SYNTHESIS OF HETEROGENEOUS MESOPOROUS PHOSPHATE GRAFTED CaO –MoO_3–SBA-15 NANOCOMPOSITE OXIDE CATALYST FOR SUSTAINABLE BIOMASS CONVERSION TO BIODIESEL.

JOHN ADJAH (ID: 10272809)

UNIVERSITY OF GHANA, LEGON
COLLEGE OF BASIC AND APPLIED SCIENCES
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

A Thesis Submitted To the School Of Graduate Studies Of The
University Of Ghana In Partial Fulfilment Of The Requirement For The Award Of Master Of
Philosophy Degree In Materials Science
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DECLARATIONS

Candidate's Declaration

I hereby declare that the thesis entitled "SYNTHESIS OF HETEROGENEOUS MESOPOROUS PHOSPHATE GRAFTED CaO–MoO$_3$–SBA-15 NANOCOMPOSITE OXIDE CATALYST FOR SUSTAINABLE BIOMASS CONVERSION TO BIODIESEL" is my own bona-fide record of research work conducted in accordance with the University of Ghana's academic regulations and guidelines, and that the contents of this thesis in full or in parts have not been submitted to any other University for the award of any degree.

Candidate: **Mr. John Adjah**

Signature: ………………. Date: …..28th July, 2016.....

Supervisors' Declaration

This is to certify that the thesis work submitted by **John Adjah** to the School of Graduate Studies of the University of Ghana for the award of Master of Philosophy degree is his own research conducted by him under our supervision. We are satisfied that the thesis has met the standard fulfilling the requirements of the regulations and guidelines on supervision of MPhil thesis laid down by the University of Ghana.

Supervisor: **Dr. Johnson Kwame Efavi**	Co-supervisor: **Dr. Abu Yaya**
……………………………… Signature	…………………………… Signature
Date: .28th July, 2016	Date: 28th July, 2016.

Head of Department's certification

I hereby certify that this MPhil thesis report has been prepared, supervised and accepted in accordance with the guidelines on the MPhil thesis works laid down by the University of Ghana.

Head of Department: DR. DAVID DODOO-ARHIN

Signature: ………………

Date: …28th July, 2016…………………

ABSTRACT

The current commercial production of biodiesel is via transesterification reaction, catalysed by homogeneous or heterogeneous catalysts. The most commonly used catalyst in biodiesel production is the homogeneous alkaline catalysts such as NaOH, KOH, CH_3ONa and CH_3OK. The choice of these catalysts is based on their higher kinetic reaction rates. However because of high cost of refined feedstocks and difficulties associated with the use of homogeneous alkaline catalysts to transesterify low quality feedstocks for biodiesel production, the development of various heterogeneous catalysts have attracted great attention in recent times. The development of heterogeneous catalyst such as solid and enzymes catalysts could overcome most of the problems associated with homogeneous catalysts. Therefore this study critically analyses the effects of catalysts on biodiesel production using findings available in open literature. This review revealed research areas to explore and improve the catalysts performance for biodiesel fuel production. The main aim of this project works however is to develop efficient and environmentally benign heterogeneous catalysts for biodiesel production. For this purpose, heterogeneous $CaO–MoO_3/PO_4$–SBA-15/$CaO–MoO_3$–SBA-15 catalysts were prepared by incipient wetness impregnation method, and the prepared catalyst was subsequently functionalized by phosphate ion. The synthesized catalyst was tested for the transesterification process of waste cooking oil to produce biodiesel. The synthesized solid catalyst was characterized using different analytical techniques such as X-ray diffraction, Fourier transform infrared spectroscopy, sorptometric technique, and optical microscopy techniques. The catalytic activity was dependent on the catalyst modification and calcination temperature. The solid catalyst, $CaO–MoO_3/PO_4$ calcined at 823 K, showed very high catalytic activity. A 3 wt % use of catalyst with methanol/oil molar ratio of 6:1 at reflux of methanol, gave the oil conversion of 99.4 % after 6 h of reaction.

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Finally I wish to thank God Almighty for making my MPhil studies reality.

DEDICATION

I dedicate this thesis to the memory of my late father, Mr. Kwadzo Ntodo Ameyikpo Dekpo, to my mother, Mrs. Nyatorwotso Mary Ewe and my siblings for their encouragement, guidance and unflinching support throughout my education. I also dedicate this work to my uncle, Mr. Dekpo Godwin Kwadzo for his support during this work as well as all those who played a vital role in my life.

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LIST OF ABBREVIATIONS

AV	Acid value
AFR	Stoichiometric air/fuel ratio
AOC	American Oil Chemists' Society
ASTM	American Standards and Measurements
ATR	Attenuated Total Reflectance
BET	Brunauer Emmett Teller
BJH	Barret-Joyner-Halenda
CN	Cetane Number
CFPP	Cold-filter plugging point
CO	Carbon monoxide
CO_2	Carbon dioxide
DG	Diglyceride
Dp	Pore diameter
EN	European National Standard
EU	European Union
ECOD	Economic Co-operation and Development
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GDP	Gross Domestic Product
GHG	Green House gases
GL	Glycerol

HC	Hydrocarbons
HCl	Hydrochloric acid
HDO	Hydro-deoxygenation
IEA	International Energy Agency
IEE	Institute of Energy and Environment
ICDD	International Centre for Diffraction Data
ICPS	Inductively coupled plasma spectroscopy
IPCC	International Panel on Climate Change
ISO	International Standards Organisation
IUPAC	International Union of Pure & Applied Chemistry
JCPDS	Joint Committee on Powder DiffractionStandards
JIC	Joint Implementation Committee
K	kelvin
KOH	Potassium Hydroxide
MCF	Meso cellular form
MCM	Mobil Crystalline Material
MG	Mono-glyceride
MSN	Mesoporous Silica Nanoparticle
MSU	Michigan State University
MW	Molecular weight
Na	Sodium
NaOH	Sodium Hydroxide
NO_2	Nitrogen dioxide

NOx	Nitrous oxide
OPEC	Organisation of the Petroleum Exporting Countries
P123	Pluronic copolymer
PEO	Polyethylene Oxide
PM	Particulate Matter
Ppm	Parts per million
PSD	Pore Size Distribution
RETs	Renewable energy technologies
SBA	Santa Barbara Amorphous
SDA	Structure Directing Agent
SDC	Sustainable Development Commission
STP	Standard temperature & pressure
TEOS	Tetraethylorthosilicate
TG	Triglycerides
TLC	Thin Layer Chromatography
TR	Transesterification Reaction
UN	United Nations
USEPA	United States Environmental Protection Agency
UNECA	United States Economic Commission for Africa
US	United States
UFOP	Union zur Förderung von Oel- und Proteinpflanzen
WEC	World Economic Council
Wt	Weight

W.r.t	with respect to oil
WCO	Waste cooking oil
XRD	X-ray diffraction

CHAPTER ONE

1.0: INTRDUCTION

Sustainability has now become a watchword for modern society. This has prompted developed and developing nations and multinational corporations to take key interest in promoting international research programmes into energy materials, sustainable food and even in city planning [1]. The advancement in methodologies to meet the requirements of the present without compromising those of future generations is of essence. Despite significant growth in proven and predicted fossil fuel reserves for the next three decades, including heavy crude oil, deep-water wells, tar sands, and shale oil and gas, there are still uncertainties in the economics of their exploitation through current extraction methodologies [1]. This will cause serious increase in the percentage of such carbon resources which was estimated to vary between 65-80 % [2-4]. These carbon resources cannot be combusted without breaching the **United Nations Framework Convention on Climate Change** (UNFCCC) targets for an average of 2 ℃ increase in global temperature relative to the pre-industrial level [5, 6]. This however poses a challenge in meeting ever rising energy demands, (predicted to increase by 50 % globally by 2040) and also to mitigate current CO_2 emissions level and its associated climate change. The quest for sustainable resources to meet the demands of a rapid growing global population presents one of this century’s major challenges [6, 7].

Globally, the transportation sector is the second largest after the industrial sector in energy consumption accounting for about 30 % of the world’s total energy requirements, out of which 80 % is road transport [8]. The transportation sector however has continuously relied on fossil fuel resources [8]. The over reliance on fossil fuels to meet the progressive global increase in energy demand as a result of urbanization, industrialization and population growth is unsustainable due to the dwindling crude oil reserves, escalating crude oil prices and its associated environmental concerns [9]. There is still a need to explore renewable energy resources in order to increase the percentage of renewables in the global energy mix [10]. According to the International Energy Agency (IEA) report [11] and Shahid and Jamal [12], the world will require 50 % more energy than today in 2030, out of which 45 % will be accounted for by China and India. Over the past three decades, the transportation sector has experienced a steady growth especially due to the increasing numbers of cars around the world. It has therefore been estimated that the global transportation energy consumption will increase by an average of 1.8 % per annum from 2005 to 2035 [13].

However, biodiesel has been recognized globally as a viable alternative renewable source of fuel required to increase the percentage of renewables in the total energy mix [15]. Biodiesel can be produced from either first generation feedstock (edible vegetable), second generation feedstock (non-edible vegetable) or third generation feedstock (microalgae, microbes) [15]. Furthermore biodiesel as an alternative to petro-based diesel has the advantages of being renewable, non-toxic, biodegradable, low emission profiles and ecological friendliness [15]. However, the application of costly refined edible oils would not only cause the scarcity of the cooking oil but also increases the cost of biodiesel production [15]. These problems could be overcome by using either non edible vegetable oils or waste cooking oils as feedstock for biodiesel production. But, such oils usually contain high concentrations of free fatty acids (FFA) and moisture contents [15, 16]. However, biodiesel production from feedstock containing high FFAs (>0.6 wt. %) required two-step processes; acid catalysed esterification to reduce the FFA contents followed by base catalysed transesterification of the ester rich feedstock to produce biodiesel [17].

One major hurdles facing scientists for the commercialization of biodiesel production in the world is non-availability of adequate feedstock and viscous nature of either edible or non-edible oils. Different methods have been proposed and used to reduce the high viscosity of oils to enable their use through various technologies such as blending with petro-base diesel, pyrolysis, emulsification and transesterification. However pyrolysis and emulsification produce heavy carbon deposits resulting from incomplete combustion and increase lubricating viscosity [18].

Currently, the most commonly used scientific process for biodiesel production is via transesterification of vegetable oils with short-chain alcohols in the presence of a suitable catalyst [18]. For commercial biodiesel production, homogeneous basic catalysts such as NaOH, KOH, or CH3COONa, are often used for the transesterification process but this presents difficult separation of the homogeneous catalyst from the esters [19]. Homogeneous mineral acid catalyst (e.g. H_2SO_4, HCl) [19], used for the esterification of FFAs are non-reusable, highly corrosive and require high temperature (>100℃) [19]. Moreover, acid catalysts must be neutralized with alkali which generates salt during the process, and this must be washed from feedstock prior to base catalysed transesterification [19].

However, these catalysts, even though effective, have shown to be sensitive to water and free fatty acid (>0.6wt %) present in the feedstock [20]. And this has resulted into the formation of unwanted soap by-products, which makes the product separation difficult and also reduces the performance of the catalyst. As a result, a tedious and ecologically unfriendly water washing process is required for the removal of the catalyst from the final product for homogeneous base-catalysed approach and thus, a huge amount of wastewater would be inevitably produced to effectively separate and purify biodiesel [21, 22].

To circumvent the aforementioned problems associated with the use of homogeneous catalysts, heterogeneous catalysts are proposed and expected to substitute homogeneous ones. This choice is because heterogeneous catalyst separation and purification from the reaction products is easy, elimination of the water washing procedure currently required for the neutralization of the biodiesel during production process, easy reuse of the catalyst in the reactor and the reduced corrosion problems of catalyst separation. This however, makes the transesterification process more practical from both commercial and environmental perspective [23]. Heterogeneous catalysis also has a rich history of facilitating energy efficiency in selective molecular transformations and contributes to 90 % of chemical manufacturing processes and to more than 20 % of all industrial products [24, 25]. Furthermore in a post-petroleum era, catalysis is expected to play a central role in overcoming the engineering and scientific barriers to economically feasible routes to alternative source of both energy and chemicals, notably bio-derived and solar-mediated via artificial photosynthesis [25]. Various heterogeneous basic catalysts used for the transesterification reaction have currently been investigated, including alkaline earth oxides, supported alkali or alkaline earth metals, basic zeolites and hydrotalcites [25, 26].

The transesterification of triglycerides with short-chain alcohol is a reversible reaction; therefore excess amount of alcohol is generally required to drive the reaction towards completion in order to produce more methyl esters as products. Moreover transesterification reactions are usually carried out in amore polar medium. The dissolution however, of the solid catalyst in the polar media cannot be ignored due to its hindrance to the heterogeneity of the catalyst [27]. Among heterogeneous bases, calcium-based catalysts show greater potential for the transesterification reaction due to their high activity and low cost [28-30]. However the application of these catalysts depends on several parameters such as oil nature type, molar ratio of alcohol to oil, temperature and catalyst type [31]. This suggests that calcium oxide (CaO) is a viable heterogeneous solid base catalyst for transesterification of oils.

From literature, the calcium oxide alone and its binary metal were usually used for biodiesel production but generated some instability and reusability issues as a catalyst. The instability of calcium-based catalysts restricts their application in industrial biodiesel production. Due to this, it is very importance to improve stability and reusability of calcium-based catalysts for long-term transesterification.

This problem has drawn recent attraction to mesoporous molecular sieves especially in their application in catalysis [31]. A hexagonally ordered mesoporous material (SBA-15 silica), is considered as an excellent support for heterogeneous catalysts due to its high surface area, large pore size and very high stability [31]. For the heterogeneous catalyst, large pore sizes are favourable for the mass transfer, and the high surface area could lead to a high concentration of active site. It has been shown that the amino-functionalized mesoporous SBA-15 possesses a high catalytic activity towards the Claisen-Schmidt condensation and Knoevenagel reaction [32]. However, for developing an environmentally benign process, CaO mixed oxides were intended to reduce the level of leaching by the interaction of CaO with other oxides [33].This interaction could cause the dispersion of calcium species on mesoporous silica supports and hence improve the stability and reusability of calcium-based catalysts.

This research is aimed at developing efficient and ecologically benign heterogeneous catalysts for biodiesel production. For this purpose; CaO-MoO3-SBA-15/CaO–MoO3/PO4–SBA-15 solid catalysts were prepared by aqueous wetness impregnation method. Upon calcinations, it would be expected that the acid–base interaction between the basic CaO and the acidic MoO_3 in the solid catalyst could promote high and stable dispersion of catalytically active sites in order to enhance the stability of the catalyst [33]. The novelty of this work is associated with the surface functionalization of the CaO–MoO_3 mixed oxide supported on

SBA-15 silica to enhance its surface properties and pore network for the transesterification reaction in a heterogeneous sense. In this study there was evaluation of the catalytic activity of the CaO-MoO3-SBA-15/ CaO–MoO_3/PO_4–SBA-15 catalysts in the transesterification of waste cooking oil regarding the conversion to methyl esters.

1.1: Research justification

The production of bio-fuels is considered as an essential technology by both developing and industrialized nations aimed at addressing energy security, environmental concerns, foreign exchange savings, and socioeconomic issues regarding rural sector development. The sustainability, environmental and inflationary problems associated with conventional fuels has recently attracted a global search for alternative renewable biofuel [34]. If biodiesel production is well sourced and produced in a sustainable fashion would play a key role in meeting high percentage of global renewable energy targets. However, developments in materials design and architecture remain critical in achieving significant improvements in biodiesel production in a heterogeneous sense [34]. The architecture of solid acid and base catalysts with tailored surface properties and pore networks present process improvements over existing homogeneous catalysed production. This however, promotes and facilitates simple catalyst separation and fuel purification, coupled with continuous biodiesel synthesis. The architecture of surface hydrophobicity of heterogeneous catalysts can strongly influence oil transesterification and FFA esterification through water expulsion from active catalytic centres hence limiting undesired reverse hydrolysis processes [34]. Solid materials capable of multi-faceted functions of FFA esterification and TAG transesterification under mild conditions present a major challenge for catalytic scientists. Although insoluble high area super acids lead a step in this direction [34].

1.2: Problem statement

The major concern over the economics of accessing fossil fuel reserves, and the widespread acceptance of the anthropogenic origin of rising CO_2 emissions and the associated climate change from combusting such carbon resources, has drawn academic and commercial research into new routes to sustainable fuels to meet the demands of a rapidly growing global population [37].

Biodiesel offers a suitable and sustainable renewable alternative to petroleum based diesel. Despite the successes chalked in the biodiesel industry there are still substantial challenges in the industry, as developments in materials design and construction are instrumental in achieving significant improvements in heterogeneously catalysed biodiesel production. The design of solid acid and base catalysts with tailored surface properties and pore networks present process improvement over existing homogeneous catalysed production employing liquid bases.

It has been observed that grafting anionic species such as sulphate, phosphate ions onto mixed oxides surface generate new acidic sites of higher strength [38, 39]. Tuning the surface area and pore networks of heterogeneous catalyst can strongly influence transesterification and FFA esterification of oil via surface functionalization. Therefore the synthesis of nanostructure catalysts and the application of surface-initiated as well as controlled phosphate to functionalize oxide surfaces with high active site loading would prove valuable in the quest for enhanced catalyst performance [39].

1.3: Research aims and objectives

The literature review has shown different options for synthesizing heterogeneous catalyst for biodiesel production. These different methods have their disadvantages. This research therefore seeks to achieve the following specific objectives;

- Synthesis of template mesoporous materials and surface functionalization.
    - ✓ Functionalization of supports into solid acid and base catalysts via aqueous incipient wetness impregnation techniques.
- Characterization of the solid catalyst using XRD, BET/BJH, FTIR and Optical microscopy.
- Application of the catalyst in transesterification process to produce biodiesel.
- Characterisation of the biodiesel produced in order to confirm its quality, purity and also compare with the international standards and specifications.

1.4: Research questions

i. Can surface modification of heterogeneous catalysts lead to potentially favourable yield of methyl esters from waste cooking oil and easier refining of the produced biodiesel?

ii. Will the use of $CaO–MoO_3/PO_4–SBA\text{-}15$ present a catalytic system that is environmentally benign processes?

iii. Will the biodiesel produced from heterogeneous transesterification catalytic reactions systems meet or compare with standard quality specifications?

1.5: Research approach

The research methods used in this study in order to achieve the aims and objectives are hereby emphasized.

1.5.1: Heterogeneous catalysis of waste oils to biodiesel

This section of the study involves preparation of heterogeneous catalysts using SBA-15 as support. The synthesised catalysts were used in the transesterification reactions of waste cooking oil feedstock with methanol to form methyl esters. The synthesized SBA-15 was impregnated with $CaO–MoO_3$ (using calcium nitrate& ammonium heptamolybdenate as precursors) via a wetness impregnation method. The use of SBA-15 could improve dispersion of the active species, CaO, MoO_3 and provide available adsorption sites for the reagents (methanol and triglycerides) prior to the conversions to methyl esters. The prepared catalyst was then grafted using phosphoric acid.

The solid catalyst was characterized using powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, Optical Microscopy and Sorptometric techniques to determine catalysts chemical and mineralogical compositions as well as analyse the morphology, and BET surface area, pore size distribution, pore diameter and pore volume.

1.6: Research hypothesis

The use of $CaO–MoO_3/PO_4–SBA\text{-}15$ heterogeneous catalysts in transesterification reactions would present a process that is environmentally benign and leads to potentially favourable yield of methyl esters and easier refining of the produced biodiesel, and improved recovery of the catalyst.

1.7: Scope and limitation

To address the limitations and problems posed by the homogeneous catalytic process, heterogeneous catalyst prepared was characterized and used for the transesterification reactions required to produce methyl esters. Esterification reactions using an acidic catalyst (in this case waste cooking oil with high amounts of free fatty acids (FFA) was carried out in this study.

1.7.1: Limitations of study

The following were not covered in the study;

i. The effect of different phosphoric acid concentration on the catalyst surface modification was not investigated.

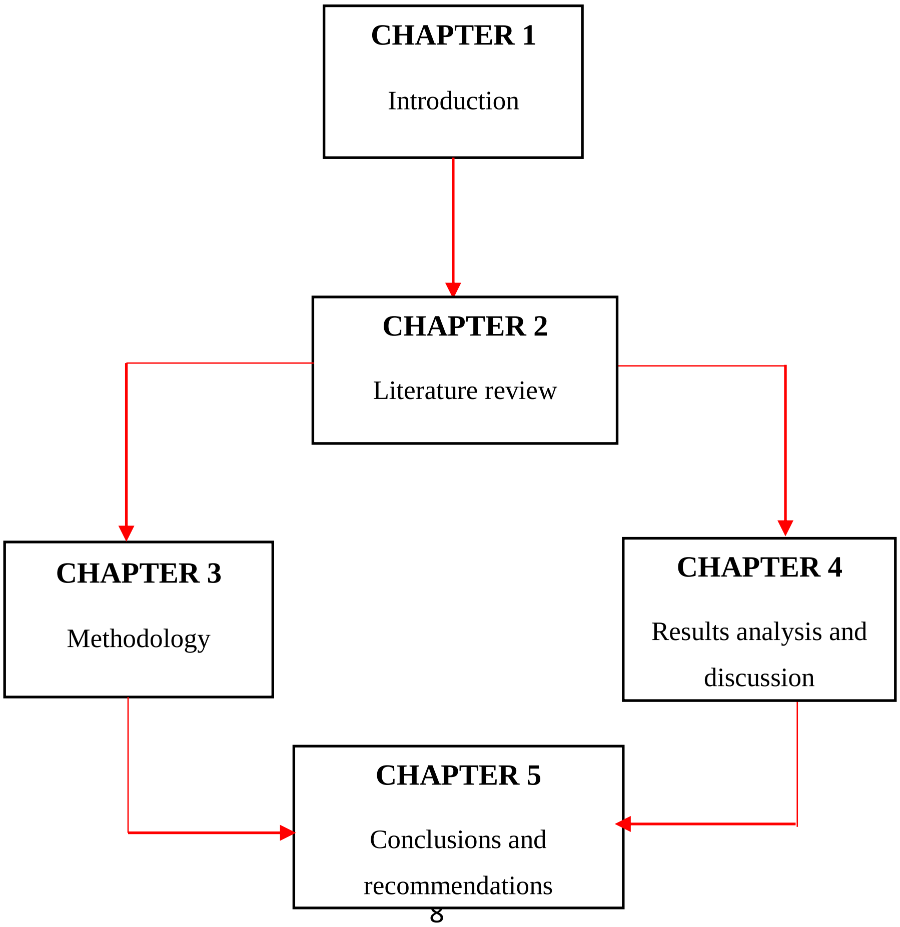
ii. Determination of the purity and yield of the glycerol produced from the transesterification reactions carried out during the study was not investigated.

iii. An investigation of the effect of molar ratio of alcohol: oil on transesterification reactions with the heterogeneous catalyst was not conducted.

iv. Determination of the effect of different catalyst loading on methyl ester yield was also not investigated.

1.8 Thesis structure

This thesis is grouped into six chapters.



CHAPTER TWO

2.0 LITERATURE REVIEW

This chapter reviews the history, application, advantages and disadvantages of bio fuels and particularly biodiesel, global biodiesel production and the chemistry of biodiesel production. The requirements of biodiesel feedstocks and characteristics are also highlighted. The properties and quality control of biodiesel and its role in biodiesel production is emphasized in the literature review. The applications of mesoporous molecular sieves to increase the activity of heterogeneous catalyst in production of biofuel are also highlighted.

2.1 Background

The world market is much concerned with issues of the escalating petro-diesel fuels cost, the negative effect of greenhouse gas emissions and the depleting petroleum resources. This has necessitated an urgent need for an alternative fuel. Biodiesel therefore is an answer to all these major concerns [39]. Biodiesel has been recognized as the “fuel of the future”. Some of the early biodiesel initiatives take place in South Africa, Austria, Germany and New Zealand. However a small pilot plant was built in Austria in 1985 using rapeseed oil as a test run for the production of biodiesel [40]. Furthermore in 1990 the first farmers’ cooperative union was established for the commercialization of biodiesel. Soon afterwards there were fleet tests that have led to engine warranties by most tractor producers such as Massey-Ferguson, John Deere, Ford and Mercedes [40]. In 1991, the first introduction of fuel standard ON C 1190 for biodiesel by the Austrian Standardization Institute to ensure quality control measure for the fuel. Subsequently, biodiesel plants were installed in other parts of the European Union, East Europe, Malaysia and the USA [40, 41]. In 2006, Canada commissioned the first commercial scale biodiesel plant with a production capacity of 35 million litres per annum [40].

2.2: Renewable Energy/Bio-Energy

The success and development of any nation is directly linked to its socio-economic advancement. Energy is one of the most important driving factors that play a key role in achieving such development. Energy plays an integral part in quest for industrialization and overall sustainable development of societies. These developments would be attained when energy is delivered on time, in sufficient quantity, under reliable economic conditions with consideration and mitigation of the environmental impacts [40]. The demand for energy has a parallel increase with the population increase, industrialization and technological advancement in developing nations [40].

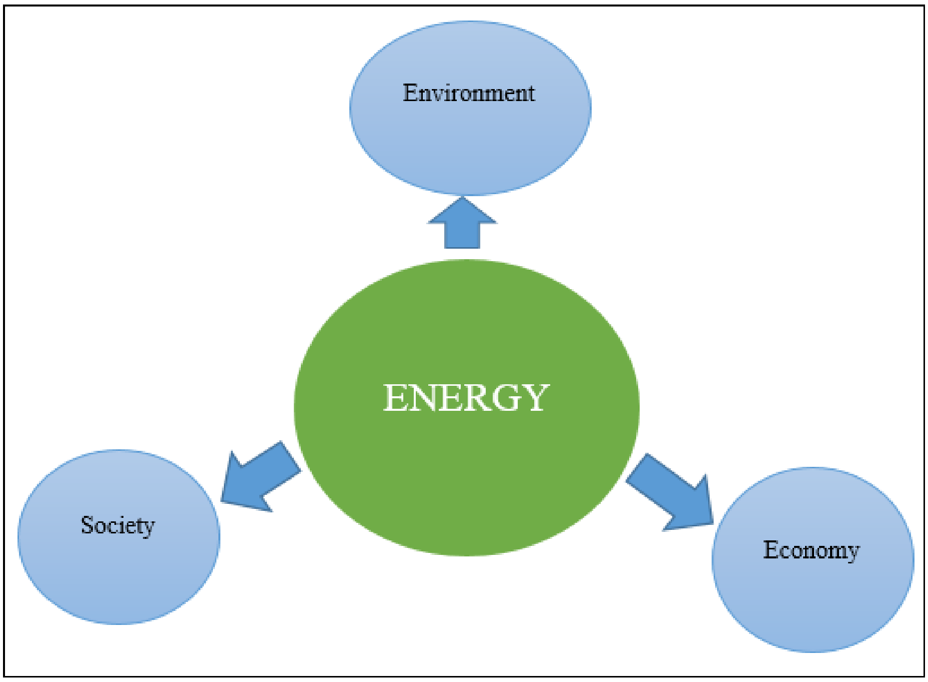


Figure 2. 1: Interrelationships between energy **and sustainable development** [40].

The continent of Africa currently constitutes 14 % of the world's population yet accounts for only 2 % of its gross domestic product (GDP) [40]. Moreover the continent produces 7 % of the world's total energy demand and consumes only 3 % of it [40, 41]. According to the World Energy Council (2002) [41], the energy resource potential in Africa is twice the world average. However the application of modern energy services is closely linked with development, provision of essential services and poverty reduction. Furthermore the consumption of modern energy sources in Sub Saharan Africa is extremely low due to the over reliance on traditional biomass [40-42]. The easy access to sustainable and affordable energy is therefore a pre-requisite for potential development in this part of the world. This access to affordable and secure energy is an essential component of achieving the millennium development goals with emphasis on education and communication, and enhances health care services with corresponding climate change [40].

There is plethora of renewable energy sources in Africa. These include more than 1.1 million gigawatts of exploitable hydropower capacity, more than 9000 megawatts of geothermal potential, substantial biomass and solar potential. However the utilization of these renewable energy resources is rather limited. The total energy requirement of Sub Saharan Africa in 1990 was approximately 267 million tons of oil equivalents [40]. The modern renewable energy resources account for less than 2 % of the continent’s primary energy demand [40]. Sub Saharan Africa also has significant amounts of renewable energy sources yet to be tapped. However renewable energy technologies (RETs) have shown a growing potential to meet energy needs where conventional energy supply options have failed. If Africa were to take its rightful place in the booming renewable energy industry, it would generate enormous developmental benefits and growth. The potential to develop modern biomass technologies in Africa such as biogas, bio-ethanol and biodiesel fuel particularly offers Africa a lot of prospect of energy self-reliant at both national and local levels with economic, environmental, social and security benefits (Figure. 2.1) [40,41]. Energy consumption in Africa is largely dominated by combustible renewable resources [40, 41]. Energy from biomass accounts for more than 30 % of the energy consumed in Africa and more than 80 % in some African countries [40]. Biomass constitutes the main energy resource for the large majority of African households for cooking, drying and space heating. From 1994 to 2004, primary energy consumption increased by 24 % in Africa according to reports on Energy for Sustainable Development in Africa (Figure. 2.2) [32]. Fossil fuels are however expected to continue supplying much of the world energy requirements. The percentage liquids share of world marketed energy consumption will fall from 35 % in 2007 to 30 % in 2035 even though liquid fuels still remain the largest source of energy in the world [40]. Many energy consumers are now turning away from liquid fuels to pave way for renewable energy sources as a result of the projected high world oil prices.

