SUSTAINABLE OPTIMIZED PRODUCTION OF BIOENERGY FROM RENEWABLE BIOMASS

BY

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Dedication

This thesis is dedicated to the One who gave me the mental capacity to do this work – Jesus Christ.

Declaration

I, Oyetola Ogunkunle, state that this doctoral research thesis is entirely my work and has not been submitted, neither by myself nor another person, elsewhere for academic merit. I recognize the meaning of plagiarism and declare that this work contains my plans, illustrations, figures, results, and arrangement except where other people's works are included as references. I acknowledge further that any academic dishonesty, including plagiarism, is not accepted by the University of Johannesburg, and there are punitive measures against it.

Signed by Oyetola Ogunkunle

On the …15th … day of … March … year … 2021.

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Publications

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4. **Ogunkunle**, O. and Ahmed. N.A. (2020). Exhaust Emissions and Engine Performance Analysis of a Marine Diesel Engine Fueled with *Parinari polyandra* Biodiesel-Diesel Blends. Energy Reports, 6: 2999 – 3007.
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Abstract

With the increasing menace of environmental pollution occasioned by fossil fuel combustion, the need for alternative clean biofuels has increased globally. Biodiesel is a popular biofuel that is mostly synthesized from plant seed oil. Every form of derived biofuels is essential because they are sustainable. Improving the production process and quality of biofuels could help achieve a cheaper and cleaner energy source for broader applications. More studies are needed to ensure that novel biofuel feedstock can pass the Sustainable Development Scenario (SDS) goals in terms of relatively high oil yield and suitable fuel properties for engine applications. Determination of optimal parameters for biodiesel production from every biomass feedstock is a necessity that must be achieved to establish its suitability and industrial relevance for sustainable production.

In order to create room for improvement and explore more studies for scientific reference, the research was conducted to examine the production of biodiesel from *Parinari polyandra* oil as a renewable biofuel for engine applications. Summarily, oil was extracted from the seeds of *Parinari polyandra* via a solvent extraction mechanism. Experimental runs for biodiesel production from extracted *Parinari polyandra* oil were developed using Central Composite and Box Behnken designs of the Response Surface Methodology (RSM). The effect of transesterification process parameters was studied under different reaction levels for statistical modeling and optimization of biodiesel production from *Parinari polyandra* oil. A test bench experiment was carried out to verify the performance characteristics of a diesel engine fueled with *Parinari polyandra* biodiesel blends.

First, the statistical optimization of reaction variables of biodiesel production from transesterification of *Parinari polyandra* seed oil was done based on seventeen (17) experimental results generated from the Box-Behnken design. Temperature, time, and catalyst amount, varied between 60 – 75 oC, 60 – 180 minutes, and 1 – 3 wt%, respectively, were chosen as independent variables while biodiesel yield was the measured response. A linear regression model was used to predict the biodiesel yield and determine the input values of an optimized yield. The multiple regression equation was used to analyze the significant effect of the input parameters on biodiesel production. The fitness of the model was determined using specific performance metrics of Analysis of Variance (ANOVA). Selected important physicochemical properties of the oil and biodiesel were determined according to American Society for Testing and Materials (ASTM) standards.

The prediction model for optimized biodiesel yield from *Parinari polyandra* oil using RSM was adequate with a high significance level of reaction parameters at 95% probability level. The *Parinari polyandra* biodiesel fuel properties were found to be within the ASTM D6751 standard, supporting its use as a vehicular engine fuel. The model developed has generated a dependable time-saving technique for estimating biodiesel yield from *Parinari polyandra* oil. The matching similarity between the optimized and validated results indicates that RSM was more efficient than conventional methods, involving lengthy iterations to solve differential equations. Validation of the optimization was achieved at reaction conditions of a temperature of 61 oC, 60 minutes reaction time, and catalyst amount of 1 wt% to produce 93.18% of biodiesel. The considerable amount of biodiesel yield obtained from optimized reaction conditions suggests that the utilization of this seed oil for biodiesel production will be viable on an industrial scale.

Second, the performance of the combustion of optimized *Parinari polyandra* biodiesel blends was evaluated biodiesel in a diesel engine. Twenty (20) experimental runs were generated from a CCD of RSM and were used to vary biodiesel production from *Parinari polyandra* oil, which was extracted using a solvent extraction mechanism. The reaction process variables, temperature, time, and alcohol to oil molar ratio, were varied between the range of 60 – 65 oC, 60 – 120 minutes, and 3:1 – 6:1, respectively. A quadratic model was used to study the efficiency of biodiesel production relative to the applied reaction conditions. A statistical model was developed, and the significant difference between the sample means was analyzed using ANOVA. The physicochemical properties of the oil and biodiesel were determined using the ASTM standards. The performance characteristics of a diesel engine were obtained via bench tests while running the diesel engine on diesel and biodiesel blends starting from 0% to 100% load conditions.

The performance evaluation results showed that the diesel engine ran smoothly on biodiesel-diesel blends without any pronounced negative effect or reduced engine performance. All the biodiesel blends exhibited combustion properties similar to fossil diesel, demonstrating that recommended blends of *Parinari polyandra* alkyl esters can be used in diesel engines with little or no modification to the engines. The flash and fire points of *Parinari polyandra* biodiesel and fossil diesel were measured to be similar in values. The brake thermal efficiency of the engine was lower when biodiesel blends were used to run the engine compared to when diesel fuel was used. This has shown that the biodiesel blends are better in terms of flammability because of their high cetane number and high oxygenated nature than diesel fuel.

Third, the exhaust emissions analysis of a marine diesel engine fueled with *Parinari polyandra* biodiesel-diesel blends was evaluated. The exhaust emissions analysis of the engine was carried out by fueling it with the varied volume of *Parinari polyandra* biodiesel-diesel blends. The performance characteristics relative to the applied torque on the engine were also measured. According to the established methods in the previous works, the oil extraction and biodiesel production from *Parinari polyandra* were carried out, and their properties were measured using standard procedures. While the engine performance parameters were computed, the concentrations of gaseous emissions from the engine exhaust, like total hydrocarbons (THC), carbon dioxide (CO_2), carbon monoxide (CO), sulphur dioxide (SO_2), and nitrogen oxides (NO_x), were detected and measured using a portable emission measurement system.

The results revealed that biodiesel–diesel blends, up to B30, demonstrated similar performance characteristics with diesel in an unmodified diesel engine. This showed that B30 does not negatively impact the engine and can be used in vehicular diesel engines without any significant modification to mitigate offensive and harmful emissions from fossil diesel fuel. B10 has the highest heating value and better performance output in terms of engine speed and power. Therefore, B30 can be used as a possible substitute for diesel fuel for better fuel economy and engine efficiency.

This study has established the optimal conditions for biodiesel production from *Parinari polyandra* seed oil using two different RSM designs. It has also revealed the suitability of the biodiesel produced as a good candidate for applications in ICEs, relative to its stable performance characteristics without any modification of the engine and lower carbon emissions.

Keywords: Biodiesel; *Parinari polyandra* oil; transesterification; fuel properties; statistical optimization; response surface methodology; engine performance; exhaust emissions.

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CHAPTER 1

INTRODUCTION

1.1 Background

Sustainable energy refers to all renewable energy sources and are not expected to diminish to be used repeatedly [1]. In our 4th Industrial World, sustainable energy offers renewable clean energy as an alternative source of energy. However, problems, such as energy shortage, fluctuating energy costs, and environmental pollution from fossil fuels, have continued to raise concerns to seek renewable technologies that can afford us sustainable energy supply without the risk of the problems mentioned above. As a result, clean energy technologies have continued to grow significantly worldwide due to the associated benefits of reducing carbon footprints and eliminating the environmental degradation and pollution occasioned by the use of fossil fuels. The various forms of sustainable energy comprise all renewable energy sources, such as biomass, biofuels, wind, solar, geothermal, and hydroelectric. Amongst all these is the capacity and renewability of biofuels to help countries reduce their dependence on fossil fuels.

Biofuels generally refer to renewable fuels (ethanol, biodiesel, and biogas) produced biochemically from organic feedstock, which have proved to be good alternatives for combustible fuels, especially in vehicular engines. The use of biofuel as energy sources can ensure energy safety and decrease gaseous exhaust emissions [2]. As a result, biofuels are sustainable and environmentally friendly due to their renewability and clean combustion, devoid of obnoxious and harmful carbon emissions. A biofuel feedstock is termed biomass and can be transformed into other biofuels through appropriate and relevant technology [3]. Biofuels can be grouped into primary and secondary fuels. Primary biofuels include solid fuel like wood which is commonly used for cooking in rural areas. Secondary biofuels include liquid biofuels such as ethanol and biodiesel processed from biomass and can be applied in vehicles and industrial processes.

Bioenergy products like biogas, bioethanol, biohydrogen, and biodiesel can be obtained from lignocellulose biomass, a considerably sizeable renewable bioresource obtainable from plants. The use of these fuels, which are free from impurities and renewable with adequate supply, will assist in cutting down the negative environmental impacts of fossil energy and help grow the economy. Therefore, investing much research and environmental management of energy resources is essential to fostering economic growth, shielding the ecosystems, and ensuring sustainable use of natural resources [4].

