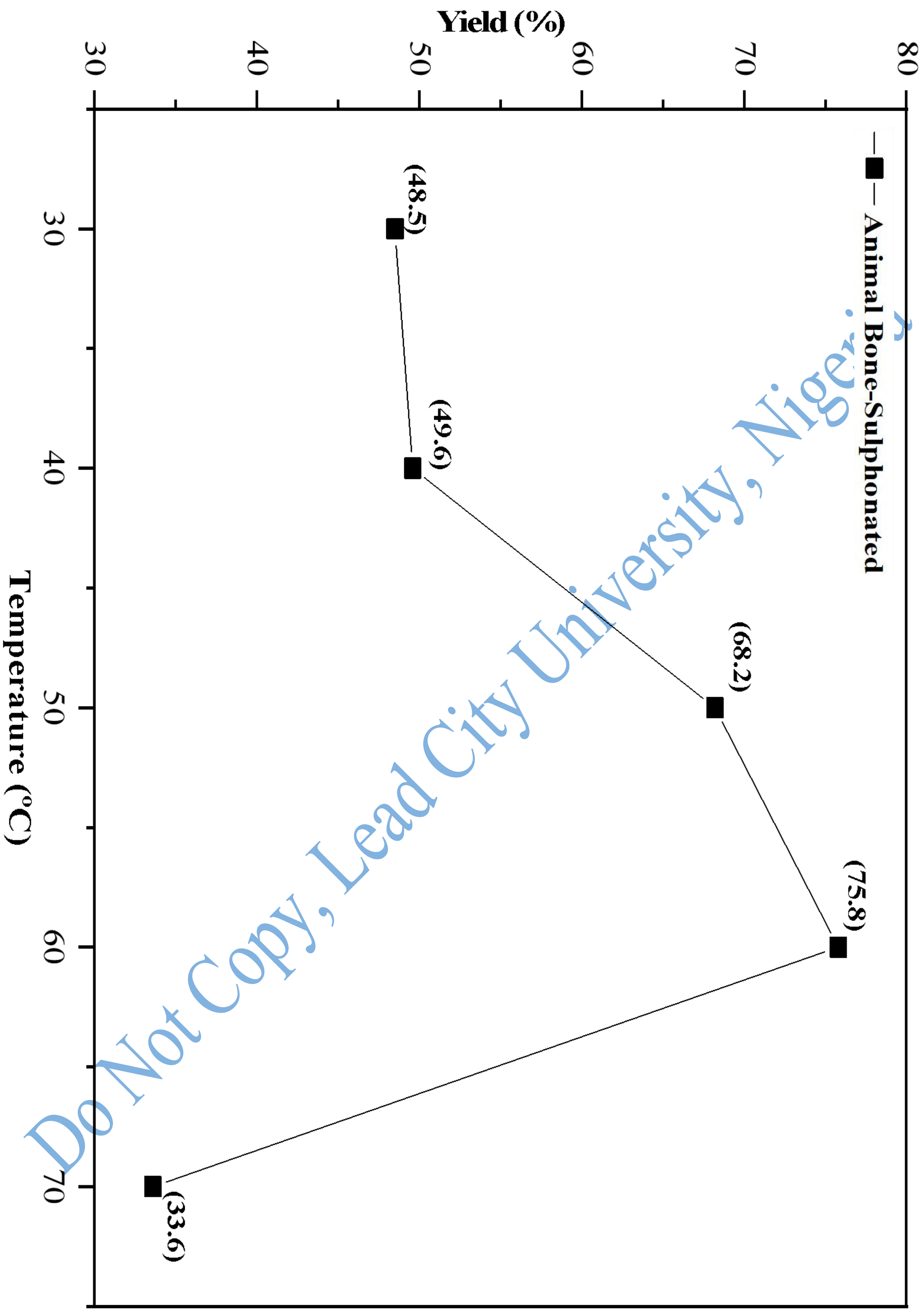


Figure 4.12: Effect of temperature on biodiesel yield using cow bone sulphonated[4]

Source: Fieldwork, 2023

4.3.3Effect of Dosage on Biodiesel Yield Using ASA Shell Pristine Catalyst

The effect of catalyst dosage on biodiesel yield using African Star Apple shell pristine catalyst was reported in Table 4.11 and Figure 4.13.

Table 4.11 Effect of Catalytic Dosage on Biodiesel Yield Using ASA Shell Pristine Catalysts

Catalytic Dosage (g)	Biodiesel Yield (%)
0.5	49.5
1.0	**72.9**
1.5	67.8
2.0	66.4
2.5	59.6

Source: Fieldwork, 2023

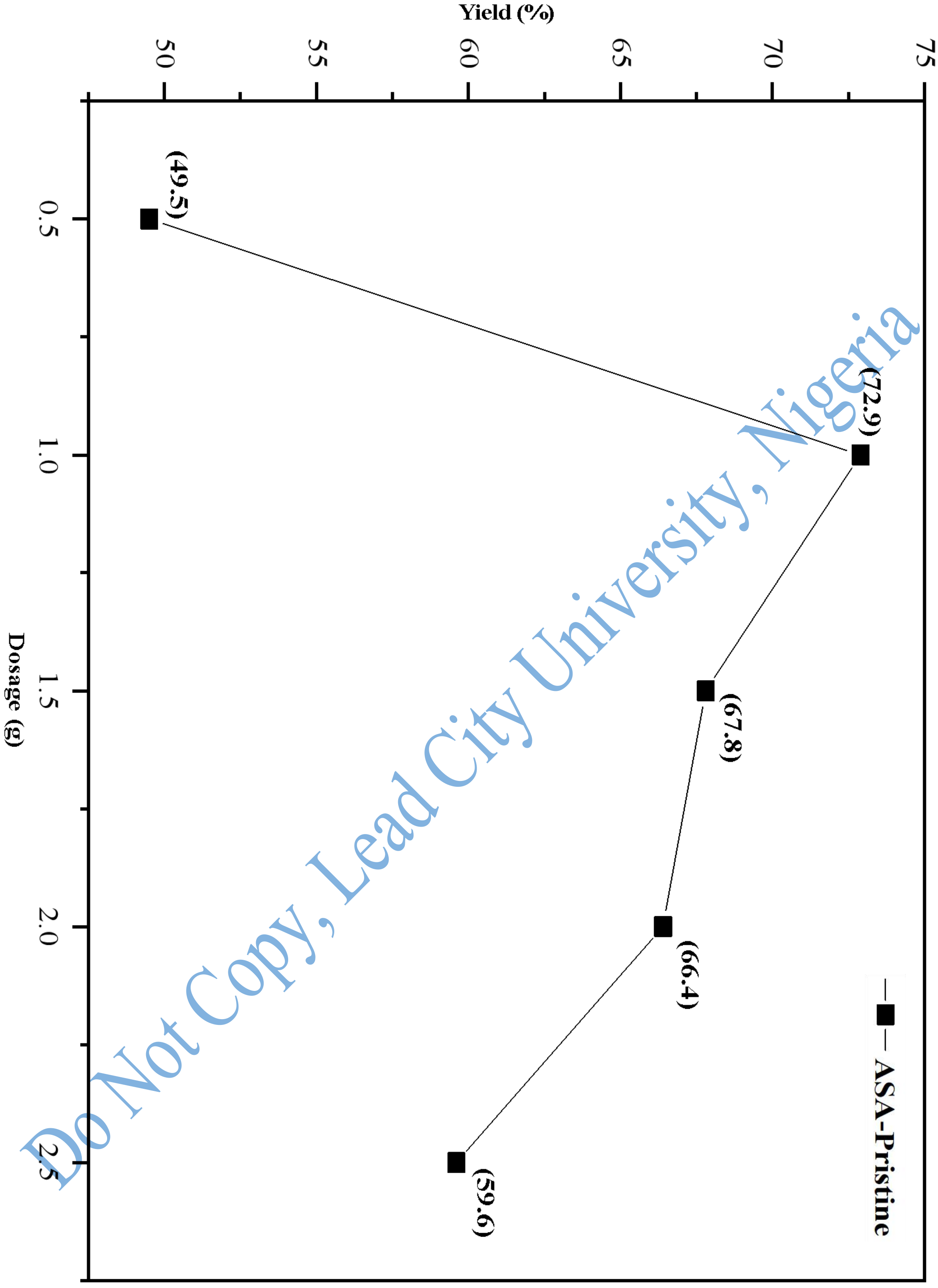


Figure 4.13: Effect of catalytic dosage on biodiesel yield using ASA shell-pristine catalysts[5]

Source: Fieldwork, 2023

4.3.3.1 Effect of Dosage on Biodiesel Yield using ASA Shell Sulphonated Catalyst

The effect of catalyst dosage on biodiesel yield using African Star Apple shell pristine catalyst was reported in Table 4.12 and Figure 4.14

Table 4.12: Effect of Dosage on Biodiesel Yield Using ASA Shell Sulphonated Catalysts

Catalytic dosage (g)	Biodiesel Yield (%)
0.5	53.4
1.0	**75.5**
1.5	69.9
2.0	66.0
2.5	55.4

