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Biodiesel production from parinari curatellifolia seeds oil using basic heterogeneous catalyst derived from tamarindus indica fruit shells

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BIODIESEL PRODUCTION FROM *PARINARI CURATELLIFOLIA* SEEDS OIL USING BASIC HETEROGENEOUS CATALYST DERIVED FROM *TAMARINDUS INDICA* FRUIT SHELLS

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ABSTRACT

Biodiesel is an alternative fuel to mineral diesel. It is produced from abundant and easily available renewable resources of animal fats and vegetable oil. However, the cost of oil feedstock is the major obstacle towards production and commercialization of biodiesel. In this study, an economical and environmental friendly heterogeneous catalyst derived from *Tamarindus indica* fruit shells (TIFSs) was prepared by calcination method, and it was used in transesterification of *Parinari curatellifolia* seeds oil (PCSO) to produce biodiesel. The seeds were characterized by having high oil content 36.2%, which makes the feedstock a reasonable candidate for biodiesl production.

The catalyst was prepared by calcination of TIFSs at 800 °C in muffle furnace for 3 hours to obtain *Tamarindus indica* fruit shells ash (TIFSA), a heterogeneous catalyst. Various techniques were used to analyze physicochemical properties of TIFSA. The catalyst exhibits high basic strength (pH>9.7), with the mesoporous structure of pore diameter d = 3.2 nm, high specific area 378.2 m^2/g, pore volume of 0.203 cm3/g and CaO crystals as a major active phase of the catalyst. The calcinated catalyst TIFSA was tested in the production of biodiesel through transesterification process using PCSO to obtain *Parinari curatellifolia* methyl ester (PCUME). During production, the best operating parameters were 5% wt. catalyst loading, 2 hours reaction time and 9:1 methanol to oil molar ratio with the maximum yield of 96.2%. In addition, the catalyst was easily separated and reused again four more times with biodiesel yield above 74%.

Furthermore, the produced biodiesel was analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) and composed mainly of unsaturated acids 63.6% and saturated acid 36.39%. Also, fuel properties of produced PCUME were investigated as per ASTM methods and compared to ASTM D6751 standard limits and mineral diesel. Most of the determined fuel properties were observed to be in good agreement with the global standards. Therefore, *Parinari curatellifolia* seeds oil and *Tamarindus indica* fruit shell are ideal feedstock for low-cost biodiesel and catalyst production respectively.

DECLARATION

I, Christian S. Nabora do hereby declare to the Senate of The Nelson Mandela African Institution of Science and Technology that, this dissertation is my own original work and that it has neither been submitted nor being currently submitted for degree award in any other institution.

Mr. Christian Samwel Nabora Date
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The above declaration is confirmed

Dr. Thamas T. Kivevele Date
(Supervisor 1)

Dr. Cecil K. Kingondu Date
(Supervisor 2)

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CERTIFICATION

The undersigned certifies that they have read and hereby recommend for acceptance by The Nelson Mandela African Institution of Science and Technology a dissertation entitled *“Biodiesel Production from Parinari Curatellifolia Seeds Oil Using Basic Heterogeneous Catalyst Derived from Tamarindus Indica Fruit Shells”* in partial fulfillment of the requirement for the degree of Masters of Science in Sustainable Energy Science and Engineering of the Nelson Mandela African Institution of Science and Technology.

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LIST OF ABBREVIATIONS

AOCS	American Oil Chemistry Society
ASTM	American Standard of Testing and Measurement
AV	Acidic Value
BET	Barrett Emmett Teller
BJH	Barrett-Joyner-Halanda
CFPP	Cold filter plugging point
CI	Cetane index
CN	Cetane number
CP	Cloud point
CPA	Cocoa Pods Ash
EDS	Energy Dispersive X-ray spectroscopy
EN	European
FAME	Fatty Acid Methyl Ester
FBP	Final Boiling Point
FFA	Free Fatty Acid
FT	Fischer Titration
GC	Gas Chromatography
IBP	Initial Boiling Point
IV	Iodine Value
LTFT	Low temperature filterability Test
PCUME	*Parinari curatellifolia* Oil Methyl Ester
PCSO	*Parinari curatellifolia* Seed Oil
PP	Pour point
RHA	Rice Husk Ash

SEM	Scanning Electron Microscope
SV	Saponification Value
TG	Triglycerides
TGA	Thermal Gravimetric Analysis
TIFSA	*Tamarindus Indica* Fruit Shells Ash
TIFSs	*Tamarindus Indica* Fruit Shells
WCO	Waste Cooking Oil
XRD	X-ray Diffraction

CHAPTER ONE

INTRODUCTION

1.1 Background

Energy is among of the basic want for social and economic growth and development. As development increases, the energy demand also increases resulting to energy crisis. The sustainable solution is required to address these issues of the energy crisis. For more than a century, petro fuel has been used as a main source of energy to run internal combustion engines for transportation, electric power generation and household uses (cooking and lighting). But these fuels have limited supply (Vedharaj *et al*., 2014), expensive, and their combustion by - products are toxic resulting to health effect. Nevertheless, their by-products are major sources of greenhouse gases emission which results to global warming and environmental pollution. For this reason, looking to other reasonable alternative renewable sources of energy which are sustainable, economically reasonable and environmentally benign is inevitable.

Biodiesel is a potential substitute fuel to mineral diesel. It is among the bio-fuels derived from various biomass sources using different technologies such as pyrolysis, gasification, fermentation and transesterification reaction. Transesterification is a process whereby a number of moles of triglyceride molecule of complex free fatty acid, reacts with moles of alcohol in the using the catalyst and at given temperature to form a methyl/ethyl ester (biodiesel) and glycerol (Demirbas, 2005; Chen *et al*., 2013). Biodiesel is a mixture of mono-alkyl esters of long chain fatty acids resulting from renewable lipid feedstock of animal fats or plant oil through transesterification process (Kafuku and Mbarawa, 2010; Burton, 2008).

Biodiesel fuel produced through transesterification process is biodegradable, non-toxic and its carbon emission has not exceeded carbon cycle, hence it can be recycled in the photosynthesis process. Also, it is characterized by having good fuel properties such as good lubricity, less exhaust emission, sulfur free, and has high flash point (>100 °C) make fuel safe for handling and storage. Also, the fuel can be produced from renewable, abundant, easily available and affordable feedstock that will make its production cheaper, hence reduces the dependence on imported fossil fuels (Kivevele and Mbarawa, 2010). Apart from good fuel properties, it also exhibits some drawbacks such as slightly lower calorific value, low cetane number, poor cold flow properties (pour and cloud point) and less oxidation stability caused by feedstock properties (Encinar *et al*., 2002; Ramadhas *et al*., 2005).

Generally, cost of production of biodiesel depends on oil feedstock, type and amount of catalyst used and the technology used in the same. But more than 70% of its production cost depends on oil feedstock and catalyst to be used (Leung *et a*l., 2006 ; Dehkhoda *et a*l., 2013; Zhang *et al*., 2014). According to Sanli; Gui and Lee (2008), more than 95% of biodiesel production is accomplished by using food grade edible oils, for example, sunflower oil, palm oil, soybean oil and rapeseed oil using homogeneous catalysts. The extensive use of refined oils for biodiesel production results into food insecurity and price competition. Also uses of homogeneous catalysts result into high production costs caused by use of high amount of water during washing, number of purification steps, high wastewater management and the catalyst is not reusable after reaction. These factors contribute to rise the costs of producing biodiesel and become a major obstacle towards commercialization processes. Therefore, it is inevitable to look for cheaper oil feedstock and low cost catalyst so as to reduce the cost of producing biodiesel.

In real sense, many researches in producing biodiesel by using non-edible, waste oil and lignocellulosic as viable feedstock have been done (Adewale *et al.*, 2015). The refined feedstock are less expensive and with no conflicts with food stuffs, but they are challenged by having very high amount of FFA (greater than 2%), density, greater amount of saturated fatty acids, land competition and technological challenges (Tang *et al*., 2018). Currently, more researches are on exploring unutilized cheap oil feedstock sources such as *Parinari curatellifolia* seed oil (PCSO). According to (Benhura *et al.* (2012), *Parinari curatellifolia* commonly known as Mbula tree is a tropical evergreen seedling tree, with pulp and seeds used as food during food deficiency especially on drought season. Their seeds kernel have reported to contain high oil content of about 38.5% (Bazongo *et al*., 2014). The oil is less commonly used as food stuffs, hence possible feedstock for production of biodiesel. The feedstock has not yet been reported to be used as feedstock in producing biodiesel in the open literature.

Apart from oil feedstock, further research is on how to overcome drawbacks caused by homogeneous catalysts towards biodiesel production and its commercialization. To overcome the drawbacks of homogeneous catalyst during biodiesel production, heterogeneous catalysts are mostly preferred. The catalysts are easy to separate, reused, it can work with low-quality oils feedstock, does not require much washing stage during biodiesel production, hence less expenses in sanitary water treatment and most of all it can be manufactured from cheap renewable agricultural wastes biomass. Biomass in nature has the variable composition of inorganic constituents such as C, O, N, H, Ca, Si, K, Mg, S, Al, P, Fe, Cl, Mn, Ti, Na, and other small trace elements and are easily converted to their metal oxides when burned (Jenkins *et al.*, 1998; Vassilev *et al.*, 2013). Also, biomass with large amount of carbonate can be converted easily into their metal oxide through thermal treatment (calcination process) (Maneerung *et al.*, 2015; Tang *et al.*, 2018).

In recent days, CaO has drawn attentions to be used as heterogeneous catalyst in biodiesel production. Calcium oxide is highly active earth metal oxide, easily available from several natural calcium sources of wastes and organic materials which are renewable such as egg shells, sea shells and *Tamarindus indica* fruit shells (TIFSs). TIFSs have enough amount of $CaCO_3$ (11.1%) (Borges and Diaz, 2012; Stadelman, 2000; Wadekar *et al.*, 2006), hence it can be considered as a possible solid basic heterogeneous catalyst precursor.

TIFSs are among agricultural wastes from juice processing industry naturally rich in calcium compounds (Sivasankar *et al.*, 2012; Meher *et al.,* 2014). It has resulted from Tamarind tree plant which belongs to the dicotyledonous family: *Caesalpiniaceae,* indigenous to tropical Africa. TIFSs wastes are abundant and cheap made up with $CaCO_3$ 11.1% by weight (Wadekar *et al.*, 2006). Furthermore, various elements such as K (13.08), Ca (36.6), Mn (12.1), Mg (10.4), Na (8.90), Zn (7.0), Fe (4.5) and Cu (2.10) mg/100g of dry matter are present as reported by Ajayi *et al.* (2006). TIFSs like any other biomass wastes with high amounts of alkaline earth metals, when burned to ashes are ready to form metal oxides to be used as basic solid heterogeneous catalyst for transesterification process (Zabeti et al., 2009). Therefore, the aim of this research is to produce and characterize biodiesel from *Parinari curatellifolia* seeds as a possible alternative fuel feedstock in biodiesel production using solid basic (alkaline) heterogeneous catalysts calcinated from waste *Tamarindus indica* (ukwaju) fruit shells, a waste agricultural biomass.

1.2 Problem statement

Biodiesel made from animal fats and vegetable oil through transesterification process is regarded as an ideal alternative fuel to mineral diesel. Biodiesel is renewable source, bio - degradable, non-toxic, emits less exhaust gas, and is environmentally friendly addressing drawbacks emanating from fossil fuels (Tshizanga *et al.*, 2017). In most cases, biodiesel made from edible and refine vegetable oil through transesterification process are not economically feasible since they increases price of both edible oil and biodiesel itself. During transesterification, homogeneous catalyst such as NaOH and KOH or heterogeneous catalyst such as CaO catalyst is needed to accomplish the process. Most of these catalysts are expensive and originating from non-renewable sources, with complicated preparation and purification steps.

Furthermore, homogeneous catalysts are not reused; they are susceptible to soap formation, need high amount of washing water and purification steps resulting to high cost of wastewater management. On the other hand, most heterogeneous catalysts are delivered from non-renewable sources such as calcite rocks that need various preparatory stages and high energy consumption (temperature) during their production. Thus, the use of these catalysts contributes to increasing costs of biodiesel production and hinders the commercialization processes. Currently, more researches focus on finding feasible oil feedstock and cheap catalyst to minimize the cost of biodiesel production towards its commercialization. Therefore, researching for cheap oil feedstock like unutilized seed oils together with using the agricultural biomass wastes as a cheap source of solid basic heterogeneous catalysts for production biodiesel inevitable.

Therefore, the aim of this study is to produce and characterize biodiesel from *Parinari curatellifolia* seed oil using solid base heterogeneous catalyst derived from *Tamarindus indica* fruits shells (agricultural waste) as low-cost for transesterification process. *Parinari. curatellifolia* seeds kernel contain high oil content and it is less commonly used as foodstuff may be used as feasible feedstock for biodiesel production. Also, *T. indica* fruit shells rich in potential metal elements and abundant agricultural biomass waste can be used as cheap source of heterogeneous catalyst.

1.3 Problem justification

The use of waste material and less commonly used feedstock in the biodiesel production draws great attention towards its commercialization process. Cost of feedstock, type and amount of catalyst have a major role in defining the competitiveness of biodiesel produced. Use of edible foodstuff in biodiesel production increases both food prices and cost of biodiesel production. Waste and less commonly used foodstuffs are economically feasible toward the commercialization of biodiesel. Furthermore, most of the chemicals used in the production of catalysts are typically expensive and hazardous to both human and environment. Use of readily available renewable organic wastes as alternative source, helps to minimize the production cost of the catalyst as well as biodiesel and are environmentally benign. Therefore, the use of agricultural wastes TIFSs and less commonly used PCSO make biodiesel produced economically feasible and reasonable.

1.4 Objectives

1.4.1 General objective

The main objective of this study is to produce and characterize biodiesel from *Parinari curatellifolia* seeds oil via transesterification process by using low-cost solid base heterogeneous catalyst derived from *Tamarindus indica* fruits shells, an agricultural waste biomass.

1.4.2 Specific objectives

The specific objectives meet the required goals for this study are as follows:

(i) To characterize *Parinari curatellifolia* seeds oil.
(ii) To characterize calcinated TIFSA a solid base heterogeneous catalyst derived from TIFSs an agricultural waste.
(iii) To produce and characterize biodiesel from *P. curatellifolia* seeds oil.

1.5 Research questions

The principal questions to be answered by this research work study are:

(i) What are the potentials of *P. curatellifolia* seeds oil in biodiesel production?

(ii) How effective is the TIFSA as basic heterogeneous catalyst for biodiesel production?

(iii) To what extent are fuel properties of produced biodiesel from *P. curatellifolia* seeds oil using TIFSA as a catalyst agreed with global biodiesel standard limits?

1.6 Significance of the research

With the problems of environmental pollutions, depletion and higher cost of petro fuels, biodiesel become a promising alternative fuel in today's world. Biodiesel is non-toxic with less exhaust emissions, it is biodegradable, renewable source of energy and needs less or no modification required to current engines. This study aim on the production and characterization of biodiesel fuel from *P. curatellifolia* seeds oil using *Tamarindus indica* fruit shells (agricultural waste) that will contribute to social and economic issues with consideration of their low costs and environmentally friendly.

CHAPTER TWO

LITERATURE REVIEW

2.2 Background

Energy is a driving force for socio-economic development in any society all over the world. Due to this fact, and with respect to the increase in the global population, issues of energy crisis are inevitable. So, the trend of the world is toward looking for a clean, sustainable, environmentally friendly and economically feasible energy. For many years, fossil fuel is been used as the source of energy in transport, power generation and domestic uses. These fuels are non-renewable and their by-products are harmful and pollutant resulting to environmental pollution. To overcome this, there are strong investigations of alternative fuel such as biodiesel to fossil fuel (Canakci and Van Gerpen, 2001; Sanli, 2008; Berrios and Skelton, 2008).

Biodiesel is a renewable source of energy produced from vegetable oils and animal fats using alcohol and catalysts are possible alternative fuel to mineral diesel. They are derived from renewable sources which are abundant, non-toxic biodegradable, and environmentally friendly. Biodiesel is receiving increasing attention in day to day lives as an alternative to mineral diesel. The diesel fuel demand is increasing steadily because of economic growth caused by the growth of the industrial sector with the fact that, diesel fuel is the most useful petroleum fuel used in the transport sector and power generation.

2.2 Biodiesel

Biodiesel is a non-fossil fuel produced from animal fats and vegetable oils via esterification and/or transesterification of triglycerides (TG) using low molecular weight alcohols in the presence of catalyst to form mono-alkyl esters (Chopade *et al.*, 2012). Generally, the fuel is oxygenated, non–toxic, biodegradable, renewable, sulfur-free and eco-friendly alternative to mineral diesel. Its properties resemble that of mineral diesel and can be used direct or with little modification in diesel engine as substitute for mineral diesel (Mittelbach *et al.*, 1992: Peterson *et al.*, 1992. 1994). Biodiesel is mainly composed of carbon chains consist of alkyl (methyl, ethyl and propyl) esters ranging from C_{14}-C_{25} and can be expressed as C_{14-25} H_{28-48} O_2 by Yusuf *et al*. (2011). In order to produce a biodiesel of high-quality and maximize yield at low cost, there are three thing of important: (a) it depends on the technology to be used (batch process, supercritical alcohol process, microwave irradiation methods, and ultrasounds used), (b) type of oil feedstock used (refined or crude oil) and (c) is the reaction parameters applied (reaction time, amount and type of catalyst, amount of alcohol, reaction temperature, and agitation speed) (Ejikeme *et al*., 2010; Vyas *et al*., 2010; Talebiankiakalaieh *et al*., 2013).