1.1.1 Oil seeds for biodiesel production

From the emergence of renewables, there has been a large growth in the adoption of biodiesel in several parts of the world. Biodiesel adoption is one of the solutions to prevalent energy crises in our present technology. Biodiesel is renewable because they are obtained from replaceable resources, unlike the dependence on the fleeting reserves of fossil fuels. Biodiesel is currently one of the major renewable biofuels being utilized in internal combustion engines. If wider attention is focused on its production and adoption, it can help to achieve energy security in the future. The use of non-edible plant oil as raw materials for biodiesel production is pertinent to overcome the associated need for edible oils and costs. The extraction of oil from plant seeds for biodiesel production has become prominent amongst sustainable energy technologies. This technique has attracted huge attention as research activities are continually made to assess the energy trapped in these natural seed oils. Nearly all plants produce seeds that contain oil. The value and application of oil can be determined by the assessment of its fatty acid composition. The use of oils extracted from seeds for biofuels and other chemical feedstock in recent years has been largely influenced by the depletion of petroleum resources, rising costs, negative environmental impacts of fossil fuels, and the necessity to advance the availability of renewable clean fuels for engine applications [5]. There are extensive amounts and quantities of energy plants and several agricultural waste biomass that have been widely used as feedstock for biodiesel production [6]–[8]. The availability of oil seeds in specific places determines the choice of oil to be explored for biodiesel production. To meet up with the desired biofuel adoption required for every nation's energy security and economy, there would be abundant use of oil seeds with relatively high oil yields [9].

As a richly endowed land with grasslands and dense vegetation, Africa has many varieties of oil-producing seeds that have not been thoroughly studied and exploited. Africa is a continent whose rich resources have not been fully used [10]. A continent blessed with naturally existing grasslands, rainforests, and green vegetation has various organic oilseeds bearing plants that require no expensive agricultural inputs for their production [10]. An extensive literature study revealed that oil plants such as karanja, castor, rubber, jojoba, mahua, yellow oleander, sand box, neem, etc. have properties suitable for biodiesel production. The study showed that 37 out of over 300 species of oil seeds bearing trees existing in Africa have oil properties suitable for biodiesel production [11], [12]. In Africa, common biodiesel feedstock plants are recorded in Table 1.1

under different geographical distributions and varying oil yields. The numbers written in ratio forms depict the numeric representation of the acid type, while the numbers in parenthesis represent the percentage composition in the oil.

Table 1.1: Selected non-edible African plants grouped under different geographical distribution and fatty acid composition

Common name	Geographical distribution	Oil yield (seed) %	Oil yield (kh/ha)	Fatty acid composition
Jatopha	Angola, Zambia, Ethiopia, etc.	20 – 60	1900 – 2500	14:0(1.4), 16:0(15.6), 18:0(9.6), 18:1(40.8), 18:2(32.1) 20:0(0.4)
Jojoba	Botswana, Ghana	45 – 55	1818	16:1 (0.2), 16:0(17.8), 18:0(14.0), 18:1(46.3), 18.2(17.9), 20:0(3.0)
Mahua	Ethiopia, Tanzania, India	34 – 50	–	14:0(1.0),16:0(17.8),18:0(14.0),18:1(46.3),18:2(17.9),20:0(3.0)
Moringa	Ghana, Kenya	33 – 41	4680	16:0(7.6), 16:1(1.4), 18:0(5.5), 18:1cis (66.6), 18:2cis (8.1), 18:3 n3 (0.2), 20:1(1.7), 20:0(5.8)
Petroleum nut	South Africa	–	–	–
Tung oil	Zimbabwe, Uganda, Sudan	–	940	16:0(2.3), 18:0(2.4), 18:1(5.6), 18:2(6.3), 18:3(0.1), 18:3(82.2), 20:0(0.2), 20:1(0.9), 24:0(0.1)
Camelina	Zambia, Ghana	–	800 – 1200	14:0(0.05), 16:0(5.16), 16:1(0.04), 18:0(2.68), 18:1(15.21), 18:2(17.90), C18:3(34.64), 20:0(1.44), 20:1 (15.14), 20:2(2.17), C20:4(1.47), 22:0(0.3), 22:1(2.57), 22:6(0.62), 24:0(0.14)
Castor oil	Nigeria, South Africa	45 – 50	450 – 2300	16:0(1.09), 18:0(0.94), 18:1(3.70), 18:2(4.44), 18:1 –OH (methylricinoleate) (89.93)
Derris indica	Ethiopia, Tanzania	30 – 40	225 – 2250	16:0(10.6), 18:0(6.8), 18:1(49.4), 18:2(19.0), 20:0(4.1), 20:1(2.4), 22:0(5.3), 24:0(2.4)
Baobab	Malawi, Zimbabwe, Mozambique, Mali, Benin	–	–	14:0(4.6), 15:0(2.5)16:0(37.3), 16:1(0.2), 17:0(0.2), 17:1 (0.3)18:0(4.2), 18 CE (6.2)18:1n-9(19.7), 18:1 n-7 (1.6), C18:2 n-6 (13.5), 19:CE (6.5), 18:3 n-3 (0.1), 19:CA (1.8), 20:0(0.7)20:1n-9(0.1), 22:0 (0.1)

Citrullus	Morocco and the Cape Verde, Egypt	17 – 19	45 – 50	–
Croton oil	Ghana, Gambia, Egypt	32	–	14:0(0.1), 16:0(6.5), 16:1(0.1), 17:0(0.1), 18:0(3.8), 18:1(11.6), 18:2(72.7), 18:3(3.5), 18:3(0.4), 20:1 (0.9), 20:2(0.2)
Milk bush	Southern, and central Africa	60 – 65	930 – 1060	16:0(15.6), 18:0(10.5), 18:1(60.9), 18:2(5.2), 18:3(7.4), 20:0(0.3), 22:0(0.1)
Algae	Gambia, Mali, Ghana	60 – 62	840 – 4160	16:0(18.42), 16:1(2.31), 16:2(3.26), 18:0(3.43), 18:1(49.64), 18:2(11.30), C18:3(8.26)
Parkia	Sierra Leone, Cameroon, Gabon, Congo, Brazzaville, Uganda, Ghana	64.4	–	–
Rubber tree	South Africa, Ghana	40 – 60	4280	16:0(10.2), 18:0(8.7), 18:1(24.6), 18:2(39.6), 18:3(16.3)
Tobacco	Ghana, Nigeria, Liberia	35 – 49	950 – 1150	6:0(0.69), 14:0(0.09), 16:0(10.96), 16:1(0.2), 18:0(3.34), 18:1(14.54), 18:2(69.49), 18:3(0.69)
Neem	Ghana, Togo, Mozambique	20 – 30	2670	16:0(14.9), 18:0(14.4), 18:1(61.9), 18:2(7.5), 20:0(1.3)

Sources: [12]–[35]

Amidst the growing research studies and activities on the exploitation of oil seeds for industrial applications, specific regulations restrict edible oil seeds for biodiesel production to prevent a food shortage crisis against the growing global populations [36], [37]. As a result, researchers have continued to exploit the use of inedible seeds, which have relatively high oil yields, for biodiesel production. Yang et al. [38] reported that the utilization of non-edible oils could be affirmed as adequate and acceptable for biodiesel production because the plants can be grown on wastelands that do not compete with limited lands for food crops production. Also, they are relatively cheap, available, and provide higher biodiesel yields and similar fuel properties as the fuel obtained from edible oils. Energy resources are raw materials that require extensive explorations by man for sustainable development. Access to affordable and sustainable energy is one of the SDS. The availability of information on oil-rich feedstock, technological know-how, and performance evaluation will help develop biodiesel and embrace the technology for establishing viable low-carbon projects in the transportation sector. The use of different oil seeds, their oil contents, extraction mechanisms, and biodiesel production methods are explicitly discussed in chapter two. It is an adaptation of a recent published review study on global production and adoption of biodiesel combustion in diesel engines.

The global community is currently facing an intense crisis of environmental deterioration from the combustion of fossil fuel, which is fleeting in reserves year on year [39]. In light of this, concerted efforts are being made globally to salvage our environment. This has led to a realistic appraisal of sustainable use of natural resources by applying engineering science principles and technology to ensure fuel security and environmental sustainability [2], [40]. Over the years, there has been a paradigm shift to renewable biofuels in balancing increasing energy demand and environmental pollution [41], [42]. The development of clean, renewable fuels for domestic and industrial use has become the earnest goal of every renewable energy researcher [43].

The relevance of renewable biofuels from vegetable oil to the conservation of our environment cannot be underestimated. Different processing technologies suitable for converting plant seed oil to biodiesel have been developed over the years to have an alternative clean fuel with comparable combustion properties as fossil fuels for engine applications [44]. The narrative application of plant oil as engine fuel can be traced to the exhibition of Rudolf Diesel's first diesel engine in 1897, which was powered by vegetable and peanut oil with an efficiency of 75%. As such, it can be concluded that the evolution of diesel engines and biofuels emerged concurrently [45]. With the environmental advantages biofuels bring [46], it remains an essential medium-term solution to reducing the waste burden and global warming crises on our planet arising from GHG emissions [47]. The energy demand has increased over the years due to the increasing population globally, especially in the transport sector. The associated benefits of renewability and lower pollutant emissions with biodiesel combustion in diesel engines have continued to intensify interests in the production and use of inedible oil biodiesel in combustion ignition (CI) engines [48], [49]. Bioenergy Australia estimates that biodiesel and bioethanol combustion could reduce emissions by over 85% and 50%, respectively, compared to diesel [50].

