

Production and Life Cycle Assessment of Biodiesel from Three Waste Oils

By

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A Thesis Submitted in the Department of Chemical Engineering to the
School of Post Graduate Studies

As part of the requirements for the award of the degree of Doctor of Philosophy
(Ph.D.) in Chemical Engineering, College of Science and Technology, Covenant
University, Nigeria.

April, 2015

CERTIFICATION

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DEDICATION

To Omniscience God: the author of knowledge

To Omolola Ayoola, a virtuous and dependable wife

To IbukunOluwa, Oluwadamilola and Toluwani: God's heritage

To Pa Felix Adeyefa (Late) and Madam Esther Adeyefa: dependable and caring parents

To Oluwabunmi Mary Faniyan (Late): my loving sister who made indelible impacts on Earth.

ACKNOWLEDGEMENT

If I have seen further it is by standing on the shoulders of giants.

Isaac Newton (Letter to Robert Hooke, February 5, 1675).

God Almighty, the author and the finisher of my faith, deserves all the glory over my life. He fashions, guides and sustains me on the path of success in this feat through the inspiration of Holy Spirit and intervention of angelic human beings.

With deep sense of humility and respect, I appreciate the Chancellor of Covenant University, Dr. David Oyedepo; a visionary and revolutionary leader that provided a platform through which this dream of mine comes to limelight. Indeed, you are success personified. I owe the entire management team of Covenant University gratitude; particularly, the kind-hearted Vice Chancellor, Prof. Charles Ayo and the amiable Deputy Vice Chancellor, Prof. Taiwo Abioye. May God continue to crown your endeavours with outstanding results (Amen).

This research work would not have been made possible without the valuable contributions of my supervisor, Prof. Kofi Hymore. His wealth of knowledge, guidance and keen observations paved the right direction for the work. He persistently ensured that comprehensive and thorough work was done. I would like to express the deepest gratitude to my co supervisor, Dr. Conrad Omonhinmin, who has the attitude and substance of a genius: he constantly and convincingly convened a spirit of possibility mentality in regard to this task. His persistent help and corrections have made this work a reality.

I greatly cherished the unrelenting efforts of Prof. J. Omoleye, Prof. J. Odigure, Prof. S. Adefila and Prof. O. Omatete. They demonstrated high level of effective mentoring skills. I can never forget the role of Dr. O. Ayeni, he assisted me a lot in this research work. Many thanks to Dr. T.

Adebayo, Dr. V. Efevbokhan, Engr. O. Adeeyo, Engr. (Mrs) M. Ojewumi,. I received a lot of encouragement, support and cooperation from them all. Also, I cherish the efforts and valuable contributions of the following members of staff of the department: Engr. S. Udohiltinah, Mrs. T. Oladimeji, Mr. S. Sanni, Mrs. O. Abatan, Miss. R. Oresangun, Mr. J. Omodara, Mrs. O. Oyeniyi, Mrs. E. Ogunniyi, Mrs U. Imo, Mrs. B. Omote and Mr. A. Jasper. May God remember them all for good as well (Amen).

Analysis of this work would not have been made possible without the generosity of Dr. P. Anawe, Mr. O. Nwaogu, Miss. R. Adeyemi, Miss. R. Anwuri and Mr. I. Eromosele. I am indeed grateful for all you did for me. I greatly appreciate the efforts of Late Dr. M. Obande, a humble and selfless man that was unreservedly committed to the progress of everyone that he had contact with. Thanks to Dr. O. Nwinyi for his excellent work in the proofreading of this thesis.

Finally, I am overwhelmed by the support received from my wife, Omolola Ayoola. Her prayers, encouragement and advice contributed to the success story of this task.

May God Almighty perfect all issues of concern in the life of everyone that made my PhD dream a reality (Amen).

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ABBREVIATIONS

Symbol	Meaning
ARCN	Agricultural Research Council of Nigeria
ASTM	American Society for Testing and Materials
BB(4)	Box-Behnken Fractional Factorial Design
BEC	Bio-Fuel Energy Commission
BRA	Bio-Fuel Research Agency
B100	Pure biodiesel
CPKO	Crude Palm Kernel Oil
CN	Cetane Number
DAG	Diacylglycerol
DALY	Disability Adjusted Life Year
DG	Diglyceride
DOE	Design of Experiments
EN	European Committee for Standardization
EPD	Environmental Product Declaration
FA	Fatty Acid
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FIIRO	Federal Institute of Industrial Research Oshodi
FRIN	Forestry Research Institute Nigeria
FSCS	Federal Soil Conservation School

GWP	Global Warming Potential
IARES	Institute for Agricultural Research and Extension Services
IITA	International Institute of Tropical Agriculture
IPP	Integrated Product Policy
ISO	International Standard Organisation
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
MAG	Monoacylglycerol
MG	Monoglyceride
NABDA	National Biotechnology Development Agency
NAC	Nigerian Automotive Council
NASC	National Agricultural Seeds Council
NCAM	National Centre for Agricultural Mechanisation
NCRI	National Cereal Research Institute
NIFOR	Nigerian Institute for Oil Palm Research Council
NNPC	Nigeria National Petroleum Corporation
NRCRI	National Root Crops Research Institute
NSPRI	Nigerian Stored Products Research Institute
PDF	Potentially Disappeared Fraction of species
PM _{2.5}	Particulate Matter with diameter of 2.5 micrometer or less
RMRDC	Raw Materials Research and Development Council
STCO	Science and Technology Complex

TAG	Triacylglycerol
TEG	Tri-Ethylene Glycol
TG	Triglyceride
WCO	Waste Cooking Oil
WGO	Waste Groundnut Oil
WO	Waste Oil
WSO	Waste Soyabean Oil

ABSTRACT

Converting the huge amount of waste cooking oils presently generated globally to biodiesel as complementary energy source to fossil fuel is one of the major routes to sustainable energy management. However, producing quality biodiesel at established optimum conditions, through a clean technology with favourable environmental implications is of greater importance. This research focused on achieving the latter through alkali catalysed trans-esterification process of biodiesel production and life cycle assessment (LCA) of the biodiesel produced using SIMAPRO 7.3.3. In this research, the comparative analysis of the use of KOH and NaOH, as catalysts in the trans-esterification of Waste Groundnut Oil (WGO), Waste Soyabean Oil (WSO) and Crude Palm Kernel Oil (CPKO); as well as the life cycle assessment of the biodiesel produced from WGO, WSO and CPKO were established. The results obtained showed that, under similar conditions, biodiesel yields from the trans-esterification of oils using KOH as catalyst are higher than the yields from the NaOH catalysed process. Comparatively, the optimum conditions for biodiesel yield from KOH catalysed trans-esterification of WGO are; 10.67 methanol/oil mole ratio, 0.86 w/w Oil catalyst concentration at 60⁰C and 71 minutes reaction time. For NaOH catalysed trans-esterification of WGO, the optimum conditions are 9.94 methanol/oil mole ratio, 0.70 w/w Oil catalyst concentration at 60⁰C and 72 minutes reaction time. Optimum conditions for biodiesel yield from KOH catalysed trans-esterification of WSO are; 9.76 methanol/oil mole ratio, 1.04 w/w Oil catalyst concentration at 60⁰C and 70 minutes reaction time. For NaOH catalysed trans-esterification of WSO optimum conditions are 9.00 methanol/oil mole ratio, 0.70 w/w Oil catalyst concentration at 61⁰C and 70 minutes reaction time. The optimum conditions for biodiesel yield from KOH catalysed trans-esterification of CPKO are; 9.51 methanol/oil mole ratio, 1.24 w/w Oil catalyst concentration at 62⁰C and 80 minutes reaction time. For NaOH

catalysed trans-esterification of CPKO, the optimum conditions are 9.57 methanol/oil mole ratio, 1.10 w/w Oil catalyst concentration at 62⁰C and 85 minutes reaction time. The accuracy of the optimal conditions obtained in all cases was justified by the optimal desirability values of approximately 1 in all cases. A simple, cost effective and energy efficient model for the prediction of biodiesel cetane number (CN) was derived. Statistical analysis showed low value of 3.28 % of Average Absolute Deviation (% AAD) for the proposed biodiesel CN model from the reported biodiesel CN model (experimental). The values of biodiesel CN calculated using the proposed model fall within ASTM specification. Analysis of the possible environmental impacts through the LCA of the biodiesels from WGO, WSO and CPKO recorded the possible emissions from the production processes as well as the products; and reports on the impacts of these emission on human health, ecosystem quality and climate change. The emission effects are potentially more pronounced on the ecosystem quality, followed by human health and least on climate change.

CHAPTER ONE

INTRODUCTION

1.0 Background of the Study

Global energy demand is sky-rocketing due to increased world population and more industrialised countries. The world is dependent heavily on coal, petroleum and natural gas for energy and as feedstock for chemicals. These sources are commonly termed as fossil or nonrenewable resources (William, 2006). Fossil resources are extracted from the Earth's crust, processed and burnt as fuel or converted to chemicals. The process of combustion of fossil resources involves the oxidation of carbon and hydrogen atoms to produce carbon dioxide, water vapour and heat released. The burning fossil fuels cause environmental concerns such as greenhouse gases (GHG) emission, the major substance responsible for climate change. Other harmful substances released during fossil fuel production and utilisation include sulphur oxides (SO_x), nitrogen oxides (NO_x) and methane (Lee and Shah, 2013).

However, the world economy depends on energy generation. Hence, the consequences of inadequate energy could be severe. These have prompted world leaders, organisations, industries and educational institutions to look for alternative energy sources that are sustainable, with less negative environmental impact. Energy production from biomass such as crop oils, woody and waste materials has a great advantage over fossil fuels (Lee and Shah, 2013).

Biomass has been explored as a nearly carbon neutral substitute for fossil fuels because of its ability to recycle carbon during its growth. Biomass can be classified broadly as recent biological origin of all matter on the earth's surface (Debalina and Ralph, 2013). Examples of biomass

(energy feedstocks) are plant oils, animal fats, cellulose and lignin. The energy producing substances derived from biomass are referred to as biofuels.

As reported by Lee and Shah (2013), biofuel technologies (both the processes and energy feedstocks) are not potentially equal in their abilities to contribute towards the attainment of clean environment and sustainability. The sources of biofuels determine the environmental, economic and social impacts of such biofuels.

Considering Nigeria as a case study, biodiesel (liquid biofuel from vegetable oils or animal fats) seems to be of the promising alternative to fossil fuels. This is because the crops required for biodiesel production are cultivated in large quantity, under favourable climatic conditions. Biodiesel technology involves simple procedures that can be practiced by even rural dwellers (making biodiesel easily available). Also, the fuel is renewable, sustainable and environmentally friendly. In addition, it does not require petroleum-diesel engine modification (William, 2006).

However, high yield and high quality biodiesel can only be achieved through scientific assessment of production process. Biodiesel can be produced from trans-esterification process which involves chemical reaction between plant oil and methanol (alcohol) in the presence of a catalyst (such as KOH) to give biodiesel and glycerol. The assessment of biodiesel production includes the use of different feedstocks for biodiesel production (in order to evaluate such feedstocks in terms of their yields), consideration of the most suitable alkali catalyst, consideration of the effect of varied factors of production and establishment of optimum conditions for biodiesel production (Filemon, 2010).

Waste vegetable oils are the preferred feedstocks for biodiesel production. This practice is cost effective and also proffers solution to the pollution problem resulting from the wrong disposal of

waste oils (Sunisa *et. al.*, 2011). The three waste oils that would be assessed in this research work are waste groundnut oil, waste soyabean oil and crude palm kernel oil. The choice of these three oils is based on the fact that they are readily available in large quantities in Nigeria (Abila, 2010).

Case-specific analyses of these feedstocks and the production processes are required in order to understand the environmental implication and benefits associated with the biodiesel as biofuel (Lee and Shah, 2013). These analyses can be achieved by considering the life cycle assessment of the biodiesel produced.

Life cycle assessment (LCA) is an analytical tool that is useful for evaluating and comparing the environmental impacts of materials and technologies (existing and emerging). LCA of biodiesel production from different waste oils (as feedstocks) will aid in the decision making process of choosing the most suitable Nigerian waste oil for biodiesel production, because LCA reveals both the kind and amount of harmful substances released (during production or consumption) by the feedstocks and/or products.

Results from LCA can be utilised to incorporate green design objectives into engineering-related decision making. Governments, consultants, academicians, and industries can use LCA to help identify environmental impacts associated with “cradle-to-grave” activities of biodiesel and even the processes involved (William, 2006). Life cycle assessment is of particular importance in providing information to ensure that environmental burdens are not shifted from one life cycle stage to another.

1.1 Statement of the Research Problem

The current demand for energy is insatiable. The crisis surrounding the cost and environmental effects of fossil fuels both in the present and nearest future has brought up the need to look for alternative source of energy (William, 2006).

Biodiesel is one of the promising alternatives to fossil fuels in Nigeria, because the nation has in abundant the resources required for biodiesel production. Embracement of biodiesel in Nigeria will address the issue of recurrent fuel scarcity, poor electricity generation in rural areas and environmental pollution.

Converting the huge waste cooking oils around to biodiesel is not enough, producing quality biodiesel at established optimum conditions, through a clean technology with good economic value is of great importance. This research is to provide answer in this direction, so that people in rural areas can successfully embark on biodiesel production.

Nigeria, as a developing nation, need not only to make significant impact in global biodiesel production, but also to ensure that the biodiesel technology adopted (which include procedures and feedstocks) meets the international standards, putting into consideration the environmental implication associated with it. The life cycle assessment (LCA) of biodiesel is one science based tool that can address such task.

1.2 Aim and Objectives of the Study

The aim of this research work is to establish optimum conditions for the production of high yield and environmental friendly biodiesel from the trans-esterification of waste groundnut oil (WGO),

waste soyabean oil (WSO) and crude palm kernel oil (CPKO) and investigate the life cycle assessment of biodiesel produced from these oils.

The objectives of the research study are:

1. To determine a more suitable alkali catalyst (between KOH and NaOH) for waste oil trans-esterification.
2. To establish optimum conditions for biodiesel production by considering methanol/oil mole ratio, catalyst concentration, reaction time and reaction temperature.
3. To formulate a model suitable for the prediction of biodiesel cetane number.
4. To perform the Life Cycle Assessment (LCA) of biodiesels produced from waste groundnut oil, waste soyabean oil and crude palm kernel oil.
5. To predict the environmental impacts of utilising the biodiesel produced.

1.3 Significance of the Study

Many advanced countries (Germany, USA, France, Malaysia etc.) pay a lot of attention to research and development of biodiesel technology and this has resulted into huge profit in these countries. Nigeria, with a population of over 160 million people, ought not to be left out in this development, considering the huge amount of waste vegetable oils carelessly dumped into our streams, land and sewage on daily basis (Abila, 2010). Converting these less valued oils to biodiesel, at commercial level, is a right and timely step in developing our economy and improving the health of our environment.

The research work, among other things, will guide in the choice of suitable feedstocks for the production of biodiesel through the application of LCA of biodiesel (considering the human

health and environmental implications). In addition, the LCA will assist in the evaluation of the sustainability of a future biodiesel industry. Some of the benefits the nation stands to derive from biodiesel production and LCA of biodiesel produced include:

- Reduction in total reliance on petroleum and crude oil products,
- Reduction in emissions of greenhouse gases.
- Economic growth in the form of employment in rural areas.
- Reduction or elimination of waste oil pollution
- Diversification of income and economy in the country
- Improved knowledge on environmental impact of biodiesel production and utilisation.

1.4 Scope and Limitation of the Study

Research work was restricted to the trans-esterification of crude palm kernel oil, waste groundnut oil and waste soyabean oil. The determination of the molecular weight of the oil triglycerides was based on the fatty acids profiles obtained from Gas Chromatography system. Methanol was the only alcohol considered during trans-esterification process, and the two catalysts used were KOH and NaOH. Laboratory scale batch reactor was simulated and used. Cetane number of biodiesel produced could not be measured because of equipment limitations (an important parameter in the assessment of biodiesel). Life cycle assessment of biodiesel was based on biodiesel purification stages.

CHAPTER TWO

LITERATURE REVIEW

2.0 Basic Concepts of Biofuels

This chapter considers the basic or fundamentals on energy from biomass as reported by researchers. These will be the baseline information upon which further research work would be made in the subsequent chapters.

2.1 Biofuels

Fuels are substances that are burned to produce energy. Biofuels are fuels derived from biomass. Biomass is organic matters obtained from plants and animals. It comprises mainly wood, agricultural crops and products, aquatic plants, plant and animal wastes (Filemon, 2010). This implies the sources of biofuels are renewable.

In its most general meaning, biofuels are all types of solid, gaseous and liquid fuels that can be derived from biomass. Examples of solid biofuels include wood, charcoal and bagasse. Wood and charcoal are widely used as fuel for domestic purposes such as cooking in the rural areas of most developing countries. Waste bagasse, the fibrous material produced from sugar cane processing, is extensively used for steam and electrical power generation in raw sugar mills (Debalina and Ralph, 2013; Filemon, 2010).

Examples of gaseous biofuels include methane gas and producer gas. Methane can be produced from the anaerobic fermentation of animal wastes, wastewater treatment sludge and municipal wastes in landfills. On the other hand, producer gas can be made from the pyrolysis or

gasification of wood and agricultural wastes. Examples of liquid biofuels include ethanol, plant oils and biodiesel.

2.2 Development Status of Biofuels

2.2.1 Development Status of Biofuels in Africa

Renewable energy technologies and specifically biofuels offer developing countries a self-reliance energy supply both at local and national levels, with potential economic, environmental, social and security benefits (Feto, 2011). Governmental and research institutions are playing leading roles in establishing and implementing rational energy policies and incentives to encourage investment in biofuel across the continent. Information exchange and experience sharing have been encouraged among institutions and practitioners who engaged in the sustainable energy development. But a lot still need to be done in order for Africa (as a continent) to be seen as a force to reckon with in the global map of biodiesel production.

According to United States Energy Information Administration (2013) biodiesel production and consumption both in Africa and the global world are shown in Figure 2.1 and 2.2. The figures show that the insignificant biodiesel barrels in reserve globally, for production almost equates consumption per day.

Edirin and Nosa (2012) reported that global energy demand is expected to grow by about 50% by 2025. This implies that efforts need to be intensified to ensure exponential rate of global biodiesel production is achieved. African countries, especially Nigeria with the highest population, have a lot to do if they are to make significant impact in global biofuel production to

generate sustainable energy which the continent requires. There was no commercial biodiesel production in Africa until 2008 (Figure 2.2). And what is being produced is not up to 0.1 percent of global production.

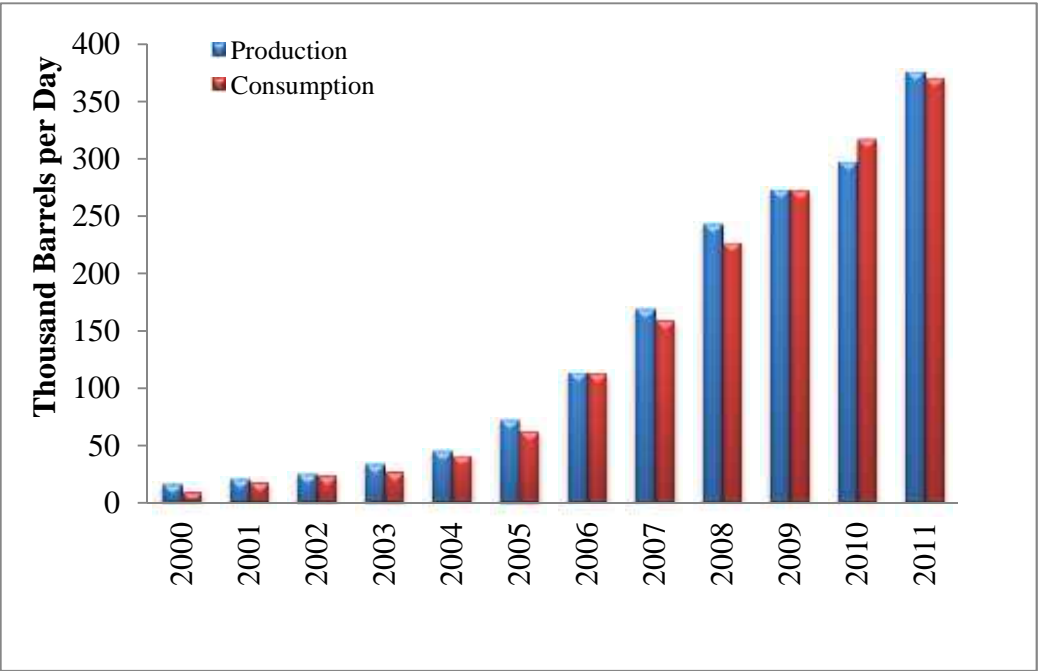


Figure 2.1: World Biodiesel Production and Consumption

Source: US EIA (2013)

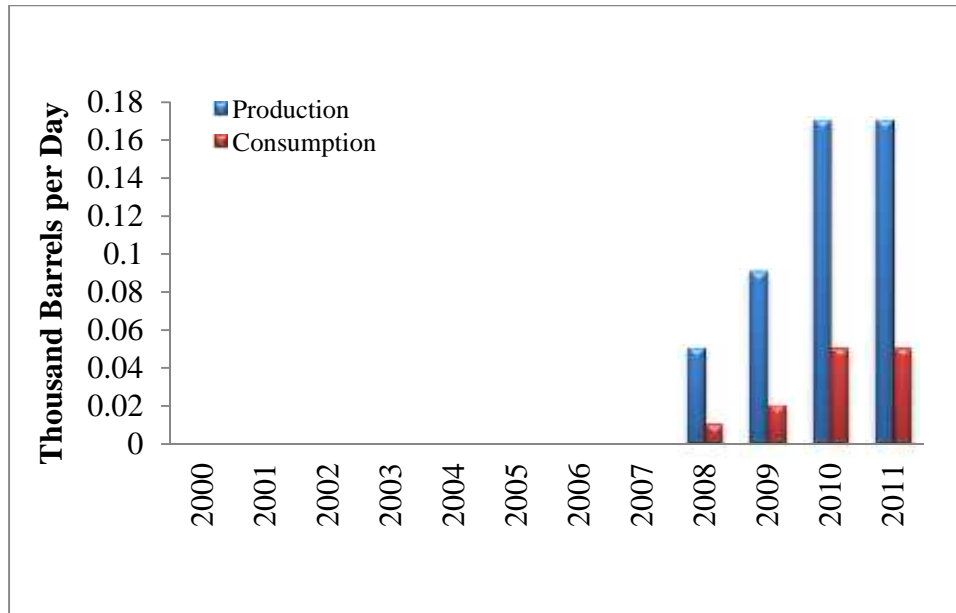


Figure 2.2: Biodiesel Production and Consumption in Africa
 Source: US EIA (2013)

2.2.2. Development Status of Biofuels in Nigeria

Nigeria is yet to announce its presence in biofuel production at commercial level, despite its abundant biofuel feedstocks. Biofuel resources in Nigeria for ethanol production include sugarcane, cassava, maize, rice, sorghum, while resources for biodiesel production include palm oil, groundnut oil, coconut oil, soyabean oil, jathropha oil and sesame oil (Edirin and Nosa, 2012; Agba *et. al.*, 2010).

According to Abila (2010), average yields of Nigerian biofuel production crops in 2007 are as shown in Table 2.1. From the table, it can be inferred that Nigeria has significant potential not only to be a great producer, but also major supplier of biofuels in the committee of nations. The report showed that Nigeria is the highest producer of cassava tuber in the world. Cassava is the main raw material required for bioethanol production. Globally, Nigeria ranked third, third and eleventh in palm kernel, groundnut and soyabean production respectively (Table 2.1). These crops are the major feedstocks for biodiesel production.

Climatic conditions in Nigeria favour the huge yearly turnover of these crops. Government, through Public-Private partnership, only need to sustain (or improved on) the production capacity of these “Golden” crops. This implies that the nation stands a good chance of becoming one of the first-ten highest producers of biofuels (bioethanol and biodiesel) in the world, provided that these resources are maximally cultivated.

Biofuels generated from the enormous magnitude of waste obtained from the cultivation and usage of these crops can even make the nation become one of the major global suppliers of Biofuels (Edirin and Nosa, 2012).

Table 2.1: Nigerian Biofuel Production Crops in 2007

Crop	2007 Average Yield [Metric Tonnes]	Biofuel Type Derivation	Derivable Biofuel Yield [L/Ha]	Nigeria’s Position in Global Ranking
Palm oil	1,300,000	Biodiesel	5,950	3 rd
Palm Kernel	1,275,000	Biodiesel	5,950	3 rd
Groundnut	3,835,600	Biodiesel	1,059	3 rd
Soyabean	604,000	Biodiesel	446	11 th
Sesame	100,000	Biodiesel	696	7 th
Cotton seed	212,000	Biodiesel	325	16 th
Cassava	34,410,000	Bioethanol	4,000	1 st
Sweet corn	6,724,000	Bioethanol	172	10 th
Coconut	225,500	Bioethanol	2,689	17 th
Sugar cane	1,506,000	Bioethanol	6,000	51 st

Source: Abila (2010)

Nigeria has formulated a policy on biofuels “Nigerian Biofuel Policy and Incentives” (Anyaoku, 2007). The policy document was approved by Federal Executive Council on June 20, 2007. Nigeria National Petroleum Corporation (NNPC) was given the mandate to create an environment for the take-off of a domestic ethanol and diesel fuel industry. The aim is to gradually reduce the nation’s dependence on imported fuels, reduce environmental pollution while at the same time creating a commercially viable industry that can precipitate sustainable domestic jobs (Oniemola and Sanusi, 2007)

The Federal Republic of Nigeria structured the implementation of this programme into blending of biofuel with fossil fuel (E10 and B20) and establishment of plantations (for growing bio-fuel feedstocks) and biofuel plants, with the aim of achieving 100% domestic production of biofuels consumed in the country by 2020.

According to Galadima *et. al.* (2011), the specific anticipated benefits of the policy are

- Diversification of the country’s sources of revenue as additional taxes could be generated from commercial activities attributed to the industry.
- Creation of sustainable job opportunities for citizens and the empowerment of rural communities who are currently neglected from enjoying the national cake
- Improving agricultural benefits by advancing farming techniques and agricultural research.
- Ensuring that the projected energy demand in the country is addressed sustainably.
- Reduction in environmental pollution due to fossil fuels.

2.2.2.1 Establishment of a Biofuels Energy Commission

For the purposes of implementing the provisions of this Policy, a Biofuels Energy Commission (BEC) was established. According to the policy, the commission is headed by a designated officer from NNPC, other members are nominated representatives of the Office of the Special Adviser to the President on Energy Matters, the Federal Ministries of Agriculture, Commerce & Industry, Finance, Environment, Science and Technology, Bankers Committee, Manufacturers Association of Nigeria, Federal University of Agriculture (as nominated by the National Universities Commission) and the Energy Commission of Nigeria.

2.2.2.2 Functions of the Biofuels Energy Commission

The Commission is charged with well-defined responsibilities for implementing the strategies for Biofuels in the country. Specifically, the Commission shall:

- Register all Biofuel Plants/Projects in the country.
- Issue license to Biofuel operators for the production of fuel ethanol or/and bio-diesel in Nigeria.
- Formulate and recommend fiscal, financial and other incentive policies for the bio-fuel industry, as well as protection measures if required.
- Periodically, review and assess the economic, technical, environmental and social impact of the use of biofuels, and shall determine changes in policies required when necessary. Monitor the supply and utilisation of biofuels and biofuel blends and recommend appropriate measures to the Department of Petroleum Resources in case of shortage in the supply of biofuels or feedstock.
- Review and adjust the minimum mandated biofuel blends as it deems appropriate.

- Determine and put in place Industry stabilization mechanisms.
- Designate and oversee the activities of the investment bank appointed to manage the Bio-fuel Industry Equity Fund.
- Establish and support the Bio-fuels Research Agency to be established under the Biofuels Programme.
- Monitor intra-industry commerce, in particular relationships between outgrowers and bio-fuel producers.
- Present quarterly reports and briefings on the status of the Bio-fuel Industry to the National Assembly.
- Disseminate and share information with investors and other interested members of the public.
- Liaise with the Energy Commission of Nigeria in the formulation, revision and implementation of the National Energy Policy.
- Liaise with the National Sugar Development Council as may be required.
- Liaise with government ministries, agencies, research institutes (e.g. NIFOR, NCRI, NRCRI, IITA) or other bodies, charged with responsibility for the development of bio-fuel feedstock such as palm oil, sugarcane, cassava, jathropha.

2.2.2.3 Establishment of a Biofuels Research Agency

To make the project a realisable objective, the federal government through the Biofuels Energy Commission is saddled with the responsibility of the establishment of Biofuels Research Agency (BRA). The research agency is headed by a Director, appointed by the Bio-fuels Energy

Commission. The agency is to act as the central coordination body for bio-fuel research in the country.

Some of the functions of biofuel research agency include:

The Agency shall

- coordinate biofuel crop production optimization programme and collaborate with the research and development efforts of International Institute of Tropical Agriculture (IITA), National Cereal Research Institute (NCRI), National Root Crops Research Institute (NRCRI), Nigerian Institute For Oil Palm Research Council (NIFOR), Forestry Research Institute Nigeria (FRIN), Nigerian Stored Products Research Institute (NSPRI), Institute for Agricultural Research and Extension Services (IARES), Agricultural Research Council of Nigeria (ARCN), National Biotechnology Development Agency (NABDA), Science and Technology Complex (STCO), Federal Soil Conservation School (FSCS), National Centre for Agricultural Mechanisation (NCAM), National Agricultural Seeds Council (NASC), Nigerian Automotive Council, Raw Materials Research and Development Council (RMRDC) and Federal Institute of Industrial Research Oshodi (FIIRO) and other relevant agencies.
- collaborate with the Ministry of Agriculture and Ministry of Science and Technology to provide direction for research in crop production, industry technology and processes pertaining to the production of bio-fuels.
- coordinate the allocation of funds set aside for bio-fuel research for mandated national research organizations.

As part of the efforts to ensure effective takeoff of this biofuels transformation agenda, Group General, Renewable Energy Division of NNPC in his presentation “Sustainable Biofuels and Economic Development” at the second Nigerian Alternative Energy Expo (2013) gave the statistical data of Nigeria’s Biofuels demand (according to National Energy Master Plan), as stated in Table 2.2.

Table 2.2: Nigeria’s Biofuels Demand

Biofuel Type	Time Frame		
	Short	Medium	Long
Biodiesel	0.233	1.951	12.7
[demand in Billion liters/year]	(10% blend)	(20% blend)	(50% blend)
Fuel-Ethanol	1.3	3.4	52.5
[demand in Billion liters/year]	(10% blend)	(15% blend)	(50% blend)

Source: Second Nigerian Alternative Energy Expo (2013)

This policy is a timely right step in the right direction, but so much success has not been recorded. However, the actualization of the objectives of this policy is subject to the efficiency of all the institutions involved. Success of this programme, among other things, has a lot to do with the encouragement of robust research clusters, rewarding mechanized farming and the implementation of enabling legislation by the government (Oniemola and Sanusi, 2007).

And there is need for a vibrant public-private partnership in the development of bio-fuels in the country. The proposed partnership should optimize benefits among parties, either public or private, by allocating responsibilities to the party that is best positioned to control the activity

that will produce a desired result. Clear and transparent legislation to develop the industry is critical and must be put in place at the right time, (Oniemola and Sanusi, 2007)

2.3 Biodiesel Production

Biodiesel is simply defined as mono-alkyl ester of vegetable oils or animal fats (Zhang *et al.*, 2003). Biodiesel fuel derivative from agricultural products reduces the dependence on fossil fuels and support local agricultural industries. Also, it offers great benefits in terms of sustainability, reduced pollutants, greenhouse gas emissions, increased energy diversity and economic security (Evangelos, 2013; Harold, 2013).

Biodiesel (methyl or ethyl ester) is considered as a very promising fuel for the transportation sector since it possesses similar properties with diesel fuel, it can be blended with diesel practically at any proportion or use directly alone (B100) in diesel engines without any modification in the engine (Yang *et. al.*, 2007).

2.3.1 Biodiesel Feedstocks

Biodiesel feedstocks are lipids. Lipids are characterised as being insoluble in water, but generally soluble in common organic solvents, such as chloroform or diethyl ether. Lipids may either be a solid or liquid at room temperature, depending on their structure and composition. Fats and oils are members of the lipids family. Normally, “oil” refers to a lipid that is liquid at room temperature, while “fat” refers to a lipid that is solid or semi-solid at room temperature (Harold, 2013).

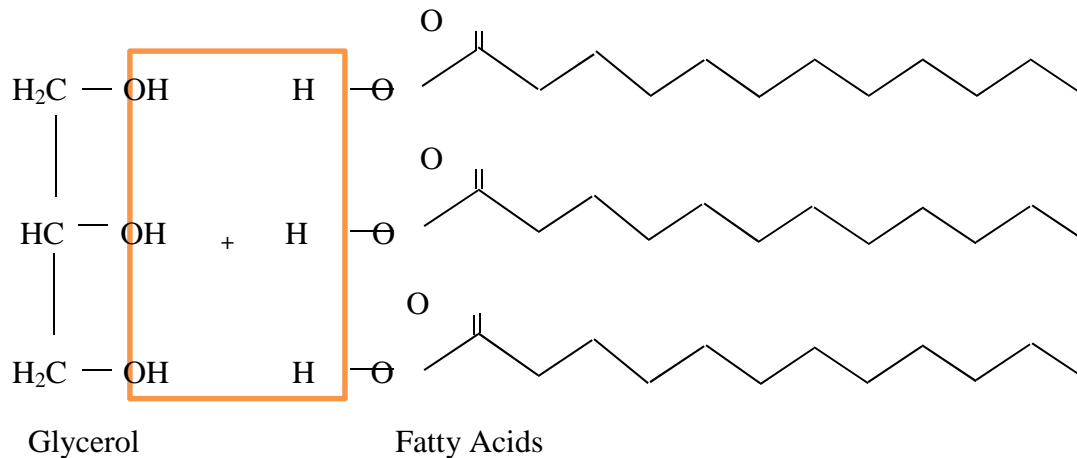


Figure 2.3: Formation of Triglycerides

Fats and oils are esters. In the special case of fats and oils, the alcohol fragment is 1,2,3-propanetriol, also known by its common name glycerol or glycerine. The acid fragments are long-chain aliphatic acids, collectively referred to as fatty acids (Figure 2.3).

Esters of fatty acids with glycerol are called glycerides. The forms of glycerides are mono-glycerides, di-glycerides and triglycerides. The structures of mono-, di-, and triglycerides (MGs, DGs, and TGs respectively) are as shown in Figure 2.4. The structures consist of glycerol (a backbone of carbon, hydrogen, and oxygen) esterified with fatty acids (chains of carbon and hydrogen atoms with a carboxylic acid group at one end) (Kaewta, 2008).

Triglyceride (TG) or Triacylglycerol (TAG) is a molecule composed of three esters of fatty acid chain (acyl group) attached to glycerol (glycerol group). When two acyl ester groups and one hydroxyl group (– OH) are present, the molecule is called a Diglyceride (DG) or Diacylglycerol (DAG). Similarly, Monoglyceride (MG) or Monoacylglycerol (MAG) or has one acyl ester group and two hydroxyl groups. The acyl groups are typically unbranched fatty acids with 10 to 24 carbon atoms.

Saturated fatty acids have no double bonds between the carbon atoms. When a pair of hydrogen atoms is removed from a fatty acid chain, one double bond is present; it is therefore called monounsaturated fatty acid. If the molecule contains two or more double bonds caused by further removal of hydrogen atoms, it is referred to as polyunsaturated fatty acids. These fatty acids are frequently represented by a symbol such as C15:0, which indicates a fraction consisting of 15 carbon atoms and no double bond while C20:2 implies a fraction consisting of 20 carbon atoms and two double bonds.

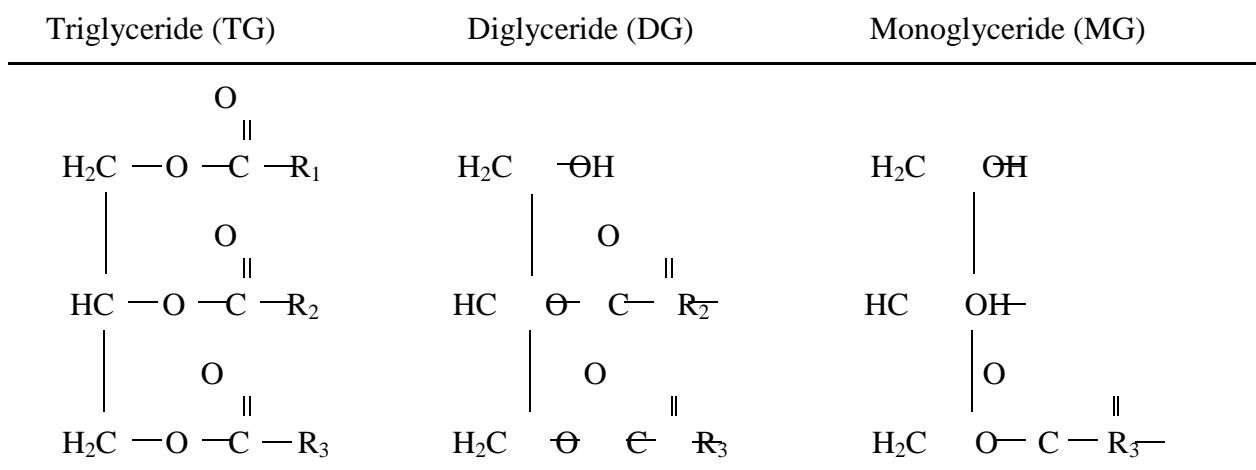


Figure 2.4: Structure of Monoglycerides, Diglycerides and Triglycerides

Source: Ramos *et.al.*, (2009). R₁, R₂, R₃ are fatty acid chains

Fatty acids can contain 4-24 carbon atoms with some degree of unsaturation (typically 1-3 C-C double bonds). Fats contain more saturated fatty acids (the compositional building blocks) than oils and this accounts for higher melting point and higher viscosity of fats. Structures of some of the common fatty acids present in fats and oils are shown in Table 2.3 (Sharma and Singh 2009).

Table 2.3: Structures of common Fatty Acids present in Fats and Oils

System name	Common name	Symbol	Formula	Double bond position
Saturated Fatty Acids				
Decanoic	Capric	C10:0	$C_{10}H_{20}O_2$	n/a
Dodecanoic	Lauric	C12:0	$C_{12}H_{24}O_2$	n/a
Tetradecanoic	Myristic	C14:0	$C_{14}H_{28}O_2$	n/a
Hexadecanoic	Palmitic	C16:0	$C_{16}H_{32}O_2$	n/a
Octadecanoic	Stearic	C18:0	$C_{18}H_{36}O_2$	n/a
Eicosanoic	Arachidic	C20:0	$C_{20}H_{40}O_2$	n/a
Docosanoic	Behenic	C22:0	$C_{22}H_{44}O_2$	n/a
Tetracosanoic	Lignoceric	C24:0	$C_{24}H_{48}O_2$	n/a
Monounsaturated Fatty Acids				
Hexadecenoic	Palmitoleic	C16:1	$C_{16}H_{30}O_2$	9c
Octadecenoic	Petroselinic	C18:1	$C_{18}H_{34}O_2$	6c
Octadecenoic	Oleic	C18:1	$C_{18}H_{34}O_2$	9c
Octadecenoic	Asclepic	C18:1	$C_{18}H_{34}O_2$	11c
Eicosenoic	n/a	C20:1	$C_{20}H_{38}O_2$	5c
Eicosenoic	Gadoleic	C20:1	$C_{20}H_{38}O_2$	9c
Eicosenoic	Gondoic	C20:1	$C_{20}H_{28}O_2$	11c
Docosenoic	Erucic	C22:1	$C_{22}H_{42}O_2$	13c
Polyunsaturated Fatty Acids				
Hexadecadienoic	n/a	C16:2	$C_{16}H_{28}O_2$	n/a
Octadecadienoic	Linoleic	C18:2	$C_{18}H_{32}O_2$	9c12c
Octadecatrienoic	Linolenic-	C18:3	$C_{18}H_{30}O_2$	9c12c15c

Octadecatrienoic	Linolenic-	C18:3	C ₁₈ H ₃₀ O ₂	6c9c12c
Octadecatrienoic	Eleostearic	C18:3	C ₁₈ H ₃₀ O ₂	9c11t13t
Octadecatrienoic	Calendic	C18:3	C ₁₈ H ₃₀ O ₂	8t10t12c

Source: Itoh (1973); c = cis formation; t = trans formation; n/a = not available

Stereo isomers of unsaturated fatty acids can be arranged in *cis* and *trans* orientation. Most natural occurring fatty acids from fats and oils have cis-double bonds whereas the unnatural trans-isomers usually only occur due to partial hydrogenation process. The Latin prefixed *cis* and *trans* describe the orientation of hydrogen atoms attached to carbon atoms at position next to a double bond. In cis-isomer, hydrogen atoms are attached on the same side causing a “V” shape of fatty acid chain (Ramos *et.al.*, 2009).

The major difference between various vegetable oils is the kind of fatty acids attached to the triglyceride molecule. Fatty acid compositions of various vegetable oils are as shown in Table 2.4. Fatty acid composition determines biodiesel properties, and this shows how important vegetable oil fatty acid composition is. Both the degree of saturation/unsaturation and molecular weight of vegetable oils determine fuel properties (Lee and Shah, 2013).

Both the edible and non-edible vegetable oils are used for biodiesel production. For instance, rapeseed oil is utilised in European countries and Canada, soybean oil used in United States of America, and palm oil in Indonesia and Malaysia; the commonly used non-edible oils is jatropha oil (Sharma and Singh 2009).

Table 2.4: Fatty Acid Profiles of Some Vegetable Oils

Vegetable Oils		Fatty Acid composition (wt. %)										
Common Name	Species	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:0	22:1
Canola (Low erucic rapeseed)	<i>Brassica rapa</i>	-	-	3.1	0.2	1.3	56.6	22.4	14.0	0.4	0.2	0.1
Canola (Low erucic rapeseed)	<i>Brassica napus</i>	-	-	4.3	0.3	1.7	61.0	20.8	9.3	0.6	0.3	-
Black mustard	<i>Brassica nigra</i>	-	1.5	5.3	0.2	1.3	11.7	16.9	2.5	9.2	0.4	41.0
Oriental mustard	<i>Brassica juncea</i>	-	-	2.3	0.2	1.0	8.9	16.0	11.8	0.8	5.7	43.3
Brown mustard	<i>Brassica juncea</i>	-	-	2.2	0.2	1.2	17.4	20.5	14.1	0.7	0.5	28.1
Wild mustard	<i>Sinapis arvensis</i>	-	0.1	2.6	0.2	0.9	7.8	14.2	13.0	0.8	1.5	45.7
White mustard	<i>Sinapis alba</i>	-	-	3.1	0.2	0.7	9.1	11.7	12.5	0.7	-	46.5
White mustard	<i>Sinapis alba</i>	-	0.1	2.8	0.2	1.1	25.0	11.6	8.6	0.7	0.6	32.8
Soybean	<i>Glycine max</i>	-	-	10.1	-	4.3	22.3	53.7	8.1	-	-	-
Soybean	<i>Glycine max (GMO^{a,b})</i>	-	-	3.5	0.1	2.8	22.7	60.3	9.8	0.2	0.2	-
Soybean	<i>Glycine max (GMO^{a,c})</i>	-	0.1	10.9	0.1	5.7	27.5	51.5	3.0	0.5	0.4	-
Soybean	<i>Glycine max (GMO^{a,d})</i>	-	0.1	23.8	0.7	3.8	15.4	44.1	11.0	0.4	0.6	-
Soybean	<i>Glycine max (GMO^{a,e})</i>	-	-	8.0	0.1	24.7	17.2	39.2	8.3	1.5	0.7	-

Palm	<i>Elaeis guineensis</i>	0.3	1.2	44.3	-	4.3	39.3	10.0	-	-	-	-
Palm	<i>Elaeis oleifera</i>	-	0.2	18.7	1.6	0.9	56.1	21.1	-	-	-	-
Palm kernel	<i>Elaeis guineensis</i>	50.1	15.4	7.3	-	1.8	14.5	2.4	-	-	-	-
Palm kernel	<i>Elaeis oleifera</i>	29.3	25.7	10.1	-	1.8	26.4	4.5	-	-	-	-
Palm kernel	<i>Aiphanes acanthophylla</i>	41.5	20.5	10.2	-	3.4	15.8	7.4	-	-	-	-
Palm kernel	<i>Buttia capitata</i>	39.2	6.4	4.2	-	3.0	11.9	3.5	-	-	-	-
Sunflower	<i>Helianthus annuus</i>	-	-	5.2	0.1	3.7	33.7	56.5	-	-	-	-
Sunflower	<i>Helianthus annuus</i> <i>GMO^{a,g}</i>	-	-	3.1	0.1	1.5	91.5	2.1	-	0.2	0.7	0.1
Sunflower	<i>Helianthus annuus</i> <i>GMO^{a,g}</i>	-	-	4.4	-	4.2	78.3	10.9	-	0.3	1.0	-
Sunflower	<i>Helianthus annuus</i> <i>GMO^{a,c}</i>	-	0.1	7.5	0.1	1.9	13.3	76.0	0.1	0.1	0.4	-
Sufflower	<i>Carthamus tinctorius</i>	-	0.1	6.4	-	2.3	11.6	79.3	-	0.3	-	-
Groundnut	<i>Arachis hypogea</i>	-	-	11.2	-	3.6	41.1	35.5	0.1	-	-	-
Corn	<i>Zea mays</i>	-	-	11.6	-	2.5	38.7	44.7	1.4	-	-	-
Olive	<i>Olea europaea</i>	-	-	13.8	1.4	2.8	71.6	9.0	1.0	-	-	-
Cottonseed	<i>Gossypium hirsutum</i>	-	-	23.0	-	2.3	15.6	55.6	0.3	-	-	-
Linseed	<i>Linum usitatissimum</i>	-	-	5.6	-	3.2	17.7	15.7	57.8	-	-	-
Coconut	<i>Cocos nucifera</i>	50.9	21.1	9.5	-	4.9	8.4	0.6	-	-	-	-
Sesame	<i>Sesamum indicum</i>	-	-	9.6	0.2	6.7	41.1	41.2	0.7	-	-	-

Rice bran	<i>Oryza sativa</i>	-	-	22.1	-	2.0	38.9	29.4	0.9	-	-	-
Jatropha	<i>Jatropha curcas</i>	-	-	18.5	-	2.3	49.0	29.7	-	-	-	-
Karanja ^f	<i>Pongamia glabra</i>	-	-	5.8	-	5.7	57.9	10.1	-	3.5	-	-
Karanja	<i>Pongamia pinnata</i>	-	-	11.7	-	7.5	51.6	16.5	2.7	-	-	-
Neem ^f	<i>Azadirachta indica</i>	-	-	17.8	-	16.5	51.2	11.7	-	2.4	-	-
Sal ^f	<i>Shorea robusta</i>	-	-	6.2	-	43.0	41.3	2.1	-	5.5	-	-

Source: Sharma and Singh, (2009); ^aGMO = genetically modified oil; ^blow saturate; ^chigh linoleic; ^dhigh palmitic; ^ehigh stearic; ^faverage value;

^ghigh oleic

2.3.2 Waste Cooking Oil (WCO)

The properties of waste (used) cooking oil depend highly on the origin of the oil. The history, duration and extent of oil exposure to water, heat, food, micro-organisms and oxygen during cooking determines both its physical and chemical properties such as viscosity, water content, FFA content, sulphur content and the presence of polymerised and oxidised compounds (Sharma and Singh, 2009).

Oil degradation during cooking occurs through three main reactions: thermolytic reaction, oxidative reaction, and hydrolytic reactions (Jacobson *et. al.*, 2008). Thermolytic reactions are heat initiated reactions which do not require oxygen and saturated fatty acids. In this form of reactions, alkanes, fatty acids, ketones, esters, and diacylglycerides are formed. Dimeric compounds are major products of thermolytic reactions of unsaturated fatty acids. Dimerization and polymerization of unsaturated fatty acids take place through Diels-Alder reactions (Jacobson *et. al.*, 2008).

Oxidative reactions occur in a series of initiation, propagation, and termination steps as shown in Figure 2.5. The initial step involves abstraction of hydrogen from unsaturated fatty acid to form a free radical ($R\cdot$) followed by a reaction of the radical with molecular oxygen to form peroxide radicals ($ROO\cdot$). The propagation phase involves intermolecular interactions, whereby the peroxide radical abstracts hydrogen from an adjacent molecule, which gives rise to hydroperoxides ($ROOH$) and a new free radical (Issariyakul, 2011).