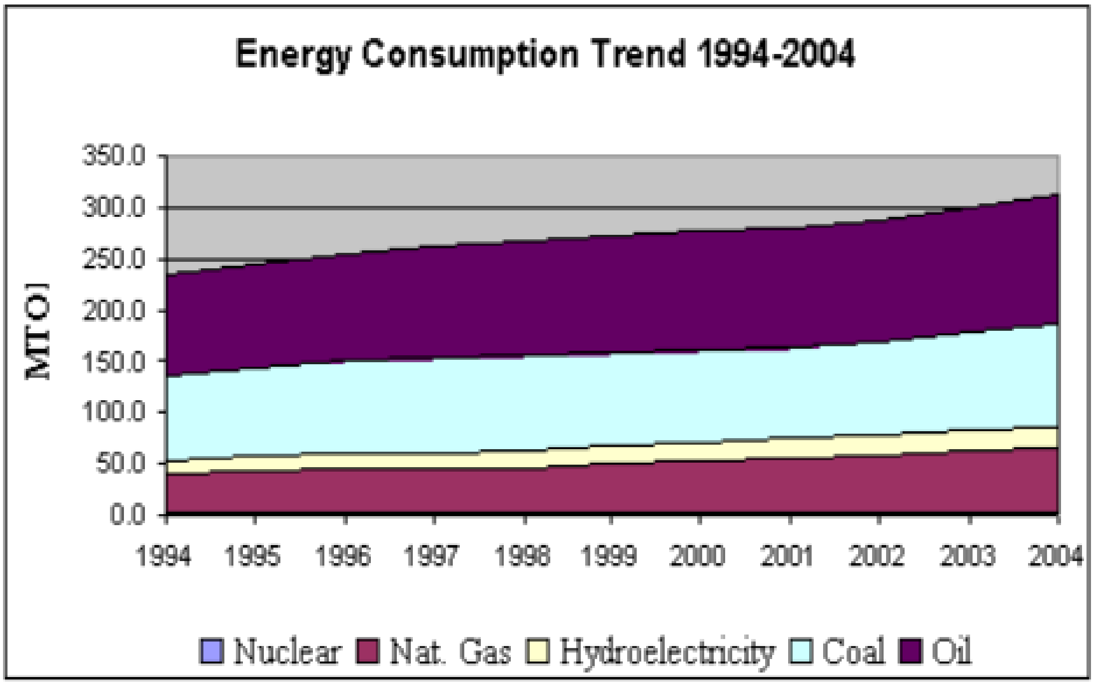


Figure 2. 2: Modern Energy Consumption trend in Africa (UNECA, 2006) [32].

The energy consumption in the transportation sector includes the energy used in moving goods and people by road, rail, air and water. The transportation sector as the second largest energy consuming sector after the industrial sector, accounts for about 30 % of the world's total energy requirement, out of which 80 % is road transport [42]. The transportation sector has continuously relied on fossil fuel resources as the main source of fuel. The transportation share of the global total liquid fuel consumption increase is projected to rise from 53 % in 2007 to 61 % in 2035(IEO2010) [43], accounting for about 87 % of the total increase in world liquid fuels consumption [43]. In U.S. over 25 % of greenhouse gas (GHG) emissions come from the transportation sector (see Figure. 2.3), making transportation sector the second largest source of GHG emissions in the United States after the electric power sector [43].However understanding the development of transportation energy consumption is one of the most important factors in assessing future trends in demand for liquid fuels.

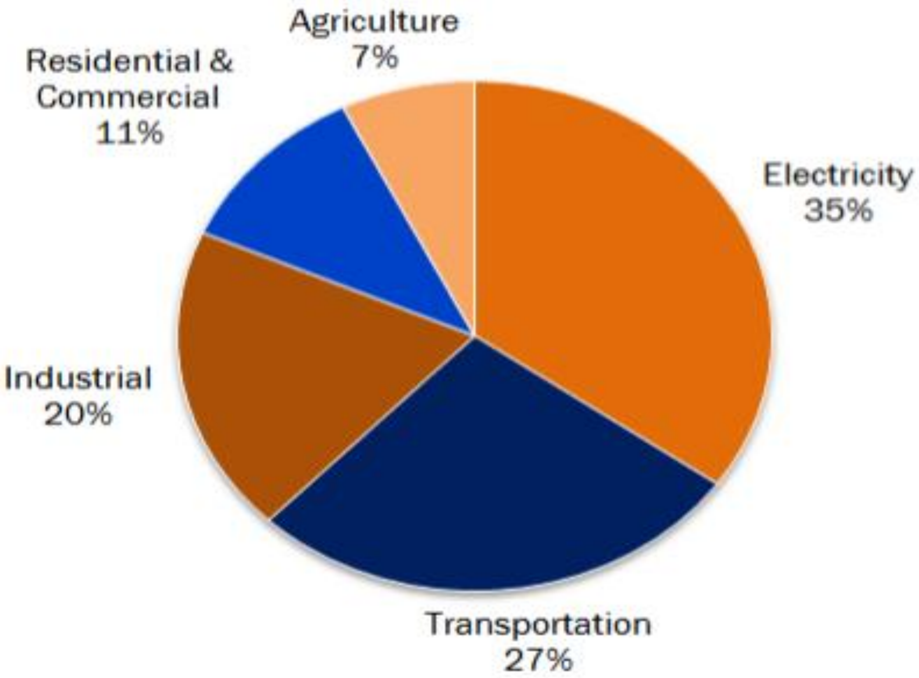


Figure 2. 3: Sectors contributing to GHG [44].

2.3: Bio-fuels

Biofuels can be broadly defined as any kind of fuel that is extracted from organic matter (biomass) of which biodiesel and bio-alcohols are the most commonly extracted. Biofuels are renewable energy sources because plants required for biofuel production can be re-grown [45]. While several sources of alternative renewable energy have the potential to meet future demands for power generation, biomass presents the most readily implemented, low cost solution to a fall in transportation fuel for blending with or replacing conventional diesel via the bio-refinery concept, as illustrated for carbohydrate pyrolysis/hydro-deoxygenation (HDO) or lipid transesterification [45, 46] to alkanes and biodiesel respectively (see Figure. 2.4).

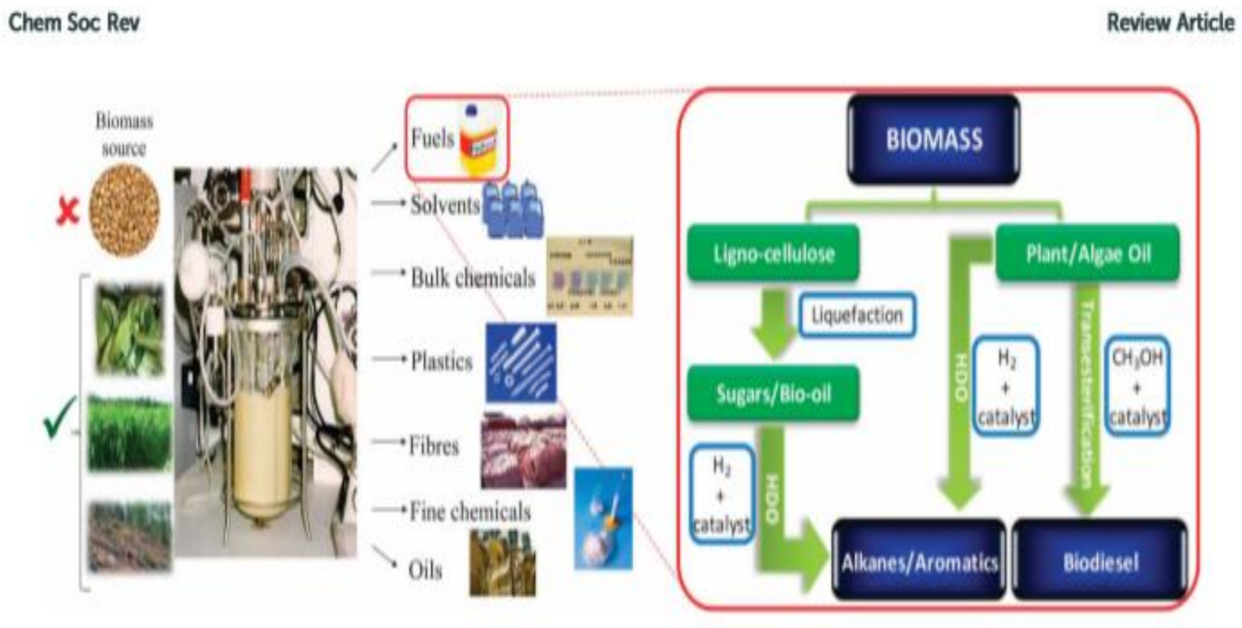


Figure 2.4: Bio-refinery routes for the co-production of chemicals and transportation fuels from biomass [1].

The derivation of first-generation bio-fuels from edible plant materials received immense criticism because of the competition between land usages for fuel crops versus traditional agricultural cultivation [47]. This raise many concerns over food versus fuel debate that might cause starvation particularly in the developing countries and other attended environmental problems caused by the utilization of the available arable land [47]. These problems can create serious ecological imbalances as countries around the world began clearing forests purely for plantation purposes. The use of these fuel crops as feedstocks could however cause deforestation and damage to the wildlife. Therefore, non-edible vegetable oils or the second and third generation feedstocks have become more viable and attractive alternative for biodiesel production [48]. These feedstocks have the potential for the sustainable biodiesel production. Furthermore, microalgae which is regarded as the third generation feedstock, has become the latest inexhaustible potential source of biodiesel production [48]. Microalgae have great economic value compared to edible oils.

To be considered sustainable, second generation bio-based fuels and chemicals use biomass sourced from non-edible components of crops, such as stems, seeds, leaves and husks or cellulose from agricultural or forestry waste. A wide variety of non-food feedstocks are potentially available globally for biofuel production. Furthermore alternative non-food crops such as energy crops (e.g. Miscanthus, Jatropha curcas, Short Rotation Copice), wastes (e.g. waste oil, food processing wastes, etc.), agriculture residues (straw, corn stover, etc) and novel feedstock such as algae [49] which require minimal cultivation are other promising prospect for biofuel feedstocks. These resources do not compete with traditional arable land or drive deforestation. There is also growing concern over extracting bio-oils from aquatic biomass, which can yield up to 80-180 times the annual volume of oil per hectare than that obtained from terrestrial plants [50]. About 9 % of transportation energy demands are projected to be met via liquid biofuels by 2030 [51].

Biodiesel which is a clean burning and biodegradable fuel derived from non-food crops or algal oils or animal fats, is considered as a viable alternative or additive to current petroleum based diesel [52].The current commercial production of biodiesel is via liquid base catalysed transesterification of triacylglyceride, C_{14}–C_{20} (TAG); components of lipids with short carbon-chain alcohols [53, 54] into fatty acid methyl esters (FAMEs) which is the main constitute of biodiesel as shown in Figure 2.5, with glycerol as economic valuable by-product [55].

However the use of longer carbon-chain (e.g. C_4) alcohols is also possible [56] and have the advantageous of producing a less polar and corrosive FAME [56] with reduced cloud and pour points.The current high cost of these alcohols and the attended difficulties of separating the heavier FAME product from unreacted alcohol and the by-product (glycerol) still remain a problem.

Biodiesel is commercially produced via homogeneous catalysed transesterification reaction. Unfortunately, homogeneous acid and base catalysts cause corrosion of reactors and engines manifolds. Also the separation of homogeneous acids from the resulting biofuel is particularly problematic and energy intensive. As it requires aqueous quench and neutralization steps which result in the formation of stable emulsions and soaps [57]. Such uses of homogeneous approaches also yield the glycerine by-product, which is of significant economic value to the pharmaceutical and cosmetic industries. The use of solid base and acid catalysts for biodiesel production has been widely reported [58]. The application of heterogeneous catalysts offer improved process efficiency by eliminating quenching and neutralisation steps by ensuring continuous operation [58] and enhance the purity of the biodiesel and glycerol. The technical advancement in catalyst and reactor design remains vital to the utilization of non-food based feedstocks. This however ensures that biodiesel remains crucial in the renewable energy sector for the 21st century. In this review, the contributions of tailored solid acid and base catalysts to catalytic biodiesel synthesis via TAG transesterification to FAMEs and free fatty acid (FFA) esterification are highlighted.

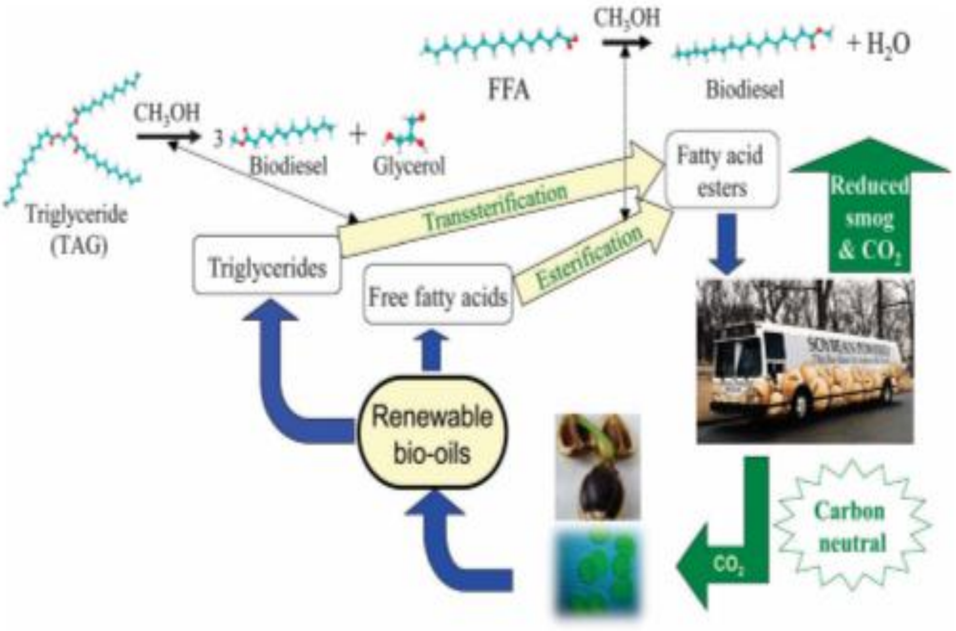


Figure 2.5: Biodiesel production cycle from renewable bio-oils via catalytic transesterification and esterification [58].

There are some assertions that biofuel is carbon neutral energy source. As crop plants cultivated for biomass production absorb exactly the same amount of carbon dioxide from the atmosphere for photosynthesis. The production and consumption of biofuel ensures that 100 % of the natural carbon cycle is achieved to completely eliminates the continuous increase in carbon dioxide rates in the atmosphere which in effect reduce global warming [58].

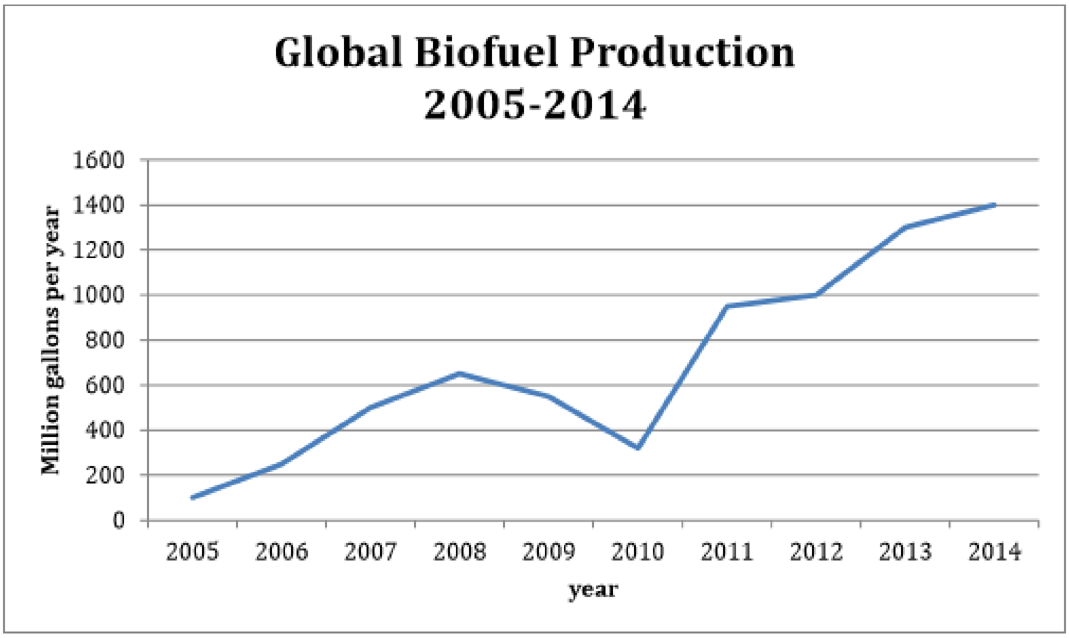
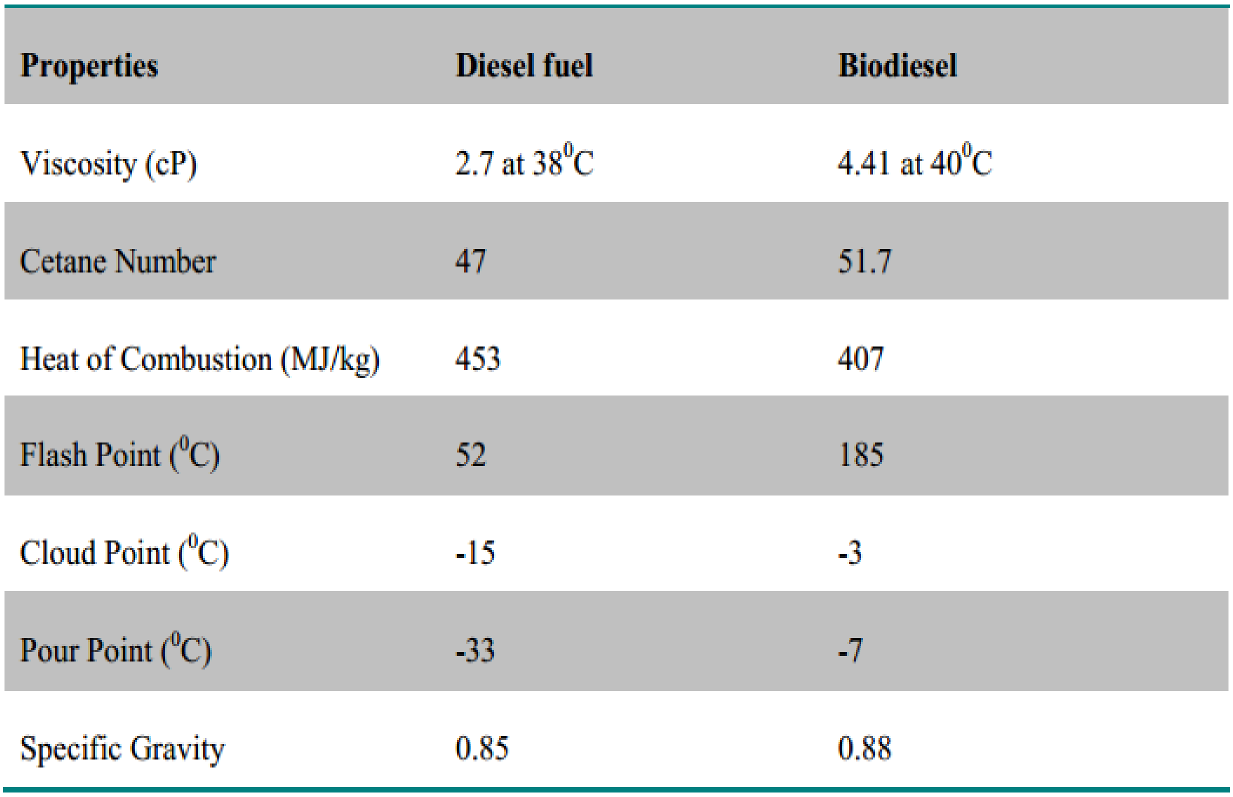


Figure 2.6: Global Biofuel production from 2005 – 2014 [3].

2.4: Biodiesel

Biodiesel is mono alkyl esters of long chain fatty acids derived from renewable feedstocks, such as vegetable oil or animal fats, for use in compression ignition engine [59]. Biodiesel is commonly made up of fatty acid methyl or ethyl esters that can be produced from triglycerides in vegetable oils by transesterification with either methanol or ethanol. The biodiesel produced is quite similar to petro-diesel fuel in its main characteristics. Furthermore, aside offering similar power to diesel fuels and having a higher flash point than diesel, biodiesel have low toxicity and provides significant lubricity improvement over petroleum diesel [58]. Table 2.1 shows the comparison of the physical properties of diesel fuel and biodiesel [58].

Table 2. 1: Properties of Diesel Fuel and Biodiesel [3]



Properties	Diesel fuel	Biodiesel
Viscosity (cP)	2.7 at 38^{0}C	4.41 at 40^{0}C
Cetane Number	47	51.7
Heat of Combustion (MJ/kg)	453	407
Flash Point (^{0}C)	52	185
Cloud Point (^{0}C)	-15	-3
Pour Point (^{0}C)	-33	-7
Specific Gravity	0.85	0.88

The production of biomass diesel is on ascendancy. The different possibilities for producing diesel oils from biomass resources have seen substantial research in recent times, and a number of catalytic methods have now been known and established. Also fats and oils can either be transesterified with alcohol to form fatty acid alkyl esters [53–58], deoxygenated with hydrogen to form n-alkanes [54–59], or cracked at high temperatures to form hydrocarbon mixtures [59]. Carbohydrates may be converted by aqueous-phase-reforming to form unfunctionalised or monofunctional hydrocarbons [53–57]. In general biomass may also be gasified to syn-gas and undergo Fischer-Tropsch-synthesis [53], or bio-oils can be produced by flash pyrolysis and upgraded by cracking or hydrogenation [59]. The possibilities are illustrated in Figure. 2.7.

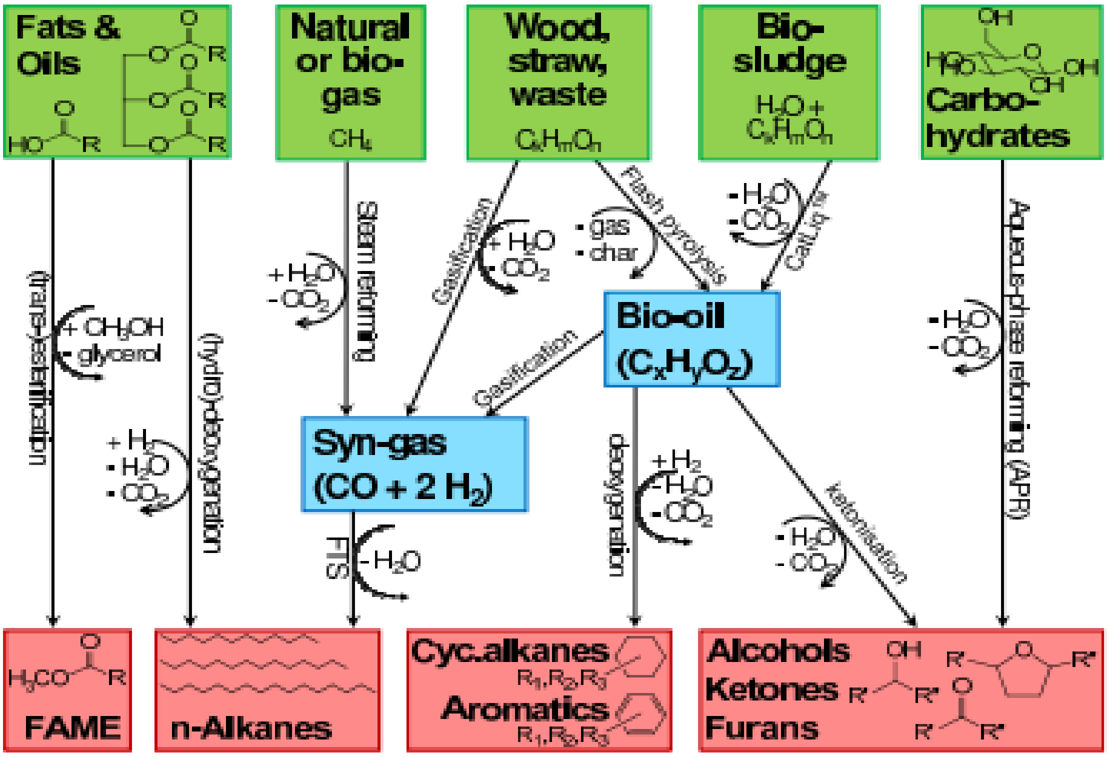


Figure 2.7: An overview of feedstocks, conversion routes and products as plau-sible components in the production of diesel from biomass [47].

One unique characteristic of diesel fuels is the ability to auto-ignites which is made possible by high cetane number. However biodiesel not only has a higher cetane number than petroleum diesel but also a higher flash point, offering better and safer performance. The redox characteristics of biodiesel qualify it a reducing agent for materials, such as brass, bronze, copper, lead, tin and zinc. For this reason these materials must avoid having contact with biodiesel [41]. Materials such as aluminium, steel, fluorinated polymers and Teflon do not react with biodiesel and can be used to store biodiesel. Furthermore, biodiesel shows mild solvent properties so when it made contact with painted or varnished surfaces as well as rubber devices may cause problems. The storage stability of biodiesel is adversely affected by the presence of unsaturated alkyl components [40, 41]. The olefinic moieties in biodiesel fuel can undergo oxidative degradation via exposure to air with deleterious results as well as formation of solids and gums [41]. Biodiesel can be used as neat fuel which is denoted as B100. However, it can be blended with petroleum-based diesel fuel which is designated as “BXX”; where XX represents the percentage in volume of biodiesel in the blend. For instance, B20 is a blend of 20 % volume biodiesel and 80 % volume petro-diesel. In USA blends of B20 or lower are acceptable standards, but there are also some interest to utilize biodiesel blends more than B20 [5]. B5 and B20 are the most common blends and can be used in unmodified diesel engines. Also biodiesel is the only alternative fuel currently available with an overall positive life-cycle energy balance (Fig. 2.8). For instance, biodiesel generates 3.2 units of fuel product energy per unit energy consumed as compared to only 0.83 units for petroleum diesel. The presence of oxygen in biodiesel (~10 %) improves combustion and reduces CO, soot, and hydrocarbon emissions while slightly increasing the NOx emissions [44].

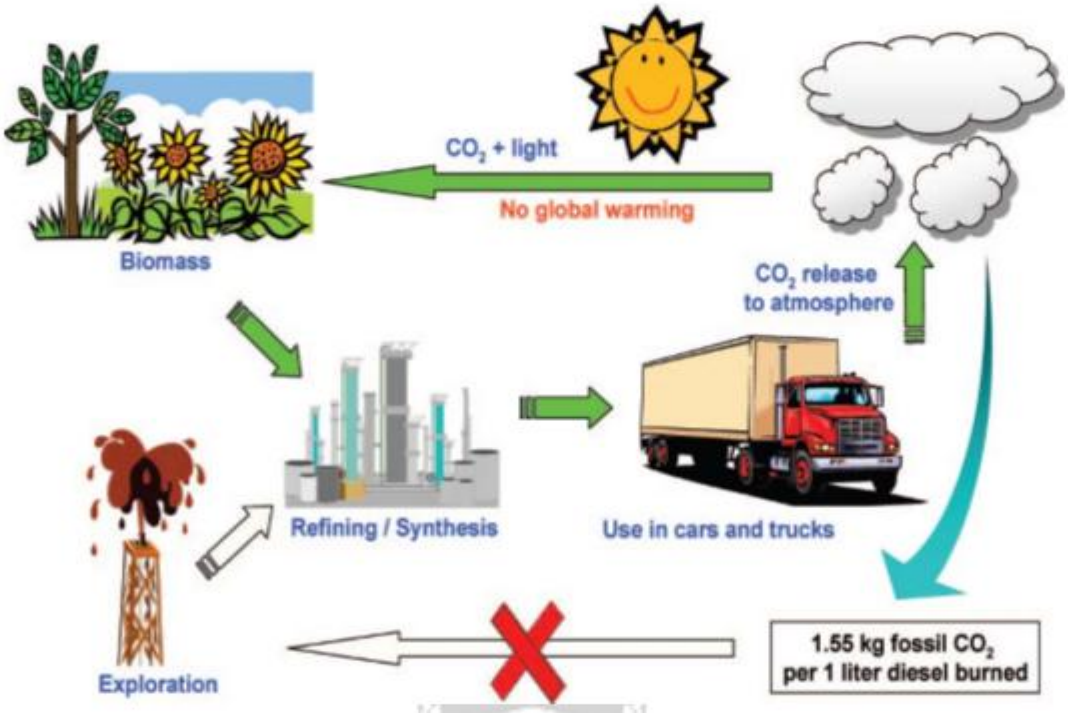


Figure 2.8: Life cycle of diesel vs. biodiesel as an environmentally friendly fuel, the CO2 cycle is closed for biodiesel but not for diesel [44].

2.4.1 Advantages and Disadvantages of Biodiesel

Biodiesel is renewable in nature and is environmentally benign in character. Biodiesel synthesis from biomass offers an option to produce a transportation fuel that is biodegradable and provides a pathway for the recycling of carbon dioxide emissions. The biodegradability was reported to be more than 90 % within 3 weeks, thereby limiting potential hazards in the case of spillage or other accidents. It was reported that biodiesel has great potential to reduce greenhouse gases by at least 3.2 kg CO_2 per1kg biodiesel [6]. The biodiesel emissions for net CO_2 are lower than petro-diesel emissions, and even for the biodiesel blends the emission level also falls depending on the blend used [45]. Figure 2.9 illustrates the comparison of the net CO_2 life cycle emissions of petro-diesel, pure biodiesel and the blend B20. And it is however indicative that there is a substantial reduction of those emission levels. The net CO_2 emissions fall by 16 % and 79 % using the blend of B20 and B100 respectively. The decline in emission levels especially of carbon monoxide by 20%, hydrocarbons (32 %), soot (50 %) and particulate matter (39 %) are well-established facts as reported by the United States Environmental Protection Agency (Figure 2.9). In addition, the fuel has essentially low emission profile of sulphur. It has been reported that the presence of unsaturated methyl esters increase NOx emissions while the emissions decrease with the use of saturated methyl esters. This slight increase in the NOx emissions when unsaturated methyl esters are used can be altered by adjusting the injection time in the engine [8]. Biodiesel also has a high lubricity so blending it with the low-sulphur diesel resolves the problem of lubricity losses when the sulphur is removed. The addition of biodiesel, even in small amount greatly enhances the lubricity of the fuel. It has been shown that the addition of 1.5 wt % biodiesel to diesel with a 15 ppm sulphur concentration change the lubricity from an unacceptable level to an acceptable level [45]. It was reported in a study that the lubricity of ethyl ester is better than methyl ester. It was also stated that lubricity of mixed fuel is better than the lubricity of pure methyl ester [44].The presence of higher amount of oxygen ensures more complete combustion of hydrocarbons and burns up to 75 % cleaner than conventional fossil diesel [44].