Renewables, whether we like them or not, are part of our future. A high level of transition to clean energy has been witnessed over the years as nations like the US, EU, and China have emerged as high producers of biofuels, coupled with the colossal research studies and publications on renewable biofuel [51]. As much as this represents a massive feat for so many developed nations, relevant information and data are still needed on promising feedstock that are energy-rich and suitable for biofuel production in the developing world [39]. Presently, energy consumption in the transportation sector has been reported to be on the increase, accounting for 60% of the total global GHG emissions [51], [52]. However, there is still a considerable gap in the large-scale production and adoption of clean-burning biodiesel fuel in the transportation industry of some developing countries.

With the present track of clean energy progress, global biodiesel production is not expectedly recording the anticipated growth to sustain global transport biofuel consumption by 2030 [53]. As of May 2019, the biofuel production records are still hovering around one-third of the Sustainable Development Scenario (SDS) biofuel consumption forecast index (Figure 1.1). A 7% expansion in transport biofuel production was recorded in 2018, and this is still less than the expected 10% production growth needed every year until 2030 to meet up with the SDS. Besides the policy supports and technological innovations needed to promote global biofuel production, consumption, and adoption, more light has to be shed on emerging feedstocks rich in oil and suitable for sustainable biofuel production.

The high availability of oil-rich biomass can command more commercialization of significant volumes of renewable clean fuel for the transport sector and provide more diesel substitutes in other industrial sectors [54]. Biodiesel production is currently being commercialized from fat, waste oil, and grease feedstock, and certain limits have been identified on their availability. Seed-bearing plants and biomass rich in oil are crucial feedstock due to their widespread availability and low-cost economic advantage.

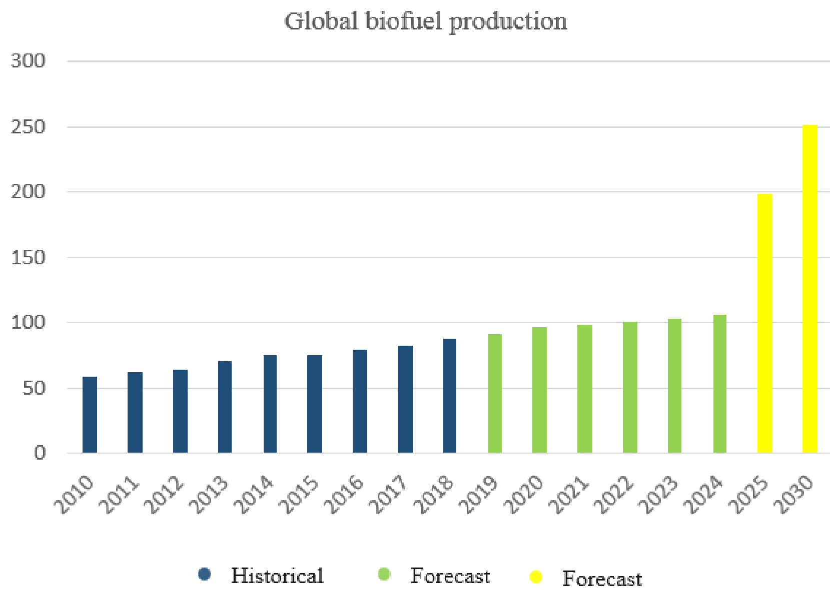

Figure 1.1: Biofuel consumption forecast 2010-24 vs. Sustainable Development Scenario (SDS) in 2025 and 2030

(Compiled by the author of this thesis)

With the availability of different potential feedstock, non-edible oils, which are second-generation biofuels feedstock, can be considered as favourable substitutes for conventional edible crops in biodiesel production. This research work has been able to show the processes and pathways of easy and cost-effective oil extraction to production of *Parinari polyandra* biodiesel and engine application of the fuel.

1.1.2 Application of biodiesel

The use of biodiesel as a vehicular fuel has become widespread owing to its similarity to fossil diesel fuel [55]–[57]. Biodiesel-diesel fuel blends, ranging from B5 to B20, have been tested and proved to run successfully in diesel engines with little or no modification of the engines [58]–[61]. Also, biodiesel has gradually gained application as a shipping fuel in the marine industry because of its clean-burning nature and unavailability of sulphur and aromatic compounds. Over the years, extracted oil from seeds jatropha, *Hura crepitans*, jojoba, loofah, neem, castor oil, *Pongamia pinnata*, etc. have been identified as favourable feedstock for the synthesis and commercialization of biodiesel for diesel engines application. The exploration of quality biodiesel in diesel engines is further discussed in the literature section, with scientific results that reveal its suitability and performance characteristics without any significant modification.

1.2 Problem statement

One of the most critical problems facing man is the insufficiency of energy. The global requirements and consumption are presumed to result from improved living standards and expanding population triggered by evolving urbanization. Fossil fuels, such as kerosene, petrol, and diesel, are becoming costlier day by day as their supplies become scarce and diminished. In the light of the increasing world population concurrent with rising fuel demands and prices, there is a need to push harder to discover feedstock that would justify the continuous production of bioenergy. It is indispensable to search for high potential feedstock and establish their fitness for bioenergy production. About 70 to 95% of the overall cost of bioenergy production is estimated to be on the acquisition of the feedstock. The populous industrial feedstock, soybean and groundnut oil, for biodiesel production, cannot stand the test of time as their continued use will interfere with the policies standing in place to ensure food security for the global growing populations. The possibility of using cheaper feedstock, such as inedible oil seeds and wastes, in biodiesel production is needed to overcome the high added value barrier to its global commercialization and adoption.

Biodiesel production from vegetable oils has been seen as an efficient way to eradicate all the problems associated with edible oils. Few issues associated with the production include restricted feedstock, which brings about non-edible oil feedstock or waste oils in this study. The industrial utilization of *Parinari polyandra* is still at its infancy and of little research interest. Available works on the plant encompass limited areas of research, which cannot provide enough clues and leads to more biofuel research studies. Studies such as phytochemical analyses of the plant extracts and oil extraction from the plant seeds are inadequate to provide relevant and substantial information about its usefulness and potential application as biodiesel feedstock for engine applications. Hence, the sustainable production of optimized biofuel from a novel feedstock and the engine applications testing are the focus of interest in this study.

1.3 Aim and objectives of the study

This study aims to optimize the sustainable production of biofuel from renewable biomass suitable for applications as engine fuel.

The objectives are:

- To extract oil from *Parinari polyandra* seeds and produce biodiesel from the extracted oil using different experimental design approaches of response surface methodology.
- To develop regression models for predicting *Parinari polyandra* biodiesel yields under different reaction conditions.
- To evaluate the performance of a diesel engine fueled with *Parinari polyandra* biodiesel blends.
- To analyze the emission characteristics from the combustion of *Parinari polyandra* biodiesel blends in a diesel engine.

1.4 Significance of the study

Remarkable progress in bioenergy production from renewable biomass would continue to promote the advancement and usage of plant-oil-derived biodiesel for engine applications without any significant modification in existing engines. The use of biofuels to reduce carbon-based greenhouse gas emission quantity is also essential to alleviate the damaging effects of these harmful and pollutant gases on the ecosystem. Increased usage of biomass-derived biofuel is needed to also facilitate wider adoption in developed and developing countries, which can also be a source of foreign exchange-earners apart from the associated environmental benefits.

1.5 Research methodology

In this work, experimental designs from RSM were used to investigate the production and optimization of biodiesel production from *Parinari polyandra* seed oil. The biodiesel production procedures and statistical modeling are shown in the following chapters of this thesis. Different regression models were generated for selected reaction parameters of the biodiesel production process. Also, the performance characteristics of Internal Combustion Engines (ICEs) operated on blended *Parinari polyandra* biodiesel were studied experimentally under different operating conditions compared to those obtained when the engines were run on fossil diesel alone. The corresponding exhaust emissions from the engines were also measured.

1.6 Scope of the study

All investigations were carried out on biodiesel production from second-generation biomass (*Parinari polyandra*) oil. Also, the performance evaluation and emission analysis of the combustion of the biofuel in internal combustion engines (ICEs) were evaluated. The study does not cover the combustion process analysis of the fuel in the ICEs. Different optimal reaction conditions for biodiesel production from the seed oil were developed using different Response Surface Methodology (RSM) designs. The performance characteristics of different diesel engines running on blended *Parinari polyandra* biodiesel under varied operating conditions were studied, and the gaseous emissions were quantified accordingly.

1.7 Research contributions

The findings from this research are enumerated as follows:

- This study is the first comprehensive work on the use of *Parinari poyandra*, a widespread feedstock in West Africa, to produce biodiesel and its use as a substitute for diesel fuel.
- Development of optimal process parameters for biodiesel production from *Parinari polyandra* seed oil using different response surface analysis experimental designs to optimize reaction parameters has been established.
- Establishing the performance evaluation and exhaust emission characteristics of different diesel engines using *Parinari polyandra* biodiesel blends without any modification of the engine was established.

1.8 Structure of the thesis

The thesis is written in line with guidelines on thesis submission by essay format as approved by the University of Johannesburg. Four research articles published in Scopus/ISI indexed journals on the subject matter are collected in this thesis. The author is the first author in all the journal articles.

