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**PRODUCTION, EVALUATION AND TESTING OF
BIODIESEL: CASE STUDIES OF *MORINGA OLEIFERA*
AND SELECTED TROPICAL SEED OILS**

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(MECHANICAL ENGINEERING)

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4th March, 2015

As the candidate's supervisor, I have approved this thesis for submission.

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Declaration 2 - Publications

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- (1) **Eloka-Eboka, A.C.**, Igbum, O.G. and Inambao, F.L. (2014). Optimization and effects of process variables on the production and properties of methyl ester biodiesel. *Journal of Energy in Southern Africa*, 25(2): 39-47.
- (2) Igbum, O.G., **Eloka-Eboka, A.C.** Ubwa, S.T. and Inambao, F.L. (2014). Evaluation of environmental impact and gaseous emissions of biodiesel fuels and blends of selected feed-stocks. *International Journal of Global Warming*, 6(1): 99-112.
- (3) **Eloka-Eboka, A.C.** and Inambao, F.L. (2014). Hybridisation of feedstocks – a new approach in biodiesel development: A case of Moringa and Jatropha seed oils. *Energy Sources Part A* (Taylor and Francis) (Accepted and in Press).
- (4) **Eloka-Eboka, A.C.** and Inambao, F.L. (2014). Engine Performance and Emission Characterization of biodiesel fuels from *Moringa oleifera* and *Jatropha curcas* seeds oils and hybrids. *Journal of Energy in Southern Africa* (submitted).

International and DoHET Accredited Conferences

- (5) **Eloka-Eboka, A.C.**, Ogunkale, B.O. and Inambao, F.L. (2013). Investigative study of biodiesel production properties of African *Thevetia peruviana* and *Jatropha curcas* seed oil feedstocks using local metallic salts as catalysts. Proceedings of 12th International Conference on Sustainable Energy technologies (SET-2013) 26-29 August 2013, Hong Kong. **Overall Best paper award**
- (6) **Eloka-Eboka, A.C.** and Inambao, F.L. (2013). Prospects and potentials of *Moringa oleifera* seed oil as a biodiesel fuel alternative in Southern Africa. Proceedings of 12th International Conference on Sustainable Energy technologies (SET-2013) 26-29 August 2013, Hong Kong.

- (7) **Eloka-Eboka, A.C.** and Inambao, F.L. (2013). Comparative case study and testing of *Moringa oleifera* seed oil as biodiesel fuel feedstock. Proceedings of the 13th Biennial Botswana Institution of Engineers, Gaborone, Botswana: 15-18 October 2013: pp. 33-42.
- (8) **Eloka-Eboka, A.C.** and Inambao, F.L. (2014). Blending of feedstocks – a new approach in biodiesel development: A case of Moringa and Jatropha seed oils. Proceedings of 22nd Domestic Use of Energy Conference, Cape Peninsula University of Technology, Cape Town, 31 March - April, 2013. pp. 189-196. (Published in IEEE Explore).
- (9) **Eloka-Eboka, A.C.** and Inambao, F.L. (2014). Effects of hybridisation of biodiesel on the fuel quality and performance of Moringa and Jatropha feedstocks and hybrids. Proceedings of 13th International Conference on Sustainable Energy technologies (SET-2014), 24-28 August 2014, Geneva, Switzerland.
- (10) Ebhota, W.S., **Eloka-Eboka, A.C.** and Inambao, F.L. (2014). Energy sustainability through domestication of Energy Technologies in third world countries in Africa. Proceedings of the 11th Industrial and Commercial use of Energy Conference, 18-20 August 2014, African Pride Crystal Towers Hotel, Cape Town. pp. 277-283. (Published in IEEE Explore).

The candidate for all the publications is the main and corresponding author respectively while Dr Freddie L. Inambao is the supervisor.

Dedication

Dedicated to my late father, Ogbueshi Marcus Eloka Nwokolo Eboka, lover of education, who passed on at the early stages of this doctoral study.

May his great soul rest in the bosom of the eternity of the beatific vision of the Most High God.

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Contents

Declaration 1 – Plagiarism	ii
Declaration 2 - Publications	iii
Dedication	iv
Acknowledgements	v
Table of Contents	vii
List of Figures	x
List of Tables	xii
Nomenclature	xiv
Acronyms and Abbreviation	xv
Abstract	xviii
Chapter 1: Introduction	
1.1 Introduction.....	1
1.2 Background of the study.....	2
1.3 Development in the use of biodiesel.....	4
1.4 History and origin.....	4
1.5 Statement of problems.....	6
1.6 Motivation	6
1.7 Aims and objectives of the study.....	7
1.8 Significance of the study.....	7
1.9 Scope of work.....	8
1.10 Layout of the thesis.....	8
Chapter 2: Paper 1, Optimization and effects of process variables on the production and properties of methyl ester biodiesel	
2.1 Introduction.....	13
2.2 Materials and methods.....	14
2.2.1 Seed plant of study: <i>Hura crepitans</i>	14
2.3 Preparation of methyl esters.....	14
2.4 Biodiesel separation.....	16
2.5 Biodiesel washing.....	16
2.6 Determination of the effects of catalyst type on yields and specific properties...	16
2.7 Preparation of methoxide.....	16

2.8	Determination of the effects of alcohol/oil molar ratio on yields.....	17
2.9	Determination of the effects of reaction time on yields.....	17
2.10	Determination of the effects of temperature on yields.....	17
2.11	Results and discussion.....	18
2.11.1	Effect of alcohol/oil molar ratio on the yields and properties of Hura biodiesel...	18
2.11.2	Effect of reaction time.....	19
2.11.3	Effects of catalyst type on yields, viscosity and specific gravity.....	21
2.11.4	Effects of temperature on yields, viscosity and specific gravity.....	22
2.12	Conclusion.....	23

Chapter 3: Paper 2, Evaluation of environmental impact and gaseous emissions of biodiesel fuels and blends of selected feed-stocks

3.1	Introduction.....	28
3.2	Emissions reductions with biodiesel.....	30
3.2.1	Lower HC emissions.....	30
3.2.2	Smoke and soot emission.....	30
3.2.3	Carbon monoxide emissions.....	31
3.2.4	Poly-aromatic HC emission.....	31
3.2.5	Nitrogen oxide.....	32
3.3	Biodiesel helps reduce greenhouse gases unlike any other ‘clean fuels’.....	33
3.4	Lower impact on marine environment.....	33
3.5	Biodegradability of biodiesel in aquatic environment.....	33
3.6	Determination of thermal and gaseous emissions.....	34
3.7	Results.....	35
3.8	Conclusion.....	39

Chapter 4: Paper 3, Hybridisation of feedstocks - a new approach in biodiesel development: A case of Moringa and Jatropha seed oils

4.1	Introduction.....	43
4.2	Materials and methods.....	46
4.2.1	Oil preparation.....	46
4.2.2	Extraction and initial characterization of oils of Moringa and Jatropha.....	46
4.2.3	<i>In situ</i> and <i>ex situ</i> hybridisation of feedstocks.....	47
4.2.4	Biodiesel production methods.....	47
4.2.5	Analysis of biodiesel and hybrids.....	48
4.3	Results and discussions.....	48
4.3.1	Results.....	48
4.3.2	Discussion of results.....	49
4.4	Conclusion.....	57

Chapter 5: Paper 4, Engine Performance and Emission Characterization of modelled biodiesel fuels from *Moringa oleifera* and *Jatropha curcas* seeds oils and hybrids

5.1	Introduction.....	61
5.2	Emission effects.....	63
5.3	Status and legislation in South Africa.....	63
5.4	Engine performance.....	64
5.5	Improvement Consideration on biodiesel feedstock.....	65
5.6	Specific study objectives.....	66
5.7	Materials/Methods.....	66
5.7.1	Development and application of biodiesel production model.....	66
5.7.2	Model formulation/calculation: base wash/neutralization.....	67
5.7.3	Model formulation: transesterification.....	68
5.7.4	Power, torque and rotational speed relationship employed.....	72
5.7.5	Emissions determination.....	72
5.8	Results and discussion.....	74
5.9	Conclusion.....	80

Chapter 6: Paper 5, Investigative Study of Biodiesel Production Properties of African *Thevetia peruviana* and *Jatropha curcas* oil feedstocks using local metallic salts as catalysts

6.1	Introduction.....	85
6.2	Yellow Oleander (<i>Thevetia peruviana</i>) plant.....	88
6.3	<i>Jatropha</i> (<i>Jatropha curcas</i>) plant.....	89
6.4	Materials and methods.....	90
6.4.1	Extraction of oils from <i>Thevetia peruviana</i> and <i>Jatropha curcas</i> seed.....	90
6.4.2	Preparation of catalysts.....	91
6.4.3	Production of biodiesel.....	91
6.4.4	Analysis and characterization of <i>Thevetia</i> and <i>Jatropha</i> oils.....	91
6.5	Results and discussion.....	92
6.5.1	Chemo-physical properties.....	92
6.5.2	Thermal properties.....	92
6.5.3	Percentage oil/biodiesel yields.....	94
6.5.4	Chemo- physical properties of the oils and biodiesel fuels.....	96
6.5.5	Thermal properties of oils and biodiesel fuels.....	97
6.6	Conclusions.....	97
6.7	Recommendations.....	98

Chapter 7: Conclusion and Future Works

7.1	Conclusion.....	102
7.2	Future works and study.....	104

Appendixes.....	105
App-A.....	105
App-B.....	106
App-C.....	107
App-D.....	108
App-E.....	109

List of Figures

Figure 2.1a	Fully grown pods of <i>Hura crepitans</i> seed hanging on the tree.....	15
Figure 2.1b	Pulverized Hura seeds.....	15
Figure 2.1c	Biodiesel and glycerine after separation.....	15
Figure 2.2	Effects of alcohol/oil ratio on some specific gravity and yields.....	19
Figure 2.3	Effects of catalyst type on some specific chemo-physical properties...	19
Figure 2.4	Effects of alcohol/oil ratio on some specific chemo-physical properties	20
Figure 2.5	Effects of reaction temp. on some specific chemo-physical properties.	21
Figure 2.6	Effects of reaction time on some specific chemo-physical properties...	22
Figure 3.1	Some structures of poly-aromatic hydrocarbons.....	32
Figure 3.2	Gaseous emission characteristics of HVO-ME and blends with AGO....	36
Figure 3.3	Gaseous emission characteristics of CVO-methyl esters with AGO.....	37
Figure 3.4	Gaseous emission characteristics of CSVO-ME and blends with AGO...	37
Figure 3.5	Gaseous emission characteristics of TVO-methyl esters and with AGO.	38
Figure 4.1	TGA analysis of Moringa Oil.....	52
Figure 4.2	TGA analysis of Jatropha Oil.....	52
Figure 4.3	TGA analysis of Moringa/Jatropha Hybrids (50:50).....	53
Figure 4.4	Chemo-physical properties of biodiesel and hybrids.....	54
Figure 4.5	Effect of hybridization on kinematic viscosity of biodiesel fuels.....	55
Figure 4.6	Effect of hybridization on cetane index of biodiesel fuels.....	55
Figure 4.7	Effect of hybridization on calorific value of biodiesel fuels.....	56
Figure 4.8	Effect of hybridization on flash and fire points of biodiesel fuels.....	56
Figure 4.9	Effect of hybridization on density and specific gravity of biodiesel.....	56
Figure 5.1	Schematics of the engine test bed setup.....	71
Figure 5.2	Engine test cell facilities and IC engines at UKZN for experimentation..	71
Figure 5.3	Experimental setup.....	73
Figure 5.4	Portable diesel smoke meter (Opacimeter).....	73
Figure 5.5	Effects of brake thermal efficiencies on load of biodiesel hybrids.....	77
Figure 5.6	Effects of specific fuel consumption on loads of biodiesel hybrids.....	77
Figure 5.7	Effects of smoke opacity on loads of biodiesel hybrids.....	77
Figure 5.8	Effects of exhaust gas temperature on loads of biodiesel hybrids.....	78
Figure 5.9	Effect of CO emission composition of loads of biodiesel hybrids.....	78

Figure 5.10	Comparison of mechanical and thermal efficiencies on loads.....	78
Figure 5.11	Effect of CO composition of the Hybrids at different loads.....	79
Figure 5.12	Effects of NOx composition on the hybrids at different loads.....	79
Figure 5.13	Effect of VOCs composition on hybrids at different loads.....	79
Figure 6.1	<i>Thevetia peruviana</i> plant.....	89
Figure 6.2	<i>Jatropha curcas</i> Plant.....	89
Figure 6.3	Comparison of heating values of oil and biodiesel with AGO.....	94
Figure 6.4	Comparison of specific heat capacities of oil and biodiesel.....	95
Figure 6.5	Fatty acid profile/composition of vegetable oils and biodiesels.....	96

List of Tables

Table 2.1	Alcohol/Oil ratio on AV, RI, CR and SA.....	18
Table 2.2	Reaction time on water and sediment, flash point and cloud point...	20
Table 2.3	Reaction time on pour point, total and free glycerine of HVO-ME...	21
Table 2.4	Effect of reaction time on acid value, refractive index, carbon residue	22
Table 2.5	Effect of reaction temperature on W & S, FP and CP.....	23
Table 2.6	Effect of reaction temperature on pour point, total and free glycerine	23
Table 3.1	Gaseous emission characteristics of AGO (Control).....	36
Table 4.1	Optimization protocol.....	49
Table 4.2	Biodiesel yields from the protocol.....	49
Table 4.3	Viscosity and shear stress of biodiesel @ 40°C.....	50
Table 4.4	Viscosity and Shear Stress of Biodiesel @ 60°C.....	50
Table 4.5	Viscosity and shear stress of biodiesel hybrids @ 40°C.....	50
Table 4.6	Viscosity and shear stress of biodiesel hybrids @ 60°C.....	51
Table 4.7	FAME composition of Moringa biodiesel.....	51
Table 4.8	FAME composition of Jatropha Biodiesel.....	52
Table 4.9	Chemo-physical properties of Moringa and Jatropha seed oil feedstock...	53
Table 4.10	Chemo-physical Properties of Moringa biodiesel (B100 methyl-ester)....	53
Table 4.11	Important biodiesel fuel properties after production.....	54
Table 5.1	Engine test bed Specification.....	70
Table 5.2	Average biodiesel (B100 and B20) emissions compared to AGO.....	76
Table 5.3	Engine emission and performance of AGO.....	80
Table 5.4	Engine emission and performance of biodiesel hybrids.....	80
Table 6.1	Percentage oil and biodiesel samples yields.....	92
Table 6.2	Chemo-physical properties of seed oils and biodiesel	93
Table 6.3	Thermal properties of the seed oils and biodiesel	93
Table 6.4	Fatty acid Composition/Profile of seed oils and biodiesels	95

Nomenclature

Greek

I Moment of inertia (kg.m^2)

τ Torque (Nm)

P Power (kJ)

ω Angular speed (rpm)

W Work (J)

η Efficiency (%)

ν Viscosity (cSt)

Roman

T Temperature ($^{\circ}\text{C}$)

t Time (mins)

v Speed (m/s)

Dimensionless

θ_1 Initial angular position

θ_2 Final angular position

π Pie

Acronyms and Abbreviation

AGO	Automotive gas oil
AOAC	American Oil Analytical Chemists
ANOVA	Analysis of Variance
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
AV	Acid value
B10	10% Biodiesel in biodiesel blend
B100	100 Biodiesel
BSFC	Brake Specific Fuel Consumption
BSTE	Brake Specific Thermal Efficiency
BME	Brake Mechanical Efficiency
BTE	Brake Thermal Efficiency
CI	Cetane Index
CO	Carbon (II) oxide
CO ₂	Carbon (IV) oxide
CN	Cetane number
CP	Cloud point (°C)
CR	Crude residue
CSVO	<i>Canarium schweinfurthii</i> vegetable oil
EPA	Environmental Protection Agency
ER	Extraction solvent
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acids
FG	Free Glyceride
FID	Flame Induced Detector
FP	Flash Point
GC-MS	Gas Chromatography-Mass Spectrophotometer
GHG	Green House Gas
GWPs	Global Warming Potentials

HC	Hydrocarbons
HVO	Hura Vegetable oil
HVO-ME	Hura Vegetable oil Methyl ester
IP	Institute of Petroleum
J ₅₀ M ₅₀	50% Moringa Hybrids
J ₉₀ M ₁₀	10% Moringa Hybrids
J ₈₀ M ₂₀	20% Moringa Hybrids
J ₇₀ M ₃₀	30% Moringa Hybrids
J ₆₀ M ₄₀	40% Moringa Hybrids
JK	Jatropha using potassium hydroxide as catalysts
JN	Jatropha using sodium hydroxide as catalysts
KOH	Potassium hydroxide
K ₃ PO ₄	Potassium Phosphate
LCA	Life Cycle Assessment
MDG	Millennium Development Goals
ME	Methyl Ester (biodiesel)
MK	Moringa using Potassium hydroxide as catalysts
MN	Moringa using sodium hydroxide as catalysts
MR	Methylation reagent
MT	Metric tonnes
NO ₂	Nitrogen (II) oxide
NO _x	Nitrogen oxides
NAC	NO _x adsorbed catalysts
O ₂	Oxygen
PP	Pour point
PAHs	Poly aromatic hydrocarbons
RI	Refractive Index
RPM	Revolution per minute
SA	Sulphated Ash
SANS	South African National Standards
SCR	Selective catalytic reduction

SOFs	Soluble organic fractions
SO _x	Sulphur oxides
sPM	Solids Particulate Matter
SR	Saponification reagents
SV	Saponification value
TG	Total Glycerides
TGA	Thermo Gravimetric Analysis
ULSD	Ultra low sulphur
VOCs	Volatile organic matter

Abstract

Production, evaluation and comparative testing of biodiesel from *Moringa oleifera* seed oil and selected tropical feedstock oils were undertaken in this study. From studies, Moringa oil has higher oil yields and excellent fuel properties and as a result is a good choice as feedstock to produce biodiesel as well as being an optimizer through the process of hybridisation with other feedstocks, to produce hybrid biodiesel fuels. Production processes were therefore designed to extract oils from the seeds of Moringa, Jatropha, Sandbox tree and Yellow oleander.

Transesterification, a biodiesel production process, was deployed using methanol in the presence of NaOH, KOH as catalysts. The use of residual ash from plantain peels as a local catalyst was evaluated as an established production variable. The study also determined production model protocols for transesterification and optimization of production variables (alcohol/oil ratios, reaction temperatures, reaction time and agitation).

The hybridization process was developed to improve the quality of biodiesel produced from other feedstocks. Hybridization is the co-mingling of oils of different feedstocks before and after transesterification. This became a major contribution of the study. Hybridisation was carried out using two process pathways termed *in situ* and *ex situ* hybridization. Fuel properties of oil feedstocks vary depending on sources and chemo-physical composition and with hybridization, the output is improved and standardized.

Oils and biodiesel from the feedstocks were analyzed and their properties determined; namely, chemo-physical, rheological, thermal and gaseous emission properties. The methodologies used and results obtained were evaluated in accordance with ASTM, AOAC, IP and SANS standards. The produced biodiesel and hybrids were further subjected to engine performance tests and analysis using a four strokes diesel engine (TD 302). The observations were simulated and computed, evaluated and analyzed.

As new players in the alternative fuel market, the biodiesel potential of these feedstocks is huge as a source of fuel for automobiles and other energy needs. Improved specific fuel properties are: viscosity, specific gravity, refractive index, cetane index, fatty acid composition, free and total glycerides, acid value, peroxide value, oxidative stability, density, flash points, pour points and calorific values.

Chapter 1

Introduction

1.1 Introduction

The growing environmental and energy concerns caused by green-house gas emissions from fossil fuels have made biodiesel fuel, which is renewable, an exceptionally attractive energy source for the future [1, 2]. Biodiesel has received increasing interest because it is a promising alternative resource for fuel replacement in compression ignition engines. The growing global demand for biodiesel has revived interest in the discovery of different oil seed feedstocks which may be sustainable, have better fuel properties and are economical [3]. The development of alternative production processes with safer, more economical and more environmentally preferred routes to produce optimized useful products is therefore a necessity.

Biodiesel fuel, which is sourced from seed oils generally, provides an economical source of energy. It has the benefit of producing less gaseous emissions than hydrocarbon fuels. It is also biodegradable and its feedstock is readily available [3, 4]. Because every seed oil does not have the potential for biodiesel production, discovering and identifying feedstocks with acceptable properties for use as biodiesel is of research concern to scientists and engineers [2]. Other sources of commercial biodiesel include canola oil, animal fat, palm oil, corn oil, waste cooking oil [4] have a limited potential because the sources are edible and are required for human consumption.

In recent years, a lot of emphasis has been put on the search for the potential biodiesel feedstocks which can be converted to liquid as well as gas fuels for energy generation. Various feedstocks have been identified as alternative sources of energy fuels. They range from various kinds of oil-based bio-wastes, energy crops (edible and non-edible oil seeds); and recently various aquatic plants identified as bio-oil sources [1].

Oils from *Moringa oleifera*, *Jatropha curcas*, Yellow oleander and Sandbox tree have been identified as potential biodiesel feedstocks in this study. These are non-edible, and they have the potential to produce considerably greater amounts of oils/lipids per hectare than most kinds of terrestrial seed oil plants [1, 3]. All of these seed plants have another advantage. They can be cultivated on marginal lands and therefore do not compete with food or other crops.

Moringa is singled out due to its exceptional qualities. It has a higher lipid content of 40 - 50%, a high level of oxidative stability, a higher percentage of oleic acid content in its fatty acid profile, and above all, it is known as a 'wonder plant' that thrives on every part of the globe.

Chapter 1: Introduction

Because of these excellent properties of Moringa oil and biodiesel produced from it, the selection of feedstocks was centred around it in this study. The author has called the method which was developed to comingle the feedstocks 'hybridisation'. Hybridisation can take two pathways: *in situ* and *ex situ* hybridization.

A critical evaluation of available information suggests that the economic viability of the production process in terms of minimizing the operational and maintenance cost along with maximization of oil-rich seeds properties is the key factor, for successful commercialization of biodiesel fuels. This study also explored and developed an optimized production process using real time models which were in accordance with American Society for Testing and Materials (ASTM) standards. Generally assisted by high petroleum prices and the desire for energy independence, biodiesel has gained political support, reflected in mandates, targets and tax incentives for production in South Africa, Nigeria, South American countries, USA, Canada, Australia and Europe. When used in sustainable manner with all attendant socio-economic benefits, its growth could be phenomenal.

1.2 Background of the study

Worldwide biodiesel production is mainly from edible oils such as soybean, sunflower, canola and palm oil. India and most countries in Africa are not self-sufficient in edible oil production unlike the developed countries. Therefore, non-edible oil seeds available are required to be researched and utilized for biodiesel production. Despite an abundance of forest and plant based non-edible oils such as *Pongamia pinnata* (Karanja), *Jatropha curcas* (Jatropha), *Madhuca indica* (Mahua), *Shorea robusta* (Sal), *Azadirachta indica* (Neem) and *Hevea braziliensis* (Rubber) being available in some countries, not much attempt have been made to use the esters of these non-edible oils as substitute for diesel with the exception of Jatropha [5-10]. Moreover, there are plenty of wastelands available in Nigeria, South Africa and everywhere in Africa, which can be utilized for growing such oil seed crops. Some investigators have obtained commercial biodiesel from some of these oils [5-10].

Moringa, Jatropha and other tropical seed oils are capable of enhancing Africa's chances of meeting the Millennium Development Goals (MDG). Most of the tropical oil seeds grow in almost all parts of the continent of Africa and most significantly in the wild [1].

The socio-economic benefits of developing the entire value chain of Moringa cannot be quantified. It grows in the wild in all parts of the continent of Africa [11, 12]. Based on our findings, a few plantations have been established in South Africa. In Cape Town, Port Shepstone and Pretoria, experimental farms have been established for the development of Moringa biodiesel industry. Mozambique is developing a Moringa biofuels industry with the hope of

Chapter 1: Introduction

contributing to 15% of the national fuel consumption in the next five years [13]. Situated in the Indian Ocean coast of Southern Africa, the Republic is an emerging market and is growing rapidly compared to its developed neighbor, South Africa. Mozambique is currently positioning itself as a major biofuels producer from *Moringa* and *Jatropha*. Biofuels project in Mozambique started in 2007 and so far, foreign companies have invested approximately US \$710 million [13].

Commercial sustainability of *Moringa oleifera* has proven itself over the past decade with the investment project the first of its kind from the wonder plant which confidently returns 14.5% for the harvest and sale of the crop with constant harvest and sales of the seeds [13]. Global energy companies are purchasing post-harvest for biodiesel production. Platinum Management Associates have established the first biofuel station in Africa. Though the global market price for *Moringa* oil is in its infancy, researchers foresee prices equal to that of crude soy bean oil (currently US\$871 per MT) for biodiesel or crude palm oil (currently US\$798 per MT) [13]. *Moringa* is supported for water treatment in replacement of alum; Senegal is exploiting *Moringa* to deal with malnutrition in children. Ghana is making tremendous efforts in using the leaves for nutritional supplements, and others are exploiting the seeds for its oil and the roots and barks for medicinal purposes [14].

In Nigeria, the Raw Materials Research and Development Council (RMRDC) is already domesticating *Moringa* across the country; one finds its products being marketed everywhere in Nigeria. In Southern Africa, Zimbabwe and Mozambique, plantations have been established and fuelling stations based on *Moringa* biodiesel have been established. In South Africa, biodiesel researchers are making efforts to position biomass bioenergy with *Moringa* and *Jatropha* at the forefront. Some plantations are at the pioneering stages. *Moringa* has great potential for the benefit of humankind. There is ongoing research by the Green Energy Solution Research Group at the University of KwaZulu-Natal, South Africa, which is pioneering the use of *Moringa* for internal combustion engines. The Department of Agriculture in Malawi has set up a system to develop the plant's seed for use as feedstock in biofuel production.

The *Moringa* Oil Manufacturing Plant of SECRA in Malawi is intending to use the oil harvested from the *Moringa* seeds to produce biodiesel which will be exported to the United States [13]. The plant's capacity is 150 million gallons of *Moringa* seed oils per year. While *Moringa* oil is already being anticipated as a source of second generation biodiesel, it wasn't considered to be an oil source by many because it has so many food uses. However, experts have advocated its use as a viable and sustainable biodiesel feedstock [13].

Of general significance is the fact that the increased use of diesel in the agriculture and transportation sectors has resulted in a diesel crisis. Finding an alternative fuel for petroleum

Chapter 1: Introduction

diesel fuel is critically important for many nations' economy and security [13]. The complete substitution of oil imports for the transportation and agricultural sectors is the biggest and toughest challenge for Nigeria and South Africa. Bio-diesels as an alternative to diesel can make farmers self-sufficient in energy requirements.

Quite a number of researchers have shown interest in studies of this nature on different seed oils. Eloka-Eboka *et al.* [15] (Jatropha and Yellow oleander oil), Agarwal and Das [7] (Linseed oil), Eloka-Eboka [2] (*Prosopis africana* seed oil), Igbum and Eloka-Eboka [16] (*Hura crepitans*, *Telfaria occidentalis*, *Cucumeropsis manii* and *Canarium schweinfurthii*) and Raheman [17] (Mahua oil) have investigated the suitability of different vegetable oils in diesel engines as biodiesel fuels.

1.3 Developments in the use of biodiesel

Biodiesel fuel is a nearly colourless liquid made of less viscous, saturated and/or unsaturated and short-chained aromatic hydrocarbons containing mainly carboxylic acids. It has properties similar to petroleum-based diesel. It has been improved from its poly-saturated bond nature as original vegetable oils with lower viscosities. In particular, it has a relatively high cetane index/number, which makes it an attractive blend component to improve petroleum-based oil, or as a direct substitute (Ajiwe *et al.*) [18], or as hybrids.

The first commercial production of biodiesel took place in Austria in 1988 and since then the Austrian Biofuels Institute has played a pioneering role in establishing the European market for biodiesel. By 1996, production in Europe peaked at 570 MLpa, but in the last few years, it has grown to nearly 2 300 MLpa and is geometrical [24].

The International Energy Agency reported in 1998 that 21 countries around the world had implemented biodiesel projects but mostly at relatively small capacities. The North American market has only now just started to grow. In all, world biodiesel production in 2003 has reached 3200 MLpa with the expectation of high growth rates for the future [19]. Africa's contribution to biodiesel production has just begun with research at different developmental stages. At present, there is an emphasis on biofuel/bioethanol production in Nigeria with the federal government's establishment of its plants and ethanol crop plantations across the country. In fact, within the last few years, the Nigerian government has seen the need to de-emphasize the total dependence on petroleum-based fuels especially with the uneasy calm of the Niger Delta (the major source of petroleum in Nigeria), and to focus on alternative and renewable energy for sustainable development [20].

1.4 History and origin

Rudolph Diesel was educated at the predecessor school to the Technical University of Munich, Germany. In 1878, he was introduced to the work of Sadi Carnot, who theorized that an engine could achieve much higher efficiency than the steam engines of the day [21]. Carnot envisioned a cycle in which a gas is compressed, heated, allowed to expand, and then cooled. After the gas is cooled, the new cycle begins. Mechanical energy is used to compress the gas and thermal energy to heat it. In turn, expansion of the gas yields mechanical energy, and its cooling yields thermal energy. The net result is conversion of thermal energy to mechanical energy [22]. Diesel sought to apply Carnot's theory to the internal combustion engine.

The efficiency of the Carnot cycle increases with the compression ratio – the ratio of gas volume at full expansion to its volume at full compression. Nicklaus Otto invented an internal combustion engine in 1876 that was the predecessor to the modern gasoline engine. Otto's engine mixed fuel and air before their introduction to the cylinder, and a flame or spark was used to ignite the fuel-air mixture at the appropriate time [23]. However, air gets hotter as it is compressed, and if the compression ratio is too high, the heat of compression will ignite the fuel prematurely. The low compression ratios needed to prevent premature ignition of the fuel-air mixture limited the efficiency of the Otto engine. Rudolph Diesel wanted to build an engine with the highest possible compression ratio. He introduced fuel only when combustion was desired and allowed the fuel to ignite on its own in the hot compressed air. Diesel's engine achieved efficiency higher than that of the Otto engine and much higher than that of the steam engine [23].