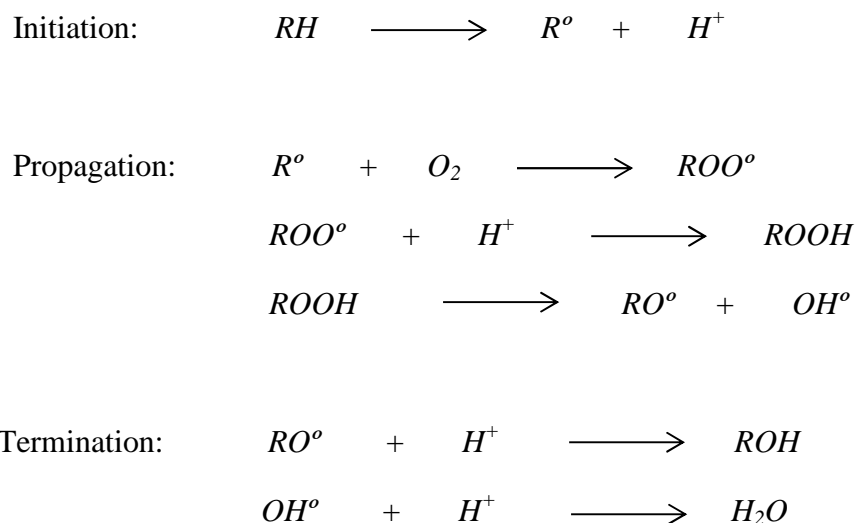


Figure 2.5: Scheme for Oxidative Reaction Mechanism
 Source: Nawar (1984)

Carbon-hydrogen bond dissociation energies of fatty acid are lowest at bisallylic, followed by allylic positions (Figure 2.6). It is reported that lower bond energies for bisallylic and allylic hydrogens have 75 and 88 kcal/mol, respectively, while those of methylene hydrogens are 100 kcal/mol (Erickson, 2002). Hence, hydrogens at bisallylic and allylic locations are favoured sites for proton abstraction by peroxide radicals. Once formed, hydroperoxides tend to proceed toward further oxidation degradation, leading to secondary oxidation derivatives such as aldehydes, acids, and other oxygenates (Nawar, 1984). Hydrolytic reactions take place between the oil and water present during food preparation. Formations of DAG, MAG, FFA, and glycerol are the main products of the hydrolysis of TAG (Mittelbach and Enzelsberger, 1999).

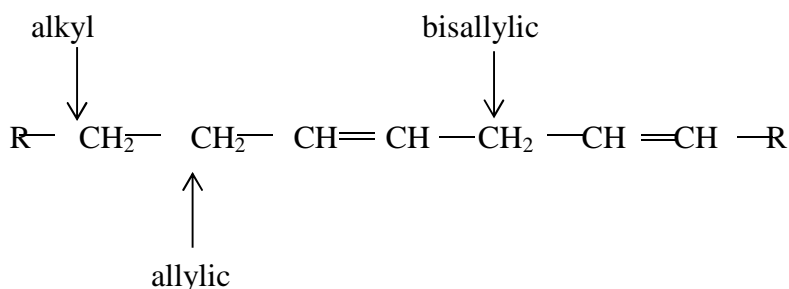


Figure 2.6 Carbon-hydrogen bond positions in fatty acids.

The combination of these reactions during food preparation resulted into various reaction derivatives; leading to an increase in polar content of the oil. It is advised that used cooking oil should no longer be used for edible purposes if its polar content exceeds 25% (Kulkarni and Dalai, 2006).

An obvious advantage of used cooking oil (as feedstock for trans-esterification) over virgin vegetable oil is its cheaper price. The availability of used cooking oil as a feedstock for biodiesel production is highly related to area population. In comparison to used cooking oil, biodiesel produced from fresh vegetable oils cost more. Zhang *et al.* (2003) reported that raw material cost is responsible for approximately 70 - 95 % of biodiesel production costs; hence a lot of money is saved when waste cooking vegetable oil is used as feedstock. Commercially, this economic benefit makes the use of used cooking oil as feedstock for biodiesel production attracts the attention of many.

2.3.3 Methods of Biodiesel Production

Some of the biodiesel production methods are discussed below.

2.3.3.1 Pyrolysis

The word “pyrolysis” is from the Greek-derived elements *pyro* means "fire" and *lysis* means "separating". Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogen). It involves the simultaneous change of chemical composition and physical phase; it is an irreversible process. That is, it involves the conversion of one substance into another by means of heat or with the aid of catalyst (Edward, 2010).

The pyrolysed material can be vegetable oils, animal fat, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years especially in those areas of the world that lack deposit of petroleum. The first pyrolysis of vegetable oil was conducted in an attempt to synthesized petroleum from vegetable oil (Edward, 2010).

Since World War I, many researchers have investigated the pyrolysis of vegetable oil to obtain products suitable for fuel. The cetane number (CN) of plant oils was found to increase by pyrolysis, and the concentration of sulphur, water and sediment for the resulting products were acceptable (Edward, 2010).

In modern standards, viscosity of the pyrolysed oil is considered too high, ash and carbon residue far exceed the values for fossil fuel, and the cold flow properties are poor (Ma *et. al.*, 1999). In addition, the technology contributes to global warming and it is also a very expensive technology. All these hinder its wide acceptance as a major process of biofuel production.

2.3.3.2 Micro – Emulsification

According to Schwab *et. al.* (1987), micro-emulsion is a colloidal equilibrium dispersion of optically isotropic fluid which has micro structures with dimensions generally in the 1 – 50 nm range formed spontaneously from two normally immiscible.

The fuels produced through micro-emulsion leads to incomplete combustion, formation of carbon deposits, and an increase in the viscosity of the lubricating oil. Micro-emulsions display considerably lower volumetric heating values as compared to hydrocarbon – based diesel fuel due to their high alcohol contents (Srivastava and Prasad, 2000). When assessed, it has been found to be inadequate due to low value of cetane number and cold temperature behaviours

(Marchetti *et. al.*, 2007). Many researchers suggested that micro-emulsions of vegetable oils with alcohols should not be recommended for long – term use in diesel engines.

2.3.3.3 Trans-esterification

Low volatile and high viscous vegetable oils cause particle agglomeration and injector fouling when used as diesel engine fuel (Xiaohu, 2008). To increase the engine fuel volatility and reduce its viscosity, the oil is subjected to a process called trans-esterification. It is a chemical process that involves the reversible reaction of triglyceride in vegetable oil (or animal fat) and alcohol (methanol, ethanol, propanol), in the presence of a catalyst to yield fatty acid alkyl ester (biodiesel) and glycerol (Mekhilef *et. al.*, 2011). The chemical reaction involved is as represented in Figure 2.7.

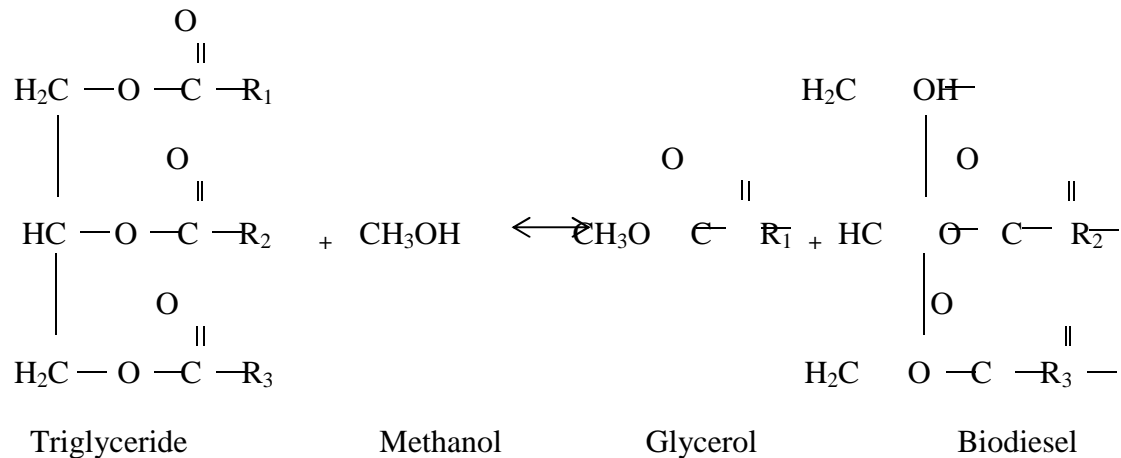


Figure 2.7: Trans-esterification Reaction

The process is also known as Alcoholysis (methanolysis, if methanol is used and ethanolysis, if ethanol is used). Based on the catalyst used, it can be referred to as enzyme-catalysed trans-esterification, acid-catalysed trans-esterification or base-catalysed trans-esterification.

It can also be seen as a process of exchanging the organic group R' of an ester with the organic group R'' of an alcohol, as shown in Figure 2.8.



Figure 2.8: Trans-esterification Reaction of Biodiesel Production

2.3.4 Pretreatment of Waste Cooking Oil as Feedstock

Waste cooking oil (WCO) is the oil obtained after using the edible oil for frying. The amount of WCO generated at homes and restaurants is increasing exponentially as a result of tremendous growth in human population (Chen *et. al.*, 2009). Despite the changes that occur during frying, WCO is a good option as feedstock for biodiesel production, once it is treated by being free of unwanted materials (Kulkarni *et. al.*, 2006).

The chemical reactions that occur during frying process (depending on level and condition of usage) include oxidative and thermolytic reactions, result in the formation of oxidation derivations composing of various acids and polymerized materials (Issariyakul, 2011; Kulkarni and Dalai, 2006). These resulted into increase in acid value and oxygen content of the used cooking oil.

WCO contains unwanted contents such as FFA, water and other solid impurities. The presence of water in oil sample often leads to hydrolysis and high FFA content leads to saponification. Both reactions results in low biodiesel yield and catalyst consumption (Zahira *et. al.*, 2013).

To reduce the high FFA content in oil, several techniques have been proposed, such as acid esterification with methanol and sulphuric acid, esterification with ion-exchange resins,

neutralisation with alkalis followed by soap removal, and extraction with polar liquids along with acid esterification and distillation of FFA (Cvengros, 2004).

To remove water present, WCO is heated to temperature above 100 °C. Vacuum distillation (0.05 bar) is used at the industrial scale. And suspended solids and other impurities can be removed by centrifugation and filtration (Chen *et. al.*, 2009).

2.3.5 Glycerol Separation

Separation of glycerol from biodiesel (desired product) is very important, being the first step in obtaining pure biodiesel and also to avoid possible reversible process. Glycerol can cause clogging of injectors and carbon residues in the engine if not completely removed (Lamers, 2010). The common laboratory practice of glycerol removal is decanting using a separating funnel. After about 24 hours of allowing trans-esterification products separate to a clear light (biodiesel) phase and a denser phase (glycerol) are obtained (Erickson, 2002).

There is often a quality control check, for if there is no distinct separation (but emulsion or soap formation), then problems may have occurred during reaction as a result of any (or combination) of the followings: insufficient/excess usage of methanol or/and catalyst, extreme high/low reaction temperature, presence of water. Glycerol removed has a wide range of applications; it can be used in chemical, pharmaceutical, food, paint and automobile industries (Feto, 2011).

2.3.6 Biodiesel Purification

In order to get pure biodiesel that meets the ASTM or EN standards, raw FAME obtained from the reaction must essentially be free of residual glycerol, methanol, un-reacted oil and traces of catalyst. Common raw FAME refining processes include water washing, ion exchange resins, membrane separation and use of adsorbents such as magnesium silicate (Atadashi *et. al.*, 2010).

The purpose of refining the biodiesel is to remove glycerol, methanol, free fatty acids (or soap) present and to neutralize any residual catalyst present. The best practice for reducing the amount of warm water required for biodiesel refining is to ensure proper trans-esterification reaction (Berrios and Skelton, 2008). The adverse effects of impurities found in unrefined FAME are listed in Table 2.5.

Table 2.5: Effects of Impurities in Biodiesel on Engines

Impurity	Effect
Free Fatty Acids (FFA)	Corrosion Low oxidation stability
Water	Hydrolysis (FFA formation) Corrosion Bacteriological growth (filter blockage)
Methanol	Corrosion of Al and Zn engine components
Metals (soap, catalyst)	Deposits in the injectors (carbon residue) Filter blockage Engine weakening
Glycerol	Deposits in the injectors (carbon residue) Increase aldehydes emissions

Source: Lamers (2010)

2.3.7 Biodiesel Washing Water

Water is both a polar and universal solvent, this makes water a good solvent for purification purposes. Through the application of water for washing, high quality FAME can be obtained from raw FAME which is insoluble in water (Gonzalo *et al.*, 2010). Water washing involves mixing distilled water with raw FAME for a given short period of time in order for impurities in biodiesel to dissolve in water. Different methods of introducing water are possible, simple settling and decanting allows for water to be removed. Water Washing is preferred to other purification technologies available not only because it is economical, but also it does produce high quality FAME (Atadashi *et. al.*, 2010).

Water acts as a good medium for the addition of acid for neutralisation of catalyst and as a carrier of impurities (Gonzalo *et al.*, 2010). 0.2 % sulphuric acid solution is added to the distilled warm water, and the mixture is added to raw biodiesel. The content is agitated for a short period of time and allowed to settle into two clear layers (biodiesel on top and cloudy washing water as bottom layer). Methanol, glycerol and catalyst are all soluble in warm water and therefore taken out with washing (bottom layer). It is important to note that agitation of the content is a must for the total dissolution of impurities in water. And biodiesel is less dense than water, these make the separation very easy to achieve (Evangelos, 2013).

2.4 Factors Influencing Biodiesel Yield and Properties

2.4.1 Effects of Free Fatty Acid (FFA) and Water Content

Presence of Free fatty acid (FFA) and water content in the raw materials used for biodiesel production will significantly affect both the quality and quantity biodiesel in alkali-catalysed trans-esterification. It implies that all starting materials (lipid feedstock, alcohol, and catalyst)

should be substantially anhydrous. Prolonged contact of alkali catalysts with atmospheric air will reduce catalyst efficacy through the catalyst's interaction with moisture and carbon dioxide in air. Also, it is critical that feedstock used during alkali-catalysed trans-esterification should contain free fatty acid that is less than 1.0 wt.% (Rashid and Anwar, 2008). The higher the acidity of oil, the lower is the conversion and yield of biodiesel. FFA present in the feedstock oil is converted to soap and then removed, through the addition of calculated alkali catalyst to the oil (Figure 2.9).

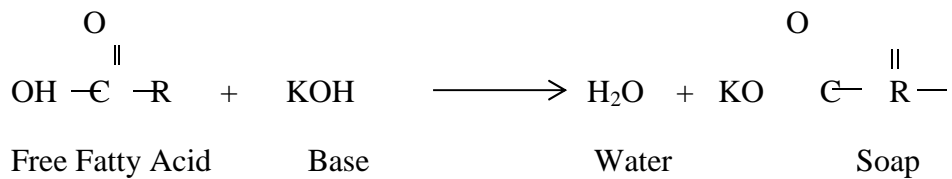


Figure 2.9: Saponification Reaction between Free Fatty Acid and Base

In addition, presence of water can promote hydrolysis of alkyl ester (biodiesel) to form FFA, which lowers ester yield (Figure 2.10). Soap formed during saponification causes increased viscosity or gel formation, which interferes with the trans-esterification reaction as well as glycerol separation.

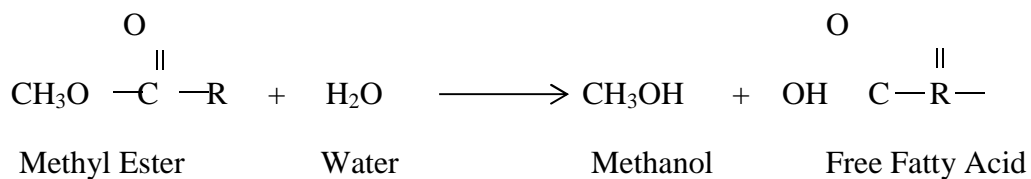


Figure 2.10: Formation of Free Fatty Acid from the Hydrolysis of Biodiesel

Ma *et al.* (1999) investigated the effects of FFA and water on trans-esterification of beef tallow using sodium hydroxide and sodium methoxide as catalyst. It was discovered that when 0.6 % FFA was added, the yield of beef tallow methyl ester was minimal. Additional water present in the reaction mixture intensely diminished the ester yield. From their studies, they concluded that FFA and water content should be maintained below 0.5 and 0.06 wt.% respectively.

Waste cooking oils usually contain large amounts of FFA and water due to prolonged exposure of heat and moisture from food. Therefore, direct alkali-catalysed trans-esterification of these oils is not applicable. Pre-treatment of these oils to remove FFA and water is usually required. In this process, 12% aqueous sodium hydroxide solution is required to neutralise FFA. The treatment temperature and duration can be either 90°C for few seconds (short-mix process) or 40°C for 15 minutes (long-mix process). The oil-soap mixture is then centrifuged to separate the aqueous phase containing water, soap, and precipitated phosphatides. The treated oil usually has FFA reduced to < 0.05% and phosphorus to < 2 ppm (Issariyakul, 2011; Chen *et al.*, 2009).

FFA can also be removed from vegetable oils through distillation (Martins *et al.*, 2006). The distillation process should be performed under vacuum conditions in order to lower the operating temperature. If the operating temperature is too high, glycerides will degrade to generate more acids. The distillation temperature ranged from 100 – 180 °C. However, this approach is less preferred due to the additional cost incurred during distillation process.

Alternatively, a two-step acid-alkali esterification-trans-esterification process can be used (Kaewta, 2008). In the first step, FFA is esterified with a short-chain alcohol with acid catalyst to produce ester. Since FFA is converted into ester in the first step, an alkali catalyst can be used in trans-esterification in the second step.

2.4.2 Effects of Alcohol Concentration and Type

Stoichiometrically, three moles of alcohol react with one mole of triglyceride to produce fatty acid alkyl ester (biodiesel) and glycerol during trans-esterification process. In order to have high biodiesel yield (conversion) by shifting the reaction to the products side (being a reversible reaction), excess alcohol is usually utilised. Factors that help to establish an optimum alcohol to oil mole ratio in trans-esterification include level of alcohol purity, oil quality and type of vegetable oil used. Guo and Leung (2006) reported that 98% ester content can be obtained from trans-esterification of canola oil using 6:1 alcohol to oil ratio while trans-esterification of used cooking oil requires 7:1 alcohol to oil ratio to obtain 94% ester content.

Trans-esterification of *Cynara cardunculus L.* oil requires 12:1 ethanol to oil ratio as an optimum ratio while an increase in ethanol to oil ratio to 15:1 decreases ester content (Enciner *et. al.*, 2002). Rashid and Anwar (2008) also reported that a further increase in alcohol used in trans-esterification of rapeseed oil beyond its optimum ratio (6:1) would result in reduced ester yield. When too much alcohol is used in trans-esterification, the polarity of the reaction mixture is increased, thus increasing solubility of glycerol back into the ester phase and promoting the reverse reaction between glycerol and ester or glyceride, thereby, reducing ester yield. It is important to note that more molar ratio of alcohol to oil would be required when waste cooking oil is used compared to using pure vegetable oil (Guo and Leung, 2006). Also, acid catalysed reaction requires a higher alcohol to oil molar ratio (30:1), compared to alkali-catalyzed reactions (Bhatti *et. al.*, 2008). In some cases, the alcohol to oil ratio is increased to 245:1 to obtain 99% conversion (Zheng *et. al.*, 2006).

The type of alcohol used in trans-esterification can also affect reaction performance, methanol and ethanol are the two commonly used. In general, methanol is preferred to ethanol due to economic benefit, higher yield of biodiesel and shorter reaction time (Ayoola *et.al*, 2012). Furthermore, methanol has a lower boiling point, thus excess methanol from the glycerol phase is easily recovered after phase separation.

The lower reactivity experienced in ethanolysis is due to increased carbon chain length which leads to a decrease in nucleophilicity. It was found that when waste fryer grease is trans-esterified with a mixture of methanol and ethanol at equal molar ratio, the resulting biodiesel contains 50% more FAME than FAEE, illustrating the higher reactivity of methoxide as compared to ethoxide (Guo and Leung, 2006).

2.4.3 Effects of Catalyst Nature and Concentration

A catalyst is any substance that increases the reaction rate without itself being converted during or after the reaction. Biodiesel production through trans-esterification is not possible without the introduction of a catalyst. The two natures of the catalysts are homogenous catalysts (in the same liquid form with all the chemical reagents involved in the reaction) and heterogeneous catalysts (in solid form while all the chemical reagents are in liquid form) and the catalysts can be acidic or basic in nature (Zheng and Hanna, 1996).

At commercial level, base catalysed process is mostly favoured due to high reaction yield, short reaction time, low reaction temperature requirement, and beneficial economics of the catalysts (Zlatica and Biljana, 2009). Feedstock containing higher amounts of FFA and water, such as waste cooking oil, may require the combination of both the acid catalyst and base catalyst, depending on the percentage composition of FFA and water (Marchetti *et. al.*, 2007). More

recently, solid catalysts are subjected to investigation because the use of these catalysts simplifies the biodiesel purification step, eliminates waste water generation, and makes a continuous flow biodiesel production process possible (Marchetti *et. al.*, 2007).

Also, enzymatic heterogeneous catalysis is a very good option for it neither produces soap nor waste water, but it is very expensive to operate with strict reaction conditions (Leung *et. al.*, 2010). On the other hand, attempts have been made to carry out non-catalytic trans-esterification reaction under supercritical conditions (Saka *et. al.*, 2010; Saka and Kusdiana, 2001). The process does not require catalysts and has a short reaction time; however, because it requires extreme reaction temperatures and pressures, the process is susceptible to polymerization (D'Ippolito *et. al.*, 2007). Consequently, the purification step becomes difficult due to increased viscosity. Each type of catalysis is discussed in the following sections.

2.4.3.1 Homogeneous Base Catalysis

Homogeneous base catalysis is the most commonly used in commercial biodiesel production processes, this is because the process offers high reaction yield (97 % or more) within a short time (10 minutes - 2 hours) with mild reaction temperatures (25 – 70 °C). According to Meher (2006), the reaction mechanism involves 3 steps as shown in Figure 2.11.

The first step is the attack of alkoxide ion (methoxide ion in the case of methanol as reacting alcohol) to carbonyl carbon of the TAG molecule to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with alcohol to regenerate alkoxide ion. The last step involves the rearrangement of the tetrahedral intermediate to form alkyl ester and DAG. This mechanism can be extended to the reaction of DAG and MAG in the same manner.

Homogeneous base catalysis in trans-esterification is much faster than homogeneous acid catalysis (Freedman *et. al.*, 1986). However, the effectiveness of homogeneous base catalysis is evaluated by the quality of the feedstock used, that is, acid value of lipid must be lower than two (2.0) and all chemical reagents (feed) must be substantially anhydrous (Meher, 2006).

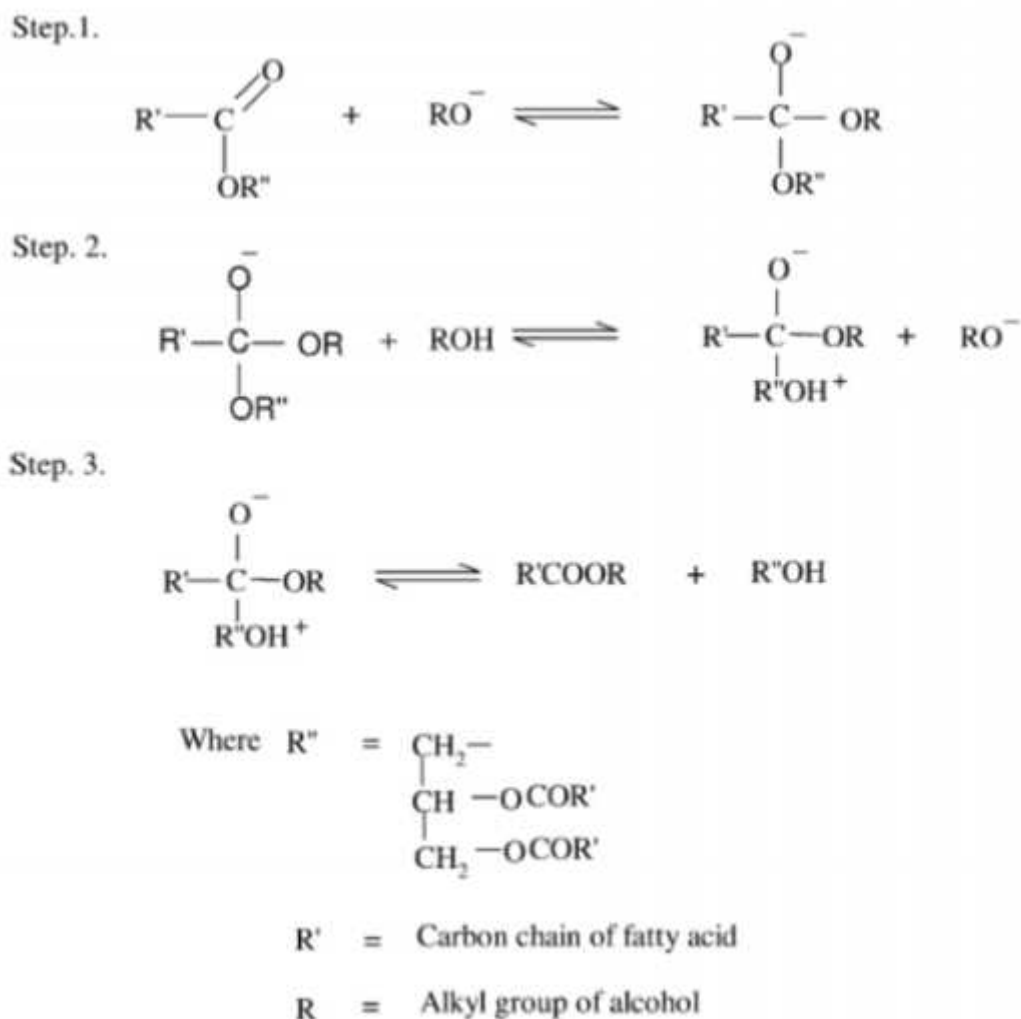


Figure 2.11: Mechanism of Homogenous Base Catalysis in Trans-esterification
 Source: Meher, (2006)

The most common homogeneous catalysts are hydroxides and alkoxides of alkali metals such as NaOH, KOH, NaOCH₃, and KOCH₃. Ma *et. al.*, 1999, found that hydroxide of alkali metal is more effective than alkoxide as NaOH and NaOCH₃ reach their maximum activities at 0.3 and 0.5 wt.% respectively when subjected to the same condition using beef tallow feedstock.

Mahajan *et. al.* (2007) showed that when NaOCH₃ was used, the acid value of the reaction product was significantly lower than when NaOH was used. However, alkali metal alkoxides are less popular than hydroxides in large-scale production due to their toxicity, higher price, and disposal problems. When alkaline metal alkoxides and hydroxides are used as catalysts in methanolysis, the active catalytic species are the same, (methoxide ion CH₃O⁻), concluding that these catalysts are equally effective (Lang *et. al.*, 2001). It was also reported that at 6:1 alcohol to oil molar ratio, the use of 0.5% NaOCH₃ is as effective as 1% NaOH (Freedman *et. al.*, 1984).

The reaction yield can also be increased by using two-step process by separating and removing glycerol at the end of the first step (Cayli and Kusefoglu, 2008). The increase in reaction yield, compared to the one-step process, stems from a shift in reaction equilibrium to the product side due to the removal of glycerol during the production process. Examples of homogeneous base catalysis for trans-esterification are presented in Table 2.6.

2.4.3.2 Homogeneous Acid Catalysis

In biodiesel production from feedstock containing high FFA and water content, acid catalysis is preferred to base catalysis. This approach is employed to avoid saponification so that FFA can be converted directly to ester through esterification while glycerides are converted into ester through trans-esterification. Therefore, acid catalysts can be used to catalyse both esterification

and trans-esterification while base catalysts only catalyze trans-esterification but not esterification (Liu, 1994).

The disadvantages of homogeneous acid catalysis are that it requires a high reaction temperature, higher concentration of catalyst, and a longer reaction time due to slower reaction rate. In addition, it is possible to have residual acid catalysts corroding the metal reactor and metal parts of the reactor (Morgenstern *et. al.*, 2006). The reaction mechanism is shown in Figure 2.12.

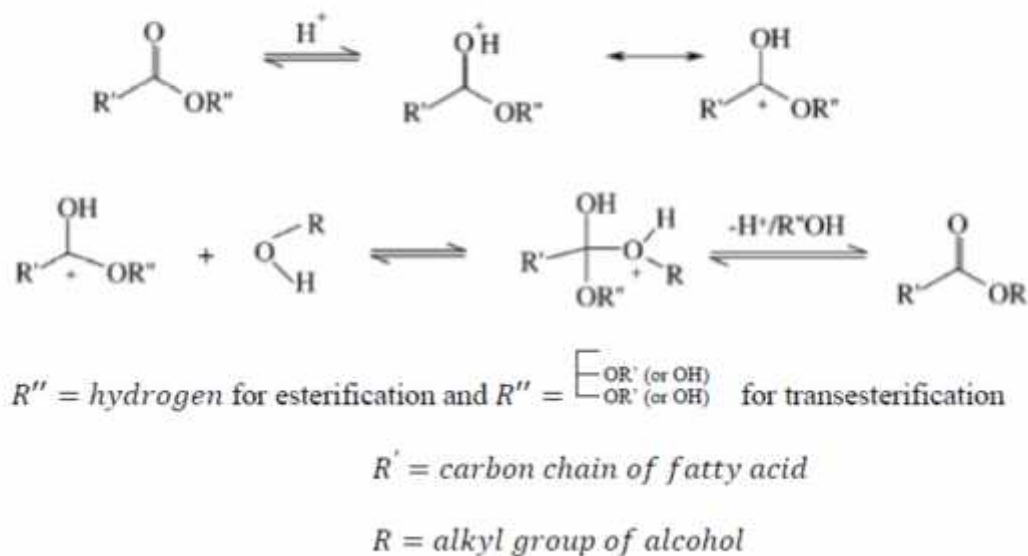


Figure 2.12: Mechanism of Homogenous Acid Catalysis in Esterification and Trans-esterification.

The first step is protonation of the carbonyl group in the glyceride molecule, which leads to the carbocation. The attack of alcohol then produces a tetrahedral intermediate and the elimination of glycerol backbone from this intermediate leads to the formation of ester. Although saponification can be avoided, water is still being generated during esterification of FFA. Water can then undergo hydrolysis, which is the reverse of esterification, but, unlike esterification, it can occur

in the presence of either base or acid. The resulting carboxylate anion from hydrolysis shows little tendency to react with alcohol to form ester, but reacts readily with K^+ or Na^+ in the presence of base to form a stable salt. Therefore, it is essential to perform acid-catalysed esterification and base-catalysed trans-esterification separately (Morgenstern *et. al.*, 2006).

Examples of homogeneous acid catalysts are H_2SO_4 , H_3PO_4 , HCl , BF_3 and CF_3CO_2H . Among these catalysts, H_2SO_4 is the most commonly used catalyst due to its good catalytic activity and simplicity in $H_2SO_4/MeOH$ preparation as concentrated liquid H_2SO_4 can be added directly to Methanol (Issariyakul, 2011). Examples of homogeneous acid catalysis on esterification and trans-esterification are shown in Table 2.7.

$HCl/MeOH$ was introduced for esterification about half century ago, but is not a very popular choice due to complexity in preparation of the solution involving bubbling hydrogen chloride gas into methanol or adding acetyl chloride slowly to methanol (Liu, 1994), using a common concentration of 5%. $BF_3/methanol$ is prepared by bubbling BF_3 gas into cooled methanol. BF_3 has an empty orbital that can accept a pair of electrons making it a Lewis acid. It has been reported that FAME can be obtained from fatty acids within a very short time (10 minutes) using 6-14% catalyst loading ((Morgenstern *et. al.*, 2006).

Due to its superior activity and short reaction time, the American Oil Chemists' Society (AOCS) has adopted BF_3 in the official method for preparing methyl ester from fatty acids (AOCS Ce 2-66). However, BF_3 is not used widely in literature as H_2SO_4 because it is expensive, toxic, and has a limited shelf life (Liu, 1994). Diazomethane (CH_2N_2) is not classified as an acid catalyst, but rather as a strong methylation reagent. Despite its inability to catalyse trans-esterification, diazomethane in ether esterifies free fatty acid at a much faster rate when compared to acid

catalysts. However, its shortcomings such as high toxicity, short shelf life, and potentially explosive have prevented it from being used widely like other catalysts (Morgenstern *et. al.*, 2006).

Table 2.6: Examples of Homogenous Base Catalysis

Feedstock	Catalyst Type	Alcohol	Alcohol/Oil Ratio	Temperature (°C)	Reaction Time	Conversion/Yield (%)
Vegetable oils	NaOH 1% wt. CH ₃ ONa 0.5% wt.	methanol	6:1	60	1hr	93 - 99% conversion
Beef Tallow	NaOH 0.3% wt. CH ₃ ONa 0.5% wt.	methanol	6:1	65	15mins	60% yield
Vegetable oils	KOH 0.5% wt. CH ₃ ONa 0.25% wt.	C1 – C4 alcohol	6:1	25	40mins	87 - 96% yield
Waste Veg. Oils	KOH	methanol	-	60	1hr	95% conversion
Vegetable oils	KOH 1% wt.	methanol	6:1	25	40mins	51 - 87% yield
Used Frying Oil	NaOH 1% wt.	methanol	7:1	60	20mins	94.6% ester content
<i>Pongamia piñata</i>	KOH 1% wt.	methanol	6:1	65	2hrs	97 - 98% yield
Grease	KOH 1% wt	ethanol	6:1	50 - 60	5 - 6hrs	97% ester content
Jatropha	NaOH or KOH 1% wt	methanol	3:1	-	2 - 4hrs	-
Mixed Canola with Used Cooking oil	KOH 1% wt.	methanol ethanol	6:1	50	2hrs	98% ester content
Rapeseed	KOH 1% wt.	methanol	6:1	65	2hrs	95 - 96% yield
Sunflower	NaOH 1% wt.	methanol	6:1	60	2hrs	97.1% yield

Source: (Dorado, 2002)

Table 2.7: Examples of Homogenous Acid Catalysis

Feedstock	Catalyst Type	Alcohol	Alcohol/Oil Ratio	Temperature (°C)	Reaction Time	Conversion/Yield (%)
Soybean	H ₂ SO ₄ 1% wt.	butanol	30:1	117	3hrs	-
Soybean	H ₂ SO ₄ 3% wt.	methanol	30:1	60	48hrs	98% conversion
Rubber seed oil	H ₂ SO ₄ 0.5% wt.	methanol	6:1	45	20 – 30mins	-
Tobacco seed oil	H ₂ SO ₄ 1-2% wt.	methanol	18:1	60	25mins	91% yield
Used Frying Oil	H ₂ SO ₄ 3.8:1 mole ratio	methanol	24.5:1	70	4hrs	99% yield
High AV Oil	H ₂ SO ₄ 0.5% wt.	methanol	20:1	120	5mins Residence time	99.5% yield

Source: Dorado (2002); AV=Acid Value

Table 2.8: Examples of Heterogeneous Base Catalysis

Feedstock	Catalyst Type	Alcohol/Oil Ratio	Temperature (°C)	Reaction Time (hr)	Yield (%)	Leaching
Rapeseed oil	MgO	22:1	reflux	22	94	n/a
Beef Tallow	BaO	6:1	reflux	1	96	n/a
Rapeseed oil	K/KOH/Al ₂ O ₃	9:1	60	1	85	yes
Soybean oil	Fe ³⁺ /Mg-Al	6:1	80	1	38	yes
Jatropha oil	MgO/Al ₂ O ₃	10:1	reflux	3	97	n/a
Rapeseed oil	K ₂ CO ₃ /Al ₂ O ₃	15:1	50	3	99	n/a
Sunflower oil	La ₂ O ₃ /ZrO ₂	30:1	200	5	85	n/a

Source: Ma *et. al.*, (2008).

Table 2.9: Examples of Heterogeneous Acid Catalysis

Feedstock	Catalyst Type	Alcohol/ Oil Ratio	Temperature (°C)	Reaction Time (hr)	Yield (%)	Leaching
Babassau oil	Amberlyst 15	300:1	60	8	74	n/a
Canola (20% FFA)	TPA/HZ ^a	9:1	200	10	90	no
Palm Kernel oil	SO ₄ ²⁻ /ZrO ₂	6:1	200	1	95	n/a
Cottonseed oil	SO ₄ ²⁻ /TiO ₂	12:1	230	8	96	n/a
Palmitic acid	SO ₄ ²⁻ /ZrO ₂ /SiO ₂	10:1	68	6	89	n/a
WCO (28% FFA)	SO ₃ H/starch	30:1	80	8	92	n/a
Cottonseed oil	SO ₄ ²⁻ /TiO ₂ -SiO ₂	9:1	200	6	92	n/a
Palm oil (5% FFA)	Arene-SO ₃ H/SBA 15	20:1	140	4	95	n/a
Cottonseed oil	SO ₃ H/starch	20:1	80	12	97	yes

Source: Watkins (2004); HZ^a = Hydrous Zirconia

2.4.3.3 Heterogeneous Base Catalysis

Heterogeneous base catalysts are gaining significant attention from biodiesel researchers because the process of catalyst removal is simple and there is no waste water generated during catalyst removal step. In addition, heterogeneous catalysts can be regenerated and reused, making biodiesel production as a continuous flow process possible. However, the use of such catalyst is limited by free fatty acid usually contained in low quality feedstock such as used cooking oil (Watkins *et. al.*, 2004). Nevertheless, these catalysts can be used with good quality feedstock and the advantages of using heterogeneous base catalysts include catalyst reusability, simplicity in catalyst removal, low reaction temperature and short reaction time; these have attracted the interest of many researchers to investigate this area (Watkins *et. al.*, 2004).

The mechanism scheme of heterogeneous base catalysis, using CaO as an example catalyst, is as shown in Figure 2.13.

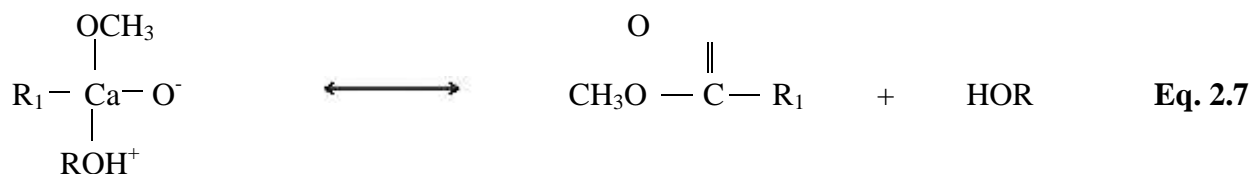
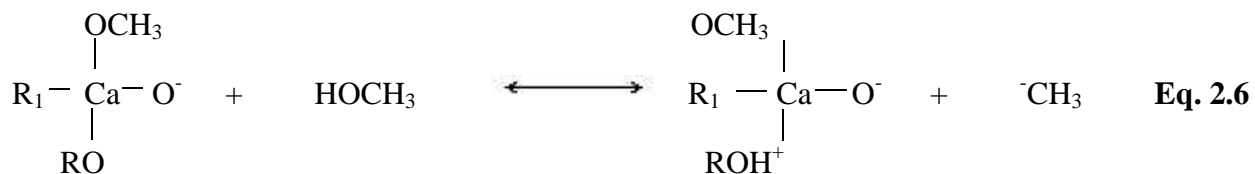
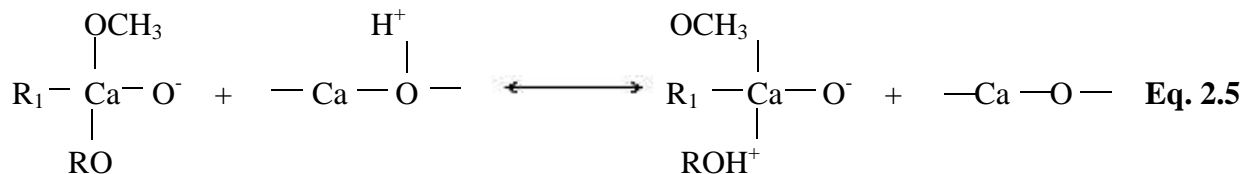
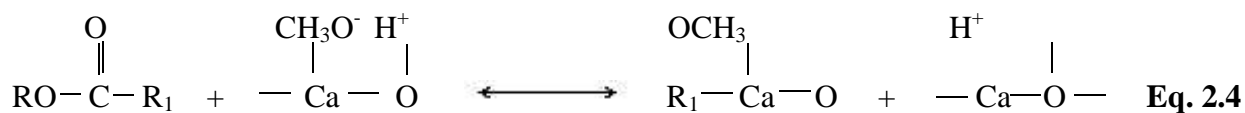
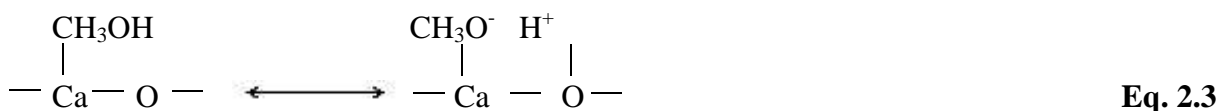
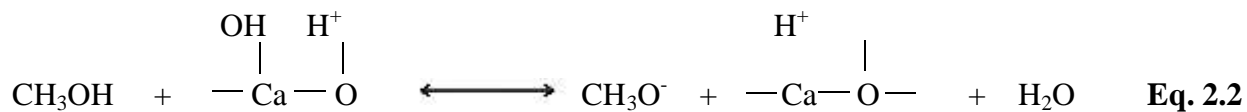
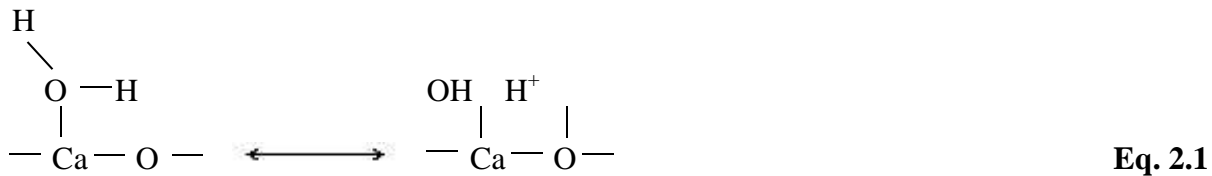


Figure 2.13: Heterogeneous Base Catalysis in Trans-esterification
 Source: Issariyakul (2011)

The first step involves the extraction of H^+ from H_2O to form surface OH^- on the basic site of CaO (Eq. 2.1). Then H^+ is extracted from methanol to form methoxide ion and water (Eq. 2.2). Also, methanol can adsorb dissociatively on CaO (Eq. 2.3). The next step is an attack of the adsorbed methoxide ion to acylglycerol molecule to form tetrahedral intermediate (Eq. 2.4) which is protonated afterward (Eq. 2.5). The tetrahedral intermediate can also react with methanol to generate methoxide anion (Eq. 2.6). In the last step, the rearrangement of the tetrahedral intermediate leads to the formation of methyl ester and glycerol or acylglycerol (Eq. 2.7).

Examples of heterogeneous base catalysis are illustrated in Table 2.8. Common heterogeneous base catalysts are those of alkaline earth metal oxides such as MgO, CaO, SrO, and BaO. BaO is not suitable in methanolysis because it dissolves in methanol and creates leaching problems, while SrO reacts strongly with CO_2 and water in the air to form $SrCO_3$ and $Sr(OH)_2$ (Issariyakul, 2011). The catalytic activity of MgO is not very high due to the low basic strength of MgO, leaving CaO the most attractive alkaline earth metal oxide catalyst. Alkali metals such as Li, Na, and K can be used to promote these catalysts. It has been shown that pure $LiNO_3$ is inactive and CaO alone has low activity towards trans-esterification of tributyrate (Watkins *et. al.*, 2004). Proper impregnation of $LiNO_3$ on CaO results in a highly dispersed monolayer Li^+ on CaO that exhibits high catalytic activity on trans-esterification. However, if too much $LiNO_3$ is added, the resulting catalyst is associated with the non-dissociative NO_3^- ions over the CaO surface and the formation of $LiNO_3$ multilayers. These inactive species have proven detrimental to catalytic activity of the Li/CaO catalyst. In addition, Li/CaO has higher basic strength and activity as compared to Na/CaO and K/CaO (Meher *et. al.*, 2006a; Meher *et. al.*, 2006b). This is because the

small size of the Li^+ ion makes it easier to be inserted more properly in the CaO framework creating oxygen gaps that contribute to the basic strength of the catalyst.

Alternatively, K_2CO_3 supported on Al_2O_3 can be used in trans-esterification. It is a commonly used catalyst in many organic chemical reactions such as isomerization, alkylation, and Trans-esterification. This is because $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ has strong basic strength and the catalytic activity of solid base catalysts depends greatly on basicity of the catalyst, rather than surface area ((Meher *et. al.*, 2006a; Meher *et. al.*, 2006b). The catalytic activity of $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ is superior to metal promoted CaO and SrO and only second to alkali metal promoted BaO. Unlike alkali metal promoted BaO, the leaching of $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ is negligible

2.4.3.4 Heterogeneous Acid Catalysis

Heterogeneous acid catalysts are most promising for biodiesel production and are expected to dominate commercial biodiesel industries in the coming years. This is due to the simplicity in the biodiesel purification step that eliminates waste water, reusability that makes continuous flow process possible and the ability to handle low quality feedstock with high FFA content through simultaneous esterification and trans-esterification reactions (Kulkarni *et. al.*, 2006). The disadvantage of heterogeneous acid catalysts is the lower catalytic activity which makes its operation effective only in high reaction temperature and high reaction time up to 22 hours (Kulkarni *et. al.*, 2006).

Catalyst leaching is another issue for this type of catalyst. If the catalyst leaches into biodiesel, purification will be required to remove the contaminated catalyst, and thereby, generating waste solvent and increase biodiesel production cost. In addition, catalyst reusability or catalyst

deactivation is usually studied for this type of catalyst. Freedman *et.al.* (1986) described the simultaneous esterification-trans-esterification reaction mechanism as shown in Figure 2.14.

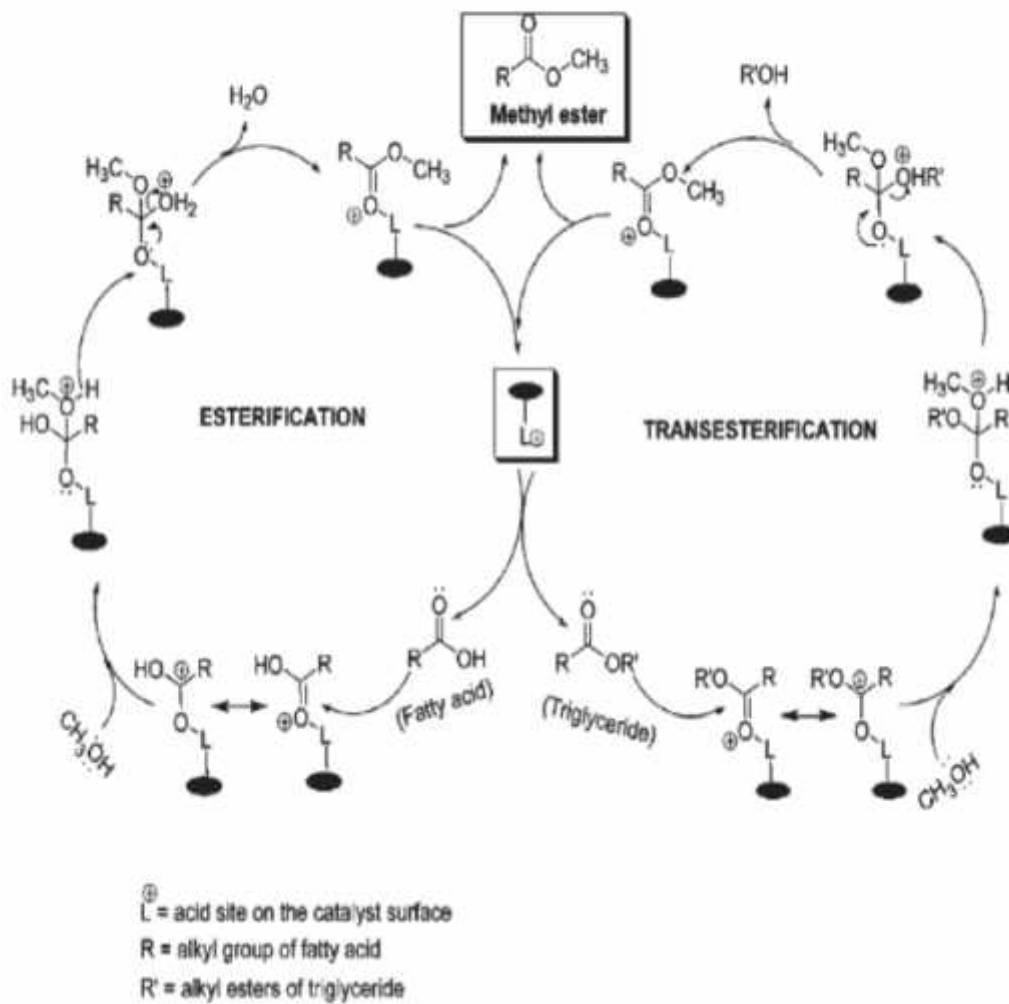


Figure 2.14: Mechanism for Heterogeneous Acid Catalysis in Esterification and Transesterification

Source: Freedman *et.al.*, (1986).

In the esterification reaction, FFA reacts with methanol to form methyl ester. The first step involves an adsorption of FFA on the acidic site on the catalyst surface. The interaction between

FFA and the acidic site leads to carbocation. An attack of methanol then results into a tetrahedral intermediate. Finally, methyl ester is formed as a result of an elimination of water molecule from the tetrahedral intermediate. In trans-esterification, acylglycerol including tri-, di- and monoglyceride reacts with methanol to form methyl ester. The reaction mechanism occurs in a similar manner as that described in the esterification reaction. The formation of methyl ester stems from an elimination of diglyceride, monoglyceride, and glycerol from the tetrahedral intermediate when triglyceride, diglyceride, and monoglyceride are adsorbed in the acidic sites, respectively. Various types of heterogeneous acid catalysts are available for esterification and trans-esterification (Table 2.9).