However, biodiesel is prone to having high cetane number, with no sulphur or aromatics compounds content, and oxygenated 10 – 11% by weight (Canakci, 2007). The fuel is miscible (it can be blended) with other organic compounds, insoluble in water and inflammable hence safe in storage. It is biodegradable, renewable, and economically feasible with high lubricity properties. For environmental purposes, it reduces the environmental effect of waste products, reduces air toxicity and net carbon dioxide emission by 78% (Abdullah *et al.*, 2017). Also, during its application, no significant modifications are required to the existing diesel engine. But biodiesel fuel exhibits some drawbacks such as lower oxidation stability than mineral diesel, lower volatility causing a deposit in the engine, higher viscosity and less by 12% of energy content when compared to mineral diesel (Ali *et al.*, 1995b). These can result in high engine emissions, lower power output and low engine performance (Math and Sudheer, 2010). Hence, biodiesel production depends more on the type of feedstock to be used.

2.2.1 Biodiesel feedstock

Choosing an appropriate feedstock in producing biodiesel is of an important factor to ensure sustainability and reducing the cost of production (Atabani *et al*., 2012). Biodiesel production feedstock as an important material can be categorized into three groups as oil feedstock (animal fat and vegetable oil), alcohol feedstock (methanol, ethanol, and propanol) and catalyst (homogeneous and heterogeneous) (Issariyakul and Dalai, 2014), and should be sustainable and of low cost. The cost of feedstock and catalyst carries consume more than 75% of the total cost in biodiesel production (Ahmad *et al*., 2011; Dehkhoda *et al*., 2013; Zhang *et a*l., 2014; Zhou *et al*., 2016). Furthermore, biodiesel can be produced from edible and non-edible feedstock, animal fats, waste cooking oil and frying oil depending on its availability and price (Adewale *et al.*, 2015). Primarily, biodiesel feedstocks are categorized into three generations. First generation feedstock includes those edible oil crops used to produce biodiesel. These include sunflower, rapeseed, soybeans and palm oil counts about 95% of edible oil feedstock. This results into impact on food insecurity by increasing both costs of edible oils and biodiesel produced and land distribute (Ahmad *et al*., 2011).

Second generation biodiesel feedstock uses energy crops and other sources of oil that are nonedible and less commonly used oils. This includes crops such as jatropha, croton, karanja, tobacco seeds. Other oil sources in this generation include waste cooking oil, animal fats, fish oil, frying oil, waste oils, and restaurant grease. These feedstocks are characterized by having high FFAs, viscosity, density and mainly composed of saturated fatty acids. All these make the process of transesterification difficult and more costful. Apart from the mentioned advantages the feedstock have the afore mentioned advantages: they are noncompetitive with foodstuffs because of some toxic components in the oils that make it unsuitable for the human being, it can be mixed with other crops resulting in less farmland, it can be grown in wetlands and other unprofitable lands hence more resourceful and environmentally benign.

Moreover, third generation feedstock are the lignocellulosic type from plant biomass. They are among the cheap, abundant nonfood materials available as plants and plant parts which are considered as more sustainable biodiesel feedstock for example microalgae and seaweed. Lignocellulosic parts are considered as future biofuels feedstock and can be processed either by hydrolysis, fermentation or gasification (i.e. Fischer–Tropsch bio-diesel (FT)). Currently, the production of fuels using lignocellulosic feedstock is not feasible in terms of cost because of the number of technical aspects that hinder their potential to be realized (Naik *et al.*, 2010). Since the main obstacle for biodiesel production and commercialization is the high cost of feedstock, the use of less commonly used seed oils such as *Parinari curatellifolia* seeds oil (PCSO) is inevitable.

2.2.2 Parinari curatellifolia

Parinari. curatellifolia (Mbula) tree is a tropical evergreen fruit tree with a mushroom-like shape. It belongs to the family *Chrysobalanceae*, found in many places in African forests along streams and also in woodland. It prefers to areas of high rainfall, and grows to a size of 23-26 m tall (Oladimeji and Bello, 2011). The plant grows well at an altitude of 0 – 1900 m with annual mean temperature of 10 – 30 °C and annual rainfall between 100 – 2700 mm (Bazongo *et al.*, 2014). The plant is wild grown with an edible pulp and less used seeds. In Tanzania, the plant grows well in northern and southern highlands where in Iringa it is known as Msawula, while in Njombe and Mbeya it is known as Mbende (Hines and Eckman, 1993). The seed kernel has high oil content of 38.5% (Bazongo *et al.*, 2014) and is less commonly used.

2.2.3 Physical chemical properties of parinari oil

The physical and chemical properties of parinari oil are the measure of the measure of biodiesel to be produced. It includes oil and water content, density, iodine value, saponification value, acid value and free fatty acid composition.

(i) Iodine value

The total unsaturated property of the oil is measured by iodine value. It is the amount of iodine expressed in grams that will react with 100g of the oil to the double bonds (Knothe, 2005). Unsaturation behavior of the oil is determined by the number of double bonds that exist in that compound. A good example is linoleic acid with 18 carbon atom (C18) is unsaturated methyl ester with 2 double bonds. The amount of iodine used during titration also determines the unsaturated level of fatty acid in a fat and is an indicator of oxidation stability of oil (AOAC, 1993).

(ii) Acid value

The amount of free fatty acids in the oil of fats is determined by the acid value (AV). It is that mass in milligrams of KOH needed to neutralize the organic acids present in 1 g of fats and oil. It is among basic parameters in describing the fats and oils (AOAC, 1993). Generally, the high acidic value in the oil promotes soap formation. Feedstock with high acid value reacts immediately with the alkali catalyst to form soap. For this matter, two steps transesterification process esterification and transesterification are needed (Ribeiro *et al*., 2011).

(iii) Saponification value

Another essential property of the oil is saponification value. It is the amount of KOH or NaOH in milligrams used to saponify 1 g of fats or oil at a given condition (AOAC, 1997). It measures the presence of free and esterified acids present in fats and fatty acids (Abdulrahman, 2016). This property indicates the ability of the oil or fats to make soap.

(iv) Free fatty acids

Free fatty acids composition is the key determinant of physicochemical properties of produced biodiesel. It includes density, acid value, kinetic value, iodine value etc. These properties are influenced by the structure of compound such as number of single bonds which determines the saturation level, the number of double bonds which determines the unsaturation level and carbon chain length i.e its atom distribution in the compound. The carbon chain length used for the biodiesel production varies depending on the feedstock source (Rashid *et al.*, 2008; Sanli, 2008). Table 1 shows the structure, the number of carbon atoms and double bonds present in the major fatty acid compounds exist in most of common triglycerides molecules. Also, the FFAs are the important factor that determines the amount of catalyst, type of catalyst to be used and storage stability of biodiesel (Gui *et al*., 2008). The higher the acidity value of the oil, the higher is the amount of the catalyst consumption and easy for more soap formation during the transesterification process. This leads to a low conversion rate and yield in transesterification (Issariyakul and Dalai, 2014). Oils with higher FFA (>2%) need two-step processes esterification and transesterification, and acid catalysts are more recommended to be used during the process.

Table 1: Common fatty acids in triglycerides molecules

Fatty acid	Carbon atom: double bond	Structure
Myristic	14:0	$CH_3(CH_2)_{12}COOH$
Palmitic	16:0	$CH_3(CH_2)_{14}COOH$
Stearic	18:0	$CH_3(CH_2)_{16}COOH$
Oleic	18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Arachidic	20:0	$CH_3(CH_2)_{18}COOH$
Behenic	22:0	$CH_3(CH_2)_{20}COOH$
Erucic	22:1	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$

Source: Sanli, (2008) and Fernandes *et al*., (2015)

2.2.4 Alcohol

Alcohol is another necessary feedstock in biodiesel production. The role of alcohol in transesterification reaction is to move the reaction equilibrium towards the product side (Guo *et al*., 2010). When it is used in excess, it usually guarantees the complete conversion and minimizes the reaction time (Tang *et a*l., 2013; Issariyakul *et al*., 2014). But too much alcohol affects reaction by increasing polarity of the reaction mixture. Also it will cause reverse reaction between methyl ester and glycerol caused by higher solubility of the glycerol back to ester phase. This will result in the reduction of ester yield (Issariyakul and Dalai, 2014). Various types of alcohols have been used in biodiesel production. This includes methanol, ethanol, butanol, amyl alcohol etc (Abdullah *et al*., 2017). But their type can affect the reaction performance caused by carbon chain when used in transesterification (Issariyakul *et al*., 2014). In most cases, during transesterification, methanol has mostly been used because is cheaper, can easily dissolve in the reaction medium and it has a short carbon chain that allows it to react quickly (Abdullah *et al*., 2017).

Generally, transesterification reaction is a stoichiometric reaction that uses a mole of triglyceride in a three moles of alcohol (1:3) to obtain a mole of glycerol and three moles methyl esters (biodiesel) (Scheme 1). The amount of molar ratios to be used will depend on the physicochemical properties of the feedstock, type of catalyst and technology to be used. Wei *et al*. (2009), managed to produce FAME of 95% yield from soybean oil over calcinated eggshell ash (CaO) as a catalyst using 1:9 oil to methanol molar ratios using3 h reaction time and 65 °C reaction temperature. Another researcher, Tang *et al*. (2013), produced a FAME of 99.5% yield from soybean oil over modified CaO using 1:15 oil to methanol molar ratio, 65 °C reaction temperature and 3 h reaction time of which it was much higher compared to 35.4% yield obtained when commercial CaO was used at the same reaction conditions.

2.2.5 Biodiesel production techniques

Biodiesel production efficiency always depends on the production technique used. In most cases, chemical and biological techniques are the two major production techniques currently used in production of biodiesel using animal fats and vegetable oils. Chemical production technique is the application of catalyst during conversion of triglycerides to biodiesel while biological production technique is the application of enzymes mainly lipase for conversion of triglyceride to methyl ester. In recent days, non-catalytic techniques and supercritical methods of conversion are also employed, but, Atabani *et al*. (2012), mention four main methods used in biodiesel production as: transesterification, pyrolysis, dilution with hydrocarbons blending and micro-emulsion.

According to Chopade *et al*. (2012), transesterification is a method mostly used in biodiesel production by mixing long chain oil compound (triglycerides) with short–chain alcohols with catalyst in order to reduce high viscosity of oil to form biodiesel. The method is commonly used because is simple, economical feasible (Atadashi *et al*., 2011; Endalew *et al*., 2011; Atabani *et al*., 2012). The advantages and disadvantages of the four methods are given in Table 2.

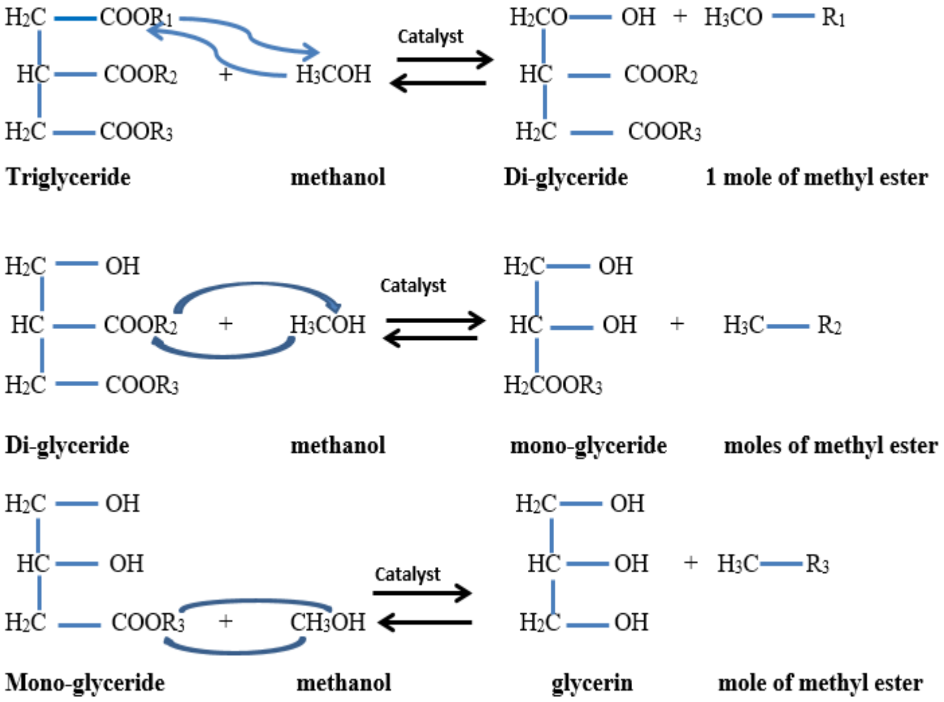
Table 2: Advantages and disadvantages of biodiesel production techniques

Technologies	Advantage	Disadvantage
Dilution (direct blending)	• A very simple and cheap process	• Very low volatility • High viscosity • Very low stability
Microemulsion	• Less reaction time • High conversion rate • Good adaptability	• High temperature and pressure is needed • It has high investment cost • It has high energy consumption
Pyrolysis	• Fuel properties closer to mineral diesel • A simple process • No pollution	• Requires high temperature • High invested capital. • Low purity
Transesterification	• High yield conversion • Low cost of production • Easy and simple in conversion	• Needs feedstock with low water and FFA content when using the homogeneous catalyst. • Few neutralization and washing steps when using the homogeneous catalyst.

2.3 Transesterification

Physicochemical properties of the fats and oil prevent them to be directly used in modern engines caused by their deviation from standard hydrocarbon fuels (Ngamcharussrivichai *et al*., 2010). Transesterification is a technique used to convert triglycerides of higher viscosity into mono-alkyl esters of lower viscosity by using short chain methyl group from alcohols, such as methanol to form biodiesel. Theoretically, transesterification is the reaction whereby a mole of triglyceride reacts with three moles of alcohols using acidic, alkaline or lipase (enzyme) catalyst to produce three moles of methyl esters and a mole of glycerol (Bobade *et al*., 2012; Abdullah *et al*., 2017).

Generally, biodiesel fuel is mostly produced via transesterification process (Tang *et al*., 2018). In history, the use of transesterification was employed by Rudolf Diesel in early 1846 by using vegetable oil (castor oil) through methanolysis (Demirbaş, 2003). The process is reversible that makes it difficult to obtain a yield of 100% (Oletoye *et al*., 2011; Tariq *et al*., 2012; Pathak, 2015). The process consists of three consecutive steps in which one molecule of the ester is formed in each step while one mole of glycerol is formed as a by-product at the end of reaction (Sharma *et al*., 2008), as shown in Scheme 1 below,



Scheme 1: Three steps on the transesterification process.

The first step deals with the conversion of triglycerides (TG) to di-lycerides (DG). In this step, one of an alkyl group is detached from triglyceride and combined with a methyl group to form a mole of methyl ester. The second step is the conversion of di-glyceride to mono-glyceride (MG), then the MG is converted to a methyl ester and one mole of glycerol is formed (Sharma *et al*., 2008; Ejikeme *et al*., 2010; Tariq *et al*., 2012).

During the transesterification process, methanol or ethanol are the most often used, but methanol is mostly used because of its physical and chemical advantages (Ribeiro *et al*., 2011). It can react with triglycerides quickly (Musa, 2016), it is inexpensive and reactive, with no complex organic compounds (Berrios and Skelton, 2008). In order for the process to occur some parameters have a big influence on its occurrence. Those parameters are type and amount of catalyst, oil to methanol molar ratio, reaction temperature, reaction time, free fatty acid composition and water content (Meher *et al.,* 2006). For the catalysts, whether acidic or basic are preferred to be used in the process but alkaline catalysts are mostly used with the fact that they are less corrosive in nature, they are faster than acid catalyst and are more environmentally benign.

2.4 Factors influencing the transesterification process in biodiesel production

In order for transesterification reaction to occur, various factors such as reaction temperature, reaction time, type of catalyst (homogeneous or heterogeneous, acid or base), methanol-to-oil molar ratio, water content, and FFA composition are to be considered. These parameters play a big role in the quality and percentage yield of the biodiesel.

2.4.1 Influence of reaction temperature

Temperature is a very essential parameter for biodiesel yield to occur during transesterification (Kotwal *et al.*, 2009). Different temperatures can be used in relation to the type of oil and alcohol used (Meher *et al*., 2006; Babajide *et al*., 2010). For normal transesterification process, evaporation of alcohol must be prevented by keeping reaction temperature less than the boiling point of alcohol (Tariq *et al*., 2012). Also, during biodiesel production, an increase in reaction temperature increases the rate of conversion of FFA to methyl esters (Shu *et al*., 2010; Babajide *et al*., 2010). But, the exposure of oil in the excessive higher temperature leads to the formation of abnormal polymeric compounds caused by the degradation of unsaturated fatty acid and triglycerides compounds (Obadiah *et al*., 2012). Also, Brito *et al*. (2007) reported that, as temperature increases, the viscosity also decreases. Rashid *et al.* (2008) studied the effect of reaction temperatures at 35, 50 and 65 °C using rapeseeds oil and KOH as a catalyst while methanol to oil molar ratio was 6:1. On their experiment, observed the yield to be 63.5, 65.0 and 68.0% respectively. They concluded that higher temperatures promote saponification of triglycerides before completion of alcoholysis when the base catalyst is used.

2.4.2 Influence of reaction time

According to Wei *et al*. (2009), the reaction time is the determinant of the methyl ester yield in a reaction. The rate of conversion depends on how long the reaction takes place (Li *et al*., 2018). Time of reaction is the main cause for adsorption of reactant and desorption of products and it depends on the catalyst activity. Algoufi *et al*. (2017) reported that, the reaction time is required to enhance the mass transfer towards the product and it is influenced by active sites of the catalyst. Any process that reaches the maximum yield conversion at a shorter period of time, is considered as economically feasible (Lin *et al.*, 2009). According to Leung *et al.* (2010), any excess reaction has its impacts of reducing product yield caused by backward reaction during transesterification. This was caused by more fatty acids form soap hence loss of ester yield.