Diesel's engine also eliminated the trouble prone electric-spark ignition system. Diesel received a patent in 1893 and demonstrated a workable engine in 1897. Today, diesel engines are classified as "compression-ignition" engines, and Otto engines are classified as "spark-ignition" engines. Diesel's motivation was not only to improve efficiency but also to bring the benefits of powered machinery to smaller companies. He used peanut oil as the fuel for demonstration of his engine at the 1900 World's Fair [23], which was successful. The early 20th century saw the introduction of gasoline-powered automobiles. Oil companies were obliged to refine so much crude oil to supply gasoline that they were left with a surplus of distillate, which is an excellent fuel for diesel engines and much less expensive than vegetable oils. On the other hand, resource depletion has always been a concern with regard to petroleum, and farmers have always sought new markets for their products. Consequently, work has continued on the use of vegetable oils as fuel [1, 23].

Early durability tests indicated that engines would fail prematurely when operating on fuel blends containing vegetable oil. However, engines burning vegetable oil that had been

Chapter 1: Introduction

transesterified with alcohols exhibited no such problems and even performed better by some measures than engines using petroleum diesel [24]. The formulation of what is now called biodiesel came out of those early experiments. The energy supply concerns of the 1970s renewed interest in biodiesel, but commercial production did not begin until the late 1990s. The National Biodiesel Board reported production of 500 000 gallons (32.6 barrels per day) in 1999 and 6.7 million gallons (437 barrels per day) in 2000 [23].

1.5 Statement of problems

There are already major problems of pollution resulting from CO₂ evolution and future crisis of energy due to shortage of energy sources in the world. Greenhouse gas emissions and fossil fuels combustion are calamities that have bedeviled our environments. Energy requirements are increasing continuously, because of increases in industrialization and population. The basic sources of this energy are petroleum, natural gas, coal, hydro and nuclear. The major disadvantage of using petroleum based fuels is atmospheric pollution and climate change created by the use of petroleum diesel. Petroleum diesel combustion is a major source of greenhouse gases (GHG). Apart from these emissions, petroleum diesel is also major source of other air contaminants including NO_x, SO_x, CO, particulate matter and volatile organic compounds (VOCs). The present work is a small step towards sustainable development by making use of a combination of renewable and alternative fuels such as biodiesels of different vegetable oils and also hybridising them for improved efficiency. Finding an alternative fuel to petroleum diesel is critical to any nation's economy and security. The complete substitution of oil imports for the transportation and agricultural sectors is the biggest and toughest challenge for South Africa and other parts of the world. In modifying existing facilities for comprehensive research studies on biodiesels and their feasibility for use in the compression ignition engines, this research work will provide the template for such design.

1.6 Motivation

Development in the biodiesel industry and the use of biodiesel in South Africa is not only in its infancy but is unfortunately, a low-priority sector. The underlying motivation of this research which has produced quite a number of publications is to developed new production pathways for biodiesel through hybridization process. Hybridization of biodiesel feedstock is a new development process presented in this study. Researchers all over have not tried such a process as an option. It is therefore a new approach in biodiesel developments. Works carried out on hybridization from this study has been accepted for publication in Energy Sources Part A as a result of its novelty and has been presented at the Domestic Use of Energy Conference (DUE-2014) in Cape Town and the proceeding published in IEEE Explore database. Another

Chapter 1: Introduction

motivation is that in producing, evaluating and testing of biodiesel from non-edible oil feedstock of Moringa and other tropical feedstock and the development of the optimization models for production, it creates an avenue for commercial scale-up and technology adaptation. The potentials of these feedstock are highlighted which will pave way for further research.

1.7 Aims and objectives of the study

The aim of this study is to produce, evaluate, and test biodiesel fuels produced from Moringa oleifera seed oils and other selected tropical feedstocks. The objectives involve the following:

1. To optimize and determine various effects of process variables on the production and properties of biodiesel by manipulating transesterification variables using NaOH, KOH and other replaceable hydrogen of metallic salts as local catalysts;
2. To carry out study of the biodiesel production properties of selected tropical feedstocks using metallic salt as catalysts;
3. To evaluate chemo-physical, thermal and rheological properties of the produced biodiesel fuels and hybrids in comparison with AGO and other feedstocks;
4. To evaluate the environmental impact and gaseous emissions of biodiesel fuels and blends of selected feedstocks; and
5. To conduct engine performance and emission profiles of biodiesel fuels from Moringa oleifera and Jatropha curcas seed oils and hybrids.

1.8 Significance of the study

This study is a step towards sustainable development of biodiesel by making use of feedstocks that are non-edible, available and have excellent properties. The choice of Moringa for the hybridization of other tropical feedstock in order to improve their quality parameters is of research interest. The engine performance testing over a period of wide range of throttle in the internal combustion engines and the lower gaseous emission shows that biodiesel fuels are energy fuels and also environmentally friendly.

Other significance of the study includes:

- To enhance research activities for biodiesel development and commercialisation.
- To modify existing facilities for comprehensive research studies on biodiesels of locally available non-edible oils of Nigerian and South African origin and their feasibility study as fuels for compression ignition (CI) engines;
- To produce and optimize biodiesel (B100) production using transesterification methods;
- To produce blends and hybrids of biodiesel of different feedstocks with AGO;
- Comparative study of bio-diesels and AGO and blends in compression ignition engines;

Chapter 1: Introduction

- Compare the results to those of conventional fuel diesels (AGO);
- To study performance, thermal, combustion and emission characteristics of biodiesel operated CI engines;
- Demonstrate the environmental benefits of biodiesel in diesel engines;
- Disseminate research results and other information on bio-derived fuels;
- To stimulate further research activity related to the biofuel industry; and
- Create awareness.

The present work is a step towards sustainable development by making use of biodiesels of the present seed oils, hybrids and blends which are renewable in nature together with the latest developments in the field of renewable and alternative diesels for internal combustion engines. It will be of immense help to the ongoing programmes undertaken by the South African project on oil seeds as it is contained in the renewable energy master plan expected to take effect from 2016 and also in creating research ambience amongst researchers.

1.9 Scope of work

- (1) Exploring the most efficient method(s) of extracting oil from *Moringa oleifera* and other selected tropical seed oils.
- (2) Production of biodiesel by transesterification process and ascertaining the appropriate temperature, reaction time, catalyst type and alcohol/oil ratio of conversion or yield.
- (3) Evaluating the chemo-physical properties of the oil, its biodiesel and blends together with thermal properties and gaseous emissions.
- (4) Performance and technical evaluation of the biodiesel and its blends in an IC engine, and making comparisons with ASTM standards.

1.10 Layout of the thesis

Chapter 1 highlights the background of the study and motivation for the research. It also presents the rationale and significance of the development of biodiesel from selected feedstocks. The overall aims and objective are succinctly presented supported by literature related to the world of biodiesel from seed oils. A historical overview of the early development of diesel engines and the need for alternative and renewable energy against the backdrop of the present utilization of fossil fuels is presented. The thesis as a whole is a research outcome of publications and conference papers as required by the University of KwaZulu-Natal for the award of the prescribed degree.

Chapter 1: Introduction

Chapter 2 is the first contribution which presents the optimization of the various effects of process variables on the production and properties of biodiesel fuels produced from selected feedstock. Specific indispensable properties of biodiesel for use in the engines were also evaluated.

Chapter 3 is the second contribution on the evaluation of the impact of gaseous emissions on the environment of the biodiesel fuels and blends from the four selected tropical seed oil feedstocks which are environmentally friendly for those in the vicinity as well as for the global environment.

Chapter 4 is the third contribution and presents a new approach in biodiesel development which is hybridization of feedstocks *in situ* and *ex situ* for improvement of properties and production of new products. Moringa and Jatropha seed oils were used as prospective case studies. This opens a new vista to hybridization and its other forms which include poly-hybridization.

Chapter 5 is the fourth contribution and presents engine performance tests which were conducted on the biodiesel and their hybrids. Also, there was a general characterization of emission from the hybrids. The engine performance was comparable to the conventional petroleum diesel and could favourably serve as a replacement with a better emission profile.

Chapter 6 is the fifth contribution which was an investigative study of the general properties of two selected non-edible feedstocks of Jatropha and Yellow oleander employing locally made catalysts for transesterification/conversion to biodiesel. This contribution attracted the best paper award at an international conference of the World Society for Sustainable Energy Technologies.

Chapter 7 presents conclusions and makes recommendations for future work.

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Chapter 2

Paper 1, OEPV-PPME

Optimization and Effects of Process Variables on the Production and Properties of Methyl-Ester Biodiesel

Optimization and Effects of Process Variables on the Production and Properties of Methyl-Ester Biodiesel

Abstract - Optimization of production process in biodiesel production holds huge prospects. A reduced cost option is the optimization of process variables that affect yields and purity of biodiesel, which was achieved in this study. Optimized production and direct effects of process variables on the production and quality of methyl ester biodiesel fuels from the non-edible seed oils of Sandbox seed was carried out. Catalyst nature and concentration, alcohol to triglyceride molar ratio, mixing speed, reaction time and temperature were taken into consideration as variables to their individual response on the yields, viscosity and specific gravity of the methyl esters produced. These are specific indispensable properties of biodiesel for use in combustion ignition engines. Optimized concentrations were 0.3 to 1.5% v/w and two mole ratios of 3:1 and 6:1. Time of reaction was varied (5 minutes to 30 minutes) with temperatures (38°C and 55°C ≤ temp. of methanol). Also, the effect of methanol in the range of 4:1 and 6:1 (molar ratio) was investigated, keeping catalyst type, reaction time and temperatures constant. Effects of KOH and NaOH on the transesterification were investigated with concentration kept constant at 1%. The general response in this study was that at optimized rate of agitation (800 rpm), optimized reaction time was as low as 5 minutes, 1% catalyst concentration of NaOH was the optimal concentration, and 55°C was the optimal temperature with attendant high yields. However, there are variations with the nature of feedstock as the work further exposed. These high points are particularly of interest to guide against process backdrop.

Index Terms - *Optimization, Process variables, Effects, Methyl-Esters, Production, Sandbox seed oil*

2.1 Introduction

Biodiesel possessing the best properties were obtained using KOH as catalyst in many studies [1-5]. Besides, many other studies achieved best results using NaOH [6-9]. Methanolysis with 1% wt of either sodium hydroxide or potassium hydroxide catalyst resulted in successful conversion giving the best yields and viscosities of the esters in most of the literature reviewed. It was observed that the product volume steadily increased from 0.5% w/v concentration of the catalyst until it reaches its peak at 0.9% wt/v catalyst concentration. Thereafter, a decrease was witnessed. Catalyst concentration levels greater than 1% may have favoured the reverse reaction [5]. One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in

which a large excess of alcohol is required to drive the forward reaction. For maximum conversion to the ester, a molar ratio of 6:1 was mostly used [1-4, 8, 10].

In other studies, the optimum ratio was 10:1 [2, 8-11]. In this study, optimization of the production process was conducted and the effects of process variables obtained as they affect the yields, purity and important properties of the methyl ester obtained during the transesterification process with the aim of reducing cost and achieving high level purity biodiesel that will be comparable with ASTM standards. This assisted in producing different grades of methyl esters and blends while the ones at optimal conditions were also established with reduced costs, better properties, effects, high yields and purities attained. The effects of transesterification variables on the yields and properties of biodiesel of four tropical seed oils were earlier studied by Igbum *et al.* [12] which provided a leeway to the present study as Sandbox seed oil was also evaluated. The objective of the present study therefore was to optimise the application of the process variables and ascertain the effects thereof on the production process and properties of the methyl ester biodiesel thereby reducing the cost and rigours of production.

2.2 *Materials and methods*

2.2.1 *Seed plant of study: Hura crepitans L [13]*

The Sandbox tree (*Hura crepitans*; syn. *Hura brasiliensis* Wild.), also known as Possum wood and Jabillo, is an evergreen tree of the spurge family (*Euphorbiaceae*), native to tropical regions of North and South America in the Amazon rain forest. The tree however extends to all regions of the world including Africa. In Nigeria, it thrives in the middle belt. Oils extracted from the derived seeds are also used as a purgative. The leaves are used against eczema. Its pale, yellow or brown soft wood is used for furniture under the name Hura. In summary, the Sandbox tree often can be found in nearly pure stands on mostly loam soil in the flat coastal regions. In Africa, it's invasiveness in Tanzania has been reported [14]. The seeds for this study were collected from Makurdi metropolis, Nigeria during the dry season (December-February). The seeds usually fall to the ground during the dry season; for this study, they were sun dried for several weeks and then crushed whole, milled and grounded together with the hard cotyledonous shells. This was due to the toughness of the shell which could not be easily separated from the mesocarp. The ground seeds were sieved to remove shells before extraction.

2.3 *Preparation of methyl esters*

One hundred millilitres of *Hura crepitans* oil was measured and poured into a large beaker. The oil was pre-treated by heating to a temperature of 70°C using a Bunsen burner to remove the

remains of solvent or moisture content and the temperature was monitored using a thermometer until it dropped to the required temperature. The heated oil was then poured into a blender which was switched off. The prepared methoxide from the PET bottle was emptied into the oil in the blender and the blender switched on; the mixture was blended for the required time of mixing.



Figure 2.1a: Fully grown pods of *Hura crepitans* seed hanging on the tree; 2.1b: Pulverized Hura seeds; 2.1c: Hura seeds and 2.1d: Biodiesel and glycerine after separation

The blender was switched off. The mixture was immediately transferred from the blender to a one litre PET bottle and closed tightly. The PET bottle was occasionally opened to allow some air in so as to avoid contraction due to cooling of the oil. The mixture was allowed to settle for 24 hours after which a dark colour glycerine by-product was observed separated from the pale liquid above with the biodiesel at the top layer. It should be noted that the biodiesel varies somewhat in colour according to the oil used and so does the by-product layer at the bottom [15]. Optimization procedures were based on a repetitive process controlled by calibrated factors, dependent and independent. This included: alcohol/oil mole ratio (6:1 and 4:1), temperature of reaction (38°C, 55°C), reaction time (5s, 30s), reaction speed, catalyst type and concentrations (KOH and NaOH); while the properties considered are: biodiesel/methyl ester yields, specific gravity, viscosity and fatty acid composition.

2.4 Biodiesel separation

Once the reaction was completed, two major products existed: glycerine and biodiesel. The clear liquid (biodiesel) found at top layer was decanted into a graduated beaker, the remainder which was difficult to decant was then transferred into a separatory funnel and allowed to settle (Figure 2.1c). The stopcock of the separatory funnel was opened and glycerine was first collected because it forms the lower layer of the mixture. The remaining liquid which was difficult to decant was transferred into a separatory funnel and allowed to settle. The stopcock of the separatory funnel was opened and glycerine collected first because it forms the layer below. The remaining top layer which is the biodiesel was siphoned off into a beaker. In some cases a centrifuge was used to separate the two materials [14].

2.5 Biodiesel washing

The biodiesel was turned into a separatory funnel and covered by a lid; equal amount of tap water was added. The funnel was swirled several times, after which it was allowed to settle for a few minutes and the water drained off from the bottom by opening the stopcock. This procedure was repeated twice using two different separatory funnels. In each washing, a separatory funnel was used until washing was effected. After washing, the biodiesel was heated to 100°C and allowed to cool. The reason for the heating was to dry the oil [14].

2.6 Determination of the effects of catalyst type on yields and specific properties

Base catalysts (NaOH and KOH) were used. Catalyzed processes dominate current commercial production. These reactions are relatively fast but are sensitive to water content and free fatty acids. Typical base concentrations are 0.3% to 1.5% based on the weight of oil. When sodium methoxide is used, the concentration can be 0.5% or less. Most researchers use NaOH as the catalyst. There are some operations that use KOH, in spite of the higher cost, because the potassium can be precipitated as K_3PO_4 fertilizer when the products are neutralized using phosphoric acid. However, this can make meeting water effluent standards a bit more difficult because of limits on phosphate levels.

2.7 Preparation of methoxide

To prepare methoxide, 1 g of KOH or NaOH was measured into a handy-sized light plastic bag using the scale (weighing balance). 20 ml of methanol was also measured using a graduated measuring cylinder and this was turned into a PET bottle. The KOH or NaOH from the plastic

bag was mixed with the methanol and the container closed tightly, the container was swirled several times until all the lye was completely dissolved [14].

2.8 Determination of the effects of alcohol/oil molar ratio on yields and specific properties

Usually 60% to 100% excess methanol is added to ensure that the reaction goes to completion. In general, the reaction can be encouraged to progress by adding an excess of one of the reactants or by removing one of the products. A base catalyzed process typically uses an operating mole ratio of 6:1 of alcohol rather than 3:1 ratio required by the reaction. The reason for using extra alcohol is that it drives the reaction closer to the 99.7% needed to meet the total glycerol standard for fuel grade biodiesel, the unused alcohol must be recovered and recycled back into the process to minimize operating cost and environmental impacts. Methanol is considerably easier to recover than ethanol. Therefore, two mole ratios of 4:1 and 6:1 were used.

2.9 Determination of the effects of reaction time on yields and specific properties

Based catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol:triglyceride ratio [16]. The typical procedure is as described above. Time of reaction was varied at 5 minutes to 30 minutes due to the speed of the mixer. It is important to note that, there is a conversion of the triglycerides to di-glycerides and then mono-glycerides/glycerol. If the reaction does not go into completion, mono-glyceride/glycerol separation will not take place and therefore the methyl ester will not meet ASTM standards. An ASTM standard for total and free glyceride specifies the minimum amount retainable in any completely reacted transesterified methyl ester. The requirements are 0.25% maximum and 0.02% maximum for total and free glyceride respectively. These parameters are very important in biodiesel development to determine complete or incomplete transesterification reaction and the quality of the products.

2.10 Determination of the effects of temperature on yields and specific properties

Temperature had no detectable effect on the ultimate conversion to ester. However highest temperatures decrease the time required to reach maximum conversion [16]. Since this reaction is between the liquids and also due to the fact that fats and alcohols are not totally miscible, transesterification therefore will be a relatively slow process. As a result, a vigorous mixing is

required to increase the area of contact between the two immiscible phases [17]. Temperature was varied between 38°C and 55°C, which is below the boiling point of methanol. The experiments performed were summarised in the table of experiment in Appendix C

2.11 Results and discussion

2.11.1 Effects of alcohol/oil molar ratio on the yields and specific properties of Hura vegetable oil methyl esters (HVO-ME)

One of the most important parameters affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3 mol of ester and 1 mol of glycerol, but most researchers found that excess alcohol was required to drive the reaction close to completion. In this work, methanol was used. The effect of methanol in the range of 4:1 and 6:1 (molar ratio) was investigated, keeping catalyst type constant; catalyst type, reaction time and temperature were varied with each reaction keeping one or two variable(s) constant at a time. It was found that the ester yields increase with molar ratio of 6:1 with 97% yield for HVO-ME (Fig. 2.2, Table 2.1, and Fig. 2.4). Lower yields were obtained when the molar ratio of 4:1 was used. For low values of molar ratio, the ester yield was sensitive to the concentrated NaOH for HVO-ME.

The specific gravity of the ester varies for the two molar ratios used; HVO-ME did not show specific trends in the values of specific gravity that can be believed to be as a result of the effects of molar ratio rather, the trends suggest that these results emanate from the catalyst type used. Figure 2.2 shows this evidence. Specific gravity was best with NaOH. HVO-ME showed viscosities that were within specification for 6:1 and 4:1 with only one catalyst type (NaOH) as shown in Figures 2.3 to 2.6. Therefore, once more, it can be observed that the alcohol/oil molar ratio has no effect on the viscosity of this methyl ester although viscosities were greatly enhanced with NaOH catalyst as shown rather than KOH.

Table 2.1: Alcohol/Oil ratio on acid value, refractive index, carbon residue and sulphated ash

	AV (mgKOH/g)		RI		CR (% mass)		SA (% mass)	
	4:1	6:1	4:1	6:1	4:1	6:1	4:1	6:1
NaOH (replicates)	0.561	0.560	1.466	1.467	0.016	0.019	0.004	0.010
	0.561	0.560	1.467	1.452	0.016	0.014	0.005	0.007
	0.561	0.560	1.467	1.452	0.017	0.017	0.006	0.006
	0.561	0.560	1.467	1.451	0.014	0.013	0.004	0.006

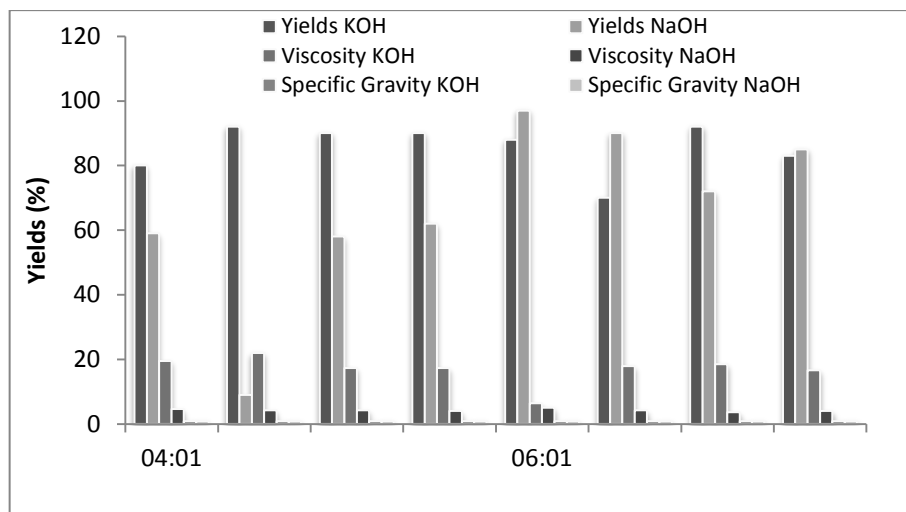


Fig. 2.2: Effects of alcohol/oil ratio on some specific gravity and yields

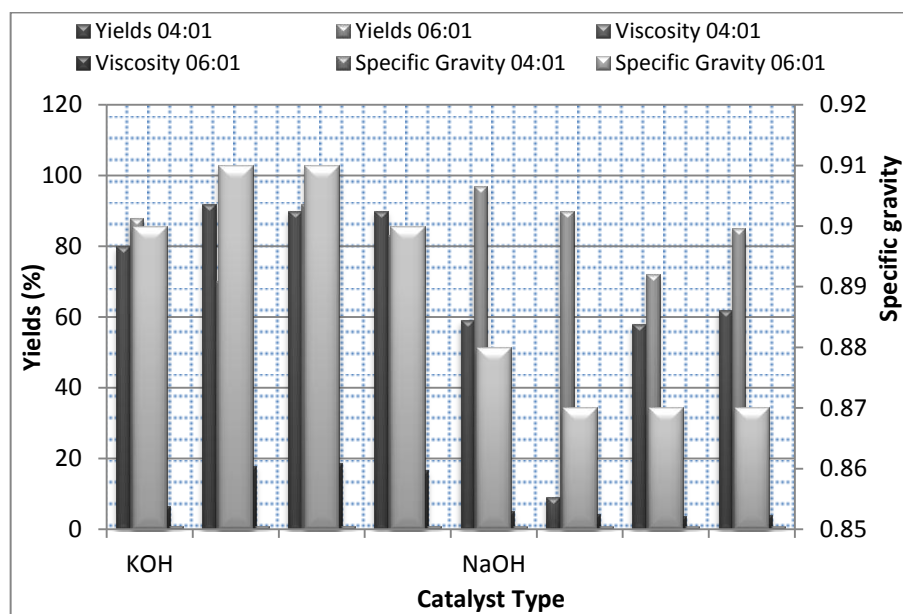


Fig. 2.3: Effects of Catalyst Type on some specific chemo-physical properties

2.11.2 Effect of reaction time

The mixing intensity appears to be of particular importance for the transesterification process. It increases the impact area between oils and catalyst-methanol solution. Mixing facilitates the initiation of the reaction. Without mixing, the reaction occurred only at the interface of the two layers and was considered too slow to be feasible. In this study, a mixing rate of 800 rpm was used. The yields, viscosity and specific gravity of methyl esters are shown in Figures 2.3, 2.5 and 2.6 and Tables 2.2 to 2.6. It was observed that the reaction of methanolysis was optimally completed at 5 minutes of mixing due to the speed of the rotor. For all cases, looking at the yields, viscosities and specific gravity, these did show significant difference when the time of

mixing was increased [17, 18]. The effect of agitation on the transesterification of vegetable oil was studied and concluded that higher agitation promoted the homogenization of the reactant and thus lead to higher yields. Rashid and Anwar [19] in their research also noted that the yield of methyl esters at 360 rpm and 600 rpm is the same which was 96% after 2 hours of reaction.

This goes to show that if the rate of agitation is very high, the time of mixing can be reduced to as low as 5 minutes of reaction as can be deduced from the graph. This is because at 5 minutes, high yields (80%) were equally obtained for HVO-ME using KOH (Table. 2.3). Specific gravity and viscosities within specification were also obtained when a reaction time of 5 minutes was used especially with NaOH. Leung and Guo [20] in their work, observed that ester content increases with reaction time at the beginning, reached a maximum at a reaction time of 15 minutes at 70°C, and then remaining relatively constant even with increasing further the reaction time. The results on an extension of the reaction time from 15 minutes to 30 minutes had no significant effect on the conversion of triglycerides, but lead to a reduction in the product yield; the yield of the product with the same ester content decreased from 87.5% to 85.3%, dropped by about 2%. This is because a longer reaction enhanced the hydrolysis of esters (reverse reaction of transesterification), resulting in a loss of esters as well as causing more fatty acid to form soap.

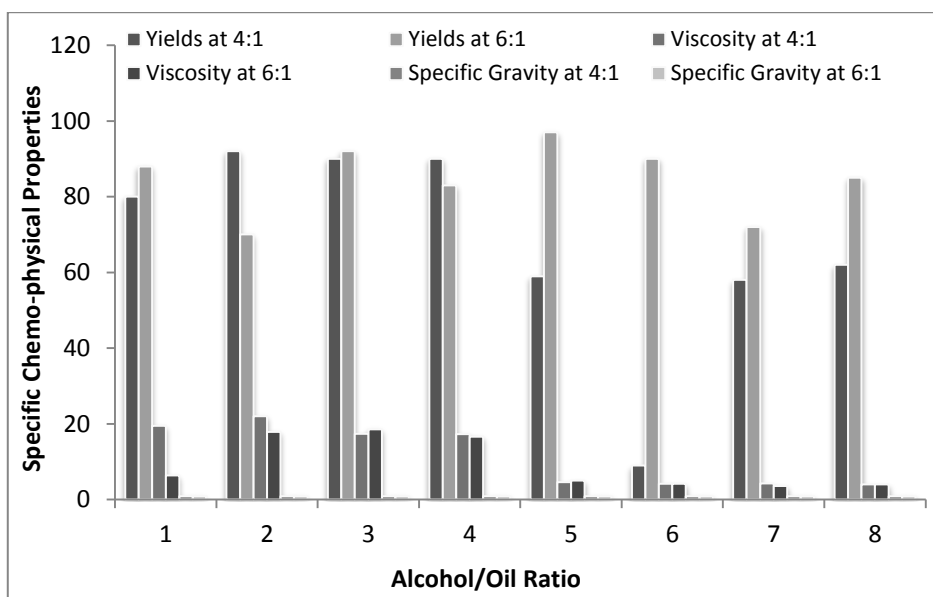


Fig. 2.4: Effects of alcohol/oil ratio on some specific chemo-physical properties

Table 2.2: Reaction time on water and sediment, flash point and cloud point

NaOH	W & S (% vol)		FP (°C)		CP (°C)	
	5	30mins	5	30mins	5	30mins
4:1	0.10	0.05	140	148	+1	+1
	0.10	0.10	142	146	-1	+1
6:1	0.05	<0.05	136	126	0	+4
	<0.05	<0.05	134	130	0	+4

Table 2.3: Reaction time on pour point, total and free glycerine of HVO-ME

NaOH	PP (°C)		TG (% mass)		FG (% mass)	
	5	30mins	5	30mins	5	30mins
4:1	-4	-4	0.126	0.129	0.006	0.006
	-6	-4	0.141	0.129	0.006	0.005
6:1	-9	-6	0.108	0.124	0.005	0.006
	-9	-3	0.107	0.124	0.002	0.007

2.11.3 Effects of catalyst type on yields, viscosity and specific gravity of methyl esters

The effects of KOH and NaOH on the transesterification of the oils were investigated with the concentration kept constant at 1%. Figure 2.3 shows the effects. This effect on ester yields as can be observed from Figures 2.3 to 2.6, showed that both NaOH and KOH catalyst exhibited appreciable behaviour especially at the ratio of 6:1 where NaOH also gave the best yield (97%) while it was poor at 4:1. Increase in reaction time from 5 minutes to 30 minutes did not improve the yields and viscosities for HVO-ME as earlier established. It also had no significant effects on specific gravity. Alcohol/oil molar ratio and the nature of catalyst can be thought to be responsible for the variation in yields, viscosity and specific gravity.