Ion-exchange resins such as Amberlyst series and Nafion silica composite solid acid catalysts are one of the first solid acid catalysts used for biodiesel production applications (Liu *et. al.*, 2006; Dos Reis *et. al.*, 2005; Liu, 1994). These resins have low catalytic activity, and therefore, require extreme reaction temperatures. Unfortunately, resins usually have low thermal stability (<140 °C) and the reaction was conducted at a mild temperature of 60 °C, which resulted in a low reaction conversion of 74% (Liu, 1994).

Alternatively, silica matrix of mesoporous solids can be used, but the catalytic activity is low. Metals such as aluminum, zirconium, titanium, or tin ions can be added to improve catalytic activity on esterification and trans-esterification. However, metal-doped materials tend to behave like weak acid, of which high catalytic activity is not exhibited. To improve catalytic activity of the catalyst, high dispersion of a strong acid species on interior surfaces of mesoporous supports is required (Chen *et. al.*, 2007b).

The Tungsten-loaded catalyst is an interesting catalyst. WO_3/ZrO_2 is used as a catalyst in esterification of palm oil and a conversion of 98% is obtained (Liu *et. al.*, 2006). However, if too much WO_3 is added, the catalyst becomes amorphous due to excess coverage of WO_3 species on ZrO_2 . The presence of the monoclinic phase of zirconia has adverse effects on catalytic activity and, therefore, the tetragonal phase is preferred. It was found that the catalytic activity of WO_3/ZrO_2 catalyst is provided by interaction between amorphous WO_3 and crystalline ZrO_2 . In addition to zirconia, Al_2O_3 has been used as support due to its high surface and large pore size that can accommodate TAG molecules with long fatty acid chains (Issariyakul, 2011; Liu *et. al.*, 2006).

A 97% ester yield was observed from trans-esterification of waste cooking oil using $\text{WO}_x/\text{Al}_2\text{O}_3$; however, the acid value was observed at 4.7 higher than that specified in biodiesel standards (Komintarachat and Chuepeng, 2009). The sulfated catalyst is another interesting catalyst. By using a conventional homogeneous acid H_2SO_4 as a precursor, SO_4^{2-} on ZrO_2 and TiO_2 can be obtained and the reaction yields a 95-96% conversion (Chen *et.al.*, 2007a; Jitputti *et. al.*, 2006).

The catalytic activity of sulfated zirconia (SZ) can be further increased by dispersing it onto mesoporous silica materials such as MCM-41 or SBA-15, thus increasing dispersion and acid sites. SBA-15 is a preferred choice in esterification and trans-esterification due to its larger pore size facilitating the long chain fatty acids. The doped zirconia on SBA-15 (unsulfated $\text{ZrO}_2/\text{SiO}_2$) shows low acidity and its acidity can be enhanced by an addition of sulfur. It is believed that an addition of sulfur causes a formation of tetragonal ZrO_2 and enhances the phase segregation by extracting zirconia to the surface of the mixed oxides and stabilizes the tetragonal phase (Chen and Fang, 2011; Chen *et. al.*, 2007a; Chen *et. al.*, 2007b).

In addition, the hydrophilicity of SBA-15 surface is partially responsible to catalyst stability. In general, water formed during esterification is adsorbed on acid sites resulting in a lower concentration of acidic sites available for the reaction. However, this water can be readily adsorbed on the neighbouring silica surface of SBA-15 and some acidic sites can thus be recovered.

Despite its high activity, SZ-type catalyst shows sulfate leaching problem, which is enhanced by hydrolysis. To counter this problem, chlorosulfonic acid is used as an alternate acid to sulfuric acid for SZ catalyst preparation. The catalyst was tested in esterification of acetic acid with *p*-tert-butylcyclohexanol and no leaching was observed (Yadav and Murkute, 2004). More recently, a high reaction conversion (92 - 97 %) was obtained using a sulphated starch catalyst (Lou *et. al.*, 2008). An interesting point about starch derived catalyst is that the reaction requires a relatively low temperature (80°C); however, sulphate leaching has been observed.

More recently, Fe-Zn double metal cyanide catalysts (DMC) have been investigated for transesterification of vegetable oil (Fang *et. al.*, 2010; Srinivas and Satyarthi, 2010; Yan *et. al.*, 2011). Cyanide is a highly toxic chemical compound containing cyano group (-C N). They have a general formula: $K_4Zn_4[Fe(CN)_6]_3 \cdot xH_2O$ (6 \leq x \leq 12) and the catalyst exhibits highest activity when x = 6. The Fe and Zn ions are linked through cyano groups.

The most interesting feature of this catalyst is its hydrophobicity as it can tolerate water content in the feedstock oil up to 20% without significant loss in catalytic activity (Srinivas and Satyarthi, 2010). The catalyst is tested with various vegetable oils and shows promising catalytic activity (84 - 99% conversion) and can be reused without loss in catalytic activity and no purification is required for catalyst regeneration.

However, when non-edible oils (such as jatropha and rubber seed oil) are used as feedstock, the acid value of the resulting biodiesel is higher than that specified in biodiesel standards, requiring further catalyst leaching investigation. Another catalyst such as zinc stearate (ZS) on silica (Si) was investigated. ZS ($\text{Zn}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$) is a zinc soap that is not soluble in polar solvents, but soluble in aromatic hydrocarbons when heated (Srinivas and Satyarthi, 2010).

When ZS/Si is tested on trans-esterification of waste cooking oil, a 98% ester yield can be obtained (Jacobson *et. al.*, 2008). In addition, catalyst leaching is not detected and the catalyst can be reused without significant loss in its activity. However, the resulting biodiesel shows an acid value of 3.3, higher than those specified in biodiesel standards. In summary, further development in heterogeneous acid catalysis is required especially in terms of ester yield, acid value of the product, and catalyst leaching (Yadav and Murkute, 2004).

2.4.4 Effects of Reaction Time, Temperature, and the Reaction Kinetics

In general, conversion and yield increase as reaction time increases. The reaction starts with the two liquid phases (alcohol and oil). Once the reaction is initiated, DAG and MAG are formed as the reaction intermediates and act as surfactants to enhance the mass transfer of TAG into methanol. At this point, the reaction mixture can be either one or two phase depending on the amount and type of alcohol used in the reaction, the amount and type of catalyst used, as well as reaction conditions. Then the glycerol is formed as the reaction by-product and separates out as an additional phase (Fogler, 1999).

In the case of homogeneously catalyzed reaction, the separation of glycerol often leads to the catalyst dissolving in glycerol phase, which lowers catalyst concentration in the reaction mixture and, therefore, slow down the reaction rate (Yadav and Murkute, 2004).

The rates of the reaction and rate constants are often used in kinetic studies in order to examine how fast the reaction proceeds. These kinetic parameters are sometimes evaluated based on the shunt (overall) reaction mechanism in which 3 moles of TAG react with 3 moles of alcohol to yield 3 moles of ester and 1 mole of glycerol (Singh and Fernando, 2007). Although the kinetic models can be simplified using the shunt reaction mechanism, it is highly unlikely that three molecules of methanol would simultaneously attack the TAG molecule to form three molecules of methyl ester. The shunt mechanism is easily disproved by the formation of DAG and MAG, which is widely reported in the literature (Singh and Fernando, 2007).

Therefore, the kinetic models should be derived based on three consecutive reversible reaction steps and the rate constants of each reaction step are usually different. The values of the rate constants indicate the rates of the corresponding reaction step, as well as reversibility of each step. Moreover, they can be used to determine the rate determining step (RDS) that controls the kinetics of overall trans-esterification. Results from the literature suggest that trans-esterification of vegetable oils (virgin oils) with low alcohol to oil ratio (6:1) using homogeneous base catalysts follows second order kinetics (Noureddini and Zhu, 1997).

The reaction step TAG to DAG is often found to be the rate-limiting step that controls the kinetics of the overall reaction. In addition, the rate constant of the reverse reaction MAG to GL is usually lowest, due to the phase separation of glycerol. However, this reaction can still take place at the glycerol-methyl ester interface rendering a small positive value of the rate constant (Mittelbach and Enzelsberger, 1999).

Trans-esterification is strongly dependent on reaction temperature and is favored by high temperatures. In the mass transfer controlled region, the higher the temperature the higher the

energy state of the reacting molecules that would be translated into faster molecular vibration and movement; thus the reacting molecules have more chance to collide with one another. In the kinetically controlled region, temperature dependency of the reaction rate is often used to calculate the activation energy of the reaction by plotting logarithm of the rate constant versus the reciprocal of the reaction temperature (Fogler, 1999). The equation is known as the Arrhenius equation (equation 2.8).

$$K = Ae^{\frac{-E_a}{R}} \quad \text{Eq. 2.8}$$

K is the rate constant; A is pre-exponential factor; E_a is the activation energy; R is the gas constant; T is reaction temperature. The activation energy is referred to the minimum energy required for a reaction to take place. From Equation 2.8, if the reaction temperature is increased, the rate constant will also increase and, therefore, the reaction will proceed at a faster rate.

A homogeneous alkali-catalysed trans-esterification can be performed at temperatures as low as room temperature. However, higher temperatures are usually employed, especially when an acid catalyst is used. Nevertheless, the reaction temperature should be below the boiling point of the corresponding reacting alcohol that is 65 °C for methanol and 78 °C for ethanol (Ma *et. al.*, 1999).

However, heterogeneous acid catalysis usually requires extreme reaction temperatures (up to 220 °C). If the reaction is operated at temperatures higher than the boiling point of the corresponding reacting alcohol, pressure needs to be applied to the reaction mixture to maintain the reacting alcohol in liquid state (Fogler, 1999).

2.5 Properties of Biodiesel

Table 2.10: Fuel Standards and Test methods for Pure Biodiesel

Property	ASTM Method	EN Method	ASTM Limits	EN Limits
Water and sediment	ASTM D2709	EN ISO 12937	0.05 max (% vol.)	500 max (mg/kg)
Total glycerol	ASTM	EN 14105	0.24 (% mass)	0.25 max (% mol)
Methanol	-	EN 14110	0.2 max (% vol.)	0.2 max (% mol)
Ash content	ASTM D874	ISO 3987	0.02 max (% mass)	0.02 max (% mol)
Sulfur	ASTM D5453	EN ISO 20846		10 max
S15 grade		EN ISO 20884	0.0015 max (% mass)	(mg/kg)
S500 grade			0.05 max (% mass)	
Cetane number	ASTM D613	EN ISO 5165	47.0 min	51.0 min
Carbon residue	ASTM D4530	EN ISO 10370	0.05 max (% mass)	0.3 max (% mol)
Flash point	ASTM D93	EN ISO 3679	130 min (°C)	120 min (°C)
Density, 15°C		EN ISO 3675		860 – 900
		EN ISO 12185		(kg/m ³)
Kin. Viscosity 40°C	ASTM D445	EN ISO 3104	1.9 – 6.0	3.5 – 5.0
		ISO 3105	(mm ² /s)	(mm ² /s)

Source: AOCS, 1998).

The use of low quality biodiesel (due to incomplete reaction or contaminants) in a diesel engine could result in several engine problems, such as coking (Ma *et. al.*, 1999). In order to prevent such problems, several fuel standards have been adopted for quality control. Among these standards are ASTM method (American Society for Testing and Materials) and EN method (European Committee for Standardisation) (AOCS, 1998). Some of these standards and methods are listed in Table 2.10. These standards serve as guide in determining the properties of biodiesel.

2.5.1 Kinematic Viscosity

Viscosity is a measure of the resistance of a fluid to flow (measure of fluid friction). In the case of liquid fuels, the less viscous the fluid is, the greater its ease of movement (fluidity) (Evangelos, 2013). This is a critical property in diesel engine because it affects the behaviour of fuel injection.

Viscosity is temperature-dependent, the higher the temperature the lower the viscosity. High viscosity can cause larger droplet sizes on injection, poorer vapourisation and narrower injection spray angle (Parag *et. al.*, 2013). This can lead to overall poorer combustion, higher emissions and increased oil dilution. The reduced fuel leakage losses in the (mechanical) fuel pump due to higher kinematic viscosity lead also to higher injection pressures and, also higher mass of injected fuel (Evangelos, 2013).

Fuels with high viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Higher viscosity value of vegetable oil (when compared to the viscosity of diesel) makes it unsafe to be used as fuel in compression

injection engine. Trans-esterification of vegetable oil produces biodiesel of very small viscosity value suitable for good diesel engine performance. According to ASTM standard, viscosity of biodiesel of good quality at 40⁰C is 1.9 – 6.0 mm²/s.

2.5.2 Density

Density of a substance is the measure of the weight per unit volume of that substance. The air-fuel ratio and energy content within the combustion chamber are influenced by fuel density. The denser the oil the higher the energy content per liter. In general, densities of biodiesel are slightly higher than that of petroleum diesel, and increasing the level of biodiesel blends increases the blend's density (Evangelos, 2013).

FAME density is strongly affected by the degree of unsaturation, with higher unsaturation leading to increased density. It has been reported that biodiesel density is also affected by chain length, that is, the higher the chain length the higher the density (Parag *et. al.*, 2013).

2.5.3 Flash Point

Flash point temperature of a fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures are required for proper safety and handling of fuel (Tan *et. al.*, 2011).

2.5.4 Pour Point

Pour point is the lowest temperature at which a material will flow due to crystal agglomeration. It is one main cold flow property and it is useful for characterizing the suitability of a fuel for large storage and pipeline distribution (Zlatica and Biljana, 2009; Chiu *et. al.*, 2004). The ASTM

specifies standard of -15°C to 10°C as the pour point of biodiesel, below the specified temperature the fuel loses its flow characteristics and becomes solid, clogging the engine (Kulkarni and Dalai, 2006).

2.5.5 Heating Value

Heating value (Heat of Combustion) of fuel is the amount of heat energy released by the combustion of a unit value of such a fuel. One of the most important determinants of heating value is moisture content. Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is negligible (Gerhard, 2005)

2.5.6 Ash Content

Ash is a measure of the amount of metals or waste materials present in the fuel. High concentration of these materials leads to injector tip plugging, combustion deposits and injection system wear. It lowers the heating value of biodiesel (Nada, 2011).

2.5.7 Sulphur Content

One important factor that should be considered is biodiesel sulphur content. This is because its release into the environment has negative effects, such as acid rain. Petroleum diesel has higher sulphur content when compared to biodiesel (William, 2006).

Therefore, of particular concern are the requirements to reduce the sulphur contents of diesel fuel. Ultra-low sulphur diesel has less than 50 ppm sulphur and new diesel regulations in most countries is sulphur content of less than 10 ppm (Miguel, 2006).

2.5.8 Cetane Number

Cetane Number (CN) is a measure of auto ignition quality of a fuel. It is a relative measure of the interval between the beginning of injection and auto ignition of the fuel. The higher the cetane number, the shorter the delay interval and the greater is its combustibility. Lower CN causes higher exhaust gas emissions and particulate matter. The CN of diesel fuel in European Union (EU) is regulated at 51, specified at 42 in Brazil and 40 in USA (Güzel, 2012). Since biodiesel is largely composed of long-chain hydrocarbon groups (with virtually no branching or aromatic structures), it typically has a higher CN than petroleum diesel (a good advantage over petroleum diesel). The CN of pure FAME molecules increases with chain length, but this effect is masked when considering complex mixtures of FAME fuels. On the other hand, the CN of FAME fuels clearly vary with average degree of unsaturation, the higher the degree of unsaturation the lower the CN (Parag *et.al.*, 2013).

In general, diesel engines will perform efficiently well with fuels of 50 cetane numbers. While fuels with low cetane numbers (of say 35) will cause difficulty in starting the engine, generate noise and thick exhaust smoke (Sivaramakrishnan and Ravikumar, 2012).

2.6 Comparison of Biodiesel and Petroleum Diesel

Zahira *et. al.* (2013) gave a comparison of the properties of WCO biodiesel and petroleum diesel in their research work. This is illustrated in Table 2.11.

Table 2.11: Comparison of the Properties of Waste Cooking Oil (WCO) Biodiesel and Petroleum Diesel

Fuel Properties	Units	WCO Biodiesel	Petroleum Diesel
Kinematic Viscosity (40 ⁰ C)	mm ² /s	5.3	1.9 – 4.1
Density	kg/L	0.897	0.750 – 0.840
Flash Point	⁰ C	198	157 – 185
Pour Point	⁰ C	-11	-19 – -13
Cetane Number		48 – 54	40 – 46
Ash Content	%	0.004	0.008 – 0.0010
Sulphur Content	%	0.06	0.35 – 0.55
Carbon Content	%	0.33	0.35 – 0.40
Water Content	%	0.04	0.02 – 0.05
Higher Heat Value	MJ/kg	42.65	45.62 – 46.48
Free Fatty Acid	mgKOH/g	0.1	-

Source: Zahira *et. al.*, (2013).

Comparison of the emission of non-environmental friendly substances from biodiesel and petroleum diesel is shown in Figure 2.15. It is important to note that damage associated with biodiesel production is by far less than the environmental damage suffered during petroleum diesel production. This has been accounted for by many researchers (Debalina and Ralph, 2013; Liang *et. al.*, 2013; Yee *et. al.*, 2009; Yusoff, 2006).

From Figure 2.15, harmful substances emitted into the environment are expressed in term of baseline of 100% petroleum diesel in each category. Air toxics from pure biodiesel is 10% of the

total air toxics released from petroleum diesel, CO released from pure biodiesel is less than 60% of CO released by petroleum diesel during utilization. Petroleum diesel releases more hydrocarbons and particulate matter than pure biodiesel, an increase in petroleum diesel in a blend of biodiesel and petroleum diesel results into increase in the release of these harmful substances. It is interesting to note that biodiesel releases higher nitrogen oxides (NO_x) than that released from petroleum diesel, this accounts for higher algae boom in water in the case of biodiesel (William, 2006).

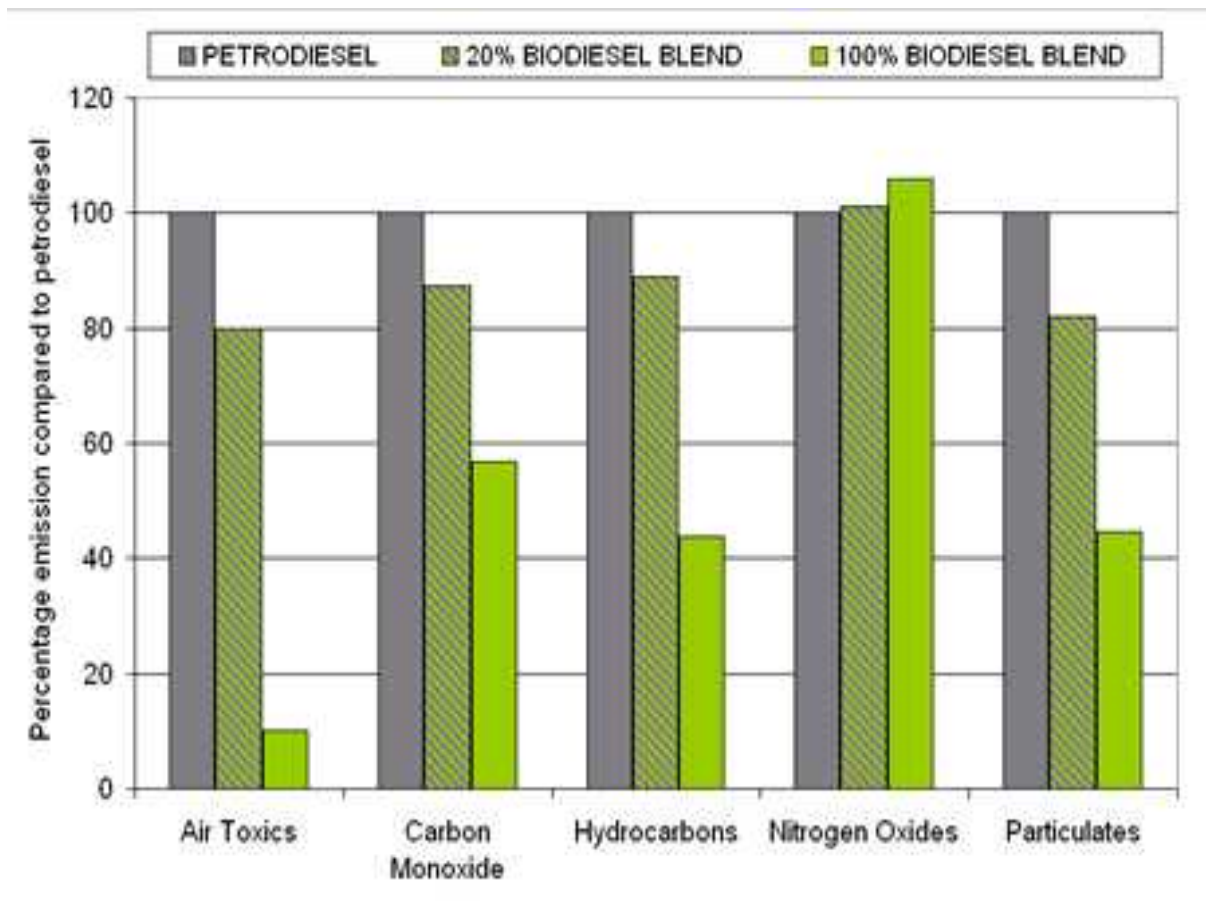


Figure 2.15: Comparison of Emission from Biodiesel and Petroleum Diesel
 Source: William (2006).

Some of advantages of biodiesel over petroleum diesel are enumerated thus:

- Biodiesel is obtained from renewable raw materials.

- Biodiesel life cycle helps to checkmate excess release of CO₂ into the environment.
- It is easily biodegradable.
- Biodiesel flash point is over 120°C (greater flash point of petroleum diesel), this makes it safer during transportation and storage.
- Biodiesel has higher cetane number than that of petroleum diesel; a quality which enhances diesel engine performance.
- Biodiesel has close to zero sulphur content

2.7 Life Cycle Assessment (LCA)

According to ISO (2006), LCA is defined as the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle.

It is an investigation and evaluation of the environmental impacts of a given product caused by its existence. It measures the whole life cycle of the product. LCA is often referred to as “*cradle-to-grave*” approach which may begin with the gathering of raw materials from the earth to create the product and ends at the point when all materials are returned to the earth. It is a concept that allows the use of reasonable and well-defined assumptions.

Most LCA studies of bioenergy from agriculture focus on the Global Warming Potential (GWP) (Bernesson and Hansson, 2006). In recent years life cycle thinking has become a key focus in environmental policy making. A clear example is the concept of IPP (Integrated Product Policy) as communicated by the European Union. Many developed countries (America, Germany, China) develop strategies that promote life cycle thinking as a key concept.

Another development is the sustainability reporting movement. Many companies now report on the sustainability aspects of their operations. In the recent years there is a sharp increase in the development of Environmental Product Declaration (Goedkoop *et. al.*, 2010).

2.7.1 Phases of Life Cycle Assessment (LCA)

Basically, any LCA study comprises of four distinct, but interrelated, phases. The phases are:

- Defining the goal and scope of study
- Making an inventory analysis of all emissions and resource consumption parameters
- Applying impact assessment method on the result
- Interpreting the result.

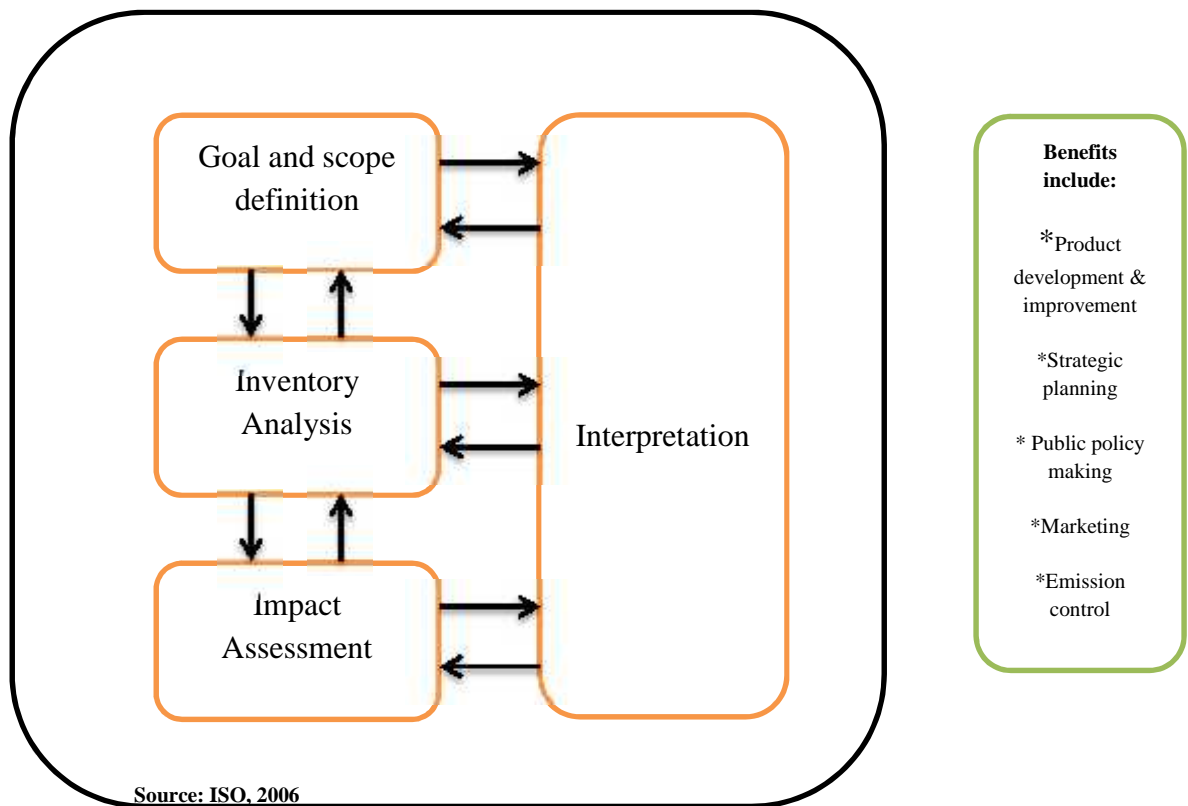


Figure 2.16: Framework of Life Cycle Assessment (LCA)

2.7.1.1 Goal and Scope

The goal and scope of an LCA are guides that provide direction and help to ensure the consistency of the LCA performed. It addresses

- The reason for executing the LCA and the questions which need to be answered.
- A precise definition of the products, its life cycle and the function it fulfils.
- Definition of comparison basis (functional unit) when products are to be compared.
- A description of the system boundary.
- A description of the way allocation problems will be dealt with
- Data and data quality requirements.
- Assumptions and limitations.
- The requirements regarding the LCIA procedures and the subsequent interpretation to be used.
- The intended audiences and the way the results will be communicated.

2.7.1.2 Inventory Analysis

Inventory analysis phase involves allocation of flows and releases, data collection and calculation procedures to quantify related inputs and outputs of a product system. Data collection can be achieved through the use of relevant in-built data in LCA software (background data) and/or use of specific data generated from your system (Debalina and Ralph, 2013).

2.7.1.3 Life Cycle Impact Assessment (LCIA)

Impact assessment phase of LCA is defined as the phase aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts of a product or system,

using the Life cycle Inventory (LCI) results and providing information for the life cycle interpretation phase. It involves

- **Selection and definition of impact categories (mandatory):** identifying relevant environmental impact categories (e.g. global warming, acidification, terrestrial toxicity).
- **Classification (mandatory):** assigning LCI results to the impact categories (e.g. classifying carbon dioxide emissions to global warming).
- **Characterisation (mandatory):** modeling LCI impacts within impact categories using science-based conversion factors (e.g. modeling the potential impact of carbon dioxide and methane on global warming).
- **Single score (optional):** emphasizing the most important potential impacts.

Table 2.12 shows some of the impact categories used in LCIA, as reported in the literatures.

Table 2.12: Impact Categories Used in Life Cycle Impact Assessment (LCIA)

Impact Category	Scale	Example of LCI Data (i.e classification)	Common Possible Characterisation Factor	Description of Characterisation Factor
Global Warming	Global	Carbon dioxide (CO ₂) Nitrogen dioxide (NO ₂) Methane (CH ₄) Chlorofluorocarbons (CFCs) Hydrochlorofluorocarbons (HCFCs) Methyl Bromide (CH ₃ Br)	Global Warming Potential	Converts LCI data to carbon dioxide (CO ₂) equivalents. Note: global warming potentials can be 50, 100 or 500 year potentials.
Stratospheric Ozone Depletion	Global	Chlorofluorocarbons (CFCs) Hydrochlorofluorocarbons (HCFCs) Halons Methyl Bromide (CH ₃ Br)	Ozone Depleting Potential	Converts LCI data to trichlorofluoromethane (CFC-11) equivalents
Acidification	Regional Local	Sulphur oxides (SO _x) Nitrogen oxides (NO _x)	Acidification Potential	Converts LCI data to hydrogen (H ⁺) ion

		Hydrochloric Acid (HCl) Hydrofluoric Acid (HF) Ammonia (NH ₄)		equivalents.
Eutrophication	Local	Phosphate (PO ₄) Nitrogen oxide (NO) Nitrogen dioxides (NO ₂) Nitrates (NO ₃ ⁻) Ammonia (NH ₄)	Eutrophication Potential	Converts LCI data to phosphate (PO ₄) equivalents.
Photochemical Smog	Local	Non-methane hydrocarbon (NMHC)	Photochemical Oxidant Creation Potential	Converts LCI data to ethane (C ₂ H ₆) equivalents.
Terrestrial Toxicity	Local	Toxic chemicals with a reported lethal concentration to rodents	LC ₅₀	Converts LC ₅₀ data to equivalents; using multimedia modeling, exposure pathways.
Aquatic Toxicity	Local	Toxic chemicals with a reported lethal concentration to fish	LC ₅₀	Converts LC ₅₀ data to equivalents; using multimedia modeling, exposure pathways.
Human Health	Global Regional Local	Total release to air, water and soil	LC ₅₀	Converts LC ₅₀ data to equivalents; using multimedia modeling, exposure pathways.
Resource Depletion	Global Regional Local	Quantity of minerals used	Resource Depletion Potential	Converts LCI data to a ratio of quantity of resource used versus quantity of resource left in reserve.
Land Use	Global Regional Local	Quantity disposed of in a landfill or other land modifications	Land Availability	Converts mass of solid waste into volume using an estimated density.
Water Use	Regional Local	Water used or consumed	Water Shortage Potential	Converts LCI data to a ratio of quantity of water used versus quantity of resource left in reserve.

Source: Debalina and Ralph (2013).

Impact indicators are typically characterized using the following equation:

$$[\text{Inventory Data}] \times [\text{Characterisation Factor}] = \text{Impact Indicators}$$

Eq. 2.9

For example, all greenhouse gases can be expressed in terms of CO₂ equivalent by multiplying the relevant LCI results by a CO₂ characterisation factor and then combining the resulting impact indicators to provide an overall indicator of global warming potential.

2.7.1.4 Interpretation

Interpretation is the phase of LCA in which the findings from the inventory analysis and impact assessment are considered together. This phase also provides results that are consistent with the defined goal and scope and which reach conclusions explain limitations and provide recommendations (ISO, 2006).

2.7.2 Why Biodiesel Life Cycle Assessment?

The increased awareness of the importance of environmental protection and the possible impacts related to products and services call for interest in the development of methods that best address their impacts. LCA addresses the environmental aspects and potential environmental impacts throughout a product's life cycle. Life cycle assessment is designed as a decision-making tool for designers, regulatory agencies, and business organizations (ISO, 2006).

Biodiesel LCA can assist in:

- identifying opportunities to improve the production process of biodiesel and its usage at various stages of its life cycle
- the choice of materials that are environmental friendly during biodiesel production
- informing decision-makers in agriculture, industry, government and non-government organizations for the purpose of short and long term strategic planning, priority setting, product or process design or redesign

- the enforcement of biodiesel production standards
- the selection of relevant indicators of environmental performance, including measurement techniques
- marketing (e.g. implementing an eco-labeling scheme, making an environmental claim, or design an environmental policy) (ISO, 2006).

CHAPTER THREE

MATERIALS AND METHODS

3.0 Introduction

In this chapter are itemised all the materials used in the study. Also described are the details of the methods used in carrying out the analysis and tests.

3.1 Materials

3.1.1 Raw Waste Oils Used

In this research work, three different waste oils were utilised basically for biodiesel production. The oils used are waste groundnut oil (WGO), waste soyabean oil (WSO) and crude palm kernel oil (CPKO). Both the WGO and WSO, obtained from Cafeteria II, Covenant University, Ota, after being used for cooking.

The CPKO used is referred to as waste oil because of the process involved in its production. It was produced (in a local plant in Ota, Ogun state, Nigeria) in a traditional way from palm kernel seeds. During the oil extraction from seeds, the seeds were subjected to very high temperature, 800⁰C, and this resulted into oxidative and thermolytic reactions, the same reactions experienced by WGO and WSO during cooking (Kulkarni and Dalai, 2006).

3.1.2 Chemicals/Reagents Used

Methanol (99.8%, Romil Ltd UK), Sodium hydroxide pellets (98%, Qualikems, India), Potassium hydroxide pellets (95%, Riedel-Dietzen, Germany), Hydrochloric acid (98%, Sigma-

Aldrich, UK), Tetraoxosulphate (IV) acid (98%, J.T Baker, USA), Benzene (97.7%, Sigma-Aldrich, UK).

3.1.3 Equipment Used

Agilent Technologies 7890A (GC System/5975C VL MSD, USA), Atomic Absorption Spectroscopy (AAAnalyst 200 Perkin Elmer precisely, USA), Cimarec Digital Magnetic Stirring Hot Plate (7.25" x 7.25", USA), Anton Paar DMA 38 Density Meter (USA), Pensky-Martens Automatic Closed Tester, (Normalab NPM 440) with Refrigerating cooling system, Julabo F12 (France), Pour Point Tester (Lawler Manufacturing Corporation, USA), C 99 Multiparameter Bench Photometer HANNA, Viscometer Bath VB-1423 (P SELECTA) with U tube Ostwald Viscometer and pipette filler (Spain).

3.2 Methods

3.2.1 Pretreatment of Waste Oils

Pretreatment of waste oils before being used for transesterification process is very important. This is because, impurities present in the waste oils would prevent high yield of biodiesel (Lou *et. al.*, 2008; Ma *et. al.*, 1999).

3.2.1.1 Removal of Particulates from Waste Oils

Waste oils contain solid particles such as sand, sticks, and fish (the kind and nature of the impurities depend on what the oil was used for). Large particles were removed through sedimentation after allowing these particles to settle at the bottom of the container. Small

particles present in the oil were removed through filtration, using industrial sieve of 70 μm pore diameter.

3.2.1.2 Removal of Free Fatty Acid (FFA) from Waste Oils

The second pretreatment process in waste oil treatment is free fatty acid removal. Frying at high temperature breaks waste oil triglyceride bonds resulting into FFAs. The removal of high level of FFA is highly essential, to prevent soap formation during trans-esterification (Zahira *et. al.*, 2013).

10mL of 0.125M NaOH solution was added to every 100g of waste oil, the mixture was continuously stirred at a temperature of 40 $^{\circ}\text{C}$ for 15 minutes, this allowed free fatty acid in oil to react with NaOH. After 30 minutes of gravitational settling, two distinct layers were formed: the top layer was less viscous waste oil lean of free fatty acid and bottom layer was an emulsion of soap formed (Figure 3.1). Waste oil was separated from the soap emulsion. Also, offensive odour of the waste oil disappeared at this stage.



Figure 3.1: Removal of FFA from Oils: (a) Treated WGO, (b) Treated WSO, (c) Soap Emulsion

3.2.1.3 Removal of Water from Waste Oils

All chemicals and materials used during trans-esterification were anhydrous. Water present in any of the reactants and catalyst will react with biodiesel formed (hydrolysis) to produce free fatty acid (Ma *et al.*, 1999). Treated waste oil (lean of free fatty acid) was heated to 120 °C for 20 minutes in an oven to allow vapourisation of water in the oil into the atmosphere. Trace droplets of soap found floating on the surface of the oil was scraped away. The filtration process was again carried out to remove any suspended particles present. A clear and bright colour of waste oil (suitable for trans-esterification) was obtained.

3.2.2 Determination of the Properties of the Raw Waste Oils

Some of the properties of the raw waste oils used for trans-esterification reaction were determined, these served as basis for the discussion of results obtained from the trans-esterification process (Figure 4.1).

3.2.2.1 Determination of the Acid Value of Waste Oils

10g of the Waste Oil was put in a conical flask. 95% alcohol was taken and neutralized with 0.1 M NaOH solution. 50ml of the neutral alcohol and 50ml benzene were added to the WCO in the flask. The contents of the flask were shaken rigorously to dissolve the FFA. This was immediately titrated using 0.1M KOH solution with phenolphthalein as indicator. The end point was the appearance of a pale pink colour. At this point, the volume of KOH that neutralised acid present in the oil was noted and simple titration calculation was carried out to determine the acid value of oil.

3.2.2.2 Determination of the Saponification Value of Waste Oils

Saponification value is the number of mg of potassium hydroxide (KOH) required to saponify the esters in 1g of a sample; and to neutralize the free acids. It also indicates the amount of average molecular weight of triglycerides contained in the oil.

1 gram of oil was weighed into 250 ml dry round bottom flask. 50ml of 0.5M alcoholic potassium hydroxide was added to the oil. Porous bits were added to ensure uniform heating. The reflux condenser was setup and the content of the round bottom flask was refluxed for about 1 hour. After refluxing, the mixture was allowed to cool and then titrated against standard hydrochloric acid and the titre values were recorded.

Similarly, 50ml of the same alcoholic KOH, blank (no oil added) was refluxed in a round bottom flask for 1hr, cooled and titrated against standard 0.5N HCl. The titre value was recorded and the saponification value was determined using the expression written in equation 3.1.

$$\text{Saponification Value} = \frac{Z \times M_1 \times 56.1}{W_1} \quad \text{Eq. 3.1}$$

where Z = volume of HCl required to neutralize excess alkali (ml) = $(X - Y)$ ml

X = titre value of HCl against oil and KOH after reflux (ml)

Y = titre value of HCl against KOH alone after reflux (ml)

M_1 = strength of HCl

W_1 = weight of oil used (g)

The number 56.1 is the atomic weight of potassium hydroxide (KOH)

3.2.2.3 Determination of Waste Oil Density

The density meter machine was switched on and the stability of the temperature was ensured (Figure 3.10). The ultrapure water was used for the calibration (measuring cell was cleaned and dried by flushing with n-Hexane and then Acetone). The test specimen was then injected into the density meter using a plastic syringe. This was done carefully to ensure that the filled-in sample was homogenous and free of gas bubbles. The syringe was left in the filling position, in order that the filled-in sample does not leak out. The upper hose was connected for evacuation and lower hose for injection. The upper density value was taken when reading was stable. And the specimen was evacuated from the density meter and flush with n-Hexane and then acetone.

3.2.3 Determination of Molecular Weights of Oil Triglycerides

Determination of the triglycerides in oil was achieved through the identification of the fatty acids (fatty acid profiles), the small units that made up oil triglycerides. Agilent Technologies 7890A GC System USA (gas chromatography equipment) was used to quantify fatty acids that made up oil triglycerides (Figure 3.5).

Oil samples were introduced at an initial oven temperature of 60 °C through auto-injectors, with the aid of syringe and sampling valves into the carrier gas stream (99.99% Helium) which carried the oil samples round the column (column length is 30 m, column thickness of 0.25 µm and internal diameter of 0.25 mm). The column temperature was programmed to increase to 200 °C at the rate of 10°C per minute. The flame ionization detector (FID) temperature was set at 220 °C.

Detectors identified the presence of fatty acids (and other compounds present) as they exit the column. As each compound entered the detector, an electrical signal proportional to the amount of compound detected was generated. This signal was sent to a data analysis system (a computer system connected to the device) where it showed up as a peak on a chromatogram and then quantified. Various fatty acids present and triglyceride molecular weights of the three oils considered were shown in Tables 4.2 - 4.4.

3.2.4 Statistical Design of Experiments

The effects of the four factors of this study (methanol/oil mole ratio , catalyst concentration, reaction temperature and reaction time) on biodiesel yields were obtained by using a design of experiments (DOE). The Box-Behnken factorial design of experiments was used in this study to determine the effects of the four factors on the response variable (biodiesel yield). The three levels of each of the four factors are listed in Table 3.1.

MINITAB 16 (PA, USA) is the software used for the design of experiments, plotting of response surfaces, establishment of optimum conditions for biodiesel production and statistical analysis of variation (ANOVA) of the response model. The design of experiments method used is Box-Behnken Fractional Factorial designs with four factors and one response variable (biodiesel yield) at three levels (Table 3.1).

Table 3.1: Statistical Box-Behnken BB(4) for Biodiesel Yield showing Factors and their Three Levels

Factors	Variables	Levels		
		-1	0	+1
Methanol/Oil Mole Ratio	X ₁	6:1	9:1	12:1
Catalyst Concentration (KOH & NaOH, % w/w Oil)	X ₂	0.7	1.2	1.7
Reaction Temperature (°C)	X ₃	48	55	62
Reaction Time (minutes)	X ₄	50	70	90

Table 3.2: Box-Behnken BB(4) Fractional Factorial Design (coded levels and replicates)

X ₁	X ₂	X ₃	X ₄	No of Runs
±1	±1	0	0	4
0	0	±1	±1	4
0	0	0	0	1
±1	0	0	±1	4
0	±1	±1	0	4
0	0	0	0	1
±1	0	±1	0	4
0	±1	0	±1	4
0	0	0	0	1
Total Runs = 27				

The choice of the values of the 3 levels of each of the factors is based on research work performed on waste oil biodiesel by some researchers (Enweremadu and Mbarawa, 2009; Zlatica and Biljana, 2009, Xiaohu, 2008).

The different combinations of each of the four factors for each of the 27 runs used for each of the three waste oils have been summarised in their coded formats, together with number of repetitions required for each combination in Table 3.2

The actual values of each of the factors for the different runs according to the BB(4) design of experiments is shown in Table 3.3. The experimental results of each of the 27 runs for each of the three waste oils investigated are shown in Appendix A (Table A1- A3).

Table 3.3: Interpretation of BB(4) Design of Experiments

Experimental Run	Methanol/Oil [mole ratio] X ₁	Catalyst Concentration [w/w Oil] X ₂	Reaction Temperature [⁰ C] X ₃	Reaction Time [minutes] X ₄
1	12:1	1.7	55	70
2	12:1	0.7	55	70
3	6:1	1.7	55	70
4	6:1	0.7	55	70
5	9:1	1.2	62	90
6	9:1	1.2	62	50
7	9:1	1.2	48	90
8	9:1	1.2	48	50
9	9:1	1.2	55	70
10	12:1	1.2	55	90
11	12:1	1.2	55	50
12	6:1	1.2	55	90
13	6:1	1.2	55	50
14	9:1	1.7	62	70
15	9:1	1.7	48	70
16	9:1	0.7	62	70
17	9:1	0.7	48	70
18	9:1	1.2	55	70
19	12:1	1.2	62	70
20	12:1	1.2	48	70
21	6:1	1.2	62	70
22	6:1	1.2	48	70
23	9:1	1.7	55	90
24	9:1	1.7	55	50
25	9:1	0.7	55	90
26	9:1	0.7	55	50
27	9:1	1.2	55	70

That is the experimental work was carried out considering the three levels of the three factors: mole ratio of methanol/oil (6:1, 9:1, 12:1), catalyst concentration (0.5 – 1.0 – 1.5) w/w oil, reaction temperature of (48 – 55 – 62)⁰C and the reaction time (50 – 70 – 90) minutes (Table 3.3).

3.2.5 Biodiesel Production

Biodiesel was produced through trans-esterification process (Figure 3.2). 100g of treated oil was used in each of the experiments carried out. Specified amount of catalyst (KOH or NaOH as the case may be) was dissolved completely in the required amount of methanol to form a clear solution of potassium (or sodium) methoxide. The solution was then transferred to warm oil heated to 50⁰C. The mixture was tightly enclosed, maintained at the specified temperature and continuously stirred at 400 rpm on a 7.25" x 7.25" Cimarec digital magnetic stirring hotplate. This allowed trans-esterification reaction to take place and the required reaction time (at the range of 50 – 70 – 90 minutes) for each experimental set up was observed.

At the end of the specified reaction time, the products obtained were then transferred to separating funnel and left for 24 hours after which two distinct layers were observed; light yellow biodiesel and reddish brown glycerol (Figure 3.3b). Separation of the two products was done by decanting off the glycerol (bottom layer) from the separating funnel.

Biodiesel obtained was free of impurities (unconverted methanol, catalyst, soap and traces of glycerol) by washing with warm distilled water repeatedly until water removed contained no impurity (Figure 3.4). Moisture content present in biodiesel was then removed by drying the content at 120 ⁰C in an oven for 30 minutes.

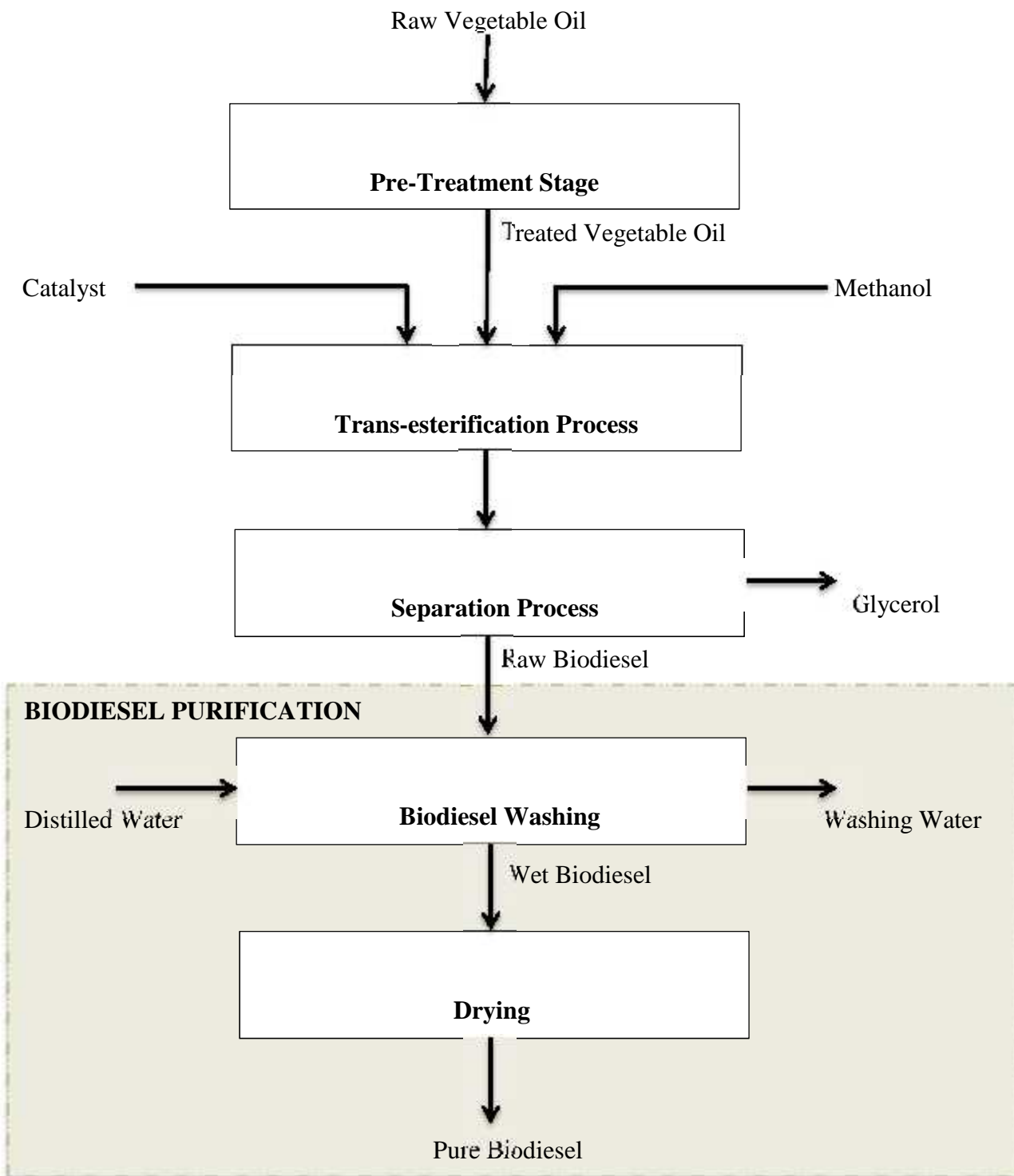


Figure 3.2: Schematic diagram of Biodiesel Production

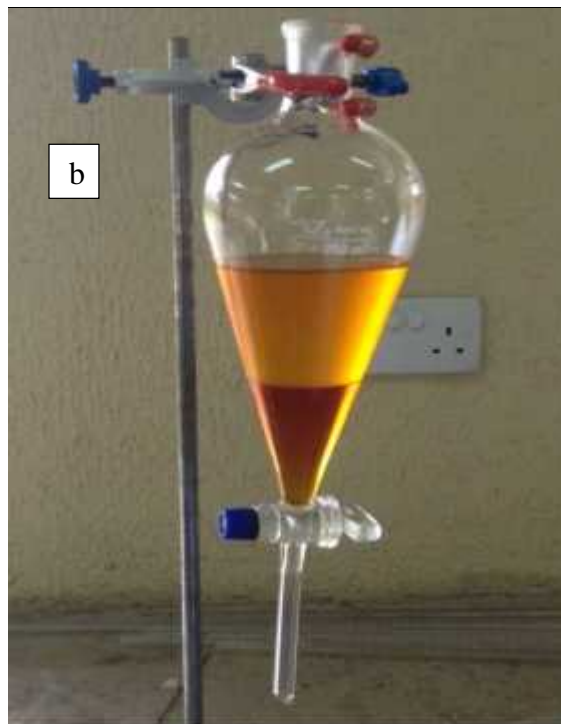
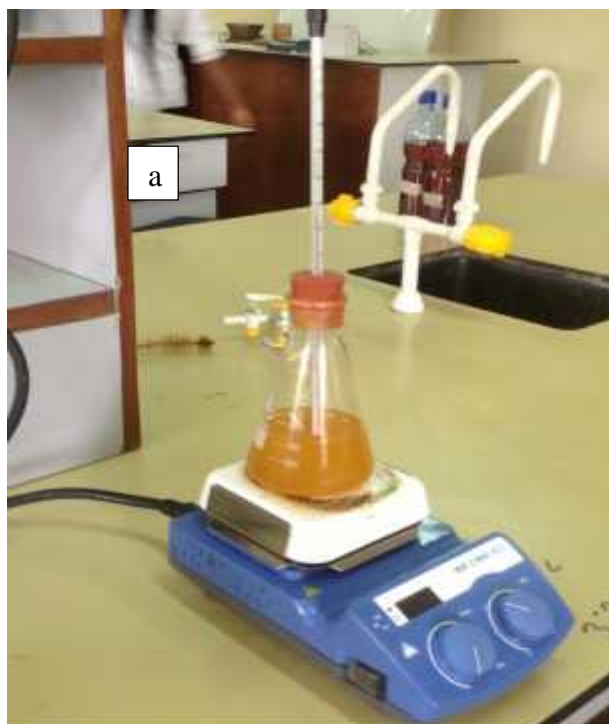


Figure 3.3: (a) Experimental set up of biodiesel production (b) Formation of biodiesel (top layer) and glycerol (bottom layer)

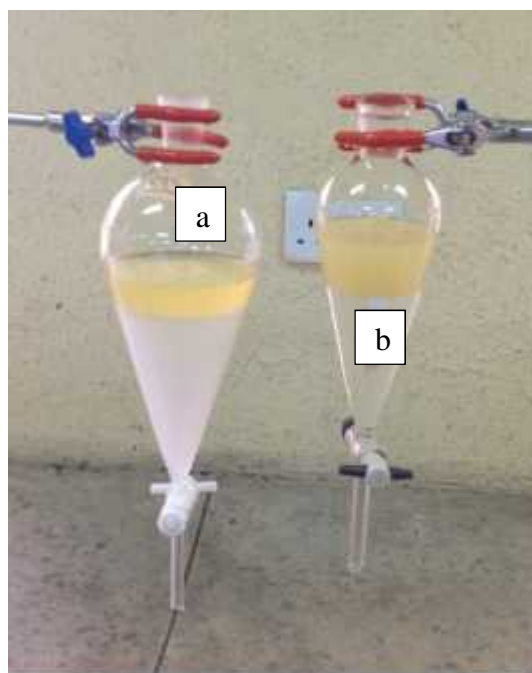


Figure 3.4: Washing of biodiesel: (a) during washing, (b & c) after washing.