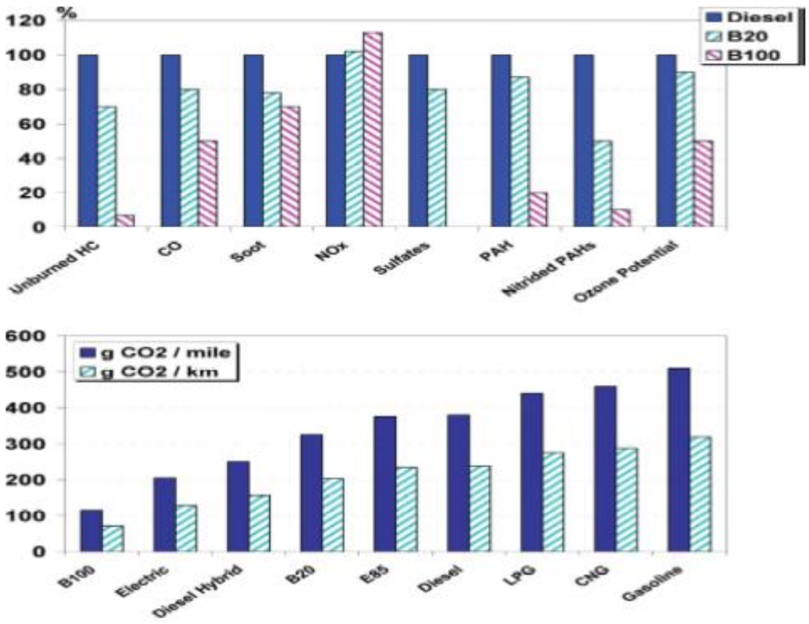
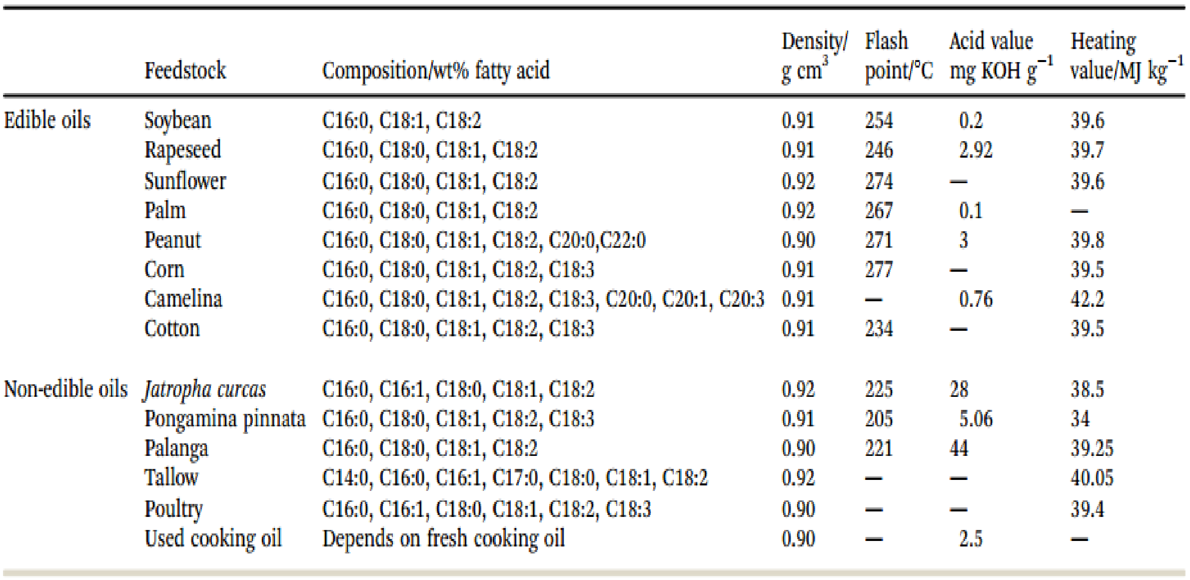


Figure 2.9: Biodiesel vs petroleum diesel emissions (top). Comparison of Net CO2 Life Cycle Emissions for most common fuels (bottom) [37].

2.4.2: Biodiesel feedstock requirements

Traditionally, major conventional feedstocks for “methyl ester process” include cotton seed oil, soybean, sunflower and peanut oil [34]. The use of Jatropha as feedstock offers a great prospects in view of the uncertainty of conventional feedstock and also to avoid conflict between energy and food (Table 2.2).

Table 2. 2: Common feedstocks for biodiesel production, free fatty acid composition and physicochemical properties. Reprinted from ref. 59, Copyright (2010), with permission from Elsevier.



	Feedstock	Composition/wt% fatty acid	Density/ g cm^3	Flash point/°C	Acid value mg KOH g^{-1}	Heating value/MJ kg^{-1}
Edible oils	Soybean	C16:0, C18:1, C18:2	0.91	254	0.2	39.6
	Rapeseed	C16:0, C18:0, C18:1, C18:2	0.91	246	2.92	39.7
	Sunflower	C16:0, C18:0, C18:1, C18:2	0.92	274	—	39.6
	Palm	C16:0, C18:0, C18:1, C18:2	0.92	267	0.1	—
	Peanut	C16:0, C18:0, C18:1, C18:2, C20:0,C22:0	0.90	271	3	39.8
	Corn	C16:0, C18:0, C18:1, C18:2, C18:3	0.91	277	—	39.5
	Camelina	C16:0, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1, C20:3	0.91	—	0.76	42.2
	Cotton	C16:0, C18:0, C18:1, C18:2, C18:3	0.91	234	—	39.5
Non-edible oils	*Jatropha curcas*	C16:0, C16:1, C18:0, C18:1, C18:2	0.92	225	28	38.5
	Pongamina pinnata	C16:0, C18:0, C18:1, C18:2, C18:3	0.91	205	5.06	34
	Palanga	C16:0, C18:0, C18:1, C18:2	0.90	221	44	39.25
	Tallow	C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2	0.92	—	—	40.05
	Poultry	C16:0, C16:1, C18:0, C18:1, C18:2, C18:3	0.90	—	—	39.4
	Used cooking oil	Depends on fresh cooking oil	0.90	—	2.5	—

Table 2. 3: Lists of oil producing crops in the world (Faupel and Al Kurki, 2002)

Plant	Latin name	Kg Oil/ht	Plant	Latin name	Kg Oil/hect
Corn	Zea mays	145	Tung tree	Aleurites spp	790
Cashew nut	Anacardium occidentale	148	Sunflower	Helianthus annuus	801
			Cocoa	Theobroma cacao	863
Oat	Avena sativa	183	Peanut	Arachis hypogaea	887
Palm	Erythea salvadorensis	189	Opium poppy	Papaver somniferum	978
Lupine	Lupinus albus	195	Rape	Brassica napus	999
Rubber seed	Havea brasiliensis	217	Olive tree	Olea europaea	1019
Kenaf	Hibiscus cannabinus	230	Indaia palm	Attalea funifera	1112
Calendula	Calendula officinalis	256	Gopher plant	Euphorbia lathyris	1119
Cotton	Gossypium hirsutum	273	Castor bean	Ricinus communis	1188
Soybean	Glycine max	374	Bacury	Platonia insignans	1197
Coffee	Coffea Arabica	386	Pecan-nut	Carya illinoensis	1505
Linseed	Linum usitatissimum	402	Jojoba	Simmondsia chinensis	1528
Hazel-nut	Corylus avellana	405	Babassu palm	Orbignya martiana	1541
Euphorbia	Euphorbia lagascae	440	Purging nut	Jatropha curcas	1588
Pumpkin seed	Cucurbita pepo	449	Macadamia nut	Macadamia terniflora	1887
Coriander	Coriandrum sativum	450	Brasil nut	Bertholletia excels	2010
Mustard	Brassica alba	481	Avocado	Persea Americana	2217
Dodder-seed	Camelina sativa	490	Coconut	Cocos nucifera	2260
Sesame	Sesamum indicum	585	Oiticica	Licania rigida	2520
Abyssinian kale	Crambe abyssinica	589	Buriti palm	Mauritia flexuosa	2743
Safflower	Carthamus tinctorius	653	Pequi	Caryocar brasiliense	3142
Buffalo	Cucurbita foetidissima	665	Macahuba palm	Acrocomia spp	3775
Rice	Oriza sativa	696	Oil palm	Elaeis guineensis	7061

Table 2. 4: Feedstock Potential in Sub Saharan Africa [40]

Crop	**Country**	**Area harvested (ha)**	**Production (tonns)**
Castor waarts	Angola	2800	1100
	Mozambique	60000	65000
Sesame seeds	Angola	2700	1700
	Mozambique	16000	11000
Castor oil	Angola	13500	3500
	Mozambique	150000	52071
	South Africa	5000	4900
Pumpkin	Mozambique	330	600
	South Africa	11000	72900
Rapeseed	South Africa	35000	32000
Avocardos	South Africa	17000	99030
	Swaziland	50	300
	Zimbabwe	170	1100
Coconut	Mozambique	70000	265000
Soybean	Malawi	70000	45000
	South Africa	174400	322995
	Zambia	10000	12000
	Zimbabwe	65000	105000
Cotton seed	Angola	2700	2700
	Botswana	1100	2500
	Malawi	69826	76761
	Mozambique	360000	240000
	Namibia	3800	5700
	South Africa	14000	26275
	Swaziland	14800	7200
	Zambia	127000	140000
	Zimbzbwe	400000	240000
Sunflower	Angola	15000	11000
	Botswana	6200	7000
	Malawi	7575	5745
	Mozambique	12000	5125
	Namibia	135	50
	South Africa	564300	885560
	Zambia	15000	8000
	Zimbzbwe	23000	23000

Maize	Angola	1115000	570000
	Botswana	56000	12000
	Lesotho	160000	105000
	Malawi	1596955	2634701
	Mozambique	1284930	1284930
	Namibia	18000	40000
	South Africa	2799000	11597000
	Swaziland	47409	26170
	Zambia	663990	1445655
	Zimbzbwe	1730000	496000

The type and quality of a feedstock greatly affect the yield of FAME. These are very important factors on the technical design of a transesterification plant and on the corresponding material and energy flows. Moreover these factors are not only indicators of technical efficiency but also affect the economic viability of biodiesel production. When choosing a feedstock for biodiesel production, it is only prudent to consider the yield per hectare, environmental and social impacts as well as the quality of the material. The yield per hectare of feedstock determines the economic viability of the biodiesel. The higher the feedstock yield, the lower the production cost. A detailed evaluation of feedstocks on the basis of a specification of the significant characteristics of oils and fats has been identified, analysed and studied [35].

The various potential feedstocks for biodiesel production that are currently available in Sub Saharan Africa are presented in Table 2.4. A wide range of oil producing crops which have the potential as biodiesel feedstock are grown globally (Table 2.3) [40]. However, only a limited number of these feedstocks are currently grown and/or have the potential to be grown in Sub Saharan Africa. Sunflower and soybean are already being widely cultivated in the region and their production can easily be expanded wherever there is available water and irrigation. They are already widely grown both by commercial and peasant farmers as a food crop and also as an industrial crop. Their wide application for biodiesel production can create additional demand and stimulate production. Although, the yield of sunflower is better than soybean, the availability and cost of the seed oils are high and low respectively. For these reasons, these seed oils were the better choice as feedstock for the transesterification reactions.

The limited availability of recycled oil poses a serious constraint to large-scale production of biodiesel using these feedstocks. These are the primary feedstocks for biodiesel production in most small to medium scale biodiesel plants in Africa. The collection and recycling of used oils is a highly competitive business. For instance, yellow grease is a promising feedstock for the manufacture of soap, textiles, cleansing creams, inks, glues, solvents, clothing, paint thinner, rubber, lubricants and detergents, etc. Apart from the quantity limitation, the quality of the oil can have a knock on effect on the quality of the biodiesel produced [36].

As “third generation” biodiesel feedstock, the use of algae has the potential to drastically expand the resource base of biodiesel production in the future. The utilization of algae can contribute to solving problems of air pollution from CO_2 and the future crises of food shortage. Algae can be grown using waste materials such as sewage and without wasting land currently used for food production. However, the production of algae on a commercial scale to harvest oil for biodiesel has not been well exploited but has the potential as promising resource. The potential of microalgae as an alternative and sustainable energy source has attracted significant research and business interest in the past few years. Currently, many companies are pursuing algae bioreactors for various purposes, including scaling up biodiesel production to commercial levels. Specifically, the Biodiesel 2020 study by Nelson and Schrock[50] reported that algae may hold the key to meeting large-scale, sustained feedstock shortages in the US, Europe and Asia.

Generally, it is relevant to note that no single agricultural feedstock or recycled product can sufficiently supply feedstock to meet national biofuel (biodiesel) targets. Constraints on land suitability for any single feedstock and competitive demands from other markets (e.g., food, feed, wood products) preclude such a research or production focus. A wide spectrum of feedstock will lead to more geographic diversity, less resource pressure on any single location, and greater resistance to drought, pests, and other production shocks. Research on feedstock that increases yield and reduces pressure on cropland should be conducted for sustainable biodiesel development in Africa.

2.4.3: Biodiesel feedstock characteristics

The sources of triglycerides are diverse, ranging from single fatty acids to waste oils with edible soybean oil being the oil most frequently used for research [38].On the other hand, vegetables oils such as rapeseed, sunflower, palm kernel and canola oils follow in terms of frequency of application [39]. Animal fats and waste cooking oils have also been investigated from the motivation to use cheap oil sources or the desire to meet the regional oil availability. But the irregularity in their chemical composition makes application difficult. In terms of chemical composition, each oil source has a specific composition of fatty acids as shown in Figure. 2.10.

The fatty acid profile of a particular oil sample is the amount of the different fatty acids present in the sample [40]. The fatty acid profile can be used to predict both physical and performance properties of the biodiesel product. For instance, biodiesel produced from tallow, a highly saturated fat, tend to have a higher freezing point that can inhibit cold flow properties [40]. In chemistry, a fatty acid is a carboxylic acid with a long unbranched aliphatic chain, which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28 [40].

Fatty acids are usually derived from triglycerides or phospholipids [44]. Free fatty acids (FFAs) are those acids that are not attached to other molecules. These fatty acids are used for the production of soap from the transesterification reaction. The FFA content of an oil sample can also be used as a guide to determine the extent of deterioration of its quality [44]. A triglyceride molecule is made up of three fatty acid units attached to a three-carbon backbone. If all carbon atoms of the free acid contain single bonds they are called saturated. For example, if a triglyceride molecule contains one double bond then it is monosaturated and it is polysaturated if it contains more than one double bond (Figure 2.12). The structure of a typical triacylglyceride molecule containing stearic acid, oleic acid and palmitic acid bound to a glycerol backbone is shown in Figure 2.11.

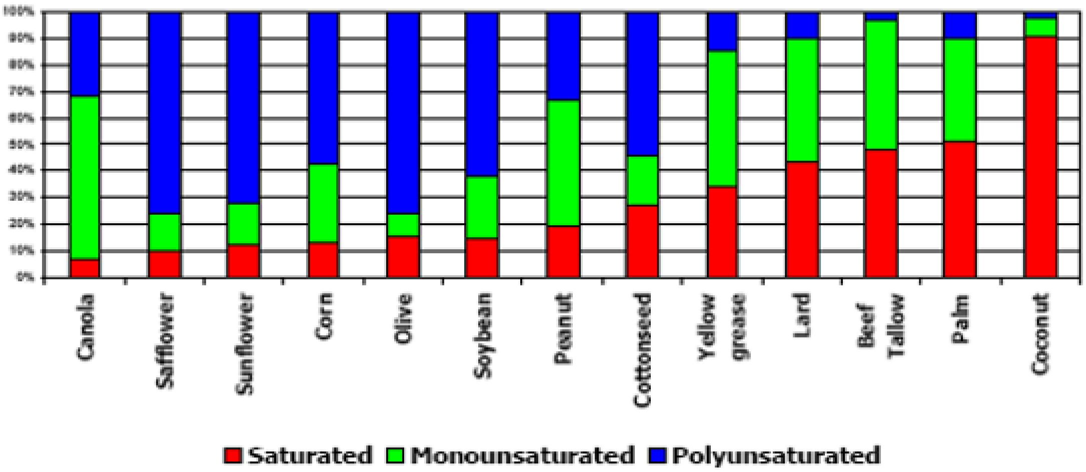


Figure 2.10: Fatty acid profile of different feedstock [61].

Figure 2.11: Composition of a triglyceride [61].

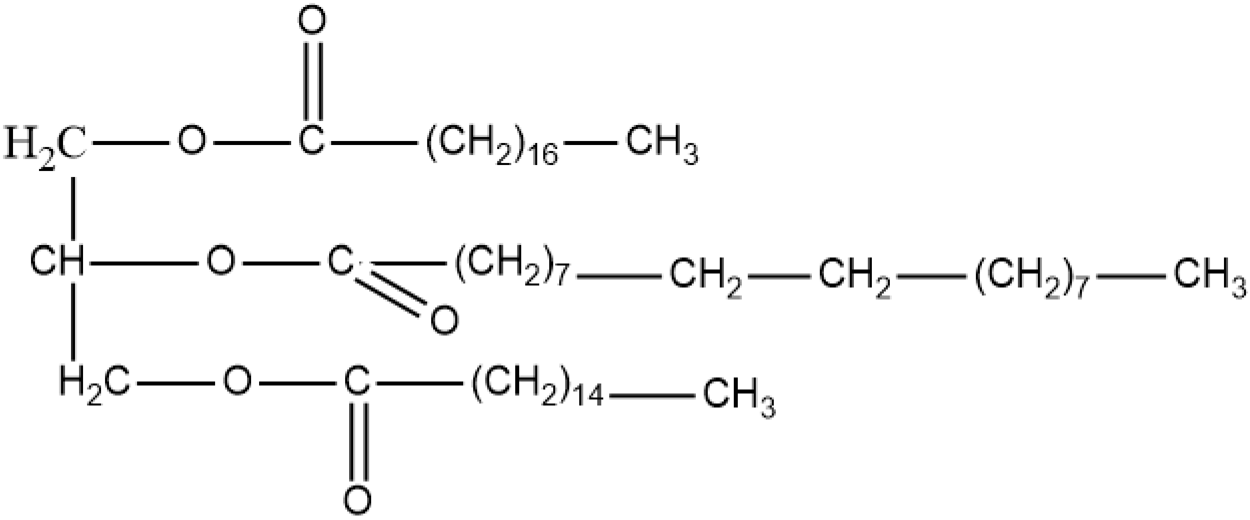


Figure 2.12: Structure of a typical triacylglyceride molecule with different fatty acids bound to the glycerol backbone.

The chemical characteristics of fatty acids are described by their carbon number and the degree of unsaturation. These characteristics affect the reactivity toward the transesterification as well as the properties of the biodiesel produced [41]. This is very important, since the FFA content affects the yield potential and hence has a major impact on the economic feasibility of the feedstock [41]. High FFA content in contact with the conventional base catalysed transesterification lowers the yield of biodiesel and produces by-products like soap stock and water as shown in Figure 2.13. The selection of the catalyst which is central to the biodiesel conversion process is also dependent on the free fatty acid (FFA) present in the oil [42]. For triglyceride stock having lower amount of FFAs, base catalysed reaction gives a better conversion in a relatively short time while for higher FFAs containing stock, acid catalysed esterification followed by transesterification is suitable [43] to avoid hydrolysis of the final ester product (Figure 2.14).

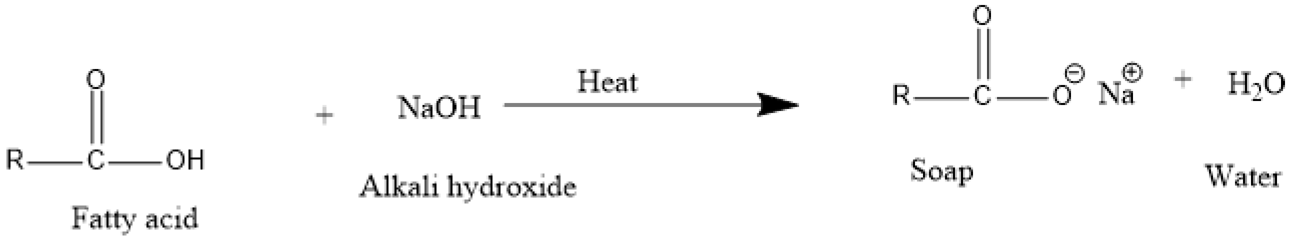


Figure 2.13: Saponification from free fatty acid with high FFA content feedstock

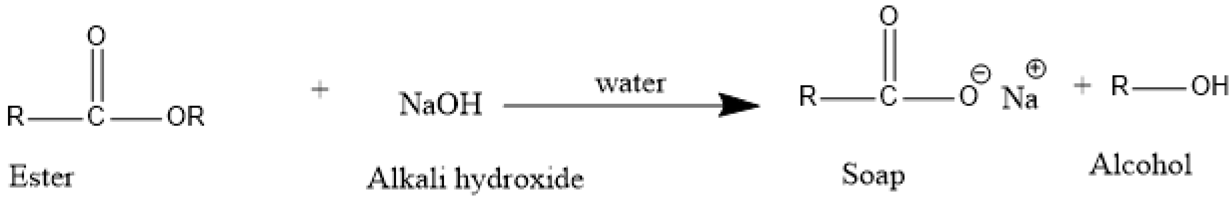


Figure 2.14: Saponification from ester by the hydrolysis of esters.

2.4.4: Biodiesel feedstock costs

A major hurdle in the commercialization of biodiesel production from vegetable oil is its high manufacturing cost, as a result of on-availability and higher cost of virgin vegetable oil. The costs of vegetable oil play a crucial role in the economics of the biodiesel. The most significant variables that affect the cost of biodiesel are cost of the raw materials, plant size and value of the glycerol by-product [46, 47]. Biodiesel feedstocks are classified by the amount of free fatty acids they contain. For example, refined vegetable oils <0.05 %, crude vegetable oils 0.5-5 %, used cooking oils 2-7 % and animal fat 10-30 % [40].

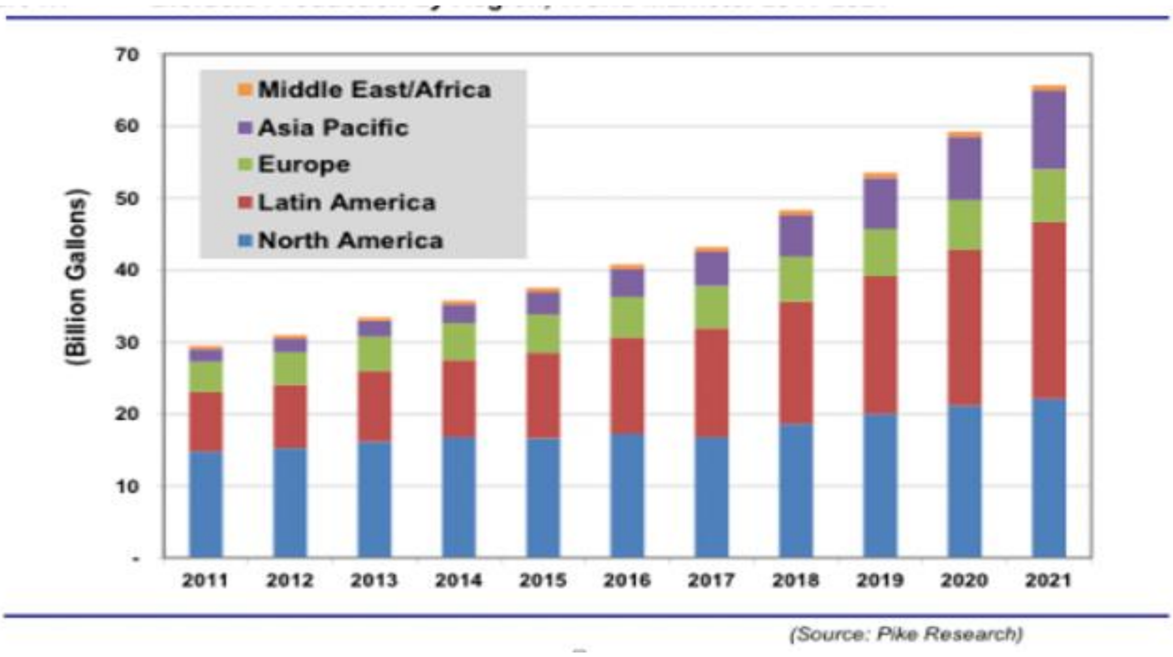
The production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically [45, 48]. The data on the requirements of diesel fuel and availability of waste cooking oil in any country indicate that the biodiesel obtained from waste cooking oil may not replace diesel fuel completely. However, a substantial amount of diesel fuel can be prepared from waste cooking oil, which would in effect reduce the dependency on petroleum-based fuel. Many developed countries have laid down policies that penalize the disposal of waste oil through water drainage systems [49].

2.4.5 Types of Alcohols.

The alcohols employed in the transesterification process include methanol, ethanol, propanol, butanol and amyl alcohol. However; for most transesterification reactions, methanol and ethanol are the more preferred ones. Methanol and ethanol are produced from natural gas and ethylene respectively. Ethanol can also be produced from renewable resources like wheat sugarcane, sugar beet and sweet sorghum etc. Ethanol is more hygroscopic than methanol, therefore is more susceptible to soap formation. Some research works so far report excessive emulsion formation during the ethanolysis of vegetable oils [30-32]. An investigation was conducted on methanolysis of menhaden oil using straight chain and branched alcohols in single-phase system at 600°C. The results suggested that the straight chain alcohols were more reactive than the corresponding branched ones [32]. It was also observed that the degree of oil conversion to fatty esters decreased with increase in the carbon chain length [33].

2.4.6: World biodiesel production

Biodiesel currently accounts for only 10 % of the world bio-fuels production with ethanol making up the rest [12]. Global biodiesel production has expanded nearly fourfold in the last decade [38] with top producers being Germany, France, USA, Italy and Austria. Biodiesel for transport energy is a potential candidate from a technical perspective, moreover high performance biodiesel with outstanding cetane numbers and flow characteristics can generate new flexibility when blended with fossil diesel [40]. According to Nelson and Schrock [50], many years of heavy investments in biodiesel production has resulted in a worldwide market. Recently published estimates projected that annual demand for biodiesel will grow within the next few years from six to nine million tonnes in the USA and from five to fourteen million tonnes in the EU (Figure 2.15) [38].



(Source: Pike Research)

Figure 2. 15: The chart show current and projected biofuel production by regions, World Market: 2011-2021.

2.4.7: Biodiesel production

Biodiesel can be prepared from a variety of feedstocks including vegetable oils such as oilseeds (rapeseed, soya bean, canola oil, and sunflower oil), animal fats, waste oils and greases [45]. Most recently algae oil is identified as more promising candidate for the production of biodiesel which have much higher yields and therefore poses less of a threat to food and water security [51]. There are five primary ways for making biodiesel: (i) direct use and blending of vegetable oil [53],(ii) use of micro emulsions with short chain alcohols [52], (iii) thermal cracking (pyrolysis) of vegetable oils [53] (iv) transesterification of triglycerides catalysed by bases or esterification of fatty acids with alcohols using acid catalysts(H_2SO_4) or solid acid catalysts [54, 55, 56] and use of enzymes [57, 59, 60] (v) catalyst free processes.

2.4.8: Direct use and blending of biodiesel

Vegetable oils may be used as neat fuels or blended with petro diesel for use in diesel engines. However several hurdles need to be overcome, as these oils typically show viscosities ten to twenty times higher than the viscosity of petro diesel. This quality leads to poor fuel atomisation and results in incomplete combustion [61]. The viscosity problem also has tendency for thermal and oxidative polymerisation leading to the formation of deposits on the injector nozzles. This can only be solved by the adapting the fuel to the engine and vice versa [61].

Moreover blending diesel fuel with vegetable oil would require vegetable oil from 0 % to 34 % if proper atomization is to be achieved [61]. Biodiesel can be used in its pure form (neat biodiesel or B100). This is the approach that provides the most reduction in exhaust particulates, unburned hydrocarbons, and carbon monoxide. It also offers the best way of using biodiesel because of its non- toxicity and bio-degradability. Although neat biodiesel would not be expected to cause any operational problems, its solvent properties are at the highest intensity and may pose problems in loosening of varnish deposits in fuel tanks and degradation of fuel lines because some elastomers (such as BUNA rubbers) are not compatible with biodiesel. It may cause paint removal near fuel fill ports [61].

2.4.9: Micro-emulsion technique

A wide range of derivatives such as micro-emulsions or blends of various vegetable oils with conventional fuel have been proposed as alternative fuels for diesel engines [61]. As the formation of micro emulsion is one of the four potential solutions for solving the problem of vegetable oil viscosity and various researchers have studied micro emulsification of vegetable oils with different alcohols and arrived at the conclusion that micro-emulsions of vegetable oils and alcohols cannot be recommended for long term use in diesel engines for similar reasons as applied to neat vegetable oils [61]. The fuels are prone to incomplete combustion, the formation of carbon deposits and an increase in the viscosity of the lubricating oil [61].