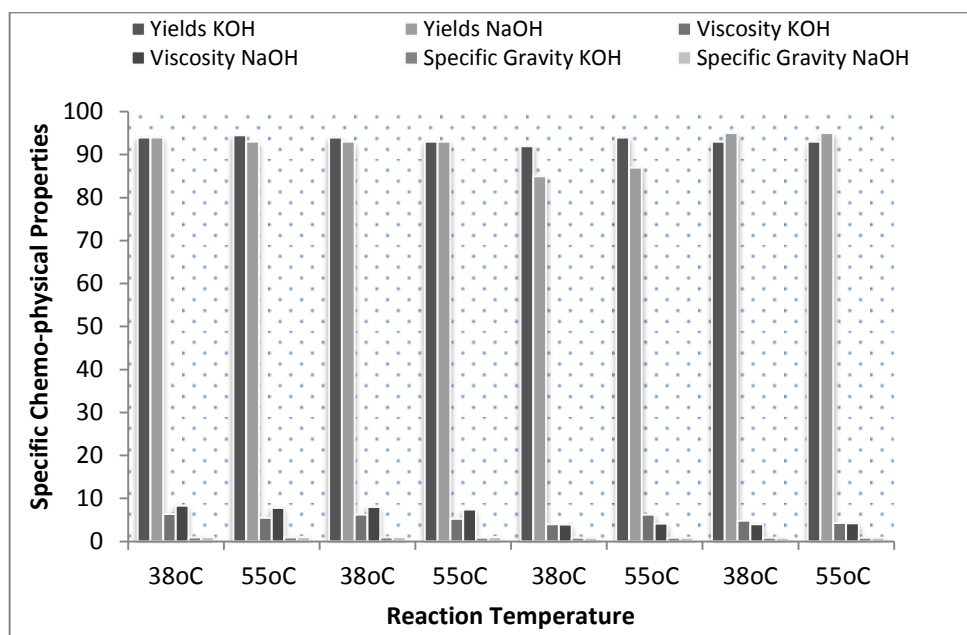


Fig. 2.5: Effects of reaction temperature on some specific chemo-physical properties

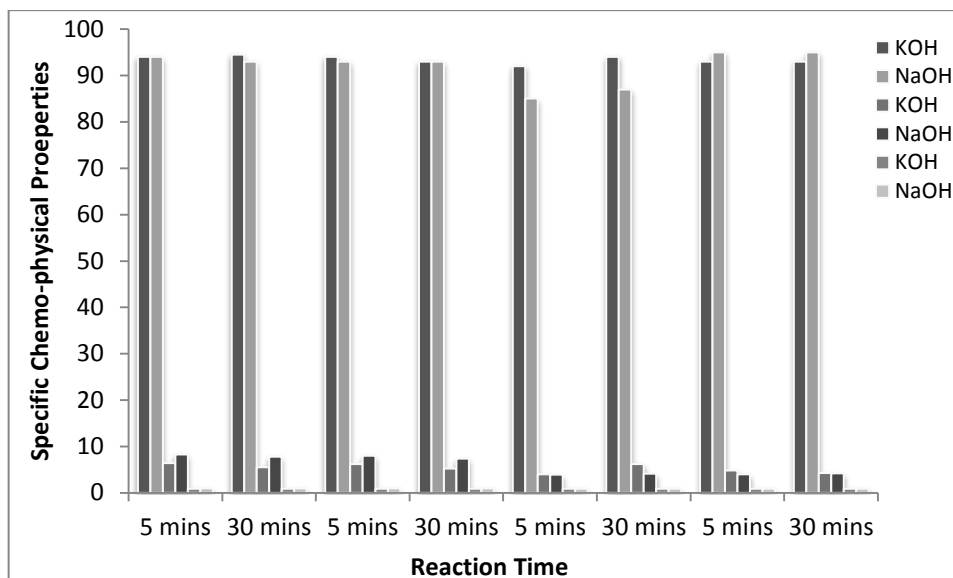


Fig. 2.6: Effects of reaction time on some specific chemo-physical properties

2.11.4 Effects of temperature on yields, viscosity and specific gravity

Alkaline alcoholysis of vegetable oils is normally performed near the boiling point of the alcohol [21, 22]. The reaction temperature above boiling point of alcohol is ignored because at a high temperature, it seems to accelerate the saponification of glycerides by the base catalyst before completion of the alcoholysis [23]. In this study, experimental trials were carried out at temperatures of 38°C and 55°C. Figure 2.5, Tables 2.5 and 2.6 show the effect of temperature on yields, viscosities and specific gravity as analysed. Several researchers found that temperature increase influences the reaction in a positive manner [24-29]. It was found that the ester yield slightly decrease above 50°C reaction temperature. This may be due to a negative interaction between the temperature and catalyst concentration following the side reaction of saponification [30, 31]. High process temperature tends to accelerate the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification process. Sinha *et al.* [32] in their study concluded that the effect of reaction temperature on the ester yield and the viscosity of the ester decreases as the reaction temperature increases above 55°C. An insignificant increase in the ester viscosity with reaction temperature is observed.

Table 2.4: Effect of reaction time on acid value, refractive index, carbon residue and sulphated ash

NaOH	AV (mgKOH/g)		RI (limitless)		CR (% mass)		SA (% mass)	
	5	30 mins	5	30 mins	5	30 mins	5	30 mins
4:1	0.561	0.561	1.466	1.467	0.016	0.017	0.004	0.006
	0.561	0.561	1.461	1.467	0.016	0.014	0.005	0.004
6:1	0.560	0.560	1.467	1.452	0.019	0.017	0.010	0.006
	0.560	0.560	1.452	1.452	0.014	0.013	0.007	0.006

Table 2.5: Effect of reaction temperature on water and sediment, flash point and cloud point of HVO-ME

NaOH	W & S (% vol)		FP (%)		CP (%)	
	38 ⁰ C	55 ⁰ C	38 ⁰ C	55 ⁰ C	38 ⁰ C	55 ⁰ C
4:1	0.10	0.10	148	142	+1	-1
	0.05	0.10	148	146	-1	+1
6:1	0.05	<0.05	136	134	0	0
	<0.05	<0.05	126	130	+4	+4

Table 2.6: Effect of reaction temperature on pour point, total and free glycerine

NaOH	PP (°C)		TG (% mass)		FG (% mass)	
	38 ⁰ C	55 ⁰ C	38 ⁰ C	55 ⁰ C	38 ⁰ C	55 ⁰ C
4:1	-4	-6	0.129	0.129	0.006	0.009
	-4	-4	0.126	0.141	0.006	0.005
6:1	-9	-9	0.108	0.107	0.005	0.002
	-6	-3	0.124	0.124	0.006	0.007

W & S: water and sediments; FP: flash point; CP: Cloud Point; PP: Pour points; TG: Total glycerine
FG: Free glycerine; AV: Acid value; RI: Refractive Index; CR: Carbon residue; SA: Sulphated ash

From Figures and Tables shown, increase in temperature did not improve the yield, viscosities and specific gravity of the methyl esters. This may be because as the reaction proceeds, there is increase in temperature naturally. Samples were introduced at 55°C during reaction; an increase in temperature as reaction proceeds further was due to interaction during mixing above 55°C which do not favour an increase in yields, viscosities and specific gravity.

2.12 Conclusion

In this study, 1% catalyst concentration which is the optimal concentration was used and established. An increase or decrease may affect the yield, viscosity and specific gravity of these methyl esters. Temperature had no detectable effect on the ultimate conversion to ester. However, higher temperature decreases the time required to reach maximum conversion [16]. Since this reaction is between the liquids and also due to the fact that fats and alcohols are not totally miscible, transesterification is a relatively slow process. As a result, a vigorous mixing is required to increase the area of contact between the two immiscible phases [33]. Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide-methanol solution. Methanolysis was conducted at different reaction speeds of 180 rpm, 360 rpm and 600 rpm; the yield of methyl esters versus time at different rate of mixing was influenced. It was observed that the reaction was incomplete at 180 rpm while the rate of mixing at higher speeds favoured biodiesel yields and was significant for methanolysis. The yield of methyl esters at 360 rpm and 60 rpm was same producing 97% after three hours of reaction time. These results are in accordance with standards already established in other studies [17].

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Chapter 3

Paper 2, EEIGE of BBSF

Evaluation of Environmental Impact and Gaseous Emissions of
Biodiesel fuels and Blends of Selected Feed-stocks

Evaluation of Environmental Impact and Gaseous emissions of Biodiesel fuels and Blends of Selected Feed-stocks

Abstract - Thermal and gaseous emissions of selected biodiesel feed-stocks: Sandbox tree (*Hura crepitans*), Fluted pumpkin (*Telfaria occidentalis*), Black date (*Canarium schwentifurtii*) and Wild melon (*Cucumeropsis manii*) whose potentials as biodiesel fuels have been established in the earlier works of Igbum *et al.* [1] were evaluated in order to ascertain and establish their environmental and emission impacts on the local and global environment. The effects of blending ratios on the thermal/gaseous emissions of the methyl esters (biodiesel fuels) of the seed oils were also investigated. The study involved the extraction of vegetable oils from the selected seeds using petroleum ether in a soxhlet apparatus, transesterification of the extracted oils with methanol at the ratio of 6:1 and Sodium hydroxide as a catalyst, reaction temperatures of 30°C and 55°C and at a reaction time of five minutes to produce the methyl esters. Thereafter, the methyl esters were blended with automotive gas oil (AGO) at different proportions and ratios to produce B5, B10, B15, B20 and B100 of each seed oil methyl ester and automotive gas oil (AGO). The blends samples were subjected to chemo-physical analysis and gaseous emission using different ASTM methods including atmospheric gas samplers and gas chromatographic Mass spectrophotometer for the trapping and subsequent analysis of the effluents. The results showed that all the blends samples of the methyl ester possess lower gaseous emissions than automotive gas oil (AGO) and are also within the ASTM standards. They are therefore more environmentally friendly than their fossil fuel counterpart. Their impact on the global and immediate environment are however friendly.

Index Terms - *Gaseous emissions, evaluation, biodiesel fuels, blends, environmental impact, feedstocks*

3.1 Introduction

Biodiesel is the only alternative fuel to have passed the EPA tier 1 and tier 11 health effects test as required by the clean air tests [2]. These tests concluded that biodiesel significantly reduces regulated emissions and does not pose any threat to human health. The majority of biodiesel used today is mixed with petroleum-based diesel in a mixture of 80% petroleum and 20% biodiesel, or B20 [2]. Thermal and gaseous emissions of selected biodiesel feed-stocks from Nigeria: Sandbox tree (*Hura crepitans*), Fluted pumpkin (*Telfaria occidentalis*), black date (*Canarium schwentifurtii*) and Wild melon (*Cucumeropsis manii*) whose potentials as biodiesel fuels have been established in the works of Igbum *et al.* [1] were evaluated in order to ascertain and establish their environmental and emission impacts on the local and global environment.

The effects of blending ratios on the thermal/gaseous emissions of the methyl esters (biodiesel fuels) of the seed oils were also investigated. The study involved the extraction of vegetable oils from the selected seeds using petroleum ether in a soxhlet apparatus, transesterification of the extracted oils with methanol at the ratio of 6:1 and Sodium hydroxide as a catalyst, reaction temperatures of 30°C and 55°C and at a reaction time of five minutes to produce the methyl esters. A study in Spain evaluated Greenhouse Gases (GHG) emissions in the production and use of biofuels considering different crop production alternatives, including the possible import of raw materials [3].

The studied biofuels reported in the Spanish study were bioethanol from cereal crops and biodiesel from crude vegetable oil and waste vegetable oil. Several blends of these biofuels with gasoline and diesel were also studied including a Life Cycle Assessment (LCA). Results showed lower GHG emissions in the production and distribution of these fuels and the benefits in terms of GHG savings for the adoption of the biofuels [3]. Diesel vehicles are a major form of transportation, especially in developing countries. Recent concerns over the environment, increasing fuel prices and the scarcity of its supply have promoted interest in the development of alternative sources of petroleum fuels [4] hence the prompting of this study.

A study on castor oil methyl ester was prepared by transesterification using potassium hydroxide (KOH) as a catalyst and tested in a four-stroke, single-cylinder compression ignition engine. The test was carried out at a constant speed of 1500 rpm at different loads. The results showed that with an increasing biodiesel percentage, the carbon monoxide (CO) emission level decreased [4]. The reduction of the CO in B05, B10 and B20 averaged 13.75%, 25.02% and 28.79%, respectively, compared to diesel (B0). The emission results of the comparative test indicated that CO, oxygen (O₂) and smoke density emissions are found to be lower when the engine is fuelled with B05, B10 and B20 as compared to B0, while carbon dioxide (CO₂) and nitrogen oxide (NO_x) with B05, B10 and B20 are found to increase emissions marginally [4].

Another study was on an experimental investigation carried out to establish the performance, emission and combustion characteristics of a diesel engine using *Jatropha* biodiesel, *Jatropha* biodiesel emulsion fuel (5% water, 93% biodiesel, 2% surfactants) and alumina-nanoparticles-blended *Jatropha* biodiesel emulsion fuels [5]. The nanoparticles were mixed with the biodiesel emulsion fuel in the mass fractions of 25 parts per million and 50 parts per million systematically. The experimental results revealed an enhancement in the performance and reduction in the harmful pollutants for the nanoparticles-blended biodiesel emulsion fuels when compared with the neat biodiesel. At the full load, the Brake Thermal Efficiency (BTE) for the nanoparticle blended fuel is 29%, whereas it is 24.9% for the neat biodiesel. However, there was

a marginal increase in the greenhouse gas emission (viz., CO₂) for the nanoparticle blended fuel compared to Jatropha emulsion fuel due to better combustion [5].

3.2 Emissions reductions with biodiesel

Non-fossil fuel energy options can help reduce or eliminate the emission of greenhouse gases and are needed to combat climate change [6]. Rosen [6] goes further to explain that though non-fossil fuel energy sources are insufficient to avoid global warming in that they are not readily utilisable in their natural forms, they can at least reduce it. Since biodiesel is made entirely from vegetable oil, it does not contain any sulphur, aromatic hydrocarbons, metals or crude oil residues. The absence of sulphur means a reduction in the formation of acid rain by sulphate emission which generates sulphuric acid in our atmosphere. The reduced sulphur in the blend will also decrease the levels of corrosive sulphuric acid accumulating in the engine crankcase oil over time [2]. The lack of toxic and carcinogenic aromatics (benzene, toluene and xylene) in biodiesel means the fuel mixture combustion gases will have reduced impact on human health and the environment. The high cetane rating of biodiesel (ranges from 49 to 62) is another measure of the additives ability to improve combustion efficiency. An engine running on 100% biodiesel would have no aromatic emission and the biodiesel would be much safer to store and handle. In addition, biodiesel blends have reduced emissions of polyaromatic hydrocarbons, another group of potentially carcinogenic substances found in petroleum [5].

3.2.1 Lower hydrocarbon (HC) emissions

As an oxygenated vegetable HC, biodiesel itself burns cleanly, but it also improves the efficiency of combustion in blends with petroleum fuel. As a result of cleaner emissions there will be reduced air and water pollution from engines operated on biodiesel blends. The studies documented the reduction in HC, carbon monoxide and particulates matter [7]. Biodiesel is comprised of vegetable oil methyl esters, that is, they are HC chains of the original vegetable oil that have been chemically split off from the naturally occurring “triglycerides”. Biodiesel HC chains are generally 16 to 20 carbons in length, and they are all oxygenated at one end, making the product an excellent fuel. Several chemical properties of the biodiesel allow it to burn cleanly and actually improve the combustion of petroleum diesel in blends [7, 8].

3.2.2 Smoke and soot emission

Smoke (particulate material) and soot (unburned fuel and carbon residues) are of increasing concern to urban air quality problems that are causing a wide range of adverse health effects for their citizens especially in terms of respiratory impairment and related illnesses. The lack of

heavy petroleum oil residues in the vegetable oil esters that are normally found in diesel fuel means that engine operating with biodiesel will have less smoke, and less soot produced from unburned fuel [8]. Furthermore, since the biodiesel contains oxygen, there is an increased efficiency of combustion even for the petroleum fraction of the blend. The improved combustion efficiency lowers the particulate material and unburned fuel emission especially in older engines with direct fuel injection system [8].

3.2.3 Carbon monoxide emissions

Carbon monoxide gas is a toxic by product of hydrocarbon (HC) combustion that is also reduced by increasing the oxygen content of the fuel. More complete oxidation of the fuel result in more complete combustion to carbon dioxide rather than leading to the formation of carbon monoxide. In the 1998 report by the Southwest Research Institute on the effect of biodiesel on truck engine exhaust emissions, the levels of carbon monoxide were shown to be reduced from 22% to 8% with a B-20 blend, depending on the type of engine [7, 22]. When the fuel was switched from low-sulphur petroleum diesel to neat biodiesel, there was a 28% to 37% drop in the carbon monoxide emission [7]. The objective of this study therefore is to evaluate the environmental impact of the gaseous emissions of the selected biodiesel fuels and blends in comparison with the fossil-fuel based automotive gas oil (AGO) with a view to advancing further bio-based fuel development for use in compression ignition engines and other applications.

3.2.4 Poly-aromatic hydrocarbon emission

Poly-aromatic HC (PAHs) are a class of heavy oil petroleum HCs defined by their complex ring structures and unique qualities. They consist of multiple benzene ring structures that make them insoluble, slow to burn and carcinogenic. Some structures of poly-aromatic hydrocarbons (PAH) are as shown in Figure 3.1. These are carcinogenic in nature. PAHs are regulated by the EPA in engine emission. In 1998 the South West Research Institute [8, 30] reported that the amines N-H engine had a 12% drop in PAHs when the fuel was switched to neat biodiesel. The Detroit diesel engine had a 29% reduction in PAHs operating on B-20 and a 69% reduction when operating on neat biodiesel. These data suggest major gains in improving the air quality around diesel engines in vehicles and boats operating on biodiesel [8].

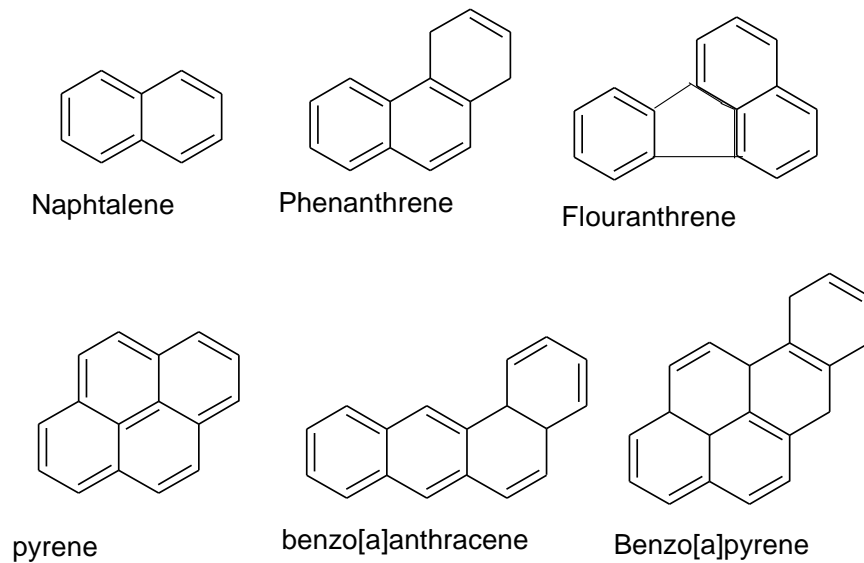


Fig. 3.1: Some structures of poly-aromatic hydrocarbons

3.2.5 Nitrogen oxide

The nitrogen oxides results from the oxidation of atmospheric nitrogen at the high temperatures inside the combustion chamber of the engine, rather than resulting from a contaminant present in the fuel. Although nitrogen oxides (NO_x) are considered a major contribution to ozone formation, they are also a reality of operating internal combustion engine [8]. There are consistent reports of slight increase (several percent) in NO_x emissions with biodiesel blends that are attributable in part to the higher oxygen content of the fuel mixture. More oxygen and better combustion of the fuel also means more formation of NO_x emission with biodiesel blends [8, 9]. In several research studies conducted since 1993 in the United States and Europe, EPA regulated emissions from an unmodified engine operating on a 20% biodiesel 80% petro-diesel blend were shown to be lower than those for petroleum diesel except for NO_x emissions, which can be 2-5% above baseline emission [8].

Some reduction in NO_x emission can be attained by retarding the timing ignition and slowing the burning rate of the fuel in the combustion chamber. Unfortunately, any improvements in NO_x emissions are usually offset by increase in HC particulate material and carbon monoxide emission caused by the mechanical adjustments to the engine [8, 9]. In Europe, the delays in engine ignition on timing have been successfully combined with the use of catalytic converters to achieve similar reductions in both NO_x emissions from transit buses. In the 1996 South-West Research Institute studied the use of a catalytic converter which improved the reduction of HC emissions with a B-20 blend of rapeseed methyl esters from 29% (without converter) to 41%

(with converter) for the Cummins test engine without any timing delays. NO_x emissions were reduced to 3% [8, 9].

3.3 Biodiesel help reduce greenhouse gases unlike any other clean fuels

Biodiesel and other bio fuels are produced from renewable agricultural crops that assimilate carbon dioxide from the atmosphere to become plants and vegetable oil. The CO₂ released this year from burning vegetable oil biodiesel will, in effect, be recaptured next year by crops grown in order to produce more vegetable oil starting materials [8]. While anthropogenic (human-made) CO₂ production accounts for only about 4%-5% of the net CO₂ emissions, it is sufficient to have caused a net gain over the past 100 years. Fossil fuel combustion accounts for 70% of the total anthropogenic CO₂ combustion. Supplementing our dwindling fossil fuel reserves with biomass-based fuels (biodiesel, for petro diesel, biomass based alcohols or hydrogen for gasoline) helps reduce the accumulation of CO₂ [8].

3.4 Lower impact on marine environment

Water pollution should also be reduced by using biodiesel in boat engines since there will be more efficient burning of the fuel mixture, less carbon (soot) accumulation and particulate (smoke) emissions. Faster starting and smoother operation also should reduce the discharge of unburned fuel [8]. Any accidental discharges of small amounts of biodiesel should have relatively little impact on the environment compared to petroleum diesel, which contains more toxic and more water-soluble aromatics. Nonetheless, the methyl esters could still cause harm [8].

3.5 Biodegradability of biodiesel in aquatic environment

Biodiesel is a simple, straight carbon chain with two oxygen molecules at one end (mono-alkyl ester). It is more readily metabolized by bacteria that normally break down fats and oils in the environment while petro diesel hydrocarbons (HC), lack oxygen and represent a very complex mixture of HCs with multiple double bonds and many other branched cyclic and cross linked chains. The more complex chemical structures of diesel HCs makes them more difficult to biodegrade and many are toxic. The biodegradation rate of rapeseed biodiesel in shake flakes with fresh H₂O was found to be comparable to dextrose (a test sugar) and about twice as fast as for petroleum diesel. In the Idaho study [10], the rapeseed esters were degraded by 95% at the end of 23 days whereas the diesel fuel in this test was only about 40% degraded after 23 days.

3.6 Determination of thermal and gaseous emissions

This test method covers the determination of the gaseous emission properties of fuels, quantitatively determining their gaseous emission properties. The fuel samples were burned for 3hrs in a specified lamp under specified conditions. Apparatus include: lamp assembly (essential to ensure that the burner fits vertically into the fuel reservoir and that the wick guide has parallel sides and is centrally disposed in relation to the slot in the dome of the burner), and wick, comprising 19 mm paraffin flat super quantity, containing approximately 43 ends of three-ply yarn, woven double plain wave with stitching ends, one blue stripe on one face and one green stripe on the reverse face, woven with approximately 16 picks per 10 mm and weighing normally 15 g/m. After weaving, the wick should be boiled in distilled water and dried thoroughly.

The test lamps were placed at least 300 mm apart and 300 mm from any wall or other obstruction and the test room temperature was maintained above 15°C to allow the temperature of the fuel to approach equilibrium room temperature within at least 5°C. The wick was dried in an oven at 105°C for 1 hour. While still hot, it was soaked in the sample and inserted into the wick guide. The reservoir was rinsed several times with the sample while the sample was passed through a coarse textured filter paper, to remove suspended matter and 100 mL of it poured into the reservoir. Then the lamp was assembled to test for Hydrocarbons/Volatile Organic Compounds (CxHy/VOCs), Nitrogen Oxides (NOx), Sulphur Oxides (SOx) Carbon Monoxide (CO) and Carbon dioxide (CO₂).

A TESTO 350 flue gas analyzer model as shown in Appendix E was used. This instrument performs automatic analysis of gaseous emissions through the use of physical properties, and provides a cyclic or continuous output signal. Emissions are continuously extracted from the lamp assembly earlier assembled and some of the samples are sent to the analyzer for the determination of the pollutant gas of interest. The analyzer gives results in $\mu\text{g}/\mu\text{m}^3$. For Suspended Particulate Matter (SPM), a mini-volume portable air sampler (Airmetric[®]) with a pre-weighed membrane filter (47 μm) was used to collect particulate matter. After sampling, the membrane filter was dried at 105°C, cooled in desiccators and weighed to the nearest milligram. The mass concentration was calculated by measuring the mass of particulate matter and dividing by the volume of air. The volume of air was determined as follows:

$$V = Q \times t \quad (3.1)$$

Where: V: volume of air (m³);

Q: Flow rate (m³/m);

t: time of sampling (s)

Where q = flow rate in litres per minute; t = time of sampling in minutes and 0.001 (the conversion from litres to cubic meters) and V in (m^3) = $0.0001 m^3/l \times q \text{ l/min} \times t \text{ (mins)}$

$$\text{Conc. of SPM} = (1000 (\mu\text{g})/\text{mg} \times W_n (\text{mg}))/V \quad (3.2)$$

Where: W_n (mass change of the filter); V in (m^3) (volume of air sample); 1000 (conversion from milligram to micrograms).

3.7 Results

Global warming is of particular interest when assessing the sustainability of bio-based fuels as one of the main drivers of their development is their potential to mitigate GHG emissions. Greenhouse gases are expressed in terms of Carbon Dioxide Equivalent (CDE). The International Panel on Climate Change (IPCC) has presented these Global Warming Potentials (GWPs) and regularly updates them in new assessments. Looking at Table 3.1 and Figures 3.2, 3.3, 3.4 and 3.5 generally, it is evident that most of the gaseous emissions of the biodiesel and blends – methyl esters of *Hura crepitans* vegetable oil (HVO); *Telfaria occidentalis* vegetable oil (TVO); *Canarium schwentifurtii* vegetable oil (CSVO) and *Cucumeropsis manii* vegetable oil (CVO), produced less emissions than AGO except CO_2 which was more than AGO for all the cases.

Global Warming Potential (GWP) is the index used to translate the level of emissions of various gases into a common measure in order to compare the relative radiative forcing of different gases without directly calculating the changes in atmospheric concentrations. GWPs are calculated as the ratio of the radiative forcing that would result from the emissions of one kilogram of a greenhouse gas to that from emission of one kilogram of carbon dioxide (CO_2) over a period of time (usually 100 years). Therefore the contribution of organic CO_2 from biodiesel is quite advantageous. Some studies have provided evidence that continuous biodiesel use reduces greenhouse gas emissions because the carbon dioxide released in biodiesel combustion is offset by the carbon dioxide sequestered while growing the feedstock [11]. B100 generally reduces carbon dioxide emissions by more than 75% compared to diesel. Using B20 reduces carbon dioxide emissions by 15% [11]. NO_x on the other hand were significant though less than in AGO; the negative impact of this however is not very threatening because with improved unsaturation of bonds structures with blending, the impact is reduced. Studies of oxides of nitrogen emissions have provided contradictory results, and therefore further research on testing is ongoing [11]. CO were all less than that seen in AGO, SO_x less in several orders than AGO, SPM far less than AGO, C_xH_y Hydrocarbon less than AGO and the VOCs were far

less than AGO. Toluene, Benzene, Ethylbenzene, Xylene emission were more than the amount found in AGO, even exist in very small amounts measured in $\mu\text{g}/\text{m}^3$. In comparison with other studies, the ozone (smog) forming potential of biodiesel hydrocarbons is less than diesel fuel.

Sulfur emissions are essentially eliminated with pure biodiesel [12]. The exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel. In these studies, criteria pollutants are reduced with biodiesel use [11, 12]. Tests show the use of biodiesel in diesel engines results in substantial reductions of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides stay the same or are slightly increased. The exhaust emissions of carbon monoxide (a poisonous gas) from biodiesel are on average 48 percent lower than carbon monoxide emissions from diesel [11, 12].

Table 3.1: Gaseous emission characteristics of AGO (control)

All results in $\mu\text{g}/\text{m}^3$

AGO	CO ₂	NO _x	CO	SO _x	sPM	C _x H _y	VOCs	Toluene	Benzene	Ethyl benzene	Xylene
	18.6	178	15.63	200	224	171	114	11.14	30.96	30.84	5.79

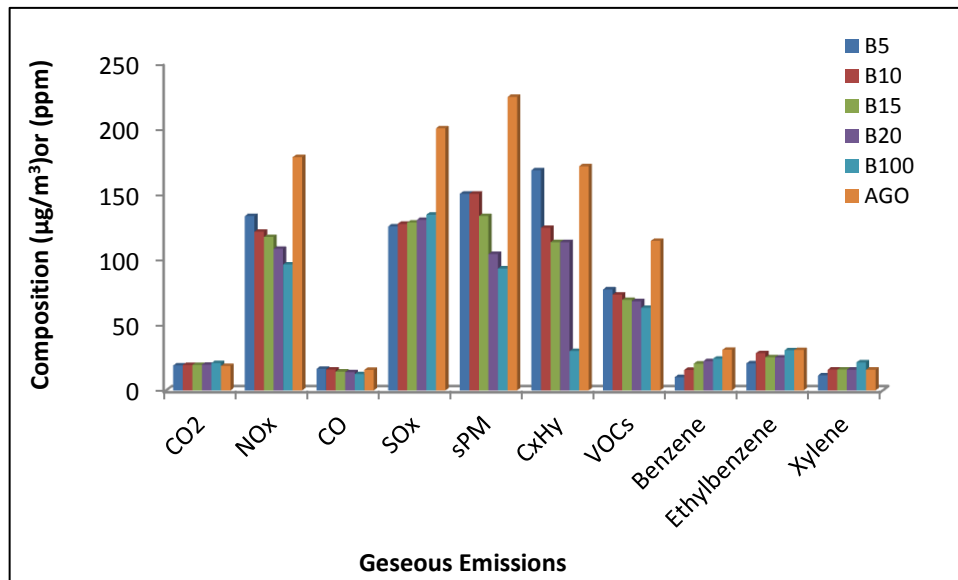


Figure 3.2: Gaseous emission characteristics of HVO-Methyl esters and blends with AGO

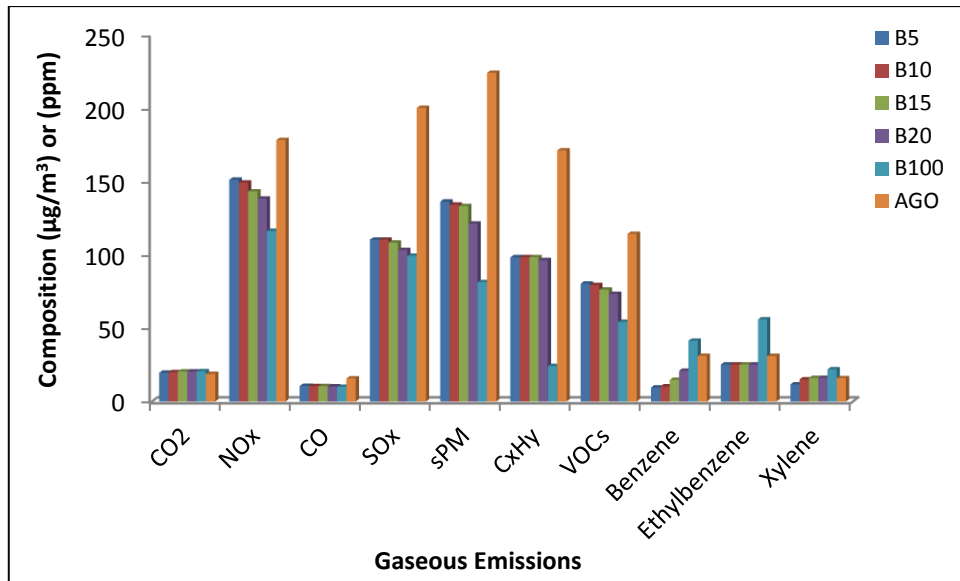


Figure 3.3: Gaseous emission characteristics of CVO-methyl esters and blends with AGO

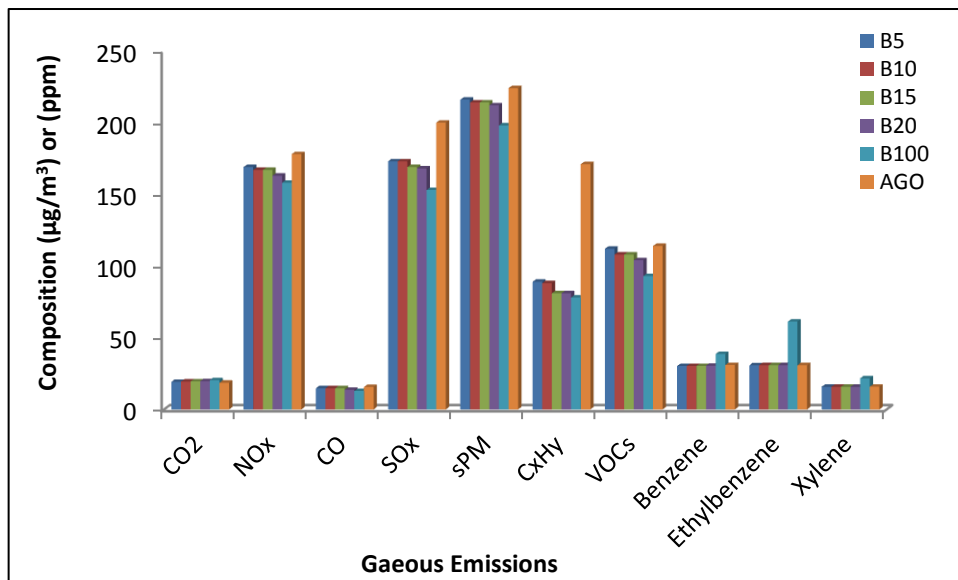


Figure 3.4: Gaseous emission characteristics of CSVO-methyl esters and with AGO

Breathing particulate matter has been shown to be a human health hazard. The exhaust emissions of particulate matter from biodiesel are about 47% lower than overall particulate matter emissions from diesel. Biodiesel reduces tailpipe particulate matter (PM). Biodiesel reduces Hydrocarbon and Carbon monoxide emissions. These benefits occur because the fuel (B100) contains 11% oxygen by weight; the presence of fuel oxygen allows the fuel to burn more completely, so fewer unburned fuel emissions result. This same phenomenon reduces air toxicity, because air toxicity is associated with unburned or partially burned HC and PM emissions. Testing has shown the PM, HC and CO reductions are independent of the feedstock

used to make biodiesel. Some PM and HC emission from diesel fuel combustion are toxic or are suspected of causing cancer and other life threatening illnesses [11, 12].