2.4.3 Influence of FFA

The free fatty acid in oil determines the applicability of fats or oil in the transesterification process, also it predicts the yield during the reaction (Guo *et al.*, 2010). High FFAs are prone to soap formation, high catalyst consumption, reduces efficiency of the catalyst, increases the reactant viscosity and reduces yield. If FFA concentration in the feedstock is higher than 1%, alkaline homogeneous catalysts are unfavorable to use in the transesterification because they are easy to form soap. Rather, acid catalysts or heterogeneous catalysts are preferred.

2.4.4 Influence water content

The water content in the feedstock has a significant effect on the biodiesel yield when the transesterification process is employed for biodiesel production. Guo *et al.* (2010) in their study, learnt the influence of water content in a feedstock by synthesizing biodiesel from soybean oils with different water contents using sodium silicate as the catalyst. At low water content, high yields of biodiesel were observed, and at higher water content the yield was clearly decreased. The high amount of water in the oil causes hydration to occur by producing OH^- that causes soap to occur.

2.4.5 Influence of methanol to oil molar ratio

Alcohol to oil molar ratio plays an important role in the conversion of triglycerides to methyl or ethyl esters. Generally, during conversion by transesterification using stoichiometric ratio, three moles of alcohol is required per one mole of triglyceride to form products methyl esters and glycerol. Any excess of methanol will increase the rate of transesterification reaction for catalyzed reaction (Kim *et al.*, 2004*;* Guo *et al.,* 2010*;* Issariyakul *et al.*, 2014).

Obadiah *et al.* (2012) used calcinated waste animal bones to produce biodiesel from palm oil while varying oil to methanol molar ratio from 1:1 to 1:18. On their study experience the significant increase of methyl ester yield as oil to methanol molar ratio increases. At the high amount of methanol to oil molar ratio, it was observed to promote the formation of methoxy species on the surface of CaO. This tends to shift the equilibrium toward product direction and increase the rate of conversion to 96.78%. No more yields were observed when methanol to molar ratio exceeds 1:18.

Rashid *et al.* (2008) studied the influence of methanol to oil molar ratio of 3:1 to 21:1 in the production using NaOH catalyst on rapeseed oil. In their observation, they found that as molar ratio increased from 3:1 to 6:1 the methyl ester also increased from 57 to 96.0% and at lower molar ratios, the reaction was incomplete. Furthermore, they observe more time to allow decantation by gravity during separation of biodiesel and glycerol takes more time. Other researchers, Lim *et al.* (2009) in their study came up with an observation that, the interference of the glycerol separation was caused by the amount of glycerol largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the reactants and catalyst. Also, Guo *et al.* (2010) confirmed that, at higher content of oil to methanol molar ratio, stable emulsions would be formed, that lead to complex separation and cleansing of biodiesel.

2.4.6 Influence of catalyst loading

The biodiesel yield depends mostly on the catalyst loading whereby increasing amount of catalyst results in increasing the number of active sites (Omar and Amin, 2011). An excessive amount of catalyst results in an increase of viscosity of the mixture resulting in poor mixture formation (Kim *et al.*, 2004; Obadiah *et al.*, 2012). Various types of the catalyst at different amount using different types of feedstock have been used in biodiesel production. Catalysts mainly used in biodiesel production are of three types: homogeneous, heterogeneous and biocatalyst (enzymes) catalyst differs according to their physical presence in the reaction.

2.5 Catalysts in the transesterification reaction

The catalyst is an essential raw material for biodiesel production. It plays a big role in increasing the reaction rate and yield during the transesterification process. Correct selection of type and amount of catalyst to use is governed by number of factors: (a) The type and quality of feedstock (FFA and water content), (b) The operation conditions (oil to alcohol molar ratio, reaction temperature, agitation rate, and pressure applied), (c) Catalytic activity (chemical nature and texture), (d) Cost of implication (availability and environmentally benign) (Chouhan *et al*., 2011). For cheap and economically feasible biodiesel production, developing new and active cheap catalysts for effective transesterification of various kinds of oil feedstock is inevitable (Atadashi *et al*., 2013). Generally, three types of catalysts can be used in the transesterification processes: homogeneous, heterogeneous and enzymic (biocatalyst) catalysts. Its chemical nature allows the catalyst to be classified into alkali or acid.

2.5.1 Homogeneous catalyst acidic and basic

Homogeneous catalyst refers to the type of catalyst acting in the same phase as the reaction mixture (oil). They are the most used catalyst in the production of biodiesel through transesterification process. The most frequently used homogeneous catalysts are NaOH, KOH, CH_3OK, and CH_3ONa which are alkaline catalysts while homogeneous acidic catalysts include H_2SO_4, HCl, H_3PO_4 (Ribeiro *et al*., 2011; Thanh *et al*., 2012). These catalysts are simple to use, easily soluble in methanol, require less reaction time with high yields during biodiesel production. Apart from that, the catalyst shows great disadvantages in transesterification processes of high production costs due to high washing and purification steps, sensitive to the high water content in feedstock leading to soap formation, high wastewater management, difficult to separate from the reaction mixture and not reusable. Alkaline catalysts are restricted to low FFA while acidic catalyst takes more time to convert triglycerides to methyl esters (Sanli, 2008; Jimenez-lopez *et al*., 2011; Endalew *et al*., 2011; Borges *et al*., 2012; Thanh *et al*., 2012; Tang *et al*., 2018). These drawbacks motivated intense research and use of heterogeneous catalysts in the transesterification process.

2.5.2 Heterogeneous catalysts

In recent years, there is great concern on using heterogeneous catalysts to replaced homogenous catalysts due to their great advantage in transesterification reactions (Abdullah *et al*., 2017). Basically, heterogeneous catalysts are the ones that act in different states from the reaction mixture, and for biodiesel production is in the solid phase. The catalysts are insensitive to high FFA, they do not dissolve or not consumed in the reaction mixture, easily to separate from reaction mixture, handle with less washing steps, with low cost, reused, less toxicity, high catalytic activity, longer life catalyst and are environmentally friendly. Also, it can be derived from both renewable and non-renewable resources which are naturally abundant (Helwani *et al*., 2009; Ngamcharussrivichai *et al*., 2010; Naik *et al*., 2010; Abdullah *et al*., 2017). The effectiveness of the heterogeneous catalyst in catalytic conversion depends on the activity of the solid catalyst used (Lee *et al*., 2009). Generally, heterogeneous catalysts can be classified as acid or base.

(i) Heterogeneous acidic catalysts

Heterogeneous acid catalysts have got much attention against homogeneous catalyst due to their sensitivity to high FFA feedstock, easy to separate from a reaction mixture and their stability of not losing catalytic activity when used in number cycles (Lee *et al*., 2014; Shu *et al*., 2010). These catalysts are characterized by having lower catalytic activity, required higher reaction temperatures (~200 °C), and higher reaction times hence increasing the biodiesel production cost (Christopher *et al*., 2014; Issariyakul *et al.*, 2014). Good thing on acid catalysts is the ability to simultaneously esterify and transesterification oil with FFA greater than 2%. It can work in the feedstock with a high water content of more than 20% without deactivation and show better yield results but likely to cause corrosion of equipment due to acidity property (Endalew *et al.*, 2011*;* Chouhan *et al.*, 2011). The most known catalysts of this type are sulfated zirconia (SZ), sulfonated saccharides, sulfonic acid group and sulfonic acid modified mesoporous silica (Jimenez-lopez *et al*., 2011; Guo *et al*., 2011; Rachmat *et al*., 2017; Issariyakul *et al*., 2014)

(ii) Heterogeneous basic catalysts

In improving transesterification process of triglycerides, various types of heterogeneous basic catalytic materials such as metal oxides, metallic salt, and supported base catalyst have been used. Heterogeneous base-catalysts are of higher reaction rates in transesterification greater yield as compared to the acid-catalysts (Christopher *et al*., 2014). According to Lee *et al.* (2009), there are six categories of heterogeneous catalyst namely: mixed metal oxides, single metal oxides, supported alkaline metals, alkaline earth metals, hydrotalcites and organic base solids. Among these, alkaline earth metal oxides are the most frequently used catalysts in the transesterification process for biodiesel production.

In many cases, metal oxides such as CaO, K_2O, MgO, and MnO are among good examples of solid base catalysts abundant in nature and widely used to produce biodiesel (Viriya-empikul *et al*., 2010; Zabeti *et al*., 2009). Calicium oxide is the most used and can be derived from calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), natural earth occurrences rocks, animal bones, seashells and agricultural wastes (Algoufi *et al.*, 2017). For example, Ngamcharussrivichai *et al.* (2010) calcinate CaO from calcite and dolomite rocks at a temperature of 800 °C with burning time of 2 h and use as a catalyst (6% wt.) with methanol to oil molar ratio (30:1) and 3 h reaction time while reaction temperature kept at 60 °C in transesterification of palm oil. The FAME of 98% was yielded while catalyst reused for the next seven runs.

Nevertheless, the high price of commercial catalyst, multi-steps on preparation procedure of catalyst from non-renewable sources and environmental issues, raise a concern of looking for greener and cheaper catalyst from renewable sources to replace conventional catalysts (Abdullah *et al.,* 2017). Most of the utilized catalysts have been derived from abundantly discarded materials which are rich in calcium carbonate for example shells, bones, and agricultural biomass wastes. Among many other advantages; the catalysts are simple and safe to handle and store, abundantly available, cheap, comes from renewable sources and are environmentally benign (Smith *et al.,* 2013). The number of materials rich with $CaCO_3$ was mentioned to be a good precursor for the organic catalyst which includes: waste seashells, eggshells, waste fish scale, animal bones and some of the plant biomass (Viriya-empikul *et al*., 2010; Wei *et al.,* 2009*;* Chakraborty *et al.,* 2010*;* Correia *et al.,* 2017*;* Chakraborty *et al.,* 2011; Smith *et al.,* 2013).

Generally, there are three main ways of transforming biomass into a solid base catalyst purposely for biodiesel production: (a) Thermal treatment (calcination method), is the way in which biomass can be directly transformed into catalyst by direct burning to form metal oxide example $CaCO_3$ to CaO, (b) Using impregnation method to support materials such as silica into reactive metals, (c) Using activated carbon materials to attach basic active compounds of alkaline and metal hydroxides (Tang *et al.*, 2018).

In most cases, calcination processes are simple and popular in use. Birla *et al.* (2012) calcinated snail shells at 900 °C for 3.5 h and got very effective heterogeneous CaO catalyst.

The catalyst was used in the transesterification process of waste frying oil for under optimum conditions and yield obtained was 87.28%. Wei *et al*. (2009) generated an active catalyst from waste eggshell, the catalyst was calcinated at 800 °C for 2 h and used for the transesterification of soybean oil resulted to a yield of 97–99%. Correia *et al*. (2017) used calcinated waste quill eggshells at 900 °C for 3 h to produce FAME and yield of 99.99% was observed. Chakraborty *et al*. (2011) converted waste Rohu fish (Labeorohita) scale into very high efficiency, of low cost and reusable heterogeneous catalyst for transesterification of neem seeds oil. The fish scale was calcined at a temperature above 900 °C for 2 h and used for transesterification process giving the maximum yield of 97.73%. The catalyst also confirmed better reusability results that could be reused up to six times in biodiesel production.

Generally, the active sites of heterogeneous catalyst are the ones which determine the effectiveness of the heterogeneous catalyst during conversion. The active site in various alkaline solid metal catalysts such as CaO, K_2O and MgO make them to be widely used in biodiesel production. CaO has been used frequently as catalyst due to its advantages such as long life catalyst, does not yield soap, has high activity and needs moderate reaction temperature (Math and Sudheer, 2010; Janaun and Ellis, 2010).

Apart from catalyst derived from shells and rocks, several studies investigate the potential use of biomass ashes as a heterogeneous catalyst for biodiesel production. Most of the organic compounds including biomass contain more carbon, oxygen, and metals such as sodium, calcium, potassium and magnesium (Jenkins *et al*., 1998; Luque *et al*., 2012). The carbon and oxygen will be reduced in the material when burned at higher temperature and results to formation of metal oxides of CaO, K_2O, MgO and other metal oxides present in the sample (Jenkins *et al.*, 1998). According to Maneerung *et al*. (2015) and Tang *et al*. (2018), biomass containing the high amount of carbonate can be converted into their metal oxide like CaO through thermal treatment (calcination process) and used as the solid base heterogeneous catalyst for biodiesel production in catalytic conversion. The ashes of these biomass materials are oxides of high basic strength, with high catalytic properties for biodiesel production. Furthermore, the biomass-derived catalysts are sustainable, safe and of more environmental friendly (Abdullah *et al.*, 2017).

Tamarindus indica fruit shells are among agricultural wastes from juice processing industry naturally rich in calcium compounds (Sivasankar *et al.*, 2012). They result from Tamarind (ukwaju) tree-type plant that belongs to the dicotyledonous family: *Caesalpiniaceae*, indigenous to tropical Africa. The pulp is edible used to make food, sauces, curries and juices and other commercial drinks leaving shells with no value (Meher *et al*., 2014). The fruit shell wastes are abundant with $CaCO_3$ (11.1%) by weight (Wadekar *et al.,* 2006). Other elements such as K (13.0%), Mn (12.1%), Mg (10.4%), Na (8.90%), Zn (7.0%), Fe (4.5%) and Cu (2.10%) mg/kg are present as reported by Ajayi *et al.* (2006). TIFSs like any other plant biomass have high amount of alkaline earth metal compounds. When burned to ashes they are ready to form metal oxides, a heterogeneous catalysts and can be used in biodiesel production (Zabeti *et al*., 2009). Good examples of catalysts derived from agricultural wastes and used for transesterification are: Amos *et al.* (2016) used cocoa pods and rice husks calcinated at 600 °C as catalysts for the transesterification of *Parinari polyandra* seeds oil resulting in a better biodiesel yield of 98.61% and 88.85% respectively. Sulaiman *et al.* (2017) used calcinated coconut waste and eggshells at 900 °C as the catalyst in palm oil resulting in a yield of 81%. Another researcher Andherson (2018), produced biodiesel from waste cooking oil (WCO) using two agricultural wastes K_2CO_3 from cocoa pods and CaO from waste chicken eggshells and compared their yields with their counterpart commercial catalyst. The catalysts were calcinated at 900 °C and achieved a yield of 73.33% and 81.43% compared to 66.67% and 83.59% of commercial catalysts respectively. Also, Li *et al.* (2018) used green biomass ash from old camphor tree burned in the air and then supported with K_2CO_3 to form a solid base heterogeneous catalyst. They evaluated its performance on biodiesel production from soybeans oil with a yield of 92.27%.

Furthermore, Osakwe *et al.* (2018) investigated the use of Kolanut pod husk ash burned at 600 °C as a catalyst in *Thevetia peruviana* (yellow oleander) seeds oil resulting to a yield of 84.50%. Also, Kouzu *et al.* (2008) examined the use of banana trunk (*Musa balbisiana Colla*) ash as heterogeneous solid base catalyst in producing biodiesel from *Thevetia peruviana* with a yield of 96% obtained. Tang *et al.* (2018) concluded that biomass waste utilization can be used to produce catalysts of low cost with the good catalytic performance of more than 80% biodiesel. Apart from biodiesel production, the process will decrease the problem of waste materials and the issue of their disposal as produced from agricultural industries and other various human activities. Also, the use of this method is of various advantages such as producing a high and efficient bio-based heterogeneous catalyst of low cost, non-toxic, biodegradable, non-corrosive and both method and catalyst are of more environmentally friendlily.

(iii) Zeolite catalysts

In recent studies, zeolite has gained a great concern on using it as a heterogeneous catalyst for biodiesel production (Kozhevnikov, 2007; Suppes *et al.*, 2004; Sharma *et al.*, 2011). Zeolites catalyst are characterized by having acidic or basic nature depends on metal attached to it, high thermal stability, less toxicity, non-corrosive, reused and environmentally friendly but are much expensive and needs higher temperature during reaction for transesterification (Shu *et al.*, 2010; Sharma *et al.*, 2011).

2.5.3 Enzymic catalysts

In recent years, enzymatic reactions using lipase for biodiesel production have attracted growing attention. An enzyme like any other catalyst can be used in transesterification reaction and has been considered the most effective method for biodiesel production. Various Enzymes (lipases) catalysts such as Candida Antartica (Royon *et al.*, 2007), Candida rugosa (Linko *et al.*, 1998), Pseudomonas cepacia (Shah *et al.*, 2007), immobilized lipase (Lipozyme RMIM) (Vieira *et al.*, 2006) Pseudomonas spp. (Ming *et al.*, 1999) or Rhizomucarmiehei (Ming *et al.*, 1999) have been used. Enzymatic catalysts possess both homogeneous and heterogeneous catalysts properties. Enzymic catalysts have various advantages over chemical catalysts: they have easy product recovery, environmentally friendly properties, high selectivity, and a low oil to alcohol molar ratio (Zhao *et al.*, 2013). It tolerates on oil having a high amount of water and FFA and facilitating easy purification of biodiesel and glycerol (Zhao *et al.*, 2013; Tang *et al.*, 2018). Enzyme catalysts have their drawbacks such as: being expensive, easily deactivated and require long reaction time. These major drawbacks limit the industrial application of enzymes in the biodiesel production (Helwani *et al.*, 2009; Zhao *et al.*, 2013).

2.6 Catalyst reusability

One of the advantages of heterogeneous over the homogeneous catalyst is its being easy to separate from mixture and reusability. The texture and its physical properties made heterogeneous catalyst to be easily separated from reaction mixture just by filtration or centrifugation, washed, dried and reused for several runs without deactivation. But reusability depends on the active site on the catalyst and texture structure. The catalyst activity always depends on its surface area, base strength, surface morphology, chemical composition and base site concentration which depends on the preparation method (Kiss *et al.*, 2006).