Source: Fieldwork, 2023

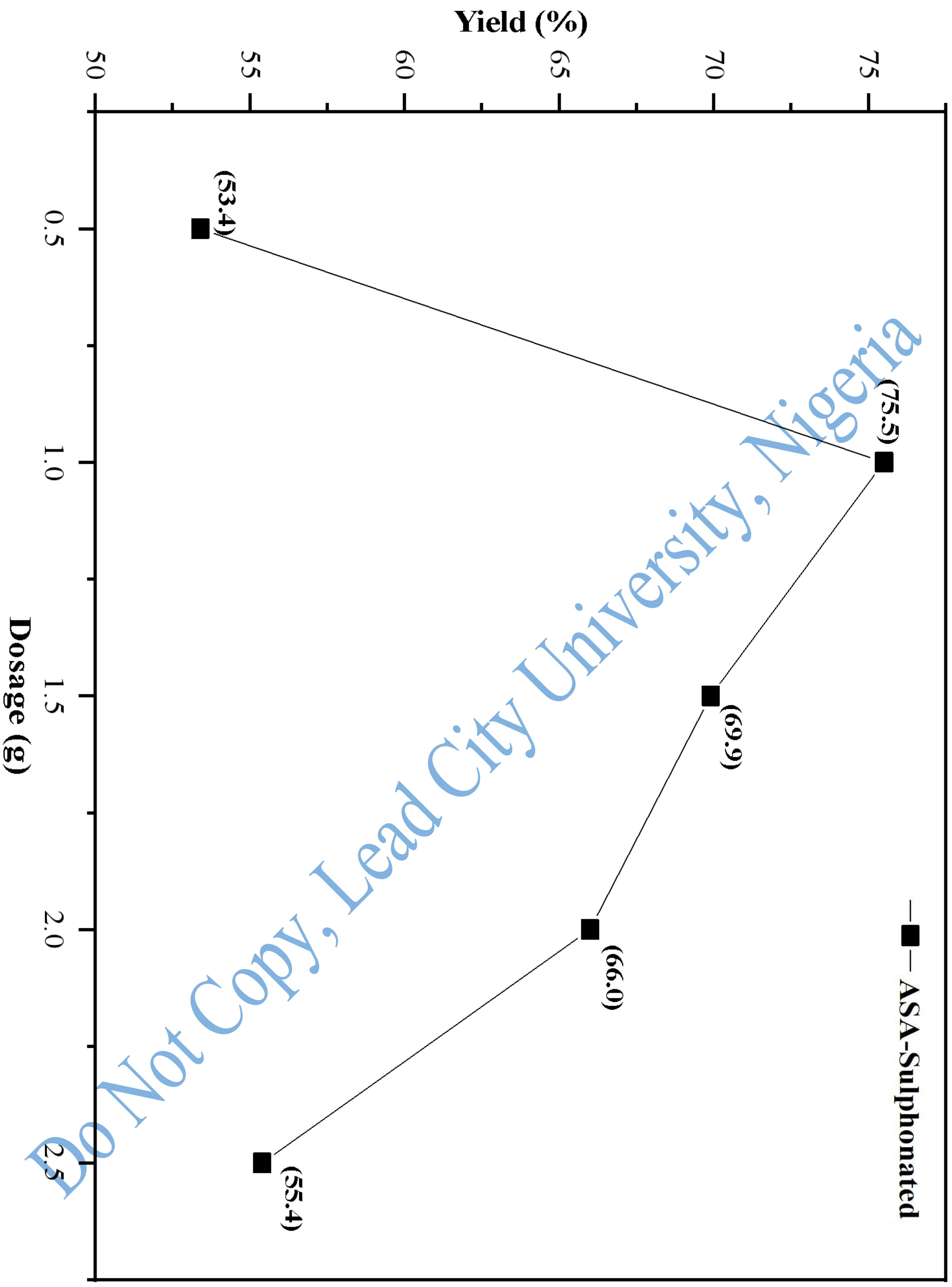


Figure 4.14: Effect of catalytic dosage on biodiesel yield using ASA shell-sulphonated catalysts[6]

Source: Fieldwork, 2023

4.3.4 Effect of Dosage on Biodiesel Yield Using Cow Bone Catalysts

The effect of catalyst dosage on biodiesel yield using cow bone pristine catalyst was reported in Table 4.13 and Figure 4.15.

Table 4.13: Effect of Dosage on Biodiesel Yield Using Cow Bone Catalysts

Catalytic Dosage (g)	Biodiesel Yield (%)
0.5	73.1
1.0	**74.6**
1.5	68.9
2.0	65.2
2.5	60.3

Source: Fieldwork, 2023

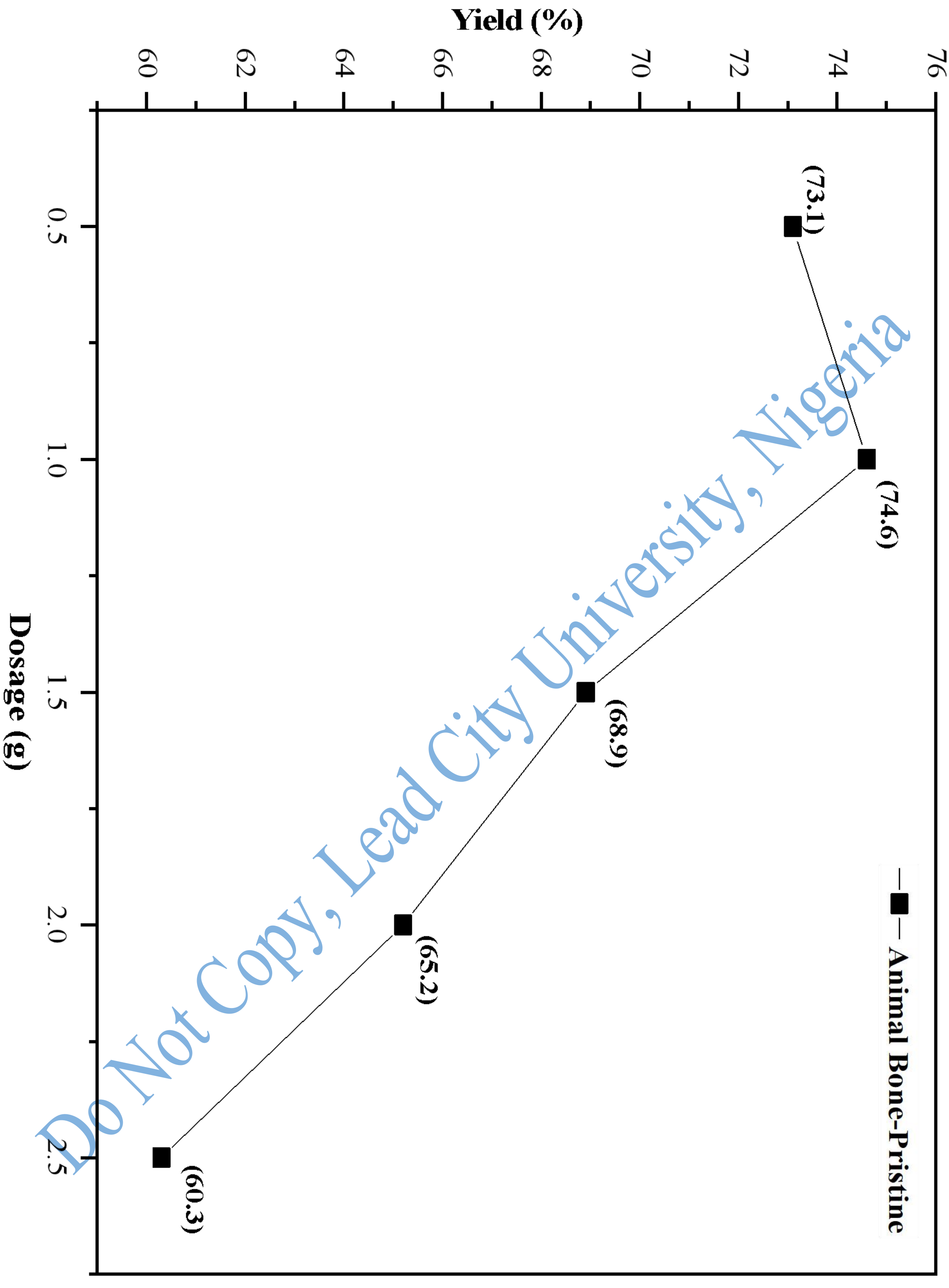


Figure 4.15: Effect of catalytic dosage on biodiesel yield using cow bone catalyst[7]

Source: Fieldwork, 2023

4.3.4.1Effect of Dosage on Biodiesel Yield Using Cow Bone Sulphonated Catalysts

The effect of catalyst dosage on biodiesel yield using cow bone sulphonated catalyst was reported in Table 4.14 and Figure 4.16.