2.4.10: Pyrolysis/Hydrocracking

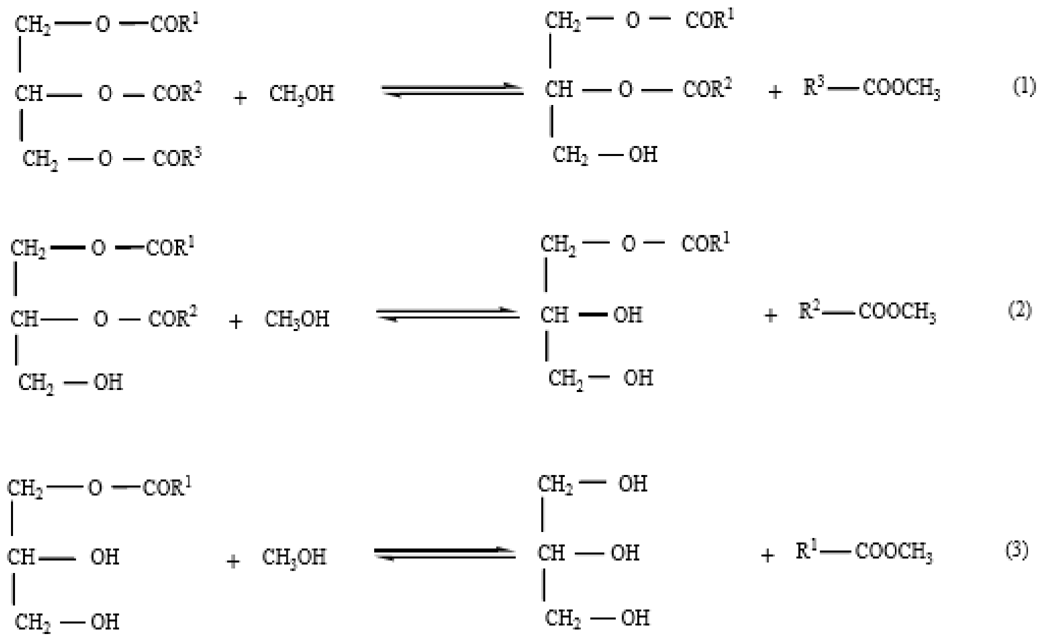
Pyrolysis of fats has a long history of more than a century and has been used particularly in the regions where there was no fossil fuel [40]. Pyrolysis means thermal decomposition reactions, normally in the absence of oxygen. This treatment give rise to a mixture of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids; which is similar in character to the hydrocarbon –based diesel fuel. But the cetane number of the oils is increased and the concentrations of sulphur, water and sediment for the resulting products are acceptable. However according to modern standards, the viscosity of the fuels is considered too high, ash and carbon residues far exceed the values for fossil diesel and the cold flow properties of the resulting fuel is poor [62]. It has also been argued that the removal of oxygen during this process eliminates one of the main ecological benefits of oxygenated fuels [62].

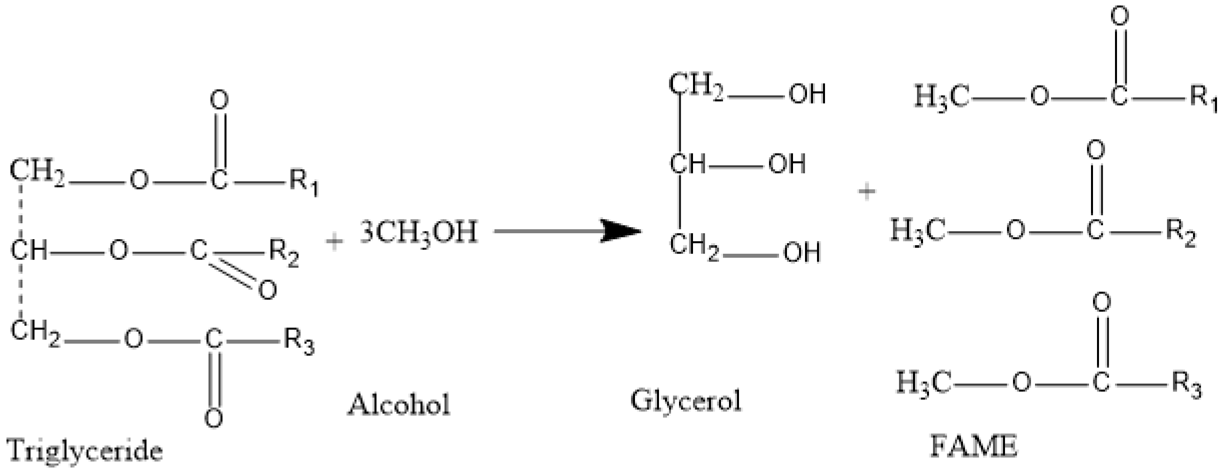
2.5: Transesterification of triglycerides

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. The applicability of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds.

In industrial practice, the reaction is carried out at 60-70 °C and is catalysed by a strong base. The hydroxides or methoxides of sodium or potassium are mostly used as homogeneous catalyst due to its low cost [60 - 63]. One molecule of glycerol is obtained as a by-product for every three FAME molecules produced. The transesterification is equilibrium-driven and indeed reversible. However, this requires the use of molar excess of methanol to drive the reaction to completion [61 - 63]. The oil- and FAME-phase (non-polar) and the alcohol phase (polar) are not directly miscible. This means from onset the reaction is slow and dependent on vigorous mixing of the two phases (e.g. by stirring) to get a large contact area between the two phases. During reaction, di- and mono-glycerides are formed, and these compounds act as emulsifiers for the reaction mixture. Once the transesterification is nearing completion, the two phases start to separate again by settling [13]. Industrially the transesterification is usually performed in a stirred batch-reactor, and as sufficient settling often requires longer time than the transesterification reaction itself, the settling is often performed in a separate settling-tank [63].

There are three stepwise reactions that occur with the formation of the diglycerides (DG) and monoglycerides (MG) intermediates from the parent triglyceride under the transesterification reactions resulting in production of 3 mol of FAME and 1 mol of glycerol (GL) from 1 mol of TG as shown in the steps 1-4 of Figure 2.16 [63].





(4)

Figure 2.16: Reaction scheme showing the transesterification of triglycerides with methanol [43].

2.6: Esterification Reaction

The homogeneous, base-catalysed transesterification is most efficient, but have a number of drawbacks. First and foremost oils and fats may contain free fatty acids (FFA). Most fresh vegetable oils usually do not contain problematic amounts of free fatty acids, but especially waste fats are challenging; 2 to 7 wt % FFA for used cooking oils, 5 to 30 wt % for waste animal fats and abattoir waste, and some trap greases can contain over 50 wt % FFA [64]. The FFAs will react with the basic catalyst and form soap, and when the feedstock contains more than about 0.5-1 wt % the reaction becomes unacceptably slow due to consumption of base otherwise intended for transesterification, and the formed soap emulsifies the phases and hinders the settling and separation after reaction [64]. For this reason, the FFAs must first be reacted with methanol to form FAME. Esterifications are acid-catalysed, and in the industry a few wt % sulphuric acid, H_2SO_4 is often used for this purpose. An acidic esterification step is therefore performed prior to the basic transesterification. Sulphuric acid is the cheapest acid and has the advantage of being both strong and very hygroscopic. The mixture of methanol and fat is esterified for a few hours at 60-70 °C, around the boiling point of methanol, with stirring so as to bring the content of free fatty acids below 0.5 wt% (Figure 2.17) prior to the transesterification [64]. Thus, two consecutive reaction steps are needed. The esterification by homogeneous acid leads to a number of other challenges: First of all the acid solution from esterification must be neutralized and made alkaline with the addition of the base for the transesterification, and even by the end of transesterification acid must again be added to neutralize the alkaline alcohol-phase. This naturally yields large amounts of salts as by-products (usually K_2SO_4 and $KHSO_4$). This has no immediate use. Furthermore it is necessary to use new homogeneous catalysts for each FAME batch. Another issue with this is the purification of glycerol and excess methanol afterwards, which is often contaminated with water and salt [65]. An immediate decantation removing most of the salt can however be made after settling.

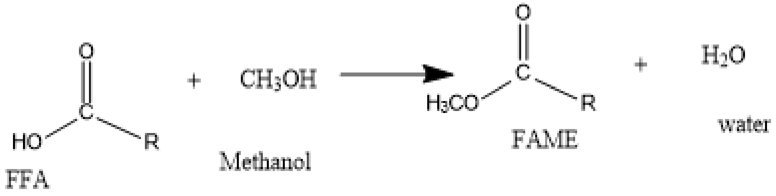


Figure 2.17: Esterification of a Free Fatty Acid (FFA) with methanol to yield FAME and water.

In principle, the transesterification can be catalysed by both bases and acids leaving room for a one-step acid-catalysed process, but the base-catalysed reaction is 3-4 orders of magnitude faster than the acid-catalysed reaction [66]. Heating the batch to at least 150-200 ℃ must be performed for completion of the transesterification with acid catalyst within an acceptable time-scale. This requires working with pressurized equipment (due to the vapour pressure of methanol, which has a normal boiling-point of 64.6 ℃ (STP)), and is therefore usually disregarded and considered uneconomical at least with sulphuric acid.

It is of great interest to substitute the homogeneous catalysts with heterogeneous catalysts. This would avoid the formation of inapplicable salt by-products, lower the expenses for buying catalysts for each batch of FAME, and prevent the equipment corrosion by dissolved H_2SO_4 in the methanol. Water formed by the neutralization of H_2SO_4 with KOH will contribute to soap formation of FFAs formed via basic hydrolysis of glycerides. Also, a solid catalyst would allow easier operation in a liquid-liquid-solid plug-flow-reactor with static mixers, which may be much more desirable with regards to labour demand, process control, -layout and -supervision, and optimization of product quality [66].

2.7: Base catalysed reaction process

Biodiesel is produced mostly by the transesterification of triglycerides of refined/edible type oils using methanol and alkaline catalyst but it has several disadvantages [57]. The alkaline catalyst corrodes equipment and also reacts with free fatty acids (FFA) to form unwanted soap by products thus requiring extensive and expensive separation. However, the base catalysis in the homogeneous state is fast and need less of methanol [64].

The molar ratio of alcohol: vegetable oil is one of the main factors that drive the transesterification [64], and excess alcohol is required to shift the equilibrium towards completion to favour fatty esters production. Salt waste streams are as a result of the use of homogenous catalysts and require neutralization. Alcohol provides the alkyl group that substitutes the fatty fraction of triglyceride. Methanol is most frequently used, mainly because the reaction rate is higher and the price is cheaper than any other commercial alcohol. The fuel qualities of alkyl esters have received varying evaluations in terms of alcohol used. A higher or branched alcohol can produce biodiesel with better fuel characteristics [67]. But it has been reported in contrast that a methyl ester and ethyl ester are similar in heat content but that the former is slightly less viscous than the later [61]. It was reported that methyl ester was better than ethyl ester from the standpoint of engine performance [68]. Furthermore when methyl ester was used as fuel in engines gave higher power torque [68]. It has been established that high alkyl esters caused more injector clogging than methyl ester and that their industrial uses were hindered by some technological problems [69]. With regards to this study, methanol was the alcohol of choice based on these reports.

An alternative multistep process allows the use of feedstock having high FFA concentrations by first carrying out the acid-catalysed pre-esterification of the FFAs prior to the base-catalysed TG transesterification. For commercial biodiesel production, alkali-catalysed process for the transesterification of the oil (with a low content of free fatty acids) with methanol is and most economical, and typically referred to as the ‘methyl ester process’. This is illustrated in Figure 2.18. The reaction mechanism of base catalysed transesterification is detailed under homogenous catalysts.

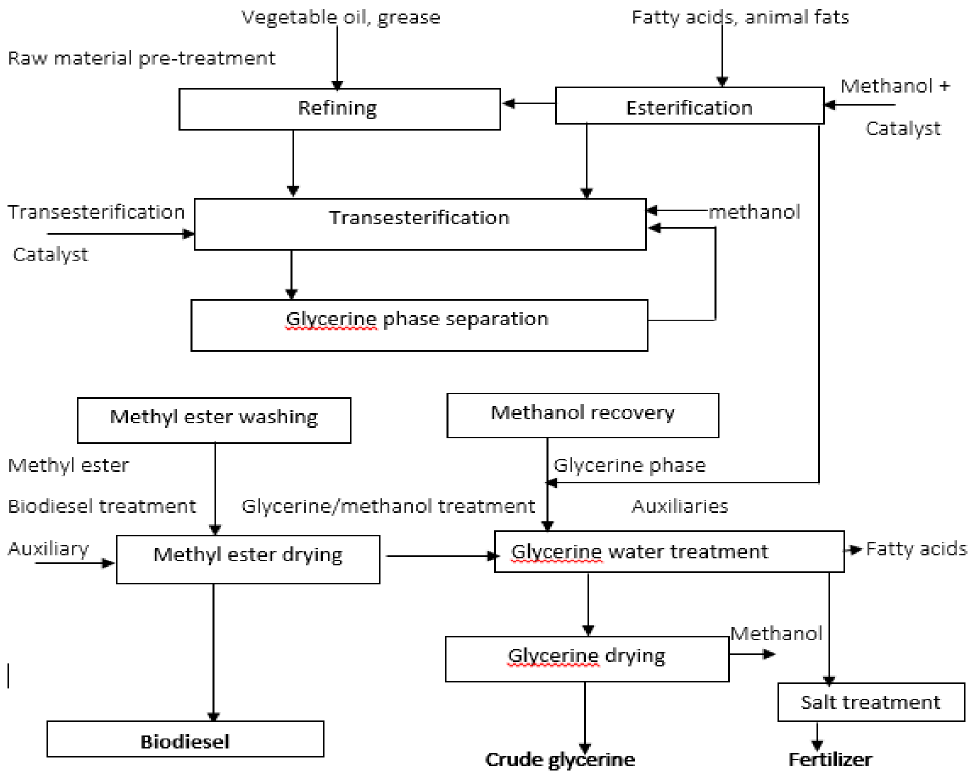


Figure 2.18: General scheme of biofuel production (IEE, 2006).

A multistep acid-catalysed FFA pre-esterification followed by base catalysed transesterification is commonly used in an integrated process [60]. Despite the added cost of production, integrated process is increasingly being applied to produce biodiesel from low-cost and high-FFA feedstock with good fuel qualities [65]. A basic technology of the flow diagram of the process is shown in Figure 2.19. Due to the limitations of the base catalysed transesterification reaction, the use of solid acid catalysts is an attractive solution to solve the problems associated with this conventional process as the catalysts could be separated more easily from reaction products and the reaction conditions could be less drastic. Additionally, the glycerol co-product arising from biodiesel production appears to be of higher quality when compared to the conventional homogeneous catalysis method [55].

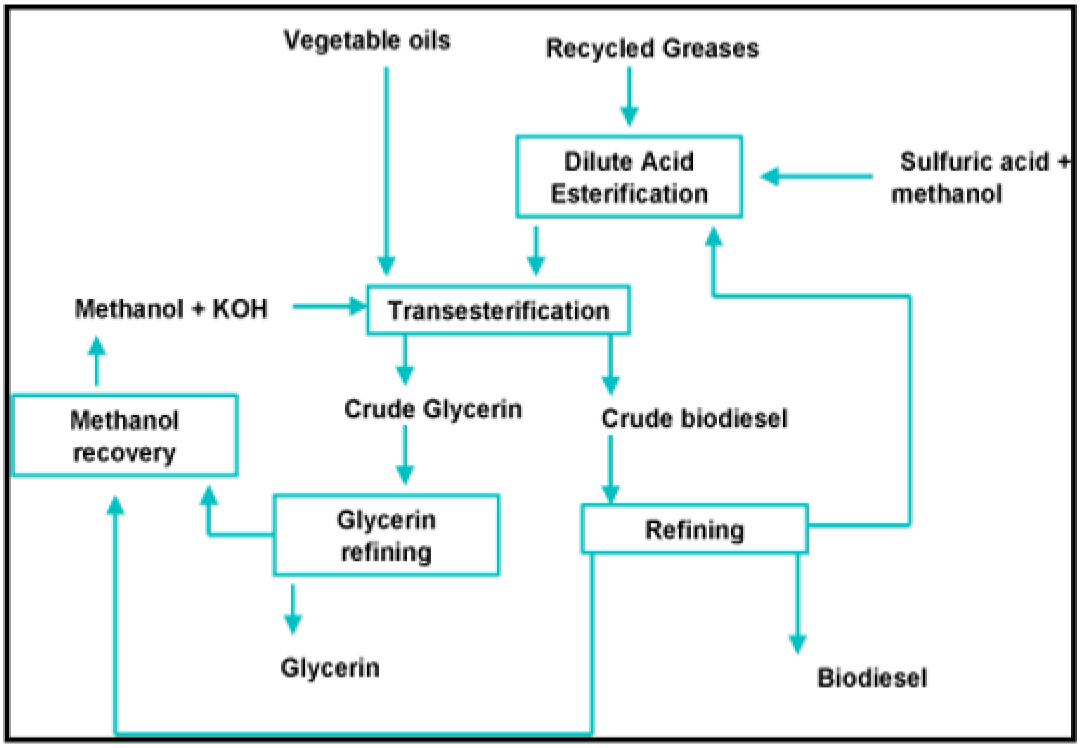


Figure 2.19: Basic technology involved in an integrated biodiesel process (USDOE, 2011).

2.8: Acid catalysed process

Acid catalysed transesterifications are usually far slower than alkali catalysed reactions and require higher temperatures and pressures as well as higher amounts of alcohol. Although they have the advantage of esterifying free fatty acids contained in the fats and oils [67]. This route is therefore especially suited for the transesterification of highly acidic fatty materials such as waste edible oil. Moreover it enables the production of long and branched chain esters, which poses considerable difficulty in alkaline catalysis [52] but the presence of water in the reaction mixture proves absolutely detrimental for acid catalysis [66]. The transesterification process is usually catalysed by Bronsted acids, preferably by sulfonic [67] and sulphuric acids [52, 68]. These catalysts give very high yields in alkyl esters, but the reactions are slow, typically requiring temperatures above 100 °C and more than 3hrs to reach complete conversion [54]. Figure 2.20 shows the mechanism of the acid catalysed transesterification of vegetable oil.

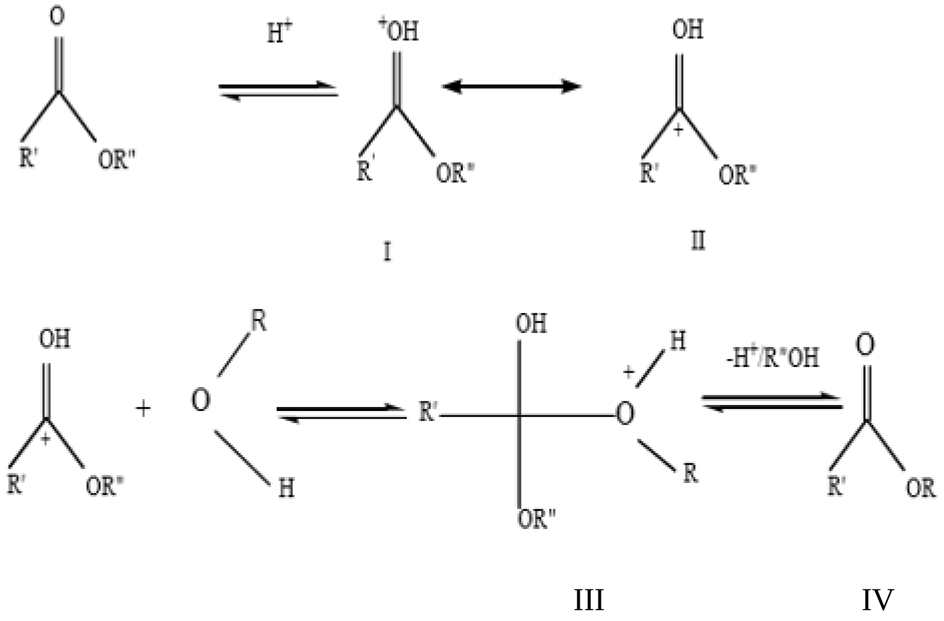


Figure 2.20: Mechanism of the acid catalysed transesterification of vegetable oil.

It should be noted that acid catalysed transesterification reactions are seldomly used as the sole reactions in industrial biodiesel production [69].They often serve as preliminary steps for the de-acidification of fatty materials followed by conventional alkaline operation [70]. The main drawback of the pre-esterification method is the difficulty of removing the homogeneous acid catalyst from the oil after pre-esterification [70, 71]. So in order to improve the process, the need for a heterogeneous acid catalyst is inevitable [71]. In order to circumvent these problems there is a need to introduce solid heterogeneous catalyst in biodiesel production [70].

2.9: Enzyme–catalysed reaction processes

Enzyme-catalysed reactions have a lot of advantages over the previously mentioned methods. The merits include; no generation of by-products, easy product recovery, mild reaction conditions, and catalyst recycling, insensitivity to FFA and water content in waste cooking oil [70, 71]. Enzyme-based transesterification reaction is performed at moderate temperatures with high yields [70]. But this method cannot be used in industry today due to high enzyme costs and the problems of deactivation caused by feed impurities [71]. The enzyme can be immobilized on a support to obtain a heterogeneous catalyst; however the use will only be applicable if the enzyme costs are reduced as in the case of enzymes used in detergents, dairy products, textile, and leather processing [71]. The enzymatic alcoholysis of pure triglycerides with or without solvent has been well-documented in literature [72, 73]. Efficient and low energy intensive procedures of biodiesel production from waste oils and animal fats combining lipases with alkali catalysts have also been reported [74].

2.10: Catalyst free processes

One of the methods of transesterification without any catalyst is the use of alcohols in the supercritical state (heated above the critical temperature) [71, 75].

Mittelbach [76] demonstrated that preheating to a temperature of 350°C and treatment for 40 minutes in supercritical methanol was sufficient to convert the rapeseed oil to methyl esters. Also the properties of the methyl esters synthesized by this method were similar to those prepared by known methods with a basic catalyst [75]. The yield of methyl ester obtained by the supercritical method was reported to be higher [75].

The disadvantages that result from the use of a catalyst and its removal from the products are eliminated if a non-catalytic transesterification reaction of vegetable oils with alcohol is conducted. Although the use of supercritical alcohol for the transesterification of pure vegetable oil is well reported in literature, the application of this technique for the transesterification of waste cooking oil is not well-documented [74]. However the supercritical methanol method is reported to be more water-tolerant than the conventional method using an alkaline catalyst and proves those crude vegetable oils as well as their wastes could be readily used for biodiesel production by this same method [68, 74].

Despite all these advantages, the supercritical methanol method has some serious drawbacks which include the requirement of high temperature, high pressure and a large amount of methanol (ie 1:42 molar ratio of oil to alcohol) [68, 75]. Therefore to apply this method on an industrial scale, further investigations of the production process, such as continuous operation and scaling up, as well as economic evaluations need to be carried out. However Van Kasteren and Nisworo [68] in their publication refuted previous claims and reported that the supercritical transesterification process of biodiesel production can comparatively compete with the alkali and acid catalysed processes.

2.11: Kinetic and mass transfer studies

There are different kinetic studies on the transesterification of esters with alcohol reported in literature [34]. Kinetics is a relevant process that describes the rate of chemical reactions with rate equations typically expressed in terms of concentrations of the reactants. These rate equations can be derived by the application of the law of mass action. This law relates the rate of reaction to the concentrations of reactants. The application of this law is restricted to elementary reactions. Elementary reactions are those reactions which possess the mechanism at the molecular level and occur in one step. Simple test are carried out by chemists to determine whether the reaction is elementary or not. These tests include number of collisions, number of bonds broken, number of bonds formed, integer reaction coefficients, and simplicity of reverse reaction [77]. The study of kinetics will provide parameters that can be used to predict extend of the reaction at any time under particular conditions. In literature, the kinetic studies on the methanolysis of various feed-stocks have been carried out as methanol is used more commonly in the process [34, 78]. Stamenkovic and co-workers [34] conduct kinetic study on ethanolysis of sunflower oil. According to Knothe [79], the kinetics of the reaction depends on the degree of mixing between alcohol and triglyceride (TG) phases. Reaction temperature and the alcohol oil molar ratios are other criteria which are important in kinetic studies [79]. The triglyceride (TG) and alcohol are two immiscible phases and hence form two separate layers upon introduction into the reactor [79]. All the kinetic studies carried out so far considered mixing as one of the criteria, however the effect of mixing intensity are not fully addressed.

2.11.1: Factors affecting the kinetics and mass transfer

2.1 1.1.1: Mixing Intensity

The degree of mixing between the alcohol and triglyceride (TG) phases is of essence. In most cases mechanical mixing is applied to increase the contact between the reactants and hence increases the rate of mass transfer. The influence of mixing on the reaction rate was observed in the 1980s. For instance the change in mixing intensity can alter the kinetics of the transesterification reaction [79]. However understanding the effect of mixing on the kinetics can be utilised in scaling up of the design [80]. Mixing intensity can be determined by Reynold‟ s number (N_{Re}). In fluid dynamics, Reynold number, N_{Re} (dimensionless number) can be defined as the ratio of inertial forces to viscous forces as shown in Eqn.(1)

$$N_{Re} = \frac{nDa^2}{\mu}\rho \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (1)$$

Where n is the rotational speed of the impeller, Da is the impeller diameter, and ρ and μ are the fluid density and viscosity respectively. Noureddini and his group [80] investigated the effect of Reynolds number on the transesterification reactions. In their study, the rotational speed of 150, 300 and 600 rpm were used. They observed that the increase in Reynolds number decreases the viscosity of the biodiesel produced. It was also noticed that mass transfer region was short for higher mixing intensities. Mechanical mixing is ideal for the reaction in a batch reactor [80]. Another group reported that agitation is an important parameter in the study of kinetics of methanolysis of beef tallow [81]. The study correlated drop size with the speed of mixing with mechanical agitation in the reactor. It was stated that smaller size of droplet increases the rate of reaction with stable emulsion [81]. Furthermore it was proven later that agitation plays an important role in the transesterification of vegetable oil and has a strong influence on the kinetics of the reaction [80]. Kinetic studies observed the mass transfer limitations in the initial stages of the reaction [78]. This initial mass transfer regime was eliminated by increasing the mixing speed of the reaction. Vicente and his co-workers [82] conducted a study for the kinetics of sunflower oil at high agitation to eliminate the mass transfer region but observed that the phase became homogenous due to the 'self enhancement' of the interfacial area.The droplet breakage was vigorous as the mixing was done at high speed of 600 rpm [82]. The study also noted the effect of temperature and catalyst concentration on the reaction. The increase in catalyst concentration or increase in temperature increases the rate of reaction [82]. This was explained by the increase in the rate constant values.

Stamenkovic and his co-workers [34] thoroughly investigated the intensity of the agitation speed using sunflower oil as the feedstock. Mean Drop diameter and drop size distribution was also investigated at different mixing speeds. The reaction was performed at low temperature of 20℃ in order to increase the mass transfer regime and decrease the reaction rate in the initial stages. Better understanding of this regime can help develop an efficient model for the kinetics. The agitation speeds of 60 and 200 rpm were observed to have

Reynolds numbers in the range of 56 and 151. This for instance indicates that the agitated emulsions were in transition state, the flow was fully turbulent near the impeller and the behaviour became laminar away from the blade [34]. However; Stamenkovic and his co-workers [34] contradicted the results obtained by Noureddini and Zhu [80]. They demonstrated the existence of two phases till the completion of the reaction unlike Noureddini and Zhu [80]. It was also observed that the other products of monoglycerides, diglycerides and soaps act as emulsifying agents. This will enhance the stable emulsion of small drops leading to the progress of the reaction [34, 80]. Mixing effect was studied for beef tallow, the relationship between the droplet size and the speed was developed. It was shown that the droplet diameter was inversely proportional to the square of the rotation speed. But in the latter case, the droplet diameter was inversely proportional to $n^{1:2}$ [81]. Mass transfer region was not significant with increasing the mixing speeds to 600 rpm at 65 ℃ [82]. Slinn and Kendall [83] confirmed their results with the results of the other developed models. The reaction was predicted to be mass transfer limited and the droplet size affected the end point of the reaction. Increasing the mixing intensity increases the conversion of methyl esters, although reaction time was observed as controlling factor in terms of conversion [83]. Recently mixing model is developed which can demonstrate the relation between mixing speeds and its effect on the transesterification reaction. The models developed in past are specific and can be used only on the particular systems. This model has been validated by the literature data and is claimed to be useful in any transesterification systems [84].

2.11.1.2: Effect of Reaction Temperature

Temperature has always been considered an important factor for the conversion of triglycerides into methyl/ethyl esters. It plays a vital role in the kinetics of the transesterfication reaction. Many studies were carried out at different temperatures (from 25℃ -200℃) to analyse the optimum temperature for the reaction to take place. Noureddiniand Zhu [80]; conducted an investigation on the temperature dependency on the overall reaction rate. The study was carried out for the temperatures of 30℃, 40℃, 50℃ and 60℃ and observed that the increase in temperature decreases the mass transfer regime in the initial period of the reaction. The study on the activation energies concluded that the forward reaction rate increases with higher temperatures [80]. Similar results were confirmed by Darnoko and his co-workers [78] for the transesterification of palm oil. The rate of conversion increased with increasing the temperature [78]. Similar trend was also observed by Vicente and his team [82] when they conducted an experiments using temperature range 25°C to 65°C. Although, it was reported that mixing intensity is more important than temperature for the transesterification of sunflower oil since the conversion results were similar for 25°C and 65°C for the mixing intensity at 600 rpm [82]. Klofular and his team [] investigated on the effect of temperature on the duration of mass transfer controlled regime and the TG mass transfer coefficient [85]. The overall results stated that the rate of forward reaction dominated the rate of reverse reaction. Temperature was significantly reported as an important parameter for the reaction kinetics of waste sunflower oil and natural rapeseed oil [85].

Investigations have also been conducted to ascertain the effect of low temperature on the kinetics for the methanolysis of sunflower oil. The study was conducted for temperatures such as 10°C, 20°C and 30°C and it was observed that the initial drop in size of the dispersed phase reduced up to 10 times as the reaction proceeded. As the reaction temperature increase, the droplet size decreases drastically. The intermediates formed during the reaction were reported as emulsifying agents. However the total interfacial area increased with formation of stable emulsions, giving rise to an enhance TG mass transfer rate [34]. The kinetic behaviour for different systems with different reaction temperature varies, thus it is appropriate to consider the kinetic studies for each case separately. Therefore it can be concluded that, reaction temperature plays a key role in the reaction kinetics. But mixing intensity is considered more important criterion than the temperature of the reaction.