Catalysts reusability has a great potential industrial application in reducing the costs of biodiesel production (Jegannathan *et al*., 2008; Wei *et al*., 2009). The ability of the catalyst to be reused several times depends on the preparation technique and their chemical properties. Various studies have been conducted on catalyst reusability. For example, Wei *et al*. (2009) studied the reusability of the eggshells derived catalyst calcinated at 800 °C. The catalyst was reused 13 times without loss of the catalyst activity property. Hu *et al.* (2011) reported the use of a catalyst (CaO) derived from freshwater mussel for 12 cycles with 80% yield from tallow oil. Correia *et al*. (2017) studied the reuse of quail eggshells calcinated at 900 °C with three cycles on transesterification of sunflower oil with slightly loose in catalyst activity. They concluded that the deactivation was probably attributed to washing and sample handling between each cycle. Chakraborty *et al*. (2010) also studied the reusability of waste fish scale derived heterogeneous catalyst calcinated at 900 °C on soybean oil. The developed catalyst was chemically stable and was used consecutively for six experimental runs without remarkable deactivation.

Generally, heterogeneous catalysts are recovered easily from the reaction mixture and reused in the transesterification reaction. But these catalysts experience the deactivation caused by structure change due to the presence of CO_2 and water in the reactor (Wei *et al*., 2009; Endalew *et al*., 2011). Also, the stability and reuse of solid catalysts have an important role in determining the economic application for biodiesel production on a large industrial scale (Correia *et al*., 2017).

2.7 Biodiesel purification and yield estimate

Biodiesel and glycerol are the products resulted from mixture of oil/fats; alcohol and catalyst reacted in the same reactor at a given time, temperature and agitation speed. Production of biodiesel using homogeneous catalyst results into a product of homogeneous mixture while that uses heterogeneous catalyst resulted into heterogeneous mixture. The heterogeneous mixture needs more separation of catalyst using filters to separate catalyst from mixture and remain with homogeneous solution. The separation of biodiesel and glycerol from the product solution is made by gravity settling and/or by centrifugation. After removal of glycerol, the remaining methyl ester may consist of traces of alcohol, glycerol, catalyst (metals), tri, di and mono-glycerides and water elements (Garcia *et al*., 2015). These traces of impurities must be removed in order to attain the quality biodiesel that meets specifications that will not harm the engine by poor performance, contaminants and emissions during burning. To remove these traces of impurities two types of washing techniques as wet and dry washing have been employed.

2.7.1 Wet washing technique

Wet washing technique is the most widely used method using warm water to remove impurities from the product. According to Atadashi *et al*. (2011), wet washing techniques involve washing biodiesel using deionized water (Ali and Isis, 2013; Grubb, 1948), acid and water (Garcia *et a*l., 2015; Grubb, 1948) or using of organic solvents (Grubb, 1948; Ma *et al*., 1998). The technique is simple to use and of low cost since water is abundant, furthermore, biodiesel is insoluble in water. But the method is prone to allow soap and free fatty acid formation resulting in reducing yield and also it generate large amount of waste water (Garcia *et al*., 2015); Manique *et al*., 2011). Garcia *et al*. (2015) successfully purify their biodiesel using acidified hot water (HCl 1N-1:4) at 85 °C followed by neutralizing it with distilled water at 85 °C. The pure biodiesel was dried in oven at 105 °C for 1 h to remove water content. Also, $MgSO_4$ or Na_2SO_4 can be used as an absorbent to remove water content from the washed biodiesel (Akhtar *et al*., 2017).

2.7.2 Dry washing technique

Dry washing technique uses adsorbents in purifying biodiesel. Various adsorbents such as silicates (megasol), ionic exchange resin, cellulosic materials, activated carbons, activated clays, etc have been developed and used to purify biodiesel. These adsorbents consist of both acidic and basic adsorption sites where polar compounds such as methanol, glycerides (tri, di or mono), glycerol, metals and soap are absorbed remaining with pure biodiesel. The technique is characterized by being waterless, with lower purification time (10-20 min) and of low reaction temperature 65 °C but expensive (Atadashi *et al*., 2011)

2.7.3 Product yield estimation

Purification of biodiesel helps to know the amount of biodiesel produced in a given reaction. During transesterification process the product yield is purified to enable finding the actual percent purity of biodiesel produced. According to Vicente *et al*. (2007), various methods have been used such as: (a) Analytical method where gas chromatogram is used to estimate percentage yield. (b) Statistical method use to analyze various variables involved in biodiesel production. Such methods include Response Surface Methodology (RSM), Artificial Neural

Network (ANN) etc and (c) Use of mathematical expression to find the percentage yield. The mathematical expression has mostly been used by many scholars in estimating the product yield as shown in Eq (7).

2.8 Physical and chemical properties of methyl esters

The quality of the oil feedstock, type and amount of catalyst and alcohol used have great influence into the properties of biodiesel produced but will be closely related to mineral diesel (Canakci, 2007). Before the use of the biodiesel, analyses of the physical and chemical properties are required to assess the suitability of its use in diesel engines. Globally, two major international standard limits, American Society for Testing of Materials ASTM D6751 and European Union Standard for biodiesel fuel (EN 14214) were used to standardize the quality of fuel produced. Various biodiesel physical and chemical properties include density, viscosity, moisture content, oxidative stability, cloud point, flash point, free fatty acids, glycerol, cetane number, acid number, sulphated ash test, and carbon residue. Table 3 shows the ASTM standard limits and methods used to analyze the property respectively. Since biodiesel is made from different feedstock and process, some of properties differ from one product to another.

Table 3: American standards limits (ASTM D6751) specification for biodiesel test

Property test	Test method	Limits	Units
Density at 15 °C	D 4052	840 - 880	kg/m^3
Kinematic viscosity at 40 °C	D 445	1.9 – 6.0	mm^2/s
Cetane number	D 613	47 min	-
Flashpoint open or closed cup test	D 93	130.0 min	°C
Cloud point	D 2500	-	°C
Water and sedimentation	D 2709	0.050 max	Volume (%)
Sulfated ash	D 874	0.020 max	Mass (%)
sulfur	D 5453	0.05 max	Mass (%)
Carbon residue	D 4530	0.050 max	Mass (%)
Acid value	D 664	0.80 max	mgKOH/g
Free glycerol	D 6584	0.020 max	Mass (%)
Distillation temperature (95% recovered)	D 1160	360 max	°C

Source: (Sanli, 2008)

2.8.1 Kinematic viscosity

The kinematic viscosity of any fuel used in the internal combustion engine is one of the most essential fuel properties which measure the effectiveness and completeness of biodiesel production. It specifies the ability of a fuel to: flow, spray, mix with other hydrocarbons, atomize and make combustion (Sanli, 2008; Atabani *et al*., 2012). The fuel injection process depends much on the viscosity of the fuel and it is a measure of fuel atomization processes. Higher viscosity leads to poor atomization, poor cold engine start-up process, ignition delay hence poor burning in the combustion chamber, increased smoke and emission (Abbaszaadeh *et al*., 2012; Hamamre *et al*., 2014). Generally, biodiesel has higher kinematic viscosity 10 – 15% times greater than that of diesel fossil fuels caused by its large molecular mass and large chemical structure. Also, it depends on feedstock and amount of oxidation (Halikia *et al*., 2001; Atabani *et al*., 2012). According to ASTM D6751 and EN 14214 standard limits the maximum limits of viscosity at 40 °C in biodiesel are 6.0 mm^2/s and 5.0 mm^2/s respectively.

2.8.2 Density

The density of the biodiesel is mostly influenced by the FFA composition in a feedstock, the saturated and unsaturated level and the chain length of methyl ester produced. The saturated methyl esters tend to have a higher density than unsaturated ones (Ong *et al*., 2013). Since heating values of fuel depend on density, denser oils contain more energy than less dense energy (Demirbaş, 2003; Atadashi *et al*., 2011). Most of the biodiesel fuels produced from animal fats or vegetable oils are denser and less compressible than the mineral diesel. The limit of density at 15 °C in biodiesel, according to ASTM D6751and EN 14214 limits varies between 840 – 880 $kg/m^3$and 860 – 900 kg/m^3 respectively. Both density and compressibility influence atomization and better mixture formation in the engine (Tat *et al*., 2000; Sanli, 2008). Fuels with high density generally cause increase in exhaust emission, nitrogen oxide (NOx) and particulate matter (PM) from the engines.

2.8.3 Cold flow properties

Cold flow properties of biodiesel fuel depend on pour point (PP), cloud point (CP), cold filter plugging point (CFPP) and low-temperature filterability test (LTFT) (Verma *et al.*, 2016). Biodiesel like any other liquid when subjected to lower temperatures, it solidifies and forms the crystal. As temperature decreases the crystal nuclei grow to visible state hence cloud point. Further decrease in temperature will cause more increase in crystal nuclei and prevent free pouring of fluid and hence pour point. According to Verma *et al*. (2016), pour point and cloud point are the vital parameters to define the cold flow quality property of biodiesel.

The cloud point refers to the temperature at which a cloud of wax crystals first appears over a liquid when cooled. It is the temperature at which smallest observable cluster of wax crystals first occur during cooling under stated conditions (ASTM Products and Fuels, 2017) while *Pour point* is the temperature at which a fluid begins to flow under specific conditions (Ali *et al*., 1995; Sanli, 2008). From the literature, most of the biodiesel fuels have higher pour and cloud points than the mineral diesel. The major cause of this property is nature and amount of fatty acid composition in the methyl or ethyl ester. According to Knothe (2005), an increase in the number of carbon atoms in the chain will increase the freezing point of a biodiesel fuel but decreases with increasing double bonds. So, it is expected that biodiesel with large amounts of saturated fatty acids have higher cloud points and pour points than unsaturated one. Cloud and pour point causes major engine operation problems of hard starting, blockage of fuel filters and fuel. This will cause engine fuel starvation resulting to poor driving force and engine damage (Atabani *et al*., 2012; Ong *et al*., 2013). Also, cold flow properties are barriers towards commercialization of biodiesel worldwide.

2.8.4 Acidic value

The acid number is an indicator of FFA content in a fresh fuel sample. The acid value is the amount of KOH in mg required to neutralize 1 g of methyl ester (ASTM, 1997). Free fatty acids are the unsaturated or saturated mono-carboxylic acids that naturally occur in animal fats, vegetable oils or waste greases and are determined by gas chromatography (GC) (Ali *et al*., 1995a). The higher acid value results from the high amount of free fatty acids. The higher acid content in the fuel causes: lower energy efficiency and severe corrosion in the fuel supply system of an engine (Atabani *et al*., 2012). This acid value in the fuel can be higher if the process of producing biodiesel was not properly maintained or the fuel was allowed to undergo oxidation caused by contamination with water during processing or storage (Meher *et al*., 2014). Pure biodiesel, however, is not acidic, but can lead to FFA formation. The maximum limit of acidic value in biodiesel for both ASTM D6751 and for EN 14214 is 0.50 mg of KOH/g (Sanli, 2008).

2.8.5 Flash point

Flashpoint is the minimum temperature at which the liquid fuel will start burning when it comes in contact with fire. Flashpoint is determined by Pensky-Martens open or closed cup tester using ASTM test method D92 and D93-90, respectively (Ali *et al.*, 1995a). This temperature goes simultaneously with fuel volatility, which specifies fuel feature for an engine's starting, warming, and the fuel safety point view during storage and transportation (Sanli, 2008). Flashpoint goes contrariwise with the fuel's volatility and for biodiesel is higher than the prescribed limit of mineral diesel (Atabani *et al.*, 2012). The minimum limit of a flashpoint for pure biodiesel according to ASTM D675 is 130 °C and for EN 14214 is 120 °C respectively. Fuels with low flash point result in less NOx emission due to low combustion pressure and temperature (Canakci *et al.*, 2005). Apart from the advantages, fuel with higher flash point may result in higher carbon deposits in the combustion chamber of an engine (Sanli, 2008).

2.8.6 Cetane Number

Cetane number (CN) value defines the ignition quality of the fuel. The higher the cetane number the better is the ignition quality of fuel. Cetane number is a diesel fuel property that quantifies the fuel's readiness to auto-ignite after injected in the cylinder (Tat *et al.*, 2000). Higher cetane number tallies with shorter ignition delay after fuel injected into the cylinder. The CN of most of the biodiesel from animal fats and vegetable oils is higher than 51 while that of petroleum-based diesel usually is between 40 and 52 (Issariyakul and Dalai, 2014; Sanli, 2008). CN depends on the level of unsaturated FFAs in the methyl ester. The higher the unsaturated FFAs the higher is CN. Other factors contribute to CN are the number of carbon atom in straight chain, position of the double or triple bond in the chain, density and boiling point of the methyl ester (Atabani *et al.*, 2012; Knothe, 2005, 2014).

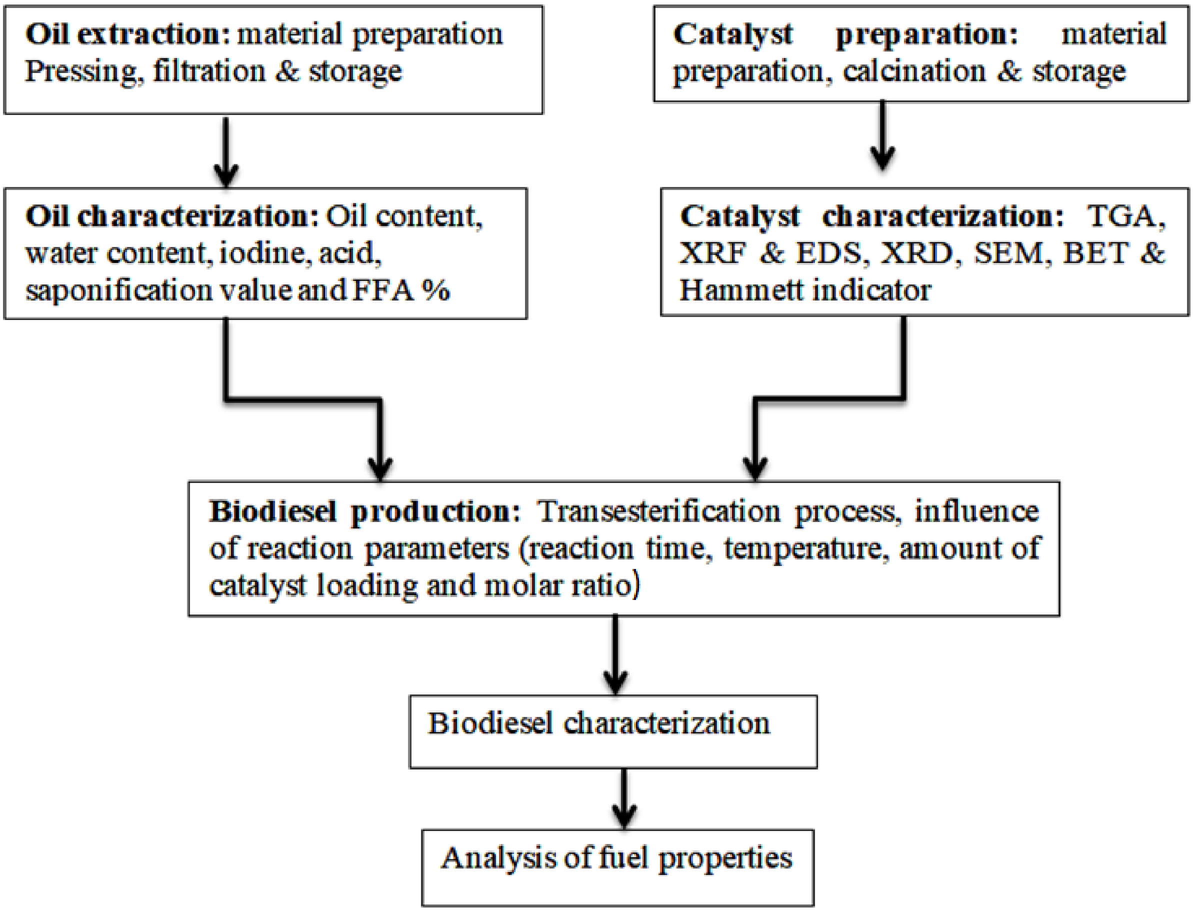
2.8.7 Oxidation stability

Oxidation stability is another biodiesel property that shows the ability of the fuel to resist oxidation during extended storage (Sanli, 2008). Oxidation causes deterioration of the fuel due to gum formation and it is promoted by fuel chemical structure (Atabani *et al.*, 2012; Neff *et al.*, 1992). Biodiesel that contains substantial amounts of linolenic, linoleic or oleic acid are more susceptible to the oxidation (Knothe, 2005). The higher amount of unsaturated fatty acid chains (double bonds) in the oil will promote oxidation to occur by reacting with oxygen in the air (Atabani *et al*., 2012). Other factors that facilitate oxidation are elevated temperatures and presence of reactive metals in methyl ester.

CHAPTER THREE

MATERIALS AND METHODS

This chapter describes materials, equipment, techniques and procedures used in preparation and analysis of both the catalyst and the biodiesel fuels produced. Various steps have been followed as summarized in the flow chart Scheme 2. All experimental procedures and measurements were done in triplicate and their average value used in determination of required property.



Scheme 2: Flow chart of this research work.

3.1 Materials

Ripen Parinari fruits were collected from Njombe - Tanzania, dehulled to obtain the seeds kernel (Fig. 1(a)) and sun-dried to remove moisture ready for oil pressing process. The waste *T.indica* fruit shells (Fig. 1(b)) were collected from market place landfills and juice processing industries in the Arusha Municipalities, washed, dried and grounded to fine particles for catalyst calcination. The reagents methanol (99.8%), ethanol absolute pure, isopropyl alcohol (95%), NaOH extra pure, KOH extra pure were from LOBA Chemie. Phenolphthalein indicator (GRIFFChem), HCl (37%) from BDH Chemicals, Wijs (iodine monochloride) reagent, benzene and benzoic acid were from Sigma Aldrich. All chemicals used were of analytical grade and used without further treatment.