Table 4.14: Effect of Dosage on Biodiesel Yield Using Cow Bone Sulphonated Catalysts

Catalytic Dosage (g)	Biodiesel Yield (%)
0.5	60.5
1	**78.4**
1.5	72.6
2	70.4
2.5	53.8

Source: Fieldwork, 2023

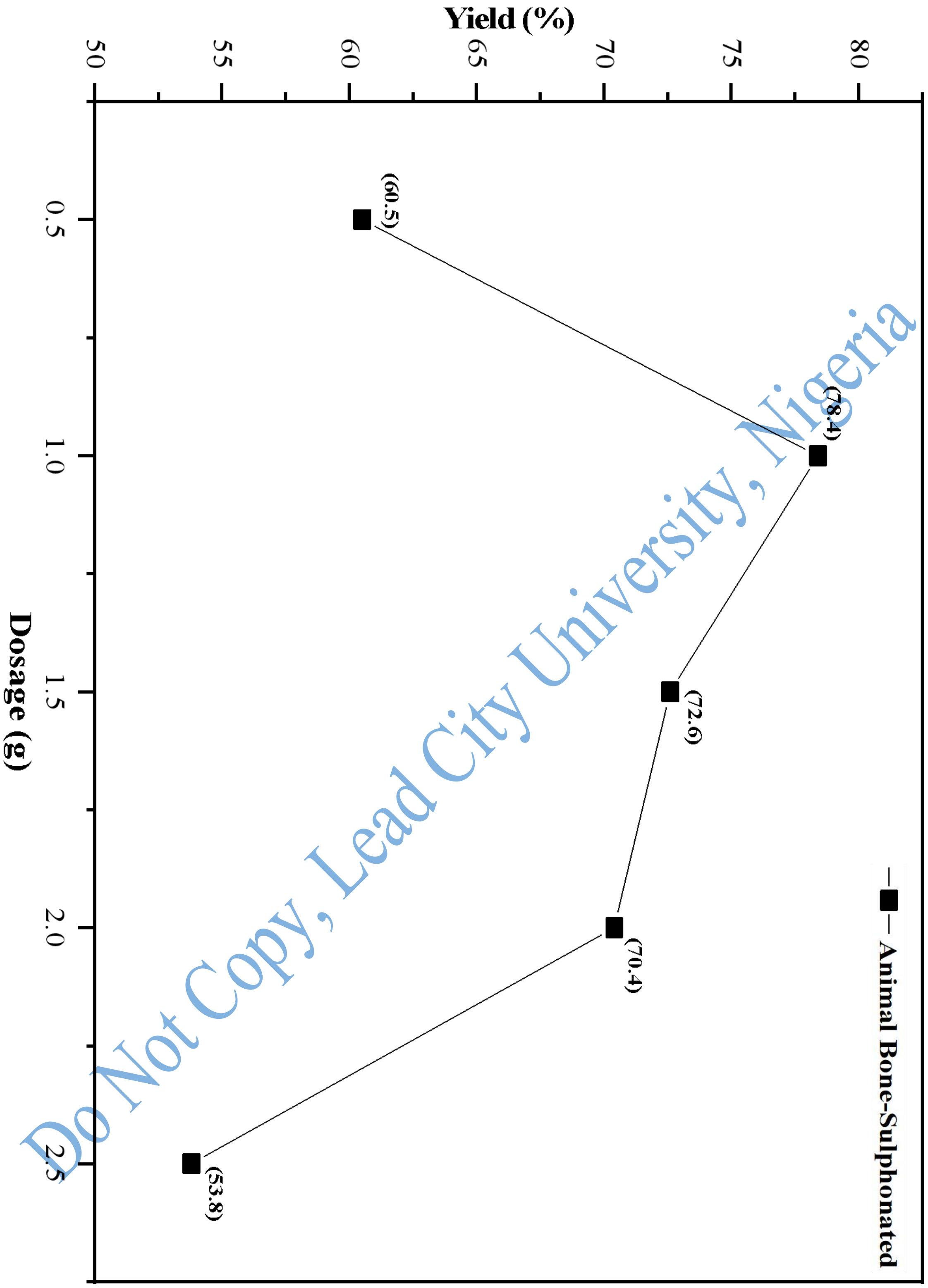


Figure 4.16: Effect of catalytic dosage on biodiesel yield using cow bone sulphonated catalyst

Source: Fieldwork, 2023

4.3.5 Effect of Time on Biodiesel Yield

The result of the effect of time on the biodiesel yield using pristine African Star Apple shell in Table 4.15 and Figure 4.17 and pristine cow bone in Table 4.16 and Figure 4.18 as catalyst is presented respectively.

Table 4.15: Effect of Time on Biodiesel Yield Using Pristine African Star Apple Shell

Time (h)	Biodiesel Yield (%)
1	73.9
2	74.5
3	76.1
4	76.7
5	**79.2**
6	74.8

Source: Fieldwork, 2023

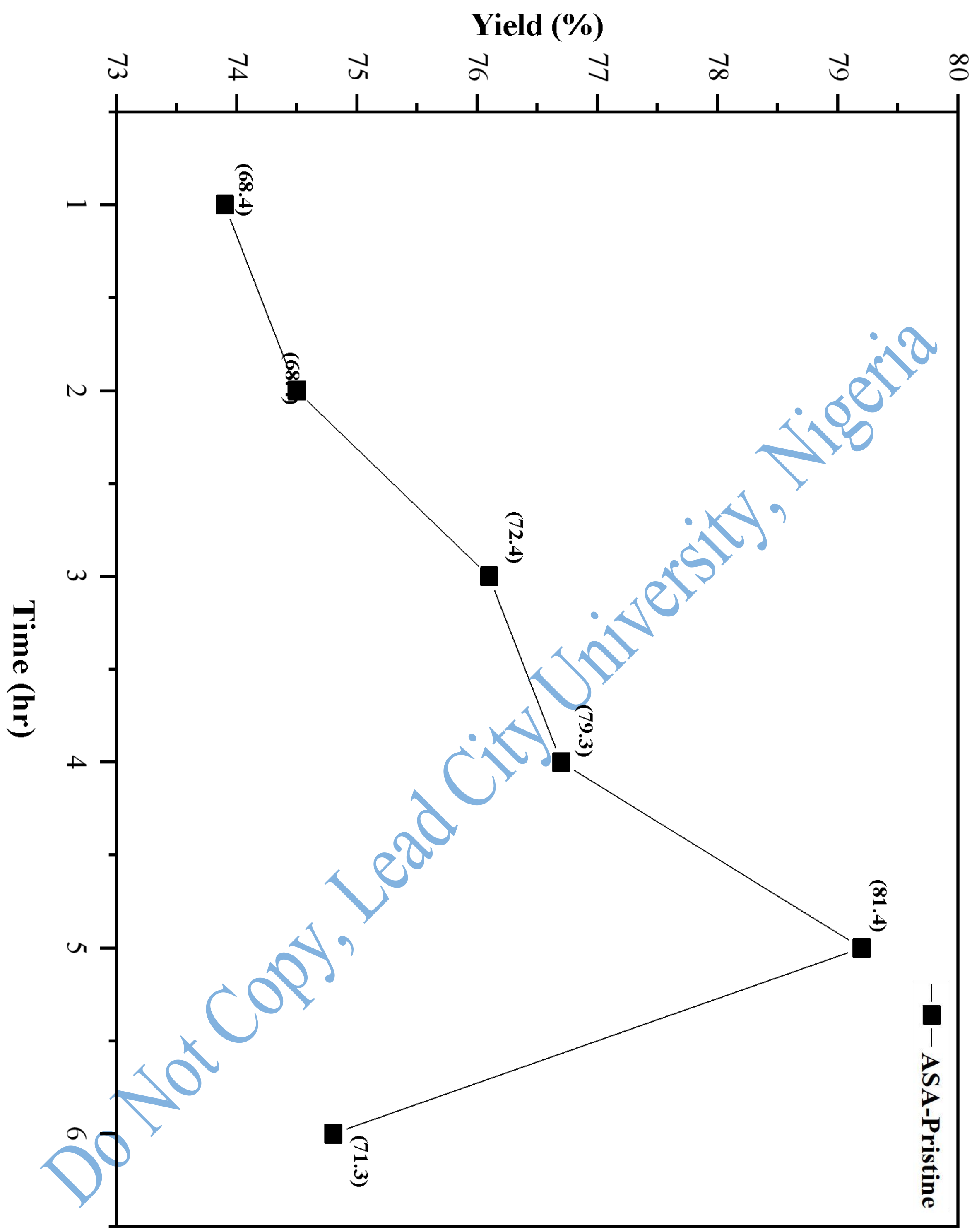


Figure 4.17: Effect of Time on Biodiesel Yield at 60 °C and 1g of using African Star Apple shell- pristine^8

Source: Fieldwork, 2023

Table 4.16 Effect of Time on Biodiesel Yield Using Pristine African Star Apple Shell Sulphonated