2.11.1.3: Molar Ratios

In general a molar ratio of 6:1 for alcohol to vegetable oil is preferred. According to the literature, it was proven to be an optimum molar ratio for the conversion [68]. To drive the reaction towards the right, excess of alcohol is used. Moreover increasing the molar ratios to 12:1 has given a reasonable yield by increasing the conversion. In the study of transesterification of cynara oil, a range between 9:1 and 12:1 gave better results [86]. For higher molar ratio of 15:1, the separation of glycerine in the reaction becomes complicated as the solubility increases due to the higher alcohol concentration. Freedman reported on the transesterification of soy oil using butanol and methanol with varying molar ratios of alcohol to oil of 30:1 and 6:1. At higher molar ratios of 30:1, the order of the reaction becomes pseudo first order using both butanol and methanol. While at the molar ratios of 6:1, the order obtained was second and fourth order using butanol and methanol respectively [77]. As homogenous base catalyst, the studies were carried out using NaOH and KOH. Later the investigations were also conducted for the methoxides and ethoxides as catalyst in the transesterification. Normally the catalyst and catalyst concentration is the least important factors to develop a model for the kinetics of methanolysis/ethanolysis. The molar ratios selected for almost all the studies were 6:1 for alcohol: oil [77]. It was also reported that the system follows a second order reaction rate for the ratios of 6:1 [77, 86]. While for higher ratios of 10:1 and higher, pseudo first order reaction rate was observed [77, 86].

2.12: Ultrasonic application in biodiesel production

For the past two decades, sonochemistry (the chemical reaction during ultrasound homogenization) has developed as an interesting research area [87]. The ultrasonic field is known to produce chemical and physical effects that arise from the collapse of cavitation bubbles. Low frequency sonication can be employed to produce emulsions from immiscible liquids and this effect could be used for biodiesel preparation as the mixing intensity or agitation is a very important parameter that must be considered during the production of biodiesel because of the fact that oil and alcohol are immiscible [69, 71, 86, 87]. The application of ultra-sonication provides a promising alternative to the use of conventional transesterification [69, 71].

In previous studies, it has been demonstrated that the use of the ultrasound provides the mechanical energy for mixing and the required energy for initiating the transesterification reaction [87]. One major hurdle in the transesterification of oils using methanol is the fact that the alcohol is a poor solvent for fatty materials thus require homogenization of the reaction mixture. Since this reaction can only occur in the interfacial region between the liquids and also for the fact that fats and alcohols are completely immiscible, transesterification is a relatively slow [69, 86]. As a result, a vigorous mixing is required to increase the area of contact between the two immiscible phases, in order to produce stable emulsion. However, vigorous mixing of the components is one method of homogenization which has been found successful for both batch and continuous operations. The application of low frequency ultra-sonication to form emulsions of oils and alcohols has been reported extensively in literature [69, 71, 86, 87].

A research reports confirmed that low frequency ultrasound is an efficient, time saving and economically functional process which have a lot of advantages over the conventional process. Reaction time is reduced drastically; the static separation time is reduced remarkably, and the yields are generally higher [69, 71, 86, 88]. Ji [86] and Stavarache [69] both studied the effect of mechanical stirring, ultra-sonication, and hydrodynamic cavitation on methyl ester yields in the alkaline (KOH) transesterification of vegetable oil using methanol (alcohol/oil molar ratio of 6:1) at a temperature of 45 °C and reported that ultra-sonication gave the lowest reaction time and highest yield, while mechanical stirring gave the shortest reaction time and the lowest yield. Thanh [88] also studied the alkaline transesterification using KOH for a series of vegetable oils via mechanical stirring and ultrasonication processes and concluded that yields in both cases were identical. According to Kumari [74], it was shown that the combination of an ultrasound process and the use of a solid catalyst reduced the reaction time compared to the conventional batch processes with 98.53 % biodiesel yield. Production of biodiesel under the ultrasonic processing possess the following advantages, reduction in processing time, amount of alcohol, catalyst amount, separation time and reaction temperature as revealed in studies conducted in previous research work.

2.13: Application of Jet –mixing technology in biodiesel production

Majority of commercial biodiesel is made by transesterification of vegetable oils and animal fats with methanol or ethanol in stirred tank reactors in the presence of base or acids catalysts [89]. There is however some challenges related to this process as follows: (a) the reaction rate can be limited by mass transfer between the oils and alcohol because they are immiscible (b) transesterification itself is a reversible reaction and therefore there is an upper limit to conversion in the absence of product removal; (c) most commercial processes are run in a batch mode and thus do not gain some of the advantages of continuous operation. In order to overcome these problems, current conventional techniques involve long reaction times, high molar ratio of alcohol to oil and catalyst concentration [89]. High operating cost and energy consumption are required to purify biodiesel and recover excess amount of alcohol and catalysts during downstream processing. Significant amounts of toxic waste water may also be produced during downstream purification. Long residence times and downstream processing time incur low production efficiency [89]. Hence, some process intensification technologies have been developed and applied to improve mixing and mass/heat transfer between the two liquid phases in recent years [89]. These technologies either utilize novel reactors or coupled reaction/separation processes. Reaction rate is greatly enhanced and thus residence time may be reduced. Some of the technologies have been applied successfully in commercial production [89].

The use of impinging jets in various practical engineering applications to enhance heat transfer is as a result of the high local heat transfer coefficient [90, 91, 92, 93, 94]. For instance great number of studies have dealt with the heat transfer enhancement using impinging jets quenching of metals and glass, cooling of turbine-blades, cooling and drying of paper and other materials, and more recently cooling of electronic equipment[91, 92; 93, 94]. Jet rectors are reactors based on the impinging jet technology. This system have a very intense mixing under pressure with different nozzle sizes which were specially developed for steel cutting (with water) and further developed for the mining sector especially in the goldmine sector. Research conducted at the University of Stellenbosch identified the use of these jet reactors for biodiesel production. Nieuwoudt [94] however improved on this discovery and technique to develop a continuous process reactor mainly for the production of biodiesel.

2.13.1: Comparison of the different biodiesel processes

Table 2. 5: A comparison of the different technologies used to produce biodiesel.

Variable	**Alkali catalysis**	**Enzyme catalysis**	**Supercritical**	**Acid catalysis**
Temp. (℃)	55 - 80	60 - 70	30 - 40	239 - 385
High FFA content	Saponified methyl ester	Esters	Esters	Unwanted product
Presence of water	Interference with reaction	No influence with reaction	Interference with reaction	Inhibits reaction
FAME yield	Normal	Higher	Good	Normal

Glycerol recovery	Easy	Difficult	Difficult	Difficult
Cost of production	Cheap	Relatively expensive	Medium	Cheap
FAME purification	Repeated washing	None	Repeated washing	Repeated washing

2.14: Catalysts in transesterification reaction

Catalysts been employed in transesterification reactions are categorized into three groups namely: alkaline, acidic and enzymatic. Comparatively, alkaline (base) catalysts show better performance. Alkaline and acidic catalysts are divided into two groups: homogenous and heterogeneous [95]. Figure. 2.21 show the various classifications of both acid and basic catalyst;

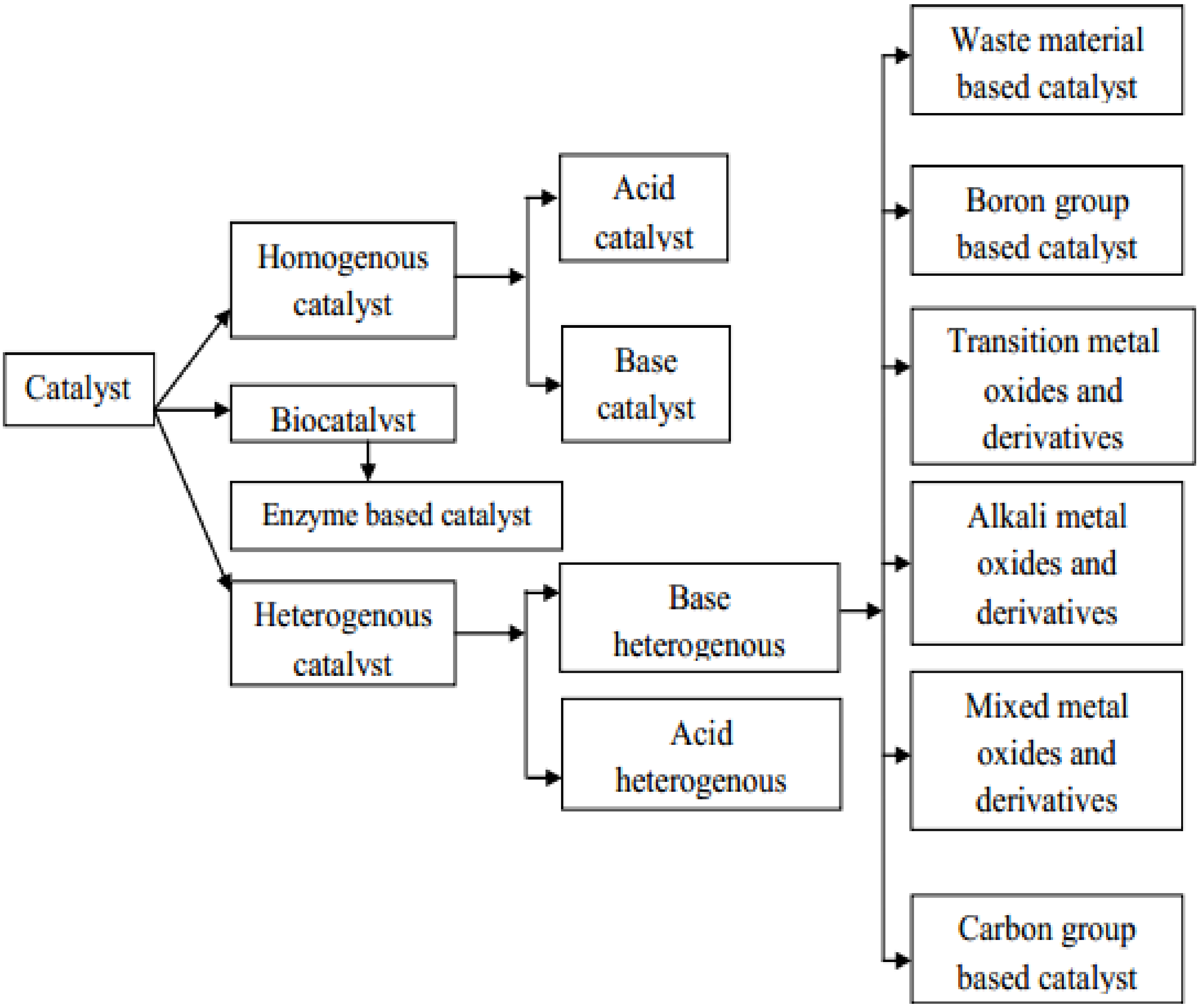


Figure 2.21:Examples of catalysts used in transesterification reaction.

2.14.1: Application of Homogeneous catalysts in biodiesel production

Homogeneous catalysts are the commonly applied technique in conventional biodiesel production via base catalysed transesterification. Normally, the alkoxide anion required for the transesterification reaction is obtained by directly dissolving the pure alkali metal in the alcohol by adding an alkali hydroxide [72, 96]. The initial step of the catalytic process involves the production of an alkoxide ion through proton abstraction from the alcohol by base catalyst (eqn.1) as shown in Figure. 2.22. The alkoxide ion attacks a carbonyl carbon of the triglyceride molecule and forms a tetrahedral intermediate ion (eqn. 2), which rearrange to form a diglyceride ion and alkyl ester molecule (eqn. 3). Finally, the diglyceride ion reacts with the protonated base catalyst, which generates a diglyceride molecule and turns the base catalyst into the initial form (eqn. 4). The resulting diglyceride is ready again to react with another alcohol molecule, thereby starting the next catalytic cycle.

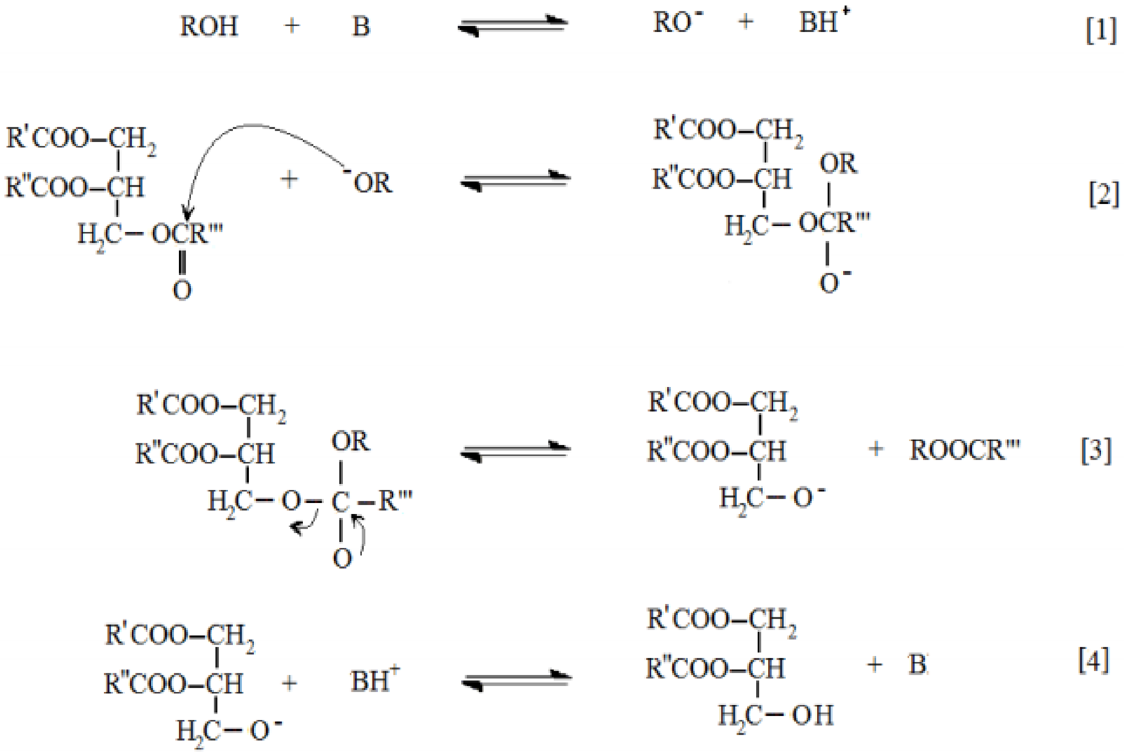


Figure 2.22: Mechanism of base catalysed transesterification reaction of vegetable oil [97].

Even though alcoholates and alkali metals give rise to high conversion, their high costs and safety risks make them unattractive for commercial production of biodiesel. However it has been recognised that alkali hydroxides are more promising because they are cheaper and easier to handle [70]. If KOH or NaOH are dissolved in an alcohol, the resulting solution would contain hydroxide and alkoxide ions in equilibrium [98]. The concentration of the alkoxide ions depends on the catalyst concentration and the pKs value of the respective alcohol and the water content of the reaction mixture. The authors also shown that for a 0.1 molar solution of NaOH in 99 % ethanol, 96 % of the total base is present in the form of the ethoxide ion and they projected similar results for anhydrous methanol [98]. Moreover alkali catalysed hydrolysis and soap formation only plays a minor role in water free alcohols [98].

Application of KOH as catalyst as compared to NaOH also reduces the amount of methyl esters dissolved in the glycerol phase after transesterification reactions. This phenomenon decreases the tendency for soap formation and hence reduces ester losses. Studies conducted by Vicente et al (2004) [82] showed only 3 mol % of methyl ester dissolution in the glycerol phase after KOH catalyzed methanolysis of sunflower oil, as opposed to more than 6 mol % methyl esters in the lower phase for NaOH catalysed reactions.

A major advantage is that there is fast separation of the glycerol phase in this process when most of the catalyst from the reaction mixture is easily removed as the esters produced will hardly have contact with the hydroxide in the first instance. This favourable behaviour is particularly pronounced if KOH is employed as the catalyst instead of NaOH as it facilitates phase separation by increasing the density of the glycerol layer due to a higher molecular weight [99].

Another advantage is that phosphoric acid can be added to the alkaline glycerol phase obtained to derive potassium dihydrogen phosphate which can be used as a fertilizer. The use of the fertilizer adds extra value to the reaction products whereas the sodium salt obtained from the use of NaOH as catalyst is noted as a by-product [79]. Finally, another advantage of NaOH as a catalyst over KOH is that sodium hydroxide catalysed transesterifications reaction is faster and its cost is cheaper [79]. A major drawback of applying homogeneous alkaline catalysts is obtaining biodiesel which has to be centrifuged and washed with water to remove impurities. Table 2.5 gives an overview of homogeneous alkaline catalysts which are frequently used in alcoholysis reactions.

Table 2.6: Overview of homogeneous alkaline catalysts used for transesterification [79].

Catalyst	Examples	Reaction conditions	Feedstock	Alcohol	Ester yield
Alkali metals	Metalic sodium	Alcohol:oil = 2-4:1	Pre-esterified waste oils Linseed oil	Methanol 2-propanol 1-butanol	87% 96%
Alkali metal alcoholates and hydroxides	CH_3ONa, CH_3OK, KOH, NaOH, LiOH	Alcohol:oil = 3-5:1 (mol/mol) T= 30-100℃	Vegetable oils, recycled frying oil and animal fats	Methanol abs. ethanol	98%
Aqueous alkali metal hydroxide solutions	40 – 55% NaOH or KOH	Alcohol:oil =3-9:1 (mol/mol) ambient temp. and pressure	Oils and waste oils with 20% FFA	Methanol 90% ethanol	-
Strong organic bases	TBD TCG	Alcohol:oil=2-3:1 (mol/mol) T=70℃, $t = 1hr$ 5 mol% of catalyst	Rapeseed oil	methanol	>99% >97%

2.14.2: Heterogeneous catalysts in biodiesel production

As enumerated earlier, conventional homogeneous catalysis offers a series of advantages but a major drawback is the fact that homogeneous catalysts cannot be reused [70]. Moreover the catalyst residues have to be removed from the ester product, requiring a lot of washing steps and the amount of waste water produced is excessively massive. These factors are related to increased production costs in this process. Solid heterogeneous catalysts have the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is however considered as a green process. This process requires neither catalyst recovery nor aqueous treatment steps. The heterogeneous catalysed transesterification of oils is an attractive alternative to reduce the costs associated with the purification and separation of reaction products [100]. Purification steps of products are much more simplified with high yields of methyl esters being achieved [98].

Heterogeneously catalysed transesterification reactions generally require more severe operating conditions with relatively elevated temperatures and pressures. Furthermore the performances of heterogeneous catalysts have been reported to be generally lower than that of homogeneous catalysts [101]. A major problem also with heterogeneous catalysts is their deactivation with time owing to many possible phenomena, such as poisoning, coking, sintering, and leaching [102]. Figure. 2.23 show a simplified flow sheet of a heterogeneous transesterification process. Application of solid catalysts to produce biodiesel however, requires a better understanding of the factors that govern their reactivity. For instance, the selected catalysts must have a multifaceted function; should catalyse transesterification and esterification reaction, be deactivated by water, be stable, should not leach, be active at low temperature, and have high selectivity [103]. To improve the performance of these catalysts, it is essential to understand the correlations between acid and base strength and catalytic activity they possess [103]. It is also obvious that the surface of these heterogeneous materials should exhibit some hydrophobic character to promote the favoured adsorption of triglycerides and to avoid deactivation of catalytic sites by strong adsorption of polar by-products such as glycerol and water [72].

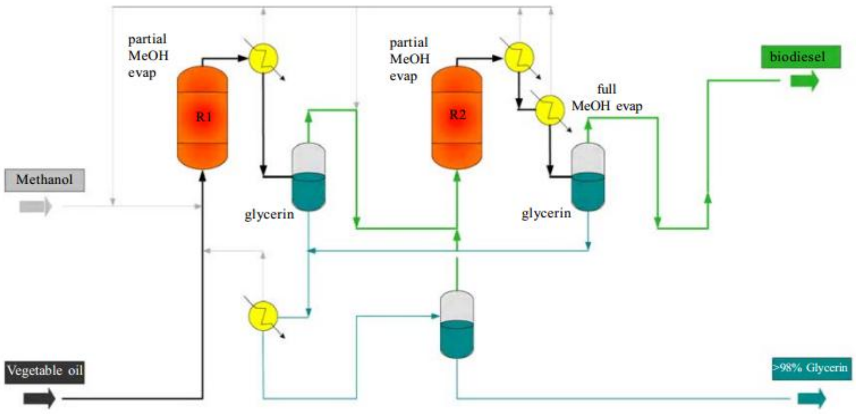


Figure 2.23:Flow sheet of heterogeneous transesterification process [104].

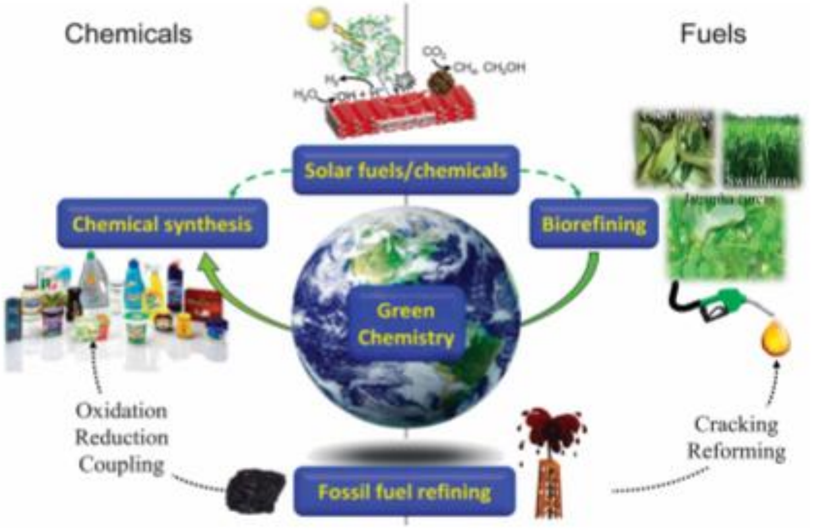


Figure 2.24: Current and future roles for heterogeneous catalysis in the production of sustainable chemicals and fuels [1].

2.15: The Metal Oxides

A plethora of metal oxides have been studied for the transesterification process of oils [1]. These include alkali earth metal oxides, transition metal oxides, mixed metal oxides and supported metal oxides [1]. Zirconium oxide, titanium oxide and zinc oxide are among the transition metal oxides that have recently drawn attention for biodiesel production due to their acidic/basic properties [1]. These catalysts have shown good catalytic activities and good stability when used to catalyse esterification and transesterification simultaneously. However, they have not been generally used in the industrial production process, mainly because of the high catalyst cost and difficulty in filtering the small catalyst particles respectively. Calcium oxide possesses relatively high basic strength and less environmental impacts due to its low solubility in methanol [1]. As compared to KOH or NaOH, calcium oxide will probably bring about similar productivity with added advantages of easy product recovery, easier handling and an environmentally benign process [101]. According to Kouzu, [105] report, transesterification of soybean oil with methanol was carried out in the presence of calcium oxide (CaO), and also via homogeneous catalysis using sodium hydroxide. Results obtained revealed an absolute conversion into FAME in both cases. According to Sakai reports, economic feasibility studies was carried out on four batch processes for the production of biodiesel using a homogeneous KOH catalyst and a heterogeneous CaO catalyst via hot water purification and vacuum FAME distillation processes. And among the four processes, the manufacturing costs involved in the CaO catalyst with hot water purification process proved to be the lowest. Conclusively, calcium oxide can be widely applied for biodiesel synthesis owing to its cheap price, minor toxicity and high availability [1].

2.16: Properties of Biodiesel fuel

The fuels that are employed for use in any engine must pass a certain number of tests and conform to specified guidelines to control their quality [84, 101]. Biodiesel and petroleum diesel widely differ in their chemical composition and character. According to Chang et al 1996, petro-diesel comprises of about 30-35 % aromatic carbons and 65-70 % paraffin and traces of olefins most of which are in the C_{10} - C_{16}range [101] and completely oxygen free. While biodiesel derived from rapeseed, soybean or sunflower seed oil primarily contains C_{16} - C_{18} fatty acids methyl esters with 1-3 double bonds per molecule and with about11 % (m/m) oxygen content as reported by Schafer, 1998. However these differences give biodiesel its characteristic physical and chemical properties. The composition and properties of the biodiesel also depend extensively on the feedstock used in the manufacturing process [71]. The fuel properties for biodiesels such as cetane number, heat of combustion, melting point and viscosity have been confirmed to increase with increasing carbon number and degree of unsaturation [71]. This however necessitated improvement of parent oil plants with specific fatty acids via genetic engineering to improve the fuel properties of biodiesel [71, 102].

2.16.1: Biodiesel standards

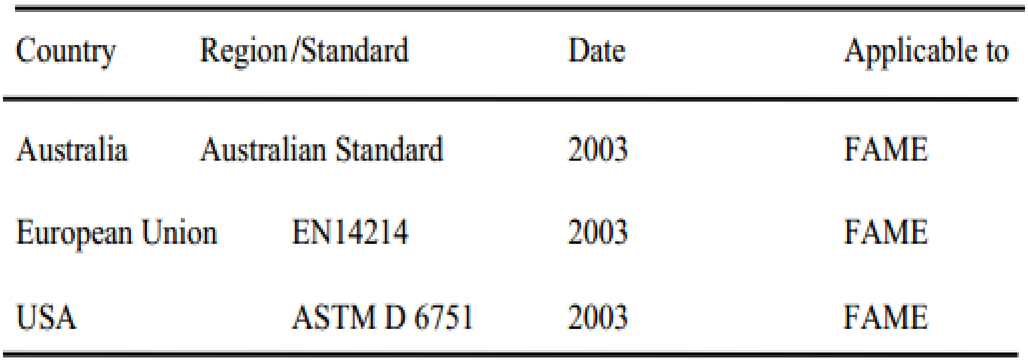
The commercialization and market penetration of fuels must meet certain standards for fuel performance and characteristics need to conform and maintained [71]. Many countries have their independent standards for biodiesel fuel. The ASTM standards are the most significant ones in order to determine the quality of the fuel [71]. With the increasing number of studies in further detail on fuel production, chemistry and performance, these standards are being revisited and significant changes are still on-going. Table 2.5shows the North American Standards for Biodiesel, ASTM (American Society for Testing and Materials) requirements for biodiesel [71].

The quality standards of any fuel are prerequisites for the commercial consumption. These standards serve as guidelines for the production process, guarantee customers of high quality fuel and provide authorities with approved tools for the assessment of safety risks and environmental pollution [71, 99]. Thus frequent tests need to be carried out on biodiesel to ensure that it meets and constantly maintains high level of industrial quality standards. There are currently no accepted international standards on the market of biodiesel [1, 71, 102].

In 1997, the European committee for standardization was mandated to develop a uniform standard for biodiesel fuels and come up with respective measurement procedures [71]. The norm EN14214 (European Union quality standard for biodiesel fuels) was formed which came into full implementation in 2004 and this is valid for all the European Union member states [71]. These standards include twenty-six (26) parameters [71]. But some of these parameters are regulated in order to control the production process and also ensure better conversion of the fatty acid into FAME [71]. The other parameters depend on the feedstock characteristics such as iodine value which in tend depends on the fatty acid profile of the oil [1, 71]. As EN14214 is very restrictive in its limits, some oil crops that would have been suitable for biodiesel production are eliminated from the selection because they exceed these limits of importance such as the iodine value, stability and cold filter plugging point (CFPP) for winter period [71]. However, some of the EU standard such as CFPP is not applicable in some parts of the Southern region due to their different climatic conditions [1, 71]. The US norm however, for FAME fuels follows the ASTM D 6571 (American standards testing and methods) (Table 2.5).

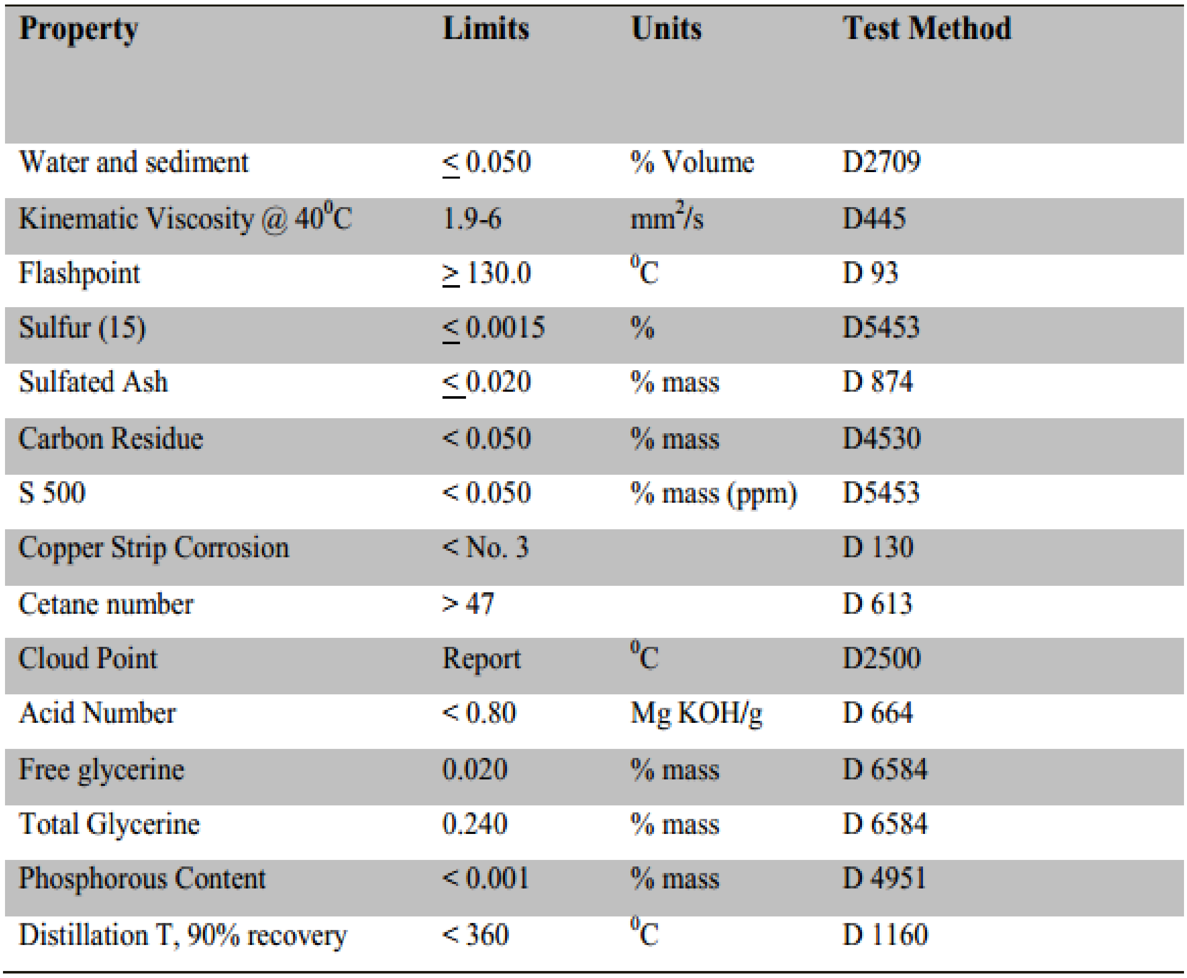
In South Africa the standard for automotive fuel for diesel engines is SANS 1935:2004 [71]. This standard specifies the requirements and test methods to be used for marketed and delivered biodiesel either as automotive fuel for diesel engines at 100 % concentration or as an extender for automotive fuel for diesel engines [71]. At 100 % concentration, fuel for use in diesel engines are designed and subsequently adapted to run on 100 % biodiesel. Table 2.6 shows the ASTM standards of maximum allowed quantities in diesel and biodiesel [71].