The remaining part of this thesis is organized as follows:

- A robust published literature review article entitled "A review of global current scenario of biodiesel adoption and combustion in vehicular diesel engines" is reported in Chapter 2.

- Chapter 3 was reproduced from a published research article entitled, "Response Surface Analysis for Optimization of Reaction Parameters of Biodiesel Production from Alcoholysis of *Parinari polyandra* Seed Oil."
- Chapter 4 contains the reports of a published research article entitled, "Performance Evaluation of a Diesel Engine Using Blends of Optimized Yields of Sand Apple (*Parinari polyandra*) Oil Biodiesel."
- A prepared manuscript on "Exhaust Emissions Analysis of a Marine Diesel Engine Fueled with *Parinari polyandra* Biodiesel-Diesel Blends" is presented in Chapter 5.
- The concluding section of the thesis and possible projections for biofuels production and adoption are detailed in Chapter 6.

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CHAPTER 2

LITERATURE REVIEW: A REVIEW OF THE GLOBAL CURRENT SCENARIO OF BIODIESEL ADOPTION AND COMBUSTION IN VEHICULAR DIESEL ENGINES

It is reproduced from Ogunkunle, O. and Ahmed, N.A. (2019): A review of the current global scenario of biodiesel adoption and combustion in vehicular diesel engines. Energy Reports, 5: 1560 – 1579.

This chapter captures a comprehensive review of all information and research studies related to the growth and promotion of biodiesel as engine fuel globally. It critically shows with much scientific evidence how the adoption of biodiesel fuel would be a socioeconomic and environmental benefit for sustainable development.

Delving into the current chronicles of research findings, explorations of biodiesel production and utilization in diesel engines have been at the forefront of sustainable and creative energy discovery. Far beyond the problems of energy crises, renewable biodiesel offers unlimited solutions to the associated issues of depleting reserves and harmful emissions with fossil fuels. In overcoming the increasing energy demand owing to the growing worldwide population, the emergence of biodiesel and its global adoption in the transportation sector has brought along a reliable fuel supply that can be used in diesel engines without any modification. This study explores the comprehensive utilization of biodiesel as engine fuel and shows the prevalent global current adoption in automobiles engines. The production rates are documented globally and promoting policies that are being mandated in many countries of the world are discussed as well. The improved state of things in achieving effective power conversion from biodiesel combustion with minimal emission impact on the environment has been documented. Worldwide technological adoption has been captured according to production rate, usage and legislation favouring the economic feasibility of diesel engines that are suitable for biodiesel with little or no modification. With the progress made so far by many researchers to establish biodiesel as a viable engine fuel, coupled with the ability to eradicate environmental issues like global warming and sustainability, it is evident that biodiesel is designed to make a future energy investment and significant addition to the domestic and industrial automobile economy.

Nomenclature

Symbols

$CoCl_2$: Cobalt (II) chloride

$CuCl_2$: Copper (II) chloride

CuO: Copper (II) oxide

$CuSO_4$: Copper (II) sulfate

$FeCl_3$: Iron (III) chloride

H_2SO_4: Sulphuric acid

CO: Carbon monoxide

CO_2: Carbon dioxide

NO_x: Nitrogen oxides

List of Abbreviations

ANN: Artificial neural network

ASEAN: Association of Southeast Asian Network

ASTM: American society for testing and materials

BHA: Butylated hydroxyl anisole

BHT: Butylated hydroxyl toluene

BP: Brake power

BSFC: Brake specific fuel consumption

BTE: Brake thermal efficiency

BtL: Biomass-to-liquid

CCD: Central composite design

CI: Compression ignition

CN: Cetane number

CRD: Common rail diesel

DI: Direct ignition

DPA: Diphenylamine

EN: European Union standard

EU: European Union

FAEE: Fatty acid ethyl ester

FAME Fatty acids methyl esters

FFA: Free fatty acid

GA: Genetic algorithm

GHG: Greenhouse gas

HEV: Hybrid electric vehicle

HHV: Higher heating value

HVOs: Hydrotreated vegetable oils

IC: Internal combustion

LHV: Lower heating value

MEFA: Methyl ester fatty acid

nPAH: Nitrated PAH's

PAH: Polycyclic Aromatic Hydrocarbons

PG: Propyl-gallate

PHEV: Plug-in hybrid electric vehicle

PL: Pyrogallol

PM: Particulate matter

RSM: Response surface methodology

SBD: Shea butter biodiesel

SDS: Sustainable Development Scenario

TBHQ: Tert-butylhydroxyquinone

THC: Total hydrocarbons

VOCs: Volatile organic compounds

2.1 Introduction

The idea of using biofuels in diesel engines emanated when the first diesel engine was displayed by its mastermind, Rudolf Diesel, at the world fair in Paris in 1900. Peanut oil was used as the fuel and he assumed that oil from locally grown crops could be used to operate his engines [1]. Basically, fossil diesel has been effectively utilized in all sectors such as agriculture, transportation and industrially because of its adaptability, availability, reliability, as well as high energy efficiency [2]. The diesel engine runs on the diesel, burnt by the heat of compression of air in the cylinder because of its desirable properties such as ignition quality, viscosity, volatility, specific gravity and lubricity. At the same time, depletion of resources has always been a concern with regard to fossil fuels, especially farmers who have always sought alternative fuel for their agricultural production [3].

In consideration of global total energy consumption and GHG emissions, transportation occupies 3rd place (after the industry and the building sectors) owing to the heavy dependence of vehicular engines on fossil fuels such as gasoline and diesel. This level of utilization is expected to rise by 60% by 2030 mainly because of industrialization, population increase and better standards of living [4]. All the technologies needed for transition to 100% renewables are already available, one of the major advantage biomass and biofuels have always had above the volume of energy they produce is their renewability. Biofuels are significant because of their sustainability while fossil fuels are a limited resource. Biofuels have the capacity to power different types of diesel engine cars regardless of the atmospheric conditions. Improving the production of liquid biofuels, such as biodiesel, would therefore lead to much availability of a cleaner, cheaper source of energy in contrast to fossil fuels.

Different seed oils have been used in several countries as feedstocks for production of biodiesel according to their availability. Soybean oil is often used in United States, Brazil and Argentina, while rapeseed oil is common to a good number of European countries, while palm and coconut oils are used in Malaysia and Indonesia for biodiesel production [5]. In Southeast Asia and India, *Jatropha cursas* [6], [7], *Pongamia pinnata* [7], [8], and *Mahua indica* [5] are utilized as significant sources of fuel. Some variety of bio-lipids can also be used for biodiesel production. Pure vegetable oil feedstocks such as rapeseed and soybean oils are commonly used, though other crops such as palm oil, sunflower, mustard, hemp, and even microalgae are promising. Used vegetable oil, animal fats including lard, tallow and yellow grease, and non-edible oils such as jatropha, neem oil, castor oil, and tall oil are some of the feedstocks being used as well [3]. The oils of the seed plants like *Cynara cardunculus* L. and *Brassica carinata* [7], residual cooking oil [9], microbial and insect oils [10], castor, tobacco seed, neem, rice bran and rubber seed oils have also been identified as other raw materials showing signs of success for production of biodiesel [11].

Several current studies focusing on utilization of non-edible oils have promoted vast discovery of non-edible oil feedstocks for production of biodiesel locally and industrially [12]. Rapeseed, soybean and palm oils remain the commonest feedstocks while mustard seed, peanut, sunflower and cotton seeds are new oil plants that are being used currently [12], [13]. Biodiesel production from non-edible oil seeds has been substantially explored over the last few years. Examples of non-edible oil seeds which have been extensively used for biodiesel production include *Jatropha curcas*, *Pongamia pinnata*, *Madhuca indica*, *Ricinus communis*, *Azadirachta indica*, *Hevea brasiliensis*, *Nicotiana tabacum*, rice bran, *Thevetia peruviana*, *Hura crepitans*, jojoba, *Ailanthus altissima*, etc. [14]–[22]. There is currently increase in extraction of oils from inedible oil seeds that are used in producing biodiesel which have the expected fuel properties for engine applications with no modification to the engine [20]–[22]. In this light, the authors recently carried out robust optimized studies on biodiesel production from *Parinari polyandra* oil [23] and made an attempt to test its engine application and performance [24], all of which are new contributions that have not been addressed before.

From established reports, the continuous combustion of fossil fuels in engines have brought about release of GHG that are contributing to increase in global warming [25]. However, biofuels possess a number of benefits, among which is the reduction of GHG in our atmosphere. The exhausts from combustion of diesel in IC engines portray a serious threat to our existence by contributing to global warming. Biodiesel is one of the renewable sources of energy for meeting increasing energy demand for transportation and reducing GHG emissions remarkably. The present review provides a comprehensive account on sustainable production and utilization of biodiesel synthesized from inedible and waste edible oils as engine fuel that will be useful for researches, engineers, fuel suppliers and end users, manufacturers and investors who are into biodiesel production and manufacturing of diesel engines.