Time (h)	Biodiesel Yield (%)
1	68.4
2	68.9
3	72.4
4	79.3
5	**81.4**
6	71.3

Source: Fieldwork, 2023

Table 4.17 Effect of Time on Biodiesel Yield Using Cow Bone Pristine

Time (h)	Biodiesel Yield (%)
1	74.6
2	74.9
3	76.4
4	77.6
5	**81.8**
6	75.2

Source: Fieldwork, 2023

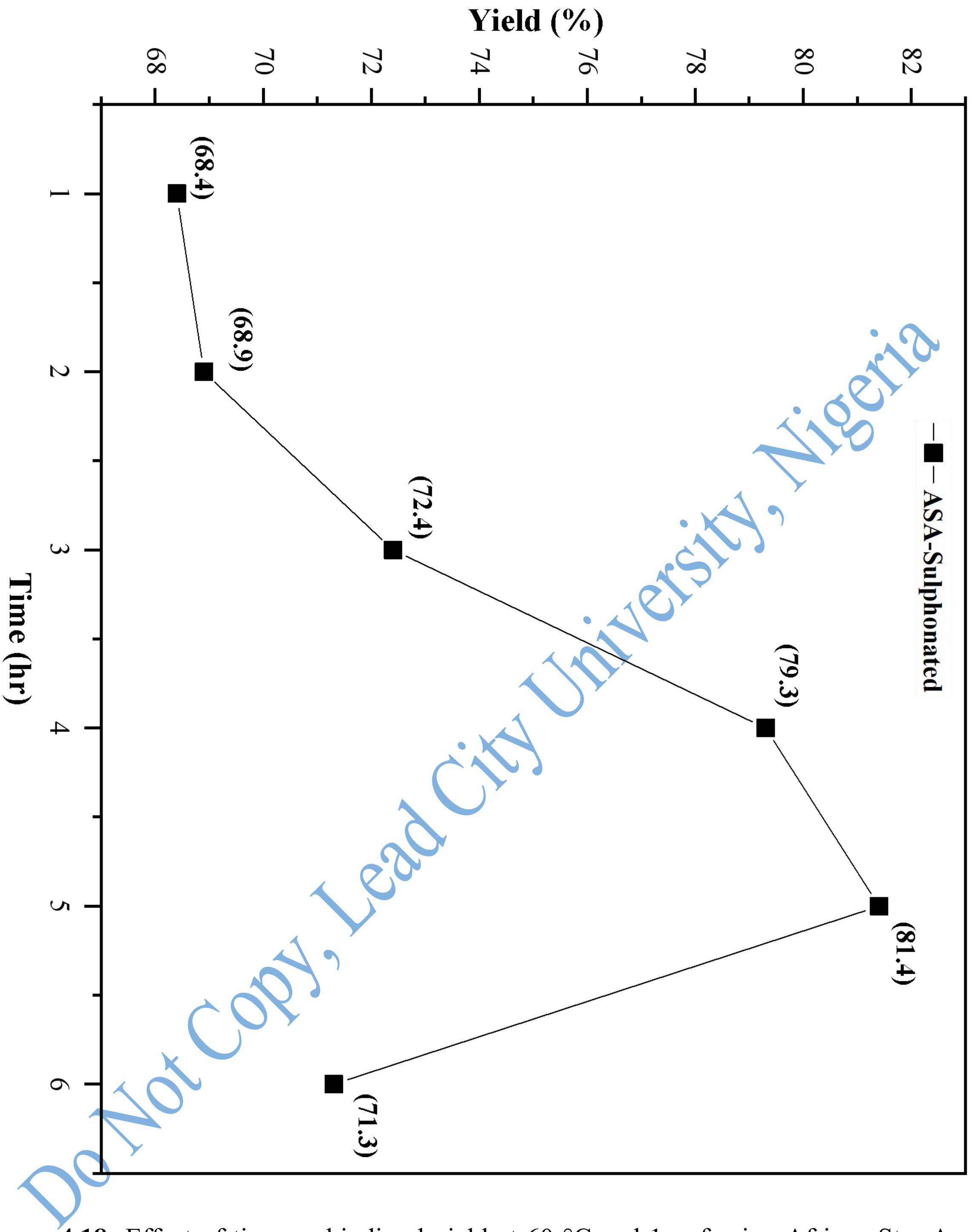


Figure 4.18: Effect of time on biodiesel yield at 60 °C and 1g of using African Star Apple shell sulphonated[9]

Source: Fieldwork, 2023

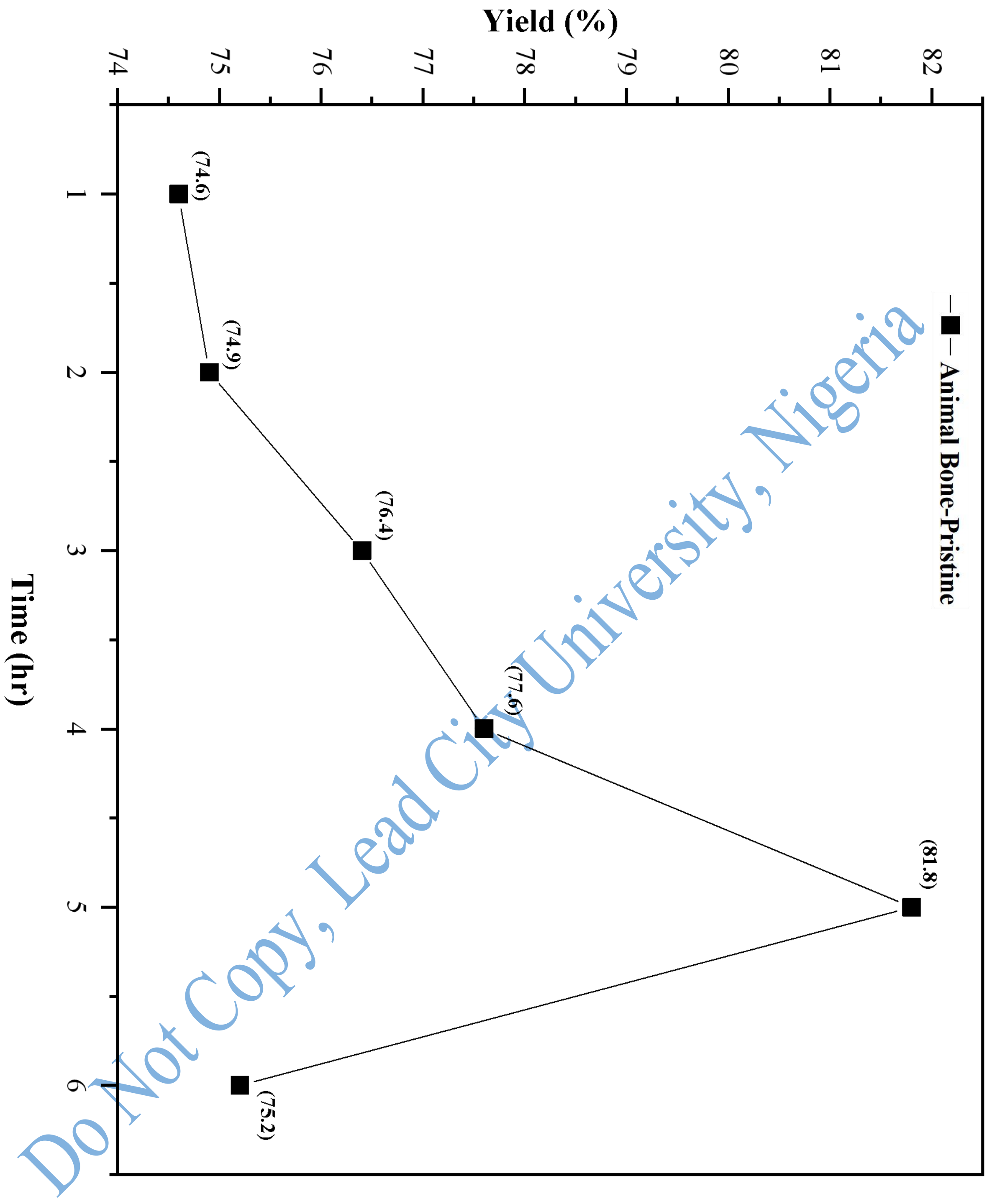


Figure 4.19: Effect of time on biodiesel yield at 60 °C and 1g of pristine cow bone catalyst[10]

Source: Fieldwork, 2023

4.3.6 Effect of Time on Biodiesel Yield Using Cow Bone Sulphonated Catalyst

The result of the effect of time on the biodiesel yield using cow bone sulphonated catalyst is presented in Table 4.18 and Figure 4.20.

Table 4.18: Effect of Time on Biodiesel Yield Using Cow Bone Sulphonated

Time (h)	Biodiesel Yield (%)
1	68.9
2	70.4
3	72.8
4	73.6
5	**86.7**
6	66.2

Source: Fieldwork, 2023

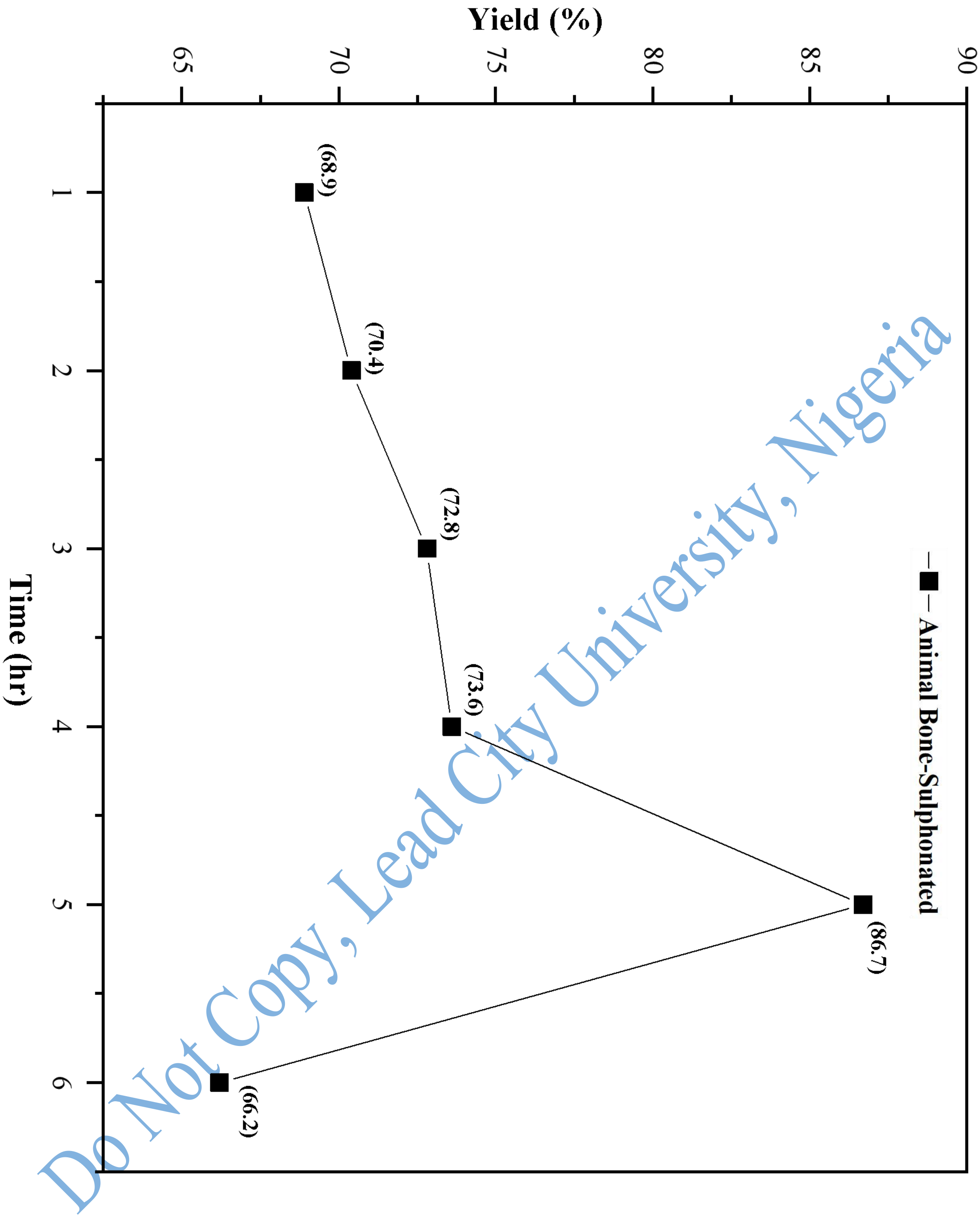


Figure 4.20: Effect of time on biodiesel yield at 60 °C and 1g of cow bone sulphonated catalyst[11]