Using B100 can eliminate as much as 90% of these “air toxics”. B20 reduces air toxics by 20% to 40%. The composition of the biodiesel will affect how much NO_x it will produce. Some kinds of B100 such as those high in polyunsaturated fatty acids produce more NO_x than B100 high in saturated fatty acids. Blends of less than 5% do not have a measurable effect on NO_x [11]. When biodiesel displace petroleum, it reduces global warming gas emission such as Carbon dioxide (CO₂). When fossil fuels are burned, however, 100% of the CO₂ released adds to the CO₂ concentration levels in the air. Because fossil fuels are used to produce biodiesel, the recycling of CO₂ with biodiesel is not 100%, but substituting biodiesel for petroleum diesel reduces life-cycle CO₂ emission by 78%. B20 reduces CO₂ by 15.66%.

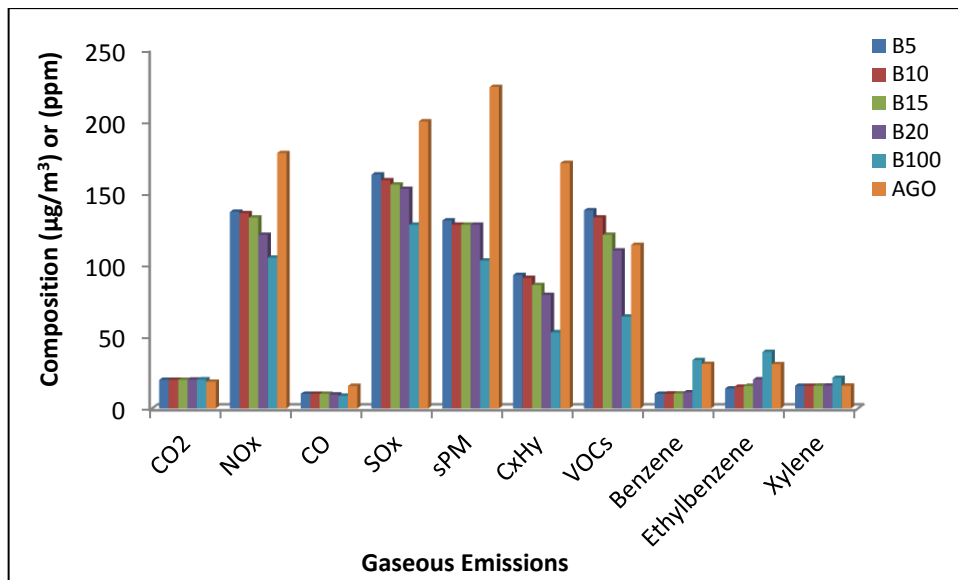


Figure 3.5: Gaseous emission characteristics of TVO-methyl esters and blends with AGO

NO_x is reduced linearly with increasing biodiesel content; for every 1% biodiesel added, NO_x decreases by 1%. A B20 heating oil fuel will reduce NO_x by about 20%. A number of studies have shown that biodiesel fuel is low in CO and HC emission, but high in NO_x emission compared to petroleum diesel [13-20]. Similar trends were observed in this study, except for NO_x emissions, although most of the differences between the biodiesel and B20 fuels used were not statistically significant. For most aromatic pollutants, biodiesel fuels generally have lowered emission compared to conventional diesel. Although emissions of benzene and several other VOC sometimes increases [13], the EPA reported consistent reductions in ethylbenzene, naphthalene and xylene with biodiesel; however, the EPA did not draw conclusions for benzene, toluene and styrene due to the variation in the literature (USEPA, 2002). For instance, using a 8

L, 6-cylinder diesel engine without after treatment systems B20 (20% rape seed oil, 80% diesel fuel) increased benzene emission compared to diesel fuel (sulphur < 300 ppm) [18]. It is not negotiable that biodiesel reduces the health risks associated with petroleum diesel with decreased levels of polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (nPAH), which have been identified as potential cancer causing compounds.

3.8 Conclusion

It is quite evident that the study on the thermal and gaseous emissions of selected Nigerian biodiesel feedstocks viz. Sandbox tree (*Hura crepitans*, HVO), Fluted pumpkin (*Telfaria occidentalis*, TVO), Black date (*Canarium schwentfurtii*, CSVO) and Wild melon (*Cucumeropsis manii*, CVO) and their blends showed significant difference compared to their fossil counterpart, the AGO, which had higher emissions. The impact however is that of environmental friendliness and comparative advantage in relation to the AGO.

The general trend is that all the fuels produced and tested together with their blends have lower gaseous emissions than AGO. Pollutants of sulphur, nitrogen, organic compounds were visibly reduced in low AGO blends. Biodiesel fuels and blends have continued to confirm their environmental friendliness in most studies of this nature. Biodiesel vegetable oil methyl esters contain no volatile organic compounds that would give rise to any poisonous or noxious fumes. The biodiesel does not contain any aromatic hydrocarbons (benzene, toluene, xylene and others) or chlorinated hydrocarbons. There is no lead or sulfur to react and release harmful or corrosive gases.

However, in blends with petro-diesel, there will continue to be significant and/or insignificant fumes released by the benzene and other aromatics present in the petroleum fraction depending on their percentages as exposed by this study. The recommendation here is that biodiesel and blends are therefore to be better and qualitatively developed to the level that they will compete favorably with the conventional fossil fuels in terms of availability and cost as this has always been the bone of contention. The studied feed-stocks could comfortably be combusted in compression ignition engines without fear of polluting the environment.

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Chapter 4

Paper 3, HF-NABD: MJ

Hybridisation of Feedstocks - A new Approach in Biodiesel
Development: A Case of Moringa and Jatropha seed oils

Hybridisation of Feedstocks - A New Approach in Biodiesel Development: A case of Moringa and Jatropha seed oils

Abstract - The search for improvement in the development of biomass and biofuels as renewable energy sources have continued within the last decades. Biodiesel fuels from different crude vegetable oils have been explored and evaluated as sustainable and unsustainable fuels energy. The fuel properties of these feedstocks vary depending on source, physico-chemical configuration and biological compositions; with processes like hybridisation, these properties may be improved. In this study, two selected feedstocks, *Moringa oleifera* and *Jatropha curcas* seed oils and their methyl esters (biodiesel) were subjected to different hybridization processes at varying proportions experimentally. The hybrid compositions were J₅₀M₅₀, J₄₀M₁₀, J₃₀M₂₀, J₂₀M₃₀, and J₁₀M₄₀ from crude oil samples (*in situ*) and BM₅₀J₅₀, BM₄₀J₁₀, BM₃₀J₂₀, BM₂₀J₃₀ and BM₁₀J₄₀ from biodiesel produced by transesterification (*ex situ*) using production variables and optimisation sequences. The produced hybrids were evaluated for chemo-physical and thermal properties using ASTM and SANS standards for each specific test(s). Results obtained revealed the efficacy of hybridisation in improving specific biodiesel properties as fuels. Specific tests included viscosity, specific gravity, refractive index, cetane index, fatty acid composition, free and total glycerine, free fatty acid composition, flash point, pour and cloud points and calorific values. These were all higher and better than the single stock biodiesel fuels. *Moringa oleifera* biodiesel which has proved itself an excellent biodiesel fuel in our previous studies having high oleic acid content (> 70%) impacted positively on *Jatropha* in enhancing its potential with positive correlation at a 95% confidence level ($\alpha > 0.05$) and on analysis of variation (ANOVA). This is a new approach in biodiesel development as studies of this nature are scarce in the literature. Hybridisation of biodiesel feedstock *in situ* and *ex situ* will no doubt give rise to new products of improved energy qualities that may bring about the much needed difference in the biodiesel industry.

Index terms - Effects, hybridisation, biodiesel, fuel quality, performance, *Moringa*, *Jatropha*, seed oil, hybrids, feedstock

4.1 Introduction

Vegetable oils are potential biodiesel fuels possessing similar characteristics to fossil fuels but also having attendant difficulties due to higher viscosities and the poly-unsaturated nature of the bond structures [1]. These are no doubt solvable with the recent developments of biodiesel in the world. Processes such as transesterification, pyrolysis or thermal cracking, and micro-emulsification can be employed to produce biodiesel from vegetable oils. Transesterification is

now common and was the first breakthrough. Thermal conversion has not been explored yet but works at different research stages portray its possibility as a processing option [2].

Worldwide biodiesel production is mainly from edible oils such as soybean, sunflower and canola oils. Since most developing countries including South Africa, India, China and other Brazil Russia India China and South Africa (BRICS) countries are not self-sufficient in edible oil production, some non-edible oil seeds available in the country are required to be tapped for biodiesel production. Despite the abundance of forest and plant based non-edible oils being available in some countries such as *Pongamia pinnata* (karanja), *Jatropha curcas* (Jatropha), *Madhuca indica* (mahua), *Shorea robusta* (Sal), *Azadirachta indica* A Juss (neem) and *Hevea braziliensis* (rubber), *Trichilia emetic* (Natal Mahogany), not much attempt has been made to use esters of these non-edible oils as substitute for diesel except Jatropha. Finding an alternative fuel for diesel fuel is critically important for nations' economy and security. The complete substitution of oil imports for the transportation and agricultural sectors is the biggest and toughest challenge for Nigeria and South Africa. Bio-diesels as an alternative to diesel, makes farmers self-sufficient in their energy requirements. Many researchers such as Eloka-Eboka *et al* [3] (Jatropha and *Yellow oleander* oil), Agarwal and Das [4] (Linseed oil), Eloka-Eboka and Ibrahim [1] (*Prosopis africana* seed oil), Igbum and Eloka-Eboka [5], Igbum *et al.* [6] (*Hura crepitans*, *Telfaria occidentalis*, *Cucumeropsis manii* and *Canarium schweinfurthii*) and Raheman [7] (Mahua oil), investigated suitability of different vegetable oils in diesel engines and as used as biodiesel fuels. Jatropha is one biodiesel feedstock that has stunned the world in the past decade as it is the first established non-edible feedstock that possesses acceptable chemo-physical, thermal and engine performance properties for use as biodiesel without engine modification.

Its other potentials in the area of clean development mechanisms (CDM) as carbon sinks, as used for organic fertilizer, and reduced climatic impact have already been well established. With the trust and attention of the world's energy experts focussed on the continuous search for alternative energy feedstock, any discovery could be possible and that is why experimental processes like hybridisation of feedstocks is timely. Hybridisation entails blending two or more different feedstocks at varying proportions to produce an entirely new product which may have new enhanced characteristics or properties derived from the initial parent stock depending on initial properties. Hybridising feedstocks like Jatropha and Moringa oils will present great possibilities of improved properties which may perform better in CI engines. When the crude hybrids are converted to biodiesel, it can be termed *in situ* hybridisation but when they are initially converted to biodiesel before hybridisation, it is termed *ex situ* hybridisation. Numerical or computational hybridisation can also be an option. This can also be explored. Early durability

tests at the early stage of biodiesel development indicated that engines would fail prematurely when operating on fuel blends containing vegetable oil. Engines burning vegetable oil that had been transesterified with alcohols now known as biodiesel, however, exhibited no such problems and even performed better by some measures than engines using petroleum diesel [7]. The formulation of what is now called biodiesel came out of those early experiments.

There are plenty of wastelands available in Nigeria, South Africa and everywhere in Africa which can be utilized for growing such oil seed crops. Among various options investigated for diesel fuel, biodiesel obtained from vegetable oils has been recognized the world over as one of the strong contenders for reductions in exhaust emissions. Several countries including India have already begun substituting conventional diesel by a certain amount of biodiesel. However, as compared to other non-edible oils, not much work has been reported on biodiesel production from *Moringa* oil although some facts have been presented. Some investigators have already obtained biodiesel from some of these oils: Hamilton [8]; Agarwal and Das [4]; Altin *et al.* [9]; Boehman *et al.* [10] and Eloka-Eboka, [11]. To this end, *Moringa oleifera* seed oil has so far shown signs of taking over the pride of place that *Jatropha* seed oil has occupied over the years with the potentials of even greater properties. The fatty acid profile of any biodiesel feedstock is better unsaturated, ideally mono-unsaturated for better performance and stability; this means that any feedstock that possesses oleic acid which is mainly a mono-unsaturated fatty acid is considered the most suitable because it confers a higher cetane number/index to any diesel which is the measure of any diesel quality and has reduced gaseous emissions.

Hybridisation of different feedstocks can bring about better and improved qualities which one feedstock may not possibly present. Studies so far have proved that *Moringa oleifera* in its raw nature has oleic acid content of above 70% which can be used to raise other feedstocks of lower content like *Jatropha*. This will improve the quality and properties of the new feedstock for biodiesel production. The growing concern due to environmental pollution caused by conventional fossil fuels and the realizations that they are non-renewable has led to the search for more environment friendly and renewable fuels. In the light of the above information, the present study was undertaken at the discipline of Mechanical Engineering of the University of KwaZulu-Natal to determine the suitability and potential of hybridising *Moringa oleifera* and *Jatropha curcas* seed oil (*in situ* hybridisation) and gain biodiesel (methyl esters) from them (*ex situ* hybridisation) as a new approach to fuel development in the biodiesel industry.

In situ hybridisation in this study refers to the blending or the chemical combination of different oil feedstock at different compositions to produce an entirely new product with properties distinct from their parent feedstock before conversion to biodiesel via transesterification,

pyrolysis, emulsification and thermal cracking. *Ex situ* hybridisation allows for the initial conversion to biodiesel followed by hybridising the feedstock. The process can be bi-hybridisation and poly hybridisation involving more than two feedstocks [12]. This approach has not been adopted or experimented in literature but this work will lead the way to hybridisation of very many other biodiesel feedstocks (bi-hybridisation, poly-hybridisation, *in situ* and *ex situ* hybridisation, blending of hybrids and so on). Most of the biodiesel produced today is by transesterification, because the process does not require exotic materials of construction; there is direct conversion to methyl esters with no intermediate steps under a low temperature and pressure environment, and a high percentage (98%) of the input is converted to the final product with minimal side reactions and reaction time [13]; and so hybridisation after transesterification does not pose any extra cost nor difficulty except precision of accuracy and proper manipulation and a wide range of opportunities. The present work is a small step towards sustainable development by making use of biodiesels of the present seed oil and blends which are renewable in nature. The hybridization expressed here is limited to the production process and therefore other forms of plant or crop hybridization are not the focus of this study.

4.2 *Materials and methods*

4.2.1 *Oil preparation*

The biodiesel was produced after oil extraction and preparation following the method adopted by Ajiwe *et al.* [14] (Appendix D). During the production process, two main products, crude biodiesel and crude glycerin, were obtained. Crude biodiesel is refined by washing and drying. The methanol obtained in this process was sent for methanol recovery, and the refined biodiesel becomes ready for use. The crude glycerin is also refined by chemicals and water and finally through distillation and bleaching techniques. The obtained glycerin can be used for pharmaceutical purposes. The methanol recovered in the methanol recovery plant was again used for the esterification process of the vegetable oils. The schematics of the whole process are as shown in Appendix D.

4.2.2 *Extraction and initial characterization of oils of Moringa and Jatropha*

Five (5) litres each of Jatropha and Moringa oils were extracted from dried seeds purchased from Kaduna, Northern Nigeria where Moringa seeds are in abundance and from, Abuja, also in Nigeria where plantations of Jatropha exist. The seeds were pulverized and subjected to mechanical extraction, solvent extraction and micro-wave extraction. Three solvent types (hexane, petroleum ether and gasoline) were explored to evaluate their effectiveness. The extracted oils were pre-treated by aqueous and base washing/neutralization using sodium

hydroxide and running water. Base neutralization process or reaction using sodium hydroxide solution (w/w) of the oil and in water depended on the free fatty acid composition of the oil. It was conducted at varying temperatures of between 60°C and 80°C for between 15 minutes to 1 hour at reaction speeds of 500 rpm to 600 rpm in an electromagnetic stirrer. The solution was subjected to rigorous filtration using filtration vacuum pump. Sodium salts (soap) formed from free fatty acids and gum, phospho/total lipids present in the oil were filtered away.

4.2.3 *In situ and ex situ hybridization of feedstocks*

In situ hybridization was carried out on five samples formed by blending the two feedstock oil after pre-treatment at different ratios and coded as follows: J₁₀M₄₀ (10% Jatropha:40% Moringa); J₂₀M₃₀ (20% Jatropha:30% Moringa); J₃₀M₂₀ (30% Jatropha:20% Moringa); J₄₀M₁₀ (40% Jatropha:10% Moringa) and J₅₀M₅₀ (50% Jatropha:50% Moringa). These are hybrids of oil feedstocks ready for transformation to methyl esters (biodiesel). The properties of *in-situ* hybrids may be quite distinct from hybrids of *ex situ* hybridization and therefore, *ex-situ* hybridization was also conducted on feedstock. This was achieved by independently converting them to methyl esters (biodiesel) by transesterification at the crude oil level and then hybridized at different ratios and composition. They were coded as: BJ₁₀M₄₀ ((10% Jatropha Methyl Ester (ME): 40% Moringa ME), BJ₂₀M₃₀ (20% Jatropha ME: 30% Moringa ME), BJ₃₀M₂₀ (30% Jatropha ME: 20% Moringa ME); BJ₄₀M₁₀ (40% Jatropha ME: 10% Moringa ME); BJ₅₀M₅₀ (50% Jatropha ME: 50% Moringa ME). All the hybrids were characterized using ASTM and SANS standards.

4.2.4 *Biodiesel production methods*

FAME methodology approach was adopted after extraction and pre-treatment of the oils from seeds. Preparation of reagents: saponification reagents (SR), methylation reagents (MR) and extraction agents (ER) which were termed transesterification reagents were conducted as:

1. SR: 45 g NaOH +300 ml (methanol:water) (1:1);
2. MR: 325 ml 6NHCl + 275 ml methanol
3. ER: 200 ml Hexane : 200 ml Diethyl ether

Oil samples (100 g +1000 ml SR) was closed tightly in a reactor, agitated by boiling (30 minutes @ 80°C); 200 ml of MR was added and heated @ 80°C for 20 minutes; 120.0 ml of ER was added; and 300 ml of boiling water or running was passed through the filter funnel and agitated for 5 minutes. They were closed tightly and allowed to settle by sedimentation in the funnel thus separating the methyl ester and the glycerin (by-product). The simple approach for transesterification which was conducted was: setting up for solvent recovery for the solvent

extracted oils; SR, MR and ER were prepared and subsequently employed for transesterification.

An optimization protocol was developed for production using NaOH and KOH as independent catalysts in transesterification in the varying multiple experiments. For the biodiesel production via transesterification, two catalyst (KOH and NaOH) processes were established and applied for optimum yields of biodiesel either as *in situ* hybrids or *ex situ*. The protocol developed is shown in Table 4.1 and the subsequent yields of biodiesel in Table 4.2. The hybridization of biodiesel feedstock using Moringa as the main constituent is because of its excellent biodiesel qualities and therefore was limited to 50% hybridization. The two way hybridizations in this study were limited to Jatropha alone using Moringa oil.

4.2.5 Analysis of biodiesel and hybrids

Viscosity tests at different temperatures and speeds with shear stress were conducted. This is an important parameter for biodiesel processing. In fact, the essence of transesterification is to reduce the viscosity of the oil and at the same time break the bond structure for proper atomization and combustion in the engine cylinder and combustion chamber. Other physiochemical analysis conducted to assess the properties of the produced biodiesel and hybrids are free fatty acid (FFA), total glycerine (TG) and free glycerine (FG), density/specific gravity, flash point, calorific values, flash point, cloud point and cetane index which is the measure of the fuel qualities. Thermal analysis and stability using thermal gravimetric analysis and Fourier infra-red spectroscopy was conducted. Fatty acid composition of the oil samples (crude) and biodiesel was subjected to gas chromatography (GC), using Shimadzu GC-MS analyzer.

4.3 Results and discussions

4.3.1 Results

The results of the oil preparation, extraction and initial characterization of oils of Moringa and Jatropha, *in situ* and *ex situ* hybridization of feedstocks, biodiesel production methods and analysis of biodiesel and hybrids are presented in Tables 4.1 to 4.11 and Figures 4.1 to 4.3.

4.3.2 Discussion of results

The properties of the produced biodiesel and hybrids are quite close to the petroleum based diesel AGO used as control standards yet possessing renewable properties of environmental friendliness and potential for less exhaust and gaseous emission obtainable in every biodiesel

are seen in all the Tables and Figures. The optimization protocol of biodiesel production of this study in Table 4.1 gave rise to the result in Table 4.2. It presents the yields of biodiesel from Moringa and Jatropha seed oil and the *ex situ* hybridization. *Ex situ* hybrids had up to 92% biodiesel yield with potassium hydroxide as catalyst while sodium hydroxide catalyst yielded 90%.

Table 4.1: Optimization protocol

Jatropha		Moringa		<i>Ex-situ</i> Hybrids	
J _N	J _K	M _N	M _K	JM _N	MJ _K
1	1	1	1	1	1
2	2	2	2	2	2
3	3	3	3	3	3
4	4	4	4	4	4
5	5	5	5	5	5

Subscripts represent catalysts type employed: N for Sodium hydroxide (NaOH); and K for potassium hydroxide (KOH): These are independent catalysts and do not take part in the reaction.

Table 4.2: Biodiesel yields from the protocol

Jatropha		Moringa		<i>Ex situ</i> Hybrids				
J _N : Yields	%	J _K : % yields	M _N : yields	%	M _K : % yields	JM _N : yields	%	MJ _K : % yields
1: 93		1: 94	1: 96		1: 98	1: 90		1: 92
2: 91		2: 92	2: 95		2: 96	2: 85		2: 85
3: 90		3: 89	3: 90		3: 91.5	3: 83		3: 85
4: 84		4: 88	4: 83		4: 90	4: 82		4: 83
5: 82		5: 85	5: 80		5: 88.0	5: 78		5: 80

This is quite interesting as most single stock biodiesel have not yielded such high percentages. The works of Igbum *et al.* [5] on *Hura crepitans* and *Canarium schweifurthii* recorded 85% as peak yield. *In situ* hybrids were not considered for biodiesel yields because they were already hybridized before transesterification and so ascertaining their production yields would be pretty difficult. Tables 4.3 to 4.6 are the viscosity and sheer stress output of the biodiesel and hybrids at the temperatures of 40°C and 60°C.

It is evident to observe that hybridization (*in situ* and *ex situ*) made significant progress in lowering the viscosities of the single biodiesel feedstock and their biodiesel. All hybrids have lower viscosity and sheer stress (measure of lubricity for proper atomization in the combustion chamber), although transesterification played a key role notwithstanding. Having a cursory look at the FAME composition of Moringa and Jatropha, hybridization of both will make up for the inadequacies of octadecanoic acid methyl ester which is a mono-saturated bond fatty acid and oleic underivatized acid to increase on the combustion quality of Jatropha in the hybrids. GC-MS analyses of the hybrids are still at WIP stage and outside the purview of this paper.

Table 4.3: Viscosity and shear stress of biodiesel @ 40°C

Samples Codes	Viscosity @40°C (RPM)				Shear Stress @ 40°C (D/cm ²)			
	20 rpm	40 rpm	50 rpm	60 rpm	20 rpm	40 rpm	50 rpm	60 rpm
B ₁₀₀ M	7.1	6.1	5.8	5.6	1.9	3.2	3.8	4.4
B ₁₀₀ J	6.6	5.9	4.4	5.2	1.7	3.1	3.6	5.7

B₁₀₀M = Moringa biodiesel (B100), B₁₀₀J= Jatropha biodiesel (B100)

Table 4.4: Viscosity and shear stress of biodiesel @ 60°C

Samples Codes	Viscosity @ 60°C (cP)				Shear Stress @ 60°C (D/cm ²)			
	20 rpm	40 rpm	50 rpm	60 rpm	20 rpm	40 rpm	50 rpm	60 rpm
B ₁₀₀ M	20.9	12.4	9.84	8.60	5.37	6.73	6.49	6.77
B ₁₀₀ J	19.7	11.7	9.30	8.10	5.17	6.14	6.14	6.37

Table 4.5: Viscosity and shear stress of biodiesel hybrids @ 40°C

Samples Codes	Viscosity @ 40°C (cP)				Shear Stress @ 40°C (D/cm ²)			
	20 rpm	40 rpm	50 rpm	60 rpm	20 rpm	40 rpm	50 rpm	60 rpm
J ₅₀ M ₅₀	6.90	6.07	5.64	5.45	1.82	3.21	3.72	4.32
J ₄₀ M ₁₀	6.90	6.15	5.76	5.60	1.86	3.25	3.84	4.43
J ₃₀ M ₂₀	7.05	5.85	5.46	5.25	1.74	3.13	3.48	4.16
J ₂₀ M ₃₀	6.60	6.07	5.52	5.35	1.78	3.17	3.64	4.24
J ₁₀ M ₄₀	6.75	6.07	5.46	5.25	1.74	3.09	3.60	4.16
BM ₅₀ J ₅₀	6.6	5.92	5.64	5.45	1.74	3.09	3.72	4.32
BM ₄₀ J ₁₀	6.60	4.70	3.42	3.20	1.19	2.18	2.26	2.53
BM ₃₀ J ₂₀	4.5	4.62	3.48	3.25	1.23	2.14	2.30	2.57
BM ₂₀ J ₁₀	4.65	4.57	3.42	3.20	1.90	2.38	2.26	2.57
BM ₁₀ J ₄₀	6.70	6.01	5.64	5.45	1.74	3.09	3.72	4.32
AGO	4.50	3.92	3.06	2.80	1.07	2.06	1.98	2.22

J₁₀M₄₀ (10% Jatropha:40% Moringa); J₂₀M₃₀ (10% Jatropha:40% Moringa); J₃₀M₂₀ (10% Jatropha:40% Moringa); J₄₀M₁₀ (10% Jatropha:40% Moringa) and J₅₀M₅₀ (10% Jatropha:40% Moringa); BJ₁₀M₄₀ ((10% Jatropha Methyl Ester (ME): 40% Moringa ME), BJ₂₀M₃₀ (20% Jatropha ME: 30% Moringa ME), BJ₃₀M₂₀ (30% Jatropha: 20% Moringa); BJ₄₀M₁₀ (40% Jatropha: 10% Moringa); BJ₅₀M₅₀ (50% Jatropha: 50% Moringa).

Table 4.6: Viscosity and shear stress of biodiesel hybrids @ 60°C

Samples Codes	Viscosity @ 60°C (RPM)				Shear Stress @ 60°C (D/cm ²)			
	20 rpm	40 rpm	50 rpm	60 rpm	20 rpm	40 rpm	50 rpm	60 rpm
J ₅₀ M ₅₀	20.25	12.85	9.78	8.40	5.34	6.81	6.41	6.61
J ₄₀ M ₁₀	20.25	12.45	9.60	8.35	5.38	6.53	6.33	6.61
J ₃₀ M ₂₀	19.65	12.22	9.48	8.20	5.23	6.32	6.26	6.53
J ₂₀ M ₃₀	20.10	12.30	9.48	8.25	5.31	6.53	6.26	6.53
J ₁₀ M ₄₀	19.65	12.07	9.36	8.10	5.23	6.27	6.18	6.41
BM ₅₀ J ₅₀	18.45	11.32	8.46	7.25	4.91	5.98	5.58	5.74
BM ₄₀ J ₁₀	18.90	11.70	8.46	7.25	4.99	6.37	5.58	5.74
BM ₃₀ J ₂₀	18.62	11.70	8.46	7.20	4.91	6.18	5.58	5.70
BM ₂₀ J ₃₀	19.65	11.77	9.48	8.30	5.19	6.18	6.26	6.57
BM ₁₀ J ₄₀	19.2	11.5	9.45	8.20	5.12	6.15	6.18	6.48
AGO	18.15	10.57	8.16	7.00	4.79	5.02	5.38	5.54

The fatty acid composition of both feedstocks have great prospect as biodiesel in CI engines as less or infinitesimal percentage of NO_x and SO_x are likely to be present during engine utilization. The thermal gravimetric analysis in Figures 4.1, 4.2 and 4.3 proved the oxidative stable nature of both the feedstocks and 50% blends at temperatures up to 500°C where only residual compositional weight losses becomes prevalent. The chemo-physical properties of Moringa and Jatropha oils in Table 4.9 and Moringa biodiesel in Table 4.10 show that both feedstocks are suitable for hybridization but that Moringa stands out as a more suitable hybridization agent than any other feedstock for improved characteristics and performance. Refer to Figure 4.4.