Figure 3.5: Gas Chromatography (GC MS) System



Figure 3.6: Atomic Absorption Spectrometer



Figure 3.7: Flash Point Tester



Figure 3.8: Viscometer Bath with U-tube Ostwald Viscometer



Figure 3.9: Hach Spectrophotometer



Figure 3.10: Density meter



Figure 3.11: Multiparameter Bench Photometer



Figure 3.12: Turbidimeter (HI 98703 Fast Tracker).

3.2.6 Determination of Biodiesel Properties

Different methods used in the determination of the properties of biodiesel produced are explained below.

3.2.6.1 Density of Biodiesel Sample

Density meter machine was switched on and the stability of temperature was ensured. The measuring cell was cleaned and dried using little quantity of n-Hexane and then Acetone. The test sample was then injected into the density meter using a 10ml plastic syringe. It is important to ensure that the filled-in sample is homogenous and free of gas bubbles. And the syringe was left in the filling position to prevent the filled-in sample from leaking. The upper hose was connected for evacuation and the lower hose for injection. And the upper density value was taken when reading was stable. Finally the sample of biodiesel from the density meter was evacuated and flushed with n-Hexane and then Acetone.

3.2.6.2 Pour Point of Biodiesel

Biodiesel was poured into the test jar to the level mark and then closed with the cork carrying the high-pour thermometer. The test jar was put into the pour bath already set at -15°C . The appearance of biodiesel was checked for, at 3°C interval, when its temperature was 9°C above the expected pour point. The condensed moisture, that limits visibility, was removed by wiping the surface with a clean cloth moistened with alcohol. The jar was tilted to ascertain whether there was movement of oil. (The complete operation of removal, wiping and replacement should not be more than 5 seconds).

As soon as the oil in the jar did not flow when tilted, the jar was held in an horizontal position for 5 seconds using a stop watch for timing (if the oil shows any movement, replace the test jar immediately in the jacket and repeat test for flow at the next 3⁰C lower). The procedure was repeated until a point was reached when biodiesel showed no movement when the test jar was held in horizontal position for 5 seconds. The observed reading of the test thermometer was then recorded as the pour point of biodiesel.

3.2.6.3 Flash Point of Biodiesel

Biodiesel was poured into the cup up to the indicated mark of flash point tester (Figure 3.7). Both the flame dipper and flame presentation control arm were placed in position. Chiller bath was switched on and set to ambient temperature. The analyser from the electrical panel was switched on. Using the icons and cursors on the front panel, the expected flash point was typed and supplied, method was selected as well. The minimum temperature at which biodiesel ignited (flash) on the application of the ignition source was displayed and noted.

3.2.6.4 Water Content of Biodiesel

Water test cell was first switched on. The screen displayed the range interface (0 – 10% and 0.02 – 1%) and the appropriate water content range was selected. And the right method (EasySHIP Paste method) was selected. The cell was open, Reagent A (part of equipment accessories) was shaken rigorously and 20ml of the reagent was added to the cell. All the content of a EasySHIP Paste bottle was added, 5ml of the biodiesel sample was added, agitator was added. The lid was replaced and the start button was pressed. Cell was shaken vigorously for 3 minutes till the end of the test. And the result was displayed at the end of the test.

3.2.6.5 Kinematic Viscosity of Biodiesel

Viscometer bath was almost filled to the brim with pure water and other gadgets were connected and powered (Figure 3.8). The set up was left for a while until the set temperature and the warm water equilibrated. Biodiesel sample was then poured into the U tube viscometer, using pipette filler. The time taken for certain quantity of the sample at the two marked points on one side of the U tube to the other side was noted. Viscosity of each sample was calculated at the equilibrated temperature as the product of the average time taken and a constant C (value of C depends on the kind of viscometer used).

3.2.7 Elemental Analysis on Biodiesel and Washing Water

The results of elemental analysis on biodiesel and washing water are shown in Appendix B.

Sample preparation (digestion) on biodiesel was first carried out. 50 ml of the sample and 10 ml of Aqua-regia (combination of nitric acid and hydrochloric acid in the ratio of 1:3) were poured into 250ml conical flask. The mixture was heated on a hotplate in the fume cupboard until the brown fume disappeared, leaving a white fume. The sample was then made up to 50 ml with distilled water and filtered with the aid of filter paper and funnel, prior to AAS analysis.

3.2.7.1 Atomic Absorption Spectrometer

The Perkin Elmer AAnalyst 200 system was employed for elemental analysis. It consists of a high efficiency burner system with a high sensitivity nebulizer and an atomic absorption spectrometer. The burner system provides the thermal energy necessary to dissociate the chemical compounds, providing free analyte atoms so that atomic absorption can occur. The

spectrometer measured the amount of light absorbed at a specific wavelength using a hollow cathode lamp as the primary light source, a monochromator and a detector. A deuterium arc lamp corrects for background absorbance caused by non-atomic species in the atom cloud.

Each sample was aspirated into nebulizer compact. In nebulizer compact, air, acetylene and the sample were mixed together to form aerosol (about 10% of aerosol is transferred into the flame and 90 % comes out as waste). The flame burned and atomised the sample from ground state to the excited state.

At excited state, absorption occurs and monochromator select the wavelength in agreement with the atom that is coming in, based on the source of light. The source of light is hollow cathode lamp. The detector detects the atom and transfers the reading to reader in mg/L

3.2.7.2 Determination of Chloride ion (Cl⁻) in Washing Water

20 ml of the sample of washing water was taken into a conical flask, 3 drops of potassium dichromate was added and a yellow colouration was observed. The solution was titrated with 0.1M silver nitrate until a pink colour end point was reached.

$$\text{Chloride ion (mg/L)} = \frac{V_t \text{ of } \text{AgNO}_3 \times 0.1 \text{ M} \times 35.5 \times 1}{2 \text{ ml of sample}} \quad \text{Eq. 3.2}$$

3.2.7.3 Determination of the Hardness of Water (Mg²⁺ / Ca²⁺)

20 ml of the water sample was put into a conical flask, ammonia buffer was added, then erichrome black T indicator was added (about 2 drops). The water solution was titrated with 0.01M EDTA and a sharp blue point was observed.

$$\text{Hardness (mg/L)} = \frac{V_t \text{ of } \text{EDTA} \times 0.01 \text{ M} \times 1}{2 \text{ ml of sample}} \quad \text{Eq. 3.3}$$

3.2.7.4 Determination of SO_4^{2-} , PO_3^- , NO_3^- in Water

Hach Spectrophotometer and Multiparameter Bench Photometer were used for the analysis. 10 ml of water sample was put into a vial bottle and standard sample of the anion to identify was added, giving a colour of the standard sample. Anion method was selected on the equipment, sample was inserted into the sample compartment and read button was pressed. Concentration of the anion was displayed in mg/L

3.2.7.5 Determination of Turbidity and Colour of Washing Water

Turbidity is the cloudiness or haziness of a fluid caused by individual particles (suspended solids) that are generally invisible to the naked eyes, similar to smoke in air. It is expressed in NTU (Nephelometric Turbidity Unit). Distilled water has zero NTU. The equipment was first calibrated using the recommended water samples of known NTU values (including distilled water). Water sample was now poured into the sample bottle and placed in turbidimeter where the turbidity value could be read directly.

Colour of the water sample was determined by using Multiparameter bench photometer. Colour of water sample is expressed in PCU (Platinum Cobalt Unit), with distilled water having zero PCU. The apparent colour value of the sample was first determined before the true colour value was then taken. These values were read directly from the equipment the moment samples were introduced, once the equipment is electrically powered.

3.2.8 Modeling of Biodiesel Cetane Number

The Stavrov *et. al.* (1981) model calculates the petroleum diesel cetane number as a function of the density and the viscosity of the diesel. This model was improved upon to obtain a biodiesel cetane number model that considers other important properties of biodiesel. These important properties of biodiesel include: carbon chain length, number of double bonds and mole fraction of biodiesel.

3.2.8.1 Model of Petroleum diesel Cetane Number - Stavrov *et. al.*, (1981)

According to Stavrov *et.al.* (1981), petroleum diesel cetane number is expressed as

$$CN_{\text{Petroleum diesel}} = \left\{ (v_{20} + 17.8) \left(\frac{1.5879}{\rho_{20}} \right) \right\} \quad \text{Eq. 3.4}$$

where $CN_{\text{Petroleum diesel}}$ = Petroleum diesel cetane number

v_{20} = Petroleum diesel kinematic viscosity at 20 °C, mm²/sec

ρ_{20} = Petroleum diesel density at 20 °C, g/cm³

3.2.8.2 Proposed Model of Biodiesel Cetane Number

The modification of Stavrov *et. al.* (1981) model for petroleum diesel cetane number to biodiesel cetane number model was made possible by considering the following findings and assumptions:

1. Biodiesel has 100 % straight chain structure (Debalina and Ralph, 2013; Evangelos, 2013; Muradov and Veziroglu, 2013; Starr and McMillan, 2003).

2. Petroleum diesel has 75 % straight chain HCs and 25 % aromatic HCs (alkyl benzene, naphthalene) (ATSDR, 1995).
3. Average molecular formula of petroleum diesel is $C_{12}H_{23}$, ranging from $C_{10}H_{20}$ to $C_{15}H_{28}$, (Collins, 2007; ATSDR, 1995).
4. Cetane number is inversely proportional to the number of double bonds of fatty acids and biodiesel (Evangelos, 2013; Parag *et.al.*, 2013; Zlatica and Biljana, 2009).

Based on the above research findings, the proposed model of biodiesel is

$$CN_{\text{Biodiesel}} = \frac{C_{100}}{C_{75}} \left\{ (u_{40} + 17.8) \left(\frac{1.5879}{\rho_{25}} \right) - \sum \left(\frac{C_{DB} \cdot x}{C_D \cdot N_{DB}} \right)_i \right\} \quad \text{Eq. 3.5}$$

where $CN_{\text{Biodiesel}}$ = Biodiesel cetane number

$\frac{C_{100}}{C_{75}}$ = ratio of straight chain carbon of biodiesel to petroleum diesel

= conversion factor = $\frac{100}{75}$

u_{40} = Biodiesel kinematic viscosity at 40 °C, mm²/sec

ρ_{25} = Biodiesel density at 25 °C

$\sum \left(\frac{C_{DB} \cdot x}{C_D \cdot N_{DB}} \right)_i$ = correction terms

C_{DB} = Carbon with double bond in biodiesel

C_D = Average number of carbon in petroleum diesel, $C_{12}H_{23}$

N_{DB} = Number of double bond in biodiesel

x = Mass fraction of biodiesel

Findings number 1 and 2 accounted for the introduction of conversion factor in the predicted model while finding number 3 and 4 gave the reason why correction terms were considered in the model.

3.2.9 Life Cycle Assessment (LCA) of Biodiesel

Life Cycle Assessment of biodiesel was carried out using SimaPro 7.3.3 software. The software is one of the most widely used LCA software that has unique features such as parameterised modelling and interactive results analysis. The method of Life Cycle Impact Assessment (LCIA) used was IMPACT 2002+ which connects Life Cycle Inventory (LCI) results to their corresponding environmental impacts (damage).

As defined by International Organisation for Standardisation 14044 (ISO 2006) LCA of biodiesel consists of four stages:

- Goal and scope definition under which the objectives of the analysis, spatial and temporal system boundaries, and the functional unit(s) are defined
- Life cycle inventory (LCI) analysis which involves mainly data collection
- Life cycle impact assessment (LCIA) which involves the determination of the environmental impacts of a process or product, based on LCI results
- Interpretation which is the process of analysing LCI and LCIA for the purpose of conclusion, recommendations and discussions.

3.2.9.1 The Goal and Scope of the LCA of Biodiesel

The goal of this study is to assess the potential impacts of laboratory scale biodiesel produced from three vegetable oils (waste groundnut oil, waste soyabean oil and crude palm kernel oil). The scope of this study is potential impact assessment of laboratory scale biodiesel (from WGO, WSO and CPKO) with emphasis on biodiesel purification process (Figure 3.13). The functional unit in this work is 1 kg of biodiesel produced. Data used were generated from the analysis of biodiesel produced and washing water. Data were expressed in International System of Units (*Système international d'unités*, SI units).

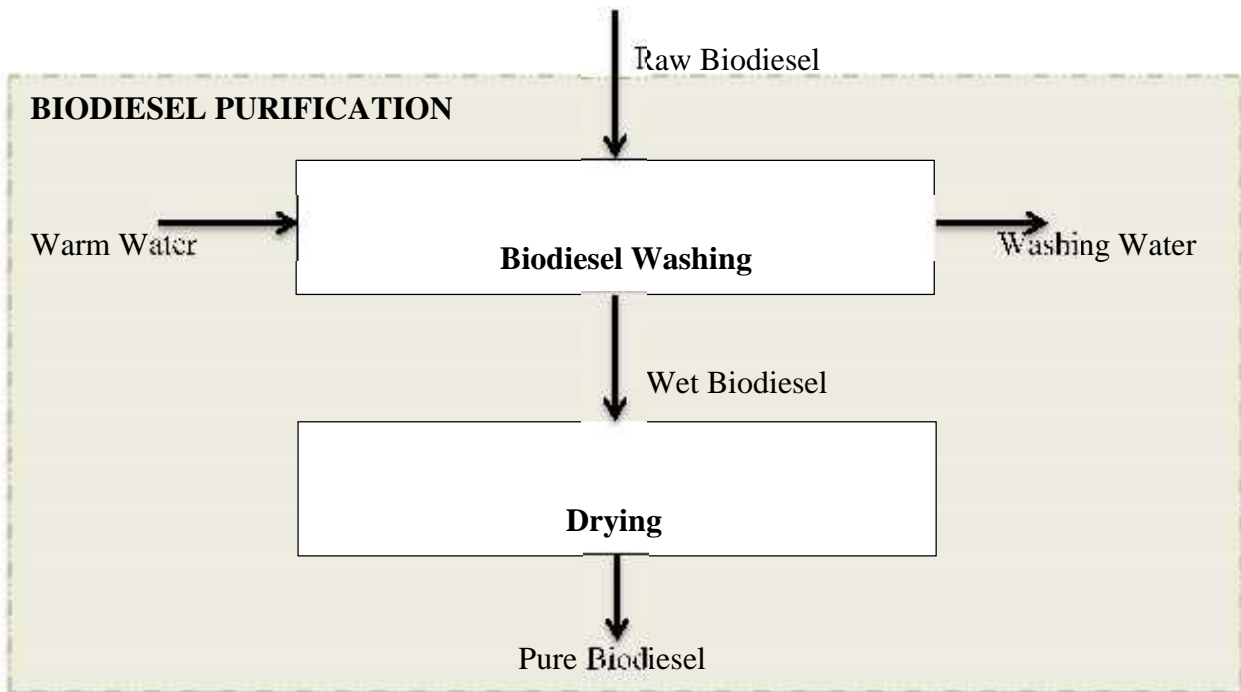


Figure 3.13: Scope of Biodiesel Life Cycle Assessment

3.2.9.2 Life Cycle Inventory (LCI)

In the LCI analysis, emissions to the environment during biodiesel washing and drying were identified and quantified and then aggregated for the unit system considered. It is assumed that the water that escaped into the atmosphere (in form of vapour) during biodiesel drying was pure. Elemental analysis (of elements that may impose danger on man and its environment) was carried out on biodiesel produced and washing water using Atomic Absorption Spectroscopy (AAS, AAnalyst 200 Perkin Elmer precisely, USA), Hach equipment, C99 Multiparameter Bench Photometer (HANNA, USA). In addition, likely anions present in the washing water were also analysed through titration method (Appendix B).

3.2.9.3 Life Cycle Impact Assessment

In Life Cycle Impact Assessment (LCIA) phase of LCA, emissions were characterised, the evaluation of potential damage to human health and environment was done by quantifying the LCI identified into two different damage categories (Figure 3.14).

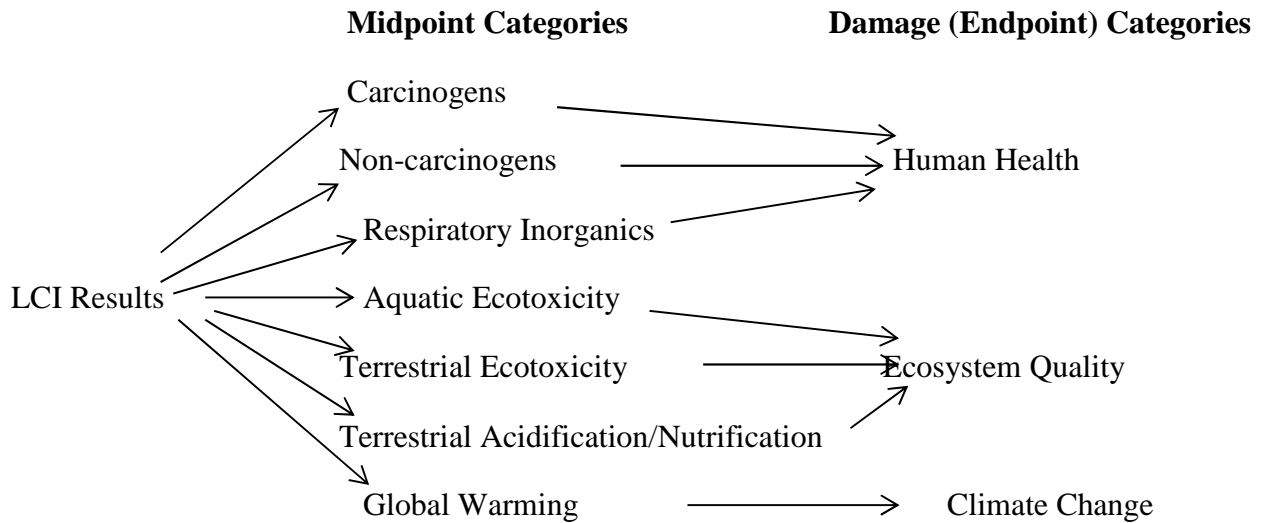


Figure 3.14: IMPACT 2002+ Framework

SimaPro 7.3.3 allows in-built models to calculate each of the damage categories, considering the LCI results of the chemical analysis. IMPACT 2002+ models account for multiple exposure pathways that link a chemical's concentration in the atmosphere, soil, surface water or in vegetation to human uptake through inhalation and ingestion (Olivier *et. al.*, 2003).

3.2.9.3.1 Human Toxicity

Model for the determination of Human Damage Factor of a substance, in DALY (Disability Adjusted Life Years) per kg_{emitted}, is given as

$$HDF_1 = iF_1 \times EF_1 = iF_1 \times \beta_1 \times D_1 \quad \text{Eq. 3.4}$$

where

iF_1 = fraction of mass of a chemical released into the environment that is ultimately taken in by the human population, as a result of food contamination, inhalation or dermal exposure (Bennet *et. al.*, 2002).

EF_1 (Effect factor of a substance) = product of the dose-response slope factor (, in risk of incidence per kg_{intake}) and of the severity (D, in DALY per incidence).

Health Effect metric for non-cancer toxicological impacts is obtained thus:

$$\beta_{\text{human}} = \frac{0.1}{ED_{10}} \times \frac{1}{BW \times LT_h \times N_{365}} \quad \text{Eq. 3.5}$$

where

β_{human} = Human health effect factor [risk of an incidence per kg cumulative intake]

ED_{10} = Benchmark dose resulting in 10% effect over background [mg/ kg/day]

BW = Average body weight in considered population [kg/pers]

LT_h = Average lifetime of humans in considered population in years [yr]

N₃₆₅ = Number of days per year [days/yr]

As reported by Olivier *et. al.*, (2003), the characterization factors at midpoint are simply obtained by dividing the Human Damage Factor of the considered substance by that of the reference substance, which is chloroethylene (for human carcinogen with well-defined fate data and a main impact pathway by air inhalation)

That is,

$$HTP_i = \frac{HDF_i}{HDF_{\text{chloroethylene}}}, \quad \text{in kg}_{\text{eq}} \text{ chloroethylene into air per kg} \quad \text{Eq. 3.6}$$

3.2.9.3.2. Aquatic and Terrestrial Ecotoxicity

Impacts on aquatic ecosystems are treated similar to human toxicity, but with certain noticeable differences. For instance, interest is in effect at species level rather than on individuals (Olivier *et. al.*, 2003).

For aquatic freshwater ecosystems, the time- and space-integrated Potentially Affected Fraction of species per unit of emission (APAF) is estimated on the basis of a fate factor (product of F and F , in years) and an effect factor (β_i) as follows:

$$APAF_i = F_j^m \times \theta_i^w \times \beta_i, \quad \text{Eq. 3.7}$$

that is,

$$\theta_i^w = 1/k = \Delta C \times V \times \Delta t/M \quad \text{Eq. 3.8}$$

$$\beta_i = \frac{0.5}{H \cdot 50_i^w} \quad \text{Eq. 3.9}$$

where

F_i^{mw} = dimensionless fraction of the emission of substance, i, in compartment m transferred to freshwater.

θ_i^w = equivalent residence time of substance, i, in water

k = the overall decay rate constant in water

M = mass of chemical released into the aquatic environment

ΔC = concentration increase in the volume of water (kg/m^3)

V = Volume of water (m^3)

HC50 = mean hazardous concentration affecting 50% of the species present in the ecosystem.

At midpoint level, the freshwater Aquatic Ecotoxicity Potential (AEP_i in triethylene glycol in water per kg_i) is derived by normalization to the reference substance

$$AEP_i = \frac{A_i}{A_{ref}} \quad \text{Eq. 3.10}$$

Terrestrial ecotoxicity potentials are calculated in a similar way, with the exception that the mean hazardous concentration affecting 50% of the species ($HC50_i^s$) is calculated using the model proposed by Hauschild and Wenzel (1998)

$$HC50_i^s = HC50_i^w (K_{di} \times \rho^s + f^w) \quad \text{Eq. 3.11}$$

where

K_{di} = adsorption coefficient of the substance (m^3/kg)

ρ^s = soil density (kg/m^3)

f^w = dimensionless volumetric water content of soil

The characterisation factors for the other midpoint categories (respiratory effects, terrestrial acidification/nitrification, and global warming potential are obtained from Eco-indicator 99 (Goedkoop and Spriensma 2000).

3.2.9.3.3 Damage (Endpoint) Categories

Damage characterisation factor of any substance is obtained by multiplying the midpoint characterization potentials with the damage characterization factors of the reference substances.

Damage characterisation factor of some reference substances are shown in Table 3.4.

Table 3.4: Damage Characterisation factors of the various reference substances

Midpoint categories	Damage factors	Units
Carcinogens	1.45E-06	*DALY/kg chloroethylene
Non-carcinogens	1.45E-06	DALY/kg chloroethylene
Respiratory inorganics	7.00E-04	DALY/kg PM _{2.5}
Aquatic ecotoxicity	8.86E-05	\wedge PDF·m ² ·yr/kg·triethylene glycol
Terrestrial ecotoxicity	8.86E-05	PDF·m ² ·yr/kg·triethylene glycol
Terrestrial acidification/nutr.	1.04	PDF·m ² ·yr/kg SO ₂
Global Warming	1	kg CO ₂ /kg CO ₂

Source: Olivier et. al. (2003), *DALY = Disability Adjusted Life Year, \wedge PDF = Potentially Disappeared Fraction of species

3.2.9.4 Interpretation

The results of LCA on biodiesel produced were reported in section 4.8 and discussed in detail in the section 5.4. Ultimately, interpretation involves the explanation of the safety and health implications of the values obtained from each of the damage categories and indicators considered. This guides in decision making process, among other things.

CHAPTER FOUR

RESULTS

4.0 Introduction

The results obtained from the various experimental work and analysis are reported in this chapter. The results are presented under appropriate subsections.

4.1 Properties of the Raw Oils Used

The physico-chemical properties of the three waste oils used in this research works are as shown on Table 4.1.

Table 4.1: Properties of the Raw Waste Oils

Oil	Flash Point (°C)	Viscosity (mm ² /s @ 40°C)	Density (g/cm ³)	Acid Value (mg KOH/g)	Sap. Value (mg KOH/g)	Water Content (%)
WGO	243	32.64	0.9090	1.561	220.0	0.63
WSO	232	31.67	0.9110	1.843	240.1	0.67
CPKO	230	36.72	0.9100	1.106	203.7	0.56

4.2 Molecular Weight of Oil Triglycerides

It is necessary to establish the molecular weights of the raw WGO, WSO and CPKO used since they are needed to determine the stoichiometric quantities of the raw materials (methanol and oil) in the trans-esterification reaction. The computation of the molecular weight of oil triglycerides is based on the determination of the various fatty acids that constituted each triglyceride. The GC analysis of WGO, WSO and CPKO gave the fatty acid profiles and mass fraction of the fatty

acids that constituted the oil triglycerides (Tables 4.2 – 4.4). The results of the calculation of the molecular weights of WGO, WSO and CPKO are shown in this section.

Table 4.2: WGO Triglyceride Molecular Weight

Fatty Acid	Weight Percent	Weight	Molecular Weight	Mole
	%	[x_i] g	[MW_i] g/mol	[x_i / MW_i] g mol
9,12-Octadecadienoic acid [C ₁₈ H ₃₂ O ₂] C18:2 (Linoleic acid)	0.42	0.42	280.4455	0.001498
9-Octadecenoic acid (Z) [C ₁₈ H ₃₄ O ₂] C18:1 (Oleic acid)	90.21	90.21	282.4688	0.319363
Total	90.63	90.63		0.320861

$$\begin{aligned} \text{Average Molecular Weight of Fatty Acids} &= \frac{\sum(x_i)}{\sum\left(\frac{x_i}{M_i}\right)} \\ &= \frac{9.6}{0.3} \\ &= 282.4587 \text{ g/mol} \end{aligned}$$

$$\text{Molecular Weight of Glycerol backbone} = 41.049 \text{ g/mol}$$

Molecular Weight of WGO Triglyceride

$$\begin{aligned} &= 3[\text{Average Molecular Weight of Fatty Acids}] + \text{Molecular Weight of Glycerol backbone} \\ &= 3[282.4587] - 3[1] + 41.049 \\ &= 885.4251 \text{ g/mol} \end{aligned}$$

Table 4.3: WSO Triglyceride Molecular Weight

Fatty acid	Weight Percent	Weight [x_i]	Molecular Weight [MW_i]	Mole [x_i / MW_i]
	%	g	g/mol	g mol
9,12-Octadecadienoic acid [C ₁₈ H ₃₂ O ₂] C18:2 (Linoleic acid)	34.86	34.86	280.4455	0.124302
9-Octadecenoic acid (Z) [C ₁₈ H ₃₄ O ₂] C18:1 (Oleic acid)	39.14	39.14	282.4688	0.138563
Dodecanoic acid [C ₁₂ H ₂₄ O ₂] C12:0 (Lauric acid)	10.39	10.39	200.3228	0.051866
Total	84.39	84.39		0.314731

$$\begin{aligned} \text{Average Molecular Weight of Fatty Acids} &= \frac{\sum(x_i)}{\sum\left(\frac{x_i}{M_i}\right)} \\ &= \frac{8.3}{0.3} \\ &= 268.1337 \text{ g/mol} \end{aligned}$$

$$\text{Molecular Weight of Glycerol backbone} = 41.049 \text{ g/mol}$$

Molecular Weight of WSO Triglyceride

$$\begin{aligned} &= 3[\text{Average Molecular Weight of Fatty Acids}] + \text{Molecular Weight of Glycerol backbone} \\ &= 3[268.1337] - 3[1] + 41.049 \\ &= 842.4501 \text{ g/mol} \end{aligned}$$

Table 4.4: CPKO Triglyceride Molecular Weight

Fatty Acid	Weight Percent	Weight	Molecular Weight	Mole
	%	[x_i] g	[MW_i] g/mol	[x_i / MW_i] g mol
Dodecanoic acid [C ₁₂ H ₂₄ O ₂] C12:0 (Lauric acid)	2.58	2.58	200.3228	0.012879
Tetradecanoic acid [C ₁₄ H ₂₈ O ₂] C14:0 (Myristic acid)	0.64	0.64	228.3768	0.002802
n-Hexadecanoic acid [C ₁₆ H ₃₂ O ₂] C16:0 (Palmitic acid)	38.34	38.34	256.4308	0.149514
9-Octadecenoic acid (Z) Cis-13-Octadecenoic acid [C ₁₈ H ₃₄ O ₂] C18:1 (Oleic acid)	49.29	49.29	282.4688	0.174497
Total	90.85	90.85		0.339692

$$\begin{aligned}
 \text{Average Molecular Weight of Fatty Acids} &= \frac{\sum(x_i)}{\sum\left(\frac{x_i}{M_i}\right)} \\
 &= \frac{90.8}{0.3} \\
 &= 267.4481 \text{ g/mol}
 \end{aligned}$$

Weight of Glycerol backbone = 41.049

Molecular Weight of CPKO Triglyceride

$$\begin{aligned}
 &= 3[\text{Average Molecular Weight of Fatty Acids}] + \text{Molecular Weight of Glycerol backbone} \\
 &= 3[267.4481] + 3[1] + 41.049 \\
 &= 840.3933 \text{ g/mol}
 \end{aligned}$$

Analysis of the results shows that CPKO contains 41.59 wt. % saturated fatty acids ($n = 0$) and 49.29 % unsaturated fatty acids ($n = 1$), WSO contains 10.39 wt. % saturated fatty acids and 74 % unsaturated fatty acids ($n = 1, 2$), while WGO contains no saturated fatty acid but 90.63 % unsaturated fatty acids (mostly $n = 1$).

4.3 Biodiesel Yields obtained from Trans-esterification Reactions

The results of the biodiesel obtained from the trans-esterification of WGO, WSO and CPKO (under the same experimental conditions) are shown in Figures 4.1 – 4.3 and Appendix A (Tables A1 – A3). Higher biodiesel yields were obtained with KOH as catalyst when compared to the yield from the NaOH catalyzed experimental runs, under the same conditions. For example, WGO biodiesel yield for experimental run 1 using KOH and NaOH catalysts separately were 91.33% and 87.73% respectively. Similar trends were observed in the other experimental runs catalyzed separately by KOH and NaOH for WGO, as well as for yields obtained from WSO and CPKO trans-esterification.

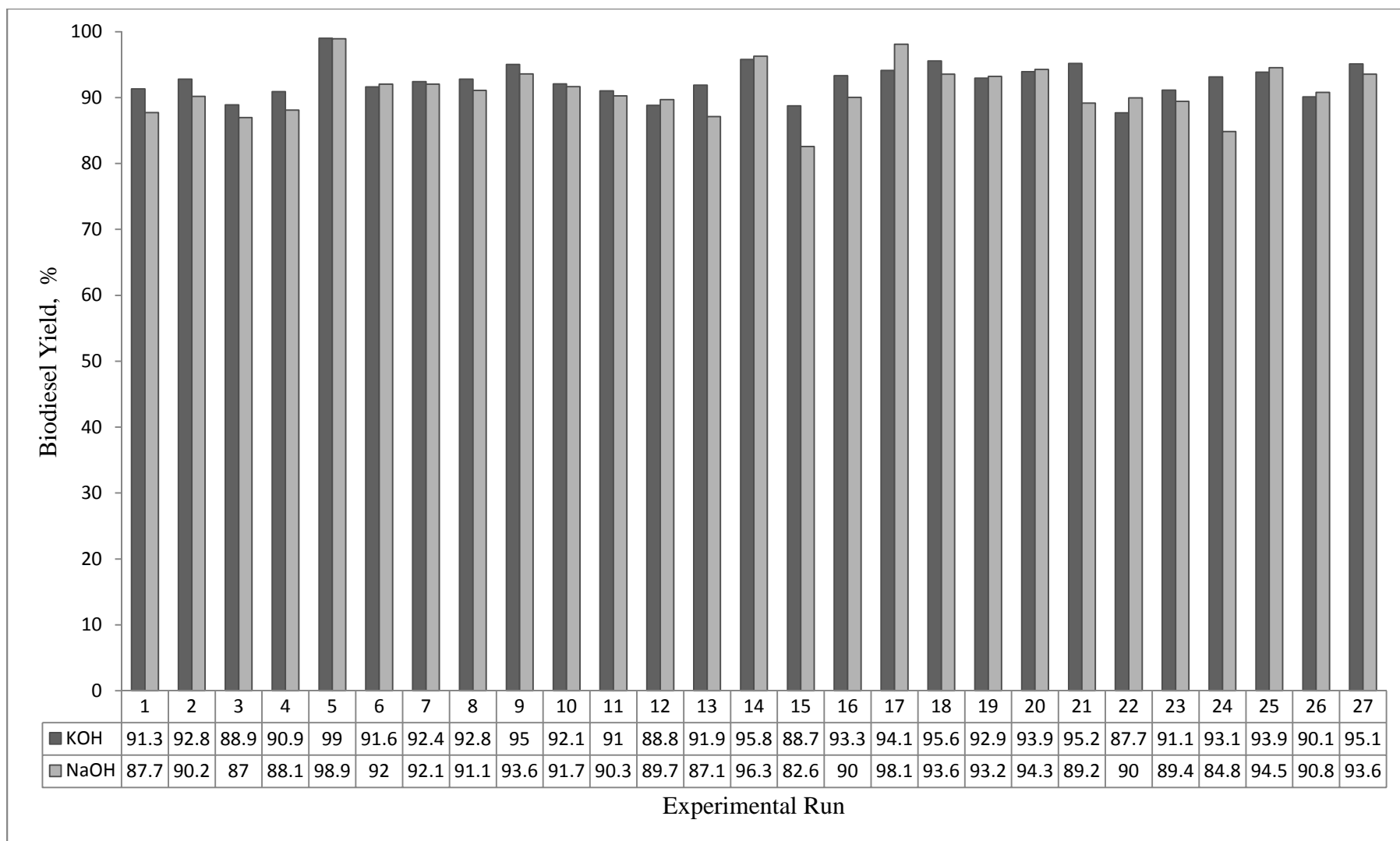


Figure 4.1: Biodiesel Yield from WGO Trans-esterification

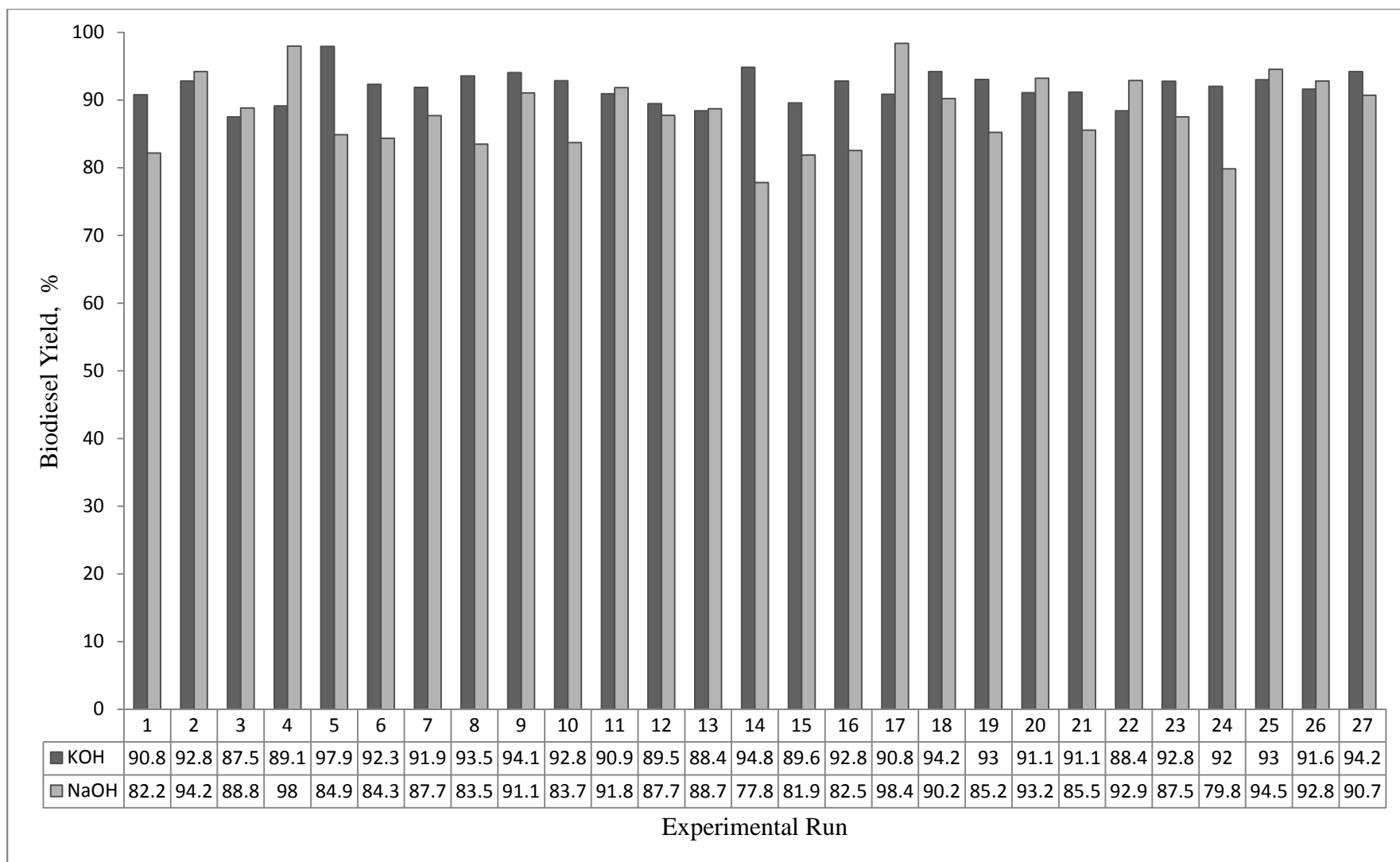


Figure 4.2: Biodiesel Yield from WSO Trans-esterification

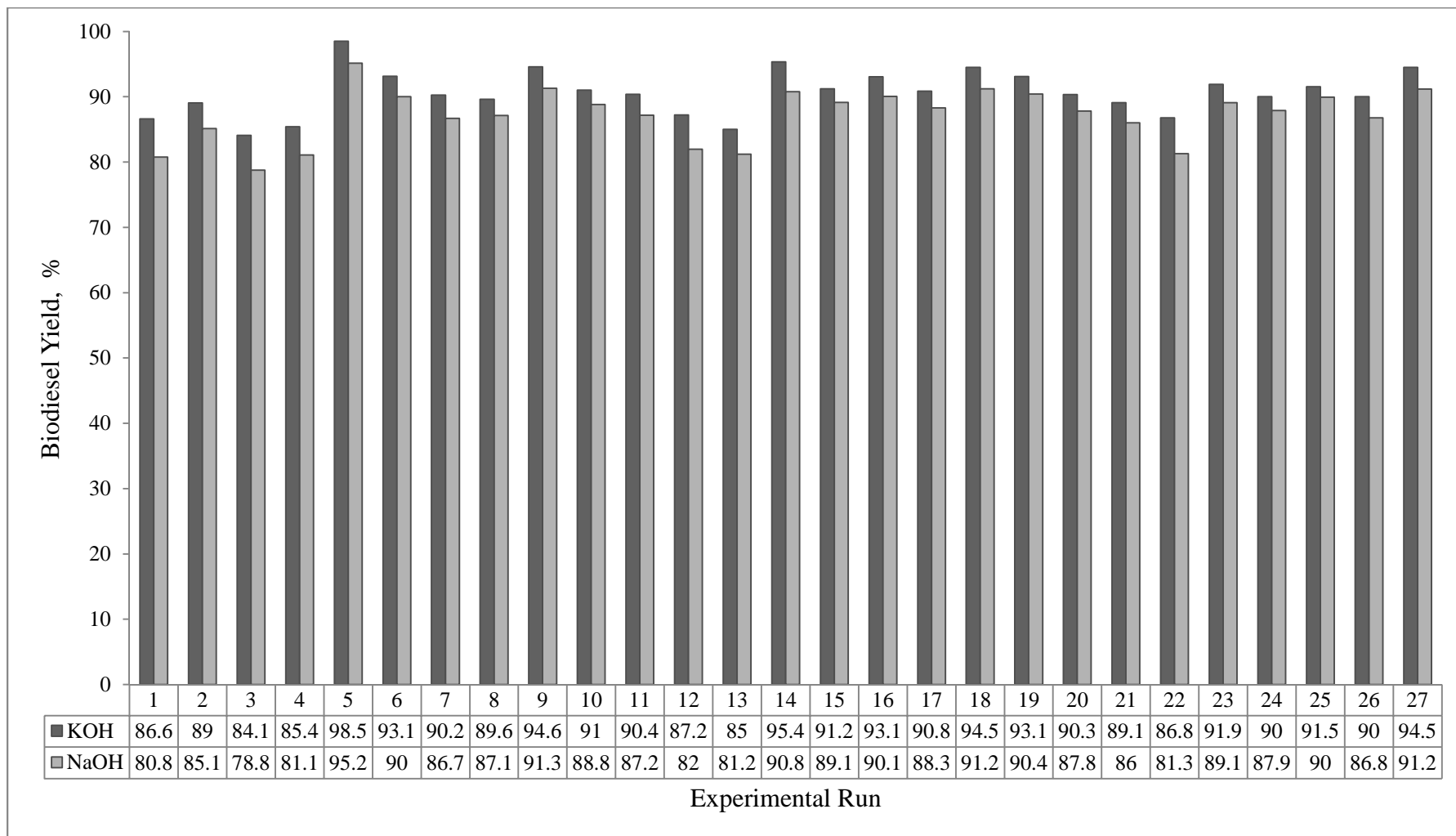


Figure 4.3: Biodiesel Yield from CPKO Trans-esterification

4.4 Surface and Contour Plots of Biodiesel Yields

The effects of operating parameters (methanol/oil mole ratio, catalyst concentration, reaction temperature and reaction time) on the yields of biodiesel for each of WGO, WSO and CPKO were represented in graphical forms using Minitab 16 software.

With the aid of both the surface and contour plots, the maximum WGO and CPKO biodiesel yields obtained from the varied methanol/oil mole ratio, catalyst concentration, reaction temperature and reaction time are as shown in Figures 4.4 – 4.21. Surface plots of WSO biodiesel yields obtained are shown in Appendix C.

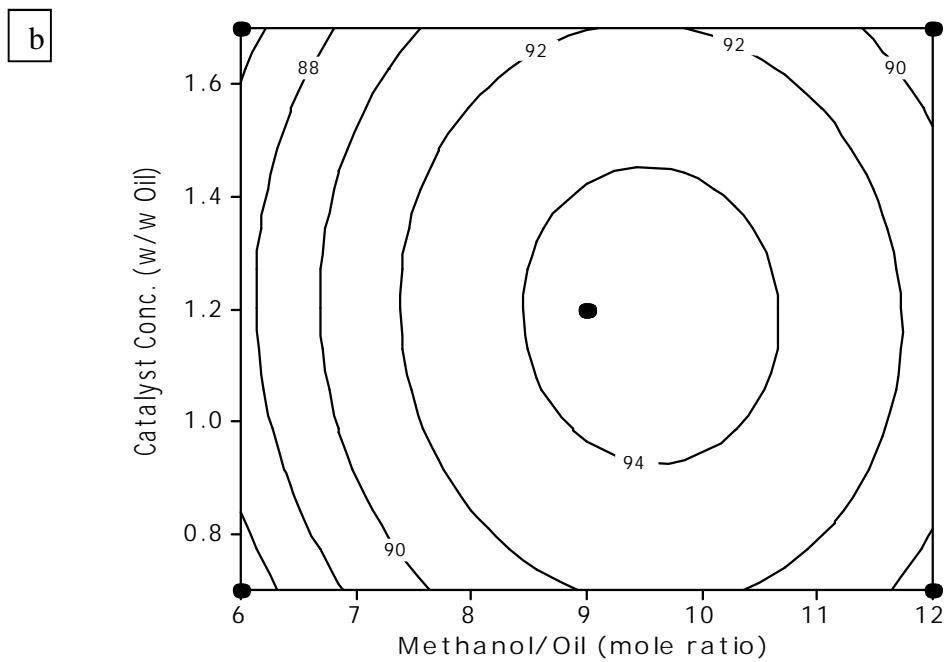
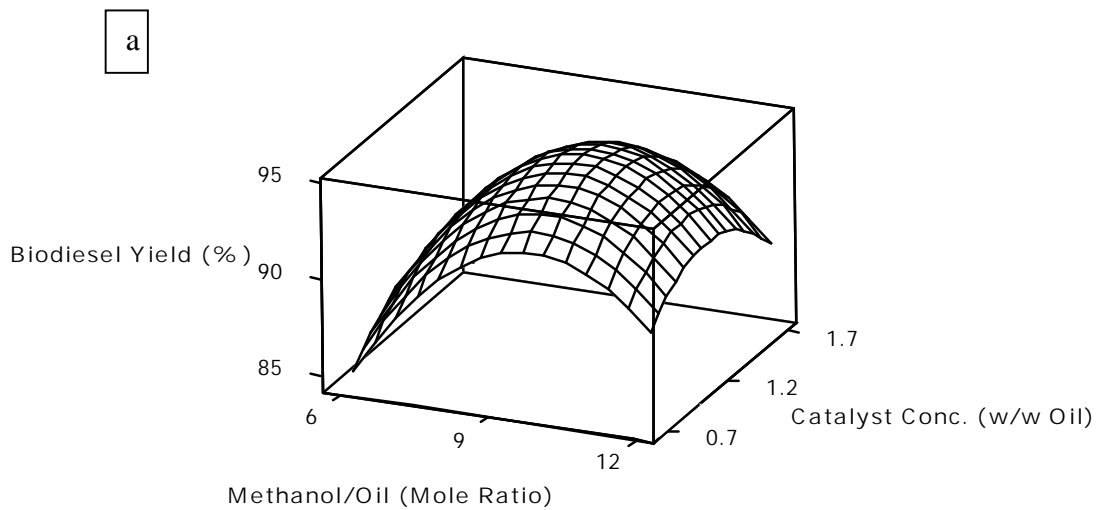


Figure 4.4: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Methanol/Oil mole ratio and KOH Catalyst Concentration, at 55 °C temperature and 70 minutes time.