Source: Fieldwork, 2023

4.4 Recyclability of the Catalysts

The catalysts used in this study were used to run more reaction cycles. This was reused for four reaction cycles. The recycle reaction was carried out separately using each of the catalysts after separation from the products. All the reaction parameters, temperature (60 °C), duration of 6 h and catalytic loading 4 wt.% were fixed. This was in line with the maximum yield conditions. In addition, the methanol to palmitic acid ratio of 10.0 v/wt was used. The result is shown in Table 4.19.

Table 4.19 Recyclability Test

Feed Catalyst (Cycle)	FAME Yield (%)
1	88.5
2	81.3
3	76.7
4	71.5

Source: Fieldwork, 2023

4.5 Discussion of Findings

4.5.1 Introduction

This section discusses the findings of this project was presented under the following sub-topics.

i. Catalyst characterization

ii. Oil characterization

iii. Recyclability of the catalysts

4.5.1 Catalyst Characterization

4.5.1.1 Physiochemical Properties of Catalysts

Table 4.1 revealed that the pH of the catalysts was in the range 3.35-3.46. The pH found is in the acidic region, which indicated that the surface is positively charged. The pH has an influence on the surface chemistry and on the surface acidity of catalyst. In other words, the activity and selectivity may affect the side reaction such as formation of carbon dioxide.

4.5.1.2 The X-Ray Diffraction Analysis of the Catalysts

The crystalline nature and chemical composition of the catalysts used in the study were carried out and the result was presented in Figures 4.1 and 4.2. For the cow bone AB-Pristine and AB-Sulphonated. According to the spectra in Figure 4.1, it could be observed that the catalysts, ABP and ABS were composed of crystals with several distinct peaks at 2θ of 21.009° (0 0 4), 27.046° (1 1 2), 32.820° (1 1 4), 42.968° (0 0 8) and 50.054° (1 1 8) corresponding to the standard patterns of hexagonal lattice of Vaterite, $CaCO_3$ [JCPDS Card No. 33-0268] and at 2θ of 26.433° (1 1 5), 30.195° (2 1 1), 40.081° (2 0 8) and 40.693° (3 0 1) corresponding to the standard patterns of tetragonal lattice of calcium phosphate, $Ca_2P_2O_7$ [JCPDS Card No. 09-0346]. The appearance of these peaks could be ascribed to the formation of hydroxyapatite might show basic characteristics in transesterification reaction. However, on sulphonating the pristine animal bone (ABP) to form ABS (sulphonated animal bone), it could be seen that some of the previously identified peaks undergo decrease or increase in intensity, especially with the peaks at 42.968° (0 0 8) and 50.054° (1 1 8) for ABP which changes to 42.825° (0 3 1) and 50.316° (1 3 2) corresponding to the standard pattern of monoclinic (primitive) of calcium sulphate sulphite, $Ca_3(SO_3)_2SO_4$ [JCPDS Card No. 38-0701]. Also, the peak appearing at $2\theta = 9.199°$ (0 2 0) corresponding to monoclinic $Ca_2P_6O_{17}$ [JCPDS Card No. 43-0224] in the ABP disappeared completely on sulphonation.

The diffractogram of the ASA shell pristine (ASP) in Figure 4.2 exhibited disordered and amorphous carbon structure with very broad peak centered at $2\theta = 22.765°$ (1 2 0) corresponding to hexagonal carbolite, C [JCPDS Card No. 50-0926] and a very small, peak at $2\theta = 32.172°$ (2 0 0) corresponding to hexagonal carbon nitride, CN [JCPDS Card No. 50-0664], as well as a sharp, intense peak centred at $2\theta = 38.336°$ (1 0 1) corresponding to hexagonal-R, O_2, [JCPDS Card No. 38-0902]. Consequently, upon sulphonation to form ASS, the peaks at $2\theta =$ (2 0 0) and (1 0 1) disappeared.

Furthermore, the crystallite sizes, *Dc*, of the catalysts were determined according to Scherrer's equation which is given as:

$$Dc = 0.89\lambda/(\beta\cos\theta) \qquad \text{Equation} \quad \ldots 3.9$$

where Dc is the crystallite diameter, λ is wavelength (0.15418 nm), θ is Bragg's diffraction angle, and β is full width at half maximum of the diffraction plane. Based on the calculation from the intense diffraction peak (1 1 2) for the animal cow bone, the crystallite size of the pristine cow bone is found to be 80.57 nm, with reduced intensity, while that of sulphonated cow bone is 80.32 nm, even with increased intensity along the same peak. This indicated that sulphonation process reduces the size of the catalyst, hence increasing reaction rate and yield. Moreover, using the ASA shell and from the intense diffraction peak (1 2 0), the crystallite size of the pristine ASA is found to be 98.86 nm, while that of sulphonated ASA shell is 98.79 nm.

4.5.2 Fourier Infrared Transformation Characterization of the Catalysts

The FT-IR spectra of the four catalysts used in this study were presented in Figures 4.3 4.4 and 4.5 and Tables 4.2a, 4.2b, 4.3a and 4.3b respectively.

4.5.2.1 Biochar from Animal Cow Bone Pristine and Sulphonation

FT-IR spectroscopy was used to determine the functional groups present in the carbonised (pristine) and sulphonated cow bone, as shown in Figures 4.2a and 4.2b. For the animal bone, three bands at 1412.7 cm^{-1}, 1012.0 cm^{-1} and 871 cm^{-1} were observed. The band at 1412.7 cm^{-1} is ascribed to the asymmetric stretching of CO_3^{2-} groups. This is attributed to the carbonate skeleton of the bone. The band at 874.1 cm^{-1} is attributed to the vCO_3^{2-}, while the band at 713.8 cm^{-1} is due to Ca–O bond. Furthermore, the band at 699 cm^{-1} is assigned to the vibration mode of carbonate ions, while the 1063 cm^{-1} is assigned to the C–O stretching and bending vibration modes of calcium carbonate species formed [1]. However, the absorption band peak 1012 cm^{-1} is the characteristic absorption of SO_3-H group. The absorption band peak is attributed to O=S=O stretching vibrations. This is consistent with the bands reported in literature. This shows that the cow bone has been successfully sulphonated and the -SO_3H group have been attached into the structure of the biochar. The implication of this was that the sulphonated catalyst was successful. The peaks around 1034.3 cm^{-1} to 1105.2 cm^{-1} observed in the pristine cow bone catalyst correlates with asymmetrical P–O bonds stretching vibrations. The implication of this could be that the cow bone catalyst contain phosphate. Furthermore, hydroxyl (−OH) groups correlate with 633 cm^{-1} and can be ascribed to bending mode of −OH group. Thus, all the functional groups observed in as-synthesized material makes it suitable to be employed in transesterification reaction for biodiesel. The two bands at 1105.2 and 1541.3cm^{-1} observed in the pristine cow bone is attributed to the bending vibration of O–Ca-O in calcium carbonate.

4.5.2.2 FT-IR Spectra of Pristine and Sulphonated African Star Apple (ASA) Shell

The functional groups present in the pristine and sulphonated ASA shell catalysts were determined, as depicted in Fig. 4a and 4b. The sulphonated ASA shell was revealed to possess a broad band at ~3200−3600 cm^{-1}, which is ascribed to the adsorbed –OH on the catalyst, while the appearance of 1578.5 cm^{-1} is ascribed to aromatic C=C while fingerprint peaks of C–H groups were observed in the range of 700–885 cm^{-1}. All of these peaks were the basic bands found in sulphonated ASA shell. The appearance of new peaks at 1440 cm^{-1} and 873 cm^{-1} for both ASA-pristine and ASA-sulphonated indicated the availability of CO_3^{2-} on the surface [2]. The ASA-pristine and ASA-sulphonated catalysts revealed similar infrared absorptions at 2180 cm^{-1} and 1654.9 cm^{-1}, which are attributed to the νO−H and νC=O in −OH and −COOH groups, respectively [3]. A broad absorption band at 3386.3 cm$^{−1}$ to 3108 cm$^{−1}$ showed hydroxyl group (ν-OH) due to moisture adsorption on the catalyst surface, while the vibration of aromatic ring groups (νC−C) appeared at absorption bands of 1599 cm$^{−1}$ to 1418 cm$^{−1}$ [4]. The presence of C=O stretching vibration of the carbonyl group is shown by the middling and strong peak at 1654.9 cm^{-1}, indicating the presence of carbonate [5]. The absorption band at 1146.2 cm$^{−1}$ is assigned to the νC-O-C on the surface of the ASA-Pristine [6]. For the ASA-Pristine and ASA-Sulphonated, the bands at 747.3 cm^{-1} and 1146.2cm^{-1} corresponds to =C–H and C–O–C were observed [7].