Table 4.7: FAME composition of Moringa biodiesel

S/No	FAME	Area %	Base m/z
1.	9-Hexadecenoic acid ME	1.36	55.05
2.	Hexadecanoic acid ME	6.01	74.00
3.	Heptadecanoic acid ME	0.11	74.00
4.	9-Octadecenoic acid ME	51.76	55.05
5	Octadecanoic acid ME	5.46	74.00
6	Oleic Acid (underivatized)	21.69	55.05
7	11-Eicosenoic acid ME	2.14	55.05
8	Eicosenoic acid ME	0.13	55.10
9	Eicosanoic acid ME	3.57	74.00
10	Docosanoic acid ME	6.70	74.05
11	Tetracosanoic acid ME	1.08	74.00

Table 4.8: FAME composition of Jatropha biodiesel

S/No	FAME	Area %	Base m/z
1.	9-Hexadecenoic acid ME	0.19	55.05
2.	Hexadecanoic acid ME	2.01	74.00
3.	Pentadecanoic acid ME	12.66	73.00
4.	9,12-Octadecadienoic acid ME	7.45	67.05
5.	9-Octadecenoic acid ME	6.64	55.05
6.	Octadecanoic acid ME	1.47	74.00

The results of thermal gravimetric analysis (TGA) of oil samples and 50% hybrid are presented as Figures 4.1, 4.2 and 4.3.

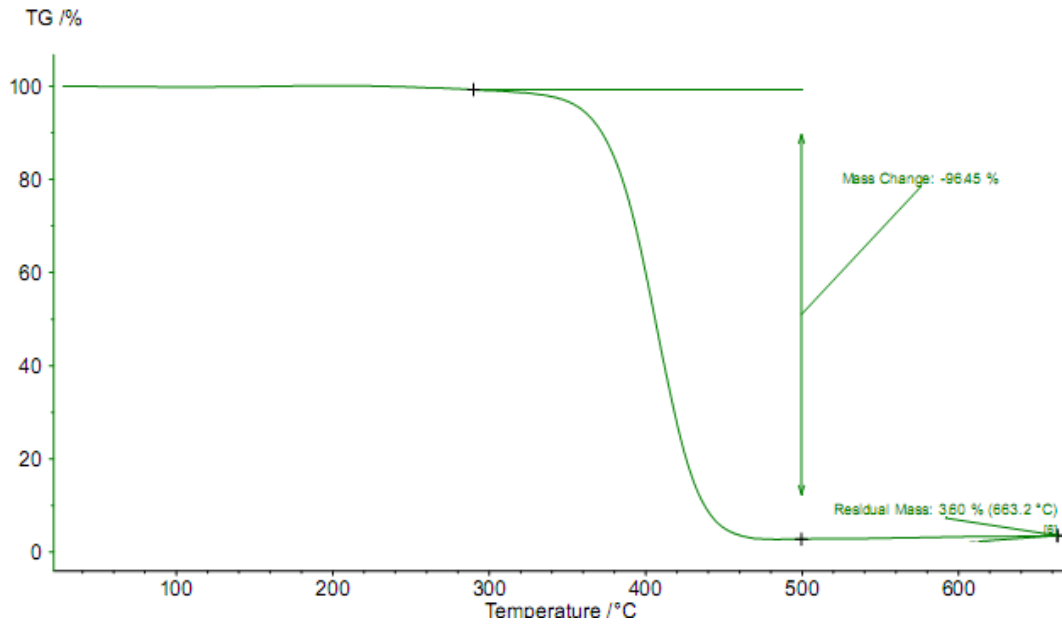


Figure 4.1: TGA analysis of Moringa Oil

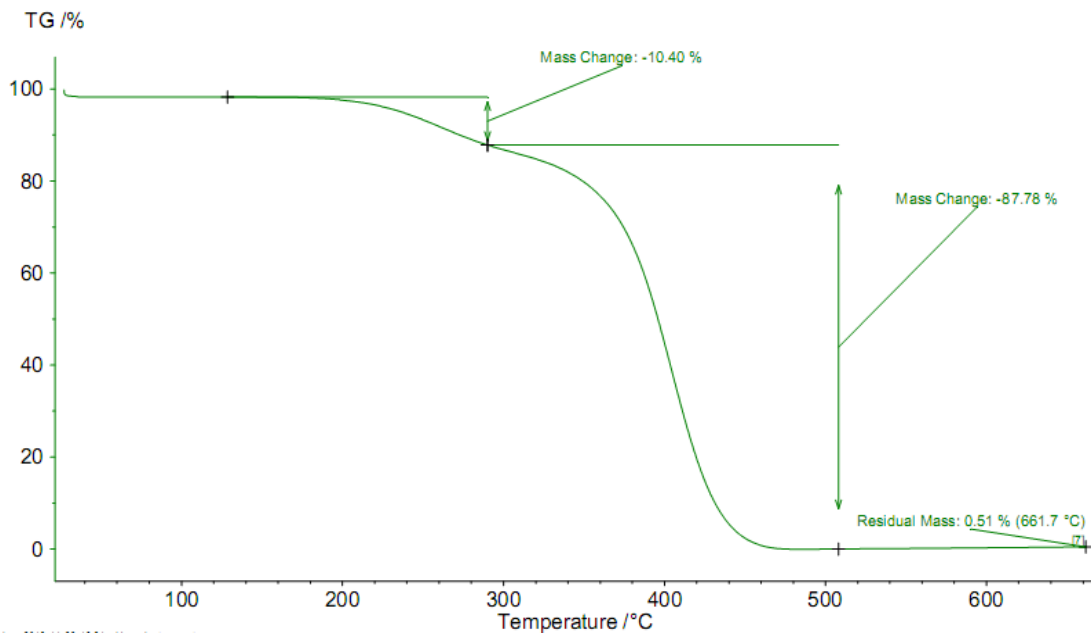


Figure 4.2: TGA analysis of Jatropha Oil

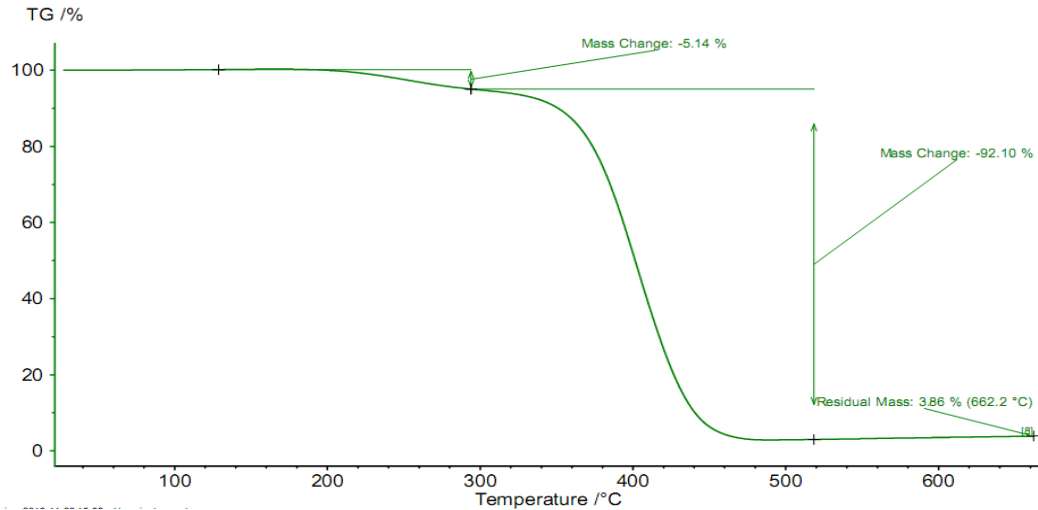


Figure 4.3: TGA analysis of Moringa/Jatropha Hybrids (50:50)

Other important and indispensable biodiesel properties like total glycerine (TG), free glycerine (FG) and free fatty acid (FFA) compositions in accordance with ASTM standards are presented in Table 4.11. These parameters are very important in biodiesel development to determine completeness or incompleteness of transesterification reaction and the quality of the products [15]. So far, the result appeared within the range of the ASTM standard [16] for the biodiesel and all the hybrids compare favourably. Different optimization protocol produced different results for better performance. Optimization therefore becomes important in order to determine quality and standard especially for hybridisation.

Table 4.9: Chemo-physical properties of Moringa and Jatropha seed oil feedstock

Some Properties	Moringa Oil	Jatropha Oil
Flash point (°C)	308	302
Pour point (°C)	8	-2
Cloud point (°C)	9	-4.5
Viscosity @ 40°C	35	31.04
Calorific value (cal/g)	8845.66	8990.23
Density (g/ml)	0.8767	0.8751
Free Fatty acids	6.678	9.45

Table 4.10: Chemo-physical properties of Moringa biodiesel (B100 methyl-ester)

Properties	Value /Unit	ASTM standards	EN/ SANS
Flash point	204°C	130 min	120 min
Acid Value	0.012	< 0.80	< 0.50
Pour Point	3.5°C	-	-
Cloud point	12°C	Not -	-
Kinematic Viscosity @40°C (cSt)	4.89	1.9 – 6.0	3.5 – 5.0
Cetane number	63	> 47	> 51
Density/Specific gravity @ 20°C	0.88g/m ³	0.850 – 1.0	0.86 – 0.90
Carbon residue	0.050 wt%	0.050	

The potential efficacy of hybridisation of biodiesel feedstock in this study and the innovative future it holds can be inferred from Figures 4.5, 4.6, 4.7, 4.8 and 4.9. In these Figures, the effects and interaction of hybridization on important biodiesel parameters were computed and plotted. As can be seen this innovative concept was quite promising; there are closer comparisons with AGO and standards for all the parameters evaluated. Comparisons with the two approaches to hybridization are also x-rayed. Flash points for all the hybrids are better than AGO because of better thermal stability and therefore are safe in handling and haulage. Their heating/calorific value is quite high, none is less than 42 MJ/kg in as much they are slightly lesser than AGO. Cetane index, the measure of diesel quality is superb for all the hybrids and better than the fossil diesel, AGO.

Table 4.11: Important biodiesel fuel properties after production

Biodiesel/Hybrids	TG (%)	FG (%)	FFA (%)
ASTM standard	0.25 max	0.02 max	0.8 max
BM ₁₀₀	0.250	0.060	0.134
BJ ₁₀₀	0.226	0.059	0.192
BM ₅₀ J ₅₀	0.268	0.0602	0.152
BM ₄₀ J ₁₀	0.251	0.129	0.336
BM ₃₀ J ₂₀	0.396	0.059	0.190
BM ₂₀ J ₃₀	0.220	0.10	0.119
BM ₁₀ J ₄₀	0.198	0.089	0.142
J ₄₀ M ₁₀ ME	0.224	0.079	0.348
J ₃₀ M ₂₀ ME	0.234	0.80	0.348
J ₂₀ M ₃₀ ME	0.234	0.080	0.349
J ₁₀ M ₄₀ ME	0.235	0.081	0.349

TG: Total glycerine; FG: Free glycerine

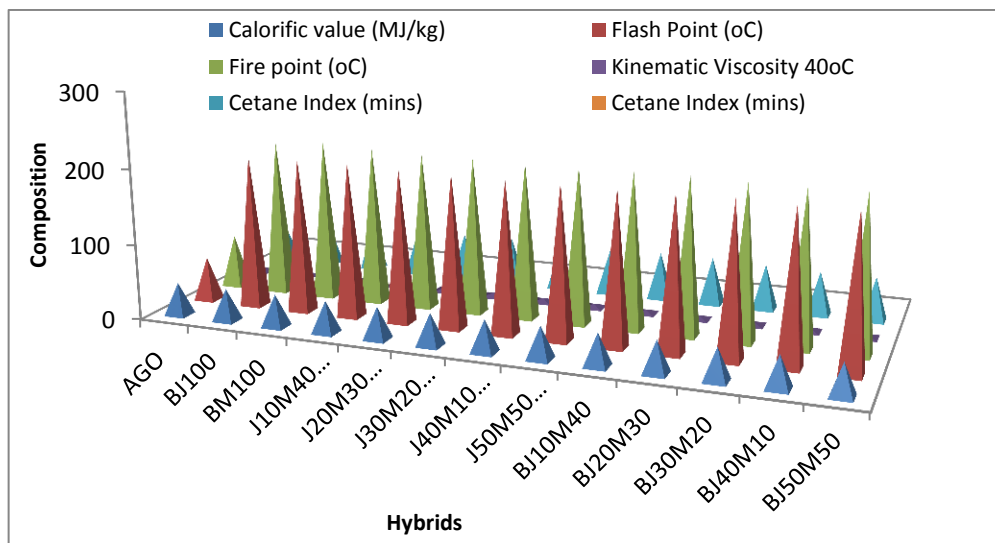


Figure 4.4: Chemo-physical properties of biodiesel and hybrids

Viscosity of the *ex situ* hybrids are superior to those of the *in situ* hybrids and are quite very close to that of the AGO which is very acceptable for the CI engine because the atomization in the combustion chamber will be quite high and will enhance complete combustion in excess of oxygen because biodiesel fuels are high oxygenated.

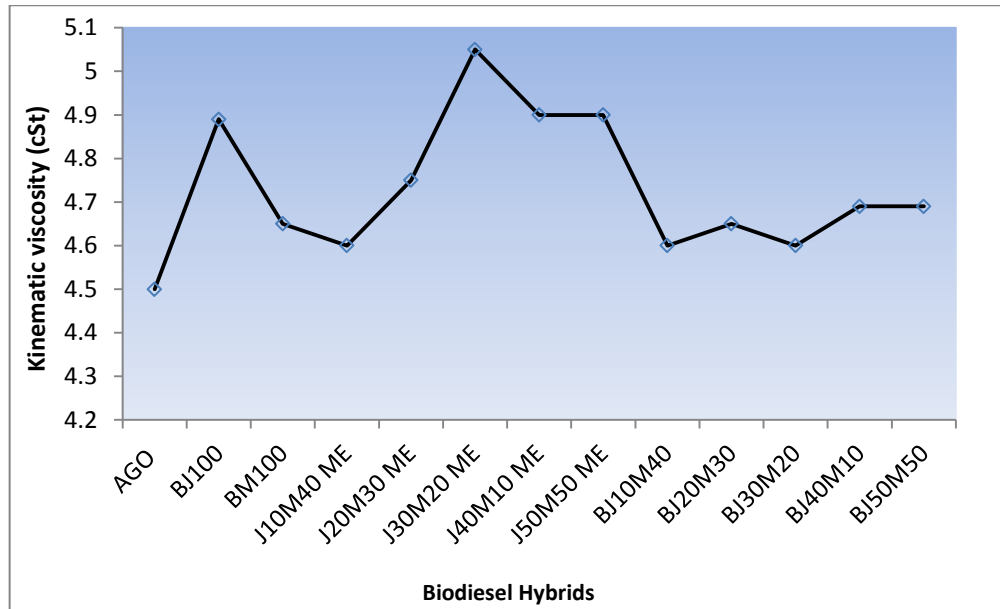


Figure 4.5: Effect of hybridization on kinematic viscosity of biodiesel fuels

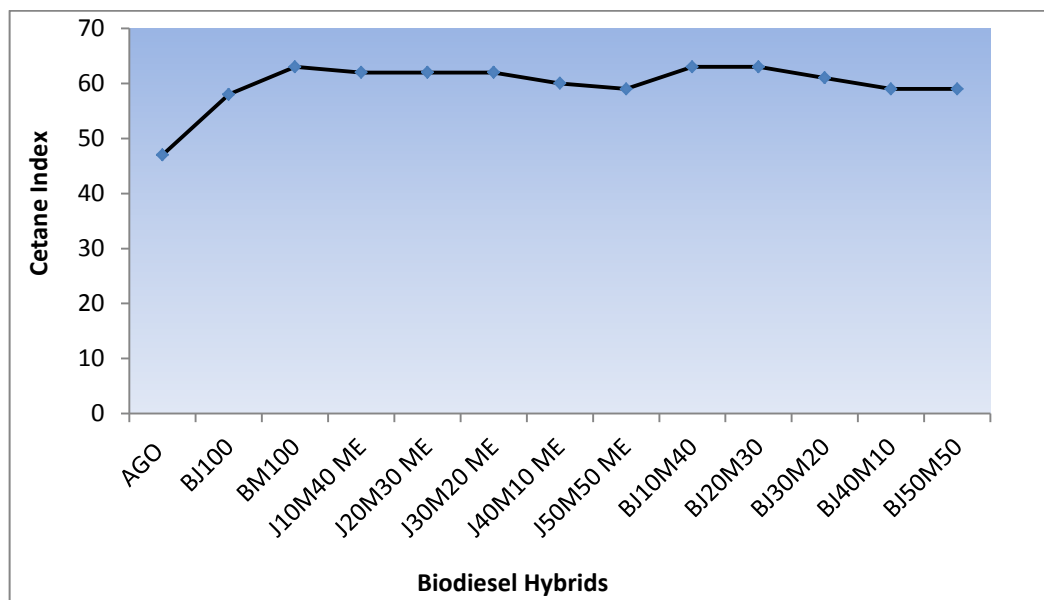


Figure 4.6: Effect of hybridization on Cetane index of biodiesel fuels

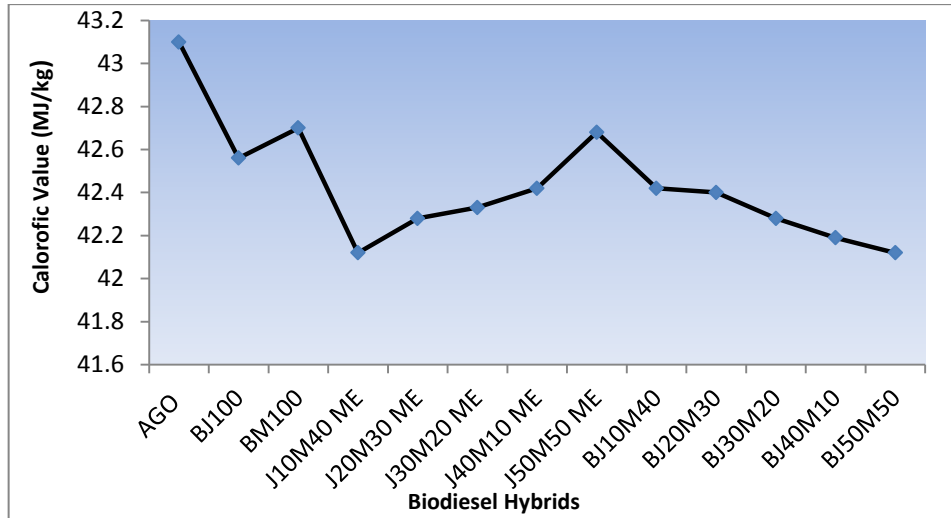


Figure 4.7: Effect of hybridization on calorific value of biodiesel fuels

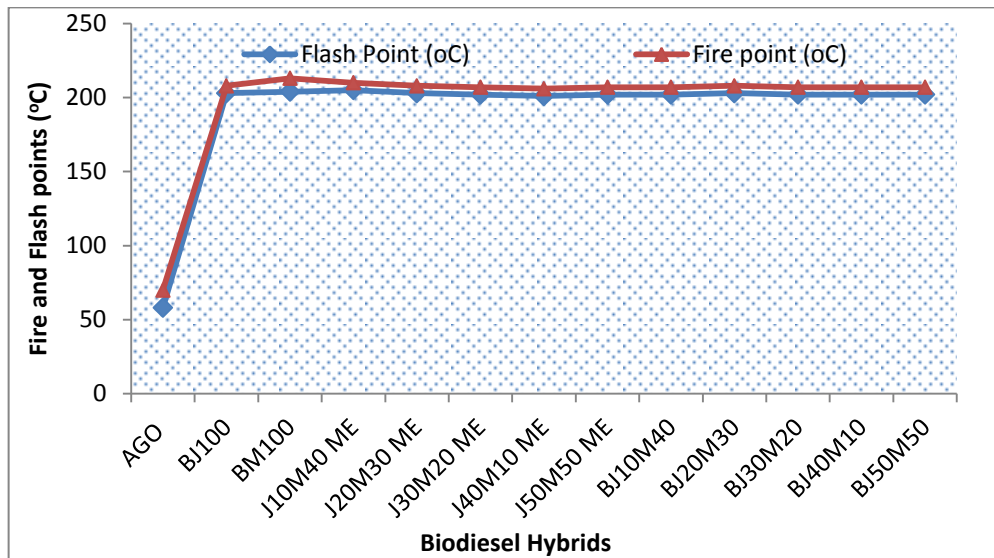


Figure 4.8: Effect of hybridization on flash and fire points of biodiesel fuels

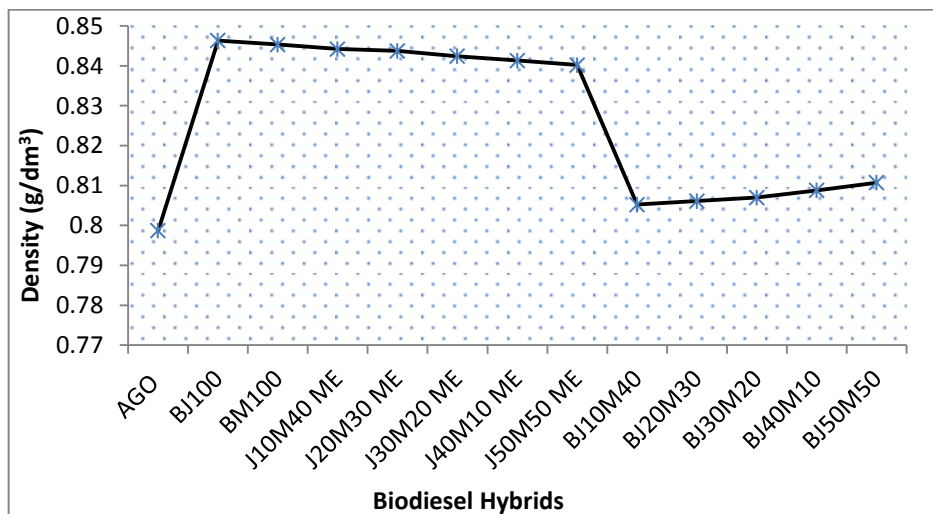


Figure 4.9: Effect of Hybridization on Density and Specific gravity of biodiesel fuels

4.4 Conclusion

Hybridisation of biodiesel feedstock *in situ* and *ex situ* has no doubt given rise to new products of improved energy qualities that may bring about the much needed difference in the biodiesel industry. In determining the suitability and potential of hybridising *Moringa oleifera* and *Jatropha curcas* seed oil (*in situ* hybridisation and *ex situ* hybridisation) a new approach to fuel development in the biodiesel industry is hereby conceptualised, articulated and developed. This approach has not been adopted or experimented in literature but this work will lead the way to hybridisation of very many other biodiesel feedstocks (bi-hybridisation, poly-hybridisation, *in situ* and *ex situ* hybridisation, blending of hybrids and so on). The study is still ongoing as other aspects beyond the scope of this present study are yet to be materialised.

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Chapter 5

Paper 4, EPEC: BMJH

Engine Performance and Emission Characterization of modelled Biodiesel fuels from *Moringa oleifera* and *Jatropha curcas* seeds oils and Hybrids

Engine Performance and Emission Characterization of modelled Biodiesel fuels from *Moringa oleifera* and *Jatropha curcas* seeds oils and Hybrids

Abstract - Biodiesel fuels are one of the easiest alternative fuels to be utilized in compression ignition engines. They are renewable, environmentally friendly and produce less gaseous and exhaust emissions. A variety of biodiesel feedstocks have been experimented with using different engine types and for various performance evaluations. In this study, overall engine performance tests and gaseous/emission characterizations were conducted in a four stroke versatile internal combustion engine (TD 300) over a wide range of throttle from the feedstocks of Moringa and Jatropha biodiesel and their resultant biodiesel hybrids. The hybrid compositions were J₅₀M₅₀, J₄₀M₁₀, J₃₀M₂₀, J₂₀M₃₀, and J₁₀M₄₀ from crude oil samples (*in situ*) and: BM₅₀J₅₀, BM₄₀J₁₀, BM₃₀J₂₀, BM₂₀J₃₀ and BM₁₀J₄₀ from produced biodiesel (*ex situ*). The biodiesel hybrids were produced by transesterification at specific optimization protocols and subjected to a novel approach in biodiesel development, hybridization using *in situ* and *ex situ* processes as reported in our earlier studies (Eloka-Eboka and Inambao [16]). The single stock biodiesel of Moringa and Jatropha and their hybrids performed favourably in comparison to AGO following ASTM standardized procedures. The torque, air consumption, ambient air temperature and pressure, specific fuel consumption, brake thermal and mechanical efficiency, brake power, engine noise, exhaust temperature and smoke opacity were determined. Also, gaseous emission was conducted using an online sampler which was subjected to a GC-MS spectrophotometer interacting with a flame induced detector (FID) for all comparisons. Results show greater improvement in performance from the hybrids and Moringa biodiesel with close similarity to AGO. The emissions were however insignificant to the immediate environment as against those of AGO. Biodiesel development continues to be currently researched until the much needed breakthrough is achieved globally.

Index Terms: *Engine, performance, emission, characterization, biodiesel, Moringa, Jatropha, seed oil, hybrids, hybridization, in situ, ex situ*

5.1 Introduction

The civilization of any country has come to be reckoned on the basis of the number of automotive vehicles being used by the populace of the country. The tremendous rate at which population explosion is taking place imposes expansion of cities to larger areas and the common person is forced to travel long distances even for his/her routine work [1-3]. This in turn is causing an increase in vehicular population at an alarming rate thereby creating huge pressures

for different governments in raising substantive foreign exchange for the import of crude petroleum products to meet the fuel requirements of automobiles and engines. The large amount of pollutants from the exhausts of engine applications running on fossil fuels have drastically increased in proportion to the number of vehicles on roads [4]. In view of the need and heavy demand for diesel fuel involved in transport in the domestic, industrial and agricultural sector and also the fast depletion of unevenly distributed fossil fuels, the search for alternate fuels has become pertinent apart from effective fuel utilization which has been the concern of the engine designers and manufacturers, developers, users and researchers involved in fuel, renewable and alternate fuel research and combustion [5-7].

When Rudolf Diesel [8] first invented the diesel engine, about a century ago, he demonstrated the principle by employing peanut oil and hinted that vegetable oil would be the future fuel in diesel engines. However, the higher viscosity and chemical composition of unprocessed oils and fats have been shown to cause problems in a number of areas: (i) piston ring sticking; (ii) injector and combustion chamber deposits; (iii) fuel system deposits; (iv) reduced power; (v) reduced fuel economy and (vi) increased exhaust emissions. The above mentioned problems can be solved once vegetable oils are converted chemically into biodiesel [6, 7]. Biodiesels derived from vegetable oils present a very promising alternative to diesel fuel since biodiesels have numerous advantages compared to fossil fuels as they are renewable, biodegradable, provide energy security and foreign exchange savings besides addressing environmental concerns and socio-economic issues [9-14]. These biodiesels have lower viscosity, density, molecular weight and ratio of carbon to hydrogen. Experiments were conducted [5-9] with conventional engine fuelled with biodiesel and it was reported that performance was comparable with conventional engines [10, 11, 13]. The drawbacks associated with biodiesel for use as fuels in compression ignition engines call for improvement in biodiesel production and processes [14, 15]

Biodiesel as mono-alkyl ester made from natural and renewable vegetable oil and animal fats based feedstock can be improved upon by chemical processes such as hybridization [16, 17]. Biodiesel is an environmentally friendly alternative diesel fuel consisting of the alkyl esters of fatty acids which are expected to play a significant role in reducing overall CO₂ emissions which will in turn clean and sustain the environment [14, 15]. Biodiesel is produced commercially by a chemical reaction, transesterification, which lowers the viscosity of the vegetable oils, breaks the poly-unsaturated nature of the bonds and improves its performance, combustion and atomization in the combustion chambers. Since biodiesel is an oxygenated, sulphur-free fuel, it typically reduces engine and gaseous emissions except for the oxides of nitrogen (NO_x) which are slightly higher than fossil diesel [14, 15]. The chemical and physical properties of the fatty acids, as well as the effect of molecular structure determine the overall

properties of biodiesel fuel. Investigations into the impact of FAME properties on diesel engines are highly topical, as hybrids of different feedstocks and higher blends with automotive gas oil (fossil diesel) of biodiesel are introduced [12, 18].

5.2 Emission effects

Global warming is considered to be one of the greatest environmental threats facing our modernized and technological world. Climate change has mainly been caused by the increase in atmospheric greenhouse gases due to human activities since the start of the industrial era which includes burning fuel to run engines [18]. When fuels are burnt, the exhaust products contain gaseous, solid, and liquid emissions. For internal combustion (IC) engines, there are just a few basic types of emissions to consider: Carbon (IV) oxide, oxides of Nitrogen (NO_x), oxides of Sulphur (SO_x), Carbon (II) oxide (CO), hydrocarbons (HC), and particulate matter (PM). In addition to these primary pollutants, reactions in the atmosphere generate secondary pollutants, namely acid rain, photochemical smog and tropospheric ozone [18]. Many of these pollutants have serious implications on human health, safety and the environment. Consequently, many countries have established strict environmental regulations that must be met by all automobile manufacturers and fuel developers.