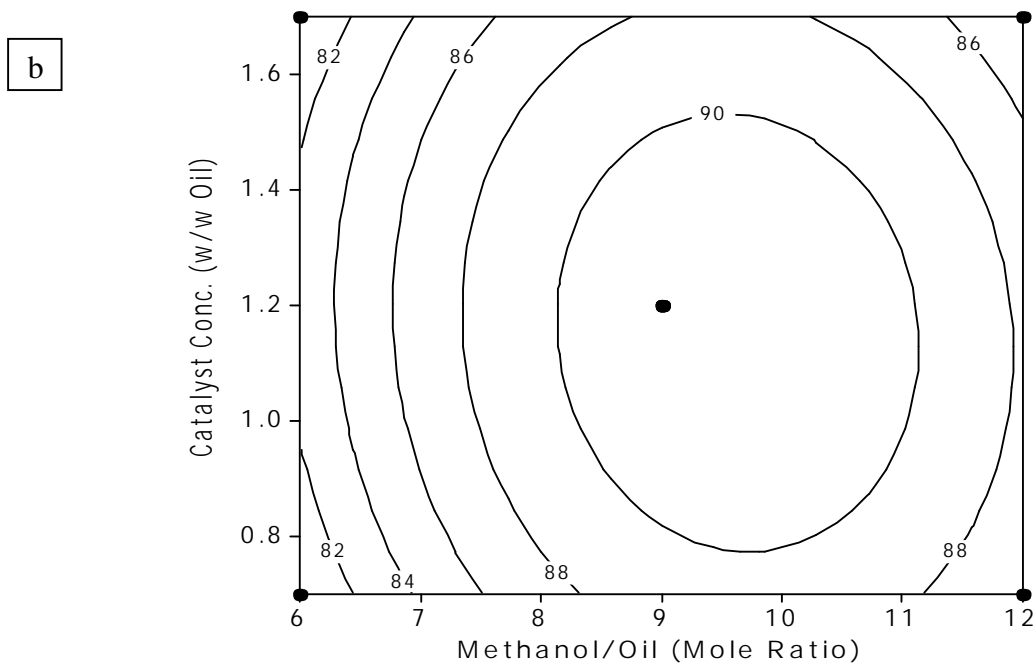
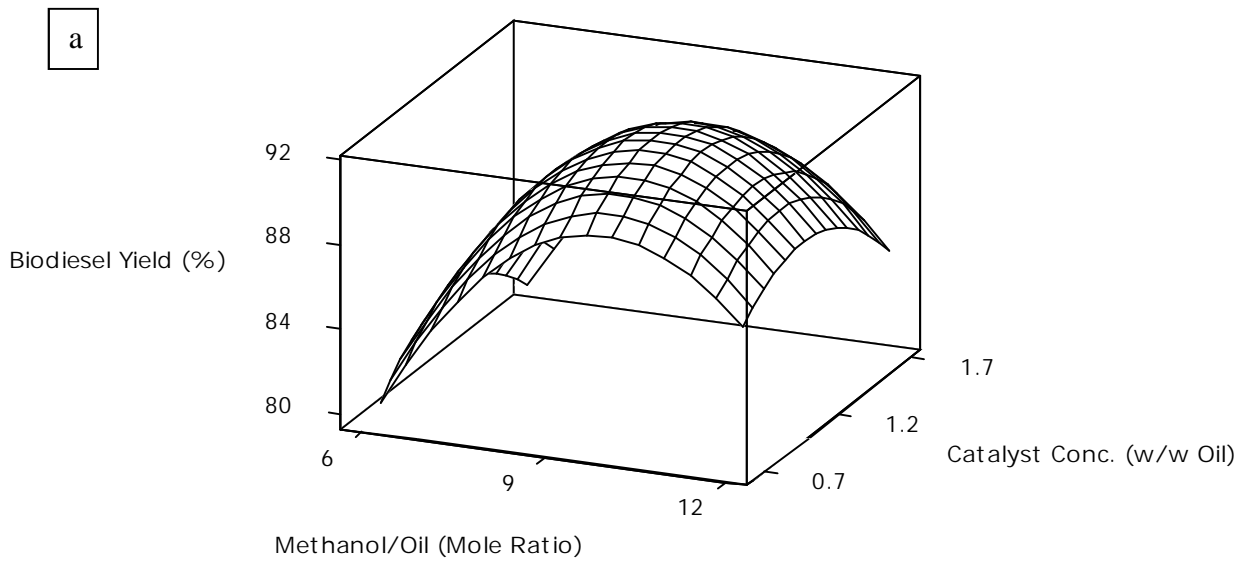


Figure 4.5: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Methanol/Oil mole ratio and NaOH Catalyst Concentration at 55 °C and 70 minutes reaction time.

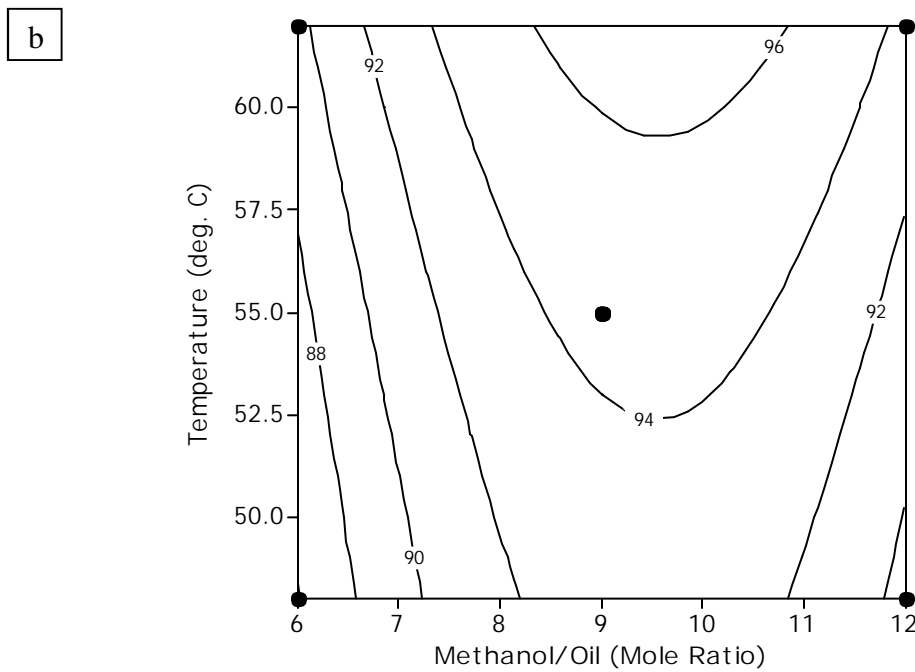
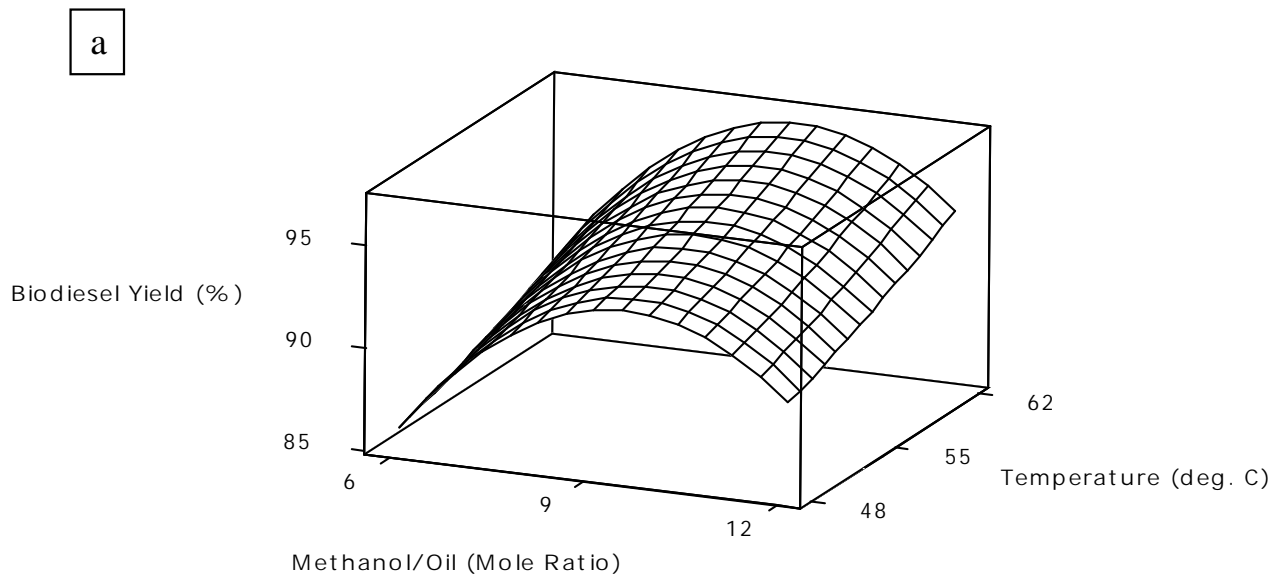
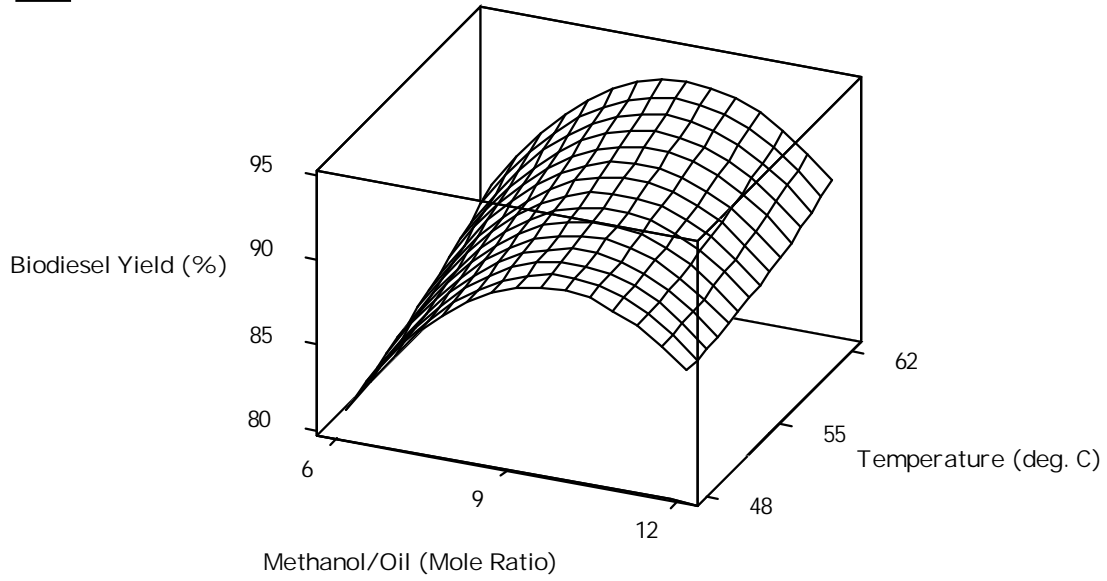


Figure 4.6: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Methanol/Oil mole ratio and Temperature, at 1.2 w/w KOH catalyst concentration and 70 minutes time.

a



b

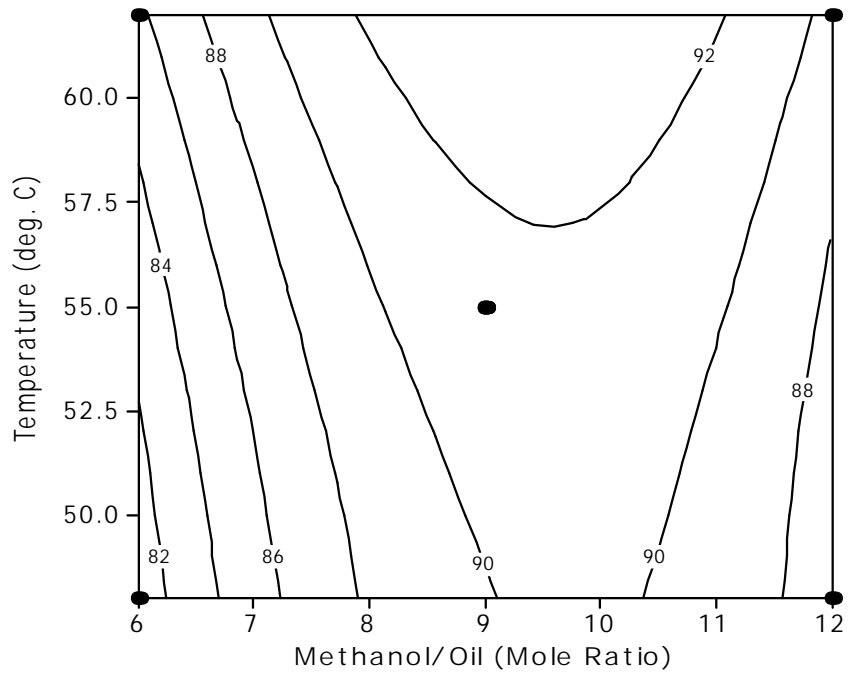


Figure 4.7: (a) Surface and (b) Contour plots of CPKO biodiesel yield, Methanol/Oil mole ratio and Reaction Temperature, at 1.2 w/w NaOH catalyst concentration and 70 minutes time.

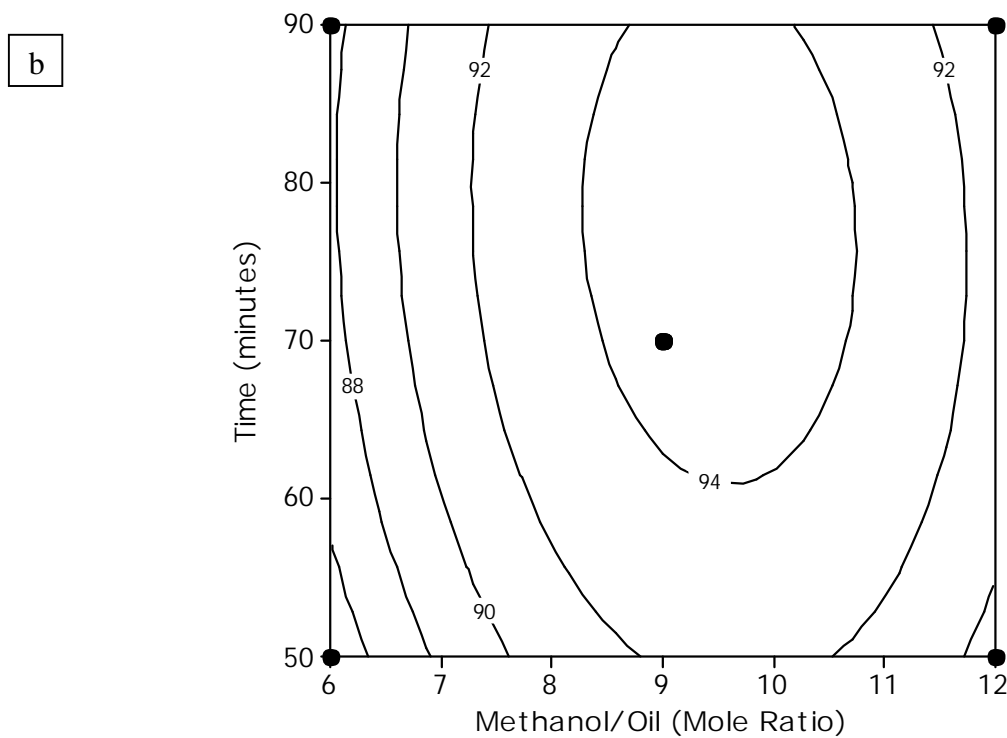
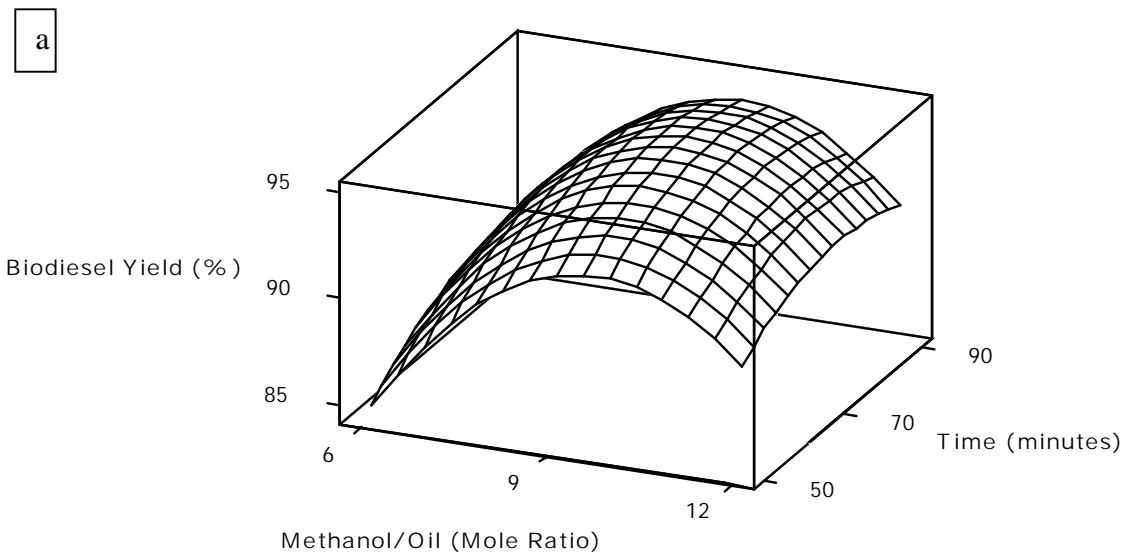


Figure 4.8: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Methanol/Oil mole ratio and Time, at 1.2w/w KOH catalyst concentration at 55 °C reaction temperature.

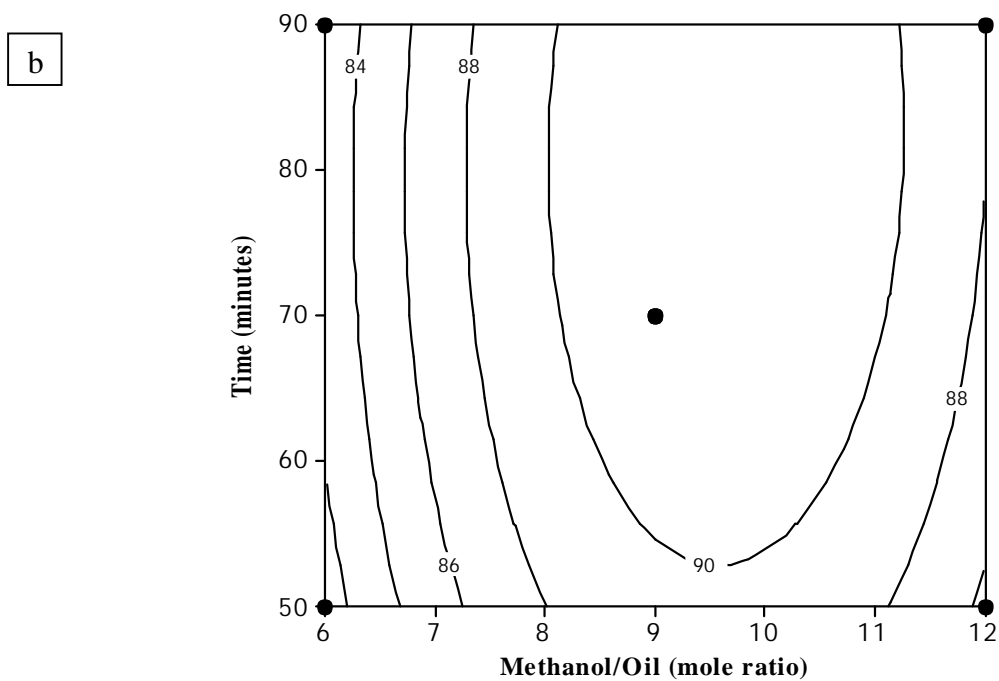
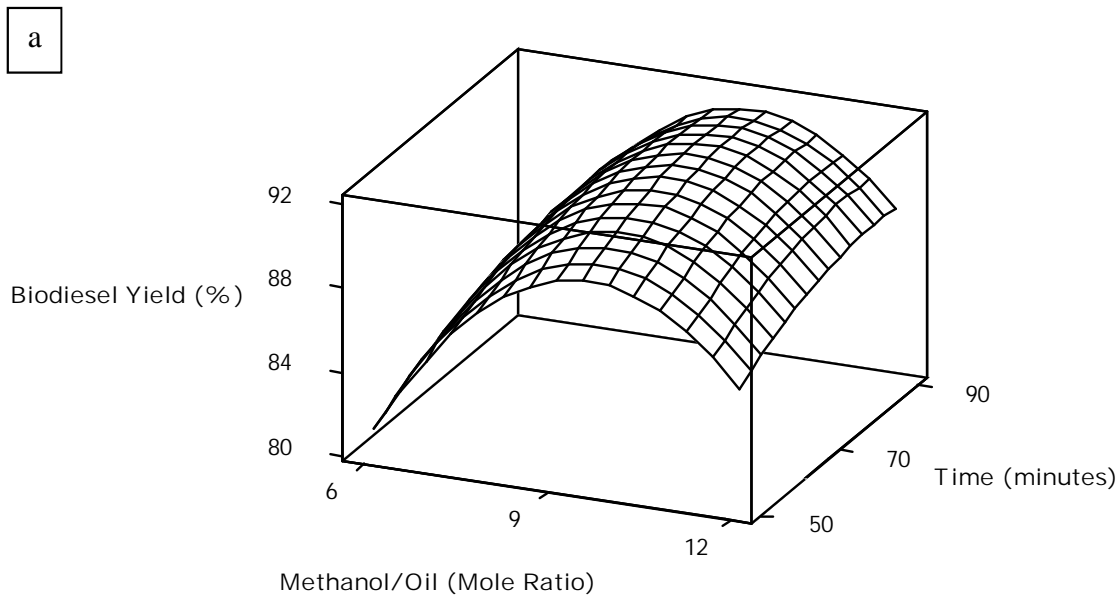
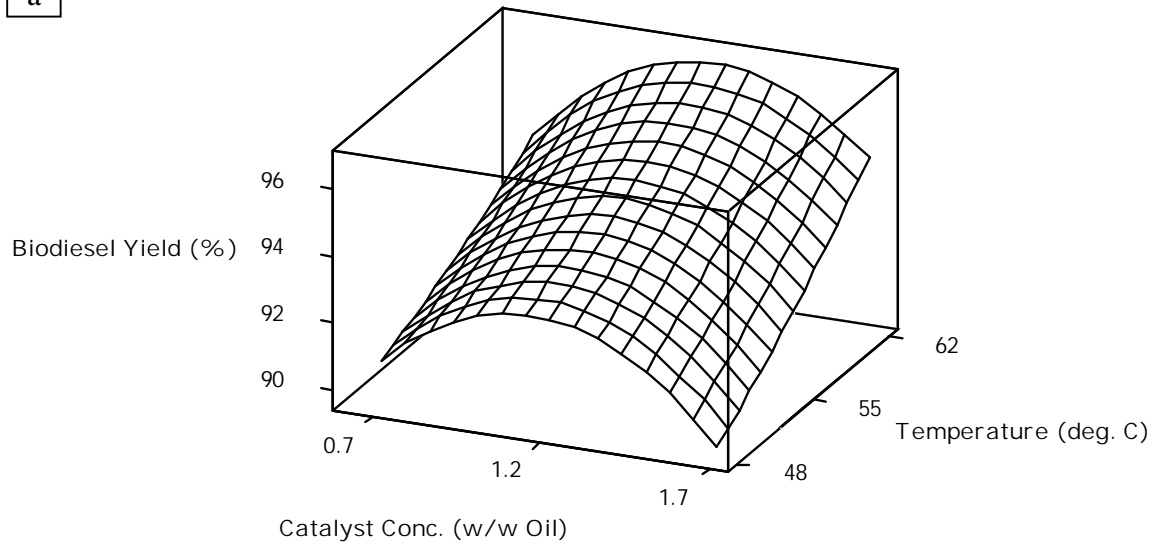


Figure 4.9: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Methanol/Oil mole ratio and Time, at 1.2w/w NaOH catalyst concentration and 55 °C reaction temperature.

a



b

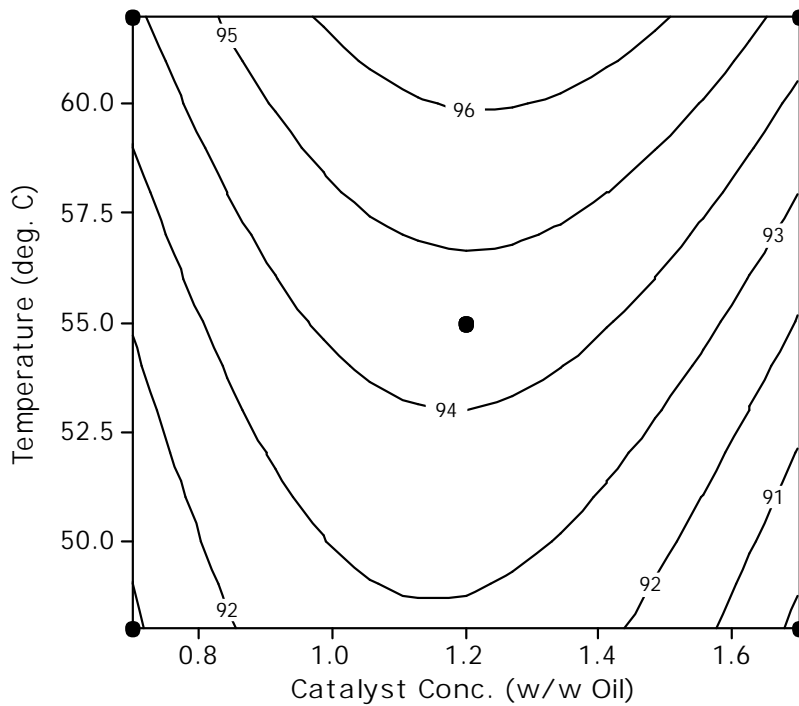


Figure 4.10: (a) Surface and (b) Contour plots of CPKO biodiesel yield against KOH Catalyst Concentration and Reaction Temperature at 9 Methanol/Oil mole ratio and 70 minutes time.

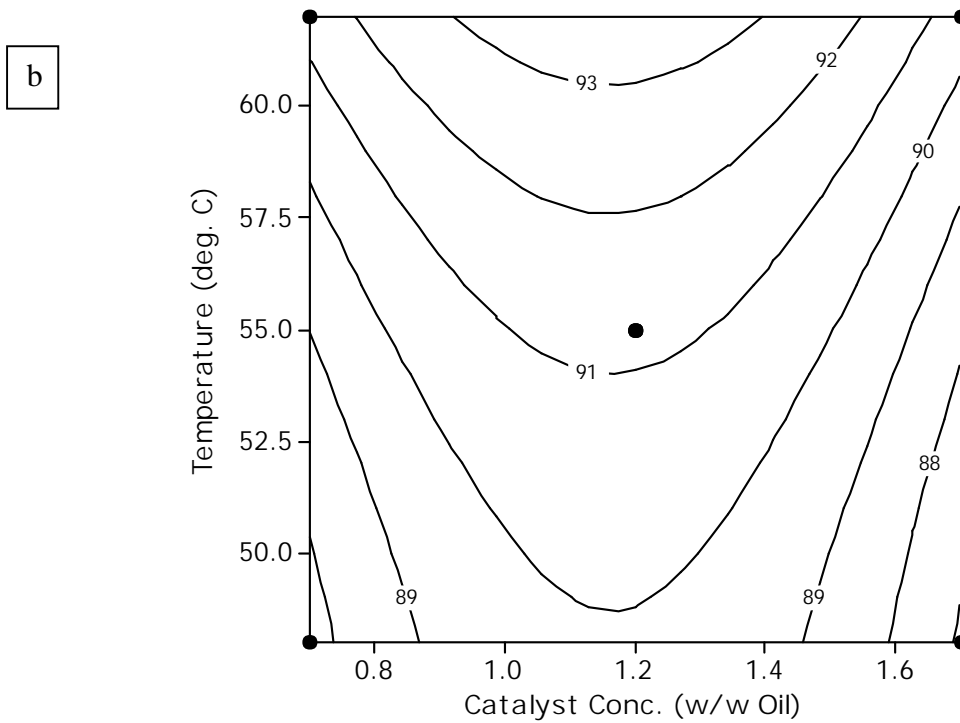
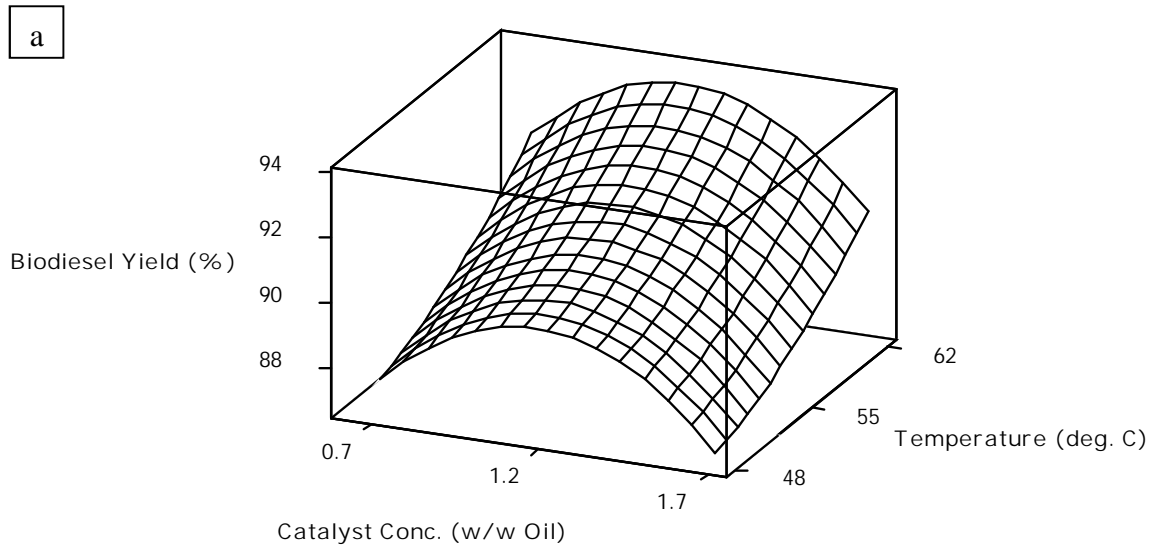


Figure 4.11: (a) Surface and (b) Contour plots of CPKO biodiesel yield against NaOH Catalyst Concentration and Reaction Temperature at 9 Methanol/Oil mole ratio and 70 minutes time.

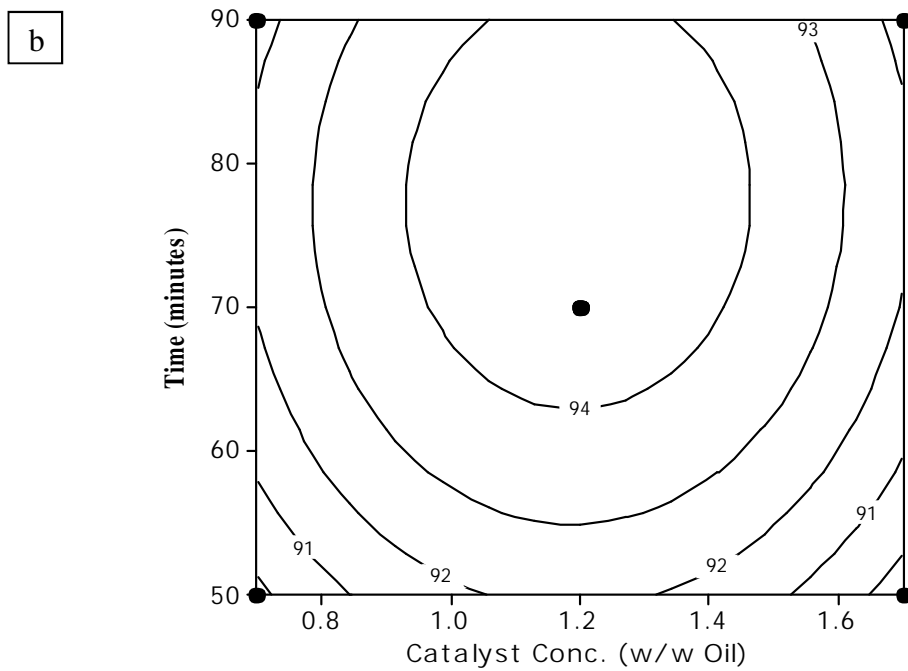
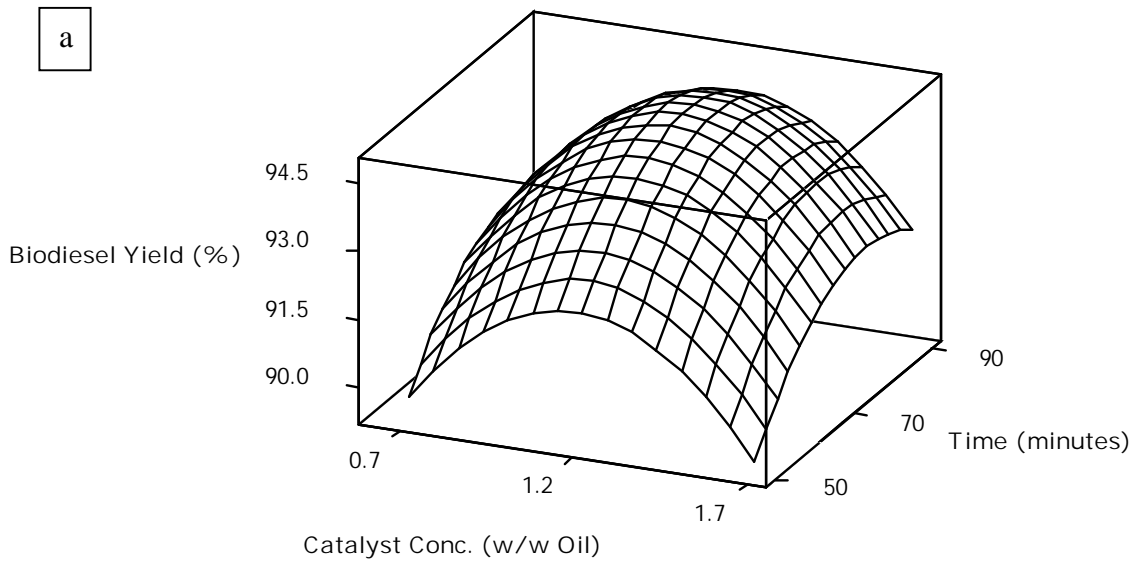
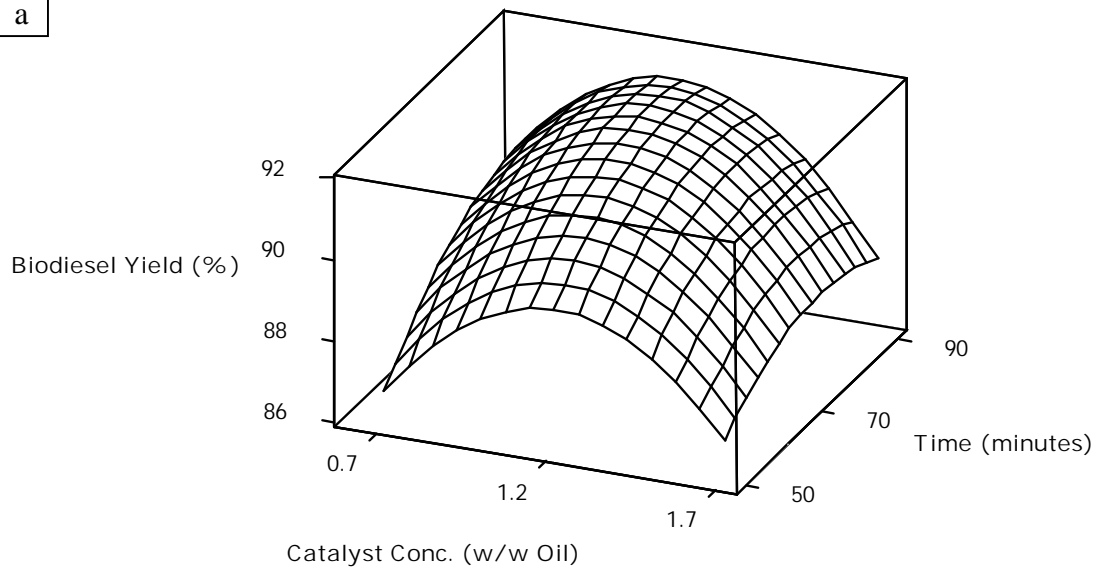


Figure 4.12: (a) Surface and (b) Contour plots of CPKO biodiesel yield against KOH Catalyst Concentration and Time, at 9 mole ratio of methanol/oil and 55 °C temperature.

a



b

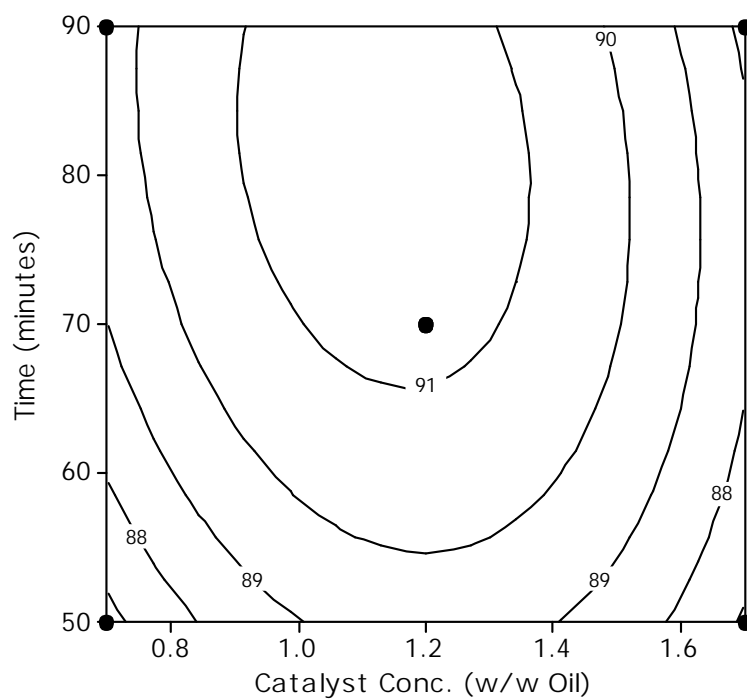


Figure 4.13: (a) Surface and (b) Contour plots of CPKO biodiesel yield against NaOH Catalyst Concentration and Reaction Time, at 9 mole ratio of methanol/oil and 55⁰C reaction temperature.

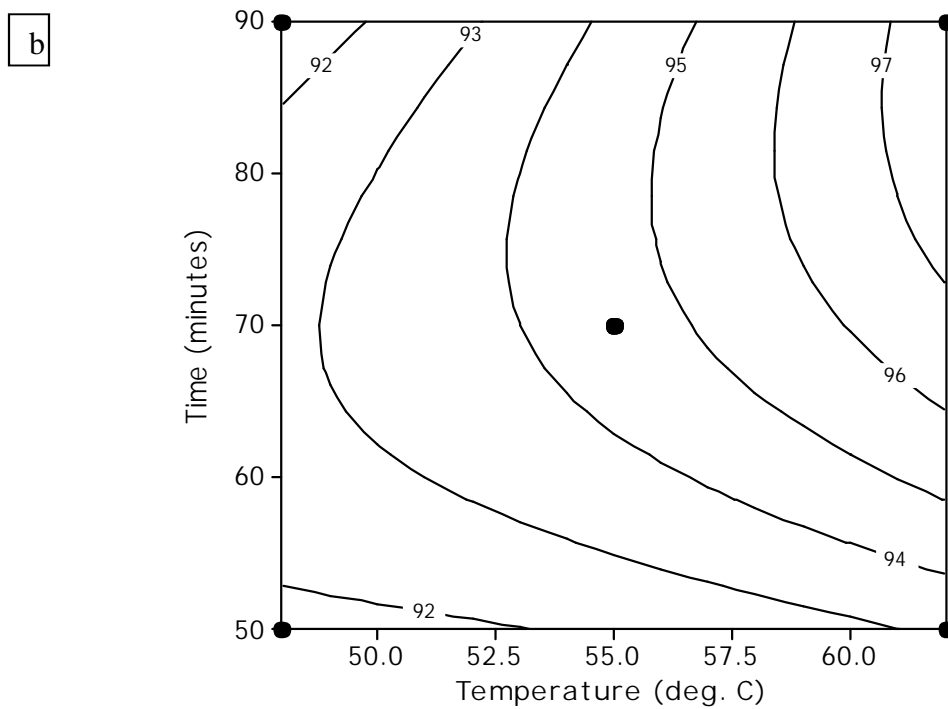
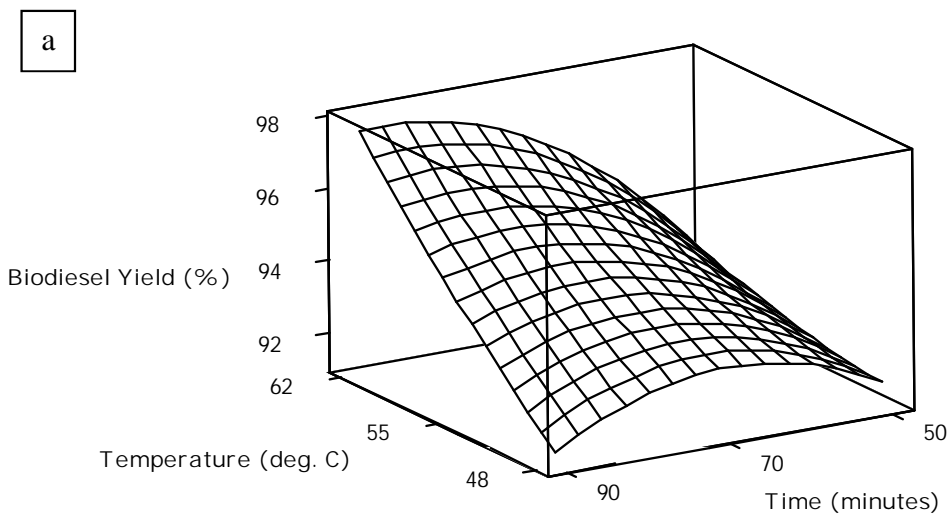


Figure 4.14: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Reaction Time and Reaction Temperature, using KOH catalyst of 1.2 w/w Oil and 9 mole ratio of methanol/oil.