4.5.3 Oil Characterization

4.5.3.1 Physiochemical Properties of the Extracted Oil

The physiochemical properties of the oil extracted from the African star apple seeds with n-hexane and chloroform in a ratio 50:50ml is as presented in Table 4.4.

The Table shows six physical parameters (colour, odour, specific gravity, percentage yield, refractive index and state of the oil) while four chemical parameters (acid-, iodine-, saponification value and percentage free fatty acid) of the oil were described.

4.5.3.2 Colour, Odour and Nature of the Oil

The oil extracted was found to be dark brown honey-like colouration, with a pleasant sweet smell odour. This was in agreement with the oil extracted in previous report [8]. However, this was different from the previously reported deep red colours [9,10]. This colour difference could be attributed to the method and specie of the African star apple fruit used in the study. In addition, there are many visual signs in the development of degradation of the oil, the most obvious of which are dark in colour and rancid flavour. The small amounts of unsaturated acid can easily undergo oxidation, especially in the solid form where oxygen can readily penetrate the crystal structure.

4.5.3.3 Viscosity

The measurement of internal fluid flow resistance is regarded as a highly significant physical characteristic of oil. The viscosity from the study showed that of African star apple seed oil was found to be 53.65 mms^{-1} at 40 °C. This is slightly lower than the previously reported value of 54.37 mms^{-1} [11].

4.5.3.4 Percentage Yield of the Extracted Oil

The percentage oil yield was 28.80% which was higher than the previously reported works of 14.92% and 11.6% yields [8,10,12]. However, the yield of 60.08% was obtained by Soxhlet extraction method of *Citrullus colocynthis* L. seed oil using chloroform and methanol in a ratio of 2:1[13]. The variations in the obtained yield could be ascribed to several factors, including the species of used African star apple, soil and climatic condition of the plantation area, seed processing methods as well as the employed extraction method [12,14,15]. However, our result is more favorable when compared to some underutilized plant seed oils, such as *Pearsea americana* (10.8% yield), *Detarium microcarpum* (7.42% yield), and mango seed (13% yield) [16,17,18,19].

4.5.3.5 Specific Gravity

The specific gravity of the oil was 0.96 at 25°C. This value was higher than the previously reported value of 0.92 [10]. This may be as a result of the process involved in the production as well as the technique.

4.5.3.6 Acid Value (mg KOH/g)

The weight in milligram of KOH required to neutralize the free acid in 1g of oil is known as the acid value of an oil. It is an important indicator of oxidation of oil. An oil in which the acid value is less than 0.1 is regarded as a good oil. However, an acid value greater than 1 denotes that the oil may cause corrosion, which could result in the formation of gum and sludge [10,11]. In this work, the obtained acid value was revealed to be 16.80 mg/KOH/g, a value higher than 0.1. This is in agreement with the previously reported literatures having 2.30 mg KOH/g and 3.23 mg KOH/g [11,20].

4.5.3.7 Iodine Value (mg/100g)

The iodine value of the oil refers as a parameter for the extent of unsaturation in vegetable oils and their resistance to oxidation, which determines the total fat of the oil to be unsaturated [21]. The iodine value of the oil extracted from ASA seed was 47.60 mg/KOH/g which is less than 100mgI/g suggesting that the oil is non-drying oil. However, the obtained value is reportedly lower compared to previous publications [20,22,23].

4.5.3.8 Saponification Value (mg KOH/g)

The saponification value is a parameter used to determine the average molecular mass of fatty acid of an oil. The saponification value was found to be 220.40 mg/KOH/g, which is higher compared to 199.50 mg/KOH/g, 134.64 mg/KOH/g, 200mg/KOH/g and 231mg/KOH/g, but slightly lower than 236 mg/KOH/g of the previously published works [8,9,10,22,23]. The obtained value revealed the presence of compounds containing long carbon chains. Despite this, the applicability of the obtained oil is not limited. Therefore, the oil may be used in production of other important products such as soap, shampoos, and lather shaving creams [24,25,26,27].

4.5.3.9 FTIR of ASA Seed Oil

The functional groups present in the ASA seed oil extracted was analyzed using FTIR. Various peaks in the spectra were then identified. The band region of 3826.83 cm^{-1} and 3197.11 cm^{-1} can be ascribed to the free *v*O−H, indicating the presence of alcoholic groups. Also, the band at 2952.01 cm^{-1} is ascribed to *v*C−H, while the bands around 1700 cm^{-1}, 1600cm$^{-1,}$ 1400cm^{-1}, and 1200 cm^{-1} are attributable to C=O stretching, C=C stretching of the aromatic ring, O−H bending of the alcoholic and carboxylic groups, and C−O−C, stretching respectively [28,29,30.,31].

4.5.3.10 GC-MS Analysis on Biodiesel

The identification and quantification of fatty acids methyl ester in the biodiesel produced with the cow bone- and the ASA seed shell catalyst were conducted and the results are shown in Figures 4.7, 4.8 and tables 4.4 and 4.5 respectively. The unknown organic compounds in the biodiesel were matched with the National Institute of Standards and Technology Library.

The spectra from Figure 4.7 shows that four peaks were ascribed to five fatty acids methyl esters and other organic compounds present in the biodiesel produced using the cow bone catalysts from the African star apple seed oil. These compounds were confirmed by their retention time, organic compound name, percentage area and molecular weight in a sequential manner. The major fatty acids methyl ester found were hexan-3-yl 2-methylbutanoate (50%), methyl 2-(trimethylsilyl) ethyl malonate (17%), methyl trans-3-chloropropenoate (12%) and p-nitrophenyl hexanoate (12%) with the retention time of 8.809, 11.676, 7.679, and 9.667 respectively. In addition, Figure 4.7 showed the peaks representing concentration and hexan-3-yl-2-methylbutanoate being the highest as shown by the Peak 3. The concentration is slightly higher when compared with the previously reported value in a seed oil but lower to the value reported by another conducted research on a different seed oil [8,10]. This may be as result of the smaller pore size of the cow bone catalyst and the specie of the seed oil used for the study.

On the other hand, the biodiesel generated from the seed oil using the African star apple shell catalyst was subjected to GC-MS analysis. The result was as shown in Table 4.5 and the spectra was shown in Figure 4.8. The table displayed three major free fatty methyl esters with the name, area coverage and the retention time. Hexan-3-yl -2-methylbutanoate (50%) was the most abundance with coverage area of fifty percent and retention time of 8.809 with molecular weight of 186.162 while the least of the compounds in terms of concentration was methyl trans-3-chloropropenoate (12 %).

Comparing the effect of these different catalysts on the biodiesel and the concentration of the free fatty acid esters, they both yield hexan-3-yl-2-methylbutanoate (50 %) as the most abundance while cow bone catalyst contains four free fatty acid ester and the African star apple shell contain three similar compounds. It was also observed that the biodiesel produced from the cow bone catalyst contain p-nitrophenyl hexanoate to the tune of twelve percent

(12 %), however this was completely absent from the African star apple shell catalyst-biodiesel. This may be because African star apple shell catalyst, a form of amorphous carbon has extremely porous surface such that it has large surface area available for adsorption or chemical reactions. In other words, the cow bone catalyst was crystalline while the ASA shell was amorphous.

4.5.4. Effect Catalytic Performance

Four different catalyst was used in this study. These are the pristine ASA shell, pristine cow bone, sulphonated ASA shell and sulphonated cow bone catalysts. They were used in the study in relation to the percentage yield of biodiesel production relative to the study parameters of temperature, catalytic dosage and time taken for the production. Each of the parameters were discussed.

4.5.4.1 Temperature Effect on Biodiesel Yield Using ASA Shell Pristine and Sulphonated Catalyst

An important factor that will impact the production of biodiesel is reaction temperature. For instance, due to the reduced viscosity of oils at higher reaction temperatures, the reaction rate is increased and the reaction time was lowered. The output of biodiesel was reduced, however, when reaction temperature was raised above the ideal range since this speed the saponification of triglycerides and causes the vaporization of methanol.

The temperature effect on the biodiesel yield using 1 g of ASA shell pristine for 1 h is presented in Fig. 4.9 and Table 4.7. When pristine ASA shell catalyst was used, it was observed that the biodiesel yield was 32.4 % at 30 °C. As the temperature increases from 40 to 50 °C, the biodiesel yield increased from 39.8 to 56.1% respectively. At 60 °C, the highest percentage yield of biodiesel was obtained to be 71.2 %. But with the sulphonated ASA shell catalyst, the highest yield was obtained to be 74.6 %. This is presumably due to increased mass transfer, causing the catalyst to quickly diffuse into the reactant system which is usually conducted slowly at low temperature [32]. As a result, it is believed that the heat at this temperature is sufficient to support the reactant molecules colliding, hence increasing the rate of catalyst and methanol penetration into ASA seed oil[33]. Additionally, the viscosity of the oil decreases as a result of the increase in temperature, thus improving the contact between the oil and methanol[34]. However, the biodiesel yield drops to 32.9% and 42.5% as the temperature increased to 70 °C for the pristine ASA shell catalyst and the sulphonated ASA shell catalyst respectively. At that temperature, large amount of methanol changes to vapour from the system because methanol has a low boiling point of 65 °C, leading to inadequate contact of methanol with the seed oil. Furthermore, at higher temperature, biodiesel yield drops due hydrolysis of fatty acid methyl ester[35].