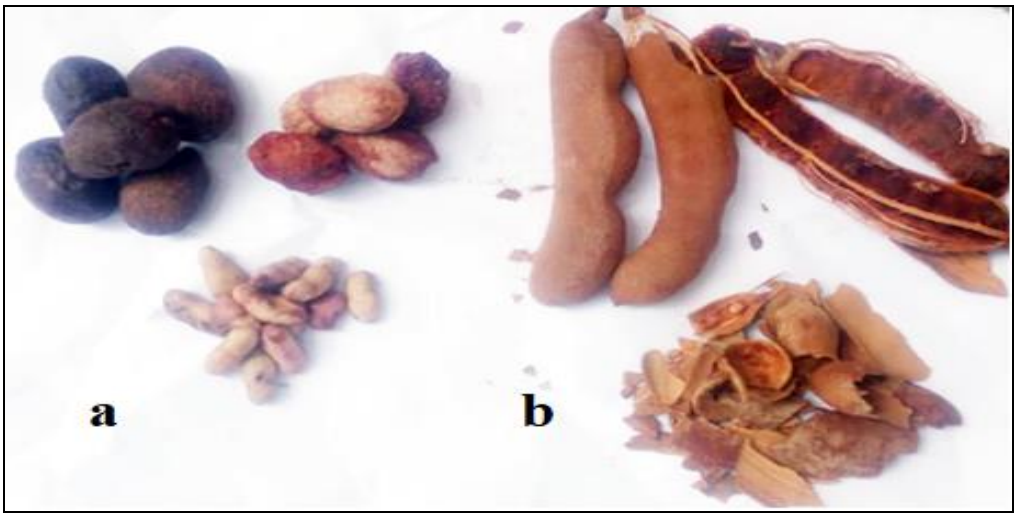


Figure 1: Photos for (a) *P. curatellifolia* fruits, pulps and seeds and (b) *T. indica* fruits, pulps and shells

3.2 Extraction and characterization of *Parinari curatellifolia* oil

3.2.1 Oil extraction

Oil from dried *P. curatellifolia* seeds kernel was extracted using a mechanical oil pressing machine. Pre-treatment of oil obtained was conducted in two steps: filtration and dehydration. Filtration is the process used to remove solid dirt content in the vegetable oil using filter paper. Dehydration involves removing traces of water content present in oil by using a low pressure distillation process (105 °C). The fresh produced clean oil was stored in a freezer for subsequent physicochemical analysis.

3.2.2 Characterization of *P. curatellifolia* Seeds Oil

The physicochemical properties PCSO like acid value, oil content, saponification value, iodine value and percentage free fatty were determined in this study. The properties were determined and analyzed according to American Standard Testing Method (ASTM, 1983) and American Official for Analytical Chemistry Standard method (AOAC, 1993; AOAC, 1997).

(i) Determination of oil content

The 20 g of dried *P. curatellifolia* seeds were weighed in weighing balance per each experiment. Then, they were subjected into a mechanical pressing machine and pressed at different pressures 200, 250 and 300 kPa, allowing oil to be flittered out while weighing the residual. The pressure was increased until no more change in weight was observed on the residual. The triplet experiment was taken for the maximum pressure attained and the average value of residual was used in the calculation of percentage oil content of the seeds using equation

$$\% \, of \ oil \ content = \frac{weight \ of \ dried \ seeds - weight \ of \ residual}{weight \ of \ dried \ seeds} \ x \ 100 \qquad (1)$$

(ii) Determination of moisture Content

In determining moisture content, the given mass of sample of clean dry seeds of parinari were taken at random and weight to contain 5.42 (g). The seeds were dried in the oven for 12 hours at temperature of 105 °C to remove moisture and then allowed to cool in a desiccator for 30 min. The dried seeds were weighed again and contain 5.09 g. The procedures were repeated three times and average weights were used in the calculation moisture content using Eq. (2) as per AOAC, (1995) procedures.

$$\% \, water \ content = \frac{weight \ of \ seed \ before \ dried \ - weight \ of \ dried \ seeds}{weight \ of \ seed \ before \ dried} x \ 100 \qquad (2)$$

(iii) Acidic value

Acidic value (AV) is the measure of FFA present in the oil. It is the weight of millimeters of KOH required to neutralize 1 gram of the organic acid present in the oil. Exactly 1 g of oil was dissolved in the solution made by 25 mL of diethyl ether and 13 mL of ethanol in 250 mL elernmeyer flask followed by gently warming. The mixture was titrated using 0.1 N of KOH using phenolphthalein as an indicator until pale pink color was observed. According to AOCS (1993) procedures, the value of AV was calculated as follows.

$$AV = \frac{titre\ volume\ x\ grams\ of\ NaOH\ in\ 0.1\ M\ of\ KOH\ solution}{sample\ weight\ in\ grams} \qquad (3)$$

(iv) Free fatty acids (%)

The FFAs are expressed as the percentage of half of value of acidic value and calculated according to equation

$$FFA = \frac{Acidic\ value}{2} \text{ x } 100 \qquad \mathbf{(4)}$$

(v) Saponification value

In determining the saponification value of PACO, 1 gram of oil was dissolved in 25 mL of ethanolic potassium hydroxide solution made by 0.5 M in 95% ethanol. The solution was heated for one hour with gently stirring using magnetic stir. While hot, 3 drops of phenolphthalein indicator was added, the color changed to pink and immediately titrated with 0.5 M HCl until the pink color disappear. According to AOCS, (1997) procedures, the saponification value was obtained by using equation

$$SV = \frac{(b-a)x \text{ grams KOH in 0.5 M KOH solution}}{sample\ weight\ in\ grams} \qquad (5)$$

where a = volume of oil solution and b= volume of titre blank solution.

(vi) Iodine value

The unsaturation level of the oil or fats is measured by iodine value (IV) of the oil. The IV in PACO was determined by calculation method after carrying out laboratory titration using carbon tetrachloride, Wijs reagent, 10% potassium iodide solution, 0.1 N sodium thio – sulphate solutions and starch indicator. In determining Iodine value two experiments were carried parallel as titrant and blank.

During experiment, two elenmeyer flasks of 250 mL each were used per each titration. In each flask, 5 mL of carbon tetrachloride was added in the flasks. Ten grams of oil sample was added in one of the flask and the other save as blanks solution. Exactly 10 mL of Wijs reagent was measured and added to each flask. According to AOCS (1997a), the flask was stoppered followed by gently swirling of the content to make a mixture and stored in dark place at 25 ± 5°C for 30 min. The mixtures were stored in a dark place at 25±5 °C for 30 min (AOCS, 1997a). After 30 min, 8 mL of potassium iodide solution (10%) followed by 60 mL of distilled water were added in each solution and immediately titrated with 0.1N of sodium thiosulphate solution until yellow disappeared. Then, 0.5 mL of starch solution was added until blue coloration appeared. This followe by titration drop by drop while stirring vigorously until blue color disappear. The average value was used to calculate the iodine value using

$$IV = \frac{(b-a)x\ N(Na_2SO4)\ x\ \text{mass of iodine in 0.1M ICI}}{Sample\ weight\ (gm)} \qquad (6)$$

where a and b are average titration volumes (mL) of blank and oil solution respectively, N = normality of sodium thiosulphate.

3.3 Catalyst preparation and characterization

3.3.1 Catalyst preparation

The TIFSs were thoroughly washed with tap water and rinsed with distilled water to remove organic materials. The catalyst precursor TIFSs were oven dried at 105 °C for 12 h grounded and calcinated (Scheme 3). Before calcination, TGA analysis was carried out using Linseins thermal analysis machine (STA 1000). The weight of the sample used was 4.33 mg and heating temperature range from 29.6 to 900 °C with a ramp rate of 5 °C min$^{-1.}$was used. The grounded catalyst precursor was burnt in the furnace (Cole parmer furnace-USA) at temperature of 800 °C with ramp rate of 5 °C min^{-1} for 3 h to form *Tamarindus indica* fruit shell ash (TIFSA).The formed TIFSA were collected, cooled in desiccator for further analysis and used as heterogeneous base catalyst for transesterification of *P. curatellifolia* seeds oil.

Scheme 3: Preparation and calcination process of TIFSs.

3.3.2 Characterization of the catalyst

In characterization process, various techniques were used to analyze the calicinated TIFSA. TGA was used to analyze thermal decomposition of catalyst precursor material ie. TIFSs, XRF and EDS were used for elemental composition, and crystalline phases of the catalyst were determined by XRD. In determining porosity/texture of the TIFSA, BET was used while Hammett Indicator solution was used to determine its basic strength. Furthermore, SEM was used to analyze the microstructures of TIFSA catalyst.

(i) Thermal Decomposition of the material

For the purposes of studying thermal decomposition of the material to form ash (catalyst) was done through TGA technique. TGA analysis was carried out using Linseins thermal analysis machine (STA 1000) made in Germany. The catalyst precursor of 4.33 mg was measured in the ceramic crucible and heated at temperature range 29.6 °C and 900 °C with ramp rate of 5 °C min^{-1}. The decomposition of the material was observed on both mass losses and heating time taken for accomplishing the process. According to Abdullah *et al*. (2017), depending on the biomass type during combustion, carbonates of calcium and potassium dissociate at 700 – 900 °C to form metal oxides while releasing CO_2. For material with $CaCO_3$, $CaCO_3$ decomposes to CaO and CO_2 according to the following equation:

$CaCO_3 \rightarrow CaO + CO_2$ and takes place between 635 °C and 865 °C (Halikia *et al*., 2001).

(ii) Catalyst composition (Elemental analysis)

The catalyst TIFSA obtained after calcination was manually grounded into fine powder and sieved by using 120 μm sieves to obtain a very fine powder. The sample was analysed at Tanzania Atomic Energy Commission (TAEC) Arusha using SPECTRO XEPOS machine fitted with ED-XRF made in Germany. The 5 g of TIFS powder was mixed with 0.9 g of a binder (Cereox, Bedburg-Hau) and homogenised by using RMP(FRITSCH Industriestr 8 55743 Idar-Oberstein, Germany) at 180 rpm for 10 min. Each harmonized sample was pressed in hydraulic press (Retsch GMbHR, Haan, German, type PP25) at 12.5 mm/Hg for 1 min to form the pellets/tablets. The pellets were subjected to SPECTRO XEPOS machine for quantification of the elements composition in the sample. EDXRF is a non-destructive method with high resolution elemental data, limited preparation required for solid samples, decreased production of hazards wastes, portability and capability of analysing all range of elements from sodium to uranium so as to capture the elements of interest. The procedure was based on the XRF-SPECTRO XEPOS protocol.

(iii) Catalyst basic strength

The quality of the catalyst was determined by using Hammett indicator method where 250 mg of calcinied sample of catalyst was added into 100 mL Erlenmeyer flask fitted with rubber stopper. 10 mL of anhydrous methanol was added in the flask and gently stirred. Then 0.5 mL of Hammett indicator solution (65 mg of phenolphthalein powered and 50 mL of benzene) was added in the flask, gently stirred and left for 2 h to equilibrate. The color changes were noted. According to Xue *et al.* (2009), wherever a solution shows a color change, it means that, the catalyst has stronger basic strength than the indicator used and vice versa.

(iv) Catalyst structure (surface area, pore diameter, pore volume)

The textural parameters of the catalyst were evaluated using BET analysis technique. The surface area, pore volume and pore diameter of the prepared catalyst was determined by Quanta chrome Nova 4200 (Win ©1994-2013, v11.03) with nitrogen adsorption-desorption isotherm at 77.3 K at University of Dar es Salaam. The mass of 0.0862 g of TIFSA was pre – treated by applying a combination of heat, vacuum and flowing gas to remove adsorbed contaminants acquired from atmospheric exposure. The solid was then cooled under vacuum, usually to cryogenic temperature. An adsorptive (N_2 [2 mL/min], CO_2, 10% NH_3 in helium ramped at 1 °C/min for 1 h for CO_2-TPD and NH_3-TPD, respectively) was admitted to the solid in controlled increments. After each dose of adsorptive, the pressure was allowed to equilibrate and the quantity of gas adsorbed was calculated. The CO_2 and NH_3 were removed in the gas phase form at room temperature only after purging with N_2. Surface area was determined using BET equation and a nitrogen molecule cross section of 16.200 Å^2. The pore size distribution was calculated by applying the Barrett-Joyner-Halenda (BJH) method to the desorption line of the isotherm at relative pressure P/Po.

(v) Catalyst morphology

The microstructures of as-prepared catalysts were analyzed using SEM-JSM-7600F Thermo NORAN System7- Tokyo, Japan. Images were taken with a JEOL-JSM-7600F, operated at 15 kV using secondary electrons to form the image. Prior the SEM measurement, the sample was coated with a thin layer of gold, and mounted on carbon platform using PVC glue. The plate containing the sample was placed in the electron microscope for analysis with magnification of 500 to 50 000. The machine was also fitted with EDS for sample composition detection.

(vi) Catalyst major component phases

In order to determine the major component phase and crystalline nature of TIFSA catalysts, XRD patterns for catalyst ash were analyzed using XRD, MAC MXP18Tokyo, Japan at Botswana International University of Science and Technology-Botswana with Cu-Kα radiation. The analysis was performed at an angle 2Θ, with scan range from 5^o to 90^o, a scanning speed of 1^o min^{-1} and actual wavelength source of λ=1.5418 µm.

3.4 Production and characterization of biodiesel

3.4.1 Production of *Parinari curatellifolia* Oil Methyl Esters

Various experiments were conducted in a reflux system (Fig. 2) using a mixture of PCSO, methanol and calcinated TISFA as a catalyst. The 250 mL flat bottomed flask was used as reactor in which the mixture of PCSO, methanol and catalyst were added and immersed in a water bath for different reactions. During the experiment, and for the purpose of this study, a number of experiments were conducted to find the best parameter to be used for reaction. Three reaction parameters: reaction time, methanol to oil molar ratio and amount of catalyst loading were altered to maximize biodiesel yield. In the transesterification process, catalyst loading was varied from 1% to 6% at intervals of 1%, methanol to oil molar ratio was varied by 3:1, 6:1, 9:1, 12:1, 15:1 and 18:1 and the reaction time was also altered from 30 min to 3 h at intervals of 30 min. In transesterification reaction, the stoichiometric ratio of methanol to oil is 3:1 (Bobade *et al.*, 2012; Abdullah *et al*., 2017). Excess methanol were used to shift equilibrium to product side (Guo *et al.*, 2010*;* Issariyakul *et al.,* 2014). Catalyst loading and reaction time were chosen as minimal to find the best minimum value to accomplish the reaction. The mass of oil, heating temperature and agitation speed 65 °C and 3000 rpm respectively were kept constant. The reaction temperature of 65 °C was taken as maximum temperature and less than the boiling point of methanol (67.5 65 °C) to prevent evaporation of methanol (Tariq *et al*., 2012). The agitation was set to 3000 rpm to overcome viscous of the mixture during reaction.

(i) Experimental set up

For the purpose of this study, in each reaction carried out, 25 mL of oil and varied amount of methanol 3 to 18 mL and catalyst 1% to 6% of oil were measured in the 250 mL round bottomed flask reactor. The reactor was fitted with a reflux condenser, water bath, thermal heating controller, digital thermometer, magnetic stir, water pump and water jar as shown in Fig. 2. The reflux condenser was fitted on the reactor to ensure any vapors given off were cooled back to the reactor. Heating controller and water bath maintain temperature of the reactor while water pump and water jar circulate and control the water loss. The magnetic stir was used to achieve a homogeneous mixture at a constant mixing speed of 3000 rpm.

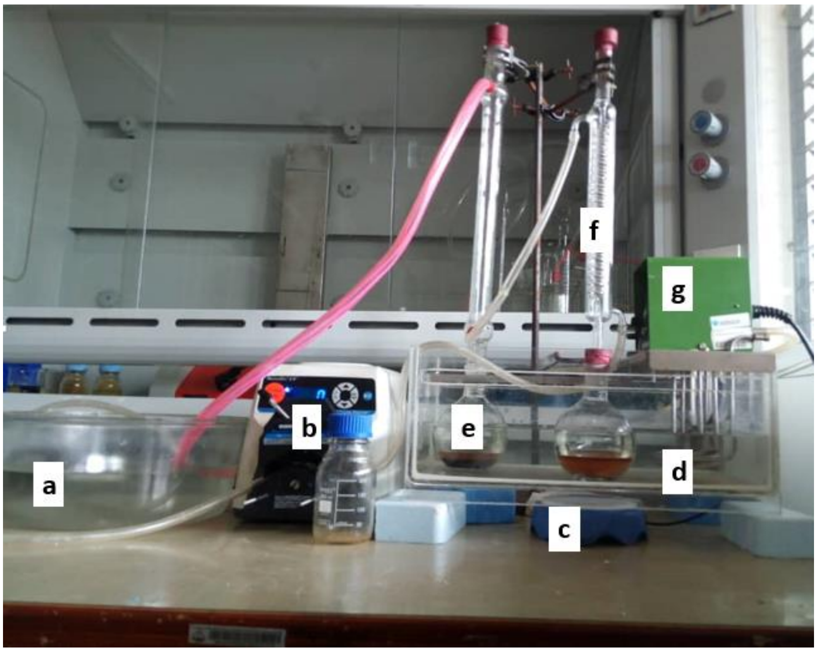


Figure 2: Biodiesel experimental set up (a) water jar, (b) water pump, (c) magnetic stir, (d) Water bath, (e) reactor, (f) reflux condenser, (g) thermal heating controller.