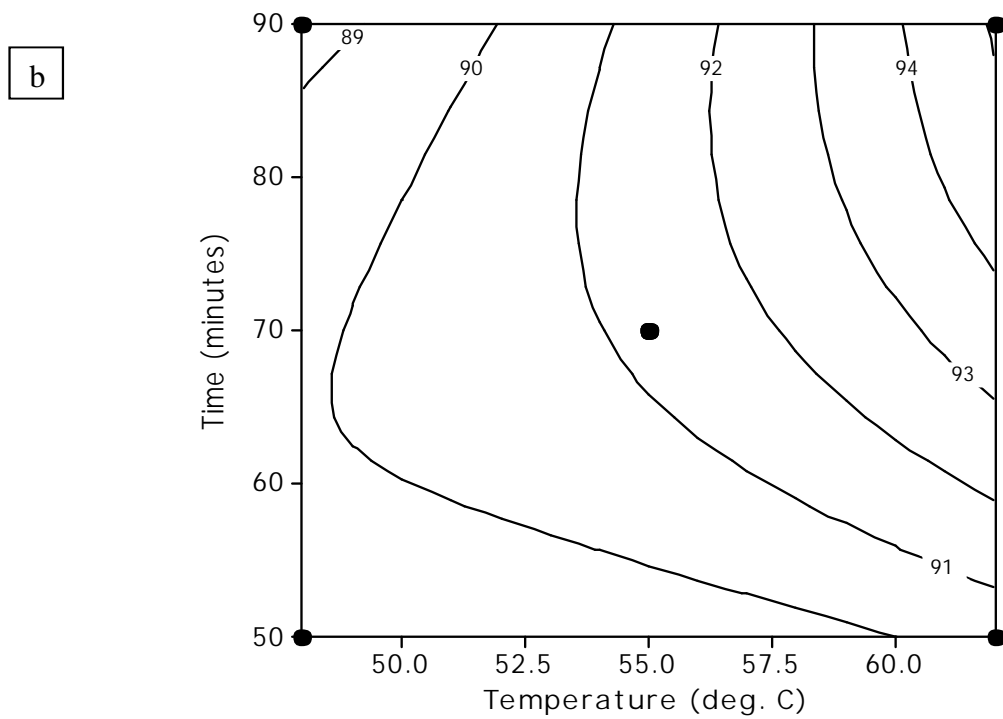
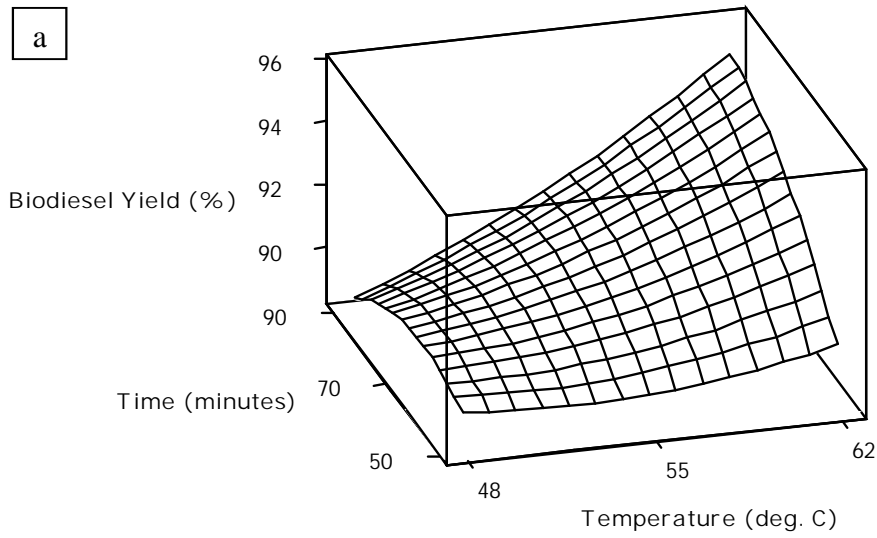
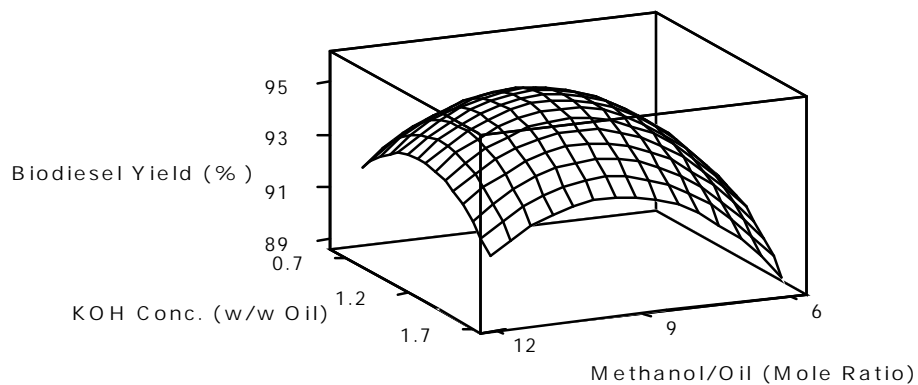


Figure 4.15: (a) Surface and (b) Contour plots of CPKO biodiesel yield against Reaction Time and Reaction Temperature, using NaOH catalyst of 1.2 w/w oil and 9 mole ratio of Methanol/Oil

Hold Values	
Rxn Temp, deg. C	55
Rxn Time, min.	70



Hold Values	
Rxn Temp, deg. C	55
Rxn Time, min.	70

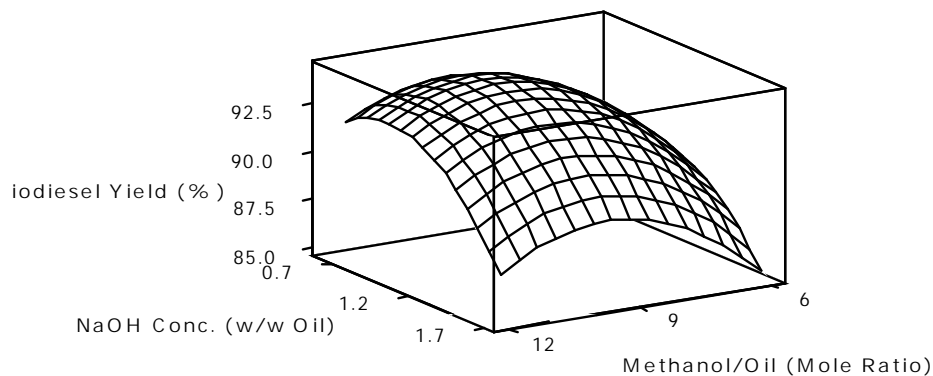
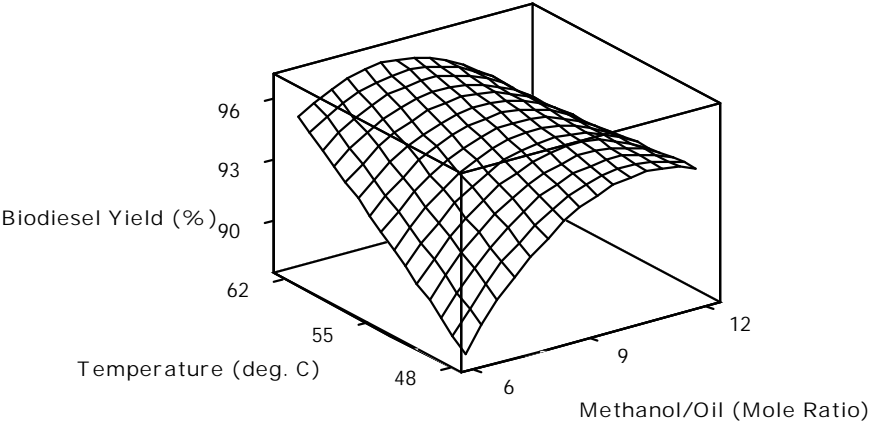


Figure 4.16: Surface plots of WGO Biodiesel Yield against Methanol/Oil mole ratio and Catalyst Concentration, at fixed 55 °C temperature and 70 minutes time

a

Hold Values	
Cat. Conc. w/wOil	1.2
Rxn Time, min.	70



b

Hold Values	
Cat. Conc. w/wOil	1.2
Rxn Time, min.	70

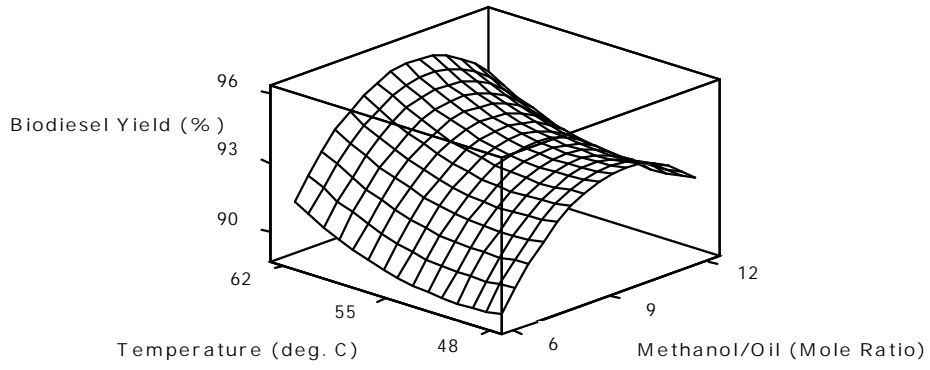
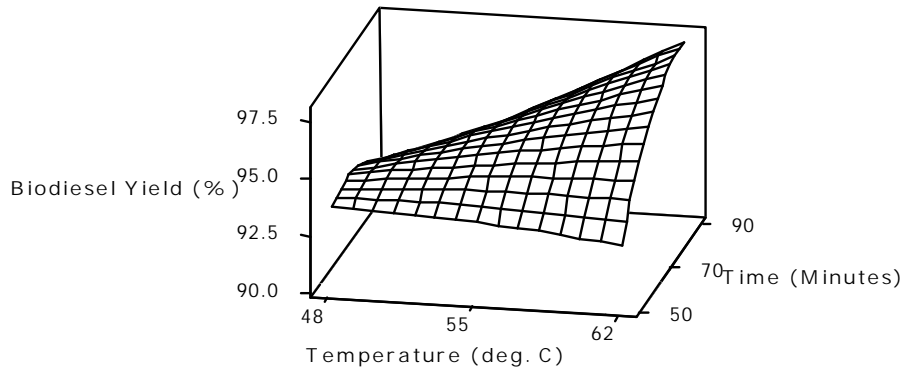


Figure 4.17: Surface Plots of WGO Biodiesel Yield against Methanol/Oil mole ratio and Temperature, at 1.2 w/w Catalyst Concentration (a) KOH, (b) NaOH and 70 minutes time

a

Hold Values	
Met./Oil, Mole Ratio	9
Cat. Conc. w/wOil	1.2



b

Hold Values	
Met./Oil, Mole Ratio	9
Cat. Conc. w/wOil	1.2

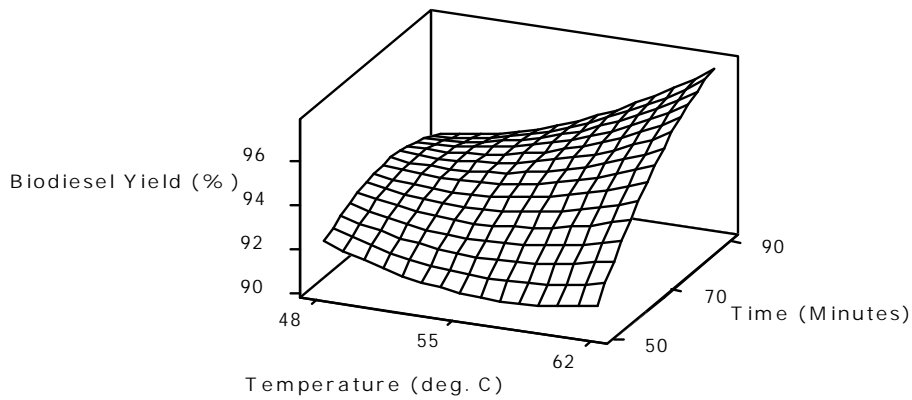
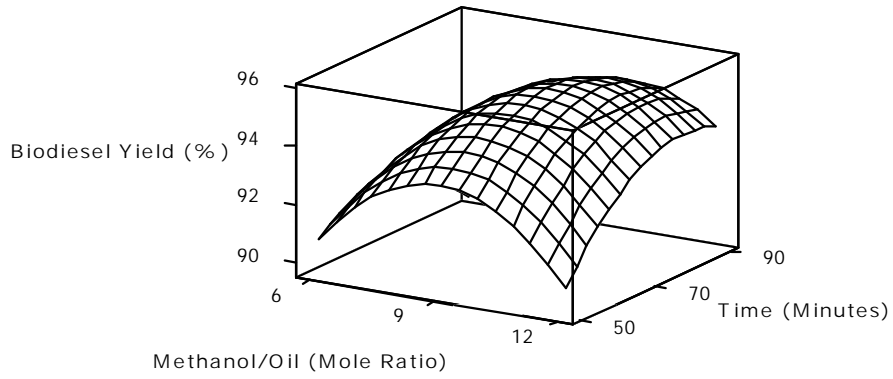


Figure 4.18: Surface Plots of WGO Biodiesel Yield against Temperature and Reaction Time, at 9 Methanol/Oil mole ratio and 1.2 w/w Catalyst Concentration (a) KOH, (b) NaOH

a

Hold Values	
Cat. Conc. w/wOil	1.2
Rxn Temp, deg. C	55



b

Hold Values	
Cat. Conc. w/wOil	1.2
Rxn Temp, deg. C	55

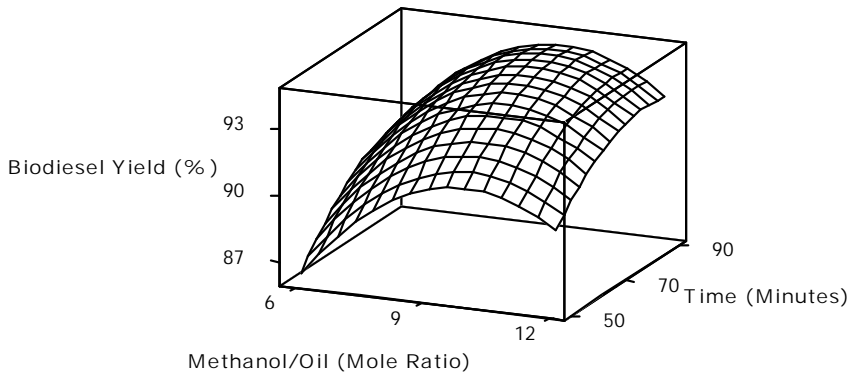
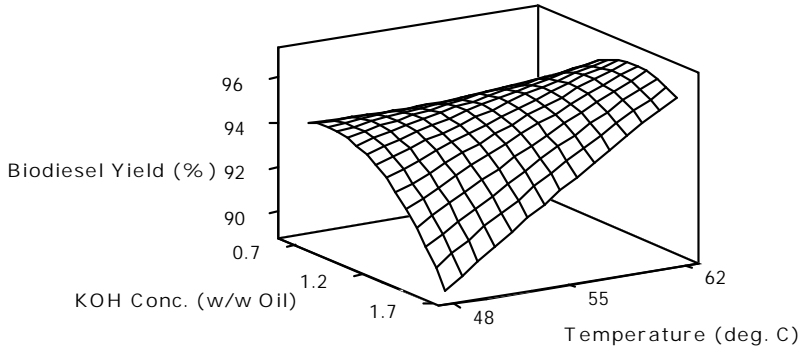


Figure 4.19: Surface Plots of WGO Biodiesel Yield against Methanol/Oil mole ratio and Reaction Time, at 55 °C and 1.2 w/w Catalyst Concentration (a) KOH, (b) NaOH

Hold Values	
Met./Oil, Mole Ratio	9
Rxn Time, min.	70



Hold Values	
Met./Oil, Mole Ratio	9
Rxn Time, min.	70

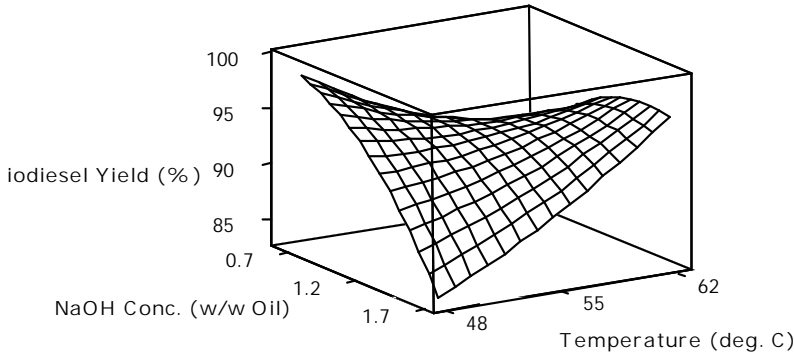
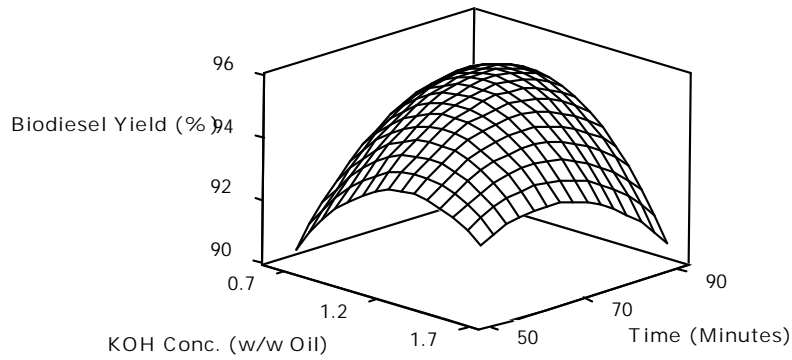


Figure 4.20: Surface Plots of WGO Biodiesel Yield against Catalyst concentration (w/w Oil) and Reaction Temperature, at 9 mole ratio of Methanol/Oil and 70 minutes reaction time

Hold Values	
Met./Oil, Mole Ratio	9
Rxn Temp, deg. C	55



Hold Values	
Met./Oil, Mole Ratio	9
Rxn Temp, deg. C	55

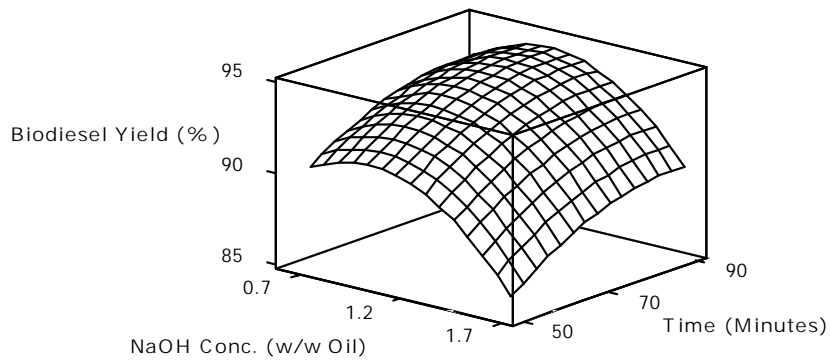


Figure 4.21: Surface Plots of WGO Biodiesel Yield against Catalyst concentration (w/w Oil) and Reaction Time, at 9 mole ratio of Methanol/Oil and 55 °C Reaction Temperature

4.5 Modeling of Biodiesel Yields

Response surface regression analysis was carried out using MINITAB 16 software. The most suitable response models generated as a function of the four factors (X_1 , methanol/oil mole ratio; X_2 , catalyst concentration; X_3 , reaction temperature and X_4 , reaction time) are second-order polynomials (with main effects, two-factor interactions and squared terms) represented as:

$$Y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 + \alpha_{1,1} X_1 X_1 + \alpha_{1,2} X_1 X_2 + \alpha_{1,3} X_1 X_3 + \alpha_{1,4} X_1 X_4 + \alpha_{2,2} X_2 X_2 + \alpha_{2,3} X_2 X_3 + \alpha_{2,4} X_2 X_4 + \alpha_{3,3} X_3 X_3 + \alpha_{3,4} X_3 X_4 + \alpha_{4,4} X_4 X_4 \quad \text{Eq. 4.1}$$

The biodiesel responses (% yields) are designated as Y associated with each factor level combinations. $\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_{1,2}, \dots, \alpha_{4,4}$ are the regression coefficients; X_1, X_2, X_3 and X_4 are the factors. $X_1 X_1, X_1 X_2, X_1 X_3, X_1 X_4, X_2 X_2, \dots, X_4 X_4$, are the interactions of the variables. The optimal process parameters for WGO biodiesel yield, WGO biodiesel yield and CPKO biodiesel yield were estimated by using MINITAB 16 software (PA, USA). The coefficients of the second-order polynomials, both the F and p values of the coefficients of the equations were determined (Appendix D). Also, the predicted responses of biodiesel yields were obtained. From the regression analysis, the most fitted models obtained are as shown in Equations 4.2 – 4.7.

$$\begin{aligned} & \text{(WGO biodiesel yield)}_{\text{KOH}} \\ & = 38.5074 + 10.8486 X_1 - 0.2922 X_1 X_1 - 0.1171 X_1 X_3 + 0.0164 X_1 X_4 - 7.1928 X_2 X_2 \\ & \quad + 0.4836 X_2 X_3 - 0.1479 X_2 X_4 + 0.0099 X_3 X_4 - 0.0034 X_4 X_4 \end{aligned} \quad \text{Eq. 4.2}$$

$$R\text{-Sq} = 90.29\%$$

$$R\text{-Sq}(adj) = 85.16\%$$

$$\begin{aligned} & \text{(WGO biodiesel yield)}_{\text{NaOH}} \\ & = 214.511 + 6.1287 X_1 - 63.8347 X_2 - 4.2363 X_3 - 0.3152 X_1 X_1 - 10.7102 X_2 X_2 \\ & \quad + 1.5557 X_2 X_3 + 0.0170 X_3 X_3 + 0.0090 X_3 X_4 - 0.0029 X_4 X_4 \end{aligned} \quad \text{Eq. 4.3}$$

$$R\text{-Sq} = 92.10\%$$

$$R\text{-Sq}(adj) = 87.91\%$$

$$\begin{aligned} & \text{(WSO biodiesel yield)}_{\text{KOH}} \\ & = 73.9378 + 6.5672 X_1 - 0.5116 X_4 - 0.3379 X_1X_1 - 5.9666 X_2X_2 + 0.2520 X_2X_3 \\ & \quad - 0.0089 X_3X_3 + 0.0125 X_3X_4 - 0.0010 X_4X_4 \end{aligned} \quad \text{Eq. 4.4}$$

$$R\text{-Sq} = 93.99\%$$

$$R\text{-Sq}(adj) = 91.31\%$$

$$\begin{aligned} & \text{(WSO biodiesel yield)}_{\text{NaOH}} \\ & = -48.6299 - 56.6067 X_2 + 5.6742 X_3 + 1.0185 X_4 + 0.1080 X_1X_1 - 0.0321 X_1X_4 \\ & \quad + 0.84 X_2X_3 - 0.0647 X_3X_3 - 0.0050 X_4X_4 \end{aligned} \quad \text{Eq. 4.5}$$

$$R\text{-Sq} = 80.18\%$$

$$R\text{-Sq}(adj) = 71.37\%$$

$$\begin{aligned} & \text{(CPKO biodiesel yield)}_{\text{KOH}} \\ & = 28.5989 + 11.0532 X_1 + 24.6909 X_2 - 0.3862 X_3 - 0.5787 X_1X_1 - 10.3358 X_2X_2 \\ & \quad + 0.0094 X_3X_4 - 0.0033 X_4X_4 \end{aligned} \quad \text{Eq. 4.6}$$

$$R\text{-Sq} = 93.24\%$$

$$R\text{-Sq}(adj) = 90.75\%$$

$$\begin{aligned} & \text{(CPKO biodiesel yield)}_{\text{NaOH}} \\ & = 12.733 + 13.3021 X_1 + 26.3284 X_2 - 0.3181 X_3 - 0.6931 X_1X_1 - 11.307 X_2X_2 \\ & \quad + 0.0082 X_3X_4 - 0.0029 X_4X_4 \end{aligned} \quad \text{Eq. 4.7}$$

$$R\text{-Sq} = 89.35\%$$

$$R\text{-Sq}(adj) = 85.43\%$$

Table 4.5: Deviation of Predicted Biodiesel Yields from Experimental Biodiesel Yields

Predicted Model of Biodiesel Yield	Range of % Absolute Deviations	Average % Deviation	R ² %
(WGO biodiesel yield) _{KOH} (Equation 4.2)	(-2.184 - 1.242)	-0.337	90.29
(WGO biodiesel yield) _{NaOH} (Equation 4.3)	(-2.291 - 2.516)	0.028	92.10
(WSO biodiesel yield) _{KOH} (Equation 4.4)	(-1.275 - 1.577)	0.073	93.99
(WSO biodiesel yield) _{NaOH} (Equation 4.5)	(-5.966 - 4.052)	-0.723	80.18
(CPKO biodiesel yield) _{KOH} (Equation 4.6)	(-2.490 - 1.527)	-0.054	93.24
(CPKO biodiesel yield) _{NaOH} (Equation 4.7)	(-4.601 - 3.000)	0.303	89.35

4.6 Properties of Biodiesel Obtained

Biodiesel properties obtained from the waste oils trans-esterification process are shown on Table 4.6.

Table 4.6: Properties of Biodiesel Obtained

Property	ASTM Mtd	Units	CPKO Biodiesel	WSO Biodiesel	WGO Biodiesel
Density @ 25 ⁰ C	ASTM D4052	g/cm ³	0.8760	0.8820	0.8903
Pour Point	ASTM D97	⁰ C	-6	-6	-9
Flash Point	ASTM D93	⁰ C	208	204	180
Water Content		%	0.004	0.006	0.005
Viscosity @ 40 ⁰ C	ASTM D445	mm ² /s	(4.70 – 5.00)	(4.55 – 4.85)	(4.30 – 4.70)
*Cetane Number			(51.7 – 53.2)	(50.6 – 52.8)	(49.4 – 51.0)

*Cetane number was calculated using the predicted model

4.7 Comparison of the reported Cetane Number (CN) and Cetane Number obtained from the predicted model

Cetane number obtained from Ramirez-Verdusco et. al. (2012) models, cetane number determined experimentally (reported by Ramirez-Verdusco et. al. (2012)) and cetane number calculated using the new predicted model are compared, as shown on Table 4.7.

Table 4.7: Comparison of Reported Cetane Number and Cetane Number obtained from the Predicted model

Biodiesel	Density (g/cm³) @ 25⁰C	Kinematic Viscosity (mm²/s) @ 40⁰C	Cetane Number (Experimental)	Cetane Number Ramirez <i>et. al.</i> (2012)	Cetane Number (Predicted Model)
Sunflower oil methyl ester	0.8820	4.05	50.0 ^a	48.7 ^b	51.4
Soyabean oil methyl ester	0.8810	4.10	51.7 ^b	50.2 ^b	51.6
Corn oil methyl ester	0.8803	4.13	53.0 ^a	51.4 ^b	51.6
Cottonseed oil methyl ester	0.8784	4.12	51.2 ^c	53.8 ^b	51.9
Beef tallow oil methyl ester	0.8774	4.29	57.8 ^d	56.2 ^b	52.2

^aRamos *et. al.* (2009), ^bRamirez-Verdusco *et. al.* (2012), ^cKnothe (2008), ^dZheng and Hanna (1996)

*Mass fractions and biodiesel compositions considered for the calculation of biodiesel cetane number in the predicted model are as reported in the work of Ramirez-Verdusco *et. al.*, 2012 (Table E1 of Appendix E)

With the aid of MINITAB 16 software, both the percentage average absolute deviation (% AAD) and pearson correlation of the CN from the predicted model and CN reported by Ramirez-Verdusco *et. al.* (2002) with CN determined experimentally were determined, as shown in Table 4.8 and Figure 4.22).

Table 4.8: Statistical Analysis of Absolute Deviation of the Results of Ramirez *et. al.* (2012) model and Predicted model from the Experimental Results

Biodiesel	CN(Exptal.)	CN (Ramirez <i>et. al.</i>)	CN (Pred. Model)	AD (Ramirez <i>et. al.</i>)	AD(Pred. model)	AAD (Ramirez <i>et. al.</i>)	AAD (Pred model)
SF	50.0	48.7	51.4	1.3	1.4	0.026	0.028
SB	51.7	50.2	51.6	1.5	0.1	0.029	0.001
CO	53.0	51.4	51.6	1.6	1.4	0.030	0.026
CT	51.2	53.8	51.9	2.6	0.7	0.051	0.013
BT	57.8	56.2	52.2	1.6	5.6	0.028	0.096
						<u>0.164</u>	<u>0.164</u>

SF = Sunflower oil methyl ester, SB = Soyabean oil methyl ester, CO = Corn oil methyl ester, CT = Cottonseed oil methyl ester, BT = Beef tallow oil methyl ester.

$$\text{Percentage Average Absolute Deviation (\% AAD)} = \frac{100}{n} \sum_{i=1}^n \frac{\text{Cetane Number (Experimental)} - \text{Cetane Number (Calculated)}}{\text{Cetane Number (Experimental)}}$$

$$\% \text{ AAD for Ramirez } et. al. (2012) \text{ model} = \frac{100}{n} \sum_{i=1}^n \frac{\text{CN (Exptal.)} - \text{CN (Ramirez et.al.)}}{\text{CN (Exptal.)}} = \frac{100(0.164)}{5} = 3.28 \%$$

$$\% \text{ AAD for Predicted model} = \frac{100}{n} \sum_{i=1}^n \frac{\text{CN (Exptal.)} - \text{CN (Predicted model)}}{\text{CN (Exptal.)}} = \frac{100(0.164)}{5} = 3.28 \%$$

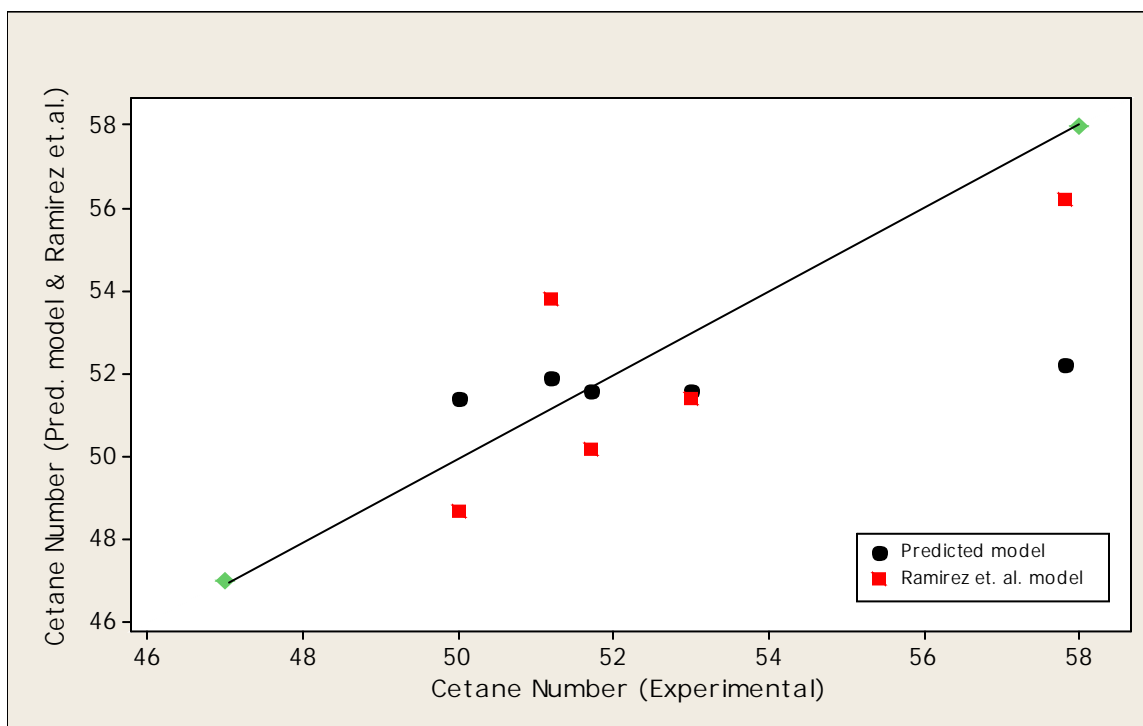


Figure 4.22: Correlation of Cetane Number using Pred. model and Cetane Number reported by Ramirez et. al. (2012) with Experimentally determined Cetane Number.

4.8 Report on Biodiesel LCA

Scaling down the amount of materials used in this process to functional unit system of 1 kg of biodiesel produced gives a table of the material balance shown in Table 4.9 (Table F1 and Table F2 of Appendix F for the actual quantity of materials involved in LCA of the laboratory scale biodiesel produced and Life Cycle Inventory respectively).

Table 4.9: Material Balance on LCA of 1 kg Biodiesel Production

ITEM	UNIT	<u>CPKO</u>		<u>WGO</u>		<u>WSO</u>	
		KOH	NaOH	KOH	NaOH	KOH	NaOH
FEED							
Methanol	kg	0.37801	0.39278	0.37017	0.37610	0.37287	0.38877
Oil	kg	1.10330	1.14641	1.08041	1.09770	1.08828	1.13468
KOH	kg	0.01324	-	0.01296	-	0.01306	-
NaOH	kg	-	0.01375	-	0.01317	-	0.01362
Warm Water	kg	0.01655	0.01720	0.01621	0.01647	0.01632	0.01702
Total	kg	<u>1.51110</u>	<u>1.57014</u>	<u>1.47975</u>	<u>1.50344</u>	<u>1.49053</u>	<u>1.55409</u>
PRODUCTS							
Biodiesel	kg	1	1	1	1	1	1
Crude Glycerol	kg	0.48132	0.53920	0.45058	0.47380	0.46115	0.52346
Water Out	kg	0.02979	0.03094	0.02917	0.02964	0.02938	0.03064
Total	kg	<u>1.51110</u>	<u>1.57014</u>	<u>1.47975</u>	<u>1.50344</u>	<u>1.49053</u>	<u>1.55409</u>

4.8.1 Characterisation of Substances Released from Biodiesel Production

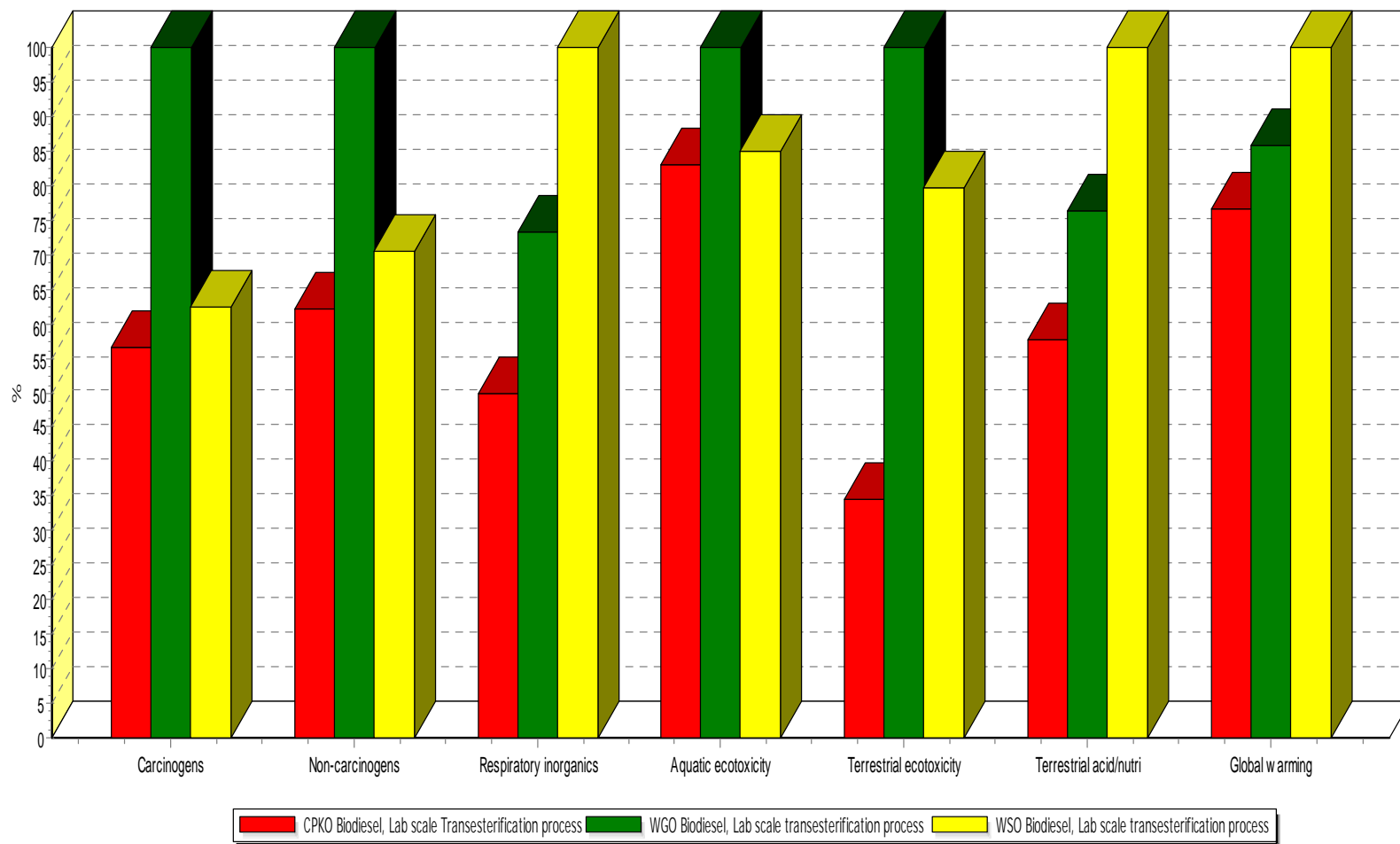
In LCA of biodiesel, non-environmentally friendly substances released are characterised into seven midpoint categories. These categories are carcinogens, non-carcinogens, respiratory inorganics, aquatic ecotoxicity, terrestrial ecotoxicity, terrestrial acidification and global warming (Figure 4.23). Table F3 of Appendix F shows the substances released into the environment and the categories that each substance belong to.

In Figure 4.23, each midpoint category is expressed in percent (%). The biodiesel that releases the highest quantity of non environmentally friendly substances was assigned 100% in each category. For example, for carcinogens, WGO biodiesel has 100% allocated to the harmful substances released because it has highest total amount (5.69×10^{-6} kg) of such substances released into the environment. While 62% of the substances released from WGO biodiesel (3.55×10^{-6} kg) were released as a result of WSO biodiesel production or/and utilisation. For CPKO biodiesel, the substances released (3.21×10^{-6} kg) was 56% of the substances released into the environment from WGO biodiesel.

Although all the seven indicators considered are expressed in unit percent (%), two categories cannot be compared at this stage because each category has its peculiar unit (Table F3). For example, carcinogens are expressed in C₂H₃Cl equivalent (C₂H₃Cl being a key substance causing cancer) and aquatic ecotoxicity substances are expressed in TEG (Tri-ethyl Glycol) equivalent in water (TEG is a key substance that damages the ecosystem quality).

The results show that WGO biodiesel production generated the highest amount of harmful substances under the following categories: carcinogens, non carcinogens, aquatic ecotoxicity and terrestrial ecotoxicity. WSO biodiesel production generated highest amount of harmful

substances under respiratory inorganics, terrestrial acidification/nutrication and global warming. While CPKO biodiesel production generated the least harmful substances in each of the seven categories.



Comparing 1 kg 'CPKO Biodiesel, Lab scale Transesterification process', 1 kg 'WGO Biodiesel, Lab scale transesterification process' and 1 kg 'WSO Biodiesel, Lab scale transesterification process';
 Method: IMPACT 2002+ V2.10 / IMPACT 2002+ / Characterization

Figure 4.23: Characterisation of Substances released from CPKO, WGO and WSO Biodiesel.

4.8.2 Damage Assessment of WGO, WSO and CPKO Biodiesel

The impact (damage) of the non-environmentally friendly substances on the environment was assessed through SIMAPRO 7.3.3, using the IMPACT 2000+ method. The results of these assessments on WGO, WSO and CPKO biodiesels are shown in Figure 4.24 - Figure 4.25. The tabulated values are in Table F4. Figure 4.24 is the damage assessment of harmful substances obtained from biodiesel production, based on midpoint categories and Figure 4.25 shows the aggregated damage assessment (endpoint category).

Similar to the characterisation of substances, each category (of midpoint and endpoint) is expressed in percentage (%) and biodiesel that releases highest quantity of non environmentally friendly substances is assigned 100% in each category.

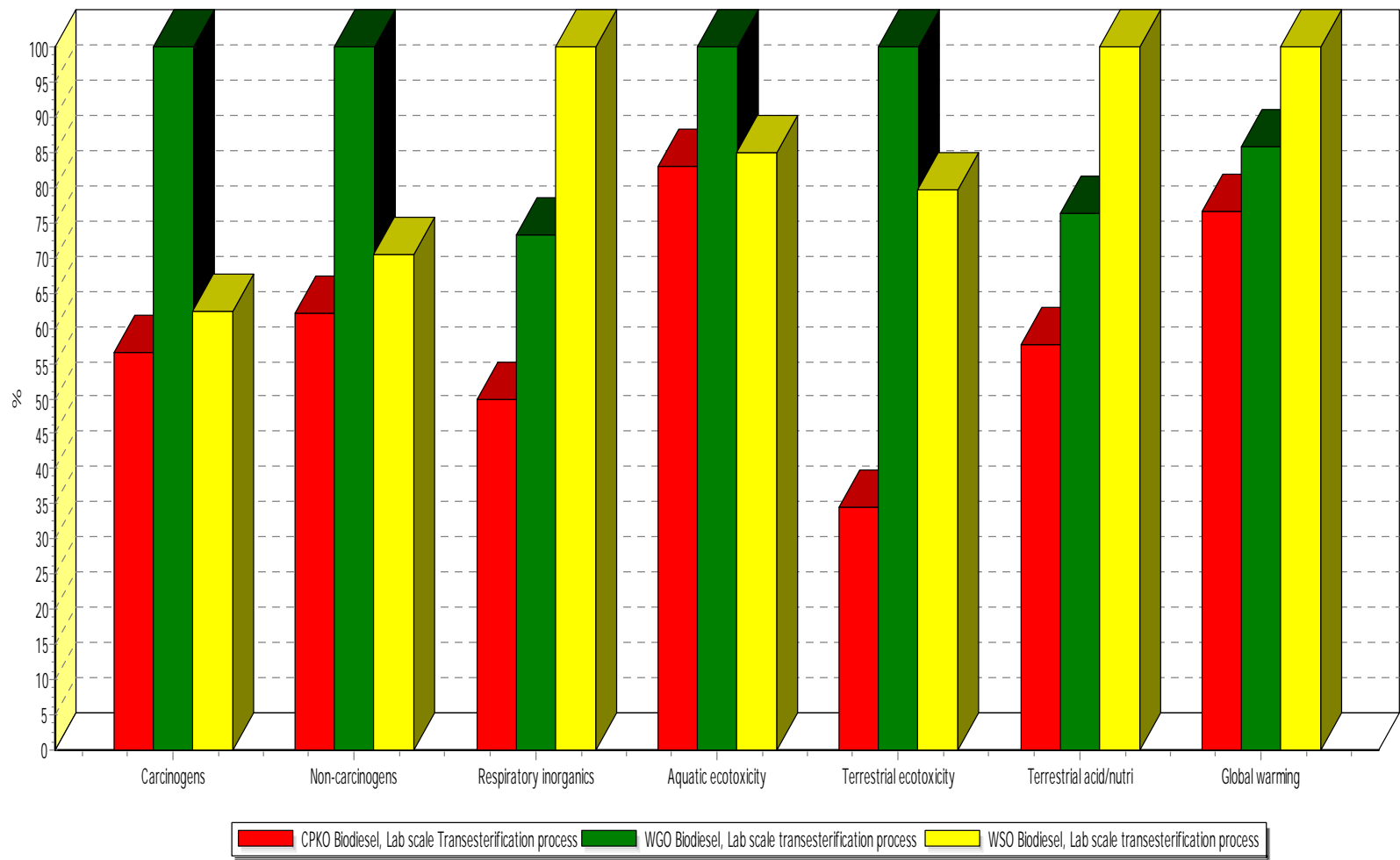
In Figure 4.24, the results trend obtained for damage assessment (based on midpoint categories) is similar to results obtained for characterization of substances. WGO biodiesel had 100 % in carcinogens category, while CPKO biodiesel had 55% and WSO biodiesel had 60%. In non-carcinogens category, CPKO biodiesel recorded 60%, WSO biodiesel recorded 70% and WGO biodiesel had 100%. The trend is similar for aquatic ecotoxicity and terrestrial ecotoxicity. However, the results show that WSO biodiesel had 100% in respiratory inorganics, terrestrial acidification/nitrification and global warming.

Each category of aggregated damage assessment (endpoint category) is obtained by adding certain midpoint categories (Figure 3.14). For example, Human Health damage is obtained from the combination of Carcinogens, Non Carcinogens and Respiratory Inorganics. Damage to Ecosystem Quality is obtained from the addition of Aquatic Ecotoxicity, Terrestrial Ecotoxicity

and Terrestrial Acidification/Nutrition. However, damage resulting in climate change is obtained solely from global warming.

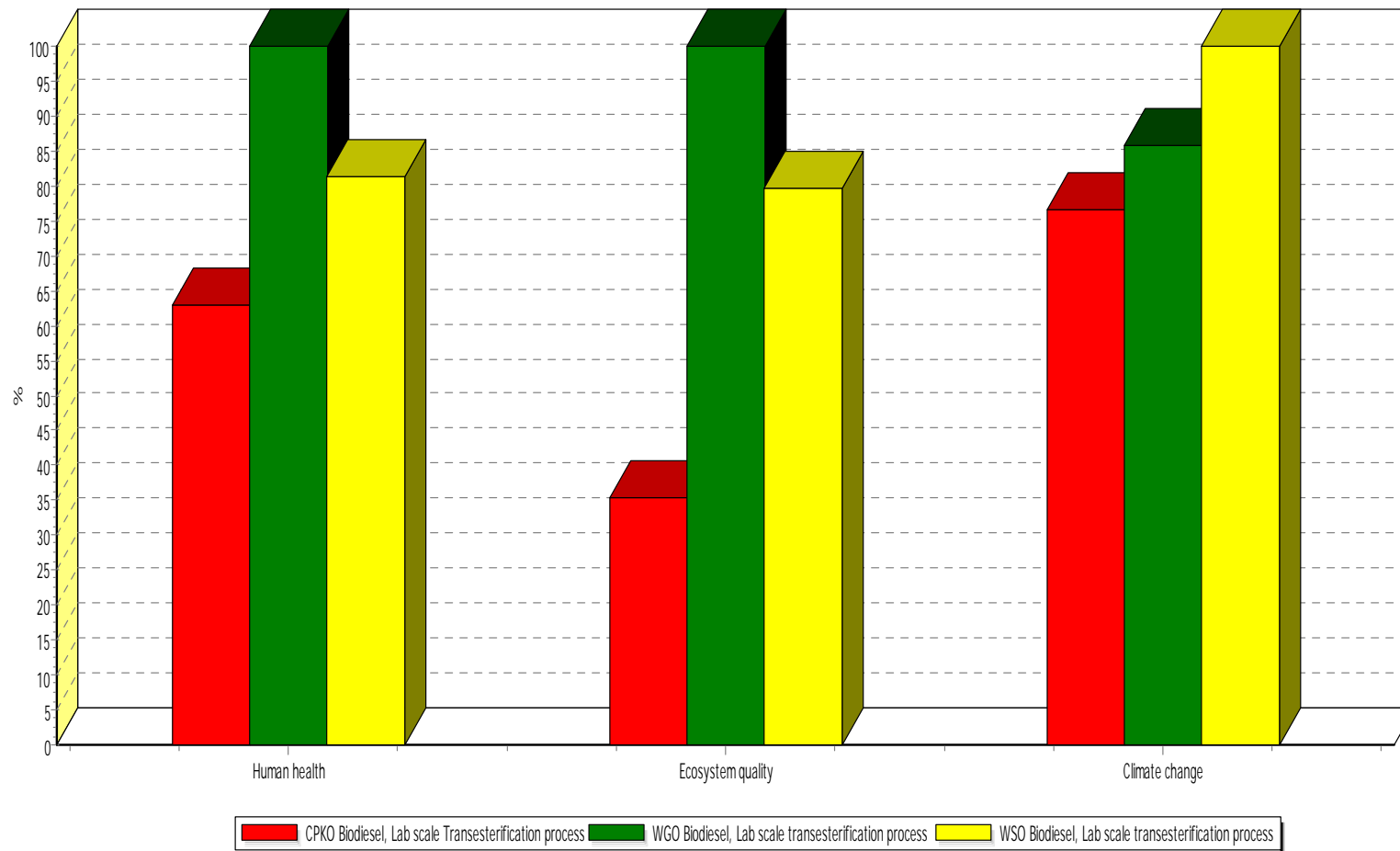
Considering damage to Human Health and Ecosystem Quality (Figure 4.25), it can be seen that WGO biodiesel generated higher amount of harmful substances. 60 % and 80 % of human health damage resulting from WGO biodiesel was recorded in CPKO and WSO biodiesel respectively. 30 % and 75 % of ecosystem quality damage resulting from WGO biodiesel was recorded in CPKO and WSO biodiesel respectively.

WSO biodiesel generated higher amount of harmful substances when damage to climate stability category is considered. CPKO biodiesel generated 75% of damage reported in WSO biodiesel while WGO biodiesel generated 85% of damage reported in WSO biodiesel.



Comparing 1 kg 'CPKO Biodiesel, Lab scale Transesterification process', 1 kg 'WGO Biodiesel, Lab scale transesterification process' and 1 kg 'WSO Biodiesel, Lab scale transesterification process';
 Method: IMPACT 2002+ V2.10 / IMPACT 2002+ / Damage assessment

Figure 4.24: Damage Assessment of Biodiesel (based on Midpoint Category)



Comparing 1 kg 'CPKO Biodiesel, Lab scale Transesterification process', 1 kg 'WGO Biodiesel, Lab scale transesterification process' and 1 kg 'WSO Biodiesel, Lab scale transesterification process';
 Method: IMPACT 2002+ V2.10 / IMPACT 2002+ / Damage assessment

Figure 4.25: Aggregated Damage Assessment of Biodiesel

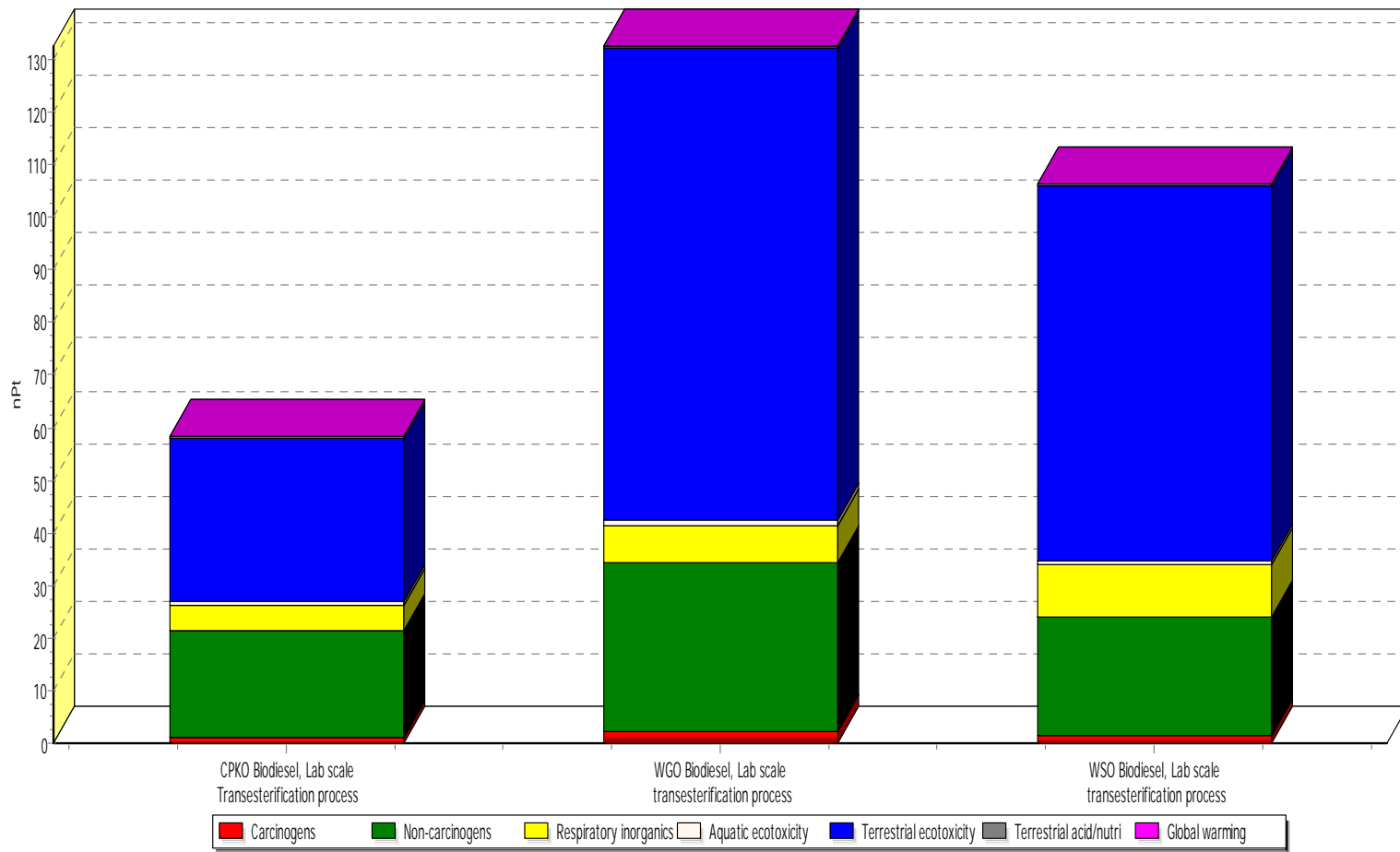
4.8.3 Single Score of WGO, WSO and CPKO Biodiesel

Single score view each product or process as a unit by making comparative analysis of the categories involved in the production of a product. By extension, it allows comparative analysis of products (WGO, WSO and CPKO biodiesel) to be easily carried out. Figure 4.26 gives the single score of biodiesels, based on midpoint categories and Figure 4.27 gives the aggregated biodiesel single score. The trend of the results of the two figures is similar with what was obtained from characterisation of substances and damage assessment of biodiesel produced.

The nano point scale used suggests how small the values of the harmful substances are. Comparing the seven midpoint categories (in each of the three kinds of biodiesel produced), the most non-environmentally friendly is terrestrial ecotoxicity (Figure 4.26). This accounts for the reason why the damage to ecosystem quality is the most pronounced one in Figure 4.27.