Table 2. 7: The international quality standards on neat biodiesel blends fuels



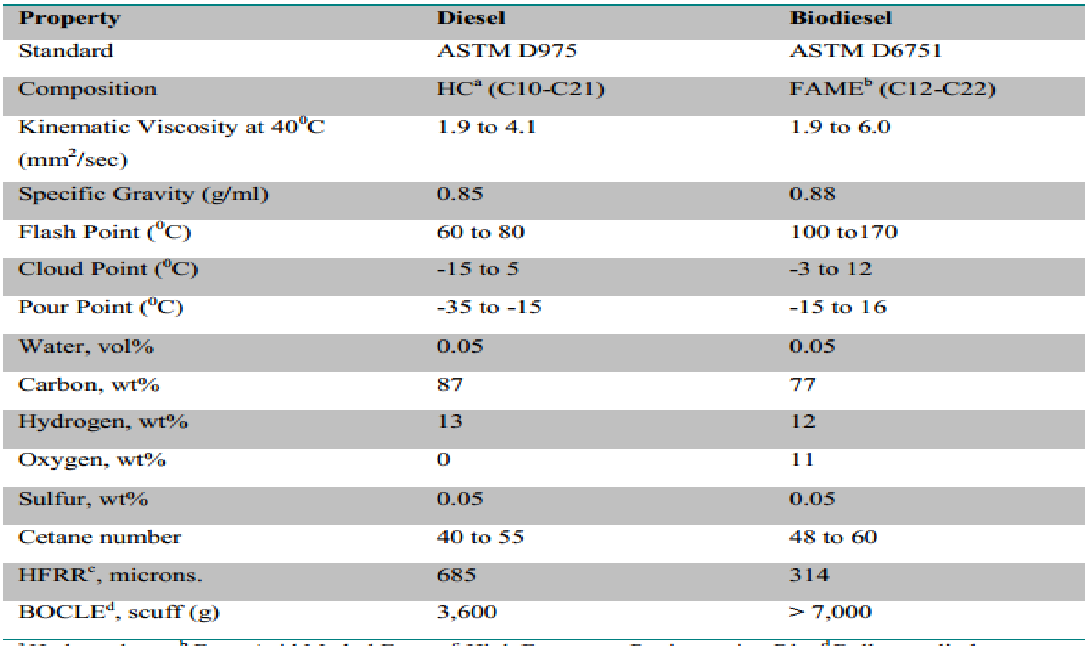
Country	Region /Standard	Date	Applicable to
Australia	Australian Standard	2003	FAME
European Union	EN14214	2003	FAME
USA	ASTM D 6751	2003	FAME

Table 2. 8: North American Biodiesel-standard ASTM D6751-03 [24]



Property	Limits	Units	Test Method
Water and sediment	≤ 0.050	% Volume	D2709
Kinematic Viscosity @ 40^{0}C	1.9-6	mm^{2}/s	D445
Flashpoint	≥ 130.0	^{0}C	D 93
Sulfur (15)	≤ 0.0015	%	D5453
Sulfated Ash	≤ 0.020	% mass	D 874
Carbon Residue	< 0.050	% mass	D4530
S 500	< 0.050	% mass (ppm)	D5453
Copper Strip Corrosion	< No. 3		D 130
Cetane number	> 47		D 613
Cloud Point	Report	^{0}C	D2500
Acid Number	< 0.80	Mg KOH/g	D 664
Free glycerine	0.020	% mass	D 6584
Total Glycerine	0.240	% mass	D 6584
Phosphorous Content	< 0.001	% mass	D 4951
Distillation T, 90% recovery	< 360	^{0}C	D 1160

Table 2.9: The ASTM standards of maximum allowed quantities in diesel and biodiesel [24].



Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10-C21)	FAME[b] (C12-C22)
Kinematic Viscosity at 40°C (mm^2/sec)	1.9 to 4.1	1.9 to 6.0
Specific Gravity (g/ml)	0.85	0.88
Flash Point (°C)	60 to 80	100 to170
Cloud Point (°C)	-15 to 5	-3 to 12
Pour Point (°C)	-35 to -15	-15 to 16
Water, vol%	0.05	0.05
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, wt%	0	11
Sulfur, wt%	0.05	0.05
Cetane number	40 to 55	48 to 60
HFRR[c], microns.	685	314
BOCLE[d], scuff (g)	3,600	> 7,000

[a] Hydrocarbons. [b]Fatty Acid Methyl Esters. [c]High Frequency Reciprocating Rig. [d] Ball-on cylinder Lubricity Evaluator

2.16.2: Cetane number

The cetane number indicates the fuel readiness to auto-ignite when injected into the diesel engine. Diesel fuels are required to have a cetane number higher than 40 and most refineries produce diesel with cetane numbers between 40 and 45 [71]. Biodiesel has a higher cetane number between 46 and 60 (depending on the feedstock used) which shortens the ignition delay in the engine and improves the combustion characteristics [106].

2.16.3: Flash point

The flashpoint of a fuel indicates the temperature at which the vapour above the fuel becomes flammable [71]. Petroleum-based diesels have flashpoints of 50 °C to 80 °C which makes them intrinsically safe [71]. Biodiesel has a flashpoint of over 160 °C which means that the fire hazard associated with transportation, storage and usage of biodiesel is much less than with other commonly used fuels (Biodiesel Education, 2009) [71].

2.16.4: Viscosity measure

Plants and waste oils have higher viscosities compared to diesel fuel [71]. But the transesterification of these oils reduces the viscosity to a large extent in converting to biodiesels [71]. Viscosity measurement is a basic parameter indicative of the extent of the reaction, since it is directly related with the fatty acid methyl ester content of the transesterified product [71]. And this is one of the specifications to comply with when producing biodiesel.

2.16.5: Sulphur content of biodiesel

According to SAPIA, 2006, the sulphur content of fossil diesel has to be below 50 ppm since high sulphur contents in fuels have been associated with negative health effects, environmental problem and also increase the cost of servicing vehicles [71]. Biodiesel is substantially free from sulphur when produce from fresh vegetable oil [71]. Biodiesel prepared from waste vegetable oil (WVO) might contain traces of sulphur and would have to be tested to fall within regulatory limits [79, 99].

2.16.6: Cold-filter plugging point (CFPP)

The cold temperature property of fuels measures the behaviour of the fuel under low ambient temperatures [71]. The cold filters plugging point is particularly important in countries where the temperatures drop below 50 °C [71]. The cloud point is the lowest temperature at which the sample may be cooled while still retaining its fluidity [71]. The cold-filter plugging point (CFPP) is considered a good indicator of operability limits of the fuel [79, 99].

2.16.7: Heat of combustion

The heat of combustion of biodiesel depends on the oil source. On the basis of mass, fossil diesel has a higher heating value which is about 13% higher than that of biodiesel [71].However because of higher density of biodiesel, its disadvantage is only about 8% lower on a volumetric basis. This means that for the same injection volumes, engines burning biodiesel have slightly lower power and torque [71]. The same power and torque can be achieved if injection volumes were altered for biodiesel [71]. Flexi-fuel vehicles use intelligent motors which can detect the type of fuel being used (biodiesel, petroleum diesel or a blend) and automatically adjust the injection parameters [71, 79, 99]. An increase of the injection volumes leads to a slightly higher specific fuel consumption when using biodiesel [71]. The above mentioned properties are those of pure (neat) biodiesel. If biodiesel is blended into fossil at 5% or 10%, the properties of the fossil diesel would not be affected to a large extent [71, 79]. However, it is only the 'lubricity' property of the biodiesel that would be affected in very low blends. This property therefore makes biodiesel an ideal additive for fossil diesel [71, 79].

2.17: History of porous materials

The history of porous materials began with zeolites having aluminosilicate frameworks [107], which are conventionally synthesized via non surfactant assisted route employing single molecule template and having small pores (micropore) inside it. The most generalized definition of a porous material is a continuous and solid network material filled through voids [108]. A material can be regarded as porous if its internal voids can be filled with gas. According to IUPAC classification, depending upon the pore size, the porous materials are of three types: mesoporous, microporous and macroporous [109]. Porous materials can be classified based on the framework building blocks: purely inorganic, hybrid organic–inorganic and all-organic porous polymers and carbonaceous materials. The classification of porous materials [110] is as illustrated in the chart.

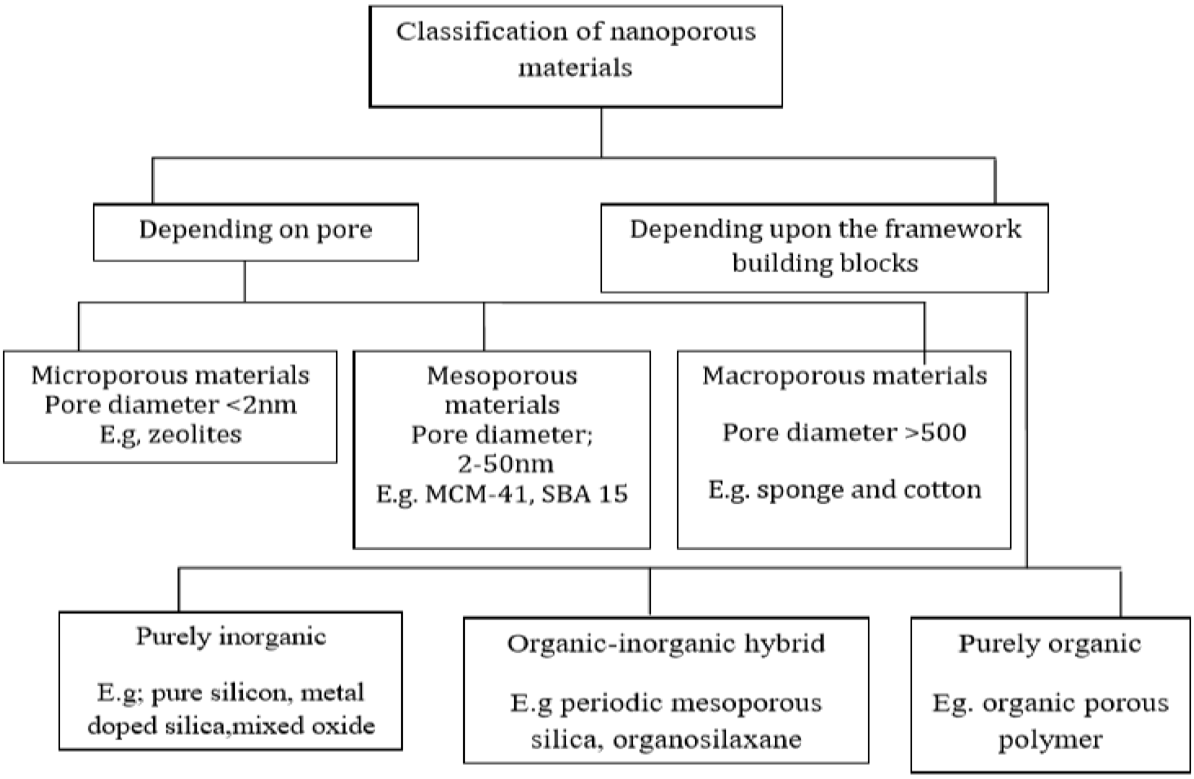


Figure 2. 25: Schematic representation of the classification of nanoporous materials [110].

Over the last two decades, various mesoporous structures have been investigated and synthesized which can be roughly classified into three (3) main categories based on their pore types; nearly spherical cage, cylindrical channel and bicontinuous [111].

2.17.1: The Mesoporous silica

Meso means "in between", has been adopted by IUPAC to define porous materials having pore dimension in between micropore and macropore i.e. typically between 2 and 50 nm [110]. Examples of mesoporous materials include silica and alumina that have similarly fine sized mesopores. A mesoporous material can be disordered or ordered in a mesostructure [159]. Ordered mesoporous silica was first reported in 1992 [111]. Ever since, significant progress has been made in their morphology control, pore size adjustment, composition variation and application development [112]. Ordered mesoporous materials such as MCM-41/48, SBA15 have uniform and regular arrangements of pore (or channel) widths whereas, atomic arrangements are not ordered. Due to their high stability, large surface areas and large pore volumes they are technically employed as adsorbents, ion-exchangers, catalysts, catalyst supports and in many other related application [113].

A procedure for synthesizing mesoporous materials (silica) was patented around 1970. Mesoporous silica nanoparticles (MSN's) were independently synthesized in 1990 by researchers in Japan [114]. They were later produced also at Mobil Corporation laboratories and named Mobil Crystalline Materials or MCM-41. Mesoporous material requires surfactants as templating material to achieve the desired structure.

2.17.2: The mode of mesoporous materials synthesis

Mesoporous materials are basically prepared through silica formation around template micelles assemblies followed by template removal by appropriate methods such as calcinations. The findings were classified by various kinds of mesoporous materials. For example, hexagonal mesoporous silica prepared using neutral amine as template possess slightly disordered hexagonal structure and thicker walls, superior thermal stability upon calcinations in air, and a smaller crystallite size, which affords complementary textural mesoporosity for improved access to the framework-confined mesopores [115]. Michigan State University (MSU1) synthesized by using polyethylene oxide (PEO) as a structure directing agent also has a disordered channel structure [115]. This material possesses large wall thickness and small particle size with considerable textural mesoporosity due to pores formed between the relatively small particles.

A widely used material, highly ordered large pore mesoporous silica Santa Barbara Amorphous -15 (SBA-15) with thicker pore walls and two dimensional hexagonal structure by using amphiphilic triblock-copolymer of poly(ethylene oxide) and poly(propylene-oxide) (Pluronic-123) as the structure directing reagent in highly acidic media. The pore diameters of the SBA-15 materials are well tuneable in the range of 5-30nm and these materials exhibit higher hydrothermal stability as compared to other mesoporous materials [116].

Meso-cellular form (MCF) materials can be synthesized using triblock copolymer stabilized oil in water to result in aerogel like structure which offers the benefits as catalyst support and separation media [117].

Mobil Oil Corporation (USA), first successfully synthesized MCM (Mobil Composition of Matters)-41/48 through surfactant-mediated self-assembly method. This surfactant assisted templating pathway or soft templating strategy opens a new class of materials named as mesoporous materials [118]. Mesoporous materials are formed by self-assembly process from combined solutions of sol-gel precursors (example; metal alkoxides) and structure directing amphiphiles usually block copolymers or surfactants [119]. Surface functionality of the pores can be modified by adding organically modified precursors, for example; organosiloxanes to the initial mix. During the synthesis process, the SDA molecules, in the form of a lyotropic liquid-crystalline phase, lead to the assembly of an ordered mesostructured composite during the condensation with the silica precursors [118]. The mesoporous materials are obtained by subsequent removal of the surfactant by extraction or calcination [118].

2.17.3: The mechanism and synthesis pathway of mesoporous materials

In the synthesis of mesoporous material, organic surfactant molecules play a significant role to generate porosity within the building blocks and thus act as template or structure directing agent (SDA). This soft templating method is the most successful pathway for the synthesis of ordered and disordered mesoporous matrices. It is important to know what a template is or what kind of interaction occurs between a template and precursor species forming the mesoporous framework during the synthesis [120].

2.17.4: Relevance of a template in generating porosity

In broader sense, a template is a pattern or overlay used in graphic arts (drawing, painting, etc.) and sewing to replicate letters, shapes or designs. In nanoporous regime, template represents a particular molecule which helps to generate or design porosity in a matrix [116]. Thus a template acts as structure directing agent (SDA) in the synthesis of porous materials. There are some other SDAs bearing hydrophobic-hydrophilic groups in a single molecule, which are not surfactants but play a crucial role of template in designing mesopores in a material [121]. These template molecules may or may not form self-assembly. All the above templates are soft templates. There are also hard templates like porous silica or colloidal silica spheres, polystyrene etc. which generate porosity within the matrix. A template is a structure (usually organic, though hard template may be inorganic) around which a material (often inorganic) nucleates and grows in a ‘skin-tight’ fashion, so that upon the removal of the template structure, its geometric and electronic characteristics are replicated in the (inorganic) materials [121].

2.17.5: Structure Directing Agents (Surfactant)

Amphiphilic surfactant templating pathway is a process in which an organic species functions as a central structure about which precursor moieties organize to form long range ordered material [122]. The molecules have both hydrophobic and hydrophilic parts and the hydrophobic component of surfactant can solubilize organic species, while the hydrophilic or ‘water loving’ component interacts with charged inorganic precursors to direct the formation of the inorganic framework [123]. The amphiphilic surfactant molecule can arrange itself at the surface of the water such that the polar end interacts with the water and the non-polar end is held above the surface (either in the air or in a non-polar liquid). The presence of these molecules on the surface disrupts the cohesive energy at the surface and thus lowers the surface tension [124]. That is why, such molecules are called ‘surface active’ molecules or surfactants. Another arrangement of these molecules can allow each component to interact with its favoured environment [120]. Molecules can form aggregates in which the hydrophobic portions are oriented within the cluster and the hydrophilic portions are exposed to the solvent. Such aggregates are called micelles. The proportion of molecules present at the surface or as micelles in the bulk of the liquid depends on the concentration of the amphiphile [125]. At low concentrations surfactants will favour arrangement on the surface. As the surface becomes crowded with surfactant more molecules will arrange into micelles. At certain concentration the surface becomes completely loaded with surfactant and any further additions must arrange as micelles. This self-assembled micelle formed by the association of individual amphiphilic templating molecules bonded through weak forces like van der Waals, hydrogen bonding etc. but there is no covalent linkage between those amphiphiles. Normally, these SDA molecules are the ‘placeholder’, what becomes the void space to produce nanoporous material. They not only allow controlling the variation of pore size but also the shape of the pores that is the total architecture of the template molecule, its size and shape are imprinted in the porous solid [120].

2.17.6: Poloxamers

Poloxamers can be defined as a non-ionic triblock copolymers composed of a central hydrophobic chain of polyoxypropylene (poly (propylene oxide)) flanked by two hydrophilic chains of polyoxyethylene (poly (ethylene oxide)) [126]. Poloxamers are known by their trade names as Pluronic, Synperonics and Kolliphor [127]. Poloxamers exhibit amphiphilic nature and hence, the polymers have surfactant properties that make them useful in industrial applications. Also, they can be used to increase the water solubility of hydrophobic, oily substances or otherwise increase the miscibility of two substances with different hydrophobicity.

Recently in materials science, the poloxamer P123 has drawn great attraction in the synthesis of mesoporous materials, including SBA-15 [128]. Figure 2.26 shows the molecular structure of poloxamer;

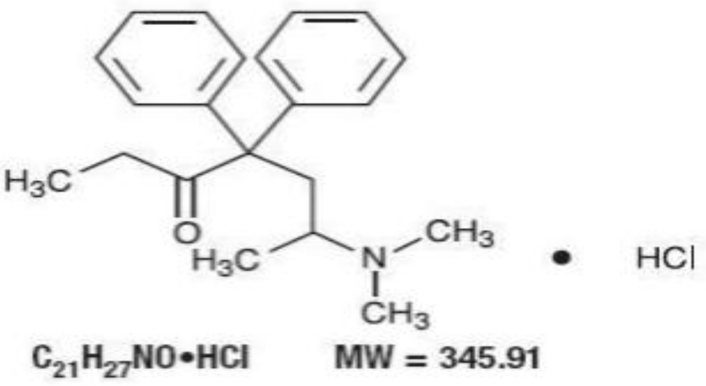


Figure 2. 26: Molecular structure of poloxamer.

2.18 Catalyst Formulation and Methods of its Preparation

2.18.1 Methods of preparation

Many catalysts consist of an active component(s) deposited on a support (such as silica, alumina, carbon etc). The role of the support may be to improve the properties (e.g. stability) of the active component(s), or to participate directly in the catalytic reaction (e.g. by providing acidic sites). The following terms define general preparation methods.

2.18.2 Deposition

Deposition describes the application of the catalytic component (e.g. nickel, as .nickel nitrate) on to a separately produced support (e.g. silica). Any treatment of the support before the deposition step must be described precisely. Deposition may be achieved by;

2.18.2.1 Impregnation

Impregnation is a method used for synthesizing heterogeneous catalysts. It is also called capillary impregnation or dry impregnation. Impregnation fundamentally involves contacting a solid with a liquid containing the elements to be deposited in the surface [129].

One or several parallel processes occur during impregnation at different rates. This includes; (i)Selective adsorption of species (charged or not) by coulomb forces, van der Waals forces and hydrogen bond (ii)Ion exchange between the charged surface and the electrolyte (iii) polymerisation/depolymerisation of the species (molecules, ions) attached to the surface (iv)Partial dissolution of the surface of the solid.

2.18.2.2 Classification of impregnation methods.

Impregnation can be done in eight different ways;

- **Impregnation by soaking, or with an excess of solution**: In this method, the excess liquid is eliminated by evaporation or by draining. A considerable quantity of active element is deposited. The quantity deposited depends on the solid to liquid ratio. This method allows high distribution and dispersions of species to be obtained. The method works best if ion/solid interactions are involved [130].
- **Pore volume impregnation:** In this method, the required amounts of active elements are introduced which corresponds to the pore volume of the support. The method is best suited to deposition of species which interact very weakly with the surface, and also for deposition of quantities exceeding the number of adsorption sites on the surface [130, 131].

- **Incipient wetness impregnation:** This process is similar to dry impregnation, but the volume of the solution is more approximately determined to correspond to that beyond which the catalyst begins to look wet [130, 131, 132].

- **Deposition by selective reaction with the surface of the support**: This process allows the carrier to be left in contact with an excess of solution for an amount of time after which the excess liquid is removed e.g., dipping technique. This is done in order to make a strong bond with the surface. The process provides better anchoring and grafting of the active elements although it is mostly not used [130, 131, 132].
- **Impregnation by percolation:** The precursor is adsorbed by percolation of the impregnating solution through a bed of carrier. The advantage of this process is that it is a faster approach to equilibrium. One can easily follow the progress of the process by analysing the effluent. Differences in the degree of deposition along the carrier bed are present [130, 131, 132].

- **Co-impregnation:** In this process, two or several active elements are introduced in a single step. Co-impregnation with uniform distribution and without segregation of species is extremely difficult to achieve [132, 133].

- **Successive impregnation**: In this method, two or several active components are introduced accordingly. Drying and often calcination takes place between the impregnations. For the second impregnation the properties of the surface to take into account are those of the solid obtained after the previous impregnation [133, 134].

- **Precipitation-deposition**: This is a special technique of impregnation often used for producing both support precursors and catalyst precursors (including precursory forms of zeolites) and occurs when two or more solutions are mixed in a suitable way [134]. In addition to providing general details of the method (e.g., concentration, temperature, pH, etc.) it is necessary to indicate specifically the order and rate of addition of one solution into the other, a description of the mixing procedure and the details of the ageing procedure, if any, where active elements are deposited onto a carrier in suspension by slow addition of the elements or *in situ* formation. This technique takes advantage of the fact that precipitation onto the carrier needs a lower super-saturation than formation of the new phase directly from the liquid. It is vital to maintain super-saturation at a constant moderate level. This is achieved, as in the homogeneous precipitation technique, by decomposition of a suitable substance, which releases the precipitating agent continuously, or by controlled and progressive addition of the precipitating agent. The technique is excellent if the primary particles of the carrier are not porous. With a porous material, support deposition takes place preferentially in the external parts [134].

CHAPTER THREE

3.0: METHOLOGY AND EXPERIMENTAL DESIGN

3.1: Introduction

This section sets out the methodology used in this study. The materials used, the research design and methods were also emphasized. The theoretical background of the analytical techniques used in this study is also discussed briefly. The general section of this experiment give a detail explanation of the laboratory procedures used.

The order of methodology employed in solving the research problems is all enumerated and highlighted in section 3.2 while the description of the chemicals used and their preparation are presented in section 3.3. This chapter comprises of two major categories namely (i) section 3.4 that details the experimental methods for the preparation of catalyst support (SBA-15) and (ii) section 3.5 deals with the preparation and functionalization of solid heterogeneous catalysts.

The experiment was conducted in the Materials Science and Engineering laboratory, Biotechnology laboratory, College of Agriculture and Ecolab in Department of Geology of the University of Ghana, Legon.

3.2: The chapter overview

The layout of this chapter includes the following:

i. Preparation of catalyst support.

ii. Catalyst preparations: The heterogeneous catalysts CaO–MoO_3–SBA-15 was prepared using the wet impregnation method and conventional hydrothermal synthesis procedure.

iii. Functionalization of solid heterogeneous catalyst.

iv. Catalyst characterization: Catalyst was characterized using different techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), sorptometric study (BET/BJH) and optical microscopy analysis.

v. Transesterification reactions: The reaction between the oil, catalyst, and methanol under different reaction conditions. The separation of phases, washing, purification and drying of the upper phase (methyl esters) were all performed in order to obtain a pure product.

3.3: Materials and chemicals

The feedstock used in the study is given in Table 3.1. All reagents used in this study were of analytical grade and the list of the chemicals**,** solvents and acids used in this work is presented in the Table 3.2.

Table 3. 1: Supply of feedstock

Material	**Source**
Waste cooking oil	Madina market

Table 3. 2: The list of chemicals and solvents used in the study

Chemicals/Solvents	**Source**	**Grade/Purity**
Tetraethylorthosilicate	Sigma Aldrich	98%
Pluronic copolymer	Sigma Aldrich	99.9%
Calcium nitrate	Merck	99.0%
Ammonium heptamolybdenate	Merck	99.5%
Hydrochloric acid	Merck	37%
Phosphoric acid	Merck	85%
Potassium hydroxide pellets	Merck	99.9%
Methanol	Paskem	99.8%
Borax	Sigma Aldrich	
Methyl orange	Merck	
Toluene	Sigma Aldrich	99.5%
Isopropanol	Paskem	40.0%
Phenolphthalein		
Deionized water		

3.4: Synthesis of SBA-15

Mesoporous SBA-15 silica was synthesized according reported procedures [18, 19].

The synthesis of SBA-15 involved 2 steps; hydrolysis and condensation, and impregnation.

3.4.1 Hydrolysis and Condensation

- 8.0g Pluronic copolymer was dissolved in 60 ml of deionised water in a 1000 ml beaker and 240 ml of 2M HCl solution was added. This mixture was stirred at a temperature of 313 K at 600 rpm until a homogenous mixture was achieved as in Figure 3.1.
- While the aqueous suspension was under constant stirring, 20 ml of tetraethylorthoilicate was added to the P123 solution dropwise. The resultant gel was stirred at 313 K at 600 rpm for 24 hours as shown in Figure. 3.2.

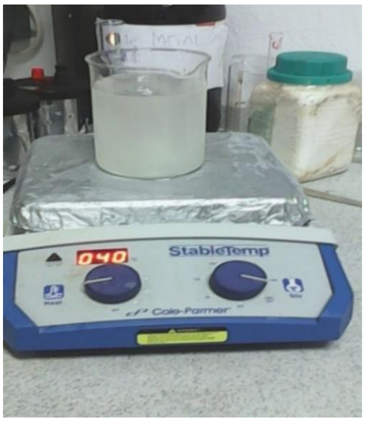


Figure 3. 1: Stirring of P123 solution **Figure 3. 2: Addition of TEOS to P123 solution**

The sol-gel solution was subsequently crystallized in an oven at 373 K for 48 hrs as shown in Figure. 3.3.

- After crystallization, the solid product was filtered, washed with deionized water several times as shown in Figure 3.3 and Figure 3.4.
- Finally, the SBA-15 powder was obtained by calcining at 823 K for 6 h as shown in Figure 3.5 and Figure 3.6below.

Figure 3. 3: Crystallization in an oven

Figure 3. 4: Washing& filtration process

Figure 3. 5: Washed, filtered & dried solid product of SBA-15.

Figure 3. 6: Calcined SBA-15 powder

Figure 3. 7: Calcination @ 823K

- The entire process of preparing SBA-15 is as illustrated in Fig. 3.8 below.