(ii) Production process

The subsequent amount of PCSO was measured in 250 mL elenmeyer conical flask and preheated at 105 °C for 5 min to reduce moisture content and allowed to cool to 65 °C. Exactly 1.25 grams (5% wt/vv of oil) of catalyst and 9 mL of methanol were measured in the rector and gently stirred to allow mixture formation. Then, 25 mL of preheated oil at 65 °C was measured and poured in the reactor to commence the reaction; 2 h were enough for reaction to take place. After reaction, the mixture was partially allowed to cool and two distinct layers of catalyst at bottom and the product which is the mixture of glycerol and biodiesel at the top was formed as depicted in Fig. 3(a). The top mixture was separated, measured and transferred into a separating funnel to cool overnight. Two more distinct layers were formed: glycerol at the bottom and the top layer was made up of a mixture of PCUME (biodiesel) and unreacted methanol as shown in Fig. 3(b). All the experiments were conducted by following identical procedures at different experimental conditions. The biodiesel was separated from glycerol ready for purification and yield estimation processes.

(iii) Catalyst separation and reusability

One of the advantages of heterogeneous catalyst is its ability to be easily separated from the mixture (Talha and Sulaiman, 2016). The Fig. 3(a) shows the product mixture with the catalyst at bottom. The catalyst was filtered from the mixture using Pittman filter paper and washed with an appropriate amount of methanol to remove traces of glycerol and/or biodiesel. The washed catalyst was oven dried at 105 °C for 2 h to remove methanol and traces of water that may present. The catalyst was reused in transesterification without further treatment while observing the yield obtained.

(iv) Product purification and yield estimation

The biodiesel obtained after separation from glycerol need to be purified to eliminate impurities such as excess alcohol, traces of catalysts, glycerol and soap caused by presence of tri, di and mono-glycerides that remain during reaction. The purification is important in order to have quality biodiesel that will comply with specification and accepted in the market. Water washing is most preferred because it is the easiest method and cheaper to apply. Before applying water washing, excess methanol was removed using batch laboratory vacuum distillation flask. The product was washed four times using warm deionized water. The washed biodiesel was dried by using anhydrous $MgSO_4$ over night to remove water content in order to obtain pure biodiesel. The weight of pure biodiesel was used to find the percentage yield using the following equation

$$\%\ yield\ of\ PCUME = \frac{weight\ of\ PCUME}{weight\ of\ product}\ x\ 100 \qquad (7)$$

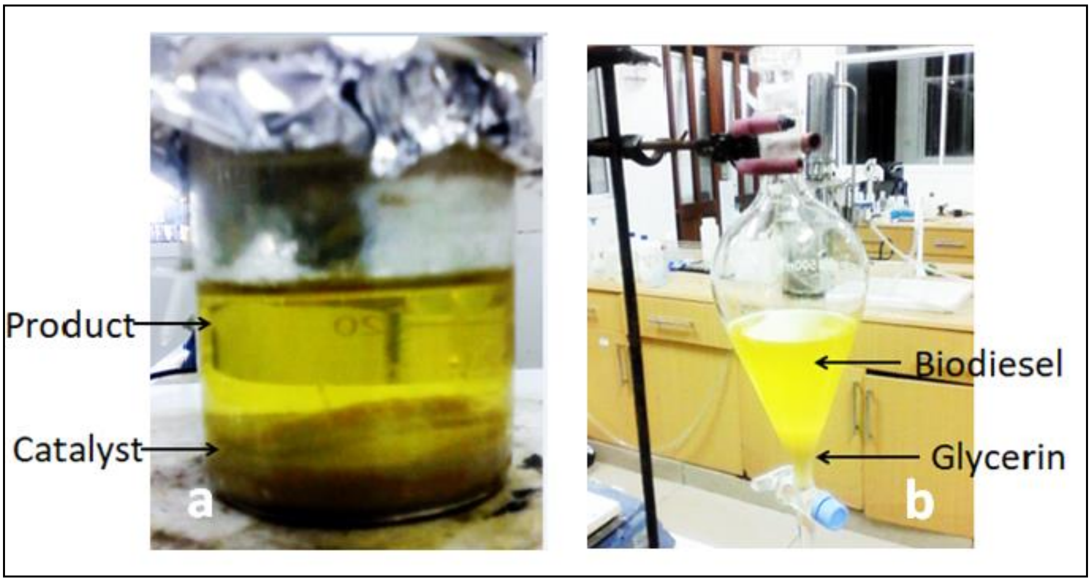


Figure 3: Photos for (a) Two distinct layers of mixture of biodiesel and glycerol at top and catalyst at bottom and (b) Two distinct layers of biodiesel at top and glycerol at bottom.

3.4.2 Characterization of biodiesel

In this study various fuel properties of PCUME were determined and tested according to ASTM testing methods for biodiesel and compared to ASTM D6751standards limits and conventional automotive mineral diesel (number 2 diesels). According to Graboski *et al*. (1996), number 2 diesel is a low sulfur diesel with 30% aromatic content. The properties determined include: fatty acid composition, density, kinematic viscosity, pour point, cloud point, calorific value, flash point and cetane index.

(i) Determination of Fatty acid composition

Analysis of fatty acid composition in the produced biodiesel was done by Gas Chromatography-Mass Spectrometry GCMS-2010 Shimadzu instrument Japan, at the University of Dar es Salam - Tanzania. The GC-MS was recorded when the instrument was operating in Electron Ionization (EI) mode (MS) at 70 ev, and Flame Ionization Detector

(FID) for GC. A Restek-5MS column with 30 m long, 0.25 mm internal diameter and 0.25 μm thick was used. The column was run in split less mode under the following conditions: the oven temperature program was 60 °C to 260 °C, and held at 60 °C for 4 min. The temperature was increased to 260 °C for 12 min (hold time) at the rate of 7 °C per min. A 6 μL injection was used for analysis in each sample. The injection temperature was 250 °C with split injection mode. The flow rate of carrier gas helium was 1.21 mL min^{-1}. The ion source temperature and interface temperature in MS were 230 °C and 300 °C respectively. The FAME and other compounds in the samples were done by scan method which involved the use of Mass Spectral Library and Search Software (NIST). Quantification of FAME and other compounds in the samples was done using Peak Integration method.

(ii) Determination of density and Kinematic Viscosity

ASTM D7042 testing method was used to test both density and kinematic viscosity of PCUME using automated Auton Paar Stabinger SVM^{TM} 300 s machine made in Germany. This test method covers and specifies a procedure for the concurrent measurement of both the dynamic viscosity (η) and the density (ρ) of liquid petroleum products and crude oils, both transparent and opaque (ASTM, 2016).

The Stabinger viscometer machine is an automated machine uses a rotational coaxial cylinder measuring system. In determining both density and dynamic viscosity, the measuring cells were cleaned by using the amount of sample injected by a syringe in a cell and dried as described in the procedures. The internal temperature control was set to 15 and 20 °C for density, and 40 °C for dynamic viscosity. The determinability limits and temperature stability criteria of the PCUME were set for biodiesel and diesel. Then, 3 mL of the PCUME was loaded into the syringe and 2 mL was injected into the into the measuring cells column while leaving the syringe in the inlet. The maximum loading per experiment is 2 mL for in-balance temperature and oscillating motion balance. Then the machine was started to commence the measurement. The instrument runs for a time until it indicates that the determination is valid and the values were recorded. Then, further injection of 1 mL was taken without taking off the syringe and the measurement was repeated in triplets. The kinematic viscosity (ν) can be obtained by dividing the dynamic viscosity (η) by the density (ρ) obtained at the same test temperature.

(iii) The Cloud and Pour Point

Cloud point and pour point were tested with cloud and pour point test cabinet made by Normalab Belgium as depicted in Fig. 6. The test cabinet is equipped with cooling bath to a temperature setting as shown in Table 4.

(iv) Cloud point test

Cloud point is tested using ASTM D2500-7 test method and according to ASTM D6751 test limits, cloud point of most biodiesel ranges between -3 to 12. Following protocol on testing cloud point, before commencement of testing, the disk and jacket was placed in the cooling medium in a minimum of 10 min before the test jar is inserted. The bath temperature was set to -18 °C with reference to Table 4. Then, the sample of biodiesel was measured to the indicated mark in a clear test tube fitted with snug–fitting cork. A glass thermometer range 50 to -38 °C was fitted through the hole centered in a fitting cork and the thermometer bulb was totally immersed in the biodiesel as shown in Fig. 4(a). The test jar was placed in the jacket and allowed to cool to form cloudy wax crystals. At each test thermometer reading that is a multiple of 1 °C when the specimen has been cooled to lowest temperature, remove the test jar from the jacket quickly but without disturbing the specimen, inspect for cloud by wrapping the test jar with cloth while gently shaking and observe the disappearances of clouds (wax) in the sample. The temperature at which cloud disappears was recorded and test jar was replaced in the jacket. Triplet experiment was carried out and average value was taken as cloud point temperature of the PCUME.

Table 4: Bath and sample temperature for cloud and pour point in testing cabinet

Bath Temperature Setting, °C	Sample Temperature Range, °C for cloud point	Sample Temperature Range, °C for pour point
0 ± 1.5	Start to 9	27 to 9
−18 ± 1.5	9 to −6	9 to –6
–33 ± 1.5	−6 to −24	–6 to –24
−51 ± 1.5	–24 to −42	–24 to –42

Source: ASTM D2500-17 (2017 and ASTM D97-17B (2009)

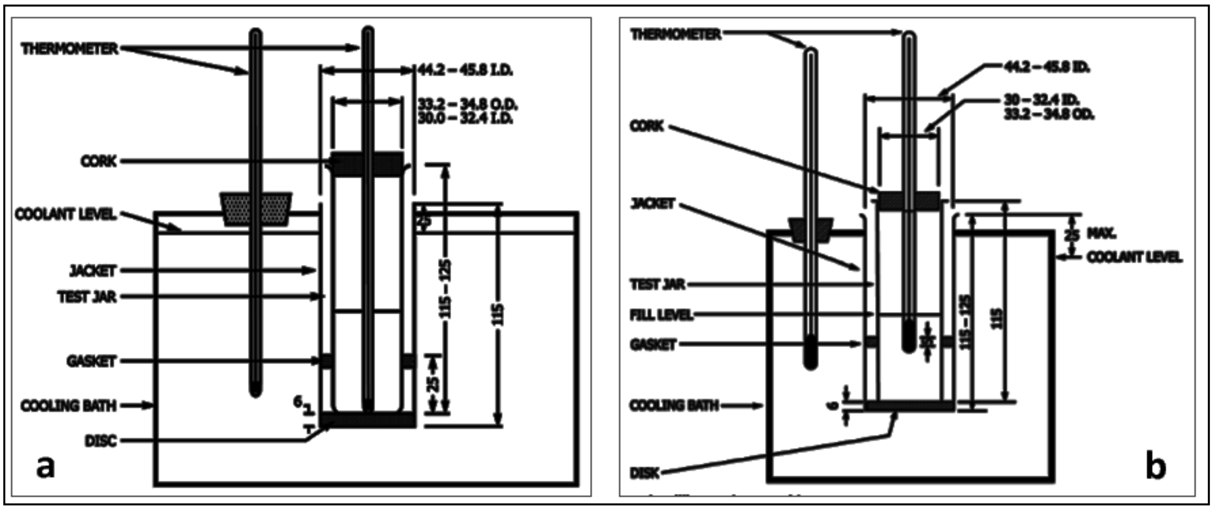


Figure 4: (a and b) Experimental set up for determination of cloud and pour points using cloud and pour point test bench respectively.

Source: ASTM D2500-17 (2017); ASTM D97-17B (2009)

(v) Pour point

Pour point of PCUME was determined using ASTM D97-17a test method. According to ASTM D6751 standard limits, pour point of most biodiesel range between -15 to 10 °C. The experimental set up follow the same protocol as for cloud point test. The bath temperature was set to -18 °C with reference to Table 4. Then, the correct amount of PCUME was measured into the test jar to the level mark. A glass thermometer range 50 to -38 °C was fitted through the hole centered in a fitting cork and fitted in the test jar. Then, the thermometer bulb is immersed 3 mm below the fill level of biodiesel in the test jar as shown in Fig. 4(b) and allowed to cool to solid state. In determining the pour point, the appearance of the specimen was examined and expressed in integers that are positive or negative multiples of 3 °C. When the lower temperature set point is reached, the test jar was removed from cooling bath jacket; wipe the surface with a clean cloth moistened in alcohol (ethanol or methanol) to remove condensed moisture that limits visibility, and then tilt the jar to ascertain whether there is a movement of the specimen in the test jar. If the specimen in the jar does not show movement when tilted and hold horizontal position for 5 s the temperature was used to determine pour point. The jar was wiped with clean cloth to ensure clear visibility and examine the points at which first drop of liquid is formed. The temperature at which first drop was observed it was recorded as pour point for that particular experiment. Triplet experiment was carried out and average value was taken as pour point temperature of the PCUME.

(vi) Flash Point

The flash point of PCUME was tested using automated Pensky-Martens open-cup apparatus (Kochler K16200) under ASTM D93 test method procedures (ASTM D93-16a). The test cup fitted in the apparatus was cleaned using paraffin, dried and returns into the apparatus. The amount of fuel sample was filled to the mark given in the cup. Locking device was tied up followed by inserting temperature measuring device in its holder. According to ASTM D6751 limits, the minimum flash point of pure biodiesel (B100) is 130 °C. Then, the operating temperature was set at 23 °C below the expected minimum flash point of biodiesel (103 °C). The flame tester was lit and flame adjusted to luminous flame. The heat was applied at heating rate of 5 – 6 °C per minute while stirring at 100 rpm. The set alarm was set at 103 °C, when the alarm buzzed; the ignition source was manually directed and passed to and fro over the test cup until the flash of fire was detected. The temperature at which flash was observed was taken as the flash point of the PCUME. Average value was used to report the actual flash point value of the sample.

(vii) Calorific value

The heat of combustion of PCUME like any other liquid hydrocarbon fuels was determined using bomb calorimeter AIKA C2000 as per ASTM D240-17 testing method. Heat of combustion was determined by burning 1 gram of PCUME sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermo-chemical and heat transfer corrections. Calorific value is a measure of the energy content in a fuel and is an important property of the bio-diesel that determines the suitability of the material as alternative to diesel fuels.

(viii) Determination of Cetane Index by distillation process

The distillation of PCUME at various temperatures was carried out using a laboratory automatic distillation machine NDI 450 Narmlab (Fig. 5) using test method ASTM D86 (ASTM D86-15, 2015). The apparatus has basic components such as: condenser, cooling bath, distillation flask, metal shield, heat source an thermometer, flask supporting device, distillate receiving cylinder and nitrogen gas as carrier gas.

The 100 mL of PCUME was precisely measured to a mark of measuring cylinder and then transferred to 125 mL distillation flask. The mercury thermometer ranging 0-400 °C was inserted in the cork plug was fitted in the neck of the distillation flask for temperature reading. The condensate was collected in the cylinder installed in condensate collection chamber. During distillation process three main temperatures reading are of great important: initial boiling temperature (IBT), mid boiling temperature (T_{50}) and the final boiling temperature (FBT). The IBT is taken as the temperature at which the first drop of the condensate strike the bottom of distillate collecting cylinder. Midpoint temperature is the temperature at which 50 mL of condensate was collected in the receiving cylinder and is the temperature used to calculate cetane index. The FBT was obtained 5 min after 5 mL of the residue liquid remaining in the distillation flask. The average value of both temperature and volume were recorded in whole process. Figure 5 (a and b) shows the distillation machine and its assembly.

(ix) Calculation of Cetane Index

Cetane Index is a calculated value used to estimate ASTM cetane number in the absence of an engine to test it. ASTM D976-06, (2016) is the test method with Cetane Index formula was used to calculate Cetane Index (CI) value for directly estimating the ASTM cetane number. For the distillate fuels, the density at 15 °C and midpoint temperature (T_{50}) is used as variable in the developed model Equation 8. The calculated value gives a reasonable close value approximated to Cetane number. Cetane index of PCUME was calculated using empirical equation

$$CI = 454.74 - 1641.416D + 774.74D^2 - 0.554T_{50} + 97.803[Log_{10}T_{50}]^2 \qquad (8)$$

where CI is the Cetane Index number, D is the fuel density at 15 °C = 0.8915 g/ml, and T50 is the mid temperature corresponding to 50% of distillation received3 = 23.42 °C.

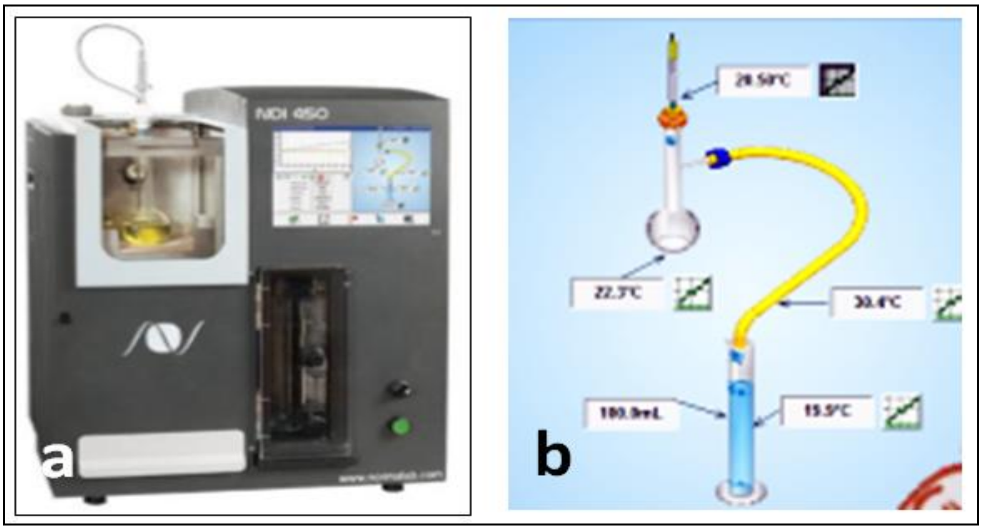


Figure 5: (a) NDI 450 distilling machine. (b) Distillation assembly

Source: Namlab, 2012 operating manual.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Physical-chemical properties of oil

Four liters of parinari seed oil were obtained from 12 kg of dry Parinari seeds which represents a yield of 36% (v/w). The results for physical chemical properties of PCSO such as oil content, moisture content, iodine value, acid value, saponification value and free fatty acid values are listed in Table 5.