5.3 Status and legislation of biodiesel in South Africa

Legislation has driven research to satisfy increasingly stringent emission requirements such as improving the combustion process and utilizing advanced after-treatment systems. Another approach has been to develop and popularize electrically powered vehicles and hybrids, and the use of alternative fuels. Of most recent and still at developmental stage is the process of hybridization of different feedstocks of biodiesel to improve general biodiesel fuel properties which this paper is related to. Studies are at top gear at the Biofuel Research Laboratories of the Green Energy Research Solutions Research group at the University of KwaZulu-Natal, Howard College, Durban, South Africa to make the required breakthrough. Different feedstocks are being experimented with to ascertain fuel properties and performance characterization (Eloka-Eboka and Inambao, 2014). Biofuels are expected to play a significant role in reducing overall CO₂ emissions [4]. Also, the possibility of substituting cleaner burning alternative fuels for gasoline and diesel has drawn increasing attention over the past decade [16]. Biofuels produced from sugar cane, corn or other vegetable oils are attracting interest as renewable energy sources that do not increase CO₂ levels [17]. That is why the South African government granted a reduction of 30% fuel tax for biodiesel thus encouraging its utilization in the country [19]. In terms of legislation, the South African Bureau of Standards (SABS) drafted a provisional biodiesel standard (SANS 1935:2011) [20] edition 2 as comparable to the ASTM D6751:2

which was based on European standards with some modification in parameters like the iodine value, and allowing the use of other esters as well [19]. Feedstocks of specific interests include soya oil, corn and physics nuts (*Jatropha*). Some studies were conducted with the objective of determining the influence of biodiesel development and application on the South Africa's economy without interfering with food production. The outcome was positive with the assessment that biodiesel especially from non-edible sources could replace 20% of imported diesel in the country [19].

5.4 Engine performance

Cetane Index (CN) is one of the main indicators of the ignition quality and combustion miscibility in diesel engines. It is a dimensionless descriptor for the ignition delay time of a fuel upon injection into the combustion chamber. The higher the cetane number, the shorter the ignition delay time and vice versa. It is an acceptable fact that the CN of biodiesel is generally higher than fossil diesel fuel due to the absence of aromatic compounds and unburnt hydrocarbons [20] and better amongst biodiesel hybrids [16,17]. The European standard for biodiesel (EN 14214:2003) specifies the minimum requirements for CN to be 51, since too low Cetane number might cause very rapid and incomplete combustion. Like other properties, Cetane number/index number is affected by the molecular structure of the source material FA [21-23]. The CN of biodiesel depends on the distribution of fatty acids in the original oil or fat from which it was produced. The longer the straight chain FA and the more saturated the molecules in the fuel, the higher the CN [7, 10, 20].

Higher Cetane numbers of the fuel was also correlated with reduced NO exhaust emissions for conventional diesel fuel as stated by Knothe and Steidley [22], however this is not always true for all types of engine technologies, as modern engines that are equipped with more sophisticated injection systems that control the rate of injection are less sensitive to CN variations [20, 22-23]. In addition, several other properties of biodiesel are important for determining its suitability as an alternative to petroleum diesel fuel. It is generally known that biodiesel fuels have lower heat release values than petroleum diesel. Fuel density and number of double bonds also have an effect on the fuel's calorific value but not significantly. Hybridization alters this structural sequence to suit desired fuel needs. A review conducted by some biodiesel researchers concluded that the FAMES have slightly higher combustion efficiency than baseline diesel fuel due to the structural oxygen content of the biodiesel which improves the combustion process, as also and similar observations reported by Lapuerta *et al.* [24-26].

Lubricity properties of fuel are very critical for reducing friction wear in engine components which are normally lubricated by the fuel rather than crankcase oil. Mechanical wear and fuel leaks can cause many problems in the engine fuelling system, as fuel pumps and injectors depend on the fuel for lubrication of moving parts. It has been known that biodiesel improves the lubricity of diesel fuel, and it is a common practice among most of the diesel fuel producers to add 1-5% of biodiesel in the ultralow Sulfur diesel (ULSD) fuel to improve its lubrication quality [19, 22].

Particulate Matter (solids or liquids) emissions have been of considerable concern with the manufacturers of diesel engines, as it is very visible and often contains some carcinogenic aromatic hydrocarbons such as benzene. According to an EPA technical report issued in 2002 [12, 14], the particulate matter emissions of B100 and B20 are less than petroleum diesel by 47%, and 12% respectively. Lapuerta *et al.* [24] reported that particulate matter emissions were investigated by a few authors and their results did not show any significant correlation either with the chain length or with the unsaturation level. But Monyem and Van Gerpen *et al.* [27, 28] reported an increase in particulate matter with increasing number of double bonds in the fatty acid and no significant impact of FA chain length was observed. NO_x formation is influenced by the oxygen concentration in the fuel, combustion duration, and mixture richness in the combustion chamber [2]. The formation of NO_x emissions is also effected by fuel properties, such as cetane number, aromatics content and iodine number. Lapuerta *et al.* [24] reported that the use of biodiesel fuels leads to a slight increase in NO_x emissions, especially in the case of highly un-saturated biodiesel fuels.

5.5 Improvement consideration in biodiesel feedstock

When considering the total amount of greenhouse gas emissions it is therefore important to consider the whole production process and what indirect effects such production might cause. The effect on carbon dioxide emissions is highly dependent on production methods and the type of feedstock used. Calculating the carbon intensity of biofuels is a complex and inexact process, and is highly dependent on the assumptions made in the calculation. A calculation usually includes:

1. Emissions from growing the feedstock (e.g. petrochemicals used in fertilizers);
2. Emissions from transporting the feedstock to the factory;
3. Emissions from processing the feedstock into biodiesel.

Based on these, production methodology is as important as quality of biodiesel. In cases where there is incomplete transesterification process, the end product(s) may be undesirable for utilization in the engines which may also affect the environment

5.6 *Specific study objectives*

Engine testing facilities are commonly used in engine development and catalyst performance research laboratories to achieve further emission reductions. A variety of biodiesel feedstocks have been experimented with using different engine types and for various performance evaluations but the aim of this study is overall engine performance tests and gaseous/emission characterizations on a four stroke versatile internal combustion engine (TD 300) over a wide range of throttle from the feedstocks of Moringa and Jatropha biodiesel and their resultant biodiesel hybrids produced by transesterification, at specific optimization protocols and subjected to a novel approach in biodiesel development, viz., hybridization using *in situ* and *ex situ* processes as reported in our earlier studies [16].

In this study, the single stock biodiesel of Moringa and Jatropha and their hybrids were subjected to standardized procedures and compared with AGO. The torque, air fuel ratio, ambient air temperature and pressure, specific fuel consumption, brake thermal and mechanical efficiency, brake power, exhaust temperature and smoke opacity and their individual effects were determined with significant differences; gaseous emissions were also measured to ascertain the level of improvement in performance.

5.7 *Materials/Methods*

5.7.1 *Development and application of biodiesel production model*

The biodiesel production model that was adopted for this study was derived from the production protocol of CSIR-CSMCRI, Bhavnagar [30] for Jatropha biodiesel production patented in the US which was re-evaluated and modified to suit variable feedstocks in this study. The working principle was the free fatty acid neutralization through base wash. The processes involved are a form of oil pre-treatment which conditions the crude oil for transesterification. The free fatty acid composition of any crude vegetable oil and its neutralization is the main thrust of reaction. Oil with lower free fatty acids requires less treatment procedures and less materials of reaction. The modified model is preceded by several stoichiometric calculations which are then applied in the experimental reactions. The model encompasses a dual way process consisting of two main reactions: base wash/neutralization reaction using strong base, in this case, aqueous solutions of sodium hydroxide (NaOH) and methyl-esterification reaction using methanol in the presence of potassium hydroxide (KOH) as catalyst. NaOH interacts better in aqueous medium hence the

choice in the base wash while the solubility of KOH in organic solvent makes it the choice in esterification. The effervescence reaction with NaOH in water enhances the dissolution and therefore proper pre-treatment of the crude vegetable oil.

The calculations were adopted in excel spreadsheets and values imputed to give required compositions for the reaction simply by changing the quantity of oil to be transesterified (in kg) and the fatty acid composition. The model generated the required NaOH and water for dissolution and also the required KOH needed to convert the neutralized oil to biodiesel.

Before adopting the model, four important experimental and numerical determinations were required:

1. Determination of the average molecular weight of fatty acids usually adopted as any member of the carboxylic acid family.
2. Determination of the weight of the crude oil to be transesterified (in kg).
3. Determination of the free fatty acid composition of the crude oil using any method.
4. Determination of the total free fatty acids.

From the experimental and numerical calculations of this model, the following will be determined:

1. The amount of sodium hydroxide (NaOH) required for neutralization/ base wash for any quantity and type of crude vegetable oil.
2. The amount of water (H₂O) needed to dissolve the required sodium hydroxide.
3. The amount of potassium hydroxide required as catalyst for transesterification.
4. The amount of methanol (alcohol) required for the total transesterification of vegetable into biodiesel (methyl esters).

5.7.2 Model formulation/calculation: base wash/neutralization

Average molecular weight of oil in the form of fatty acids	=	FA _{mol}
Weight of crude oil in kg	=	W
Free Fatty Acid composition (%)	=	FFA
MW of NaOH	=	molecular weight of NaOH
Total FFA	=	FFA _{Total}
NaOH _{req}	=	Amt of NaOH required for neutralization
FFA _{Total}	=	$\frac{W(kg) \times FFA}{1000}$ (gm)
NaOH _{req}	=	$FFA \times \frac{MW \text{ of NaOH}}{FA_{mol}}$ (gm)
In Excel spreadsheets: NaOH _{req}	=	= ROUND (FFA _{Total} *40/FA _{mol}), 2) (gm)
Amount of Water (H ₂ O) required	=	NaOH _{req} x 4 (gm)

5.7.3 Model formulation: transesterification

N	=	Neutralized oil
TG _{mol}	=	Moles of Total glyceride
MeOH _{excess}	=	Excess methanol (%); in this model 75% was adopted
MeOH _{mol}	=	Moles of methanol
MW of KOH	=	Molecular weight of KOH
MeOH _{req}	=	methanol required for transesterification (gm)
KOH _{req}	=	Amount of KOH required as catalyst (gm)
TG _{mol}	=	$\frac{N}{((F\text{Amol} \times 3) + \text{MW of KOH})}$
MeOH _{mol}	=	$((TG\text{mol} \times 3) \times (1 + \text{MeOH}\text{excess}))$
In Excel Spread, MeOH _{mol}	=	$=\text{ROUND} ((TG_{\text{mol}} * 3) * (1 + \text{MeOH}_{\text{excess}}), 4)$
MeOH _{req}	=	$\text{MeOH}\text{mol} \times 32 \times 1000$
KOH _{req}	=	$2.5\% \times N \times 1000$

This model allows for flexibility of experimental reaction. The two processes of base wash / neutralization and esterification can be conducted in the cold/ambient condition or heated depending on the choice of the experimental design. This study observed the effects of the cold and hot at 60°C-70°C with agitation speed of 500 rpm to 650 rpm at 30 minutes each and there was no seeming difference in the reaction products. So for energy conservation, optimization and less cost, the cold/ambient condition is recommended. There was complete transesterification while employing any of the conditions. But in subjecting to heat, care must be taken not to burn off the methanol before attaining equilibrium.

The engine test performance and emission analysis test was conducted at the Biofuels laboratory of the Petroleum Processing Engineering Technology of Petroleum Training Institute, Effurun, Nigeria. A TD 300, a versatile engine test bed with instrumentation for comprehensive investigations into the features and operating characteristics of internal combustion engines was used for the study. It enables a wide range of investigations into the characteristics of four-stroke single-cylinder petrol and diesel engines. For use with engines up to 10 kW: four-stroke diesel and four-stroke petrol engines ideal for group demonstrations and student projects; Includes comprehensive control console and instrumentation; Optional ancillaries available to extend the range of study even further; Quick, convenient and accurate engine mounting and changeover; Test bed includes anti-vibration mounts; Uses four-quadrant drive to start and load the engine, giving excellent stability; Self-sealing couplings enable quick and efficient connection and disconnection of fuel lines with minimum loss or spillage of fuel; Works with TecEquipment's Versatile Data Acquisition System (VDAS®).

The main components of the system are: a heavy fabricated floor-mounting bed; an instrument console with instrument frame; a fuel tank support frame that supports the fuel tank and optional fuel gauge. The bed is held on anti-vibration mounts. It includes a robust trunnion-mounted d.c. machine. An electronic load cell connected to the machine measures the driving torque of the test engine. The engines are supplied pre-mounted on a sturdy precision base plate. When the engine is initially mounted onto the test bed or exchanged with an alternative engine, dowels and slots locate the engine quickly, accurately and reliably. Each engine includes a colour-coded fuel tank with self-sealing couplings. The couplings ensure the engines can be connected and disconnected quickly and efficiently with minimum loss or spillage of fuel. For convenience and safety, the fuel tank can be removed for filling or for storage in a fuel locker when not in use. Removing the fuel tank also prevents unauthorized use of the equipment.

The control has an electrical cabinet which houses a four-quadrant drive to start and load the engine. The motor can also be used to drive the engine while the fuel and ignition are off, so students can establish frictional losses. The control includes an air-box and orifice plate to enable students to measure air flow. The instrumentation and display units are mounted on a sturdy frame, which is part of the control. The control also includes a convenient work top for use as a writing desk, or for positioning other equipment such as a computer. The control and test bed are separate in order to avoid vibration being transmitted from the engine to the measuring devices. In addition, it allows the instrumentation to be thermally and acoustically screened from the test bed, using suitable shielding or a wall. The engines (available separately) include an exhaust thermocouple, dynamometer coupling, colour-coded fuel tank, hoses and fittings. They have modified cylinder heads and cranks for connection to TecQuipment's Engine Cycle Analyzer (ECA100 available separately). An Exhaust Gas Calorimeter (TD300a) is also available to enable students to measure energy lost through exhaust gases and to determine the energy balance of the engine. Table 5.1 and Figure 5.1 are the test bed specification and schematic diagram respectively. See also Figure 5.2 showing engine test bed for biodiesel experimentation in Mechanical Engineering Laboratory at Howard College, Durban for high volume experimentation.

Table: 5.1: Engine test bed specification

Engine Test bed and Instrumentation	Specifications
Available Experiment Modules	Four-stroke petrol engine (TD301) Four-stroke diesel engine (TD302)
Essential Ancillaries	Manual Volumetric Fuel Gauge (AVF1) or Automatic Volumetric Fuel Gauge with Digital Read-out (DVF1)
Recommended Ancillaries	Exhaust Gas Calorimeter (TD300a) • Versatile Data Acquisition System frame mounted version (VDAS-F)
Essential Services	<i>Exhaust outlet:</i> Laboratory exhaust outlet to atmosphere, to comply with local emission regulations <i>Acoustic silencer:</i> Specification dependent upon exhaust system <i>Electrical supply:</i> Three-phase 415 VAC, 50/60 Hz, 20 A or Three- phase 220 VAC, 50/60 Hz, 32 A
Operating Conditions	<i>Operating environment:</i> Well ventilated laboratory environment, <i>Storage temperature range:</i> –25°C to +55°C (when packed for transport) <i>Operating temperature range:</i> +5°C to +40°C <i>Operating relative humidity range:</i> 80% at temperatures < 31°C decreasing linearly to 50% at 40°C
<i>Instrument Console dimensions</i>	Width 1400 mm x depth 300 mm x height 820 mm
<i>Test Bed dimensions (without engine)</i>	Width 950 mm x depth 475 mm x height 1050mm
<i>Weight (packed total)</i>	<i>Weight (packed total):</i> 600 kg
<i>Volume (packed total)</i>	600 kg
<i>Dynamometer</i>	4.25 m ³
<i>Maximum absorption</i>	D.C. machine with four-quadrant regenerative drive
<i>Maximum speed:</i>	10 kW
<i>Speed measurement</i>	3600 rev min ⁻¹
<i>Torque measurement</i>	Optical encoder and digital display
<i>Air consumption measurement</i>	Strain gauged load cell and digital display
<i>Ambient air temperature and barometric pressure measurement</i>	Air-box and orifice plate, pressure transducer and digital display
<i>Exhaust temperature measurement</i>	Thermocouple, pressure transducer and digital display
<i>Fuel consumption</i>	Engine thermocouple and digital display Precision volumetric fuel gauges (analogue or automatic digital versions available)
<i>Safety features</i>	Interlocks for mains power failure and engine over- speed Emergency stops on test bed and console

Source: Engine Test Bed Manual

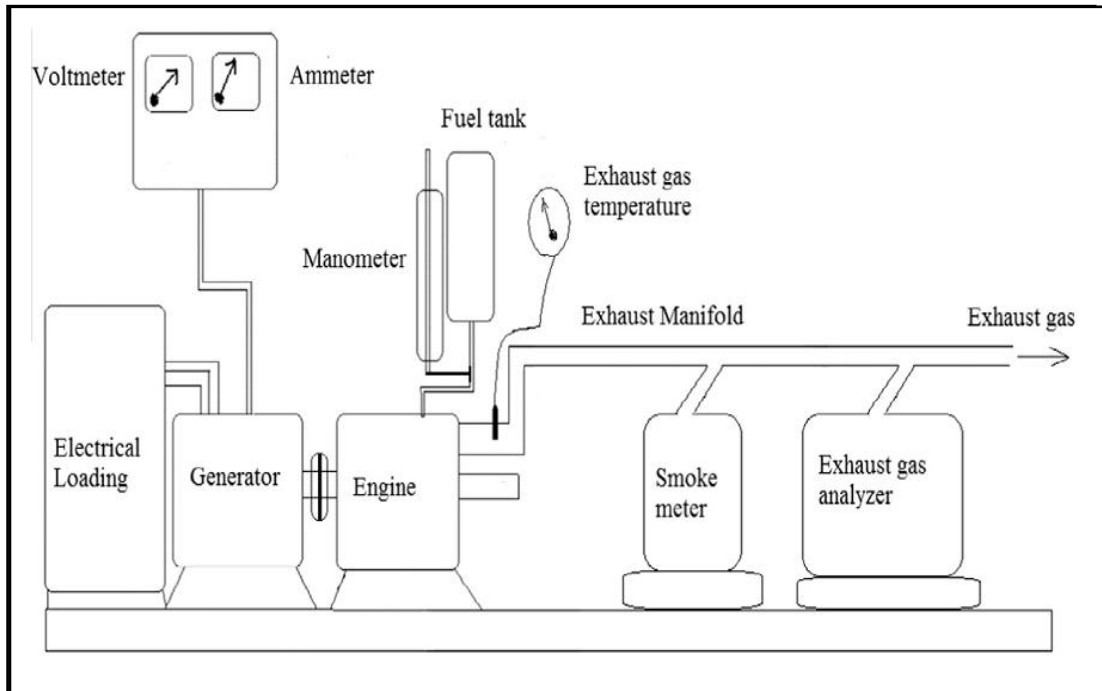


Figure 5.1: Schematics of the engine test bed setup



Figure 5.2: Engine test cell facilities and IC engines at UKZN for biodiesel experimentation

In the performance experiment, the following were tested, analyzed and recorded: torque, temperature, low and high speeds, specific fuel consumption, engine flue gas emissions, O₂, CO, VOCs and NO_x; smoke opacity, noise and vibration. Having powered the diesel engine for 30 minutes of continuous run using AGO (conventional diesel) to stabilize it, the engine was put to a hold, drained off of the AGO and ready for testing. Samples of biodiesel and blends, and AGO were measured out using a measuring cylinder. 1000 ml of each sample was poured into sample bottles. They were intermittently poured into the storage tank of the diesel engine which was modified to suit the purpose of the test. A standard 1000 ml container was constructed for use as a fuel tank and was directly connected to the injector combustion chamber so that precise data was collected without difficulty. Each sample was run for 40 minutes. A total of 15

samples and AGO were run and tested for the parameters already established. All the biodiesel and samples were able to power the engine creditably well without any iota of difficulty. The speeds (rpm) were measured for each sample at different temperatures and time; using the rated power of the engine and the power-torque-speed relationship, the torque at different speeds was determined.

5.7.4 Power, torque and rotational speed relationship employed

The relationship of power, torque and rotational speed according to Serway and Jewett [29] and general engine technology is crucial to engine performance. Mathematically for rotation about a fixed axis or point, the expression is given by:

$$W = \int_{\theta_1}^{\theta_2} \tau d\theta \quad (5.1)$$

Where W = work, τ = torque, θ_1 and θ_2 are initial and final angular positions.

From the theory of work-energy and power, W is equal to change in rotational kinetic energy, ΔE which is given by;

$$\Delta E = \frac{1}{2} I \omega^2 \quad (5.2)$$

Where I is the moment of inertia and ω is the angular speed (rpm).

$$P = \tau \cdot \omega \quad (5.3)$$

P = power, τ = torque and ω = angular velocity.

The power injected by the torque depends on instantaneous angular speed and the power output [29] is determined by the torque applied to the engine generator as schematically presented in Figure 5.1.

$$P = \tau \times \pi \times \omega \quad (5.4)$$

Which is torque multiplied by 2π multiplied by rotational speed.

5.7.5 Emissions determination

The temperature attained at different time and speeds were recorded using the thermocouple and the digital meter. The fuel consumption per sample for the period of the tests (40 minutes) was also recorded. This was accomplished by taking the difference of the volume of the initial fuel used for each run and the final volume after runs for 40 minutes. The amount of flue gas emitted (O_2 , CO , NO_2 and $VOCs$) at each interval of time, temperature and speed for each sample was

recorded in parts per million (ppm) and compared. All the data collected were analyzed, compared and graphs plotted. Inference statistics were used for this analysis and applied for the purpose of this study. An experimental setup used in the present work is shown in Figure 5.3. The engine was loaded with an eddy current dynamometer. The mass flow rate of intake air was measured with an orifice meter connected to a manometer. A surge tank was used to damp out the pulsations produced by the engine, for ensuring a steady flow of air through the intake manifold. The fuel consumption rate was determined using the glass burette and stop watch. The engine speed was measured using a digital tachometer. An AVL 444 Di gas analyzer was used for measuring the exhaust gas components such as CO, HC, and NOx. The smoke density was measured using an AVL 413 smoke meter. The exhaust gas temperature was measured with a k-type thermocouple.

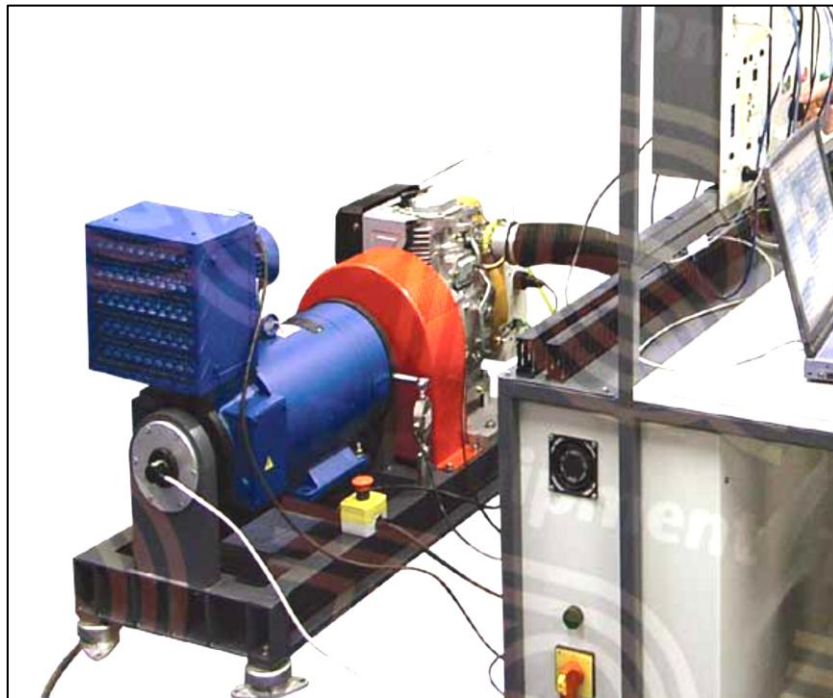


Figure 5.3: Experimental setup at PTI, Warri



Figure 5.4: Portable diesel smoke meter (Opacimeter)

Before starting the measurements, some important points were considered in order to get meaningful data from the experiments. The engine was warmed up prior to data acquisition. The lubricating oil temperature was monitored to confirm that the engine was in a sufficiently warmed-up situation. Ambient conditions should be maintained for different engine runs because the ambient pressure and temperature have an effect on intake air drawn into the engine cylinder, thereby changing the fuel-air mixing as well as combustion process. All the engine test runs were carried out in fair constant ambient conditions. During the tests with hybrids biodiesel, the engine was started with AGO until it warmed up. Then fuel was switched to biodiesel and hybrids. After finishing the tests with biodiesel B100 the fuel was always switched back to diesel and the engine was run until the hybrids biodiesel had been purged from the fuel line, injection pump, and injector in order to prevent starting difficulties at later time.

At the start of each test the test engine was operated with base fuel-diesel for about 30 minutes to attain a normal working temperature condition after that base line data were generated and the corresponding results were obtained. The engine was then operated with hybrids of biodiesel in situ ($J_{50}M_{50}$, $J_{40}M_{10}$, $J_{30}M_{20}$, $J_{20}M_{30}$, and $J_{10}M_{40}$) and ex situ ($BM_{50}J_{50}$, $BM_{40}J_{10}$, $BM_{30}J_{20}$, $BM_{20}J_{30}$ and $BM_{10}J_{40}$). At every operation the engine speed was checked and maintained constant. All the measurements were repeated thrice, and the arithmetic mean of these three readings was employed for calculation and analysis. The different performance and emission parameters analyzed in the present investigation were brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), exhaust gas temperature (EGT), carbon monoxide (CO), unburned hydro-carbons (HC), nitrogen oxide (NO), and smoke. Smoke opacity was measured using portable diesel smoke meter (Figure 5.4) according to SAE J1667 standards as adopted by South African National Standards [20].

5.8 Results and discussion

The results show that crude Moringa oil properties which include some chemo-physical properties are very determinant in its characteristics as a feedstock for biodiesel. The chemo-physical and thermal properties have been presented in our previous paper. As this study is primarily concerned with the engine performance and emission characteristics, parameters such as brake specific fuel consumptions (BSFC) on engine loads, brake specific thermal efficiencies (BSTE) on engine loads, exhaust gas temperatures on engine loads, smoke opacity on engine loads were evaluated. Also expressed are the comparisons of thermal and mechanical efficiencies, composition of gaseous emissions and the effects of engine loads on them. These are presented in Tables 5.2, Figures 5.5 to 5.13, Tables 5.3 and 5.4 respectively. As can be seen in Table 5.2, the average biodiesel (B100 and the acceptable biodiesel bend, B20) was compared with conventional AGO for regulated and non-regulated emissions. The emissions of

CO, PM and NO_x were significantly reduced in biodiesel compared to AGO and B20 (80% of AGO). Sulphates, PAHs and nPAH which were non-regulated also followed the same trend of non-pollution in biodiesel. This was as established by the National Biodiesel Board of the US and was employed as the benchmark (standard/control) for comparison of the hybrids performance of this study. The effects of engine loads on thermal efficiency in Figures 5.5 and 5.6 when AGO and biodiesel hybrids were used to power the engine exhibited close comparison with the AGO. The efficiencies increased as the engine load was increased for all the hybrids utilized.

The difference in the response of AGO and biodiesels was quite insignificant even though AGO performed better. At full load, AGO produced 40% thermal efficiency while the hybrid biodiesel fuels produced between 35% and 40%. BM₅₀J₅₀ and BM₄₀J₁₀ were as high as 38%. The presence of oleic acid and the higher oxidative stability of Moringa as a hybridization agent may be responsible for this improved performance. This was due to the higher percentage in brake power as loads are applied. The high presence of dissolved oxygen and complete combustion of the biodiesel hybrids were also responsible which enabled proper atomization of the fuel molecules. Fuel consumption (Figure 5.6) is also related to the thermal efficiencies which decreased as the loads increased. Biodiesel and hybrids combusted more than AGO so had a lesser consumption rate with superior heating/calorific value, lesser specific gravity and lower mass flow injected into the engine [19]. Viscosity as a property also played a significant role in the atomization of fuel in the combustion chambers. At full load, the specific fuel consumption of AGO was as low as 0.28 kg/kWh while the hybrid biodiesel recorded between 0.30 kg/kWh to 0.42 kg/kWh.

This is quite an improvement from non-hybridized conventional biodiesel fuels as recorded by other researchers. The mono-unsaturated oleic acid which is very prominent in the Moringa hybridizing agent with fatty acid profile of 74.0% as indicated in our earlier studies [16, 17] also made a significant contribution. Oils with high oleic acid content are desirable and give biodiesel fuels a reasonable balance or compromise of fuel properties. Considering that the other saturated fatty acid methyl esters (C20:0 and C22:0) in Moringa biodiesel as well as C22:1 likely have high cetane numbers, a high cetane number of Moringa biodiesel is anticipated [16, 17]. Figures 5.7 and 5.8 show the trend of events of the exhaust gas temperature and smoke opacity with increased engine loads. There was a general increase in smoke opacity and exhaust temperature as the engine loads increased. But in comparison to AGO, the biodiesel and the hybrids performed better. At peak load, AGO recorded 380 HSU while the hybrids fell between 290 and 320 HSU; what this means is that AGO produced more smoke than the biodiesel and hybrids. Density/opacity of smoke is used to measure the efficiency of combustion of fuel in the

engine. The lower the better and higher is the environmental protection it offers. The exhaust gas temperature is also closely linked with the former. AGO recorded higher temperatures than the biodiesel and hybrids. At peak load, it was 395°C while the hybrids were between 320°C to 375°C. Biodiesel and hybrids with lesser emissions and lower exhaust gas temperatures are not prone to tail pipe and exhaust corrosion compared to AGO. It must be noted that the quantity of fuel injected into the engine increases with engine load to maintain the power output and therefore the heat released rises proportional to the exhaust gas temperature as the load increases which is also indicative of combustion quality in the chamber.

For all the emissions, CO, CO₂, NO_x, VOCs as evaluated in Figures 5.11, 5.12 and 5.13 with AGO, there was a general trend with respect to engine loads. At constant load, there was slight variation with respect to hybrids which was very wide compared to AGO. As can be seen in Table 5.4, AGO recorded 0.035 and 0.018 % vol composition of CO₂ at 100 and 50% load respectively while the hybrids fell between 0.02 to 0.017 and 0.008 to 0.02% vol at 100 and 50% respectively. Figure 5.9 shows that AGO produced a wider variation in composition of CO than biodiesel and hybrids. The same trend is also observable in Tables 5.3 with respect to torque, temperature and rotational speed, v in rpm. Between the speed of 1000 rpm to 200 rpm, the torque, and temperature with increase in time from 5 minutes to 40 minutes, the emissions of CO, NO_x, CO, VOCs and O₂ increased for AGO and for the hybrids at 50 and 100% load respectively as seen in Table 5.4.