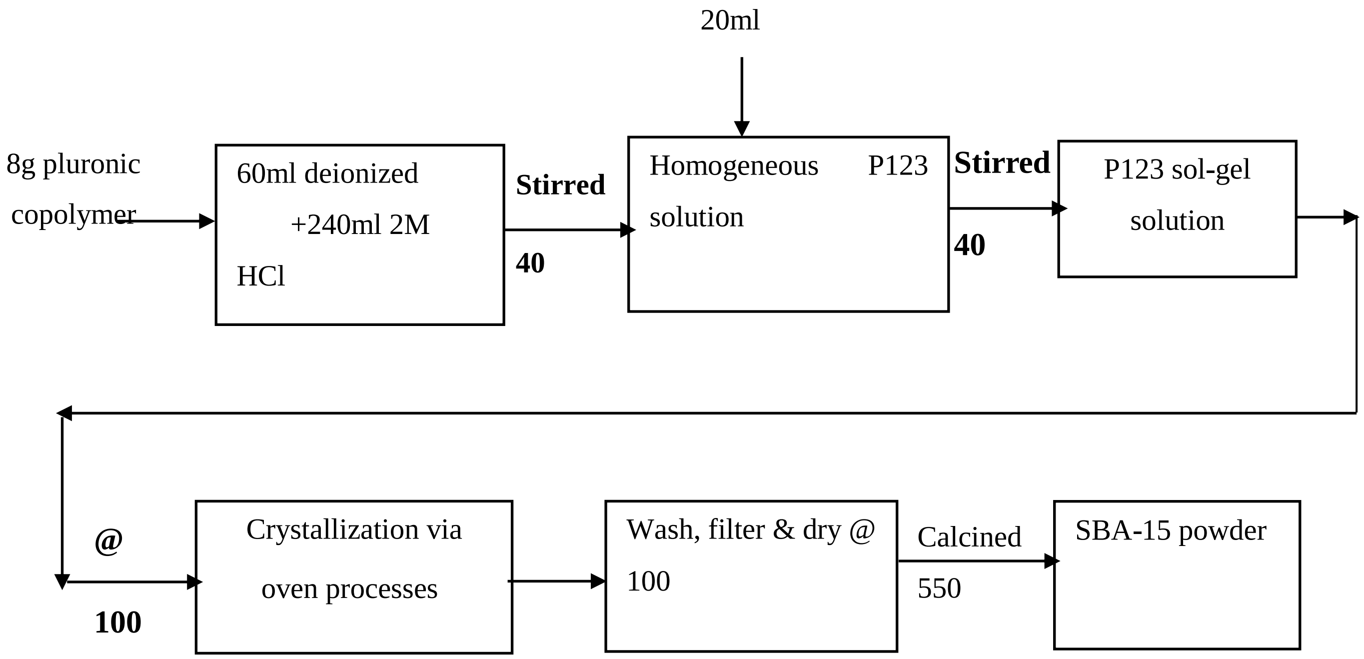


Figure 3. 8: Process Development Flow chart.

3.5: Preparation of solid catalyst

3.5.1: Impregnation method.

- A $CaO–MoO_3/PO_4$–SBA-15 catalyst was prepared by loading 3 wt % $Ca(NO_3)_2$ and 10 wt % $(NH_4)_6Mo_7O_{24}$ amounts according to the incipient wetness impregnation method using SBA-15 as template.
- Typically, 3.0 g SBA-15 support was impregnated with aqueous solutions of the precursors, namely, $Ca(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ as shown in Figure. 3.5a.
- After impregnation, the sample was dried overnight at 373 K in an oven and subsequently calcined at 823 K and 1023 K respectively for 6 hrs. as seen in Figure. 3.5b
- Upon calcination, the impregnated calcium and molybdenum compounds were decomposed to their corresponding metal oxides.

Figure 3. 9: SBA-15 with Ca(NO3)2& (NH4)6Mo7O24

Figure 3.10: Calcined impregnated SBA-15.

3.5.2: Batch formulation

Table 3. 3: The table below shows the batch compositions of the Ca (NO3)2 & (NH4)6Mo7O24 that were used.

SAMPLE CODE	**AMOUNT OF $Ca(NO_3)_2$**	**AMOUNT OF $(NH_4)_6Mo_7O_{24}$**	**AMOUNT OF SBA-15**
S_1	3wt%	10wt%	3.0g

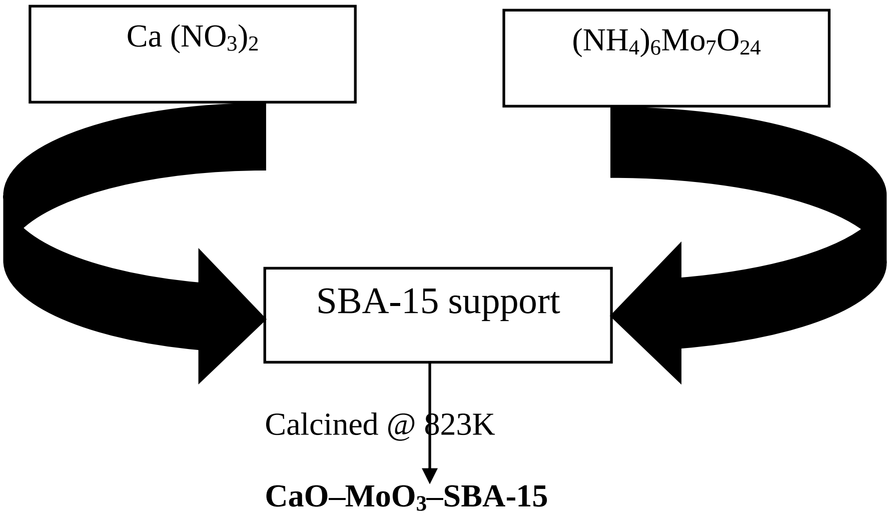


Figure 3. 11: Process of Impregnation Flow Chart.

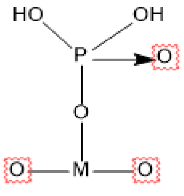
3.5.3: Surface functionalization of $CaO-MoO_3-SBA-15$

The phosphation was carried out by suspending $CaO-MoO_3$-SBA-15 powder in 2M H_3PO_4 solution. After 30 minutes of stirring, the resultant suspension was placed in an oven overnight to crystallize. The solid particles were then filtered, washed with dilute H_3PO_4

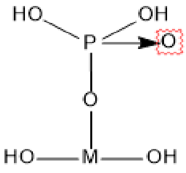
solution, dried at 120 °C and subsequently calcined for 6 hrs at 723 K, 823 K, 923 K and 1023 K respectively.

Flaig Bauman [135] proposed a mechanism in which adsorption occurs by an exchange process between surface hydroxyl groups and $H_2PO_4^-$ ions in solution, H_3PO_4 being dissociated only to the first degree at pH< 7. The following structure (**I**) is postulated.

The second mechanism involved in the dissociation of adsorption of H_3PO_4 leading to the blockage of Lewis acid sites as illustrated in (**II**). Upon heating, the dehydroxylation occurs leading to the bridged structures as shown in Figure 3.5.1. In this case Bronsted acidity was generated.



(I)



(II)

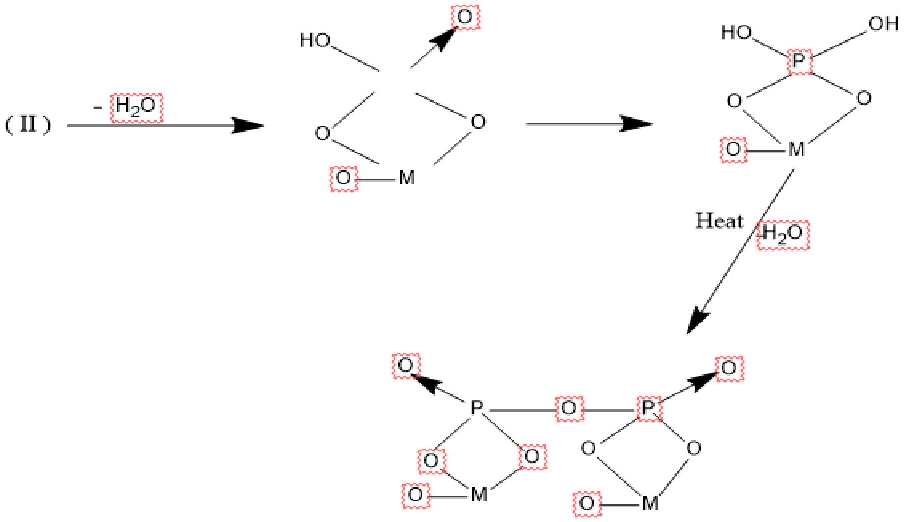


Figure 3. 12: Reaction mechanism associated with the dissociation of adsorption of H_3PO_4 leading to the blockage of Lewis acid sites.

Table 3. 4: The phosphation of CaO-MoO3-SBA-15 powder by 2M H_3PO_4 solution;

SAMPLE CODE	**AMOUNT OF CaO-MoO$_3$-SBA-15 USED**	**AMOUNT OFH$_3$PO$_4$ USED**
S$_2$	3.0 g	10 ml

3.6: Biodiesel synthesis via heterogeneous catalysis.

This section presents the transesterification reactions of the triglyceride (waste cooking oil) into methyl esters via heterogeneous catalysis. In this synthesis the catalysts used were CaO-MoO_3-SBA-15 and CaO–MoO_3/PO_4–SBA-15 for the transesterification with intense mechanical agitation necessary to enhance the emulsification of the liquid reactants into FAME. The influence of relevant process parameters and variables that affects the conversion and yield of FAME from the different feedstock are reported.

3.6.1: Experimental procedure for biodiesel synthesis.

3.6.1.1 Oil sample preparation

The waste cooking oil (WCO) was pre-treated to remove the dirt and other inert materials from the oil. The WCO was first filtered under vacuum to remove the dirt and other inert materials, then dehydrated using anhydrous sodium sulphate and again filtered under vacuum, prior to use.

A three necked round bottom flask (500 ml) was used as laboratory-scale reactor for the experimental studies in this work, and a hot plate equipped with magnetic stirrer was used for heating the mixture in the flask which was capable of maintaining the required reaction temperature of 60-80 ℃ within ± 0.1℃. An on/off controller measure was used for regulating the temperature with a laboratory thermometer. For the simultaneous transesterification and esterification reaction of oil, the mixture was stirred at a constant mechanical agitation speed of 600 rpm for all the test runs. The reactor was initially charged with 60 g of pre-treated oil and heated to 60 ℃. The reaction was timed as soon as the catalyst /methanol solution was added to the reactor and it continued for the required reaction time of 6 h. The reaction was carried out under reflux equipped with a magnetic stirrer for mixing the oil, methanol and catalyst at a stirring speed of 600 rpm. After which the reaction was stopped by cooling the reactor to room temperature. The mixture was then placed in a separating funnel and allowed to stand overnight to ensure complete separation of the methyl esters and the glycerol phase. The glycerol phase (bottom) was removed and left in a separate container.

After the glycerol layer has been separated, the methyl ester layer was centrifuged to further concentrate and purify the methyl esters by removing methanol, catalyst and the glycerol residuals. Finally the methyl esters (biodiesel) were dried with sodium sulphate (10 wt% Na_2SO_4) based on the weight of the oil. The experimental set up is illustrated in Figure. 3.6a and Figure. 3.6b shows the samples of products obtained from waste cooking oil.

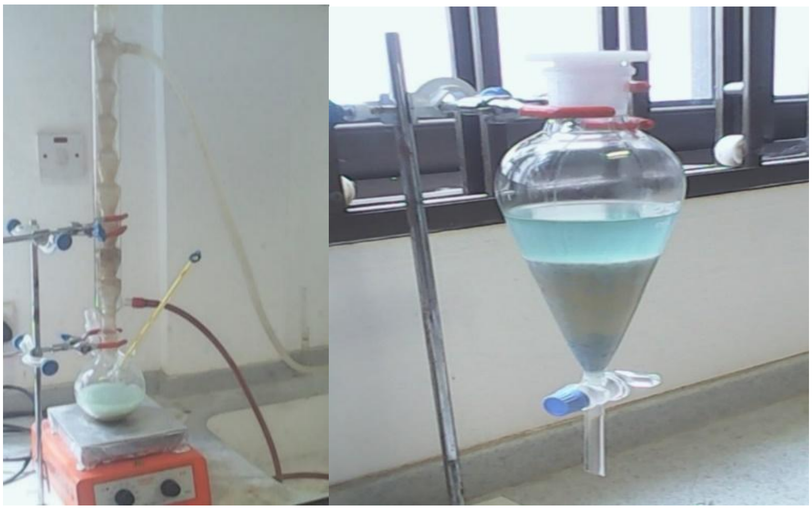


Figure 3. 13: Experimental set up of the mechanical agitation process & separation.

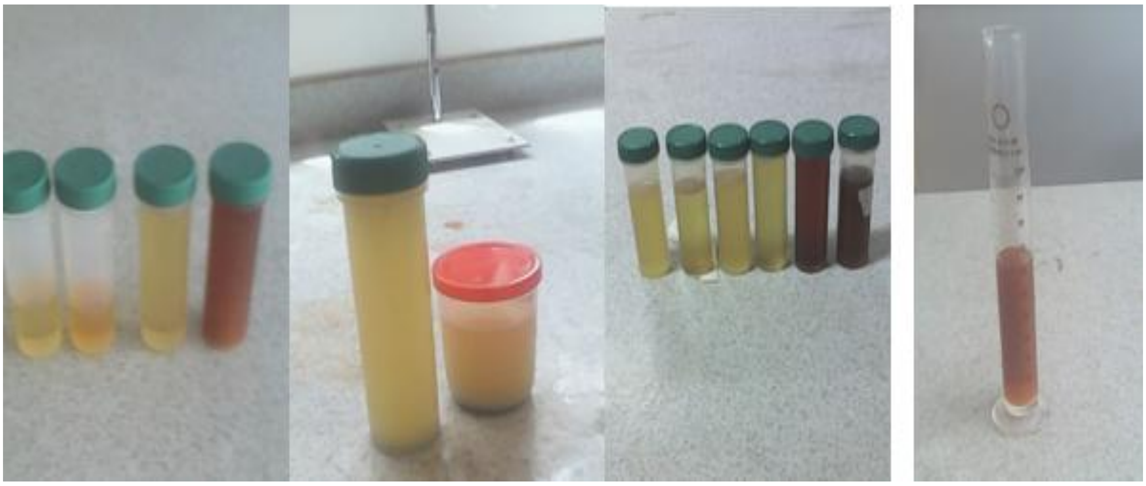


Figure 3.14: Samples of products obtained from waste cooking oil samples from experiments conducted in this study.

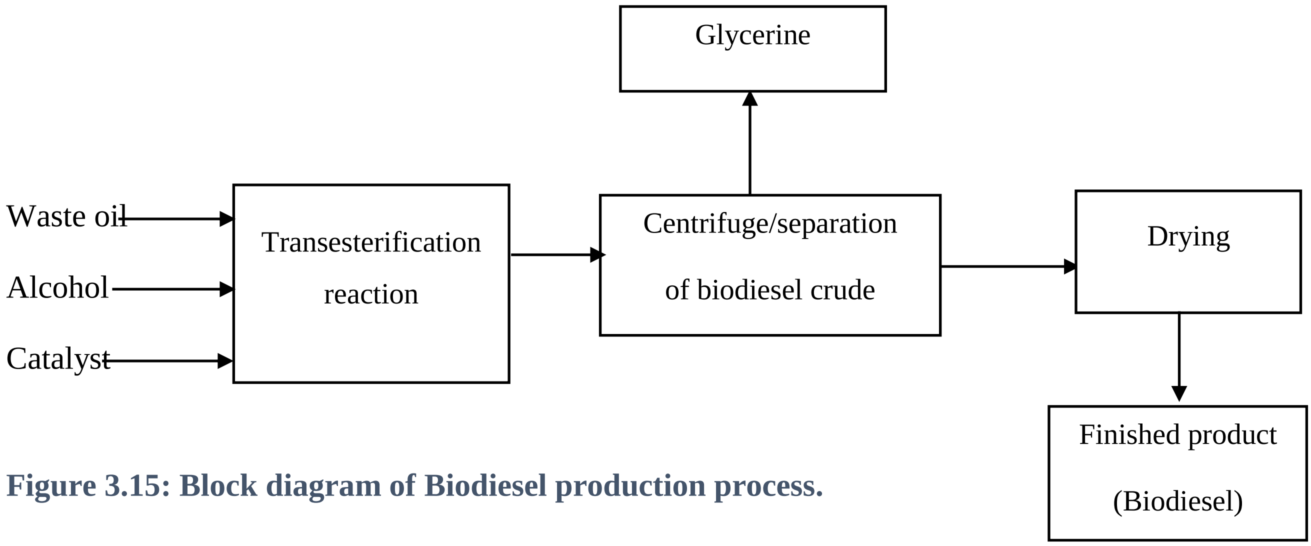


Figure 3.15: Block diagram of Biodiesel production process.

3.6.3 Characterisation of biodiesel

3.6.3.1 Methyl ester yield determination

The methyl ester yield is determined by the following procedure. A 1 ml of the sample is added to 40 mlof alkalis (NaOH, 0.1M) and reacted for 12h. After complete reaction, the sample was titrated with H_2SO_4 (0.1M) to get the percentage of methyl esters in the upper layer [135]

$$\% \text{ methyl ester yield (\%ME)} = \frac{V_{O}-V_{B} \ *C*M*100}{1000} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (1)$$

V_O = volume of blank oil in ml

V_B = volume of H_2SO_4 required for the titration of biodiesel (ml)

C = concentration of the H_2SO_4 used

M = molecular weight of ester.

Table 3. 5: The methyl ester determination of biodiesel using titration.

Burette reading	1	2	3	Blank
Initial reading	0.0	0.0	0.0	0.0
Final reading	7.7	7.8	7.8	41.8
Volume used	7.7	7.8	7.8	41.8

$$\% \text{ methyl ester yield } (\%ME) = \frac{V_{O}-V_{B} \;*C*M*100}{1000} = \frac{41.8-7.8 \;\times 0.1\times 292.2\times 100}{1000} = 99.348 \approx 99.4\ \%$$

3.6.3.2 Properties of oil samples

3.6.3.2.1 Acid value

An acid value (or "acid number" or "acidity") is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid. The acid number is used to quantify the amount of acid present, for example in a biodiesel sample. It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1 g of sample.

3.6.3.2.2: Procedure for acid value determination of biodiesel

In an AOCS Cd 3d-63 procedure, 1:1 v/v mixture of toluene and isopropanol was used. 125 ml of the mixture was neutralized with drops of 0.1 molL^{-1} KOH in isopropanol until first appearance of the pink colour of phenolphthalein indicator. 20 g of biodiesel sample was dissolved in this mixture until the pink colour disappeared and the solution was continuously and vigorously shaken during the titration until the pink colour reappears and persist for at least 30s. Each titration was repeated three times and the standard deviation calculated. The acid value (AV) is defined by the equation:

$$AV = \frac{(A-B)\times C\times 56.1}{M} mgKOH/g \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

AV = the acid value

A = titrant volume in ml for sample titration

B = titrant volume in ml for blank titration

C = concentration of KOH in molL^{-1}

M = mass of the tested sample in grams and 56.1is the molecular weight of KOH.

Table 3. 6: The acid value determination of waste oil using titration

Burette Readings	**1**	**2**	**3**	**Blank**
Initial volume/cm^3	0.0	0.6	1.4	0.1
Final volume/cm^3	0.6	1.4	2.1	0.1
Volume Used/cm^3	0.6	0.8	0.7	0.1

$$AV = \frac{A - B \ \ \times C \times 56.1}{M} mgKOH/g = \frac{0.70 - 0.10 \ \ \times 0.10 \times 56.1}{20} = 0.1683 \approx 0.2$$

Table 3.7: The acid value determination of biodiesel using AOCS Cd 3d-63 method.

Burette reading	**1**	**2**	**3**	**blank**
Initial reading/cm^{-3}	0.00	0.20	0.40	0.00
Final reading/cm^{-3}	0.20	0.40	0.60	0.10
Volume used/cm^{-3}	0.20	0.20	0.20	0.10

$$AV = \frac{A - B \ \ \times C \times 56.1}{M} mgKOH/g = \frac{0.20 - 0.10 \ \ \times 0.10 \times 56.1}{20} = 0.02805$$
$$\approx 0.03 mgKOH/g$$

3.6.3.3: **Thin Layer Chromatography (TLC) measurements**

TLC is generally used to separate and determine the concentration of different types of lipid groups in foods, e.g. Triacylglycerol, diacylglycerols, monoacylglycerols, cholesterol, cholesterol oxides and phospholipids [1]. A TLC plate is normally coated with a suitable absorbing material and placed into a suitable solvent. A small amount of the lipid sample to be analysed is spotted onto the TLC plate. With time the solvent (the mobile phase) moves up the plate due to capillary forces and separates different lipid fractions on the basis of their affinity for the stationary phase (silica material). At the end of the separation the plate is sprayed with a dye so as to enhance the spots visibility. By comparing the distance that the spots move with standards of known composition it is possible to identify the lipids present. The TLC was chosen because its rapid analytical method that gives quite accurate indication of oil and methyl esters content in the sample.

3.6.3.3.1: **Procedure for physio-chemical analysis by TLC**

The characterization of the FAME product obtained in the experiment conducted using the CaO–MoO_3/PO_4–SBA-15 as heterogeneous catalyst was analysed by silica gel TLC technique to check the conversion of the triglycerides into methyl esters according to the method described by Damyanova [136]. Silica gel TLC plates were used for analysing the methyl ester sample as shown in Figure 3.16.

A mixture of hexane/ethyl acetate/acetic acid (80:20:2 v/v/v) was used as the mobile phase and silica gel as the stationary phase. Detection was achieved by spraying the TLC plate with 10% ethanolic phosmolybdate acid solution and heating the plates for 10 min at 180ºC in an air circulating oven. Biodiesel shows a higher mobility than waste oil with the selected solvent system and complete conversion of waste oil to biodiesel was supported by the disappearance of the waste oil spot on the TLC plate.

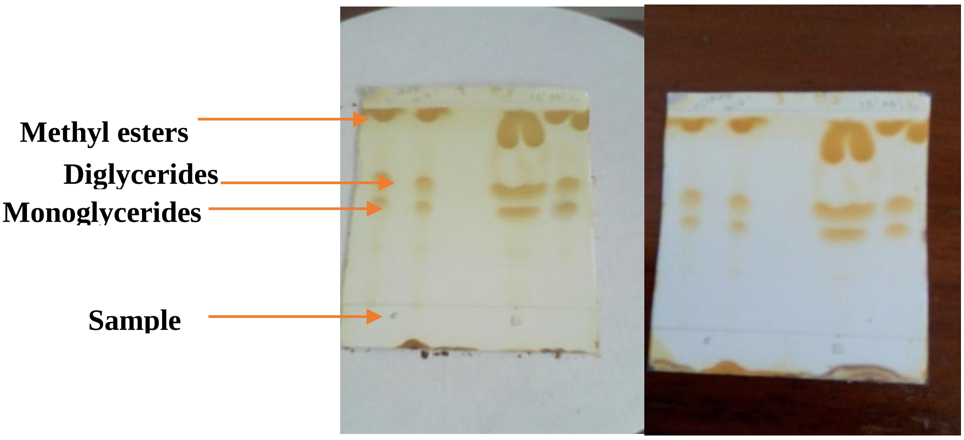


Figure 3. 16: TLC plate showing the separation of FAME constituents.

3.4: **Kinematic Viscosity.**

Kinematic Viscosity is another important parameter to analyse the quality of the biodiesel fuel. It depends on the raw materials used for the production of methyl esters. In literature many models have been proposed to predict kinematic viscosity of biodiesel and many of them are focused on the dependency with temperature. Kinematic viscosity for the biodiesel samples was measured at 25 ℃ and 40 ℃ with viscometer.

Table 3. 8: Measured kinematic viscosity values obtained at different temperatures of biodiesel.

No. of runs	**1**	**2**	**3**	**4**	**5**	**6**
η@ 25℃	6.2	6.6	6.4	5.8	6.0	5.8
η@ 40℃	3.8	3.6	3.4	3.8	4.4	3.2

CHAPTER FOUR

4.0: RESULTS AND DISCUSSIONS

This chapter presents and discusses the results of the characterization of the heterogeneous catalysts prepared and subsequently used for transesterification reactions. The results of the characterization and the catalytic activity of the heterogeneous catalysts were studied and discussed in this section as well.

4.1: XRD Analysis

XRD patterns were recorded using a Bruker D8 Advance diffractometer fitted with a Lynx Eye high-speed strip detector, both using CuKα (1.54Å) sources with a nickel filter, calibrated against SiO_2 (Bruker) standards. Wide angle patterns were recorded over a range of $2\theta = 10^o$-80^o (step size 0.02° , scan speed 0.020° s^{-1}).

The XRD patterns of the developed catalysts are as shown in Figure. 4.1. The XRD spectrum exhibited a well-defined resolved diffraction pattern with prominent peaks at 2θ =18.6°, 28.8°, 31.4°, 34.3°, 47.3°, 49.2°, 54.1°, 57.9° and 59.5° of the catalysts at the same calcination temperature as illustrated in Figure. 4.1. SBA-15 support showed no distinct diffraction peak in the XRD pattern and this implies that the SBA-15 support was mainly present in an amorphous state.

By loading CaO-MoO_3, the CaO–MoO_3–SBA-15 catalyst showed characteristic XRD peaks of MoO_3 at 2θ angles of 34.3° and 49.2° (JCPDS File No. 05-0508).

Calcination drives restructuring and sintering to expose lower coordination stepped (111) and (110) surface planes, which are more polarisable and exhibit much higher transesterification activities under mild conditions [1]. A direct correlation was therefore observed between the surface electronic structure and associated catalytic activity, revealing a pronounced structural preference for (110) and (111) facets (Figure 4.1) [198]. The X-ray diffraction pattern shown in Figure 4.1 explains the crystal structure and phase composition of CaO-MoO_3 nanocrystalline materials. The sharp diffraction peaks at (021), (101), (001), (011), (111), (121) and (002) indicate crystalline nature of CaO-MoO_3 nanomaterials, having lattice parameters **a** = 3.966Å, **b** = 13.82 Å, **c** = 3.703 Å (JCPDS: 05-0506) and strong peaks show crystalline nature of CaO-MoO_3 nanoparticles. The X-ray powder diffraction patterns of MoO_3 and CaO displayed three strong characteristic reflections (100), (110), and (200), and (111), (220) and (002) respectively of hexagonal mesoporous SBA-15 with space group P6mm. The powder diffraction patterns indicate that the primary structure of SBA-15 consists of well-ordered channels, which are maintained after the formation of MoO_3 nanoparticles inside the channels. In addition, the phase cancellation between the pore walls and the guest species MoO_3 leads to a decrease of the intensity of Bragg reflections.

A typical diffraction peak of CaO was also observed at 2θ angles of 47.3° and 54.1° (JCPDS File No. 28-0775) [183]. Obviously, the CaO and MoO_3 phases resulted from the thermal decomposition of calcium and molybdenum precursors. The solid catalyst also exhibited diffraction peaks at 2θ angles of 18.6°, 28.8°, 31.4°, 57.9°, and 59.5°, which could be ascribed to $CaMoO_4$ perovskite (JCPDS File No. 29-0351) [135].
Calcium forms a mixed oxide with MoO_3. Supporting both oxides on SBA-15 mesoporous silica offers a transesterification catalyst with improved stability relative to CaO due the presence of acidic MoO_3 sites on the SBA-15 [1]. The impact of Ca:Mo ratio and calcination temperatures were explored, with a Ca: Mo ratio of 6: 1 maximizing activity for waste cooking oil conversion to methyl esters [1].

The formation of $CaMoO_4$ compound is as a result of the reaction of CaO with molybdenum compound on the surface of SBA-15 silica during the calcination process. The solid reaction between CaO and MoO_3 could give rise to an enhanced stability of the solid catalyst, since the leaching of catalyst components can be reduced upon this interaction. Calcining the prepared sample at 823 K induced CaO and MoO_3 crystallisation, with a corresponding rise in activity; higher temperature calcination did not promote further crystallization and was not beneficial for transesterification.

When the sample was calcined at 1023 K, as indicated in Figure. 4.1c, the characteristic XRD peaks ascribed to CaO, MoO_3 and $CaMoO_4$ obviously disappeared as a result of mesostructure collapse. With functionalizing the sample, the characteristic peaks corresponding to CaO, MoO_3 and $CaMoO_4$ became less intensive in the XRD pattern.

In spite of phosphation, the XRD analysis confirmed the localization of phosphate ions mainly on the oxide surface without detectable phosphate phase. The phosphate ions can be considered to be finely dispersed on the oxide surface. The intensity of the XRD peaks was found to decrease upon phosphate modification as a result of the retardation of crystallization [137-141]. Such lower degree of crystallinity of modified oxides compared to pure oxides is already reported [1-3].

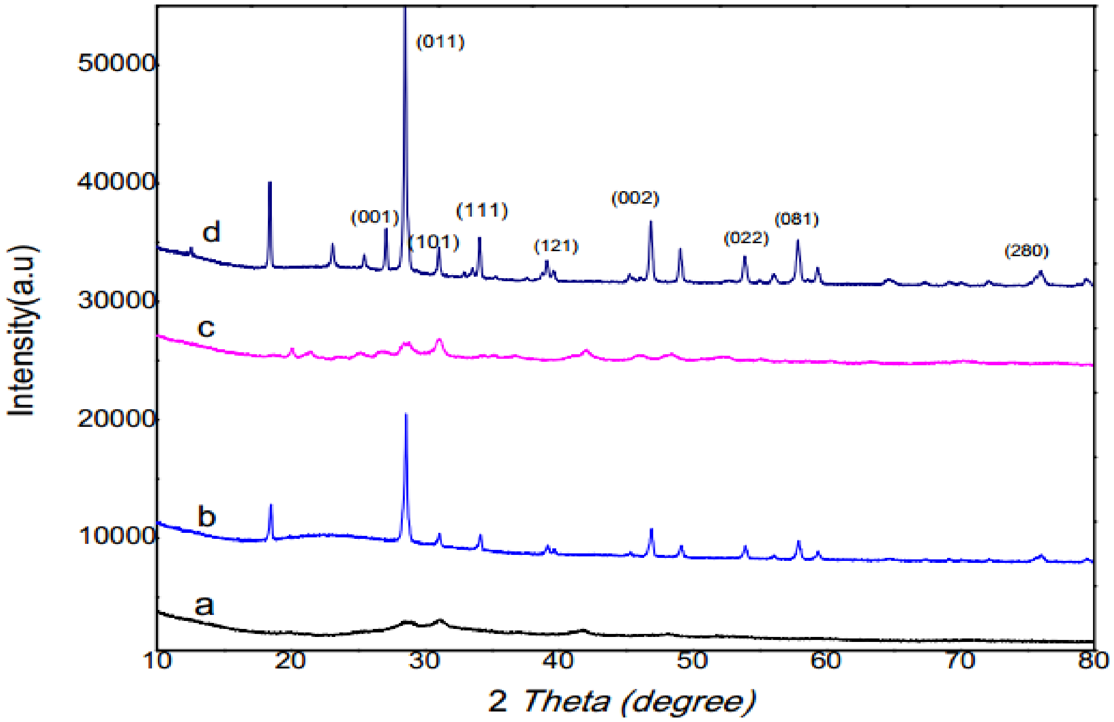


Figure 4. 1: XRD patterns for (a) SBA-15 @ 550℃, (b) CaO-MoO3/PO4-SBA-15@ 550℃, (c) CaO-MoO3/PO4-SBA-15 @ 750℃ (d) CaO-MoO3-SBA-15@ 550℃ catalysts.