The oil content was determined from the ratio of mass of oil to the mass of dry seed kernel extracted as per Eq. (1). The oil yield of 36.2% obtained was less than 36.75% and 38.5% found by Ndaba (2014) and Bazongo *et al*. (2014) for the same seeds. The *P. curatellifolia* seed oil content was favorable feedstock for biodiesel production (Ahmad *et al*., 2011; Atabani *et al*., 2012). The moisture content of PCSO was little higher 6.0% by weight compared to that found by Oladimeji and Bello (2011) of 5.1% but not used for biodiesel production. Other parameters such as acidic value, iodine value, and saponification value were not reported in the previous literatures.

The acid value was used to determine the amount of FFA in the oil, which was found to be 3.3 mgKOH/g. The amount of FFA in this study was less compared to 5.15 and 5.9 mgKOH/g of oil reported by Oladimeji and Bello (2011) and Bazongo *et al.* (2014) respectively from parinari seeds. According to Ghatikar (2015), the feedstock with high amount of FFA (>1%) are more vulnerable to soap formation, reduce the catalyst efficient, increase viscosity of the oil and hinder the separation of glycerol from the mixture. All these consequences result to reduction of biodiesel yield. For the oil with FFA greater than 1%, it is preferred to use heterogeneous catalyst to prevent more soap formation. Heterogeneous catalysts are more tolerant to higher FFAs and help to an increase the biodiesel yield (Ramadhas *et al*., 2005; Marchetti *et al*., 2007; Berchmans *et al*., 2008).

Table 5: Physicochemical properties of PCSO

Property	**Unit**	***P. curatellifolia oil***
Oil content	%	36.2
Acid value	mgKOH/g of oil	6.67
Iodine value	$gI_2/100g$ of oil	82.62
Saponification value	mgKOH/g of oil	135.5
FFA	mgKOH/g	3.33

4.2 Catalyst characterization

4.2.1 Thermal gravimetric analysis

The appropriate calcination temperature and time for catalyst precursor (TIFSs) in this study was obtained through thermo-gravimetric analysis as depicted in Fig. 6. Upon calcination significant mass loss of 35% was observed at temperature between 250 and 480 °C where volatile matter escaped from the sample. The stability of weight loss at temperature 500 °C to 750 °C in 120 min is an indication that the decomposition of the sample catalyst precursor is going to completion with metal oxide becoming the main active ingredient in the catalyst. Since TIFSs have high content of $CaCO_3$, the temperature higher than 750 °C was therefore required to decompose the carbonate-based materials to CaO (Wei *et al*., 2009; Hui *et al*., 2010). According to Lee *et al.* (2014), optimal performance of the calcinated heterogeneous catalyst was obtained at high calcination temperatures, which maximizes formation of metal oxides such as CaO content. Purposely from this study, the high content of calcium carbonate was also revealed from XRF analysis on the ash to have 47.4% CaO. On the other side, more heating time again led to particle sintering/agglomeration and decreases catalyst reactivity.

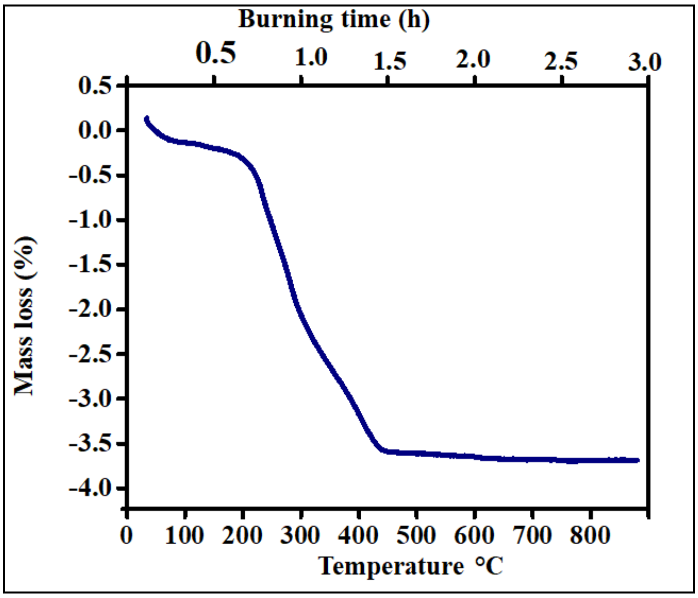


Figure 6: TGA analysis of catalyst precursor TIFSs showing decomposition of material in relation to the temperature change between 30 and 900 °C and time taken between 0 and 180 min.

4.2.2 Catalyst composition

The chemical composition of TIFSA burned at 800 ^{o}C was determined by XRF technique on the dry basis, and CaO was derived as the main component.

Table 6 shows the result of ash from TIFSs mainly composed of CaO and considered as a favorable heterogeneous base solid catalyst in biodiesel production. According to Zhang *et al*. (2010) and Wei *et al*. (2009), CaO was considered as a base catalyst with high basic strength, easy to react with water and has minor toxicity properties. Other oxides found in the catalyst are K_2O, MgO, SiO_2, P_2O_5, and other trace oxide compounds. CaO, K_2O, and MgO are basic in nature and enhance the catalytic basic strength properties (Boey *et al*., 2011; Kouzu *et al*., 2008), while SiO_2 and P_2O_5 are acidic in nature and can enhance catalytic acid properties useful for esterification of high FFA feedstock. The presence of significant amount of alkaline and alkaline earth metal oxides, CaO, K_2O, and MgO in the prepared catalyst is an indicator of the effectiveness of this base catalyst (Kouzu *et al*., 2008; Zabeti *et al*., 2009).

Table 6: Composition of TIFSA catalyst

Oxide	(% by wt.)	Nature
CaO	47.4	Basic
K_2O	19.2	Basic
MgO	5.1	Basic
P_2O_5	3.1	Acidic
SiO_2	3.0	Acidic
Others	22.2	-

4.2.3 Catalyst structure

Catalyst structure involves surface area, pore diameter, and pore volume. The prepared catalyst was characterized by large pore diameter of 3.2 nm, pore volume 0.585 cm^3/g and surface area of 378 m^2g^{-1}. This will allow easy diffusion of reactant into the surface and interior part of the catalyst (Kiss *et al.*, 2006). The structure of catalyst obtained here as well compared with what Osakwe *et al*. (2018) obtained for CaO from Kolanut pod husk calcinated at 600 °C by having specific surface area of 398.547 m^2/g, pore diameter 2.138 nm and pore volume 0.203 cm^3/g. In contrast, the BET surface area was higher while pore diameter and pore volume were low compared to TIFSA. Other researchers referenced in this study on biomass ash do not report on the observation of structures of their catalysts. According to Zabeti *et al*. (2009), the specific surface area and pores volume together make an active site of the catalyst. Also, Sharma *et al*. (2011) in their study reported that, high pore diameters are of high potential to allow higher diffusion of reactant and product molecules. Since the prepared catalyst has a higher surface area and smaller particle sizes, it could be the reason for exhibiting good performance during the transesterification process (Viriya - empikul *et al*., 2010).

Furthermore, the basic strength of the catalyst pH>9.8 was taken to be higher than the phenolphthalein indicator pH=9.8 that overcome the weak indicator properties by undergoing color change to pink. The color change of the mixture was proved that the catalyst had stronger basic property i.e. H > 9.8 (Cantrell *et al*., 2005; Kouzu *et al*., 2008).

4.2.4 Catalyst morphology

The Fig. 7 presents SEM images of the TIFSA catalyst and the chemical composition of the ash as determined by EDS. The SEM micrographs Fig. 7(a, b, c) indicate that TIFSA had a spherical and porous surface. The pore sizes are big enough to increase the active sites of the catalyst. Fig. 7(d) shows the elemental composition of TIFSA as determined by EDS. It was observed that CaO was the major detected compound in the catalyst followed by SiO_2, K_2O, and Al_2O_3, the results were in good agreement with that determined by XRF. Only MgO was not observed in this EDS technique.

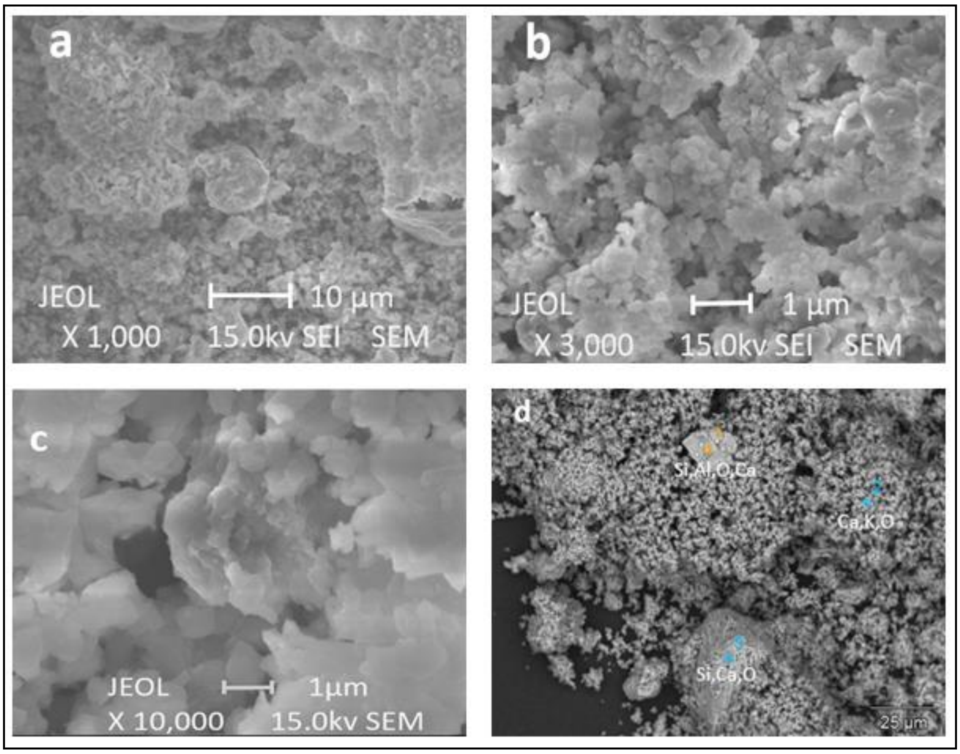


Figure 7: SEM images of the TIFSA calcinated at 800 °C: (a, b) Pores on the catalyst surface; © Regular spherical-shaped pores on the catalyst surface; (d) Elemental analysis by EDS.

4.2.5 Catalyst major phase composition

The XRD pattern of the TIFSA catalyst calcinated at a temperature of 800 ^{o}C is shown in Fig. 8. The spectra were obtained at $\lambda = 1.5418$ nm at scan range of 5 – 90 degrees. The diffraction lines at 2Θ were observed at 32.18, 37.52, 53.95, 63.75, 67.39, 79.55 and 88.31 degrees which correspond to CaO (00-044-1481 reference code of the Inorganic Crystal Structure Database – ICSD) and Joint Committee on power Diffraction Standards (JCPDS) card file number 00- 037-1497, and similar to observations reported by Wei *et al*. (2009), Chavan *et al*. (2015) and Correia *et al*. (2017). The peaks prove the presence of CaO at a higher percentage.

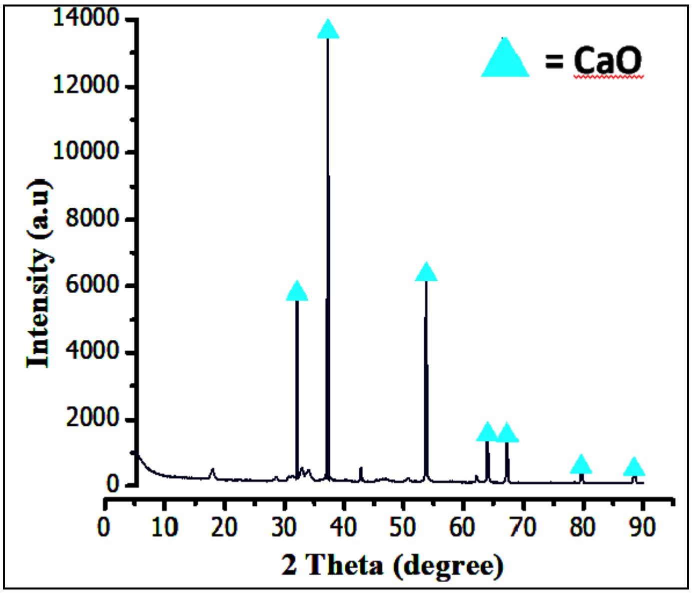


Figure 8: XRD patterns of waste TIFSA derived catalyst calcinated at 800 °C.

4.3 Production of PCUME

The experimental yield of the methyl ester from PCSO was found to be 96.2% of pure biodiesel from the mixture. The deviation from 100% yield was probably caused by the high value of free fatty acids present in the oil. This cause more glycerol and soap formation.

4.4 Analysis of PCUME

4.4.1 Fatty Acid Composition Analysis

The GC-MS analysis was used to obtain percentage of ester composition, the number of carbon bond, retention time and amount yield from PCUME as shown in Table 7. The representative GC peaks characteristic are shown in Fig. 9. The main fatty acid esters identified in PCUME are 9, 12- Octadecadienoic acid (Z, Z), methyl ester (Linoleic acid), 9-Octadecenoid acid (Oleic acid), Hexadecanoic acid, methyl ester (Palmitic acid) and Methyl stearate (Stearic acid). Other fatty acid esters were found in trace amounts. The PCUME comprise total of 63.6% by weight of unsaturated and 36.39% by weight of saturated fatty acids.

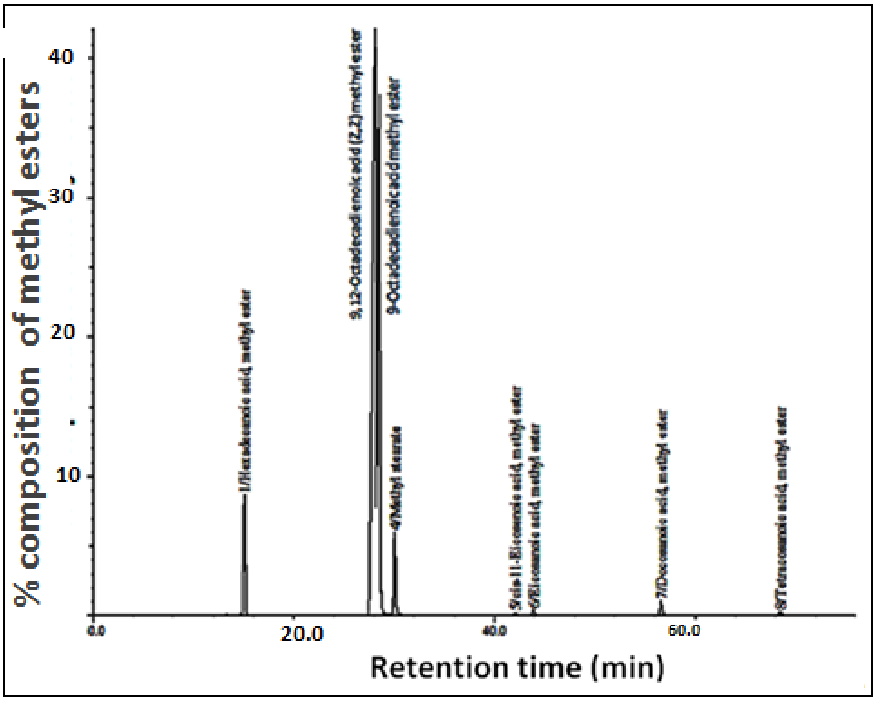


Figure 9: GC trace of fatty acid methyl esters composition derived from PCUME.

Table 7: Methyl ester composition of the PCUME

FAME (common name)	**Carbon atom and number of bonds**	**Retention time**	**% Yield**
Hexadecanoic acid methyl ester (palmitic acid)	C16:0	33.78	20.68
9,12- Octadecadienoic acid (Z, Z) methyl ester (Linoleic acid)	C18:2	37.04	36.58
9-Octadecanoic acid, methyl ester, (E) –(Oleic acid)	C18:1	37.14	26.93
Methyl stearate (Stearic acid)	C18:0	37.52	12.82
Cis-11-Eicosenoic acid, methyl ester (cis - vaccenate)	C18:1n-7	40.53	0.098
Eicosanoic acid, methyl ester (methyl arachidate)	C20:0	40.97	0.708
Docosanoic acid, methyl ester (methyl behenate)	C22:0	44.14	1.83
Tetracosanoic acid, methyl ester (Methyl myristate)	C14:0	47.12	0.357
Total saturated			36.39793
Total unsaturated			63.60207
Total yield			100

4.4.2 Fuel properties

The fuel properties of biodiesel produced were tested according to ASTM standard methods and compared to ASTM D6751 standard limits as summarized in the Table 8.

From the results, it was observed that viscosity, cloud point, pour point and acidic value were within the acceptable range as prescribed in ASTM D6751 while density was slightly higher than limits. According to Ong *et al*. (2013), the density of biofuel depends on the chain length of methyl ester and its saturation level. The higher the unsaturation of methyl esters, the higher is the density. Probably this can be the reason for the higher density of PCUME. Also, denser fuels are less compressible and that causes poor atomization process resulting to incomplete combustion when burned in an engine (Canakci *et al*., 2001; Ong *et al*., 2013).