Table 5.2: Average biodiesel (B100 and B20) emissions compared to conventional diesel

Emission Type	B100	B20
	Emissions in relation to conventional diesel	
Regulated		
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
NO _x	+10%	+2% to -2%
Non-Regulated		
Sulfates	-100%	-20% ^a
PAH (Polycyclic Aromatic Hydrocarbons) ^b	-80%	-13%
nPAH (nitrated PAH's) ^b	-90%	-50% ^c
Ozone potential of speciated HC	-50%	-10%

Source: National Biodiesel Board, Biodiesel Fact Sheets, Emissions

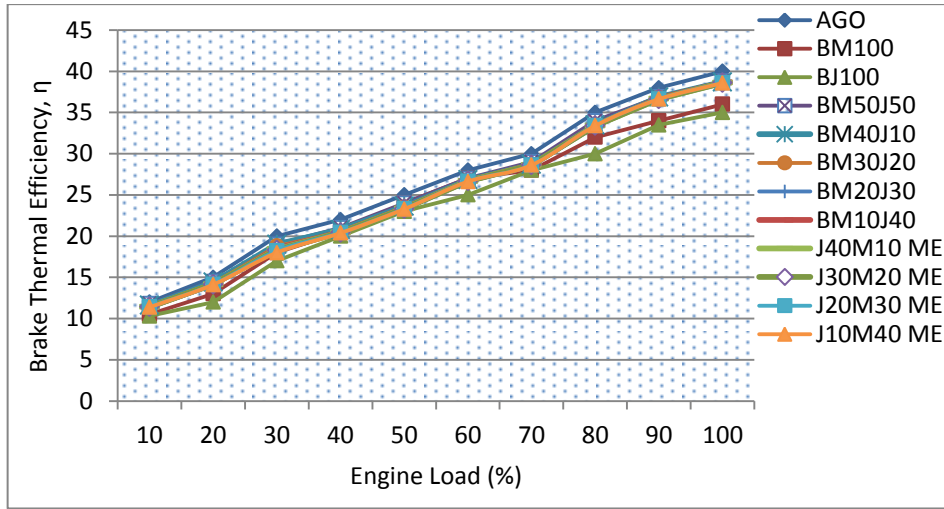


Figure 5.5: Effects of engine loads on brake thermal efficiencies of biodiesel and hybrids

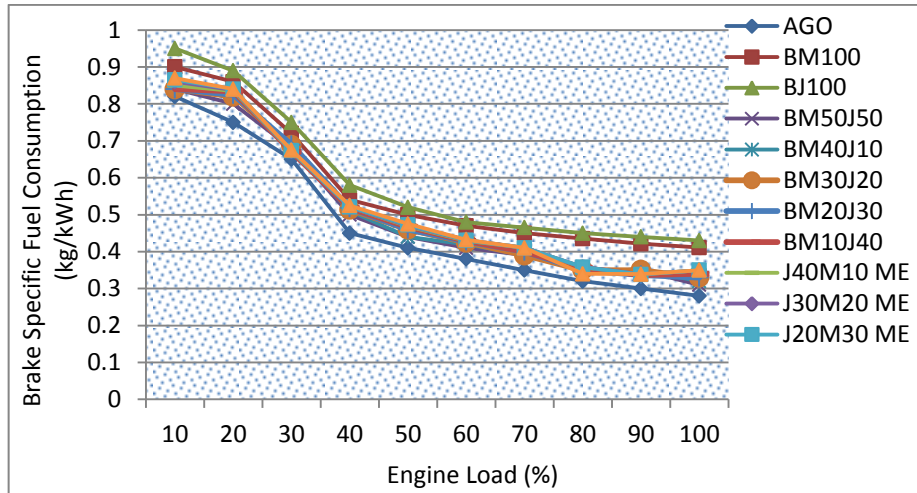


Figure 5.6: Effects of engine loads on brake specific fuel consumption of biodiesel and hybrids

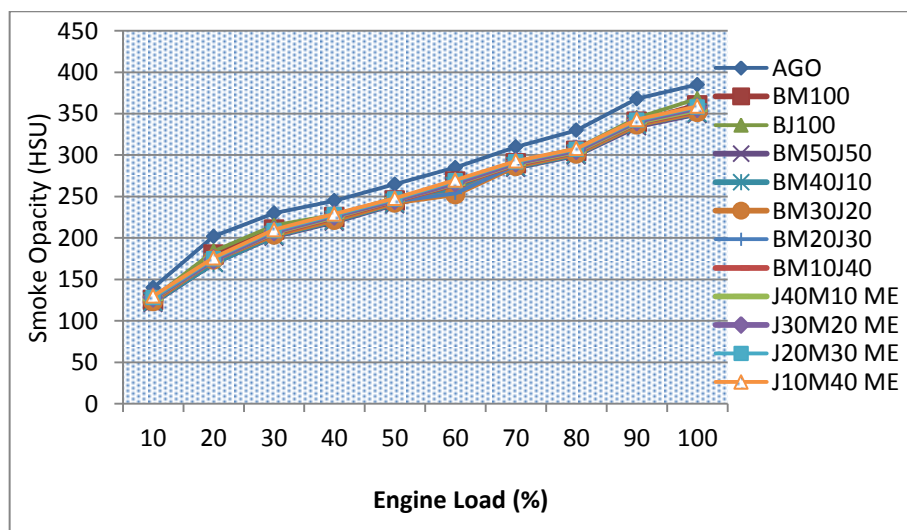


Figure 5.7: Effects of engine loads on smoke opacity of biodiesel and hybrids

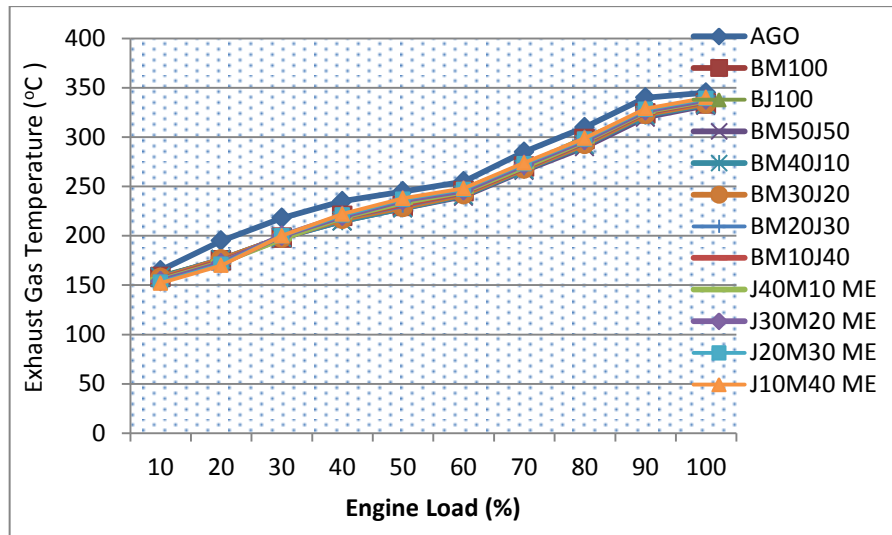


Figure 5.8: Effects of engine loads on exhaust gas temperature of biodiesel and hybrids

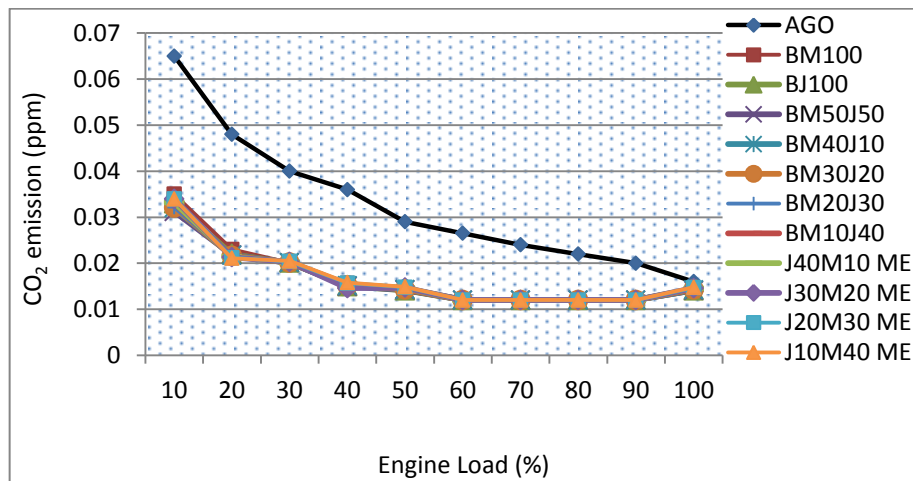


Figure 5.9: Effect of engine loads on CO emission composition of biodiesel and hybrids

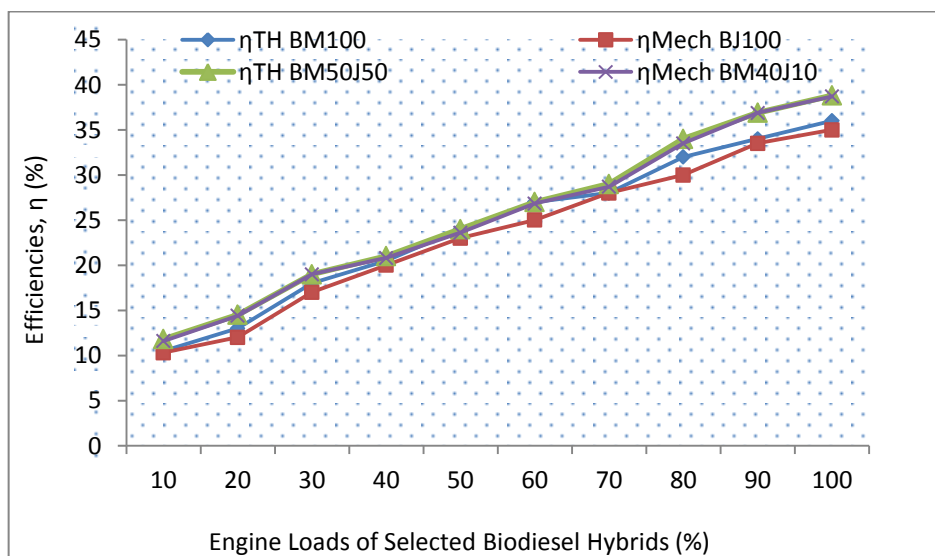


Figure 5.10: Comparison of mechanical and thermal efficiencies on engine loads

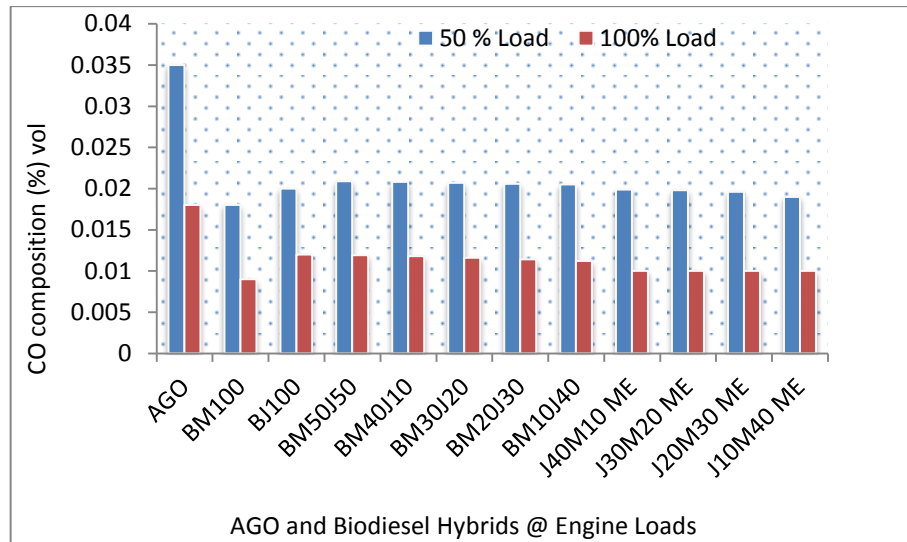


Figure 5.11: Effect of CO emission composition of the hybrids at different loads

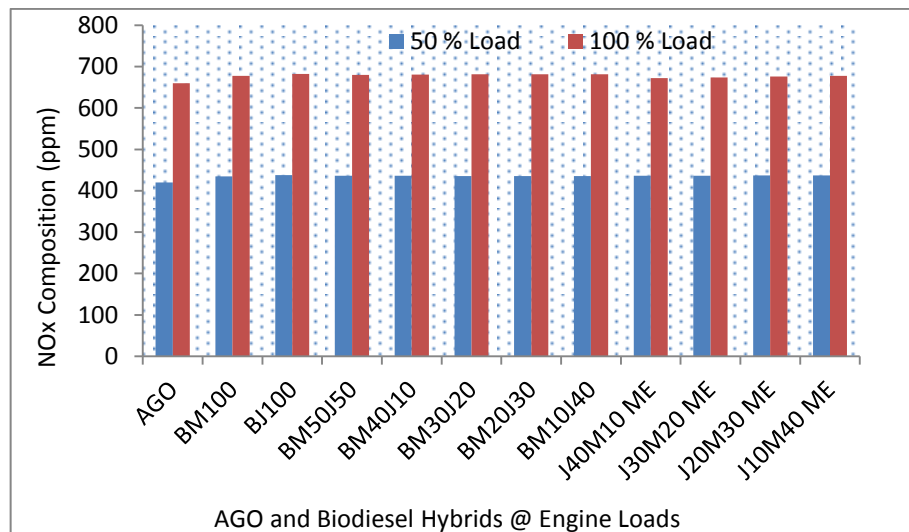


Figure 5.12: Effect of NOx emission composition on the hybrids at different loads

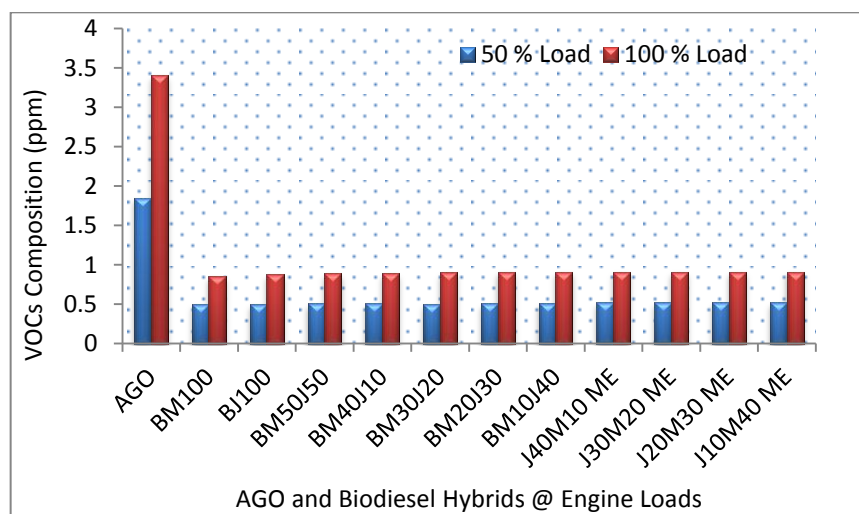


Figure 5.13: Effect of VOCs emission composition on biodiesel and hybrids at different loads

Table 5.3: Engine emission and performance of AGO

Speed (rpm)	Torque (Nm)	Temperature (°C)	Time (mins)	CO (% vol)	NOx (ppm)	VOCs (ppm)	O ₂ (ppm)
1000	6.9	73	5	36	7.8	0.9	19.2
1200	5.8	74	10	40	9.0	1.1	19.4
1400	4.9	92	25	47	13.7	1.6	19.6
1600	4.3	101	20	47	15.7	2.0	19.8
1800	3.8	105	30	53	16.5	2.2	19.9
2000	3.4	107	40	58	18.2	2.4	20

Table 5.4: Engine emission and performance of biodiesel hybrids

Engine Load	CO (%)		NOx (ppm)		VOCs (ppm)	
	50 (%)	100(%)	50(%)	100(%)	50(%)	100(%)
Hybrids						
AGO	0.035	0.018	420	660	1.85	3.4
BM100	0.018	0.009	435	678	0.50	0.85
BJ100	0.020	0.012	438	682	0.50	0.88
BM ₅₀ J ₅₀	0.0209	0.0119	436	680	0.51	0.89
BM ₄₀ J ₁₀	0.0208	0.0118	436	681	0.51	0.89
BM ₃₀ J ₂₀	0.0207	0.0116	435.8	681.7	0.5	0.90
BM ₂₀ J ₃₀	0.0206	0.0114	435.6	681.5	0.51	0.91
BM10J ₄₀	0.0205	0.0112	435.4	681.2	0.51	0.91
J ₄₀ M ₁₀ ME	0.0199	0.010	436	672	0.52	0.91
J ₃₀ M ₂₀ ME	0.0198	0.011	436.6	674	0.52	0.91
J ₂₀ M ₃₀ ME	0.0196	0.011	436.8	676	0.52	0.91
J ₁₀ M ₄₀ ME	0.0190	0.011	437	678	0.52	0.91

5.9 Conclusion

The aim of this investigation was to evaluate engine performance and usability of Moringa and Jatropha biodiesels hybridized fuels produced by hybridization as a new approach in biodiesel development and to characterize the emission from compression ignition engines. Moringa biodiesel appears to be a biodiesel fuel with one of the highest cetane numbers ever reported as biodiesel fuel. There is no doubt that Moringa is a potentially valuable oil seed crop and that its oil appears to be a viable and promising feedstock for biodiesel production and as a hybridization agent. The performance of the hybrids of Jatropha and Moringa seed oil in CI engine was very close to petroleum diesel. Therefore, they can be used in CI engines in rural area for meeting the energy requirement in various agricultural operations such as irrigation, threshing and so on.

The CI engine ran successfully during the tests conducted. The hybrids characterized for their improved chemo-physical and stable thermal properties performed favourably compared with conventional diesel (AGO). The specific fuel consumption, thermal and mechanical efficiencies,

exhaust gas emission were close to the value obtained from AGO. The smoke density produced during combustion was less than that produced by AGO while also all the emissions produced were better and more environmentally friendly, achieving higher energy efficiencies from hybridisation of biodiesel feedstock. All the hybrids showed improved properties compared to the non-hybridised or single stock biodiesel. Recommendation is that other feedstocks should be experimented with including poly-hybrids.

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Chapter 6

Paper 5, ISBPP of TJLC

Investigative Study of Biodiesel Production Properties of African *Thevetia peruviana* and *Jatropha curcas* seed oil feedstocks using Local metallic salts as Catalysts

Investigative Study of Biodiesel Production Properties of African *Thevetia peruviana* and *Jatropha curcas* seed oil feedstocks using Local metallic salts as Catalysts

Abstract - Investigative study into the potentials of African *Thevetia peruviana* and *Jatropha curcas* seed oil feedstocks as biodiesel fuels was conducted using local metallic salts as catalysts. The properties investigated were chemo-physical, thermal and fatty acid composition for the produced biodiesel fuels after transesterification of the two vegetable oils using potassium hydroxide (KOH), banana peel ash and coconut fiber ash as catalysts at the same reaction times and temperatures. Eight samples of biodiesel were produced from the two seed oils and subjected to different chemo-physical analysis including fatty acid profile using GC-MS; heating values and specific heat capacities at different temperatures using bomb calorimeter. Results revealed that *Thevetia peruviana* and *Jatropha* seed oils have oil yields of 48% and 46% respectively. The biodiesel yields from the biodiesel produced from KOH (89% and 85%) were higher than those produced from the local ashes (72%, 70%, 74.5%, and 73.8%). The densities/specific gravities of all the biodiesel samples were comparable with conventional diesel (AGO) and also fell within the ASTM (0.88 limit). The flash points of the samples (biodiesels from *T. peruviana* and *J. curcas* seed oils) were higher and better than that of AGO and conformed to standards (130°C minimum). All the samples were up to 130°C except those made using banana ash which were slightly lower but higher than reference diesel. The predominant fatty acids present in *T. peruviana* seed oils are palmitic, linoleic, linolenic, oleic, myristic and stearic acids while *J. curcas* seed oil is made up of palmitic, linoleic, linolenic, oleic, myristic and stearic acids at different proportions respectively. The heating values were considerably lower than the standard reference diesel. This work may be advanced further making use of other locally sourced materials as catalysts.

Index Terms - Biodiesel, Production, Properties, *Thevetia peruviana*, *Jatropha curcas*, feedstock, catalyst, metallic salts

6.1 Introduction

The production and consumption of bio-fuels continues to increase as more attention is paid to the environment and the depletion of fossil-fuel resources (Timothy and Timan, 2010). Biodiesel, a fuel from natural oils such as soybean oil, rapeseed oil, animal fats or used cooking oil and fat can be used as a substitute for, or as an additive to, mineral-based diesel fuel since it meets international standard specifications such as American Society of Testing and Material (ASTM D6751), European Norm (EN14214), Japan Industrial Standards, South African Bureau of Standards and so on [1].

Biodiesel fuel has received considerable attention in recent years as an oxygenated fuel, as it is a biodegradable, renewable and non-toxic fuel. It contributes no net carbon dioxide or sulphur to the atmosphere and has low emission profiles, so it is environmentally beneficial [2]. Currently, the production of biodiesel has already become a new worldwide industry [3]. In the United States of America (USA) the primary feedstock interest is on soybeans and sunflower oil as biodiesel sources [4, 5]. Most European countries are concerned with rapeseed oil; Asian countries prefer to utilize coconut oil or palm oil. African countries especially Nigeria, Kenya, Mali, Mozambique, Zimbabwe and South Africa have focused on *Jatropha*, sunflower, soya, used vegetable oil and more recently Moringa. Yellow oleander (*Thevetia peruviana*) is a new discovery while continued search for more energy crops are ongoing within various provenances [2].

Vegetable oils such as jojoba has also been investigated and found to have potential as biodiesel feedstock [6, 7]. Nowadays, people have paid more attention to shrub borne oil such as the oil of *Jatropha Curcas*, *L. pistace*, *Chinensis burge* and even Yellow oleander amongst others due to their non-edibility, high oil percentage content and wide geographical and climatic spreads [3]. The current production of biodiesel in USA is estimated at approximately 50,000 tonnes per year (57 million liters) with a potential to produce about 1.5 billion liters per year. In Europe, production capacity is estimated at 665 000 tonnes (755 million litres) per year with a planned production capacity of about 2 million tonnes (2.77 billion) per year [8]. In Nigeria and South Africa especially the KwaZulu-Natal province, vegetation distribution and rainfall activities supports agricultural pursuits that can produce the feedstock for biofuels production and presently research works are at several stages in both countries to develop and commercialize energy crops for biofuels production [9]. At current production level, oil reserves will be depleted in 40 years [10, 11]. It was estimated that Nigeria would have exploited about 21.5 billion barrel of her reserves of 22 billion barrels of crude oil in 35 years at its current export rate of about 2.1 million barrel per day [12].

For the production of renewable energy resources, the country will improve and upgrade by creating more jobs and stimulating related industries in the downstream sector of the economy by improving the socio-economic indicators of the country [12]. In line with the federal government energy policy, biofuels will create jobs for 668 000 Nigerians with a GDP impact of 30.4 billion dollars [12]. With the development of modern technology, vegetable oil feedstocks can be utilized to produce various clean alternative fuels to mineral fuel which can substitute fossil fuels. Fossil fuels such as petroleum, coal and natural gas, which have been used to meet the energy needs of humans, are associated with negative environmental impacts such as global warming, environmental pollution and others [13]. It has been widely reported

that not less than ten (10) major oil fields from the 20 largest world oil producers are already experiencing declines in oil reserves [13]. Recently published data also revealed a total of 29 major world oil producing countries already experiencing declining oil reserves from 2005 to 2007 [11, 14].

Commercially, biodiesel is produced by transesterification [15]. As fuel properties are closely related to the composition of fatty acids of the vegetable oil stock, monitoring the reaction mixture is very important to control the quality of biodiesel [16]. Some of the important quality parameters as established by the ASTM D6751 for 100% biodiesel (B100) are flash point, kinematic viscosity, specific gravity, cloud point, free glycerin and total glycerin. These must meet the values established by the specifications [16, 17] after which they can be used in internal diesel combustion engines with little or no modifications [16-18]. Also, since biodiesel is produced from renewable, domestically grown feedstock, it can reduce the use of petroleum-based fuel and possibly lower greenhouse gas contributions caused by internal combustion engines [19].

Long before these resources are finally exhausted, oil in particular will become scarce and heading for extinction and of course become more expensive. In Nigeria, bulk and sustainable production of biodiesel is yet to be explored to greater extents. With the turn of events in Nigeria where the refineries are almost down and have been heavily dependent on importation of fuel, the development of this promising biofuels sector to improve the economic fundamentals for biodiesel production is imperative. Biodiesel can meet growing energy demands in a sustainable manner, since it can be produced in large quantities, it is environmentally friendly and the cost of production can be encouraged by promoting the agricultural sector. This sector can also provide job opportunities and reduce our dependence on foreign oil and improve domestic African economies.

The production of biodiesel fuels primarily and commercially employs transesterification reaction usually with methanol and ethanol as transesterification agents and metallic bases mainly sodium and potassium hydroxides as catalysts. These are synthetic catalysts and have found uses in other chemical industries. These may be available but having to utilize localized catalysts such as ashes from coconut fiber, banana peels, fuel woods, plantain wastes and others may not be a bad idea as it will open up new vistas and as well recycle waste. Other attendant benefits of renewable and alternative energy resource will also be reaped as the final products will still maintain their biodegradability and environmental friendliness. The objective of this present research work is to comparatively evaluate the chemo-physical, thermal, and biodiesel potential of the feedstocks of typical African *Jatropha (Jatropha curcas)* and Yellow Oleander

(*Thevetia peruviana*) oil seeds for the production of biodiesel from selected local materials used as catalysts to serve as substitute to the conventional synthetic catalysts for use as biodiesel fuels in Nigeria and South Africa while establishing substitute catalysts from local ashes of coconut fiber and banana peels as transesterification catalysts agents thus presenting local content initiative in biodiesel production.

Considering the huge benefits derivable in the world of biodiesel from different feedstocks and blending, this research work is basically significant because it will produce transesterified, locally catalyzed (banana peels and coconut fiber), renewable, non-toxic, environmentally-friendly biodiesel and blends from African based *Jatropha* (*Jatropha curcas*) and Yellow Oleander (*Thevetia peruviana*) seed oils and laying bare their production properties viz. thermal, chemo-physical and gaseous emissions properties. The possibility of utilizing local ashes from organic matter as transesterifying catalysts or agents will help to reduce the cost of production, thereby reducing the general selling price of biodiesel fuels and blends.

6.2 Yellow Oleander (*Thevetia peruviana*) plant

Yellow Oleander (*Thevetia peruviana*) is a tropical shrub which grows in the wild and remains ornamental. and is grown as hedges and for its bright and attractive flowers, and is commonly planted around homes, schools and other public buildings. *Thevetia peruviana* is recorded to exist for more than 2000 years in its native countries, West Indies, Brazil and Mexico. It was taken to Europe about three hundred years ago and today it has naturalized in virtually all countries in the tropics [20]. *Thevetia peruviana* thrives very well in all the climatic and vegetation belts of Nigeria and KwaZulu-Natal province of South Africa [20]. *Thevetia peruviana* is a dicotyledon which belongs to the Aponaceae family. It is a composite evergreen shrub, found to have a milky sap. It is known as yellow Oleander (nerium), gum bush, bush milk, exile tree in India, *cabalonga* in Puerto Rico, *Ahanai* in Guyana, *Olomi Ojo* by the Yorubas of Nigeria. The plant is perennial, reaching about 3 to 3.9 meters in height. The leaves are linear, narrow, sword-like and green. The plant fruits virtually ten out of the twelve months of the year. The seed contains about 60%-64% oil on dry matter basis. The plant produces white latex (sap) that is highly poisonous, the seed is also very poisonous. Despite the toxicity of the plant, it has found useful application in several spheres of life; its latex is used as an analgesic for toothache, when the stem is chewed and also as an insecticide [20].



Figure 6.1: *Thevetia peruviana* plant



Figure 6.2: *Jatropha curcas* plant

6.3 *Jatropha (Jatropha curcas) plant*

Jatropha (Jatropha curcas) belongs to the family *Euphobiaceae*, and is a drought resistant perennial shrub, growing well in marginal/poor soil. It is easy to establish, grows relatively quickly, producing seeds for 50 years. *Jatropha* produces seeds with oil content of 37% and above [20]. The oil can be combusted as fuel without being refined; it burns with clear smoke free flame and has tested successfully as fuel for simple diesel engines. The by-product is pressed cake, a good organic fertilizer. It is found to be growing in many parts of the country, rugged in nature and can survive with minimum inputs and easy to propagate. Medically, it is used for diseases such as cancer, piles, snake bite, paralysis and dropsy. *Jatropha* grows wild in many areas of the world and even thrives on infertile soil. Several works have been conducted on *Jatropha* as a feedstock for biodiesel and currently is the most established source of biodiesel in the world especially due to its non-edibility and sustainability in any climate region/belt [21].

A good *Jatropha* crop can be obtained with little effort, depending on soil quality and rainfall. Oil can be extracted from *Jatropha* nuts after two to five years. The kernels consist of oil up to 60%. It is called purging nut, physic nut by the English, it is still uncertain where the centre of origin is, but it is believed to be Mexico and Central America. It has been introduced to Africa and Asia and now it is cultivated worldwide. It grows in tropics as well as temperate regions. Normally, it grows between three and five metres in height, but can attain a height of up to eight to ten metres under favourable conditions as shown in Figure 6.2. The seeds become mature when the capsule changes from green to yellow, after two to four months.

6.4 Materials and methods

Thevetia peruviana seeds were locally collected in Makurdi metropolis of Benue State, Nigeria while *Jatropha curcas* seeds were purchased from Gbajimba in Guma local government area of Benue State during the dry season. The moisture-free seeds were ground using a grinding machine and oil extracted using soxhlet apparatus. A rotary evaporator was used to recover the solvent (n-hexane). The extracted oil, automotive gas oil (AGO/conventional diesel) used as standard and the biodiesel fuels that were eventually produced were taken for analysis and characterizations. The extracted oils from both seed oils were used to produce biodiesel through a transesterification process using methanol but the method used in this study, was to use different local salts and alkalis as catalysts, viz., potassium hydroxide (KOH), an alkali, banana peels ash and coconut fibre ash which were metallic salts.