4.2: **FTIR Spectroscopy Analysis**

In this work, ATIR was employed as it allowed analysis on a small sample size using a single bounce diamond anvil ATR accessory fitted to a Thermo-Fisher Nicolet IS50 FT-IR spectrometer. Figure 4.2a illustrates the FT-IR spectra of the samples with CaO–MoO_3 loadings. For the SBA-15 silica, there were two IR absorption bands at 3435 cm^{-1} and 1635 cm^{-1} assigned to the O–H stretching and bending vibration of physisorbed water [33].

Figure. 4.2b depicts the FTIR spectrum of phosphate grafted catalyst calcined at 550 °C. The primary infrared bands related to the SBA-15 molecular sieves framework were the asymmetric and symmetric stretching of Si–O–Si at 1087 cm^{-1} and 820 cm^{-1}, and the absorption peak at 465 cm^{-1} could be ascribed to the Si–O bending stretching vibration [142, 143]. Moreover, a weak band at 965 cm^{-1} for the SBA-15 support was associated with Si–OH in SBA-15 silica [144]. As the CaO-MoO_3 was loaded on the SBA-15 support, characteristic IR absorption peaks of SBA-15 network emerged at 1087 cm^{-1} , 820cm^{-1} and 465 cm $^{-1}$ [139, 143]. An interesting observation to be noted was that the 965 cm^{-1} band due to silanol group disappeared upon the loading of calcium and molybdenum compounds and subsequent calcination at a higher temperature. Such a result could be ascribed to the formation of Si–O–Mo and Si–O–Ca bond in the catalyst, and probably led to the increased stability of the solid catalyst.

However, the 3435 cm^{-1} band due to hydroxyl groups on the catalyst surface appeared to be reduced in its intensity indicating that the OH group interacted with calcium and molybdenum oxides and contributed to form Si–O–Mo and Si–O–Ca bond in the calcination process [34]. With further increase in calcination temperature to 1023 K, the peaks completely disappeared as shown in Figure 4.1c. The solid catalyst showed similar IR spectra to the 823 K-calcined samples. Notably, the IR results were in better agreement with the XRD measurements and also conformed to the result of transesterification activity in Section 4.2. The solid catalysts, CaO-MoO_3/PO_4-SBA-15 and CaO-MoO_3-SBA-15 displayed similar IR spectra at 823 K calcined sample.

The presence of phosphate ions in the modified sample was confirmed by the IR spectra which showed a broad peak around 980 cm^{-1}-1087 cm^{-1}, which can be ascribed to the P-O stretching mode of phosphate ions [145].

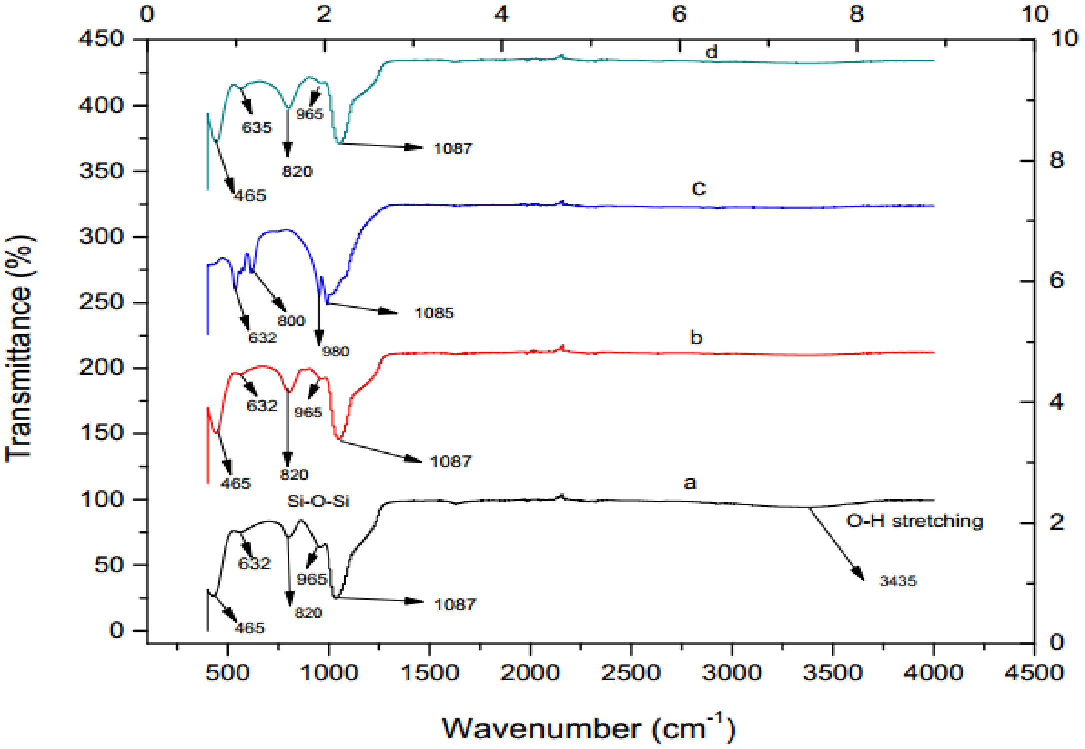


Figure 4. 2: FT-IR spectra for (a) SBA-15 @ 550℃, (b) CaO-MoO3/PO4-SBA-15 @ 550℃, (c) CaO-MoO3/PO4-SBA-15 @ 750℃ (d) CaO-MoO3-SBA-15 @ 550℃ catalysts.

4.3 **Porosity Analysis /Sorptometric Studies**

The textural properties of the catalysts prepared were studied by N_2 adsorption-desorption isotherms as illustrated in Figure. 4.3.

Porosity and surface area were measured using Quantochrome NOVA 4200e instrument by N_2 adsorption using Novawin v11.0 analysis software. Samples were degassed under vacuum at 120 °C for 24 hours prior to analysis. Adsorption and desorption isotherms were recorded at -196 °C. BET surface areas were calculated over the relative pressure range 0.05-0.5 where a linear relationship was observed. Mesopore diameters were calculated applying the BJH method to the desorption branch [146-148].

According to IUPAC classification, the isotherms exhibited type IV curve with a hysteresis loop which is an indication of mesoporous materials. The adsorption-desorption was not a reversible process which led to the appearance of the hysteresis loop between the curves of the adsorption and desorption. While the capillary condensation in the mesopores occurred at higher relative pressures than the capillary evaporation, the hysteresis loop was observed [25, 26]. The pore size distribution (PSD) which represents the structural homogeneity of the developed catalysts confirmed the mesopore structure ($2 < D_p < 50\ nm$) of the catalysts. Based on the analysis of the results, a BET surface area of 336.383 m^2/g with the pore diameter of 3.099 nm and total pore volume of 0.428 cc/g was achieved for the phosphate modified catalyst. The sample calcined at 750 ℃ for 6 hours showed a drastic increase in particle size (44.313 nm) and this is essentially attributed to the particle aggregation followed by crystal growth. The two-step desorption branch [81] and the decrease in pore volume might be attributed to the presence of a pore-blocking effect by PO_4, because the formation of CaO-MoO_3 particles inside the pores of SBA-15 would not significantly affect the pore volume due to the high density of CaO-MoO_3 (4,700 kg cm^{-3}).

The specific area of the phosphate modified sample was found to be higher than that of the corresponding unphosphated sample, which can be ascribed to delayed crystallization [139]. The phosphate groups being well dispersed on the surface prevents the oxide particles from coming closer during calcination. It was also observed that the surface area of the phosphated sample decrease with increase calcination temperature. The phosphation generally leads to an increase in surface area and a decrease in crystallinity and the samples are thermally stable. Phosphation can occur through adsorption at co-ordinatively unsaturated Lewis acid sites and exchange of OH groups by $H_2PO_4^-$ ions. The catalytic activity and surface acid-base properties mainly depend on the amount of the phosphate adsorbed and also the nature of the adsorption [139]. Also the reduction in mesopore volume observed between the non-functionalized and functionalized solid catalysts indicates the filling of the mesopores by the PO_4 particles.

Table 4.1 shows the characteristics of the particle size and crystallite size for the CaO–MoO_3–SBA-15 andCaO-MoO_3/PO_4-SBA-15 calcined at the same temperature. The crystallite size and particle size were calculated using Eqs (3) and (4) respectively. The particle size showed an increasing trend with temperature. At 750 ℃, the phosphated catalyst showed about a tenfold increase in particle size compared to the phosphate grafted one calcined at 550 ℃ which essentially was attributed to particle aggregation followed by crystal growth. This fact is additionally supported by the crystallinity data calculated using XRD data. The samples calcined at 550 °C for 6 h showed drastic decrease in particle size. The crystallinity and particle size did not show a significant variation after calcination at 550 °C. From the isotherms, it can be concluded that the mesoporosity of the support is still preserved after the incorporation of CaO-MoO_3 particles into the SBA-15 materials. The decrease in pore volume can be attributed to the presence of a pore-blocking effect by CaO-MoO_3, because the formation of CaO-MoO_3 particles inside the pores of SBA-15 would significantly affect the pore volume due to the high density of CaO-MoO_3 (4,700 kg cm^{-3}).

Table 4. 1: Shows BET surface area, pore size, pore volume, crystallite size and particle size of the catalysts.

SAMPLE NAME	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cc/g)	Crystallite size (nm)	Particle size (nm)
SBA-15@ 550°C	336.383	3.099	0.464	-	7.432
CaO–MoO_3–SBA-15 @ 550°C	187.703	5.058	0.713	6.712	7.265
CaO-MoO_3/PO_4-SBA-15@ 550°C	336.383	3.099	0.428	7.945	4.054
CaO-MoO_3/PO_4-SBA-15 @ 750°C	30.773	1.519	0.113	-	44.313

The average crystallite size was determined based on XRD peak broadening using the Scherrer equation Eq. 3 [10].

$$t = \frac{0\cdot 9\lambda}{B\cos\theta} \quad \text{..} (3)$$

t = the average crystallite size,

B = the broadening of the diffraction line measured at half maximum intensity, λ = the wavelength of the X-ray radiation and θ = the Bragg angle.

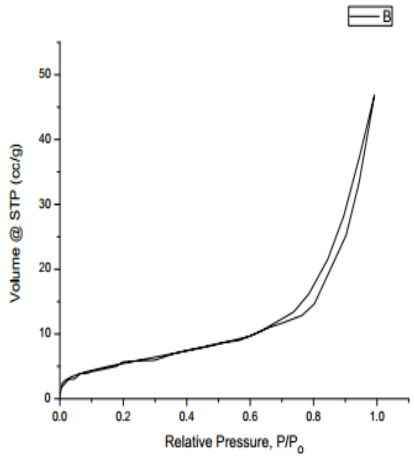
The average particle size was estimated [11] by assuming that all particles have the spherical shape and size. The particle size, D, is given by the Eq. 4;

$$\boldsymbol{D = \frac{6000}{S_{BET} \times \rho}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

S_{BET} = BET specific surface area

ρ = True density of the sample.

The pore size distribution of the meso pores present in the catalysts are presented in Figures 4.2, 4.3 and 4.4 respectively.



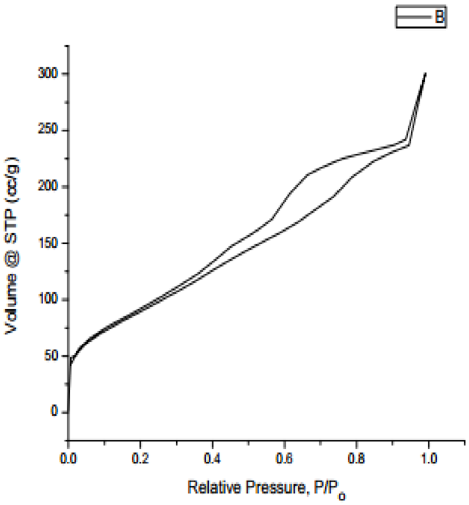
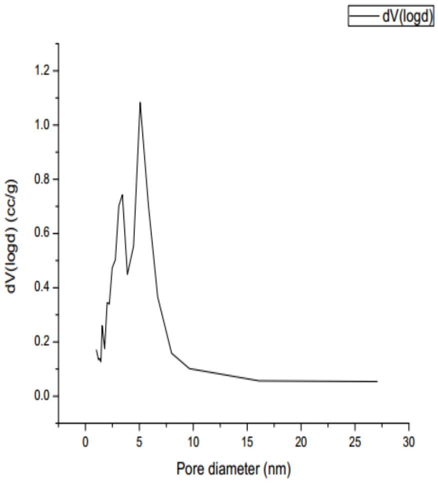


Figure 4. 3: N2-isotherm of CaO/MoO3/PO4 @ 550℃ Figure 4. 4: Pore size distribution

Figure 4. 1: N_2-isotherm of $CaO/MoO_3/PO_4$ @ 550℃ Figure 4. 2: Pore size distribution



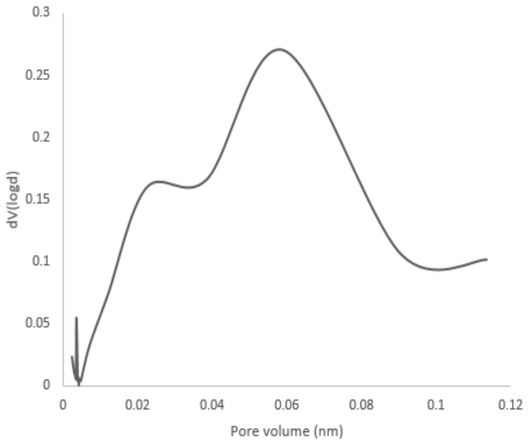


Figure 4. 5: N2-isotherm of CaO–MoO3 @ 550℃ Figure 4. 6: Pore size distribution

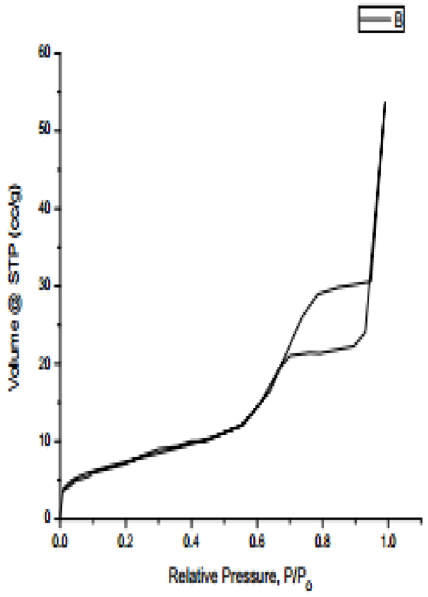


Figure 4. 7: N2-isotherm of CaO-MoO3/PO4@750℃

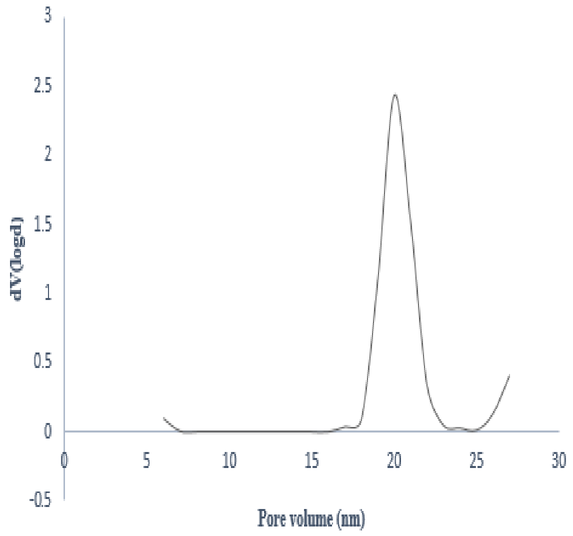


Figure 4. 8: Pore size distribution

4.4: Optical microscopic analysis

The microscopic view of SBA-15, CaO-MoO$_3$-SBA-15 and CaO-MoO$_3$/PO$_4$-SBA-15 are presented in the Figure 4.4 (a-c). Figure 4.9 shows the microscopic view of the SBA-15 before loading Ca (NO$_3$)$_2$ and (NH$_4$)$_6$Mo$_7$O$_{24}$ precursor solutions. The sample showed cloudy pores with widely dispersed particles.

Figure 4.10 shows the microscopic view of the impregnated sample. The sample showed agglomeration of particles with heavy crystal growth. The sample also demonstrated well-defined pores on the silica template support with regular and smaller particles.

Figure 4.11 illustrates the view of phosphate graftedCaO-MoO$_3$ nanocomposite oxide calcined at 550℃. The microscopic view of the phosphate modified sample shows the presence of uniform nanoparticles. Optical microscopic observation indicates that surface functionalization is quite effective in the preparation of nanosize particles.

During the hydrothermal synthesis process, the reactants are uniformly dispersed at molecular level in the mixture. When hydrolysis occurs, the nucleation and growth of the particles take place through only short-distance diffusion of the nearby atoms. Due to the shorter lifespan of hydrothermal reaction, the long-distance diffusion of the atoms is not facilitated resulting in the formation of nanosized materials.

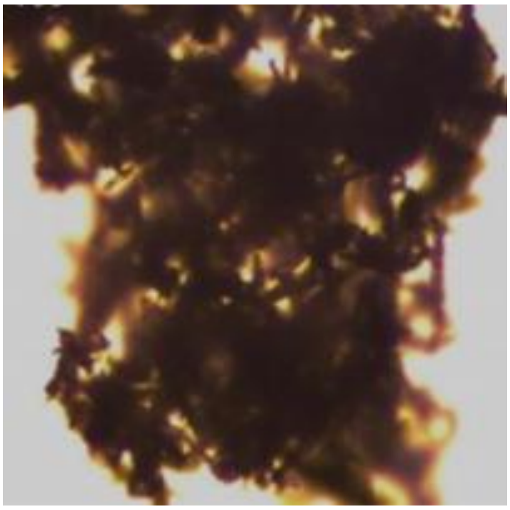


Figure 4.9: SBA-15 @ 550℃

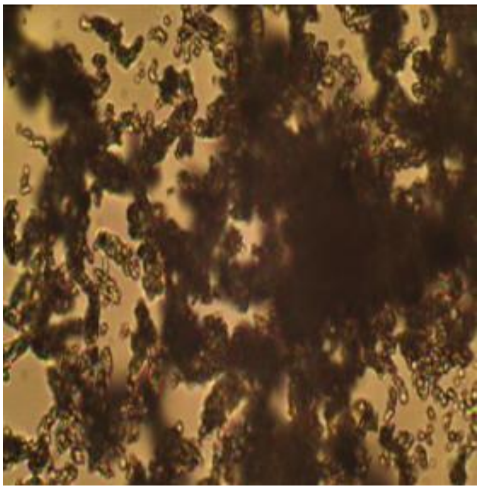


Figure 4.10: CaO-MoO3-SBA-15 @ 550℃

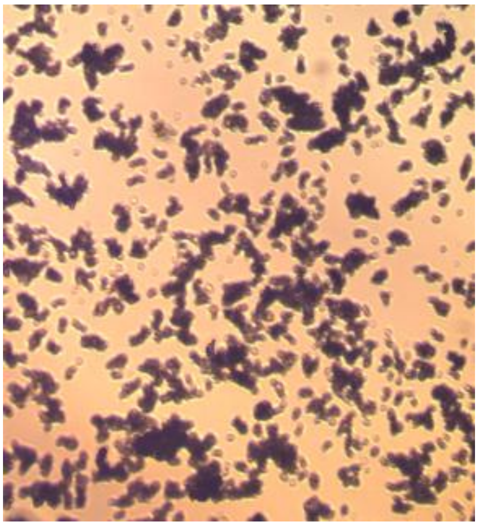


Figure 4.11: CaO-MoO3/PO4-SBA-15 @ 550℃

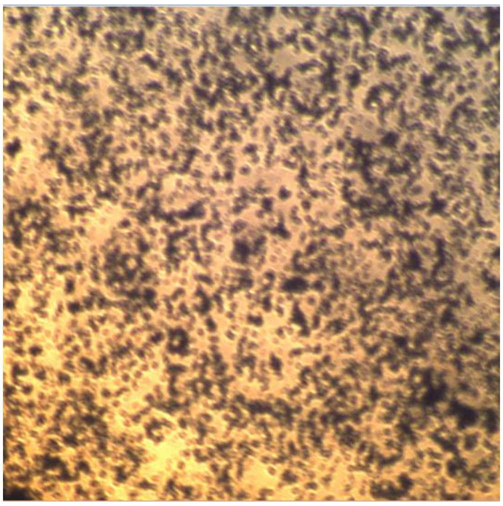


Figure 4.12: CaO-MoO3/PO4-SBA-15 @ 750℃.

4.4 Biodiesel characterization analysis

To ascertain the quality of the final biodiesel product obtained under the optimal conditions, biodiesel samples were analysed in the Materials laboratory, University of Ghana, experimentally. The following parameters were analysed using certified procedures; (i) kinematic viscosity at 40 ºC, (ii) acid value (iii) absorbance.

The maximum acid value obtained for the biodiesel produced from the waste cooking oil in this study was 0.03 and this is far below the required value. The acid value measures the content of free fatty acids in biodiesel. The presence of free fatty acids influences fuel aging, the European Standard specifies a maximum value of 0.5 mg of KOH/g of sample.

The kinematic viscosity of the biodiesel sample measured at 40 ºC in this study ranged from 3.2 to 4.4 mm^2/s (Table 3.8).The kinematic viscosity is an important property considering fuel atomization, as well as fuel distribution. For biodiesel to be used in diesel engines, the kinematic viscosity must be between 3.5 and 5.0 mm^2/s. Different viscosities are as a result of the incomplete reaction of the waste cooking oils or the inadequate biodiesel purification, which leaves conjugated or free glycerol in the methyl esters phase. The presence of glycerides alters the apparent viscosity of methyl esters, revealing the extent of the transesterification reaction and the methyl esters phase purity.

Figure 4.9 shows a typical absorbance curve for diluted waste cooking oil methyl esters in the range of 200 to 360 nm with resolution of 1 nm by using a GENESYS 10S UV-VIS spectrophotometer with optical path of 1 cm. The FAME absorbs in the ultraviolet range. The dilution was necessary to achieve the absorption within the spectrophotometer detection range. Peaks were observed at 275 and 305 nm. The absorbance for methyl esters produced very similar absorbance, with no significant differences. Therefore, it can be concluded that the absorbance in this band is not affected by the biodiesel produced at different temperatures. Analysis of the absorbance curves for various biodiesel produced at different temperatures showed that a single wavelength in the UV range could be used to detect the methyl ester level.

According to Beer's law, the absorbance of a chemical component is proportional to its molar concentration [135] Eq. (5).

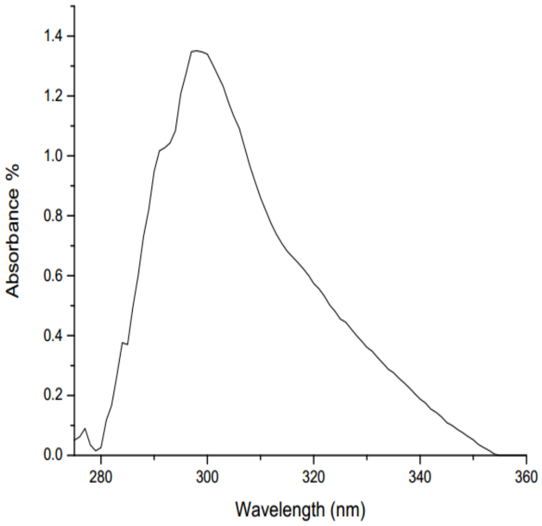
$A = \varepsilon bl$ …………………………………………………………………….. (5)

A = Absorbance

ε = molar absorptivity

b = concentration of solution sample

l = sample path length



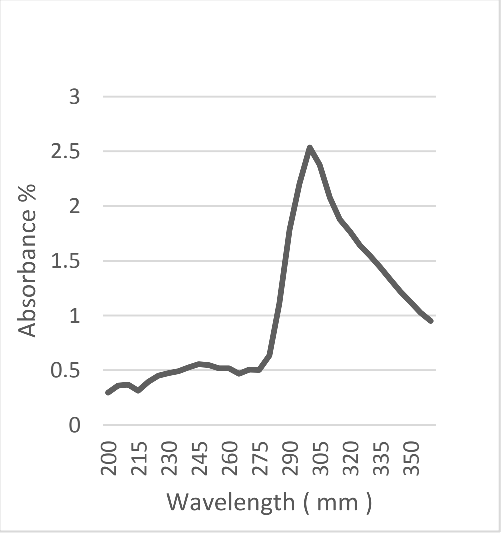


Figure 4. 9: Absorbance of biodiesel diluted in n-hexane

Figure 4. 10: Absorbance of biodiesel diluted in n-hexane.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

This section gives a brief account of the overview of the major issues addressed in the previous chapters and to what extent the stated aims and objectives were achieved and research questions answered. Subsequently a summary of the main contributions made and major findings are also enumerated. Considerations of possible future directions and recommendations for further work are also stated.

5.1 Chapter overview

The main aim of this research work is to develop efficient and environmentally benign heterogeneous catalysts for biodiesel production. The design and use of these solid catalysts aimed to address the drawbacks of the conventional homogeneous base catalysis using NaOH or KOH. For this reason, heterogeneous CaO–MoO_3/PO_4–SBA-15 and CaO–MoO_3–SBA-15 catalysts were prepared by incipient impregnation method, and the prepared catalyst was subsequently functionalized by phosphate. The synthesized catalyst was tested for the transesterification process of waste cooking oil to produce methyl esters.

Different techniques such as X-ray diffraction, Fourier transform infrared spectroscopy; sorptometric and optical microscopy analysis were used for the characterization of the solid catalyst. The catalytic activity was largely dependent on the calcination temperature and surface modification. The solid catalyst, CaO–MoO_3/PO_4 calcined at 823 K, showed very high catalytic activity.

In this study, 3 wt % of the catalyst with methanol/oil molar ratio of 6:1 at reflux of methanol was used to achieve 99.4% conversion of waste oil after 6h of reaction. The catalyst can easily be recovered and reused without significant loss of activity.

5.2 Conclusion

In this investigation, the surface and structurally modified CaO–MoO_3–SBA-15 catalyst was successfully synthesized by incipient impregnation method using calcium nitrate and ammonium heptamolybdate as precursors. The phosphate grafted CaO–MoO_3–SBA-15 nanocomposite oxide was prepared by aqueous incipient wetness impregnation method and subsequently post phosphate grafted to improve its surface properties and pore networks, in order to enhance its catalytic performance. The interaction among CaO, $MoO_3$and PO_4 on the surface of SBA-15 silica was responsible for the improvement of the catalyst stability. The molybdenate component was observed to be present in a highly dispersed state in the form of isolated tetrahedral and polymolybdenate clusters (ie perovskite) in the nanocomposite oxide material. The catalytic activities of the synthesized catalyst are evaluated for the synthesis of waste cooking oil to produce methyl esters. The catalytic activity in the transesterification reaction was largely dependent on the calcination temperature and surface functionality of the synthesized catalysts. The solid catalyst $CaO–MoO_3/PO_4–SBA$-15 calcined at 823 K for 6 h, was found to be the best catalyst, which possesses the highest textural properties and produce the oil conversion of 99.3% by using a 3 wt. % of catalyst with methanol/oil molar ratio of 6:1 at reflux of methanol.

The use of the solid catalysts in this study possesses potential to new developments in the production of biodiesel. As it allows process simplification and reduces processing costs by improving the mass transfer limitation of the three phase reaction and simplifies the product purification processes as compared to what is required in conventional homogeneous catalysis.

It was observed that biodiesel can be conveniently produced from low quality waste cooking oil feedstock using heterogeneous catalyst.

The visible absorption spectrum seems not to be suitable for direct sensing of transparent biodiesel impurities such as glycerol, mono-, di- and triglycerides, since the pure components do not have absorption in the visible range. However, the visible range with the combination of ultraviolet range could be appropriate for sensing of some parameters of biodiesel quality and is the subject of future research. Additionally, combining visible absorption spectra with ultraviolet range has a potential for sensing some properties of biodiesel quality enumerated in ASTM specification.

5.3 Recommendations for future study

The scope of this thesis work suggests that there is a plethora of further works that still need to be done in order to improve heterogeneous catalysis and design of catalysts materials.

- The effect of different phosphoric acid concentration on the catalyst surface modification should be investigated.
- In order to make the production process of biodiesel more cost effective, the chemistry of heterogeneous catalysts such as solid alkaline catalysts need to be thoroughly explored, well developed and use in biodiesel production.
- Concerted efforts should be made in order to exploit ways of improving the kinetic rate of CaO-based catalysts, since it has high catalytic activity, long lifespan and operates under mild reaction conditions.
- Determination of the purity and yield of the glycerol (by-product) from the transesterification reactions should be carried out.
- A study of the effect of molar ratio on transesterification reactions with the heterogeneous catalyst need to be investigated.
- Determination of the effect of different catalyst loading and the effect of reaction temperature on methyl ester yield must be investigated.
- The use of ultraviolet absorption spectrum and its potential application for sensing quality of biodiesel needs further investigation.
- The biodiesel produced under phosphate grafted catalyst should be characterised using GC-MS techniques to ascertain the actual yield and quality of the FAME.

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Appendices

Calculation of methyl ester yield

% methyl ester yield (%ME) = $\frac{V_{O-V_B} *C*M*100}{1000}$

……………………………………….. (1)

V_O = volume of blank oil in ml

V_B = volume of H_2SO_4 required for the titration of biodiesel (ml)

C = concentration of the H_2SO_4 used

M = molecular weight of ester.

Calculation of acid value of FAME

$AV = \frac{(A-B)\times C\times 56.1}{M} mgKOH/$

g…………………………………………………………… (2)

AV = the acid value

A = titrant volume in ml for sample titration

B = titrant volume in ml for blank titration

C = concentration of KOH in molL^{-1}

M = mass of the tested sample in grams and 56.1is the molecular weight of KOH.