4.5.4.2 Temperature Effect on Biodiesel Yield Using Pristine Cow Bone

The temperature effect on the biodiesel yield was also investigated using 1g of pristine cow bone catalyst and time was 1 h. From the results presented in Fig. 4.11 and Table 4.9, it was observed that the biodiesel yield increased steadily to a point as the temperature increased but decreased at higher temperature. At 30 °C, the biodiesel yield was found to be 41.6 % and at a 40 °C, the yield increased to 49.6 %, while at 50 °C, the biodiesel yield was found to be 61.8 %. When the temperature was increased to 60 °C, the yield correspondingly increased to 73.1%, as attributable to reduction in the viscosity of the oil at high temperature, thereby enhancing the contact between oil and methanol [34]. The reason could be that at high temperature, reaction rate is accelerated and equilibrium is reached, thereby increasing the yield. Temperature increase strengthens mass transfer and hence enhance the fast diffusion of the catalyst into the reactant system [36]. More so, increase in temperature provides enough heat which maintains the collision of the reacting molecules and therefore increases the rate of diffusion of the catalyst and the alcohol to the African star apple seed oil. As the temperature was increased above 60°C, it was found that the yield was lowered. At 70 °C, the biodiesel yield drops drastically to 28.8 % (Figure 4.11). Excess methanol is needed for the reaction to occur but at higher temperature usually above the boiling point of methanol (65 °C), the methanol volatilizes from the system. The reason could be that there was no contact of methanol with the African star apple seed oil molecules resulting to low biodiesel yield. Furthermore, at higher temperature, there is hydrolysis of the fatty acid methyl ester, thereby causing a reduction in the biodiesel yield [35].

In summary, the pristine African star apple shell and pristine cow bone catalysts biodiesel yield at the optimum temperature of 60 °C as found to be 70.2 % and 73.1 % respectively.

4.5.5 Effect Catalyst Dosage

The catalyst dosage used in this study were consider based on the catalysts used. These include the African star apple shell catalyst and the cow bone pristine catalysts. The optimum yield of biodiesel in relation to the dosage was explained.

4.5.5.1 Effect of Catalytic Dosage on Biodiesel Yield Using African Star Apple Shell Catalyst

The effect of catalytic loading of African star apple shell catalyst is presented in Figure. 4.13 but the sulphonated ASA shell catalyst was in Figure 4.14 and Table 4.12. Increasing the catalyst dosage from 0.5g to 1g increased the biodiesel yield from 49.5 to 72.9% for the pristine ASA shell. The sulphonated ASA shell catalyst yield was from 53.4 to 75.5%. This can be attributed to increase in the amount of available acid site [37]. There was a slight change when the catalyst dosage was doubled in the yield of biodiesel from 66.4 % to 59.6% but when the sulphonated ASA shell catalyst was used, the yield was 66.0% to 55.4% was observed as catalyst dosage increased from 1.5 g to 2.5 g. This may be as a result of reduction in the reactant interaction with the active site and this increase in the mass of the catalyst may result in the decrease in biodiesel yield [38]. Furthermore, increase in catalyst dosage leads to product absorption which reduces biodiesel yield [39]. In conclusion, the sulphonated ASA shell maximum yield was 75.5% and pristine ASA shell catalyst yield was 72.9%. The implication was that sulphonated ASA shell catalyst produced more of biodiesel than the pristine ASA shell catalyst when 1 g of catalyst was loaded.

4.5.5.2 Effect of Catalytic Dosage on Biodiesel Yield Using Cow Bone Catalyst

The effect of catalytic dosage of cow bone catalyst was investigated as shown in Figure 4.15. When dosage increased from 0.5 to 1 g, biodiesel yield increased from 73.1 to 74.6 % respectively. However, loading with sulphonated cow bone catalyst, the yield was increased from 60.5 to 78.4 % when 0.5 g increased to 1 g. The increase in biodiesel yield can be attributed to increase in active site of catalyst due to increasing dosage and also the smaller size of the crystal of the sulphonated cow bone catalyst [38]. However, further increase in dosage (from 1.5 to 2.5 g), resulted in decreased biodiesel yield from 68.9 to 60.3 % and 72.6 to 53.8 % for the pristine and sulphonated cow bone catalyst respectively. This may be due to product adsorption on the catalyst's surface [39]. Also, the mass transfer limitation of the reactant to the active site can lead to decrease of biodiesel yield [38]. Conclusively, the biodiesel yield of sulphonated cow bone catalyst (78.4 %) was higher than the pristine (74.6 %) counterpart when 1.0 g of the catalyst was used.

4.5.6 Effect of Time on Biodiesel Yield

The result of effect of time on the biodiesel yield using pristine African Star Apple shell and cow bone pristine as catalyst is presented in Figures 4.17 and 4.19 respectively.

4.5.6.1 Effect of Time on Biodiesel Yield Using Pristine African Star Apple Seed Shell Catalysts

From Table 4.15 and Figure 4.17, the pristine African Star Apple shell revealed that the biodiesel yield was found to increase steadily from 73.9 % to 79.2 % with increasing heating time from 1 h through to 5 h. The essence of the increase in heating time is to provide sufficient time needed to ensure that enough transfer of the immiscible phases and also to attain equilibrium [38].

4.5.6.2 Effect of Time on Biodiesel Yield Using Sulphonated Cow Bone and ASA Shell Catalysts

With pristine cow bone catalyst as shown in Table 4.17 and Figure 4.19, the biodiesel yield was found to increase steadily. This indicates that cow bone pristine is a better catalyst than African star apple shell catalyst because higher percentage of biodiesel yield was produced with pristine cow bone catalyst. This was in agreement with the report due to the fact that enough time is required to ensure the mass transfer among the liquid solid reactant system in order to attain equilibrium state and improve the yield of biodiesel [38].

However, after 6 h, the yield of biodiesel decreases to 74.8 and 75.5 % for African star apple shell pristine catalyst and cow bone pristine catalyst respectively. This could be due to the catalysts steadily deactivating in nature [40]. More so, excess reaction time would not facilitate the reaction once equilibrium status is achieved [41]. The results of the optimum conditions of the process variables affecting biodiesel yield were investigated for the oil feedstock. In

Figures 4.17 and 4.19 is presented the biodiesel yield using African star apple seed oil under optimum conditions of process variables. The biodiesel yield was found to be 79.2 and 81.8 % for African star apple seed shell pristine and cow bone pristine respectively. Thus, it can be inferred from the studies that cow bone pristine had better catalytic performance than African star apple seed shell pristine.

In contrast, the percentage yield of biodiesel when sulphonated ASA shell catalyst and cow bone sulphonated catalyst was utilized in relation of time at an interval of 1hour was showed in Tables 4.17 and 4.18 respectively. The Tables revealed that at an hour the yields were 68.4 and 68.9 %. The yield increases until the fifth hour (81.4%) for sulphonated ASA shell and (86.7 %) for the sulphonated cow bone catalyst as sheened by the figure 4.18 and 4.20 respectively. But when the reaction mixture was allowed to be on for 6 h, the yield was dropped from 81.4 to 71.3% for sulphonated ASA shell catalyst and 86.7 to 66.2% for sulphonated cow bone catalyst. This could be as result of the fact that the sulphonated cow bone catalyst has crystalline size of 80.32 nm indicating it is a crystal and the ASA shell with size of 98.79 nm which can be associated by the amorphous nature of the catalyst. Conclusively, the sulphonated cow bone catalyst which produced higher yield than the sulphonated ASA shell catalyst is a better catalyst in relation to time react.

4.5.7 Recyclability of the Catalysts

The reusability test of catalysts is an important measure of the response of FAME against the number of times the catalyst was used. The recycle reaction was carried out separately using each of the catalysts after separation from the products taken into consideration all the reaction parameters, temperature (60 °C), duration of 6 h and catalytic loading 4wt.% were fixed. The result shown in Table 4.19 revealed the optimum reaction was 4 cycles with the highest FAME yield of 88.5% recorded in the first run and the least amount was recorded at the fourth run. It was observed that the yield was declining as the cycle increases until the potency and the yield greatly dropped to 71.5%. This could be due to the fact that the sulphonic group in the catalyst have been deactivated. This finding was supported by previous work conducted[42].

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Chapter Five

Conclusion

5.1 Summary of Findings

The percentage oil extracted from the African star apple seeds with n-hexane and chloroform in a ratio 50:50 ml is 28.88 %. Non sulphonated carbon-based catalyst (Pristine) from African star apple shell and the cow bone were found to have a pore size of 98.86 nm and 80.51 nm respectively. Sulphonated carbon-based catalyst from African star apple shell and the cow bone were found to have a pore size of 98.79 nm and 80.32 nm respectively. The percentage biodiesel yield using pristine African star apple shell catalyst was found to be 72.9 % while using cow bone catalyst was 74.6 % at the highest catalyst dose of 1 g. The biodiesel yield with 1g catalyst dose of sulphonated African star apple shell catalyst was found to be 75.5 % while using sulphonated cow bone catalyst was 78.4 %. The dominant methyl ester found in the diesel from the oil produced by pristine and sulphonated ASA and the cow bone catalysts was hexan-3-yl-2-methylbutanoate. The sulphonated Cow bone catalyst was found to be more effective for the production of biodiesel. The African star apple seed oil yield is not sufficient for the feedstock of commercial production of biodiesel but can be used for some industrial purposes. The biodiesel obtained conformed to ASTM standard based on the observed physiochemical parameters conducted.