Considering the research literature on the different applications of biodiesel in engines, there is no available work which has explored the current state of the art of global biodiesel production and utilization in transportation sector and the expected outgrowth for it to pass the SDS goals by the year 2030. Also, to the best knowledge of the authors, the commercialization of non-edible oils in countries with high biodiesel production rate has not yet been established nor addressed before. With the recent records of increase in diesel vehicle sales in the United States and consistent rise in diesel car markets in Europe for the past decade, this review is intended to serve as a paradigm pointer to an imminent corresponding increase in global biodiesel policies adoption and complete switch to diesel engines in respect to improved performances of engines running on renewable and environmental friendly biodiesel fuel. The expected challenges and prospects of promoting on biodiesel as a future fuel in the transportation sector were also identified for further studies. The chosen literatures were peer reviewed scientific researches that provided significant contributions to the study area. Elsevier's reference manager software Mendeley was used for capturing, citing and listing the references of the article that were selected.

2.2 Review of biodiesel production technologies

It is generally accepted that viscosity is the main difficulty that hampers the direct use of vegetable oils in traditional diesel engines [26], [27]. Consequently, there are established techniques and processes that have been used to produce biodiesel from various non-edible feedstocks to reduce viscosity. These methods include pyrolysis, micro-emulsification, dilution, and transesterification. Of all these methods, transesterification remains the viable process that has been adopted so far for the reduction of viscosity. The flowchart shown in Figure 2.1 describes the routes to produce biodiesel from non-edible oil seeds and their final products [28]–[31]. Transesterification was found to be the most common method used in biodiesel production. More emphasis is given to this under this section.

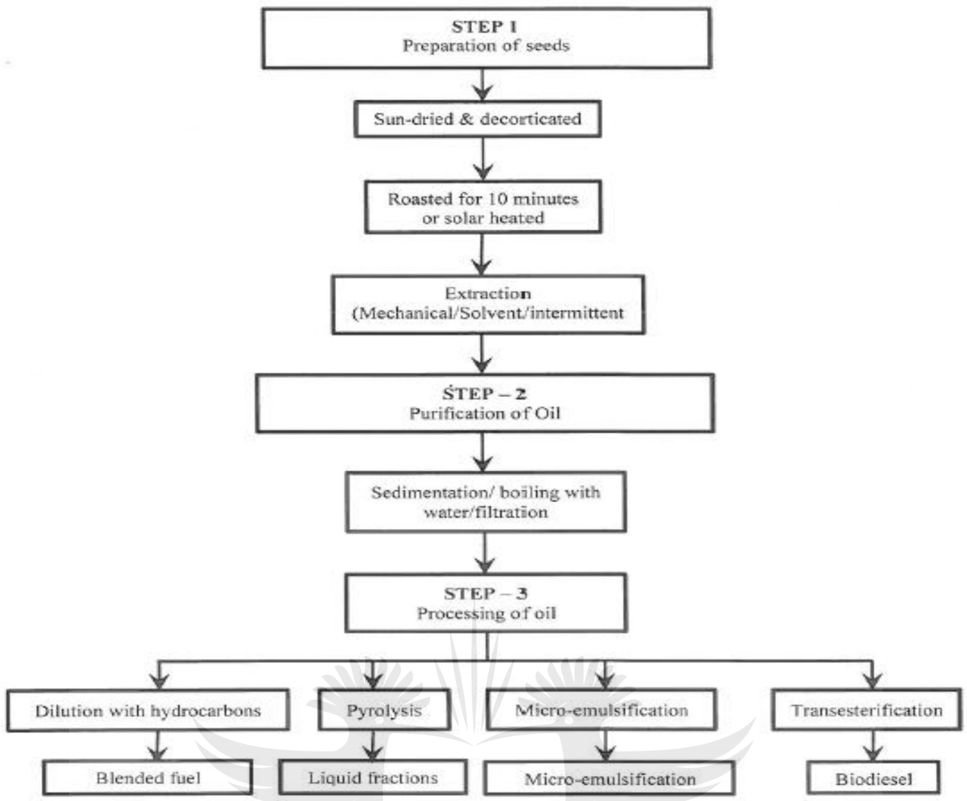

Figure 2.1: Process flowchart of non-edible crop seeds to biodiesel

(Compiled by the author of this thesis based on the works of Atabani et al. [29]; Balat and Balat [31]; Salvi and Panwar [32])

2.2.1 Pyrolysis

Pyrolysis refers to anaerobic thermal disintegration of organic materials in the presence of a catalyst. The fragmented matters can be animal fats, vegetable oils, natural triglycerides or FAME. Common products of pyrolysis of triglycerides are alkanes, alkenes, alkadines, aromatics and carboxylic acids [4], [33]. The liquid components of the disintegrated fats are similar to diesel fuels. The pyrolysis products have CN, viscosity, flash point, and pour point properties lower than diesel fuel but similar heating values [26], [27], [34].

2.2.2 Micro-emulsification

Micro-emulsification, which is also known as co-solvent blending, is the thermodynamic equilibrium dispersion of microstructures with average diameter, d, less than 0.25 of the wavelengths of visible light. Much agitation is needed for the mixture to remain in a single state.

A microemulsion can be made by using a co-solvent to dissolve immiscible substances such as vegetable oils and an ester, or vegetable oils and alcohols, such as methanol, ethanol, butanol, hexanol, with the addition of a surfactant and a cetane improver. Addition of diesel fuel is optional depending on the type of engine. Micro-emulsification is a stable technique for reducing high viscosity of triglycerides [26], [31].

2.2.3 Dilution

Dilution involves the addition of diesel fuel to triglycerides to make it thinner (reduce the viscosity) for better engine performance. No chemical process is needed for this method [3], [35]. It is established that complete replacement of some vegetable oils for diesel fuel is not realistic experimentally due to variation in the viscosity and pour points. Consequently, mixing 20 – 25% blends of vegetable oil with diesel has been examined to produce quality performance results for diesel engines [4], [24], [27], [36]–[38]. The details of diluting fossil diesel with varieties of non-edible seed oil such as turpentine, *Putranjiva roxburghii*, cotton seed, linseed, rubber seed, *Jatropha curcas* and *Pongamia pinnata* oil are reported in some literatures [39]. Diluted fuels such as, preheated palm oil and palm oil/diesel oil blends, palm oil/waste cooking oil mixtures, were prepared and successfully applied as fuels in an IC engine [40].

2.2.4 Transesterification

Transesterification has been extensively used in reducing the viscosity of vegetable oil and influencing their conversion to biodiesel. It is a process by which akyl esters are produced from chemical reactions between alcohol and vegetable oils in the presence of catalyst. The most affordable and available alcohols in this reaction include methanol and ethanol [4], [41]. The type of alcohol used does not entirely determine the biodiesel yield, the selection is determined by cost and performance. Transesterification is a reversible reaction involving a sequence of three reaction stages in which the triglyceride in oil is converted into diglyceride, and diglyceride is converted into monoglyceride (methyl or ethyl ester) [28]. Three moles of alcohol are required in this reaction for each mole of triglyceride. But usually, more molar ratio is often employed to shift the reaction forward for maximum biodiesel production. Three ester molecules are produced in the overall chemical reactions; one ester molecule from each step (Figure 2.2). Glycerol, which has commercial value, is derived as a by-product of this reaction (Figure 2.3).

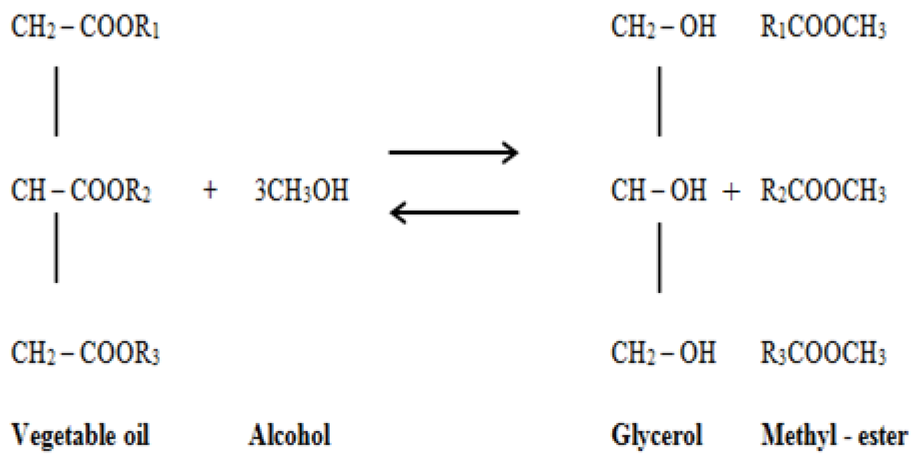

Figure 2.2: Reaction mechanism for transesterification
Demirbas [26]; Singh and Singh [27]