In this study, the PCUME exhibits higher flash point temperature of about 174 °C. It is an important temperature from the safety point of view during storage and transportation (Canakci *et al.*, 2001). The minimum allowable limit for biodiesel as per ASTM D6751 limits is 130 °C for pure biodiesel in which PCUME fall in the range. Also, the calorific value of biodiesel (39.3 MJ/kg) was found to be slightly lower than that of mineral diesel (42 MJ/kg) as in many other biodiesels (Ramadhas *et al*., 2005; Hulwan and Joshi, 2011). The cetane number was represented by cetane index obtained from the distillation process. The cetane index was found to be (44.4) which were considerably lower than mineral diesel and ASTM D6751 standard limits. Possibly the exhibited CN was caused by high unsaturated level of methyl ester (63.4) number of double bond, and mid temperature of distillate (T_{50}) during distillation process of methyl ester (Knothe *et al*., 2003; Knothe, 2005, 2014).

Table 8: Physical and chemical properties of *P. curatellifolia* methyl ester

Property	Unit	Equipment used	Petrol diesel (ASTM D975 limits)	Biodiesel (ASTM D 6751 limits)	PCUME
Density @ 15°C	kg/m^3	AutonPaar density meter	850	840 – 880	891.5
Density @ 20°C	kg/m^3		850	840 – 880	888.0
Kinematic viscosity @ 40°C	mm^2/s	Stabinger Viscometer	2.0-4.5	1.9-6.0	5.62
Flashpoint	°C	Pensky-Martin	60-80	130 min	172
Cloud point	°C	Cloud and pour point testing cabinet	-15 to -5	-3 to 12	9
Pour point	°C		-35 to -15	-15 to 10	-6.1
Calorific value	MJ/kg	Bomb calorimeter	42-46	-	39.3
Acid value	mgKOH/g	Titration	-	0.5 max	0.1
Cetane index	-	Calculated value	-	47 - 65	44.4

4.5 Influence of reaction parameters

The effective performance of the calcined catalyst was evaluated on determining biodiesel yield by studying the influence of reaction conditions. Demirbaş (2005) reported that, the reaction temperature, alcohol to oil molar ratio, and amount of catalyst loading are the main factors influencing the conversion efficiency and rate of the transesterification process. The yield of biodiesel in this study was found through experimental finding by varying these main parameters: methanol to oil molar ratio, reaction time and percentage of catalyst loading while reaction temperature and stirring speed were kept constant at 65 °C and 3000 rpm respectively. The reaction temperature was kept at 65 °C as the temperature below the boiling point of methanol to avoid evaporation.

4.5.1 Catalyst loading

The amount of catalyst loading (% wt/vv of oil) for a given reaction has great influence in determining the product yield. Since excess methanol tends to shift reaction equilibrium to the reaction product side to complete reaction, the excess molar ratio was needed for this experiment. The influence of catalyst concentration loading with respect to oil was varied from 1% to 6% at intervals of 1% and the yield was calculated using Eq. (1). The ratio of methanol to oil of 18:1 was used while reaction time was maintained at 3 h, the reaction temperature was kept 65 °C and stirring rate was 3000 rpm for all reactions. Based on the results as shown in Fig. 10(a), it was clearly observed that, as the amount of catalyst loading was increased from 1% to 5%, the rate of conversion was also increased with a maximum yield of 94.7% obtained. When the catalyst loading was increased beyond 5% wt., the yield was observed to drop. The observation was similar to that reported by Kim *et al.* (2004) and Nurul *et al.* (2017) and testified the results were caused by higher viscosity of reaction mixture that caused by poor diffusion of methanol to oil and catalyst in the system. Therefore, it can be concluded that 5% wt. of catalyst loading was the maximum amount of catalyst required to achieve the maximum yield of 94.7% understated condition.

4.5.2 Molar ration

Alcohol to oil molar ratio is another important parameter in the process of changing triglycerides to methyl esters. Generally, in using stoichiometric ratio, three moles of methanol or alcohol are required to convert one mole of triglyceride during transesterification process (Lee *et al.*, 2009). For the heterogeneously catalyzed reaction, the excess methanol helps to improve the rate of the transesterification processes (Kim et *al.*, 2004; Guo *et al.*, 2010; Issariyakul *et al.*, 2014; Lee *et al.*, 2014). In this work methanol to oil molar ratio was varied in the range of 3:1, 6:1, 9:1, 12:1, 15:1 and 18:1 and its influence was investigated in triglyceride conversion using 5% wt. of catalyst, 3 h reaction time, while reaction temperature and stirring speed were 65 °C and 3000 rpm respectively. From the experiment, it was observed that the yield was increasing as molar ration increases. When 9:1methanol to oil molar ratio was used, the maximum biodiesel yield obtained was 95.5%. No more yields were observed when higher molar ratio was used as shown in Fig. 10(b). According to Issariyakul and Dalai (2014), the polarity of the reaction mixture increases as the excess amount of alcohol increases. This causes the reverse reaction resulted by increasing solubility of the glycerol and reduces ester yield. To conclude this and for purpose of this experiment, in varying of reaction parameters, the maximum yield of 95.5% was achieved using 1:9 methanol to oil molar ratio with 5% wt. of catalyst loading 3 h reaction time at 65 °C and stirring rate of 3000 rpm.

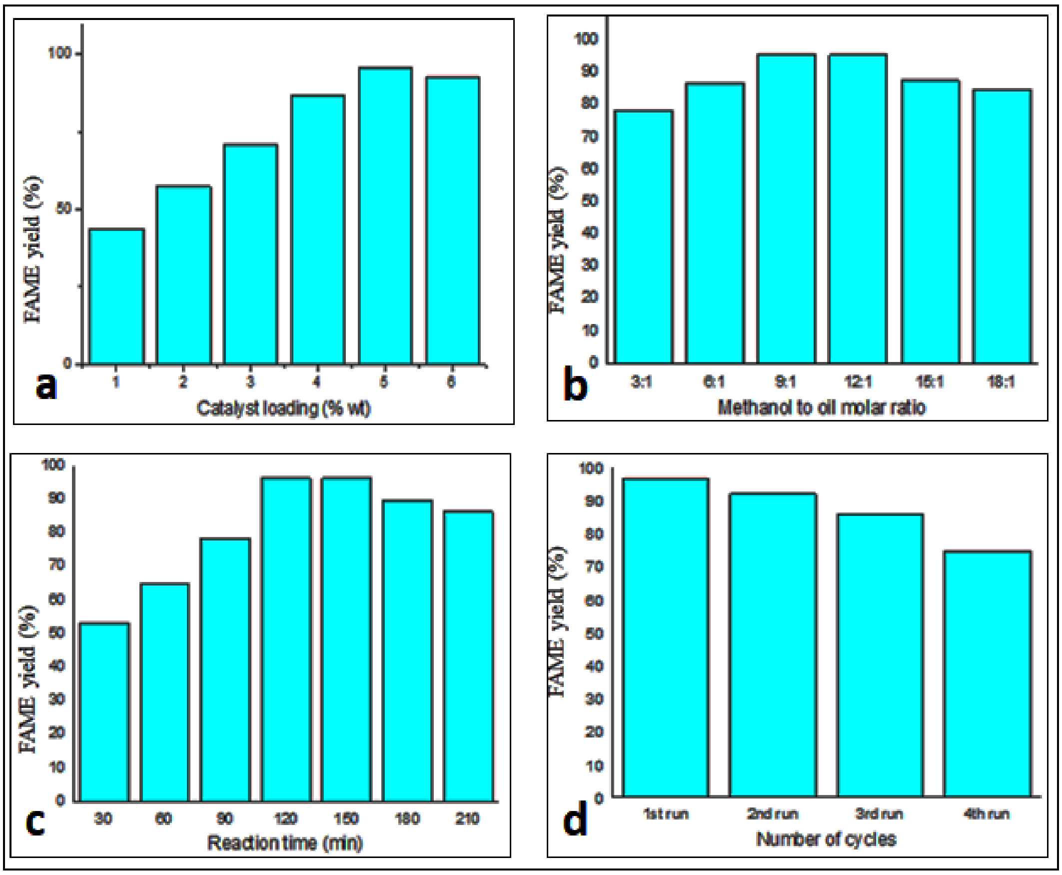


Figure 10: Graphs showing; (a) Influence of catalyst loading in biodiesel yield, (b) Influence of molar ratio in biodiesel yield, (c) Influence of reaction time in biodiesel yield, (d) Catalyst reusability and biodiesel yield.

4.5.3 Reaction time

According to Wei *et al.* (2009), the yield of the methyl esters increases with an increase in reaction time. Also, Li *et al*. (2018) in their study report that, the rate of conversion depends on how long the reaction takes place. The highest reaction time used for the production of biodiesel using PCSO, 5% wt. catalyst loading and 9:1 methanol to oil molar ratio was determined by the experimental reaction by varying time from 30 min to 3 h at an interval of 30 min under the same condition. The result obtained during conversion of triglyceride to methyl ester is presented in Fig. 10(c). From the result, there is an increase of yield from 53.3% at 30 min to 96.2% at 120 min where constant yield was observed at 120 and 180 min then followed by a decrease in yield. According to Leung *et al.* (2010), during transesterification reaction more reaction time will lead to a reduction of product yield caused by the backward reaction and it also promotes soap formation. For the purpose of this study and under given condition the favorable time for reaction was 2 h with maximum conversion yield of 96.2%.

4.6 Catalyst reusability

Calcinated catalyst from TIFSs is made up of the high amount of CaO, CaO in the catalyst shows sustained activity after being repeatedly used for several times depending on its chemical properties (Birla *et al.*, 2012). In this study, using of TIFSA (calcinated at 800 °C for 2 h) a yield of more than 74.2% was obtained in those 4 cycles with a slight decrease after each cycle/run as shown in Fig. 10(d) without complete deactivation. In the first, second, third and fourth run, the yield was 96.2%, 91.7%, 85.6%, and 74.2% respectively under the same conditions. The results show that the catalyst efficiency was decreasing after each run probably caused by deactivation of the catalyst. Similar to this study, Correia *et al.* (2017) conduct a transesterification of quill eggshell (900 °C for 3 h) on sunflower oil with a yield of 99.0% on the first run. The reuse of the catalyst in the transesterification reaction was demonstrated for 3 cycles with a slight decrease after each reuse to 78.26%.

Furthermore, Chakraborty *et al.* (2011) convert waste fish scale (900 °C for 2 h) and used for transesterification on soybean oil with a yield of 97.73%. The catalyst also confirms better reusability up to 6 times in biodiesel production without remarkable deactivation. Wei *et al.* (2009) demonstrate a similar observation from catalyst derived from eggshell (800 °C for 3 h) with 13 cycles without catalyst deactivation. According to Boro *et al.* (2011) and Birla *et al.* (2012), the loss of catalyst activity is contributed by structure changing during reaction, presence of water molecules in the oil, leaching of catalyst surfaces caused by the effect of methanol and washing, filtration process and transformation of metal oxides to other compounds such as hydroxides example $Ca(OH)_2$. Another possible cause of catalyst deactivation is the dissolution of the active metal oxide and deposition of organic compounds such as glycerol on the active sites of the catalyst (Taufiq-Yap *et al.,* 2014). Good thing is, the used catalyst can regain its catalytic activity when it was calcinied again at higher temperature for subsequent enough time (Boro *et al.*, 2011).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Biodiesel is an alternative fuel for mineral diesel produced from abundant, cheap and easily available renewable resources of animal fats and vegetable oil. It is non-poisonous, bio - degradable, with less emission of toxic gases hence environmentally friendly. Use of less expensive oil feedstock (PCSO) and cheap agricultural wastes (TIFSs) reduces the costs of production and allows commercialization of biodiesel.

The *P. curatellifolia* seed has proven as a potential oil feedstock having high oil content 36.2% to be used for suitable biodiesel production. The oil was characterized by having high amount of acidic value, saponification value and FFAs of 6.67, 135 and 3.3 mgKOH/g of oil respectively. Due to these properties, solid basic heterogeneous catalyst was mostly preferred for transesterification process in production of biodiesel. The highly active, cheap and low cost solid heterogeneous catalyst was developed by direct calcination of TIFSs (a waste agricultural biomass) for transesterification of PCSO.

The calcination process at 800 °C was reasonable to obtain an active catalyst with high basic properties due to the presence of CaO, K_2O, and MgO in a large amount. Also, the catalyst had acidic property caused by the presence of SiO_2 and P_5O_2 which favors esterification of oil since it has higher FFAs. The developed catalyst had a good catalytic property with basic strength greater than 9.8 (pH>9.8), the surface area of 378 m^2g^{-1}, a mesoporous catalyst with pore diameter 3.2 nm and crystalline phases. The best operating parameters for the production of biodiesel were 5% wt. catalyst loading, 2 h (reaction time), 9:1 (methanol to oil molar ratio) and 65 °C (reaction temperature) at 3000 rpm stirring rate. The maximum yield of PCUME was 96.2%. Moreover, the catalyst was easily separated and reused in four more runs in the production of biodiesel with more than 74% yield observed up to the fourth run. The reusability of the catalyst makes the process of producing biodiesel cheap, allow recycling the wastes and make catalyst environmentally friendly.

Also, some important fuel properties of PCUME were investigated and compared to mineral diesel and global biodiesel standards such as ASTM D6751 testing limit. The PCUME was mainly composed of unsaturated fatty acid methyl esters (63.60% wt.) and saturated fatty acid methyl esters was only 36.39% wt. PCUME was dominated by linoleic acid (36.5%) fatty acids. The physicochemical properties such as density at 15 and 20 °C, kinematic viscosity, cloud and pour points of produced PCUME were observed to be in good agreement with ASTM D6751 standard limits but little higher than petrol diesel. Also, flashpoint that was observed to be 174 °C, was higher than petrol diesel but agrees with ASTM D6751 standard limits of greater than 130 °C. This is much safer for storage and transportation process. Furthermore, the acid value was lower to specified limits which prove the fuel will not corrode the fuel pipes. Also, the calorific value of 39.3 MJ/kg for PCUME like most other biodiesel was slightly lower than petrol-diesel. The cetane index (44.4) was considerably lower than that of mineral diesel, this was probably caused by high amount of unsaturated FFAs 63.4% which resulted from Linoleic and Oleic acid present in the methyl ester. The results exhibited that most of the determined biodiesel properties were in good agreement with ASTM D6751 standard limits.

5.2 Recommendations

This study focuses on the production of biodiesel from Parinari *curatellifolia* seeds oil using heterogeneous basic catalyst derived from *Tamarindus indica* fruit shells ash wastes from agricultural biomass. Both two (seeds oil and fruit shells) have been considered as cheap and of low cost for biodiesel production. In order to minimize the cost of biodiesel production and to maximize yield, the following areas need further investigation:

(i) Future work should explore the economic feasibility for the potential use of PCSO and TIFSA to minimize the cost of production.

(ii) Further study should be carried out on the optimization process of PCUME.

(iii) Future work should investigate way on how to prevent the TIFSA catalyst from deactivation caused by contamination with water and CO_2 when exposed to air.

(iv) Future study should engine test of the biodiesel and study its efficiency and emissions.

(v) Future work should consider studies on the effect of the calcination temperature of the catalyst to minimize energy use and maximize yield.

(vi) The study should be carried out on the oxidation stability of the PCUME

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APPENDECES

RESEARCH OUTPUT

Output 1: Research Aticle

Research Article

Tamarindus Indica fruit shell ash: a low cost and effective catalyst for biodiesel production from *Parinari curatellifolia seeds* oil

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Abstract

The study evaluated the potential use of agricultural waste, *Tamarindus indica* fruit shell ash, as a solid base catalyst for production of biodiesel. The catalyst was prepared by calcination of *T. indica* fruit shell at 800 °C in muffle furnace for 3 h. Branauer-Emmett-Teller, thermal gravimetric analysis, X-ray diffraction, scanning electron microscope, X-ray florescence, and Hammett indicator techniques were used to characterize the physicochemical properties of the produced catalyst. The catalyst had basic strength of greater than 9.7 and mesoporous structure with pore size d = 3.2 nm. The crystalline phase was made up of calcium oxide, potassium oxide, and magnesium oxide. The catalyst was tested for biodiesel production using *Parinari curatellifolia* seeds oil. The results showed that the best operating parameters for the production of biodiesel were 9:1 methanol to oil molar ratio, 125 mg catalyst (5 wt% of oil), 2 h reaction time, and 60 °C reaction temperature. These optimized operating parameters afforded a maximum yield of 96.2%. Also, fuel properties of biodiesel: acid value, viscosity, and flash, pour, and cloud points were investigated and compared to the ASTM standards limits D6751. The results were observed to be in good agreement with the ASTM standards limits for biodiesel. In addition, the catalyst was easily separated and subsequently reused for four runs in biodiesel production. Thus, Tamarind fruit shell derived catalyst is very promising for the production of biodiesel due to its high performance, low-cost, easy preparation and availability.

Keywords *Tamarindus indica* fruit shell · Biodiesel · Solid base catalyst · *Parinari curatellifolia* · Transesterification

1 Introduction

Energy is a key component for economic development, poverty reduction, and prosperity [1]. Diesel and petrol are the most commonly used fossil fuels in the energy mix contributing more than 82% of the world's total primary energy. Fossil fuels are a precious resource with limited supply but their by-products affect people and the environment [2]. The use of renewable and clean energy obtained from replenishable sources such as biomass offers solutions for various fossil fuel-linked problems that challenge many societies around the world. Biofuels including biodiesel, have become more attractive due to the fact that biomass feedstocks are easily available, cheap, easily bio-degraded, and their combustion by-products are less harmful and are environment friendly [3]. Biodiesel is a mixture of alkyl esters obtained when tryglycerides are transesterified in the presence of catalyst giving glycerol as by-product [4].

The conventional production of biodiesel using homogeneous catalysts has been replaced by eco-friendly heterogeneous catalysts [5]. These heterogeneous basic catalysts are advantageous in nature since they are easily separated from reaction mixture, recyclable (cost

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