5.2 Conclusion

Oil from African star apple seed was extracted and converted to biodiesel using biowaste based catalysts of African star apple shell and cow bone. Sulphonated catalysts from the biowaste were successfully synthesized by carbonization - sulphonation method. The physiochemical characterization of the oil was evident. Results of the characterization with X-ray diffraction and Fourier transform infrared spectroscopy further confirmed the disappearance of bonds showed that sulphonated biowaste of cow bone catalyst showed improved and small catalyst pore size than biowaste of African star apple sulphonated. Both the sulphonated African star apple and cow bone catalysts can be an effective catalyst in the production of biodiesel from African star apple seed oil. However, Sulphonated cow bone catalyst is more effective for biodiesel production from ASA seed oil. The maximum yield optimal parameters of temperature, reaction time and catalyst have great effect on the yield of biodiesel.

5.3 Recommendations

i. The potential of African Star Apple seed oil be explored with more modern instrument for possible better result.

ii. Production of a better hybrid of African Star Apple through genetic reengineering to obtain a high content African Star Apple seed oil.

5.4 Contribution to Knowledge

The synthesis of sulphonated biowaste carbon based solid acid catalyst from ASA Shell and Cow bones has been achieved and established. Utilization of the synthesized sulphonated carbon-based solid catalyst in the production of biodiesel using ASA Seed oil as feedstock has also been established. Furthermore, it was established that sulphonation process reduces the size of the catalyst and hence increase reaction rate and yield. Also, it was established from the study that the cow bone catalyst was crystalline while the African star apple shell catalyst was amorphous.

5.5 Suggested Area of Further Research

i. Investigation into the possibility of using the seed of ASA for other industrial uses apart for biodiesel production.

ii. Other methods of extraction and extraction medium in relation to the mixing ratio can be investigated for better yield of biodiesel.

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Textbooks

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Bio-data

A. Personal Data

1. **Name:** Isaac Sewanu BANKOLE
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2. **Telephone Number & E-Mail Address:** +2348034719780; ibankole2015@gmail.com

3. **Date and Place of Birth:** 31st August, 1962; Idooye

4. **Nationality:** Nigerian

5. **Marital Status:** Married

6. **Number of Children:** Four (11-, 9-, 5- & 5 years)

7. **Name and Address of Spouse:** Mrs. Esther O. Bankole,
Ogun State Teaching Service Commission, Abeokuta, Ogun State.

8. **Name and Address of Next of Kin:** Same as above

9. **Date of Assumption of Duty:** 7th May, 2011

10. **Status of first Appointment in Lead City University:** Not Applicable

11. **Present Position:** Lecturer I

12. **Date of Last Promotion:** Not Applicable

13. **Date of Confirmation of**

Appointment: Not Applicable

14. **If not Confirmed, Why?** Not Applicable

15. **Present Salary:** Not Applicable

16. **Faculty:** Science

17. **Department:** Laboratory Technology

B. Educational Background

Educational Institutions Attended with Dates

(i) Primary Education:

Baptist Day Primary School, Ijebu-Ode 1970 – 1975

(ii) Secondary Education:

Egbado College, Ilaro, Nigeria. 1976 – 1981

(iii) Higher Educational Institutions Attended with Dates

i. Lagos State University, Ojo, Lagos, Nigeria.
Ph. D Science Education (Chemistry) 2017

ii. Lagos State University, Ojo, Lagos, Nigeria.
M.Ed. Curriculum Studies 2000

iii. University of Lagos, Akoka, Lagos State.
B. Sc (Ed) Chemistry (Second Class Upper Division) 1991

iv. Ogun State College of Education, Ijebu-Ode, Ogun State.1985

C. Awards and Fellowships

(i) Best paper Award at 12th Multidisciplinary International Science Technology Education, Arts, Management and Social Sciences, University of Ghana, 25th October, 2018.

(ii) Gold Award of Excellence by Chemical Society of Nigeria received at the 42nd annual Conference held in Abuja, November, 2020.

(iii) Fellow Award of Chemical Society of Nigeria, 21st September, 2015.

D. Work Experience With Dates

i) Community Grammar School, Ojo, Lagos State 1992 – 1994

ii) Gateway Polytechnic, Igbesa 2007 – 2011

iii) Ogun State Institute of Technology, Igbesa, Ogun Sate. 2011- 2022

E. Courses Taught In The Current Academic Session

- GLT 112 General Laboratory Techniques
- STC 121 Organic Chemistry I
- STC 221 Organic Chemistry II
- STC 313 Organic Chemistry I
- STC 413 Heterocyclic Compounds
- STC 220 General Chemistry
- GNS 228 Research Methods
- STC 321 Polyfunctional Compounds
- STC 415 Natural Products and Petrochemicals
- GLT 121 Preparation of Solutions and Side Shelf Reagents
- STS 222 Project Supervision
- STS 212 Seminar

E. Membership of Professional Bodies

Member Chemical Society of Nigeria (CSN)

F. Publications

1. Thesis/Dissertation

Potency of Student-Directed Concept Maps and Card Games on Achievement and Process Skills Development of Senior Secondary School Chemistry. ***PhD. Thesis***.

2. Authored Books

a) **Bankole, I.AS**, & Babajide S.O (2012). *General Chemistry for Non-Science Students* (ISBN 978-978-50882-4-3).

b) **Bankole I. Sewanu**, Babajide, S.O & Adeyinka, M O (2017, 2021)- *Introduction to Organic Chemistry for Tertiary Institutions* (ISBN978-978-55379-6-3)

(b) Edited Books: None

(c) Contributions to Books: None

(3) Published Articles in Refereed Conference Proceedings: None

(4) Papers Accepted for Publication

1) Akinlabi, A.K, Quadri, R.K, **Bankole, I. S** and Koleoso, O.K (2015). The use of Coconut Shell as Additive in Natural Rubber compounding. *Journal of Chemical Society of Nigeria, 40(1), 56-64.*

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14) **Bankole, I. Sewanu** (2018): Effect of Concept Mapping and Card Game Instructional Strategies on Senior Secondary Students' Chemistry Achievement. TASUED Journal of Pure and Applied Sciences. Vol.1 (1) 56-70.
15) **Bankole, I. A. Sewanu** (2018): Deploying Card Games as tools in learning Chemistry concepts in Nigerian Classrooms. Journal of Chemical Society of Nigeria. Vol.43 (3), pg. 482-487.
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(c) Manuscript/Book Chapters Accepted for Publication None

(d) Papers under Review for Publication

(i) Extraction and Charaterization of *Chrysophyllum albiudum* Seed Oil

(ii) Comparative Oil Extracted from African Star Apple non-edible seed using Soxhlet extractor with different solvents.

(e) Work in Progress None

5. Book Reviews and Commentaries in Scholarly Journals: None

6. Technical Report: None

7. Other Publications: None

8. Creative Work: None

G. Notable Scholarly or Professional Accomplishment:

i) **Deputy Vice Chairman**, South West Zone Chemical Society of Nigeria

ii) **Fellow**, Chemical Society of Nigeria.

H. Major Conferences/Workshop.

(i) Colloquium on Lessons from Recession for National Development Organized by Okebukola Science foundation, January 1st, 2017.

(ii) 1st South-West Zonal National Conference on relevance of Chemistry in the development of Industrial Raw materials, Abeokuta, 17 -19th, May 2017.

(iii) 40th Annual International Conference on Green Chemistry as Catalyst for Economic Growth and National Security at International Conference center, Kaduna, September, 17- 22nd 2017.

(iv) Colloquium on Youth Demographic Bulge in Nigeria: from Disadvantage to Advantage. January 1st, 2018.

(v) Improving Educational Standard in Nigeria, organized by Tai Solarin University of Education, Ijagun, Ijebu Ode. January 16th - 18th, 2018.

(vi) 41st Annual International Conference on Sustainable Chemistry, University of Ibadan, September 17th -23rd 2018.

(vii) 12th ISTEAMS Conference on Technology Renaissance for innovations and Productivity (TRIP) at OGITECH Igbesa, 27TH -29TH September, 2018.

(viii) 13th ISTEAMS Multidisciplinary Cross Border Conference, University of Ghana, Legon, Accra, Ghana. 24- 26th October, 2018.

(ix) Improving Educational standard in Nigeria organized by Tai Solarin University of Education, Ijagun, Ijebu-Ode, January 16th -18th, 2018.

(x) Repositioning Science Education in Sokoto state and Nigeria's Educational system; catalyst for self- reliance and sustainable development by North West Zonal Chemical Society of Nigeria held at Umaru Alli Shinkafi Polytechnic, Sokoto, 9th – 11th May, 2018.

(xi) 14th National Conference organized by School of Vocational Education, Federal College of Education, Abeokuta on Vocational Education and Global Learning for National Development, June 17- 21, 2019.

(xii) 42nd Annual International Conference in Collaboration with ACRICE-4 on Chemistry Education and Sustainable Development at Academy Guest house and Events Halls, Agidingbi, Ikeja, Lagos, September, 8th -13th, 2019.

(xiii) 43rd Annual International Conference on chemical Security and COVID-19 Challenges: The Chemistry perspective held at Raw Materials Research and Development Council (RMRDC), Abuja, 22nd – 27th November, 2020.

J. Extra-Curricular Activities: Playing Lawn Tennis

K. Referees

1) **Prof. Akinlabi, Akinola K**
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Signature Date

The University Compliance Certification

This is to certify that the Thesis of **Isaac Sewanu BANKOLE** With Matriculation Number **LCU/PG/001779**, in the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Nigeria is full Compliance with the Approved University Format and Style.

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Signature Date