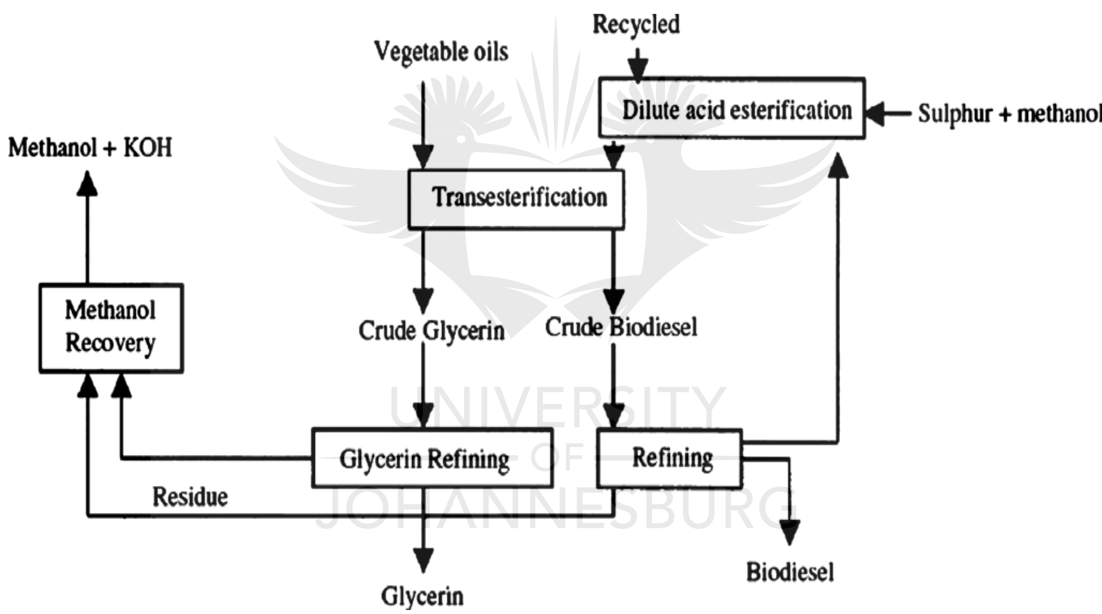

Figure 2.3: Basic schemes for biodiesel production
Marchetti et al. [42]

The catalysts that are commonly used are acid and alkali catalysts depending on the nature of the oil used for biodiesel production. Transesterification catalysis involving the use of enzymes are currently being explored for higher biodiesel production. As a result of the differences in the saturation of oil, the acid value of any chosen feedstock has to be reduced to less than 2.0 mg KOH/g for a one-way alkaline transesterification [43].

Other authors however recommend it to be below 4.0 mg KOH/g [44], but the reaction will be slowed down as a lot of water is produced along with ester [45]. To overcome this, many other studies have employed two-step transesterification processes to produce biodiesel from saturated oils with fatty acid values greater than 2.0 mg/KOH/g. The first step involves acid esterification reaction between the oil and an acid to reduce the fatty acid content. The catalyst commonly used during acid esterification of neat oil is H_2SO_4 [46]. This is then followed by transesterification reaction where the purified/neat oil is reacted with alcohol in the presence of a catalyst. Generally, alkaline transesterification would favour biodiesel production as it appears to take place about 4000 times faster than acid transesterification [47]. The alkaline catalysts used at industrial level include homogeneous catalysts such as NaOH and KOH. The use of homogeneous catalysts has been successful at industrial level for biodiesel production. However, the biodiesel and glycerin have to be purified by washing the products with hot distilled water to remove the basic catalyst [4]. A reasonable number of researchers have used non-synthetic heterogeneous solid catalysts which have relative advantages of reusability and reduction of overhead cost of washing the products [17], [48]–[57]. Methanol was also found to have high reaction potential and preferred over other alcohols due to its relatively low cost [58].

In order to meet up with high transportation demands for biodiesel fuel, both local and industrial production of biodiesel must be improved for high biodiesel yields. Optimization techniques have proved to be efficient tools in producing quality and high esters yield. It is of great significance to study the effect of applied reaction parameters on biodiesel yield because they influence directly the efficiency of biodiesel production. Statistical procedures, such as RSM [23], [24], [59], Factorial design [60], Box–Behnken factorial design [17], [61], Taguchi technique [62], D-Optimal design [18], GA coupled with ANN [63]–[66] are commonly used optimization methods for biodiesel production. The different findings on optimized yields of biodiesel production from selected inedible seed oils with high biodiesel potentials are outlined Table 2.1.

Table 2.1: Optimized biodiesel yields from different inedible oil feedstock

Oil feedstocks	Maximum Biodiesel yields	Model	Independent variables	References
Vitellaria paradoxa	99.65%	ANN coupled with GA and RSM	Catalyst amount, oil/methanol molar ratio, temperature, time	[64]
Jatropha curcas, Pongamia pinnata and Calophyllum inophyllum	93%, 91%, and 85%	NM	Mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, time,	[67]

			temperature and purity of reactants	
Jatropha curcas	>99%	RSM	Methanol quantity, acid concentration, reaction time	[6]
WCO	96.03%	NM	Temperature, time, methano-to-oil mole ratio	[53]
Hura crepitans	93.97%	D-Optimal	Temperature, time, catalyst concentration, catalyst type	[18]
Thevetia peruviana	81%	RSM	Temperature, time, alcohol-to-oil ratio	[17]
Parinari polyandra	95.62%	RSM	Temperature, time, catalyst amount	[23]
Jojoba	83.5%	RSM	Temperature, catalyst concentration	[68]
Pongamia pinnata	98%	NM	Catalyst concentration, methano/oil molar ratio, temperature, mixing intensity	[69]
Oleic acid	82.1%	RSM, ANN-GA	Methanol to oleic acid molar ratio, catalyst loading, temperature, time	[65]
Castor oil	94.19%	Factorial Design	Temperature, catalyst concentration, ethanol:castor oil molar ratio	[60]
Castor oil	99.81%	RSM	Temperature, methanol/oil molar ratio, catalyst concentration	[70]
Mahua oil	92.7%	RSM	Catalyst concentration, methanol amount, temperature, time	[71]
WCO	98%	GA	Molar ratio, catalyst, time, speed, temperature, humidity, impurity	[72]
Pongamia glabra	95%	NM	Methanol to oil molar ratio, catalyst concentration, temperature, time	[73]
Shea butter	92.16%	RSM	Temperature, agitation, methanol:oil mole ratio, catalyst loading	[74]
Black soldier fly larvae	96.18%	RSM	Temperature, methanol:fat molar ratio, enzyme loading, time	[9]
Sterculia oil	90.2%	RSM coupled with ANN	Temperature, catalyst concentration, oil to methanol ratio, agitation speed	[75]

Jatropha curcas - Ceiba pentandra	93.47%	ANN-GA	Methanol-to-oil ratio, agitation speed, catalyst concentration	[66]
Brucea javanica	94.34%	RSM	Methanol to oil ratio, catalyst concentration, temperature	[76]
Loofah	88%	RSM-ANN	Time, temperature, amount of alcohol, amount of KOH	[77]
Simarouba glauca	62%	RSM-ANN	Oil:alcohol ratio, temperature, time	[78]
Bauhinia monandra	93.33%	RSM	Catalyst loading, methanol/oil molar ratio, time	[50]
Sesamum indicum	96.62%	RSM and ANN	Time, catalyst amount, temperature, methanol to oil molar ratio	[79]
Cantaloupe	94.5%	NM	Methanol to oil molar ratio, temperature, catalyst loading	[80]

Several biodiesel optimization layouts were achieved through the use of traditional and heuristic algorithm-based support vector machines to recognize the perfect sets of reaction conditions and obtain regression models with greater precision for optimizing biodiesel production from waste cooking oil [72]. Many of these procedures for biodiesel optimization were achieved using standardized software features to achieve best utilization and performance of resources. Quadratic models were commonly used, and the ANOVA results showed that some of these reaction parameters, especially temperature, alcohol to oil molar ratio, and catalyst concentration had significant impact on biodiesel production at 95% probability level. The application of RSM to optimize biodiesel production has generated wider applications than other heuristics models (GA, ANN, ANFIS, SA, etc.). The most commonly used optimization models are RSM, ANN and GA. Analysis of Scopus indexed publications on the subject area shows that 530, 89, and 30 documents have been published on the application of RSM, ANN, and GA respectively in the last 30 years. For the Web of Science based journals, a total number of 530, 97, and 62 have been published on the application of RSM, ANN, and GA respectively.

Though there have been quite some arguments on the use of these optimized models for better prediction, it appears RSM is still scaling high as the most commonly used model over the years. A better explanation found for this is the cost effectiveness and reliable optimization methodology which requires reduced number of experimental runs for evaluating multiple applied parameters in any process control [81]–[83]. The application of RSM can be a useful utility in improvement of industrial biodiesel production. Sarve [84] reported that ANN had better prediction capability than RSM in predicting the FAEE content from crude *Madhuca indica* oil transesterification. Betiku [85] also demonstrated that ANN established a reliable model than RSM in the prediction of biodiesel production from *Azadirachta indica* seed oil. To verify the statistical predictions for the biodiesel yields, verifications experiments were carried out and a similar agreement was found between the experimental and predicted values.

2.3 Current research scenario of biodiesel combustion as vehicular fuel

Biodiesel has become an important vehicular fuel owing to its excellent and similar properties as diesel engine fuel [86]–[88]. Many researchers have tested biodiesel combustion in automobile diesel engines using different ratio of biodiesel with diesel blends. According to some reports, fuel blends above 20% generated maintenance problems and even occasionally damaged the engine [89]–[91]. Biodiesel of lower blends, B2 and B5, in diesel fuel have been used successfully in existing diesel engines as well as new designs coming off the assembly line. Biodiesel is used in the marine industry as a shipping fuel because of its non-toxicity and essential absence of sulphur and aromatics.