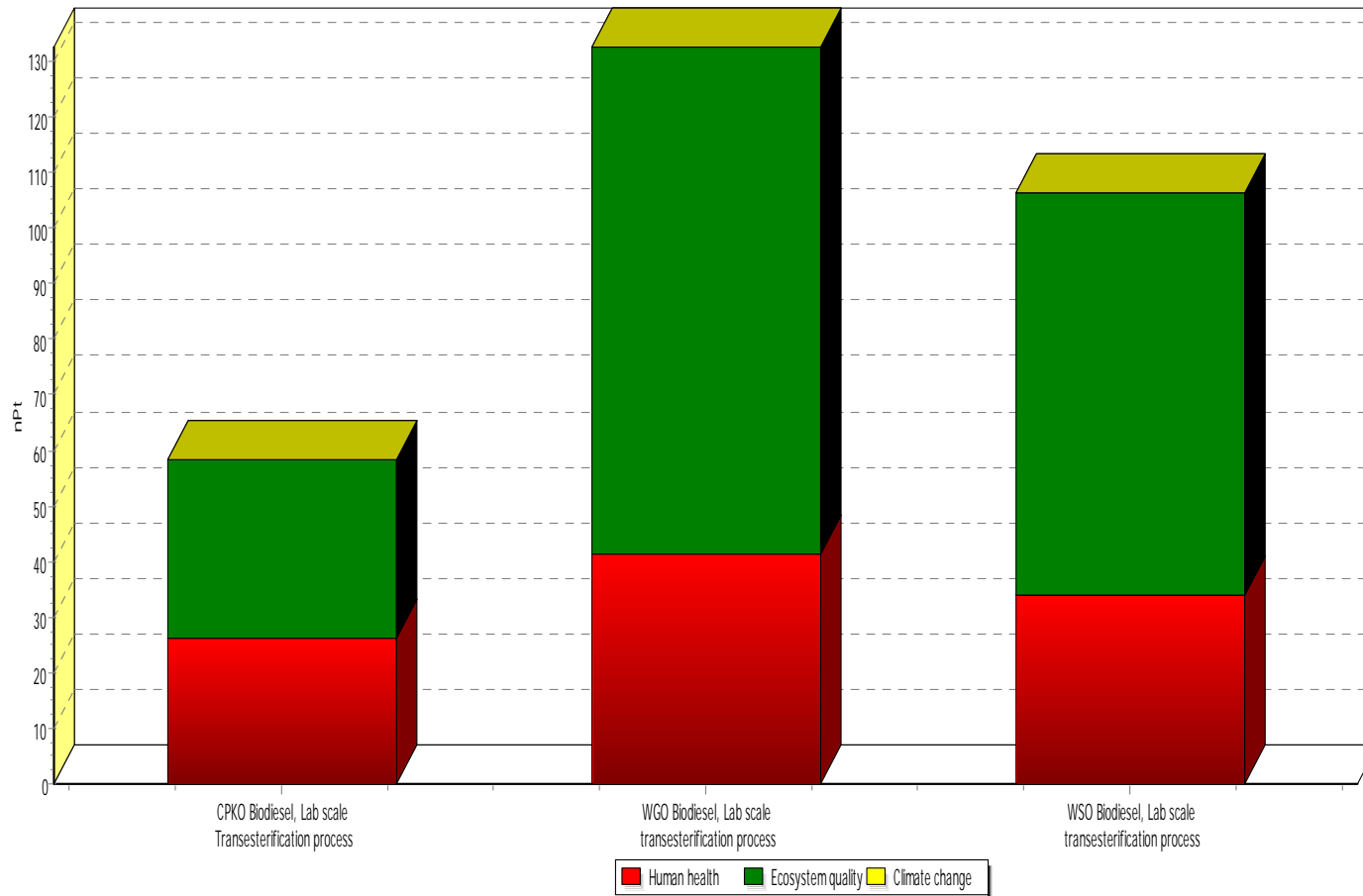
Considering the three biodiesel produced in Figure 4.26, WGO biodiesel generated highest harmful substances in each of the categories, except in respiratory inorganics and global warming categories that are dominated by WSO biodiesel (Table F5 of Appendix F), CPKO biodiesel generated the least harmful substances in each category thereby has the least potential damage to human health, ecosystem quality and climate change.

In Figure 4.27, the potential damage to ecosystem quality was the highest, for each of the biodiesels, followed by damage to human health and damage to climate stability is the least.



Comparing 1 kg 'CPKO Biodiesel, Lab scale Transesterification process', 1 kg 'WGO Biodiesel, Lab scale transesterification process' and 1 kg 'WSO Biodiesel, Lab scale transesterification process';
 Method: IMPACT 2002+ V2.10 / IMPACT 2002+ / Single score

Figure 4.26: Single Score of CPKO, WGO and WSO Biodiesel (based on Mid-point Categories)



Comparing 1 kg 'CPKO Biodiesel, Lab scale Transesterification process', 1 kg 'WGO Biodiesel, Lab scale transesterification process' and 1 kg 'WSO Biodiesel, Lab scale transesterification process';
 Method: IMPACT 2002+ V2.10 / IMPACT 2002+ / Single score

Figure 2.7: Aggregated Single Score of CPKO, WGO and WSO Biodiesel

CHAPTER FIVE

DISCUSSION OF RESULTS

5.0 Properties of the Waste Oils

Properties of the three forms of oils used in this research work are found on Table 4.1. Analysis on raw waste oils showed that CPKO had the least acid value (1.106 mg KOH/g) and lowest water content value, while WSO had highest value of free fatty acid present and with highest water content (0.67 %). These revealed the level of usage of the vegetable oils: level of free fatty acid increases with the number of frying time (Sunisa *et. al.*, 2011). Also, the higher value of viscosity of CPKO (36.72 mm²/s) accounted for the reason why cetane number of CPKO biodiesel was higher than any of the other two form of biodiesel produced. Flash point of 243 °C of WGO considered made it safer to any one of the other two forms of oils in very hot conditions. Some of these oil properties are likely indicators of the properties of biodiesel produced from the oils.

5.1 Waste Oils as Raw Materials for Biodiesel Production

In the transformation of virgin oils to waste oils by their use in harsh conditions or poor storage conditions; results in certain undesirable characteristics of the oils. These include increase in the FFA, peroxide value and change in density and viscosity of the oils (Edward, 2010).

Of these changes, it is the increase in the FFA that has the most limiting effect on the use of waste oil as a raw material for biodiesel production (Cvengros, 2004). High FFA oils result in the consumption of a portion of the oil to form soap instead of biodiesel during trans-esterification

reaction (Figure 2.9). Since the FFA result from the decomposition of the triglyceride portion of the oil, it follows that the triglyceride content of waste oil is lower. According to Ali and Tay (2013), if the FFA content of the oil is higher than 2.0 mg KOH/g a two-step instead of a single step procedure is recommended for the production of biodiesel from such oils. It is thus necessary to determine these characteristics of waste oil in order to engage the appropriate number of steps for biodiesel production.

Table 4.1 indicates the properties of the raw WGO, WSO and CPKO used. Although the oils were of different sources, they remained in the relative good state as evidenced by the low FFA content. Since the FFA content of the raw oils were less than 2.0 mg KOH/g, the single stage production process was adopted and pretreatment step carried out on the raw oils further reduced FFA of the oils. It was also necessary to establish the molecular weights of the raw oils (WGO, WSO and CPKO) used since they were required to determine the stoichiometric quantities of the other reactant (methanol) in the trans-esterification reaction. The results of the analysis and calculation of the molecular weights of WGO, WSO and CPKO are as shown in [section 4.2](#). WGO had molecular weight of 885.4251 g/mol, WSO had molecular weight of 842.4501 g/mol while the molecular weight of CPKO was 840.3933 g/mol. Although the fatty acid compositions of various oils depend on certain factors such as type and origin; the fatty acid components of each of the three oils in the present study are the major fatty acids peculiar to their respective plant sources (Issariyakul, 2011; Leung *et. al.*, 2010; Myint, 2007).

5.2 WGO, WSO and CPKO Biodiesel Yields

5.2.1 Comparison of Biodiesel Yields from KOH and NaOH catalysed Trans-esterifications

The results of the experiments show that trans-esterifications of the waste oils using KOH as catalyst produced higher yields compared with those obtained from NaOH catalysed trans-esterifications (Figures 4.2 – 4.4). With KOH as catalyst, the forward reaction of trans-esterification process was faster, resulting in higher percentage conversion under similar reaction conditions.

KOH is more chemically active than NaOH. The atomic radius of potassium is greater than that of sodium, since the single valence electron that exists in the former is located farther from the nucleus than that for sodium hence less energy is required to excite the valence electron in potassium than in sodium (Chen *et. al.*, 2007a).

Table 4.9 and Table F1 (Appendix F) show that the materials input required for the production of any given volume of biodiesel is higher while using NaOH catalyst when compared to the materials required if KOH catalyst is used during trans-esterification process. The implication of this is that to produce biodiesel of same capacity, KOH catalysed trans-esterification process will require lesser quantities of materials and reduced equipment sizes resulting in lower production cost.

Cumulative results of the biodiesel yield showed that WGO generated higher yield, followed by WSO and then CPKO. The results further showed that KOH catalysed trans-esterification process produced higher biodiesel yields when compared to yields from NaOH catalysed trans-esterification process (Tables A1, A2 and A3 of Appendix A). These findings support earlier

reports that KOH is more suitable for trans-esterification process (based on yield), especially on the industrial level of application as reported by Zlatica and Biljana, 2009; Drapcho *et. al.*, 2008.

WGO with higher number of double bonds and higher percentage of unsaturated fatty acids (90.63 % unsaturated fatty acids) yielded higher biodiesel. Gerhard (2005) justified this in his report that the higher the number of double bonds and level of unsaturated fatty acids, the more reactive the fatty acids (triglyceride components). Compounds with increasing number of double bonds are more chemically unstable than compounds with less double bonds; therefore lesser energy is required for such substance to undergo chemical reactions.

5.2.2 Effects of Methanol/Oil mole ratio, Catalyst Concentration, Reaction Temperature

And Reaction Time on Biodiesel Yields

The effects of operating parameters (methanol/oil mole ratio, catalyst concentration, reaction temperature and reaction time) on the yield of biodiesel for each of WGO, WSO and CPKO were studied by using Box-Behnken fractional factorial design of experiments. The results were analysed using Minitab 16 software. With the aid of both the surface and contour plots the maximum WGO and CPKO biodiesel yields obtained from the different levels of methanol/oil mole ratio, catalyst concentration, reaction temperature and reaction time are as shown in Figures 4.4 – 4.21. The surface plots of WSO biodiesel yields obtained are shown in Appendix C. The results are analysed in terms of the percentage yield of biodiesel. As reported by earlier researchers (Mahajan *et. al.*, 2007; Meher *et. al.*, 2006b; Freedman, 1986), percentage biodiesel yield is calculated thus

$$\text{Yield (\%)} = \frac{W}{W} \frac{a b}{a a u} \frac{p}{u} \times 100 \quad \text{Eq. 5.1}$$

Figures 4.4 and 4.5 are the surface and contour plots of CPKO biodiesel yields obtained using KOH and NaOH as catalysts, at a fixed reaction temperature of 55⁰C and a reaction time of 70 minutes. The maximum CPKO biodiesel yields of 93% using KOH as catalyst (Figure 4.4) and 90% using NaOH as catalyst (Figure 4.5) were obtained at 9 mole ratio of methanol/oil and catalyst concentration of 1.2 w/w oil.

Figures 4.4 and 4.5 show that as the catalyst concentration and methanol/oil mole ratio were increased up to 1.2 w/w oil and 9 mole ratio respectively, CPKO biodiesel yields increased. Beyond this point, the yield began to decrease. The higher biodiesel yields were obtained at 93 and 90 % at 1.2 w/w catalyst concentrations (KOH and NaOH respectively) and 9 mole ratio of methanol/oil. This is the most suitable condition for both KOH and NaOH as catalysts for trans-esterification reaction to proceed in forward reaction.

In Figures 4.6 and 4.7, CPKO biodiesel production was favoured by increase in the reaction temperature and the methanol/oil mole ratio up to 10 mole ratio. The maximum biodiesel yield was obtained at (9 – 10) w/w methanol/oil mole ratio and (60 – 62) ⁰C reaction temperature (which is very close to methanol's boiling point of 65 ⁰C). At this stage, the biodiesel yield of KOH catalysed CPKO trans-esterification reaction was 96% while biodiesel yield of NaOH catalysed CPKO trans-esterification reaction was 92% (1.2 w/w catalyst concentration and 70 minutes reaction time were constant).

From Figures 4.8 and 4.9, the increase in reaction time up to 10.5 methanol/oil mole ratio favoured high CPKO biodiesel yield, at constant 1.2w/w catalyst concentration and 55⁰C reaction temperature. 8.5 - 10.5 mole ratio of methanol/oil and 60 – 90 minutes of reaction time

(for KOH catalyzed reaction) favoured maximum biodiesel yields of 94 %. Similarly, 8.5 - 10.5 mole ratio of methanol/oil and 52 – 90 minutes (for NaOH catalyzed reaction) produced maximum biodiesel yields of 90.

At constant methanol/oil mole ratio of 9 and 70 minutes reaction time, the catalyst concentration of 1.2 w/w oil and 62 °C reaction temperature produced 96 and 93 % biodiesel yield from KOH and NaOH catalysed reactions respectively (Figure 4.10 and 4.11). Increase in catalyst concentration up to 1.2 w/w oil increased CPKO biodiesel yield.

From Figure 4.12 and Figure 4.13, at constant 9 mole methanol/oil ratio and 55°C reaction temperature, increase in reaction time and catalyst concentration of 1.0 – 1.4 w/w oil catalyst concentration resulted in maximum CPKO biodiesel yield of 91 and 94 % for KOH and NaOH catalysed trans-esterification reactions respectively. Beyond this condition, backward reaction resulting into production of triglycerides and methanol occurred.

In Figure 4.14 and Figure 4.15, surface and contour plots showed that the higher the reaction time and temperature, the higher the biodiesel yield. KOH catalysed CPKO trans-esterification reaction generated maximum biodiesel yield of 97 % while NaOH catalysed CPKO trans-esterification reaction generated maximum biodiesel yield of 94 %.

Figure 4.16a illustrates the effect of catalyst and methanol/oil mole ratio at fixed reaction temperature and reaction time on WGO biodiesel yields. The results show significant influence of these two parameters. For a fixed methanol/oil mole ratio, increasing KOH catalyst concentration to 1.2 w/w oil increases biodiesel yield. Further increase in KOH concentration to

1.7 w/w oil resulted in a decrease in WGO biodiesel yield. Similar inference can be made for the effect of methanol/oil mole ratio at constant catalyst concentration. Increase methanol/oil mole ratio from 6 to 9 increased biodiesel yield. Further increase in mole ratio of 12 resulted in a decrease. The biodiesel yield for a given catalyst concentration thus depends on methanol/oil mole ratio – a clear case of interaction between the catalyst concentration and methanol/oil mole ratio. Hence, maximum biodiesel yield was recorded at methanol/oil mole ratio of 9 and KOH catalyst concentration of 1.2 w/w oil.

A similar trend was observed for NaOH as catalyst in Figure 4.16b. The major difference in this pattern was in the magnitude of the biodiesel yield. In general, slightly lower WGO biodiesel yield were recorded with the use of NaOH than with KOH as catalyst.

Figure 4.17 shows the effect of the reaction temperature and methanol/oil mole ratio at fixed catalyst concentration and reaction time. Figure 4.17a clearly shows increased biodiesel yield with increase in reaction temperature and methanol/oil mole ratio, with KOH catalyst. The extent of increase in biodiesel yield is more for reaction temperature than for methanol/oil mole ratio in the range studied. A similar variation is seen in Figure 4.17b when the catalyst used was NaOH.

Figure 4.18a shows the effect of reaction time and reaction temperature at fixed methanol/oil mole ratio and catalyst concentration, with KOH as catalyst and Figure 4.18b with NaOH catalyst. In both cases, there was increase in biodiesel yield with increasing reaction time at higher reaction temperature than at lower reaction temperature.

Figure 4.19 shows the interaction between methanol/oil mole ratio and reaction time. While the effects of methanol/oil mole ratio on biodiesel yields are similar with either KOH or NaOH as catalyst, slightly lower biodiesel yields were obtained when NaOH was used as catalyst.

Figure 4.20a and Figure 4.20b show decreased biodiesel yield with increasing catalyst concentration and increasing reaction temperature when either KOH or NaOH as the catalyst. The results also show a clear interaction between catalyst concentration and reaction temperature.

Although the effects of catalyst concentration on biodiesel yield are similar for either KOH or NaOH as catalyst, maximum biodiesel yield values were observed in Figure 4.21 while in Figure 4.20 the biodiesel yield values decreased monotonically with increasing catalyst concentration.

In summary, it can be said that all four parameters (methanol/oil mole ratio, catalyst concentration, reaction temperature and reaction time) affected the biodiesel yields and there were obvious cases of interaction between the factors. It is therefore important that the conditions of optimum biodiesel yield should be established. This is discussed in detail in the section 5.2.3.

The effect of each of the four parameters can be explained largely in terms of the reversible nature of the reaction between the oils and the alcohol to form biodiesel. As reported by Issariyakul *et. al.* (2007), increase in biodiesel yield with increase in reaction temperature is consistent with Arrhenius equation which indicates increase in rate of reaction with increase in temperature (equation 2.8).

Another factor that influenced the yield is the mole ratio of the reactants. The use of high methanol/oil (higher than 10) mole ratio, did not favour biodiesel production; rather it pushed the reversible reaction to the right side of the reaction equation. Rashid and Anwar (2008) however reported that when too much alcohol is used in trans-esterification, the polarity of the reaction

mixture is increased, thus increasing the solubility of glycerol and promotes the reverse reaction between glycerol and biodiesel, thereby reducing biodiesel yield.

Increase in catalyst concentration increases biodiesel yield up to a certain level of 1.2 w/w oil, it is not clear why increase in catalyst concentration beyond this level results in decrease in biodiesel yield.

5.2.3 Biodiesel Yield Optimal Conditions

Table 5.1: Optimal Conditions for Biodiesel Production

Source of Biodiesel	Methanol/Oil [mole ratio]	Catalyst Conc. [w/w Oil]	Reaction Temperature[⁰ C]	Reaction Time [minutes]	Optimum Yield,%	Optimal Desirability*
CPKO (KOH catalyst)	9.51	1.24	62	80	97.7	1.0000
CPKO (NaOH catalyst)	9.57	1.10	62	85	96.4	0.9637
WGO (KOH catalyst)	10.67	0.86	60	71	98.5	1.0000
WGO (NaOH catalyst)	9.94	0.70	60	72	95.2	0.9098
WSO (KOH catalyst)	9.76	1.04	60	70	93.5	0.8256
WSO (NaOH catalyst)	9.00	0.70	61	70	95.8	1.0000

*Maximum value of Optimal desirability is 1.0

Optimal desirability shows the accuracy of the predicted optimal conditions, and the values for all the predicted optimal conditions are very high (approximately 1 almost in all cases). In Table 5.1, the optimum methanol/oil mole ratio range of (9.0 – 10.7) fall within the range reported for waste oils by several researchers (Ali and Tay, 2013; Leung *et. al.*, 2010; Zhang *et. al.*, 2003). For virgin vegetable oil, the optimal mole ratio of methanol/oil in alkali-catalysed transesterification investigations is in the range of 6:1, but waste oils (with high FFA) have optimum values higher than 6:1 mole ratio of methanol/oil (Ali and Tay, 2013; Leung *et. al.*, 2010; Zhang *et. al.*, 2003).

This implies that methanol/oil ratio of more than 6 is required to achieve high biodiesel yields and to prevent catalyst consumption by the trace of FFA that may be present (Zahira *et. al.*, 2013). KOH catalysed WGO trans-esterification reactions, with higher percentage of double bonds and higher biodiesel yield, had higher optimum methanol/oil mole ratio of 10.67.

The optimum reaction temperatures were similar in all cases (range of 60 – 62⁰C). The conversion of triglycerides to biodiesel approaches peak values at these temperatures which are very close to the boiling point of methanol (65⁰C). Higher reaction temperature favoured higher biodiesel yield, provided the boiling point of methanol was not exceeded (Lee and Shah, 2013). According to Ali and Tay (2013), higher temperature leads to a higher energy state of the reacting molecules which can be translated into faster molecular vibration and movement, thus the reacting molecules have more chance to collide with one another resulting into higher yield.

The high reaction temperatures also decrease the viscosity of oil and result in an increased reaction rate (Leung *et. al.*, 2010). But at temperatures above the optimum value, biodiesel yield decreased due to the vapourisation of the methanol (Guo and Leung, 2006).

Optimum reaction time ranged between 70 – 85 minutes. The higher the number of double bonds the more reactive the parent oil and the shorter the reaction time. The optimum reaction time of 70 minutes for WSO biodiesel production was the least and CPKO biodiesel recorded longer reaction time (80 - 85 minutes). Increasing the reaction time beyond the optimum value results in backward reaction between biodiesel and glycerol (products) leading to reduction in the biodiesel yield (Eevera *et. al.*, 2009).

The higher the number of double bonds, the more reactive the parent oil and the lesser the amount of catalyst concentration required for reaction. WGO biodiesel (with KOH catalyst) generated higher optimum yield of 98.5 %, at catalyst concentration of 0.86 w/w Oil and optimal desirability of 1. Optimum CPKO biodiesel yield required higher values of catalyst concentrations of 1.24 and 1.10 w/w oil for KOH and NaOH catalysed reactions respectively.

5.2.4 Regression Analysis of Biodiesel Yield Models

5.2.4.1 ANOVA using p and F values

The ANOVA for the six regression models of biodiesel yields obtained indicated that the models fit very well in describing the relationship between the predictor (biodiesel yields) and the factors. This is evident from the calculated large F values and very low p values ($p < 0.05$). Large F value implies that most of the variations in the responses can be explained by the regression model equations (Appendix D, Table D1 – D6). The significance of each term of the models is justified by the p values of < 0.05 for most of the main effects, two-factor interactions and squared terms. Each model recorded R^2 and R^2 (adjusted) values. These values ascertain the

fitness of the models for they describe the extent at which responses are reflected in each model (Equation 4.2 – 4.7).

Equations 4.2 and 4.3 indicate that the effects of methanol/oil mole ratio and also the interaction of the four main factors, in WGO biodiesel yield are very significant. In addition, NaOH catalysed WGO biodiesel production reveals that catalyst concentration and reaction temperature have significant effects in biodiesel yield model (Tables D1 – D2 of Appendix D).

The methanol/oil mole ratio and reaction time showed significant effects in WSO biodiesel yield model, with KOH as catalyst (Equation 4.4). The catalyst concentration, reaction temperature and reaction time have significant effects in NaOH catalysed WSO biodiesel yield model (Equation 4.5). The effects of the interactions of the four factors are significant in WSO biodiesel yield as reflected by the low p values and high F values of the coefficients of the model equation (Tables D3 – D4).

The omission of reaction time in Equations 4.6 and 4.7 shows that the effects of reaction time on CPKO biodiesel yield was not as significant as the effects of the other three main factors (methanol/Oil mole ratio, catalyst concentration and reaction temperature). Also, low p values and high F values indicate that the interaction of methanol/oil, catalyst concentration, reaction temperature and reaction time were significant (Tables D5 – D6 of Appendix D).

5.2.4.2 Accuracy of Regression Predicted Models of Biodiesel Yields

Accuracy of the regression models in predicting the experimental responses can be seen from the deviations between the predictions of the biodiesel yield models and the experimental data. The details of the calculations of the deviations are in Appendix D. Table 4.5 gives the summary of these results. The results show generally good predictions of the experimental responses. The

maximum percentage average deviation of any of the models is 0.70 %. Most of the six predicted models had lower percentage average deviations. The range of deviation is also consistent with the average deviation when it is considered that each model predicted 27 experimental data responses. The low level of the deviations is consistent with the very high R^2 of each of the equations as seen in Table 4.5.

5.3 Validation of the Predicted Model for Biodiesel Cetane Number

Validation of the predicted model for biodiesel cetane number was carried out by comparing the results obtained from the predicted model with several experimental results employed by Ramirez-Verdusco *et. al.* (2012) in their models (Table 4.7).

Interestingly, percentage average absolute deviation (% AAD) of cetane number for both the predicted model and Ramirez-Verdusco *et. al.* (2012) model using the reported experimental cetane number generated the same result of 3.28 % (Table 4.8).

Comparatively, the higher pearson correlation value and lower p-value of the predicted model (when compared to Ramirez-Verdusco model) favours the predicted model as a more suitable model. The statistical analysis yielded pearson correlation of 0.824 between the cetane number of the predicted model and experimental cetane number and p-value of 0.086. While a value of 0.812 pearson correlation between the cetane number of Ramirez-Verdusco *et. al.* (2012) model and cetane number of experimental results and p value of 0.095 were obtained.

Using the predicted model, the values of the calculated cetane number of biodiesels produced and the values of the calculated CN of the five biodiesels reported by Ramirez-Verdusco *et. al.*

(2012) fall within the ASTM cetane number specification of 49 – 61 (Ali and Tay, 2013; Magin *et. al.*, 2010). Similarly, the predicted model shows that biodiesel cetane number is directly proportional to viscosity and inversely proportional to density, as reported by several researchers (Evangelos, 2013; Güzel, 2012; Magin *et. al.*, 2010; Zatica and Biljana, 2009).

These results reveal the high level of accuracy of the predicted model and also confirm the new approach as a plausible method for the determination of biodiesel cetane number. Since the new approach utilises key indices like density and viscosity, it can be proposed as a reliable method of CN determination for biodiesel.

5.4 Life Cycle Impact Assessment of WGO, WSO and CPKO Biodiesels

IMPACT 2002+ methodology was used for the assessment of the impact of substances released during the production of biodiesel from WGO, WSO and CPKO (Figure 3.14). Under this methodology, the impact categories are grouped into three:

- Damage to human health, categorised as carcinogens, non- carcinogens and respiratory inorganics
- Damage to ecosystem quality, categorised as aquatic ecotoxicity, terrestrial ecotoxicity and terrestrial acidification and nitrification
- Damage to climate change, categorised as global warming.

5.4.1 Classification and Characterisation of Substances from Biodiesel production

Characterisation is a systematic approach of classifying substances involved in the LCA of biodiesel into midpoint categories. It involves computing the value of each substance in a category in relation to the key substance of the category (Olivier *et. al.*, 2003). Characterisation

results, obtained from the product of each life cycle inventory data and corresponding characterisation factor (Equation 2.9), using SIMAPRO 7.3.3 software are as shown in seven categories in Figure 4.23 and Table F3 of Appendix F. In a category, the values of a chemical substance released from the three kinds of biodiesel produced can be compared.

5.4.1.1. Carcinogens from Biodiesel Production

Carcinogens are cancer causing agents. Carcinogenic substances are expressed in 1 kg C₂H₃Cl equivalent. Analysis showed that Arsenic, Cadmium and Chromium VI are the key carcinogens that are likely to be released into the air from the biodiesel produced (Table F3 of Appendix F). Possible quantity of Chromium VI released into the air as a result of the usage of biodiesel produced from CPKO, WGO and WSO is 3.65×10^{-7} kg, 8.52×10^{-7} kg and 4.87×10^{-7} kg respectively. In effect, CPKO biodiesel released 55 % carcinogens; WGO biodiesel released 100 % carcinogens while WSO biodiesel released 60 % carcinogens (Figure 4.23). This projects WGO biodiesel as the biodiesel with the most health-damaging potential (in terms of cancer challenge) and the CPKO biodiesel as the least.

Comparison of the LCA of biodiesels obtained from waste cooking oils and virgin oil seeds show considerable difference in the level of carcinogens recorded for waste and virgin oil-based biodiesels. Requena *et. al.* (2010) reported that biodiesel from waste cooking oils generated 30% carcinogens of the total carcinogens obtained from the cultivated oil-bearing seeds used for biodiesel production. That is, the use of waste cooking oils for biodiesel production poses lesser health challenges.

5.4.1.2. Non-carcinogens from Biodiesel Production

Non carcinogens are substances that impose serious health problems to man in various degrees, ranging from body pain to even death, but are not cancer-causing. Non carcinogens identified include Aluminium, Beryllium, Cobalt, Chromium III, Copper, Lead, Nickel and Zinc (Table F3 of Appendix F). They are also expressed in 1 kg C₂H₃Cl equivalent.

The quantity of Aluminium potentially released into the air (as non-carcinogen) from the usage of biodiesels is 1.02×10^{-8} kg, 7.78×10^{-8} kg and 7.29×10^{-9} kg, from WGO biodiesel, WSO biodiesel and CPKO biodiesel respectively. Aluminium released from biodiesel washing water is 2.26×10^{-8} kg of WGO biodiesel, 3.08×10^{-8} kg of WSO biodiesel and 1.85×10^{-8} kg of CPKO biodiesel.

Beryllium potentially released into the air as a result of the usage of biodiesel produced from WGO, WSO and CPKO is 3.75×10^{-5} kg, 1.25×10^{-5} kg and 2.50×10^{-5} kg respectively. Potential Cobalt released into the air is 1.70×10^{-5} kg, 2.80×10^{-5} kg and 5.48×10^{-6} kg from WGO biodiesel, WSO biodiesel and CPKO biodiesel respectively.

Considering the category, CPKO biodiesel would release the least harmful substances into the environment. Cumulatively, WGO biodiesel generated 100 % non-carcinogens, WSO biodiesel generated 70 % and CPKO biodiesel generated 60 % non-carcinogens (Figure 4.23); making WGO biodiesel the potentially most harmful biodiesel produced from the three waste oils.

5.4.1.3. Respiratory Inorganics from Biodiesel Production

Respiratory inorganics are inorganic substances that cause respiratory related problems in man. Respiratory inorganics are expressed in 1 kg PM_{2.5} equivalent. Nitrogen dioxide and sulphur

dioxide are the major respiratory inorganics identified in this category (Table F3 of Appendix F). The potential amount of nitrogen dioxide released into the air is 3.69×10^{-9} kg, 4.60×10^{-8} kg and 5.80×10^{-8} kg from CPKO biodiesel, WGO biodiesel and WSO biodiesel respectively. The potential sulphur dioxide released into the air is 1.25×10^{-9} kg, 2.65×10^{-8} kg and 4.06×10^{-8} kg from CPKO biodiesel, WGO biodiesel and WSO biodiesel respectively.

In effect, CPKO biodiesel released 45 % respiratory inorganics; WGO biodiesel released 70 % respiratory inorganics while WSO biodiesel released 100 % respiratory inorganics (Figure 4.23); making WSO biodiesel the biodiesel with the most potential to release respiratory inorganics.

5.4.1.4. Aquatic and Terrestrial Ecotoxicity Substances from Biodiesel Production

The presence of aquatic ecotoxic substances in water hampers the growth, development and existence of aquatic organisms. Aquatic ecotoxic substances are expressed in 1 kg of Tri-Ethylene Glycol equivalent in water (kg TEG water). Terrestrial ecotoxicity refers to the impacts of toxic substances on terrestrial ecosystems, such as forests and wetlands. Terrestrial ecotoxic substances are expressed in 1 kg of Tri-Ethylene Glycol equivalent in soil (kg TEG soil). The amount of Zinc released is most pronounced, both as aquatic ecotoxic substance in water and as terrestrial ecotoxic substance in soil (Table F3 of Appendix F).

Though zinc is an essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity. Such toxicity levels have been seen to occur in man at ingestion of greater than 225 mg of Zinc (Ranjan and Premananda, 2003). Excessive absorption of zinc can suppress copper and iron absorption. The free zinc ion in solution is highly toxic to bacteria, plants, invertebrates, and even vertebrate fish (Ranjan and Premananda, 2003).

Comparatively, the percentages of the aquatic terrestrial ecotoxicity substances are 80 % from CPKO biodiesel, 100% from WGO biodiesel and 85 % from WSO. In terrestrial ecotoxicity category, the percentages of the substances released are 30 % from CPKO biodiesel, 100% from WGO biodiesel and 75 % from WSO (Figure 4.23); making WGO biodiesel the potentially most lethal to the aquatic and terrestrial environment.

5.4.1.5. Terrestrial Acidification and Nutrifaction Substances from Biodiesel Production

Terrestrial acidification and nutrifaction substances are compounds when released into the environment causes acid rain. Terrestrial acidification and nutrifaction substances are expressed in 1 kg SO₂ equivalent. Sulphur dioxide and nitrogen dioxide are two substances evaluated in this category. As reported by Requena *et.al.* (2010), the amount of NO₂ generated is higher than SO₂ generated from each biodiesel production (Table F3 of Appendix F).

Acid rain causes acidification of lakes and streams and contributes to the damage of trees at high elevations and certain forest soils. In addition, acid rain accelerates the decay of buildings, paints, statues and sculptures (US EPA, 2012b)

The results show that the terrestrial acidification and nutrifaction substances released are 55 % from CPKO biodiesel, 75 % from WGO biodiesel and 100 % from WSO biodiesel (Figure 4.23).

5.4.1.6. Global Warming Substance from Biodiesel Production

Global warming refers to increase in average temperature of the air and sea at Earth's surface. Substances contributing to global warming are called global warming substances or greenhouse gases. SIMAPRO expresses global warming substances in 1 kg CO₂ equivalent. Carbon dioxide

is the only greenhouse gas analysed in this category. Potential CO₂ released from the use of the three biodiesels are 1.18×10^{-6} kg by CPKO biodiesel, 1.32×10^{-6} kg by WGO biodiesel and 1.54×10^{-8} kg by WSO biodiesel. Comparatively, CO₂ released is 75 % from CPKO biodiesel, 85 % from WGO biodiesel and 100 % from WSO biodiesel (Figure 4.23).

In general, considering each category of carcinogens, non-carcinogens, aquatic ecotoxicity and terrestrial ecotoxicity; WGO biodiesel released more harmful substances than any of the other biodiesels. WSO biodiesel generated more in global warming, terrestrial acidification/nitrification and respiratory inorganics categories (Figure 4.23).

The types and amount of harmful substances released is a function of the level of usage of the parent oil during cooking (frying); the lesser the level of usage of parent oil, the lower the amount of FFA in the oil and the lesser the amount of non- environmentally friendly substances released (Sunisa *et. al.*, 2011). The level of an oil usage is determined by its duration and extent of its exposure to water, heat, food, micro-organisms and oxygen during cooking.

CPKO possessed properties that made it preferred as the most environmentally friendly raw oil. Pre-transesterification analysis of the raw waste oils showed CPKO with the least acid value (1.106 mg KOH/g) and lower water content value of 0.57 % (Table 4.6).

5.4.2 Potential Damage Assessment of Biodiesel produced from the Three Oils

A second important aspect of LCA is the potential damage assessment of the biodiesel production. The accurate prediction of such damages will help create a profile of the attributes of various organic materials as feedstocks for biodiesel production; it will also provide a reference materials both for localized (small) as well as large scale production of biodiesel while prioritising, environmental issues.

5.4.2.1. Damage to Human Health

Potential non-environmentally friendly substances (with direct impacts on human health) released into the atmospheric air are more than that released into the environment through biodiesel washing water (Table F4 of Appendix F). These substances are expressed in Disability Adjusted Life Year (DALY). According to WHO (2014), one DALY is one year lost due to ill-health, disability or early death.

The cumulative effects of carcinogens, non-carcinogens and respiratory inorganics on human health amount to the damages to human health. Cadmium, nitrogen dioxide and zinc have the most pronounced impacts on human health (Table F4 of Appendix F). Potential impacts of some of the substances released to the environment are discussed in Section 5.4.4.

Figure 4.25 shows that WGO biodiesel pose more potential damage on human health with 100 % potential non environmentally friendly emissions than 60 % estimated for CPKO biodiesel and 80 % for WSO biodiesel.

5.4.2.2. Damage to Ecosystem Quality

Damage to ecosystem quality refers to the degradation in quality of water, soil and air, which may impose varied degrees of threat to species found in the ecosystem. Substances released are expressed in PDF*m²*yr (PDF = Potentially Disappeared Fraction of species).

Considering ecosystem quality in Figure 4.25, WGO biodiesel showed greater potential damages with 100 % emission, WSO biodiesel with 75 % emission and CPKO biodiesel with 30 % non-environmentally friendly emissions.

5.4.2.3. *Damage to Climate Stability*

Climate change is due to global warming. Global warming, as a phenomenon, results from the release of greenhouse gases (GHGs) into the atmosphere among other factors and GHGs resilient permanence in the atmosphere leads to the entrapment of heat on the earth's surface. The most significant examples of GHGs are CO₂, NO₂, CH₄, H₂O and fluorinated compounds (www.epa.gov). The Global Warming Potential (GWP) measures how much a mass of GHG (in CO₂ equivalent) can contribute to climate change.

It is important to note that biodiesel production contributes to the reduction of GHGs emissions, for CO₂ utilised during the photosynthesis of oil-bearing of plants is far greater than CO₂ released into the atmosphere due to biodiesel production and/or utilization (Almeida, 2009).

In the present analysis, the amount of CO₂ released from CPKO, WGO and WSO biodiesel are expressed in kilogram (Table F4 of Appendix F) in percentage (Figure 4.25). Potentially, WSO biodiesel contributes more to climate change with 100 % CO₂ release during use; followed by WGO biodiesel with 80 % and CPKO biodiesel with 70 % emission of CO₂.

In each of the categories (Figures 4.23 - 4.25), CPKO biodiesel utilisation generated the least potential damage to man and the environment. This is due to higher level of saturated carbon chains of the oil. However, carbon atoms in WGO and WSO biodiesel are mostly unsaturated (Table 4.1 – 4.3). Due to more reactive nature of unsaturated carbons, compounds such as phospholipid are formed from WGO or WSO and materials in contact with during cooking (frying). These compounds pose a threat to the sanity of the environment when eventually released into the environment through biodiesel utilisation and/or biodiesel washing water (Choe and Min, 2007; Chung *et. al.*, 2004).

In addition, the repeated usage of WGO and WSO for cooking (frying) at high temperatures creates higher levels of harmful substances released by WGO and WSO biodiesels. At such high temperatures, weaker double bonds of fatty acid units of WSO and WGO are easily broken, resulting in the formation of environmentally sensitive substances (Choe and Min, 2007).

From the present study, proposed order of preference for diesel engine usage of the generated biodiesels is: CPKO biodiesel, WSO biodiesel and WGO biodiesel (being the least preferred). These results also relates to the cetane numbers (CN) of the three biodiesels (Table 3.5), with a CN of 51.7 – 53.2 CPKO biodiesel is preferred over WSO biodiesel (CN: 50.6 – 52.8) and WGO biodiesel (CN: 49.4 – 51.0). The higher the CN, the better the performance of the biodiesel as diesel engine oil and the lesser the release of non-environmentally friendly substances into the environment (Güzel, 2012).

5.4.3 Potential Impact Valuation using Single Score

Single score view each product or process as a unit by the comparative analysis of the categories involved in the production of a product. By extension, it allows comparative analysis of CPKO, WGO and WSO biodiesels.

From Figure 4.26 and Figure 4.27, the results show that the potential damage effects are more pronounced on ecosystem quality (especially terrestrial ecotoxicity) followed by human health (in the form of non-carcinogens and respiratory inorganics released) with the least effect on climate change. This trend agrees with the findings of Silalertruksa and Gheewala (2012). Similarly, Figure 4.27 shows that the order of preference of the biodiesel produced (based on the

impacts of the substances released), is CPKO biodiesel, WSO biodiesel and WGO biodiesel; with CPKO biodiesel being most preferred.

5.4.4 Potential Impacts of some of the Substances released to the Environment

Most of the trace elements (except Lead) responsible for damage to environment are required by organisms (plants, animals and microorganisms) for growth and development, as well as for ecosystem functioning, provided the quantities limits are not exceeded. However, when the tolerant limits of these elements of compounds are exceeded, they impose damages of varied degrees depending on the concentration, duration and frequency of exposure (ASTDR, 2012; Walton, 2009).

According to ASTDR (2012), excess of Chromium beyond the maximum level of 0.1 mg/L for total chromium in drinking water could result in stomach health challenges (such as ulcer and anemia), respiratory tract challenges (such as irritation of the lining of the nose, runny nose, asthma, cough, shortness of breath) and a long time effect of lung cancer in animals and humans (Shanker *et. al.*, 2005). Effects of Chromium on plant growth and development include alterations in the germination process as well as in the growth of roots, stems and leaves (Sabine and Wendy, 2009; Shanker *et. al.*, 2005).

The effects of excess Aluminium in animal and humans include; damage to the central nervous system and loss of memory in man, damage to tree roots located underwater, decline in number of fish and amphibians due to reactions of aluminum ions with proteins in the gills of fish and the embryo of frogs in acidified lakes (Lenntech, 2012).

Arsenic is carcinogenic and toxic if the intake dose (in form of arsenic oxide) exceeds 100 mg, it causes alteration of the genetic materials of fish as well as poor growth in plant (Muradov and Veziroglu, 2013; Sabine and Wendy, 2009).

In man, Cadmium causes stomach upset, damage to the central nervous system, the immune system, DNA damage or cancer development. Cadmium poisoning can result from animals feeding on plants from cadmium-enriched soils (Muradov and Veziroglu, 2013).

Long-term exposure to copper by humans may result in irritation of the eyes and nose, as well as headaches, stomachaches, dizziness, vomiting and diarrhea. High uptakes of copper may cause liver and kidney damage. And only a limited number of plants have a chance of survival on copper-rich soils (Lenntech, 2012).

In human, Lead causes a rise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of nervous systems, brain damage, diminished learning abilities of children and even death in animals and humans. Lead limits plant chlorophyll synthesis (Sabine and Wendy, 2009).

Nickel poisoning in animals results in respiratory failure, birth defects, asthma and chronic bronchitis, heart disorder and allergic reactions such as skin rashes. High nickel concentration on sandy soils can damage plants and high nickel concentration in surface water can diminish the growth rates of aquatic animals (Lenntech, 2012).

High concentration of Zinc in the bodies of both man and animals results in skin irritations, vomiting, anemia, damaged pancreas and disturbed protein metabolism, depending on the concentration. Only a limited number of plants can survive on Zinc-rich soils. Zinc negates the activities of micro-organisms and earthworms (Muradov and Veziroglu, 2013).

Short-term exposures to high levels of sulfur dioxide can be life-threatening. Exposure to 100 parts of sulfur dioxide per million parts of air (ppm) is considered immediately dangerous to life and health of organisms, particularly animals and humans. Being an acid gas and GHG, it causes stunted plant growths which can result into deforestation if present in high concentration both in air and water (US EPA, 1991).

Nitrogen dioxides (NO_x) promote eutrophication in coastal ecosystems, which deteriorate fish habitat and aquatic biodiversity. NO_x contribute to both the greenhouse effect and to stratospheric ozone depletion. Once released into the environment, nitrogen dioxide cascades from one negative environmental impact to another (WHRC, 2014; US EPA, 2012).

5.5 Benefits of using WGO, WSO and CPKO for Biodiesel Production

It is important to note that the benefits accrued to the use of the three waste oils for biodiesel production are far greater than the disadvantage traceable to their usage as feedstocks. The LCA of the three biodiesels produced highlights the need to carry out both preventive and corrective measures in order to minimise the release of non-environmentally friendly substances into the environment. This approach guides the choice of feedstocks for biodiesel production.

5.5.1 Reduction in Environmental Pollution

Comparatively, study by Swanson *et. al.*, (2007) justifies the use of waste cooking oils as feedstocks for biodiesel production with the least release of non-environmentally friendly substances into the environment.

The utilisation of these oils (as feedstocks at commercial level) will curb water and soil pollution problems arising from the illegal waste oil disposal into rivers and landfills. Huge quantities of waste cooking oil are generated daily throughout the world. In the United States, the Energy Information Administration estimates 100 million gallons per day (Radich, 2006). Although there are no volume estimates for waste cooking oils in Nigeria, with a rising population of about 166.21 million people (National Bureau of Statistics, 2014) and a growing fast food and eateries sector of the economy; a considerable amount of waste oils are generated annually. Recycling these huge waste cooking oils as fuel in diesel engines will reduce environmental degradation connected with the poor disposal of such waste oils (Pugazhvadivu and Jeyachandran, 2005), as well discourage prolong use due to lack of an organized disposal system by offering alternative.

It has been reported that the methyl ester processed from waste cooking oils for use in diesel engines releases lower smoke levels and higher thermal efficiencies than virgin vegetable oils (Kumar *et al.*, 2003). This encourages the use of waste oils rather than virgin oils for biodiesel production, ensuring that virgin oils with attendant high nutritional content are not sacrificed for energy production. In addition, this will not create a market hike in virgin oil price and thus compound economic hardship, or threaten food security; rather a new section of energy sector will evolve with the potential to reduce total energy cost as well as create jobs, thereby improving the economy.

The application of fertilizers is not required in the usage of waste cooking oil. This amounts to the release of less harmful substances into the environment when compared to a situation of oil-bearing seed planting and cultivation that require fertilizer applications which will end up increasing the nitrogen, phosphorus and potassium contents of such seeds. In the downstream processes that generate virgin oil, fertilizer application is discouraged hence reducing the amount

both on a primary level due to direct fertilizer application to the soil and on a secondary level due to the released of harmful N, P, K compounds from the use of the oils for energy production. Besides fertilizer production requires the use of energy which is accompanied by GHGs production.

5.5.2 No Threat to Food Security

A major critic often leveled against biofuels, particularly against large scale production of biodiesel, is that it could lead to food shortage and price increase in food commodities. However, this challenge can be overcome through research that involved the use of waste oils for the production of biodiesel, rather than virgin oils and hence possible food products with high oil content (Enweremadu and Mbarawa, 2009).

The results from the present study confirm the assertion that the use of CPKO, WGO and WSO will not threaten food security as waste oil but not virgin oil is required as feedstocks. Similarly, the use of waste oils will reduce the challenge of deforestation that arise from continuous and extensive crops cultivation, as well as reduce biodiversity loss.

5.2.3. Biodiesel Sustainability and Low Production Cost

One way to ensure the sustainability of biodiesel is to continuously utilise waste oils such as WGO, WSO and CPKO as feedstocks. A growing human population will always result in increased generation of waste cooking oils. For biodiesel to compete favourably with petroleum diesel (in terms of cost), waste cooking oils are important for low cost biodiesel production (Yang *et al.*, 2007). The low cost of production of biodiesel from waste oils and the convenience of generating such feedstocks (waste oils) from daily household and commercial activities make

biodiesel production at all societal strata even in rural areas an affordable and encourageable endeavour.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Research Conclusions

A number of useful findings and deductions is made from the biodiesel production and LCA of biodiesel obtained from WGO, WSO and CPKO. These findings include:

- i. Following GC analysis, the order of increasing molecular weight, carbon chain lengths and number of double bonds in the three oils considered in this research work is CPKO, WSO and WGO respectively.
- ii. Under the same condition, biodiesel yield obtained from the trans-esterification of oil using KOH catalyst is higher than the yield obtained from NaOH catalysed process.
- iii. Optimum conditions for biodiesel yield from KOH catalysed trans-esterification of CPKO are 9.51 methanol/oil mole ratio, 1.24 w/w oil catalyst concentration, 62⁰C reaction temperature and 80 minutes reaction time.
- iv. Optimum conditions for biodiesel yield from NaOH catalysed trans-esterification of CPKO are 9.57 methanol/oil mole ratio, 1.10 w/w oil catalyst concentration, 62⁰C reaction temperature and 85 minutes reaction time.
- v. Optimum conditions for biodiesel yield from KOH catalysed trans-esterification of WGO are 10.67 methanol/oil mole ratio, 0.86 w/w oil catalyst concentration, 60⁰C reaction temperature and 71 minutes reaction time.
- vi. Optimum conditions for biodiesel yield from NaOH catalysed trans-esterification of WGO are 9.94 methanol/oil mole ratio, 0.70 w/w oil catalyst concentration, 60⁰C reaction temperature and 72 minutes reaction time.

- vii. Optimum conditions for biodiesel yield from KOH catalysed trans-esterification of WSO are 9.76 methanol/oil mole ratio, 1.04 w/w oil catalyst concentration, 60⁰C reaction temperature and 70 minutes reaction time.
- viii. Optimum conditions for biodiesel yield from NaOH catalysed trans-esterification of WSO are 9.00 methanol/oil mole ratio, 0.70 w/w oil catalyst concentration, 61⁰C reaction temperature and 70 minutes reaction time.
- ix. Biodiesel cetane number increases with increase viscosity, decrease density and decrease number of double bonds in carbon chains of biodiesel.
- x. The order of increasing cetane number and viscosity are WGO biodiesel, WSO biodiesel and CPKO biodiesel.
- xi. LCA of the biodiesels reveals that the increasing order of potential damage to human health (based on respiratory inorganics, carcinogenic and non-carcinogenic substances released) as a result of the biodiesel or utilisation of biodiesel is CPKO biodiesel, WSO biodiesel and WGO biodiesel.
- xii. In term of potential global warming, WSO biodiesel releases higher quantity of CO₂ into the environment, followed by WGO biodiesel with CPKO biodiesel releasing the least CO₂.
- xiii. The increasing order of potential damage to ecosystem quality (based on biodiesel utilisation) is CPKO biodiesel, followed by WSO biodiesel and then WGO biodiesel.
- xiv. From the study, it can be concluded that the higher the level of carbon saturation of feedstocks the lesser the potential environmental impacts of such feedstocks. CPKO biodiesel with higher percentage of saturated carbon has greater potential to release the least non-environmentally friendly substances.

- xv. Single score of LCA of the three biodiesels showed that the increasing order of damage to both human and environment indicate that CPKO biodiesel produces the least damage, followed by WSO biodiesel and then WGO biodiesel.

6.2 Research Recommendations

- i. Further research work should be carried out on the blend of various waste vegetable oils for biodiesel production, as well as comparative study on the LCA of blended oils and virgin oils as feedstocks.
- ii. Research on the blend of alkali catalysts (KOH and NaOH) at different proportions for biodiesel production should be investigated.
- iii. LCA of biodiesel from raw materials cultivation to biodiesel utilization and energy consumption should be investigated.
- iv. Further research work should be carried out on the industrial applications of biodiesel washing water and glycerol.
- v. Comparative analysis on the use of ethanol and methanol for the trans-esterification of plant oils and LCA of biodiesel should be investigated.

6.3 Contributions to Knowledge

The thesis as presented has made specific contributions to knowledge in the following areas:

- i. Biodiesel yield obtained from the trans-esterification of oil using KOH catalyst is higher than the yield obtained from NaOH catalysed trans-esterification process, under the same

conditions. KOH is thus a preferred catalyst in the trans-esterification of vegetable oils for biodiesel production.

- ii. Optimum conditions at different temperature, methanol/oil mole ratio, catalyst concentration and reaction time have been established.
- iii. A simple model for the prediction of biodiesel cetane number has been introduced. This new approach will reduce the cost of biodiesel cetane number determination, for the conventional method involves the use of complex and costly equipment.
- iv. Analyses of life cycle assessment of biodiesel from Waste Groundnut Oil (WGO), Waste Soyabean Oil (WSO) and Crude Palm Kernel Oil (CPKO) have been achieved. This will assist greatly in decision/policy making on biodiesel in Nigeria. Quantifiable results from the LCA of the three biodiesels are a much needed baseline for future works and related applications.