These three reagents were used as catalysts for the biodiesel production. Eight different samples and AGO were finally produced for the study. They were: AGO/conventional diesel fuel, sample A; biodiesel produced from *Jatropha* seed oil using potassium hydroxide (KOH) as catalyst, sample B; biodiesel produced from *Thevetia* seed oil using KOH as catalyst, sample C; biodiesel produced from *Jatropha* seed oil using coconut fiber ash as catalyst, sample D; biodiesel produced from *Thevetia* seed oil using coconut fiber as catalyst, sample E; biodiesel produced from *Jatropha* and *Thevetia* using banana peel ash as catalyst, sample F; and samples G and H which represent vegetable oils extracted from *Jatropha* and *Thevetia* respectively.

6.4.1 Extraction of oils from *Thevetia peruviana* and *Jatropha curcas* seeds

Yellow oleander seed oils and *Jatropha* seed oils have similar extraction processes. Two hundred millilitres (200 ml) of normal hexane was charged into the round bottom flask (500 ml) of the Soxhlet apparatus and mounted in the heating mantle of the apparatus, was heated to between 65°C - 100°C in order to prevent loss of hexane vapour because the boiling point of n-hexane is 69°C. The evaporating n-hexane was condensed into the thimble by the condenser where it leached the oil out of the paste. The oil rich solvent after reaching a level siphoned back automatically into the round button flask where the process described so far was repeated. After five cycles, the thimble was discarded of its residue, while the solvent was recovered using the rotary evaporator, leaving behind pure Y. Oleander oil. The above process was repeated until enough oils were obtained. The same extraction process was employed for *Jatropha* seeds [22] and [23].

6.4.2 Preparation of catalysts

1% w/w of potassium hydroxide was dissolved in 26 ml of methanol to form potassium methoxide solution in a conical flask and covered to avoid ambient reaction. This was used for the transesterification of the extracted oils of *Y. Oleander* and *Jatropha* during the biodiesel production. 0.1 M of banana peels and coconut fiber ash solutions were also prepared by dissolving the ashes of both plant wastes in distilled water and made up to 100 ml mark in a conical flask. The ashes were made by burning the wastes in a controlled set-up and the ashes obtained after completion. The 0.1 M solutions of both ashes were then dissolved in 26 ml of methanol to form methoxides of banana ash salt and coconut respectively. The use of local catalyst is actually a deviation of what is obtainable and it is indeed the modification/novelty that this work intends to present – using a local metallic salt as catalyst for biodiesel production.

6.4.3 Production of biodiesel

100 ml each of *Jatropha* and *Y. Oleander* seed oils were used to produce six samples of biodiesel fuels using potassium methoxide; banana peels methoxide and coconut fiber methoxide earlier prepared respectively in a large beaker. The mixtures were blended in an electric blender after thorough mixing for five minutes at a temperature of about 60°C above the boiling point of methanol and poured into a large beaker. The oil was preheated to a temperature of 70°C which was monitored using thermometer until it dropped to the required temperature and blended for about 30 minutes to 60 minutes reaction time. This was to allow for complete and homogeneous reaction as adopted by Igbum *et al.* [24]. The mixtures were immediately transferred from the blender to a one litre PET bottle and closed tightly. The PET bottle was occasionally opened to allow in some air in order to avoid contraction due to cooling of the oil. The mixture was allowed to settle for 24 hours after which a dark colour glycerin by-product was observed separated from the pale liquid above which is the biodiesel at the top layer. Biodiesel varies somewhat in colour according to the oil used and so does the by-product layer at the bottom [24].

6.4.4 Analysis and characterization of *Thevetia peruviana* and *Jatropha curcas* oils

Density, flash point, pour point, cloud point kinematic viscosity, appearance/colour, refractive index, fatty acid profile, percentage free fatty acid (FFA), cetane index, degree of saturation and un-saturation, heating value, saponification value, iodine value, acid content, total and free glycerin and others are some of the chemo-physical properties with which vegetable oils and biodiesel fuels are identified as recommended by ASTM, AOAC, AOCS, API and other standards were determined for the extracted *Thevetia Peruviana* and *Jatropha curcas* produced

biodiesel fuels and AGO as control. These tests were carried out according to the methods adopted and used by Eloka-Eboka [21], Olisakwe *et al.* [23] and Igbum *et al.* [24].

6.5 Results and discussion

6.5.1 Chemo-physical properties

The chemo-physical and thermal properties of the eight seed oil and AGO with their fatty-acid composition and biodiesel samples studied are presented in Tables 6.1, 6.2, 6.3 and 6.4. The fatty acid compositions from the Gas Chromatography Mass spectrophotometer (GC-MS) and the comparison of specific heat capacities of all the samples are presented in Figures 6.3, 6.4 and 6.5.

6.5.2 Thermal properties

The results of the thermal properties of all the samples of biodiesel and raw vegetable oils of the study are presented in Table 6.3. This includes heating values and specific heat capacities at different temperatures for all the samples studied. Comparisons of heating values and specific heat capacities at different temperatures are presented in Figures 6.3 and 6.4.

Table 6.1: Percentage oil and biodiesel samples yields

Samples	Weight of dried Oil seed (kg)	Weight of oil after dehuling (kg)	Vol. of sample before transesterification (ml)	Yields of oil after transesterification (%)
A	2	1	100	89.0
B	2	1	100	85.0
C	2	1	100	72.0
D	2	1	100	70.0
E	2	1	100	74.5
F	2	1	100	73.8
G	2	1	100	48.0
H	2	1	100	46.0

A= KOH based Jatropha biodiesel; B= KOH based Thevetia biodiesel; C= Coconut Ash based J. biodiesel; D= Coconut Ash based T. biodiesel; E= Banana Ash based J. biodiesel; F= Banana based T, biodiesel; G= Jatropha Oil and H= Thevetia Oil.

Table 6.2: Chemo-physical properties of seed oils and biodiesels

Properties	Samples of Raw oil and biodiesel from different catalysts								
	AGO	A	B	C	D	E	F	G	H
Flash Point (°C)	98	137	133	131	136	121	119	139	129
Fire Point (°C)	136	147	140	139	148	148	138	150	149
Cloud Point (°C)	-2	12	10	11	9	5	7	12	5
Pour Point (°C)	-8	6	6	6	4	-2	3	5	-2
FFA (%)	N/D	0.27	0.25	0.26	0.23	0.17	0.23	0.26	0.18
Carbon Residue (%)	0.42	2.29	0.24	0.30	0.25	0.21	0.29	0.28	0.21
Cu (ppm)	0.09	0.08	0.04	0.05	0.07	0.03	0.06	0.08	0.04
Fe (ppm)	0.41	0.26	0.26	0.28	0.21	0.18	0.31	0.24	0.18
Viscosity @ 40°C (cSt)	12.63	16.03	15.88	15.67	15.98	15.81	15.76	15.99	15.97
Iodine value (wajs)	N/D	189	183	182	181	210	184	188	196
Ash content (ppm)	0.33	0.22	0.21	0.21	0.24	0.13	0.19	0.21	0.16
Sulphur content (ppm)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Density (kg/m ³)	0.870	0.872	0.856	0.850	0.882	0.874	0.900	0.910	0.886
Moisture content (% wt)	0.03	0.03	0.02	0.045	0.03	0.035	0.04	0.04	0.05
Refractive Index	1.325	1.435	1.477	1.463	1.392	1.442	1.368	1.451	1.462
Saponification value (KOH/g)	N/D	189	183	182	181	210	184	188	196

* N/D - Not Determined * N/A - Not Available

Table 6.3: Thermal properties of the seed oils and biodiesel

Properties	Samples of Raw oil and biodiesel from different catalysts								
	AGO	A	B	C	D	E	F	G	H
Heating Value (KJ/Kg)	45.28	30.21	29.84	30.69	29.84	31.93	31.27	30.14	31.42
Specific Heat @ 60°C (J/kg.K)	2978.1	3243.0	3434.2	3079.3	3149.5	3010.2	3228	3153	3002.3
Specific Heat @ 80°C (J/kg.K)	3346.3	3561.2	3611.0	3262.1	3451.1	3304.2	3433	3512.	3305.1
Specific Heat @ 100°C (J/kg.K)	3867.3	3992.4	4101.3	3721.2	3899.3	3779.1	3899	4006	3809.2

6.5.3 Percentage oil/biodiesel yields

Table 6.1 presents the results of the percentage oil yields of both Yellow oleander and Jatropha seeds and the biodiesel yields using the different catalyts. The percentage oil yield is slightly lower in Y. Oleander seeds (48%) than in Jatropha seeds (46%). This value showed high oil yields of both seed oils. Jatropha however has been worked on extensively and the percentage oil yields have never been found to be less than the values obtained in this study even though our values are less than other studies. Ibiyemi [20] found appreciable percentage oil yields of 64% for Y. Oleander. Olisakwe *et al.* [23] also reported a little higher yield for Jatropha and Yellow oleander (54.6% and 58.5%). For the biodiesel yields, samples produced from KOH (89% and 85%) were higher than those produced from the local ashes (72%, 70%, 74.5%, and 73.8%). This is understandable because the ashes were unprocessed, not optimized in production and also from the fact that potassium based catalyts are usually less effective than sodium based which usually gives up to 99% yields. The works of Igbum *et al.* [24] in their study of the effects of transesterification variables on the yields and properties of biodiesel confirm this too.

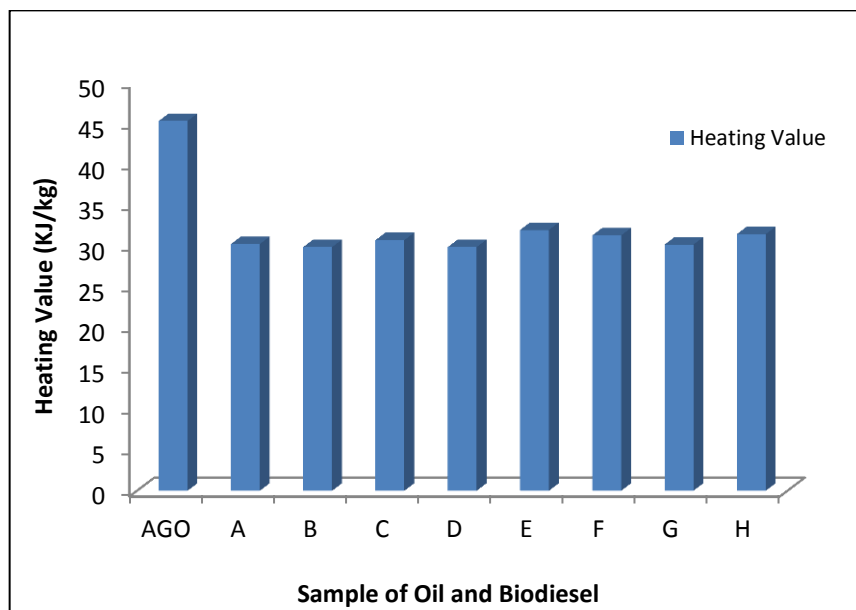


Figure 6.3: Comparison of heating values of samples of oil and biodiesel with AGO

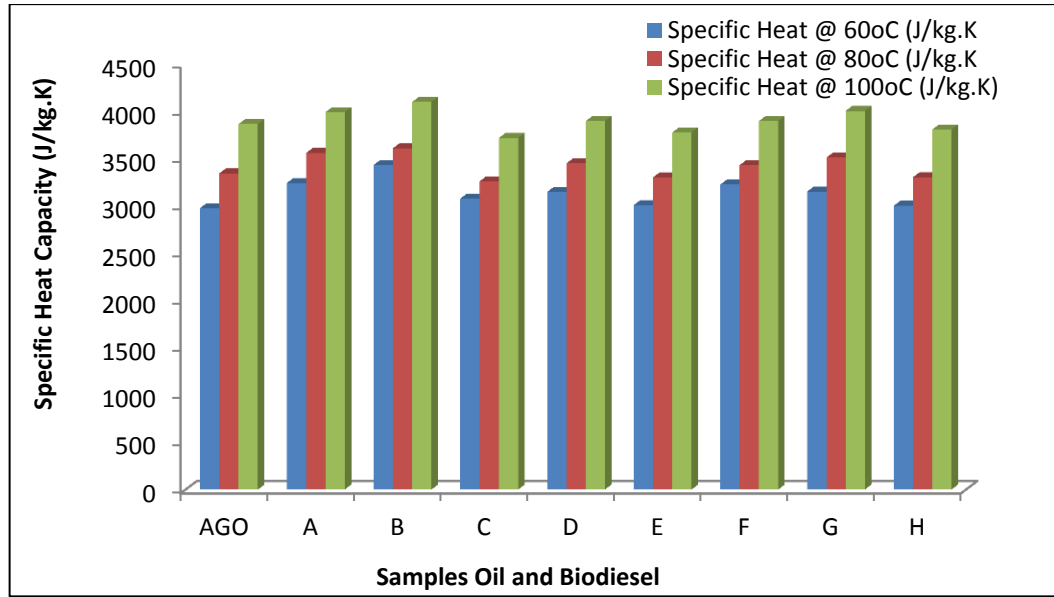


Figure 6.4: Comparison of specific heat capacities of samples of oil and biodiesel with AGO

Table 6.4: Fatty acid composition/profile of seed oils and biodiesels

Fatty Acids	Acronyms	A	B	C	D	E	F	G (JVO)	H (TVO)	Units
Stearic Acid	C18:0	0.02	0.03	0.02	0.03	0.01	0.01	0.02	0.01	%
Myristic Acid	C14:0	3.56	4.08	2.56	3.57	2.13	2.34	3.14	2.19	%
Palmitic Acid	C16:0	12.28	13.51	10.14	13.3	8.16	9.86	11.13	8.24	%
Linolenic Acid	C18:3	4.74	5.09	4.34	4.89	3.24	4.18	4.56	3.51	%
Linoleic Acid	C18:2	11.22	12.14	10.18	11.56	7.18	9.24	10.28	8.64	%
Oleic Acid	C18:1	4.13	5.91	3.96	4.28	2.14	3.81	4.06	3.22	%
Total		35.95	40.75	31.2	37.46	22.86	29.43	33.19	25.81	%
ΣSFA		15.86	17.6	12.72	16.73	10.3	12.2	14.29	10.44	%
ΣUFA		20.09	23.14	18.48	20.73	12.56	17.23	18.9	15.37	%
U/S		1.27	1.32	1.45	1.24	1.22	1.41	1.32	1.47	%
L/L		0.42	0.42	0.43	0.42	0.45	0.45	0.44	0.41	%

SFA = saturated fatty acids; UFA = Unsaturated fatty acids; U/S = unsaturated/unsaturated; L/L = linolenic/linoleic

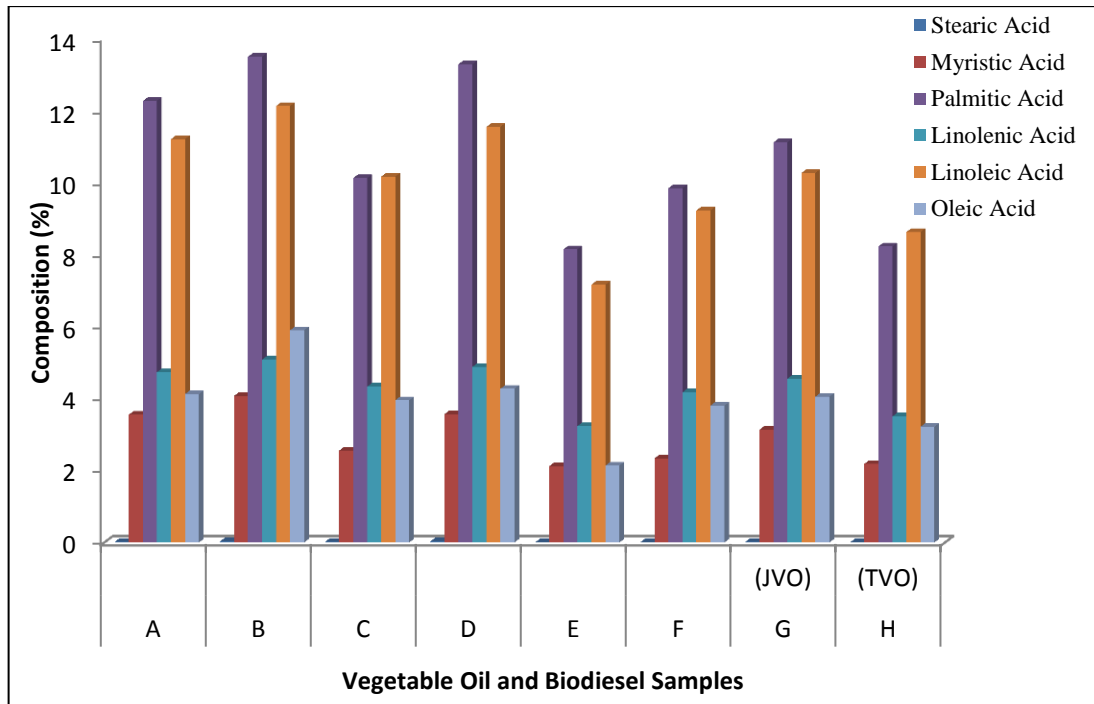


Figure 6.5: Fatty acid profile/composition of vegetable oils and produced biodiesels

6.5.4 Chemo- physical properties of the oils and biodiesel fuels

The densities/specific gravities of all the biodiesel samples were comparable with AGO and also fell within the ASTM (0.88 limit) as evident in Table 6.2. The flash points of the samples (biodiesels from *Yellow oleander* and *Jatropha* seed oils) were higher and better than that of AGO and conformed to standards (130°C minimum). All the samples were up to 130°C except samples E and F (made using banana ash) which were slightly lower but higher than AGO. Fuels with high flash points can withstand high temperature operations and are safe for handling and haulage. The same is applicable with the fire points. The pour and cloud points of the samples were not encouraging compared to AGO and standards. This suggests that AGO can withstand extreme cold condition better than all the samples; this is an indication that AGO will thrive better in temperate regions and can traverse regions without being affected by cold climates better than all the biodiesels produced [25].

The kinematic viscosities at 40°C designated for biodiesels across the samples were quite high for the produced biodiesel fuels and the two seed oils without much difference. AGO in this case is very high (12.63 cSt) and beyond the value of what AGO should give. AGOs generally have low viscosities and that is the advantage fossil fuels have over bio-fuels. Other works saw AGO with much lower values: 2.00 cSt [26], 1.62 [24], 1.69-6.0 cSt was recommended [17]. The percentage free fatty acid composition (FFA) of all the samples fell within the ASTM

recommendation (0.80 maximum) and this is quite interesting as the highest value was 0.26. AGO is not a bio-product and therefore contains no free fatty acid.

The predominant fatty acids present in Yellow oleander seed oils are palmitic, linoleic, linolenic, oleic, myristic and stearic acids (8.24, 8.64, 3.51, 3.22, 2.19 and 0.01%). while Jatropha seed oil is made up of palmitic, linoleic, linolenic, oleic, myristic and stearic acids (11.3, 10.28, 4.56, 4.06, 3.14 and 0.02%). Stearic, myristic and palmitic acids are saturated while linoleic and linolenic acids are poly-unsaturated fatty acids. Oleic acid is a mono-unsaturated fatty acid and it is desirable for biodiesel production resulting in less soot/NO_x formation. The profile of fatty acids is important in the business of biodiesel because this determines the suitability of any oil or fuel for use as biodiesel and can be used also to estimate the cetane number and index of any biodiesel [2]. Chromatograms depict the various peaks of radiation from where the functional groups of the fatty acids were determined with time and are a useful tool in chromatography which is indispensable in determining unknown chemical components. The ratios of saturated to un-saturated, linolenic to linoleic as presented are quite low but within the ASTM recommendation.

6.5.5 Thermal properties of oils and biodiesel fuels

The results of the thermal properties which include the heating values and the specific heat capacities at temperatures of 60°C, 80°C and 100°C for all the samples of the produced biodiesel fuels are presented in Table 6.3. The interactions/comparisons with AGO at the mentioned temperatures are in Figures 6.3 and 6.4. The heating values of the biodiesel fuels produced using the catalysts of study are substantially lower than the ASTM standards and of AGO. AGO has 45 280 kJ/kg; ASTM standards recommend 38 000 to 40 000 minimum but none of the samples attained this minimum value. The highest has 32 930 kJ/kg. The calorific/heating value is the energy content of any fuels, be it fossil or non-fossil (bio-based). The heat capacities at the temperatures as shown in Figure 6.4 projected the biodiesel samples as having better heat capacities than AGO with increased temperatures showing a higher degree of heat retention and as such can serve automotive or similar engines better. Studies of Igbum *et al.* [24] presented similar correlation.

6.6 Conclusions

The results of the analysis show clearly that all the biodiesels produced are suitable for use as biodiesel. The chemo-physical and thermal properties of the produced samples of biodiesel fell within the ASTM specifications for use as biodiesels hence they can be subjected to engine performance. The seed oil contents of both Y. oleander (*Thevetia peruviana*) and Jatropha (*Jatropha curcas*) are relatively high. Further, the percentage yields of biodiesel using the local

catalysts are quite satisfactory. The densities/specific gravities of all the biodiesel samples were comparable with AGO and fell within the ASTM (0.88 limit). The flash points of the biodiesel samples were higher and better than that of AGO and conformed to standards (130°C minimum). The heat capacities at the different temperatures tested projected the biodiesel samples as having better heat capacities than AGO with increased temperatures showing a higher degree of heat retention and as such can serve automotive or similar engines better. The indispensability of biodiesel applications in the modern demands for bio based products can no longer be ignored as the urgent need for a technological shift from fossil fuels continues to be an imperative.

6.7 Recommendations

The following recommendations are proffered arising from this study: firstly, further works should be conducted on co-mingling or blending of different biodiesel feedstocks with each other and with AGO at different percentages and testing their properties. This will be a new vista or direction in the search for alternative and renewable energy. Secondly, there should be an improvement with the use of local ashes as catalysts for the transesterification of vegetable into biodiesel; this study is just an eye-opener and if proper and chemically processed local catalyst(s) are employed, there may be improvement on this present work.

Acknowledgements

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Chapter 7

Conclusion and Future Works

Conclusion and Future Works

7.1 Conclusion

The aims and objectives of this study which were to produce, evaluate and analyse biodiesel fuels from selected tropical seed oils with particular reference to *Moringa oleifera* feedstock with its specific and interesting potential have been explored. These have been achieved in five or more ways as laid out in the journal and conference papers presented in this thesis. Optimization of biodiesel production processes holds huge prospects. A reduced production option is the optimization of process variables that affect yields and purity of biodiesel, which was achieved in this study.

Catalyst nature and concentration, alcohol to triglyceride molar ratio, mixing speed, reaction time and temperature were taken into consideration as variables impacting yields, viscosity and specific gravity of the methyl esters biodiesel fuels produced. These are specific indispensable properties of biodiesel for use in combustion ignition engines. In addition to variations in the nature of feedstocks as exposed in this work, several other measures such as blending and hybridization can be acceptable process options. The hybridization process was successfully explored and developed for biodiesel production application as another method towards enhancing better fuel quality and performance. This novel approach can be applied to other feedstocks and in multi-faceted dimensions in the form of poly-hybridization.

This study explored bi-hybridization. The efficacy of hybridisation in improving specific properties of biodiesel fuels has been brought to bear. Specific tests such as viscosity, specific gravity, refractive index, cetane index, fatty acid composition, free and total glycerine, free fatty acid composition, flash point, pour and cloud points and calorific values were all higher and better than single stock biodiesel fuels. *Moringa oleifera* biodiesel, which has proved itself an excellent biodiesel fuel with high oleic acid content (> 70%), contributed to enhancing the properties of biodiesel from *Jatropha curcas* hybrid biodiesel feedstock *in-situ* and *ex-situ* which will no doubt give rise to new products of improved energy qualities that may bring about the much needed difference in the biodiesel industry.

It is evident that the study of thermal and gaseous emissions of selected biodiesel feedstocks and their blends showed significant differences compared to their fossil fuel counterpart (AGO) which has higher gaseous emissions; the impact, therefore, is that of environmental friendliness on the part of the biodiesel fuels and comparative advantage compared to AGO. The general trend was that all the biodiesel fuels produced and tested together with their blends and hybrids

have lower gaseous emissions than AGO. Pollutants of sulphur, nitrogen, organic compounds were visibly reduced in low AGO blends. Biodiesel fuels and blends have continued to confirm their environmental friendliness in most studies of this nature.

However, there were continuous significant and/or insignificant fumes released by benzene and other aromatics present in the petroleum fraction depending on their percentages as exposed by this study. The recommendation here is that biodiesel and blends are therefore to be better and qualitatively developed to the level that they will compete favorably with conventional fossil fuels in terms of availability and cost as this has always been the bone of contention. The studied feed-stocks could comfortably be combusted in compression ignition engines without fear of polluting the environment. The general trend of the analysis clearly shows that all the biodiesels produced are suitable for use as biodiesel. The chemo-physical and thermal properties of the produced samples of biodiesel fell within the ASTM specifications for use as biodiesels hence they can be subjected to engine performance. The indispensability of biodiesel application in the modern demands for bio-based products can no longer be ignored as the urgent needs for technological shift from fossil fuels continues to be an imperative.

7.2 Future works and study

Future works emerging from these studies will embrace different strategies of biodiesel performance in compression ignition engines for use in the agricultural sectors. Biodiesel development in South Africa is still in its infancy. Several potential feedstocks have been abandoned; waste cooking oils, sunflower oil, corn (which was listed in the South Africa's renewable energy master plan); Jatropha and others can further be harnessed. The use of B100 and the employment of the production protocol of this study for use in vehicles and cars as obtainable in India where aspects of these studies were carried out could be experimented in South Africa. Vehicle manufacturers could experiment with real time application of biodiesel fuels in engines where emission testing and engine performance could be explored. Several specific modelling studies using computational fluid dynamic software such as Ricardo, KIVA codes, WAVE should be explored in order to study the combustion and combustion behaviours of biodiesel fuels of different feedstocks. A broad array of research and scientific incursion that combines theory, modelling and simulation using biodiesel as pseudo or surrogate fuels are not just necessities but indispensable and apt in themselves. Hybrid biodiesel with kerosene can be an option for automotive and heavy-duty vehicles or even for aviation purposes.

Appendixes

Appendix A

On Tue, Jun 10, 2014 9:58 AM PDT James.Sp840@gmail.com wrote:

>10-Jun-2014

>

>Dear Eloka-Eboka:

>

> Hybridisation of Feedstocks - A New Approach in Biodiesel Development: A Case of Moringa and Jatropha seed oils

>

>I am pleased to accept your paper in its current form which will now be forwarded to the publisher for copy editing and typesetting. You will receive proofs and instructions for transfer of copyright in due course. The publisher also requests that proofs are checked and returned within 48 hours of receipt.

>

>Thank you for your contribution to Energy Sources Part A

>

>Sincerely,

>Dr James Speight

>Editor, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

>James.Sp840@gmail.com, James.Sp840@gmail.com

>

>

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Appendix B

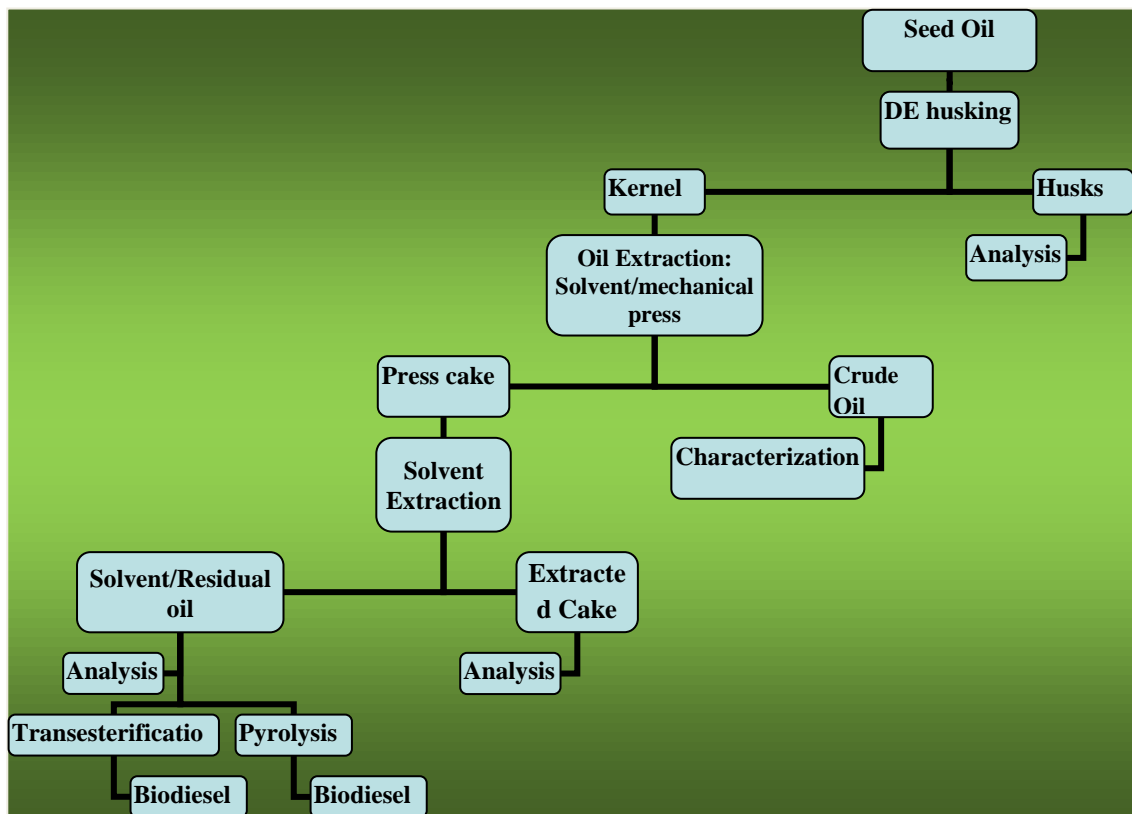


Appendix C: Recommended Table of Experiments for Chapter Two

The study in Chapter Two is a published work hence this Table of Experiments is placed in the Appendix

Activities	Experiments Performed
Pre-Treatments	Collection of Materials, Preparation of materials
Treatments	Extraction of Oil, Analysis of crude oil, identification of Process variables, optimization of process variables, production of Biodiesel
Post Treatments	Biodiesel Separation, Biodiesel Washing, Determinations of effects of process variables and specific properties, chemo-physical properties determination

Appendix D: Schematics/Process Flow of Biodiesel production



Appendix E: A Testo Flue gas Experimental set up



Testo Flue Gas Analyser can analyse up to eight (8) gases in all. These are O₂, CO, CO₂, NO, NO₂, SO₂, HC and H₂S.