While some studies have shown the possibility of using more than 20% of vegetable oils as addition to diesel fuel, the acceptable submissions are that chemically refined vegetable oil can be used to operate CI engines for prolonged period without any engine modification [24], [90], [92], [93]. In 2005, Chrysler introduced into the American market the Jeep Liberty CRD vehicles which can run on 5% biodiesel blends. This was a symbolic pointer for partial acceptance of biodiesel as a sustainable diesel fuel extender. Warranty coverage was increased to 20 % biodiesel blends in 2017 with the expectation that biofuel quality in the US will be improved [94]. The Volkswagen Group stated categorically that many of its cars are suitable with EN 14214 standardized B5 made from rapeseed oil. Mercedes Benz does not permit biodiesel fuel blends which exceeds 5% biodiesel as a result of production defects in their engine designs. The application of different fuel blends in their cars other than specified will revoke any warranty. It was also gathered that the Mercedes-Benz Limited Warranty does not cover any damages incurred by the use of restricted fuels [94]. However, extensive research in the use of biodiesel-diesel blends in CI engines have proved that seed oil-derived biodiesels have benefits relative to improved combustion performance and emissions reduction. In 2004, the city of Halifax, Nova Scotia revolutionized its transportation network by allowing the city rapid buses to run wholly on a fish-oil based biodiesel. There were few initial mechanical issues which were overcome when the entire fleet had been successfully converted after several years of refining.

Ejaz and Younis [89] in their study identified biodiesel as vehicular fuel which can be used to replace diesel fuel. The authors also concluded that its renewability and similar fuel properties to fossil diesel make it a potential useful fuel to replace fossil diesel in the nearest future. Biodiesel produced from plant sources can be modified by blending with other fuels such as diesel, biodiesel and biodiesel blends in order to complement the saturation level of fuel and attain better combustion [95]. Among several oil sources, it can be concluded that jatropha oil, depending on variety, is a leading candidate for the commercialization of non-edible vegetable oils for biodiesel production as an alternative diesel fuel in IC engines. For instance, the seed oil of jatropha was used as an alternative to diesel fuel during the Second World War in in Madagascar, Cape Verde and Benin [96]. Mofijur et al. [2] concluded that B10 and B20 blends of jatropha biodiesel can be used in a diesel engine without any modification. The results indicate that viscosities of B10 and B20 are similar to that of diesel. It was observed that BSFC increases as the biodiesel volume increases.

Ogunkunle and Ahmed [24] created fuel blends between the range of B5 and B20 from *Parinari polyandra* biodiesel and used them to run a 5Hp diesel engine. The biodiesel blends had properties which were within the ASTM standards for engine fuel. The study showed that that the flammability index of biodiesel blends is better because of its higher CN and oxygenated characteristics. The test results of two Euro 3 passenger cars diesel engines, fueled with saturated and unsaturated biodiesel fuel blends, showed that a maximum 30% blend with fossil diesel can only be permitted due to cold-flow inhibition [97]. The results indicate that higher blending ratio majorly affect the exhaust emissions, alongside the fuel unsaturation level and engine technology. It was concluded that the composition level of saturated and unsaturated biodiesel should be carefully monitored in biofuel markets in order to achieve maximum environmental and operational benefits.

The biofuel potential of different palm oil-based products was evaluated in IC engines and the results showed that a high proportion of palm oil in diesel fuel decreases the heating value of the blend, but the brake thermal efficiency increases for the palm oil/diesel blends [40]. The treatments applied include preheating palm oil and preparation of palm oil/diesel oil blends, mixtures of palm oil with waste cooking oil, which are all converted into esters by transesterification process. The methyl ester was found useful as an engine fuel without engine modification. Biodiesel produced from different inedible oil seeds have been utilized in blended forms between the range of B5 and B20 with significant similarities to that of fossil fuel combustion in IC diesel engines [2], [58], [97]–[105]. The biodiesel has better lubricating properties which reduces thermal loss, the HV of blended biodiesel were relatively high for better combustion.

Exploration of recent literature studies show that lower blends of biodiesel increase the BTE and moderates the fuel consumption of CI engines. The exhaust gas temperature increases with increasing volume of biodiesel in fuel blends. The results established that the use of biodiesel in CI engines is viable and sustainable. Amidst the use of biodiesel as an engine fuel, there lie the problems of low-temperature flow property, thermal and oxidation stability facing the suppliers and end users of biodiesel blends.

The addition of additives to biodiesel has shown to improve its combustion by inhibiting oxidation and thermal degradation of B100 and biodiesel blends. Fuel additives are now gaining interest to meet market demands for viable fuels containing biodiesel blends. Fuel additives can increase fuel economy and reduce emissions either directly or indirectly. Their use allows the operation of the engine to be maintained at ideal conditions over its entire lifespan. For example, oxygenated additives, metal based additives, antioxidants, CN improvers, smoothness and cold flow are used to meet certain automotive specifications and quality [106]. Some research findings show that the most effective method of reducing emissions and improving engine performance is by adding nano additives and using emulsified fuels [107]. Common additives used by researchers include di-ethyl ether, methyl oleate, synthetic Mg additives, orange oil, kerosene, methanol, ethanol, etc. Some of these, and many other ones that are used to improve the cold flow properties of biodiesel, engine performance and emission properties were discussed by Ali et al. [108].

Latest researches show the inclusion of Nano-sized particles in diesel-biodiesel fuel emulsion. The results obtained reveal an enhancement in the thermophysical properties, the heat transfer rate, and stabilization of the fuel mixtures. There are notable reductions in the exhaust emissions and increases in the engine performance parameters depending on the amount of nanofluid additives [109]. Metal-based additives that are commonly used include $CuCl_2$, $FeCl_3$, CuO - nano structured, $CoCl_2$ and $CuSO_4$. They have catalytic effect and are added in diesel and biodiesel based on the necessary requirements. The application is done in nano form and finely dispersed into the fuel using an ultrasonicator [110]. The use of these additives also reduces the exhaust emissions [111]. The commonly used oxygenates are alcohols (methanol, ethanol, propanol and butanol), ether and ester. The fuel-efficient groups in acetoacetic esters include dicarboxylic acid esters and dimethyl carbonate esters [106]. The addition of oxygenates will minimize the ignition temperature of biodiesel, stabilize the fuel combustion potential, and also reduce the smoke emissions [112]. Certain additives, such as nitrites, peroxides nitrates, aldehydes and tetra-azoles, are meant to improve the CN. Alkyl nitrates are commercially used with evidences of good outcomes. Alkyl nitrates have been tested as the most essential additives in commercial improvement of CN. The type which has been used for years is 2-Ethylhexyl, and has become general additive for improving CN [113]. Examples of antioxidant additives include BHA, BHT, PL, DPA, TBHQ and PG. The successful ones from literature include TBHQ, PL and PG. [114], [115].

Nano-additives that were synthesized from different sources such as ferrous material, polymeric materials, ceramics, non-organic materials, metal oxides such as aluminum, carbon, titanium, iron, and CNTs have been mixed with diesel-biodiesel blends and their effects studied in many literatures [107]–[109], [116]. The fuel additives are reported to have the capability to increase the oxygen level in the engine, reduce the exhaust emissions, improve the fluid flow properties, reduce the ignition delay for better combustion and increase the viscosity index [112]. The conclusion of Vijay Kumar [117] reveals that the improvement of combustion performance and reduction of emission characteristics of biodiesel can be achieved through the use of additives to the 2nd generation of biodiesel.

2.4 Recent trends in scientific publications for engine performance using biodiesel as fuel

In search of a renewable alternative fuel that can suitably replace fossil fuels and the environmental impacts consideration of emissions from petrochemical products, researchers have directed their interests to biomass-derived fuels. This appears to be the logical solution to the environmental concerns, energy security challenges and socioeconomic issues facing the conventional petrol-diesel. According to the records of Web of Science, publications records (Figure 2.4) focusing on development of biofuels and their applications in several areas have increased from 1988 in 2010 to 4061 in 2018, with records to show the spatial distribution all around the globe.

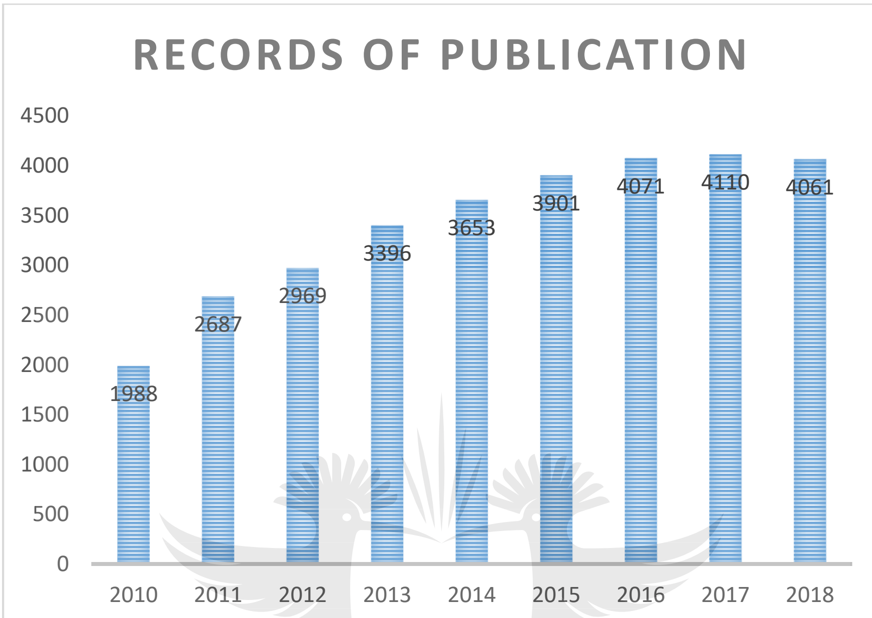

Figure 2.4: Research publication records on biofuel production and application from 2010 to 2018

(Compiled by the author of this thesis)

Scopus analysis for scientific contributions on the application of biodiesel as vehicular engine fuel suggests how research interest in this area has increased over the years. It is evident that the utilization of biodiesel fuel in diesel engines is gaining successful application as the publications by year showed increasing trend as reflected in Figure 2.5. One (1) publication was recorded on the use of biodiesel in diesel engine in 1994 while the number has increased over the years gradually to 418 documents from different parts of the world in 2018.