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APPENDICES

APPENDIX A: Experimental Results Obtained from Trans-esterification of Oils

Table A1: Results Obtained from WGO Trans-esterification

Experimental Run	Biodiesel Yield Obtained (%)	
	[using KOH Catalyst]	[using NaOH Catalyst]
WGO/01	91.33	87.73
WGO/02	92.78	90.18
WGO/03	88.90	86.98
WGO/04	90.89	88.11
WGO/05	99.00	98.92
WGO/06	91.61	92.04
WGO/07	92.43	92.05
WGO/08	92.78	91.09
WGO/09	95.02	93.60
WGO/10	92.08	91.67
WGO/11	91.00	90.25
WGO/12	88.81	89.67
WGO/13	91.90	87.10
WGO/14	95.78	96.29
WGO/15	88.74	82.58
WGO/16	93.33	90.02
WGO/17	94.11	98.09
WGO/18	95.56	93.56
WGO/19	92.94	93.21
WGO/20	93.93	94.27
WGO/21	95.16	89.16
WGO/22	87.69	89.96
WGO/23	91.11	89.44
WGO/24	93.12	84.84
WGO/25	93.85	94.52
WGO/26	90.09	90.79
WGO/27	95.10	93.55

Table A2: Results Obtained from WSO Trans-esterification

Experimental Run	Biodiesel Yield Obtained (%)	
	[using KOH Catalyst]	[using NaOH Catalyst]
WSO/01	90.79	82.17
WSO/02	92.82	94.21
WSO/03	87.51	88.80
WSO/04	89.12	97.96
WSO/05	97.90	84.88
WSO/06	92.31	84.34
WSO/07	91.88	87.68
WSO/08	93.54	83.48
WSO/09	94.06	91.05
WSO/10	92.83	83.69
WSO/11	90.91	91.84
WSO/12	89.45	87.73
WSO/13	88.40	88.71
WSO/14	94.82	77.80
WSO/15	89.57	81.88
WSO/16	92.80	82.54
WSO/17	90.84	98.38
WSO/18	94.21	90.21
WSO/19	93.03	85.19
WSO/20	91.08	93.23
WSO/21	91.13	85.54
WSO/22	88.42	92.86
WSO/23	92.77	87.50
WSO/24	92.02	79.83
WSO/25	92.98	94.52
WSO/26	91.61	92.81
WSO/27	94.18	90.68

Table A3: Results Obtained from CPKO Trans-esterification

Experimental Run	Biodiesel Yield Obtained (%)	
	[using KOH Catalyst]	[using NaOH Catalyst]
CPKO/01	86.63	80.78
CPKO/02	89.04	85.13
CPKO/03	84.10	78.77
CPKO/04	85.43	81.09
CPKO/05	98.52	95.16
CPKO/06	93.12	90.01
CPKO/07	90.24	86.68
CPKO/08	89.62	87.14
CPKO/09	94.57	91.30
CPKO/10	91.01	88.81
CPKO/11	90.39	87.19
CPKO/12	87.22	81.98
CPKO/13	85.03	81.21
CPKO/14	95.35	90.78
CPKO/15	91.23	89.14
CPKO/16	93.07	90.05
CPKO/17	90.84	88.30
CPKO/18	94.50	91.22
CPKO/19	93.11	90.40
CPKO/20	90.33	87.80
CPKO/21	89.09	86.02
CPKO/22	86.77	81.30
CPKO/23	91.89	89.08
CPKO/24	90.03	87.91
CPKO/25	91.53	89.95
CPKO/26	90.01	86.79
CPKO/27	94.52	91.18

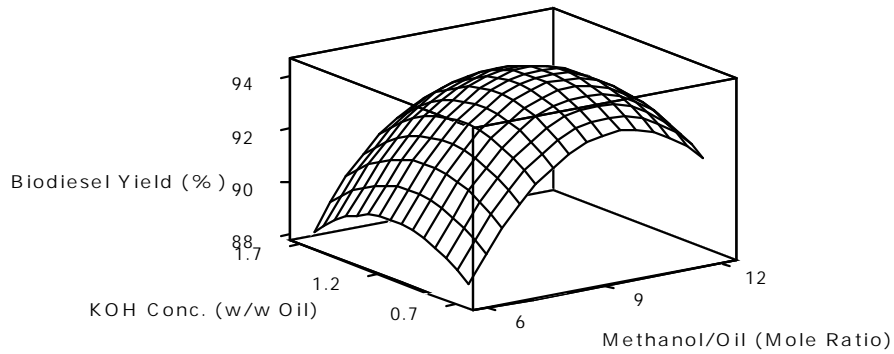
APPENDIX B: Substances Obtained from Biodiesel and Washing Water Analysis

No	Substance	Unit	CPKO Biodiesel	WGO Biodiesel	WSO Biodiesel	CPKO Washing H ₂ O	WGO Washing H ₂ O	WSO Washing H ₂ O
1	Aluminium (= 250.3 nm)	mg/L	0.015	0.021	0.016	0.009	0.011	0.015
2	Arsenic (= 329.5 nm)	mg/L	0.002	0.003	0.001	0.014	0.039	0.042
3	Beryllium	mg/L	0.009	0.011	0.007	-	-	-
4	Cadmium (= 228.8 nm)	mg/L	0.010	0.031	0.051	0.025	0.031	0.028
5	Calcium	mg/L	-	-	-	0.86	0.76	0.55
6	Carbon dioxide	mg/kg	1.18	1.32	1.54	-	-	-
7	Carbonate	µg/L	-	-	-	430	500	530
8	Chloride	mg/L	-	-	-	1.46	1.71	0.99
9	Chromium (= 357.9 nm)	mg/L	0.003	0.007	0.004	0.001	0.003	0.002
10	Cobalt	mg/L	0.002	0.004	0.003	-	-	-
11	Copper (= 324.7 nm)	µg/L	3	7	11	17	23	15
12	Hydroxide	mg/L	-	-	-	0.680	0.810	0.750
13	Lead (= 283.3 nm)	mg/L	0.020	0.013	0.014	0.004	0.006	0.010
14	Nickel (= 232.0 nm)	mg/L	0.038	0.056	0.028	0.005	0.009	0.007
15	Nitrate	mg/L	-	-	-	0.520	0.480	0.420

16	Nitrogen dioxide	µg/L	290	361	460	-	-	-
17	Phosphate	mg/L	-	-	-	0.190	0.280	0.270
18	Sulfur dioxide	mg/L	0.160	0.340	0.520	-	-	-
19	Sulphate	mg/L	-	-	-	0.640	0.650	0.700
20	Zinc (= 213.9 nm)	mg/L	0.013	0.078	0.042	0.138	0.141	0.093

APPENDIX C: WSO Biodiesel Yield Surface Plots Obtained

Hold Values	
Rxn Temp, deg. C	55
Rxn Time, min.	70



Hold Values	
Rxn Temp, deg. C	55
Rxn Time, min.	70

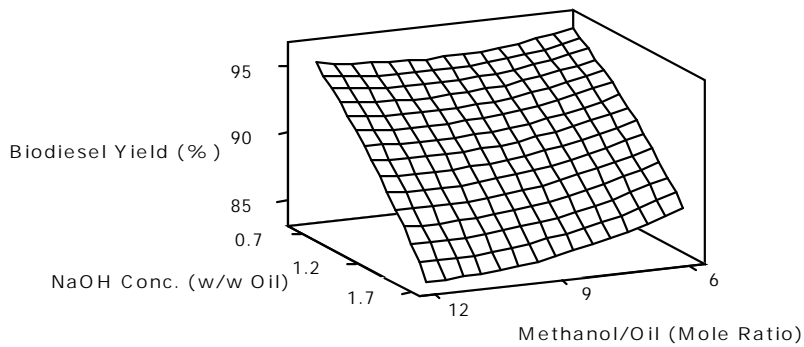
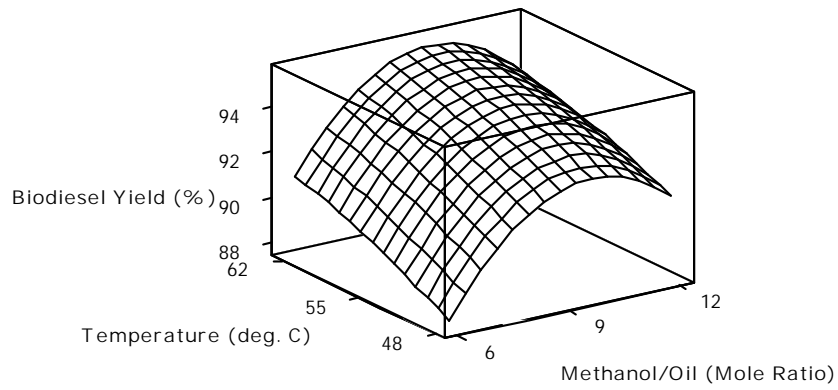


Figure C1: Surface plots of WSO Biodiesel Yield against Methanol/Oil mole ratio and Catalyst Concentration, at 55 °C temperature and 70 minutes time

a

Hold Values	
Cat. Conc, w/wOil	1.2
Rxn Time, min.	70



b

Hold Values	
Cat. Conc, w/wOil	1.2
Rxn Time, min.	70

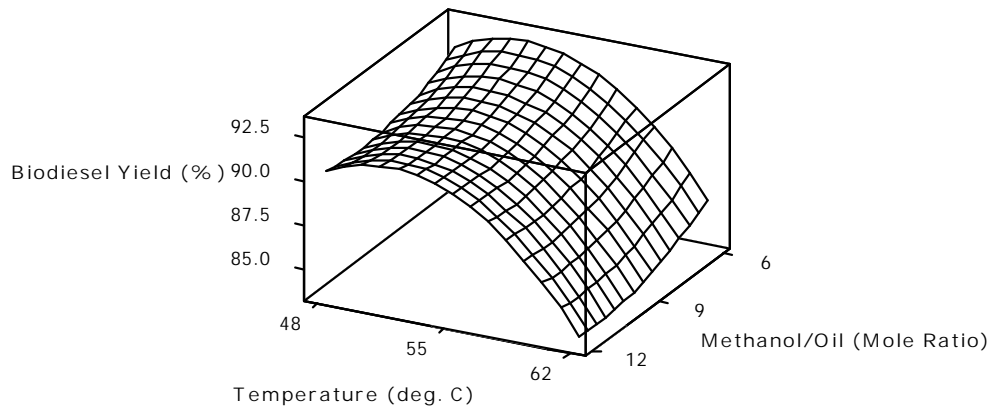
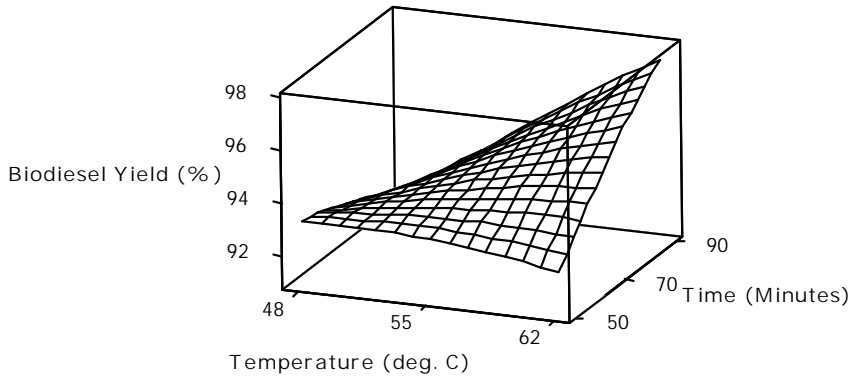


Figure C2: Surface Plots of WSO Biodiesel Yield against Methanol/Oil mole ratio and Temperature, at 1.2 w/w Catalyst Concentration (a) KOH, (b) NaOH and 70 minutes time

a

Hold Values	
Met./Oil, Mole Ratio	9
Cat. Conc, w/wOil	1.2



b

Hold Values	
Met./Oil, Mole Ratio	9
Cat. Conc, w/wOil	1.2

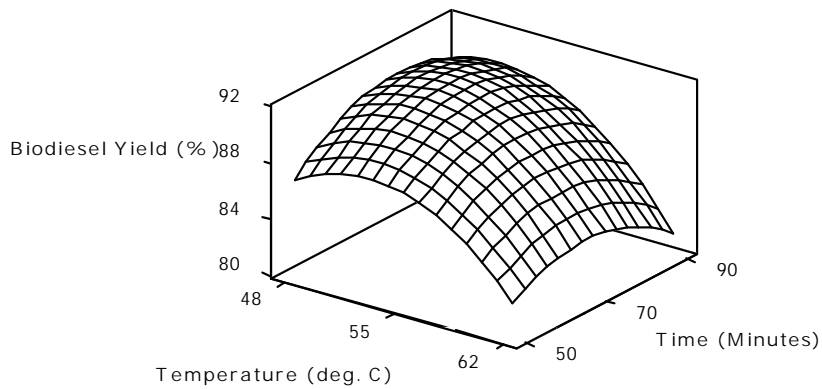
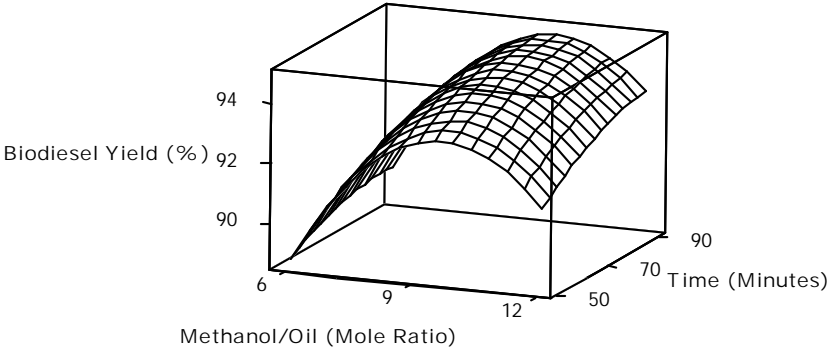


Figure C3: Surface Plots of WSO Biodiesel Yield against Temperature and Reaction Time, at 9 Methanol/Oil mole ratio and 1.2 w/w Catalyst Concentration (a) KOH, (b) NaOH

a

Hold Values	
Cat. Conc, w/wOil	1.2
Rxn Temp, deg. C	55



b

Hold Values	
Cat. Conc, w/wOil	1.2
Rxn Temp, deg. C	55

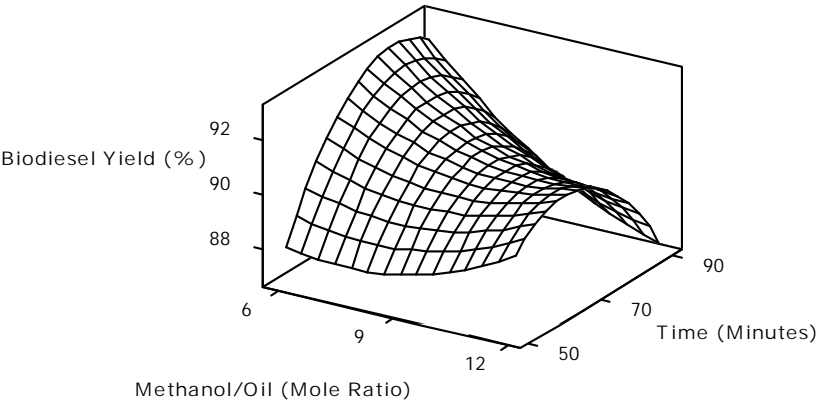
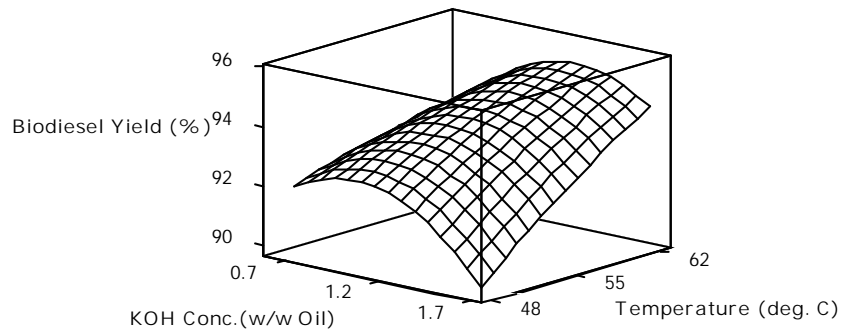


Figure C4: Surface Plots of WSO Biodiesel Yield against Methanol/Oil mole ratio and Reaction Time, at 55 °C Reaction Temperature and 1.2 w/w Catalyst Concentration (a) KOH, (b) NaOH

Hold Values	
Met./Oil, Mole Ratio	9
Rxn Time, min.	70



Hold Values	
Met./Oil, Mole Ratio	9
Rxn Time, min.	70

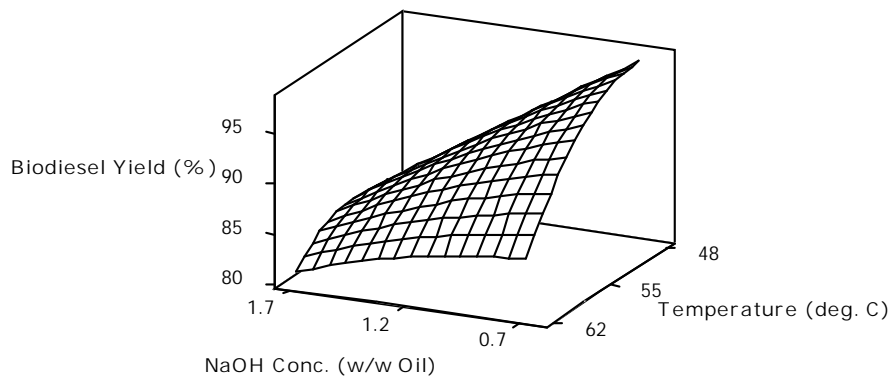
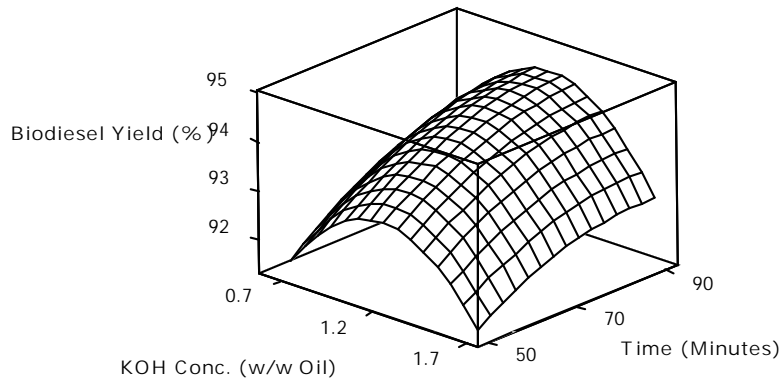


Figure C5: Surface Plots of WSO Biodiesel Yield against Catalyst concentration (w/w Oil) and Reaction Temperature, at 9 mole ratio of Methanol/Oil and 70 minutes reaction time

Hold Values	
Met./Oil, Mole Ratio	9
Rxn Temp, deg. C	55



Hold Values	
Met./Oil, Mole Ratio	9
Rxn Temp, deg. C	55

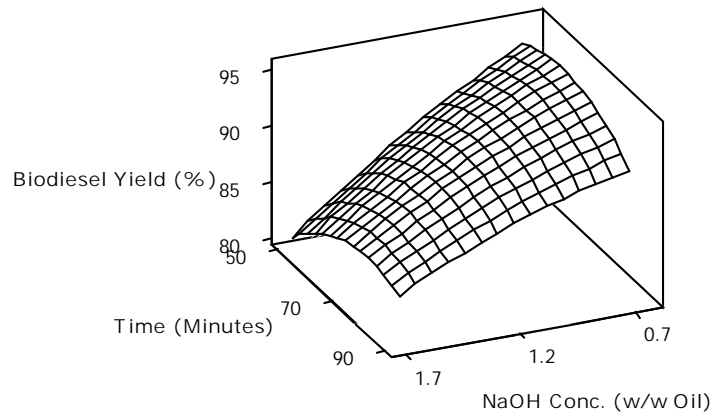


Figure C6: Surface Plots of WSO Biodiesel Yield against Catalyst concentration (w/w Oil) and Reaction Time, at 9 mole ratio of Methanol/Oil and 55 °C Reaction Temperature

APPENDIX D: ANOVA for WGO, WSO and CPKO Biodiesel Yields

Table D1: Analysis of Variance for WGO Biodiesel Yield using KOH Catalyst

Factor				Notation		
Methanol/Oil,		mole ratio		X ₁		
Catalyst Concentration,		w/w Oil		X ₂		
Reaction Temperature,		deg. C		X ₃		
Reaction Time,		minutes		X ₄		
X ₁	X ₂	X ₃	X ₄	WGO Biodiesel Yield (%) (KOH Catalyst)		% Deviation
				Predicted Value	Experimental Value	
12	1.7	55	70	91.38	91.33	-0.063
12	0.7	55	70	92.40	92.78	0.403
6	1.7	55	70	89.60	88.90	-0.797
6	0.7	55	70	90.62	90.89	0.289
9	1.2	62	90	97.76	99.00	1.242
9	1.2	62	50	93.45	91.61	-2.011
9	1.2	48	90	91.92	92.43	0.545
9	1.2	48	50	93.15	92.78	-0.402
9	1.2	55	70	95.43	95.02	-0.437
12	1.2	55	90	94.09	92.08	-2.184
12	1.2	55	50	90.57	91.00	0.462
6	1.2	55	90	90.34	88.81	-1.727
6	1.2	55	50	90.76	91.90	1.232
9	1.7	62	70	96.35	95.78	-0.602
9	1.7	48	70	89.89	88.74	-1.307
9	0.7	62	70	93.98	93.33	-0.706
9	0.7	48	70	94.30	94.11	-0.204
9	1.2	55	70	95.43	95.56	0.130
12	1.2	62	70	92.77	92.94	0.180
12	1.2	48	70	94.61	93.93	-0.732
6	1.2	62	70	95.91	95.16	-0.789
6	1.2	48	70	87.92	87.69	-0.263
9	1.7	55	90	91.06	91.11	0.052
9	1.7	55	50	92.47	93.12	0.692
9	0.7	55	90	95.03	93.85	-1.265
9	0.7	55	50	90.53	90.09	-0.493
9	1.2	55	70	95.43	95.10	-0.352
Average Value				92.86	92.55	-0.337

Term	Coefficient	SE Coefficient	F	p
Constant	38.5074	6.33702	17.5727	0.0000006
<i>Linear</i>				
X ₁	10.8486	1.42639	57.8455	0.0000007
<i>Square</i>				
X ₁ X ₁	-0.2922	0.04372	44.6725	0.0000038
X ₂ X ₂	-7.1928	1.40493	26.2114	0.0000854
X ₄ X ₄	-0.0035	0.00076	20.9299	0.0002691
<i>Interaction</i>				
X ₁ X ₃	-0.1172	0.01645	50.7454	0.0000017
X ₁ X ₄	0.0165	0.00773	4.5431	0.0479416
X ₂ X ₃	0.4837	0.06856	49.7775	0.0000019
X ₂ X ₄	-0.1479	0.04275	11.9679	0.0029960
X ₃ X ₄	0.0099	0.00180	30.5811	0.0000367

Table D2: Analysis of Variance for WGO Biodiesel Yield using NaOH Catalyst

Factor				Notation
Methanol/Oil,		mole ratio		X ₁
Catalyst Concentration,		w/w Oil		X ₂
Reaction Temperature,		deg. C		X ₃
Reaction Time,		minutes		X ₄

X ₁	X ₂	X ₃	X ₄	WGO Biodiesel Yield (%) (NaOH Catalyst)		% Deviation
				Predicted Value	Experimental Value	
12	1.7	55	70	87.52	87.73	0.237
12	0.7	55	70	91.49	90.18	-1.460
6	1.7	55	70	84.79	86.98	2.516
6	0.7	55	70	88.76	88.11	-0.745
9	1.2	62	90	97.28	98.92	1.652
9	1.2	62	50	91.20	92.04	0.906
9	1.2	48	90	92.93	92.05	-0.964
9	1.2	48	50	91.89	91.09	-0.886
9	1.2	55	70	93.65	93.60	-0.062
12	1.2	55	90	92.80	91.67	-1.240
12	1.2	55	50	89.24	90.25	1.111
6	1.2	55	90	90.07	89.67	-0.453
6	1.2	55	50	86.51	87.10	0.670
9	1.7	62	70	96.18	96.29	0.109
9	1.7	48	70	83.46	82.58	-1.074
9	0.7	62	70	89.27	90.02	0.832
9	0.7	48	70	98.33	98.09	-0.247
9	1.2	55	70	93.65	93.56	-0.105
12	1.2	62	70	93.93	93.21	-0.776
12	1.2	48	70	92.10	94.27	2.295
6	1.2	62	70	91.20	89.16	-2.291
6	1.2	48	70	89.37	89.96	0.649
9	1.7	55	90	89.61	89.44	-0.193
9	1.7	55	50	86.05	84.84	-1.429
9	0.7	55	90	93.58	94.52	0.985
9	0.7	55	50	90.02	90.79	0.838
9	1.2	55	70	93.65	93.55	-0.115
Average Value				91.06	91.09	0.028

Term	Coefficient	SE Coefficient	F	p
Constant	214.511	37.3623	22.781	0.000000
<i>Linear</i>				
X ₁	6.129	1.1061	30.70	0.000036
X ₂	-63.835	11.4936	30.85	0.000035
X ₃	-4.236	1.2175	12.11	0.002868
<i>Square</i>				
X ₁ X ₁	-0.315	0.0611	26.66	0.000078
X ₂ X ₂	-10.710	2.1981	23.74	0.000143
X ₃ X ₃	0.017	0.0112	2.32	0.146478
X ₄ X ₄	-0.003	0.0011	6.97	0.017223
<i>Interaction</i>				
X ₂ X ₃	1.556	0.1852	70.59	0.000000
X ₃ X ₄	0.009	0.0028	10.09	0.005526

Table D3: Analysis of Variance for WSO Biodiesel Yield using KOH Catalyst

Factor			Notation
Methanol/Oil,	mole ratio		X ₁
Catalyst Concentration,	w/w Oil		X ₂
Reaction Temperature,	deg. C		X ₃
Reaction Time,	minutes		X ₄

X ₁	X ₂	X ₃	X ₄	WSO Biodiesel Yield (%) (KOH Catalyst)		% Deviation
				Predicted Value	Experimental Value	
12	1.7	55	70	90.89	90.79	-0.116
12	0.7	55	70	91.35	92.82	1.577
6	1.7	55	70	87.98	87.51	-0.543
6	0.7	55	70	88.44	89.12	0.756
9	1.2	62	90	97.22	97.90	0.690
9	1.2	62	50	92.28	92.31	0.023
9	1.2	48	90	90.94	91.88	1.016
9	1.2	48	50	93.01	93.54	0.566
9	1.2	55	70	94.20	94.06	-0.152
12	1.2	55	90	92.93	92.83	-0.113
12	1.2	55	50	91.49	90.91	-0.648
6	1.2	55	90	90.02	89.45	-0.643
6	1.2	55	50	88.58	88.40	-0.214
9	1.7	62	70	94.31	94.82	0.531
9	1.7	48	70	89.77	89.57	-0.228
9	0.7	62	70	93.01	92.80	-0.228
9	0.7	48	70	91.99	90.84	-1.275
9	1.2	55	70	94.20	94.21	0.007
12	1.2	62	70	93.56	93.03	-0.580
12	1.2	48	70	90.79	91.08	0.315
6	1.2	62	70	90.65	91.13	0.515
6	1.2	48	70	87.88	88.42	0.608
9	1.7	55	90	92.79	92.77	-0.032
9	1.7	55	50	91.36	92.02	0.713
9	0.7	55	90	93.25	92.98	-0.300
9	0.7	55	50	91.82	91.61	-0.233
9	1.2	55	70	94.20	94.18	-0.024
Average Value				91.81	91.88	0.073

Term	Coefficient	SE Coefficient	F	p
Constant	73.9378	6.11326	35.169	0.000000
<i>Linear</i>				
X ₁	6.5672	0.55554	139.744	0.000000
X ₄	-0.5117	0.15424	11.006	0.003831
<i>Square</i>				
X ₁ X ₁	-0.3379	0.03065	121.552	0.000000
X ₂ X ₂	-5.9667	1.00819	35.025	0.000013
X ₄ X ₄	-0.0010	0.00069	2.132	0.161516
<i>Interaction</i>				
X ₂ X ₃	0.2521	0.04434	32.314	0.000022
X ₃ X ₄	0.0125	0.00232	29.144	0.000040

Table D4: Analysis of Variance for WSO Biodiesel Yield using NaOH Catalyst

Factor			Notation
Methanol/Oil,	mole ratio		X ₁
Catalyst Concentration,	w/w Oil		X ₂
Reaction Temperature,	deg. C		X ₃
Reaction Time,	minutes		X ₄

X ₁	X ₂	X ₃	X ₄	WSO Biodiesel Yield (%) (NaOH Catalyst)		% Deviation
				Predicted Value	Experimental Value	
12	1.7	55	70	85.42	82.17	-3.961
12	0.7	55	70	95.83	94.21	-1.721
6	1.7	55	70	87.24	88.8	1.753
6	0.7	55	70	97.64	97.96	0.316
9	1.2	62	90	82.94	84.88	2.281
9	1.2	62	50	81.75	84.34	3.059
9	1.2	48	90	89.03	87.68	-1.540
9	1.2	48	50	87.84	83.48	-5.231
9	1.2	55	70	90.56	91.05	0.532
12	1.2	55	90	87.29	83.69	-4.307
12	1.2	55	50	89.96	91.84	2.044
6	1.2	55	90	92.96	87.73	-5.966
6	1.2	55	50	87.92	88.71	0.880
9	1.7	62	70	82.08	77.80	-5.511
9	1.7	48	70	82.29	81.88	-0.507
9	0.7	62	70	86.61	82.54	-4.937
9	0.7	48	70	98.58	98.38	-0.205
9	1.2	55	70	90.56	90.21	-0.394
12	1.2	62	70	84.41	85.19	0.910
12	1.2	48	70	90.50	93.23	2.926
6	1.2	62	70	86.23	85.54	-0.809
6	1.2	48	70	92.31	92.86	0.581
9	1.7	55	90	83.95	87.50	4.052
9	1.7	55	50	82.77	79.83	-3.683
9	0.7	55	90	94.36	94.52	0.168
9	0.7	55	50	93.17	92.81	-0.395
9	1.2	55	70	90.56	90.68	0.126
Average Value				88.69	88.13	-0.723

Term	Coefficient	SE Coefficient	F	p
Constant	73.9378	6.11326	35.169	0.000000
<i>Linear</i>				
X ₁	6.5672	0.55554	139.744	0.000000
X ₄	-0.5117	0.15424	11.006	0.003831
<i>Square</i>				
X ₁ X ₁	-0.3379	0.03065	121.552	0.000000
X ₂ X ₂	-5.9667	1.00819	35.025	0.000013
X ₄ X ₄	-0.0010	0.00069	2.132	0.161516
<i>Interaction</i>				
X ₂ X ₃	0.2521	0.04434	32.314	0.000022
X ₃ X ₄	0.0125	0.00232	29.144	0.000040

Table D5: Analysis of Variance for CPKO Biodiesel Yield using KOH Catalyst

Factor			Notation
Methanol/Oil,	mole ratio		X ₁
Catalyst Concentration,	w/w Oil		X ₂
Reaction Temperature,	deg. C		X ₃
Reaction Time,	minutes		X ₄

X ₁	X ₂	X ₃	X ₄	CPKO Biodiesel Yield (%) (KOH Catalyst)		% Deviation
				Predicted Value	Experimental Value	
12	1.7	55	70	88.78	86.63	-2.490
12	0.7	55	70	88.90	89.04	0.154
6	1.7	55	70	84.96	84.10	-1.032
6	0.7	55	70	85.08	85.43	0.406
9	1.2	62	90	97.72	98.52	0.805
9	1.2	62	50	92.89	93.12	0.242
9	1.2	48	90	91.28	90.24	-1.162
9	1.2	48	50	91.72	89.62	-2.344
9	1.2	55	70	94.72	94.57	-0.166
12	1.2	55	90	91.20	91.01	-0.218
12	1.2	55	50	89.00	90.39	1.527
6	1.2	55	90	87.38	87.22	-0.194
6	1.2	55	50	85.18	85.03	-0.187
9	1.7	62	70	93.98	95.35	1.427
9	1.7	48	70	90.18	91.23	1.147
9	0.7	62	70	94.10	93.07	-1.110
9	0.7	48	70	90.29	90.84	0.596
9	1.2	55	70	94.72	94.50	-0.240
12	1.2	62	70	93.33	93.11	-0.238
12	1.2	48	70	89.52	90.33	0.889
6	1.2	62	70	89.51	89.09	-0.473
6	1.2	48	70	85.70	86.77	1.225
9	1.7	55	90	91.86	91.89	0.026
9	1.7	55	50	89.66	90.03	0.404
9	0.7	55	90	91.98	91.53	-0.492
9	0.7	55	50	89.78	90.01	0.254
9	1.2	55	70	94.72	94.52	-0.219
Average Value				90.67	90.79	-0.054

Term	Coefficient	SE Coefficient	F	p
Constant	28.5989	6.07910	37.4 40	0.0000000
<i>Linear</i>				
X ₁	11.0532	0.84301	171.914	0.0000000
X ₂	24.6909	4.06234	36.942	0.0000076
X ₃	-0.3862	0.15879	5.916	0.0250590
<i>Square</i>				
X ₁ X ₁	-0.5788	0.04650	154.888	0.0000000
X ₂ X ₂	-10.3358	1.67418	38.114	0.0000062
X ₄ X ₄	-0.0034	0.00086	15.383	0.0009154
<i>Interaction</i>				
X ₃ X ₄	0.0095	0.00218	18.782	0.0003577

Table D6: Analysis of Variance for CPKO Biodiesel Yield using NaOH Catalyst

Factor				Notation		
Methanol/Oil,		mole ratio		X ₁		
Catalyst Concentration,		w/w Oil		X ₂		
Reaction Temperature,		deg. C		X ₃		
Reaction Time,		minutes		X		
X ₁	X ₂	X ₃	X ₄	CPKO Biodiesel Yield (%) (KOH Catalyst)		% Deviation
				Predicted Value	Experimental Value	
12	1.7	55	70	84.49	80.78	-4.601
12	0.7	55	70	85.30	85.13	-0.206
6	1.7	55	70	79.53	78.77	-0.976
6	0.7	55	70	80.34	81.09	0.915
9	1.2	62	90	94.16	95.16	1.043
9	1.2	62	50	90.07	90.01	-0.067
9	1.2	48	90	88.28	86.68	-1.855
9	1.2	48	50	88.78	87.14	-1.886
9	1.2	55	70	91.48	91.30	-0.205
12	1.2	55	90	87.46	88.81	1.510
12	1.2	55	50	85.66	87.19	1.745
6	1.2	55	90	82.51	81.98	-0.647
6	1.2	55	50	80.71	81.21	0.615
9	1.7	62	70	90.04	90.78	0.806
9	1.7	48	70	86.46	89.14	3.000
9	0.7	62	70	90.85	90.05	-0.895
9	0.7	48	70	87.27	88.30	1.162
9	1.2	55	70	91.48	91.22	-0.293
12	1.2	62	70	89.51	90.40	0.973
12	1.2	48	70	85.93	87.80	2.121
6	1.2	62	70	84.56	86.02	1.695
6	1.2	48	70	80.97	81.30	0.394
9	1.7	55	90	87.99	89.08	1.216
9	1.7	55	50	86.19	87.91	1.949
9	0.7	55	90	88.80	89.95	1.273
9	0.7	55	50	87.00	86.79	-0.247
9	1.2	55	70	91.48	91.18	-0.337
Average Value				86.94	87.22	0.303

Term	Coefficient	SE Coefficient	F	p
Constant	12.7330	9.04504	22.781	0.000000
<i>Linear</i>				
X ₁	13.3021	1.25430	112.469	0.000000
X ₂	26.3284	6.04432	18.974	0.000340
X ₃	-0.3182	0.23626	1.814	0.193910
<i>Square</i>				
X ₁ X ₁	-0.6931	0.06919	100.338	0.000000
X ₂ X ₂	-11.3070	2.49099	20.604	0.000224
<i>Interaction</i>				
X ₃ X ₄	0.0083	0.00325	6.515	0.019455
X ₄ X ₄	-0.0029	0.00127	5.240	0.033691

APPENDIX E: Mass Fractions of Five Biodiesel Samples

Table E1: Mass Fraction of Five Biodiesel samples considered as reported by Ramirez-Verdusco et. al., (2012)

Carbon Chain	Mass Fraction (x_i)				
	BT	SB	SF	CO	CT
C14:0	0.005	0.000	0.001	0.000	0.008
C16:0	0.159	0.101	0.060	0.099	0.229
C16:1	0.009	0.000	0.000	0.000	0.000
C18:0	0.085	0.045	0.059	0.031	0.031
C18:1	0.317	0.243	0.160	0.291	0.185
C18:2	0.365	0.531	0.714	0.568	0.542
C18:3	0.046	0.072	0.006	0.011	0.005
C20:0	0.003	0.004	0.000	0.000	0.000
C20:1	0.008	0.000	0.000	0.000	0.000
C22:1	0.003	0.004	0.000	0.000	0.000

APPENDIX F: Life Cycle Assessment of Biodiesel

Table F1: Material Balance on LCA of CPKO, WGO and WSO Biodiesel Produced

ITEM	UNIT	<u>CPKO</u>		<u>WGO</u>		<u>WSO</u>	
		KOH	NaOH	KOH	NaOH	KOH	NaOH
FEED							
Methanol Used	kg	0.92508	0.92508	0.92508	0.92508	0.92508	0.92508
Oil Consumed	kg	2.70000	2.70000	2.70000	2.70000	2.70000	2.70000
KOH Used	kg	0.03240	-	0.03240	-	0.03240	-
NaOH Used	kg	-	0.03240	-	0.03240	-	0.03240
Warm Water Used	kg	0.04050	0.04050	0.04050	0.04050	0.04050	0.04050
Total	kg	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>
PRODUCTS							
Biodiesel	kg	2.44719	2.35517	2.49904	2.45967	2.48098	2.37951
Crude Glycerol	kg	1.17789	1.26991	1.12604	1.16541	1.14410	1.24557
Water Out	kg	0.07290	0.07290	0.07290	0.07290	0.07290	0.07290
Total	kg	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>	<u>3.69798</u>
Water Turbidity	*NTU	207	208	210	212	207	208
Colour of Water	*PCU	307	310	307	311	307	311

*NTU = Nephelometric Turbidity Unit, *PCU = Platinum Cobalt Units (Pure water has zero values of NTU and PCU).

Table F2: Life Cycle Inventory

No	Substance	Compartment	Unit	CPKO	WGO	WSO
				Biodiesel	Biodiesel	Biodiesel
1	Aluminium	Air	µg	5	21	16
2	Aluminium	Water	µg	9	11	15
3	Arsenic	Air	µg	2	3	1
4	Arsenic	Water	µg	14	39	42
5	Beryllium	Air	µg	9	11	7
6	Cadmium	Air	µg	10	31	51
7	Cadmium	Water	µg	25	31	28
8	Calcium	Water	µg	860	760	550
9	Carbon dioxide	Air	mg	1.18	1.32	1.54
10	Carbonate	Water	µg	430	500	530
11	Chloride	Water	mg	1.46	1.71	0.99
12	Chromium	Air	µg	3	7	4
13	Chromium	Water	µg	1	3	2
14	Cobalt	Air	µg	2	4	3
15	Copper	Air	µg	3	7	11
16	Copper	Water	µg	17	23	15
17	Hydroxide	Water	µg	680	810	750
18	Lead	Air	µg	20	13	14
19	Lead	Water	µg	4	6	10
20	Nickel	Air	µg	38	56	28
21	Nickel	Water	µg	5	9	7
22	Nitrate	Water	µg	520	480	420

23	Nitrogen dioxide	Air	µg	290	361	460
24	Phosphate	Water	µg	190	280	270
25	Potassium Hydroxide	Raw	g	6.875	6.5849	6.8059
26	Sodium Hydroxide	Raw	g	6.6173	6.483	6.5259
27	Sulfur dioxide	Air	µg	160	340	520
28	Sulphate	Water	µg	640	650	700
29	Zinc	Air	µg	13	78	42
30	Zinc	Water	µg	138	141	93

Table F3: Characterisation of Substances into Seven Categories

Substance	Compartment	Unit	CPKO Biodiesel	WGO Biodiesel	WSO Biodiesel
Carcinogens					
Arsenic	Air	kg/C ₂ H ₃ Cl eq.	2.49E-06	3.73E-06	1.24E-06
Cadmium	Air	kg/C ₂ H ₃ Cl eq.	3.56E-07	1.10E-06	1.82E-06
Chromium VI	Air	kg/C ₂ H ₃ Cl eq.	3.65E-07	8.52E-07	4.87E-07
Total			3.21E-06	5.69E-06	3.55E-06
Non Carcinogens					
Aluminium	Air	kg/C ₂ H ₃ Cl eq.	7.29E-09	1.02E-08	7.78E-08
Aluminium	Water	kg/C ₂ H ₃ Cl eq.	1.85E-08	2.26E-08	3.08E-08
Beryllium	Air	kg/C ₂ H ₃ Cl eq.	2.50E-05	3.75E-05	1.25E-05
Cobalt	Air	kg/C ₂ H ₃ Cl eq.	5.48E-06	1.70E-05	2.80E-05
Chromium III	Air	kg/C ₂ H ₃ Cl eq.	5.39E-08	1.26E-07	7.18E-08
Chromium III	Water	kg/C ₂ H ₃ Cl eq.	4.51E-09	1.35E-08	9.02E-09
Copper	Air	kg/C ₂ H ₃ Cl eq.	6.13E-09	1.43E-08	2.25E-08
Lead	Air	kg/C ₂ H ₃ Cl eq.	5.21E-08	3.38E-08	3.64E-08
Lead	Water	kg/C ₂ H ₃ Cl eq.	4.30E-08	6.45E-08	1.07E-07
Nickel	Air	kg/C ₂ H ₃ Cl eq.	3.37E-07	4.97E-07	2.48E-07
Zinc	Air	kg/C ₂ H ₃ Cl eq.	1.21E-06	7.23E-06	3.90E-06
Zinc	Water	kg/C ₂ H ₃ Cl eq.	1.84E-05	1.88E-05	1.24E-05
Total			5.06E-05	8.13E-05	5.74E-05
Respiratory Inorganics					
Nitrogen dioxide	Air	kg/PM _{2.5} eq.	3.69E-08	4.60E-08	5.86E-08
Sulphur dioxide	Air	kg/PM _{2.5} eq.	1.25E-08	2.65E-08	4.06E-08
Total			4.94E-08	7.25E-08	9.92E-08
Aquatic Ecotoxicity					
Aluminium	Air	kg TEG water	7.40E-03	1.04E-02	7.89E-03
Aluminium	Water	kg TEG water	3.24E-02	3.96E-02	5.39E-02
Arsenic	Air	kg TEG water	1.10E-04	1.65E-04	5.48E-05
Cadmium	Air	kg TEG water	4.28E-03	1.33E-02	2.18E-02
Chromium	Air	kg TEG water	2.01E-04	4.69E-04	2.68E-04
Chromium	Water	kg TEG water	4.53E-04	1.36E-03	9.06E-04
Copper	Air	kg TEG water	8.82E-03	2.06E-02	3.23E-02
Lead	Air	kg TEG water	8.01E-04	5.21E-04	2.64E-03
Lead	Water	kg TEG water	1.05E-03	1.58E-03	2.64E-03
Nickel	Air	kg TEG water	6.79E-03	1.00E-02	5.00E-03
Zinc	Air	kg TEG water	2.65E-03	1.59E-02	8.57E-03
Zinc	Water	kg TEG water	1.94E-01	1.98E-01	1.30E-01
Total			2.59E-01	3.12E-01	2.66E-01

Terrestrial Ecotoxicity

Aluminium	Air	kg TEG soil	1.90E-03	2.66E-03	2.02E-03
Aluminium	Water	kg TEG soil	2.04E-16	2.50E-16	3.40E-16
Arsenic	Air	kg TEG soil	8.37E-04	1.26E-03	4.19E-04
Cadmium	Air	kg TEG soil	9.12E-03	2.83E-02	4.65E-02
Chromium	Air	kg TEG soil	1.15E-03	2.67E-03	1.53E-03
Copper	Air	kg TEG soil	3.55E-03	8.29E-03	1.30E-02
Lead	Air	kg TEG soil	2.61E-03	1.70E-03	1.83E-03
Nickel	Air	kg TEG soil	2.14E-02	3.15E-02	1.58E-02
Zinc	Air	kg TEG soil	1.32E-02	7.89E-02	4.25E-02
Total			5.38E-02	1.55E-01	1.24E-01

Terrestrial Acidification/Nutr.

Nitrogen dioxide	Air	kg SO ₂ eq.	1.59E-06	1.98E-06	2.52E-06
Sulphur dioxide	Air	kg SO ₂ eq.	1.60E-07	3.40E-07	5.20E-07
Total			1.75E-06	2.32E-06	3.04E-06

Global Warming

Carbon dioxide	Water	kg CO ₂ eq.	1.18E-06	1.32E-06	1.54E-06
Total			1.18E-06	1.32E-06	1.54E-06

*kg PM_{2.5} eq.= kilogram of particulate matter with diameter equivalent to 2.5 micrometer or less

*kg TEG soil = kilogram of Tri-Ethylene Glycol in soil.

Table F4: Damage Assessment

Substance	Compartment	Unit	CPKO Biodiesel	WGO Biodiesel	WSO Biodiesel
Human Health					
Aluminium	Air	DALY	2.04E-14	2.86E-14	2.18E-14
Aluminium	Water	DALY	5.17E-14	6.32E-14	8.61E-14
Arsenic	Air	DALY	7.69E-11	1.15E-10	3.84E-11
Cadmium	Air	DALY	1.63E-11	5.07E-11	8.34E-11
Chromium	Air	DALY	1.17E-12	2.74E-12	1.56E-12
Chromium	Water	DALY	1.26E-14	3.79E-14	2.53E-14
Copper	Air	DALY	1.72E-14	4.00E-14	6.29E-14
Lead	Air	DALY	1.46E-13	9.48E-14	1.02E-13
Lead	Water	DALY	1.20E-13	1.80E-13	3.01E-13
Nickel	Air	DALY	9.44E-13	1.39E-12	6.96E-13
Nitrogen dioxide	Air	DALY	2.58E-11	3.22E-11	4.10E-11
Sulphur dioxide	Air	DALY	8.74E-12	1.86E-11	2.84E-11
Zinc	Air	DALY	3.38E-12	2.03E-11	1.09E-11
Zinc	Water	DALY	5.15E-11	5.27E-11	3.47E-11
Total			1.85E-10	2.94E-10	2.40E-10
Ecosystem Quality					
Aluminium	Air	PDF*m ² *yr.	1.54E-05	2.15E-05	1.64E-05
Aluminium	Water	PDF*m ² *yr.	1.62E-06	1.99E-06	2.71E-06
Arsenic	Air	PDF*m ² *yr.	6.63E-06	9.94E-06	3.31E-06
Cadmium	Air	PDF*m ² *yr.	7.23E-05	2.24E-04	3.69E-04
Chromium	Air	PDF*m ² *yr.	9.07E-06	2.12E-05	1.21E-05
Chromium	Water	PDF*m ² *yr.	2.27E-08	6.82E-08	4.55E-08
Copper	Air	PDF*m ² *yr.	2.85E-05	6.66E-05	1.05E-04
Lead	Air	PDF*m ² *yr.	2.07E-05	1.35E-05	1.45E-05
Lead	Water	PDF*m ² *yr.	5.30E-08	7.94E-08	1.32E-07
Nickel	Air	PDF*m ² *yr.	1.69E-04	2.50E-04	1.25E-04
Nitrogen dioxide	Air	PDF*m ² *yr.	1.66E-06	2.06E-06	2.63E-06
Sulphur dioxide	Air	PDF*m ² *yr.	1.66E-07	3.54E-07	5.41E-07
Zinc	Air	PDF*m ² *yr.	1.04E-04	6.25E-04	3.37E-04
Zinc	Water	PDF*m ² *yr.	9.72E-06	9.93E-06	6.55E-06
Total			4.39E-04	1.25E-03	9.95E-04
Climate Change					
Carbon dioxide	Water	kg CO ₂ eq.	1.18E-06	1.32E-06	1.54E-06
Total			1.18E-06	1.32E-06	1.54E-06

*DALY = Disability Adjusted Life Year,

*PDF = Potentially Disappeared Fraction of species

Table F5: Single Score

	Impact Category	Unit	CPKO Biodiesel	WGO Biodiesel	WSO Biodiesel
Human Health	Carcinogenics	Pt	1.27E-09	2.25E-09	1.40E-09
	Non Carcinogenics	Pt	2.00E-08	3.21E-08	2.26E-08
	Respiratory Inorganics	Pt	4.88E-09	7.15E-09	9.78E-09
	Total		2.62E-08	4.15E-08	3.38E-08
Ecosystem Quality	Aquatic Ecotoxicity	Pt	9.47E-10	1.14E-09	9.69E-10
	Terrestrial Ecotoxicity	Pt	3.10E-08	8.96E-08	7.13E-08
	Terrestrial Acid/Nutr.	Pt	1.33E-10	1.76E-10	2.31E-10
	Total		3.21E-08	9.09E-08	7.25E-08
Climate Change	Global Warming	Pt	1.19E-10	1.33E-10	1.56E-10
	Total		1.19E-10	1.33E-10	1.56E-10

*Pt = Point