The documents by country analysis recovered a total of 2736 peer-reviewed documents related to performance of biodiesel combustion in vehicular diesel engines between 1994 and 2018, with India leading 1339 publications. The distribution of journal publications counts for fifteen leading countries where biodiesel fuel technology is being used as fuel in diesel engines is shown in Figure 2.6. Venezuela, Paraguay, Qatar, Rwanda, Slovakia, Sudan, Tunisia and Trinidad and Tobago are some of the countries with the lowest research interests, having just one publication each on this subject area. It is worth noting that there has been an increasing number of publications on the use of fuel additives to improve the combustion efficiency of biodiesel in vehicular diesel engines. Of the total publications recorded in this study area, about 12% focused on application of fuel additives to improve the engine performance and reduce the GHG emissions from the engine exhausts. The application trend (Figure 2.7) varied from the first publication in 1999 to 66 scopus indexed documents in 2018.

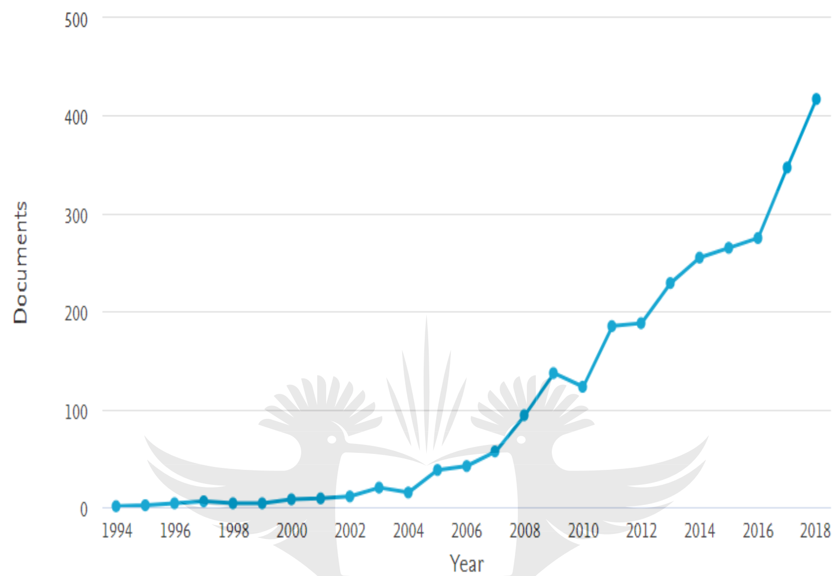

Figure 2.5: Publication trend by year on application of biodiesel in vehicular diesel engines

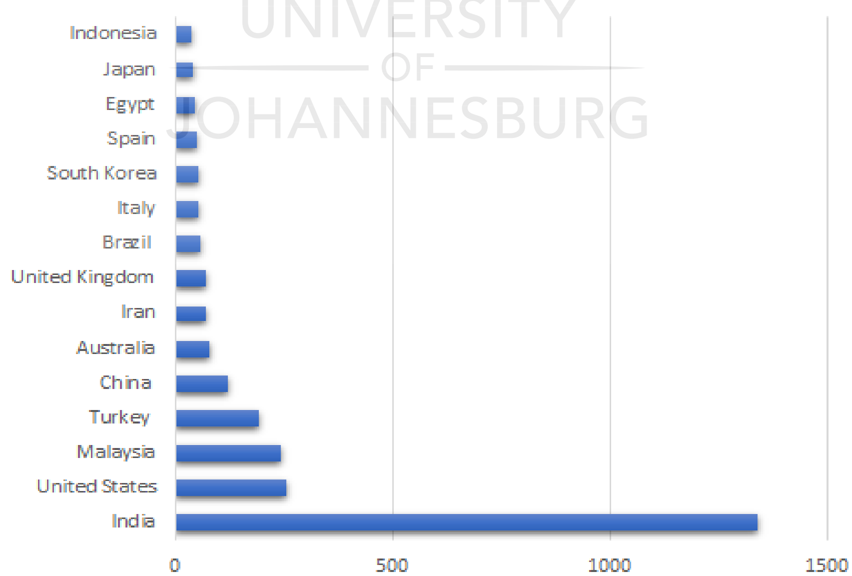

Figure 2.6: Publications by country on application of biodiesel in vehicular diesel engines

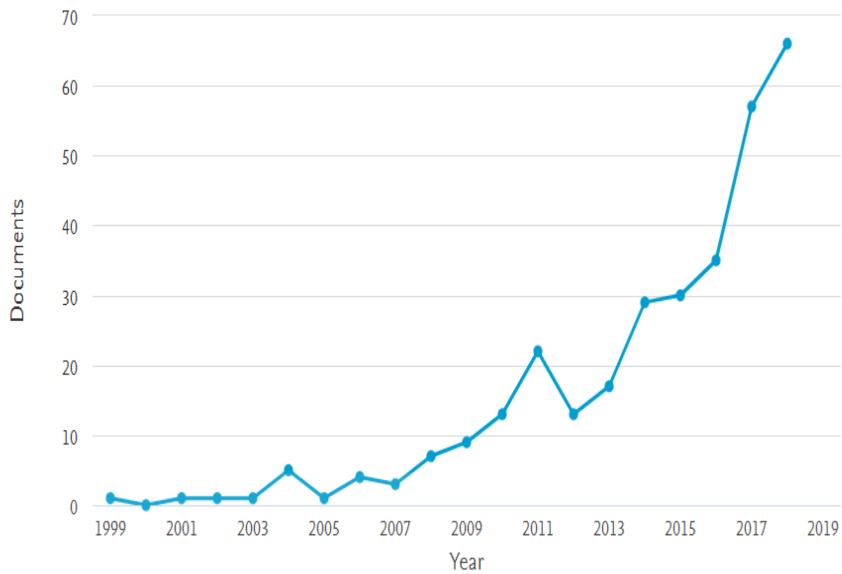

Figure 2.7: Publication trend of documents by year for application of fuel additives in biodiesel combustion technology

The increasing trend observed between these years shows that application of fuel additives is gaining popularity in the transportation sector for improvement of engine performance and reducing harmful emissions. The fluctuations observed in the trend, which is more pronounced in 2012, can be attributed to the fact that researchers are still trying to master the application of these additives in the right quantities. However, this technology, most especially the usage of Nano additives, need more research capacity and concerted efforts to make it an adoptable technology.

2.5 Advantages of using biodiesel

The benefits of using biodiesel in IC engines are profound and are marked for its wider applications based on the following highlights:

- Diesel engines have proved to be more efficient than petrol engines in term of energy conversion and power output [103], [118]–[121].
- The efficiency of engine shelf-life can now be prolonged while reducing the costs of procurement of early replacement.
- Biodiesel are clean burning fuels. The combustion of biodiesel in IC engines reduce the release and impact of GHG. Literature studies suggest that the combustion of biodiesel reduces GHG by 40 – 65% [122], [123]. Compared to the last 20 years, GHG of major cities with high automobiles usage in the world will be reduced by more than 20% [124].

- Better thermal efficiency from friction reduction as a result of smoother lubricating quality of biodiesel-diesel blends [24], [125], [126].
- The raw materials for biodiesel production are organic and easy to source. More biodiesel products can be made available from different plant oil materials and waste oil [127].
- Biodiesel is renewable and does not give rise to global warming due to its closed carbon cycle. Amount of the carbon taken by plants are returned back to the atmosphere. Biodiesel is carbon neutral because it contributes zero emissions to global warming.
- Biodiesel is non-toxic and also safe to transport from one point to another owing to its relative high flash point.
- Provision of foreign exchange earners. The availability and abundance of feedstock oil seeds in specific areas have created job opportunities for local farmers in creating more plantations of the feedstock and increasing the production for foreign exchange.

2.6 Impact of biodiesel combustion on engine performance and emissions

Current research investigations have presented that biodiesel can help in enhancing the performance and reducing harmful exhausts in a diesel engine [103]. The study of the impact of biodiesel on engine power and torque show that there is no major difference in engine power when pure biodiesel or diesel fuel is used to run the engine. [24], [118], [120], [128]–[130]. Amazing increases in power or torque of an engine from pure biodiesel were reported by some researchers [131], [132]. For instance, it was found that the difference in maximum and minimum engine power and torque at full load between petrol-diesel and some plant oil biodiesels were only 1.49% and −0.64%, 1.39% and −1.25%, respectively [133]. This was caused by higher BSFC, higher oxygen content and higher combustion rate of biodiesel. Qi et al [120] reported that soybean oil biodiesel demonstrated similar combustion properties to that of diesel, and that the power outputs were almost identical. There was also significant reduction in CO, THC, NO_x and smoke under full load conditions.

Song and Zhang [131] reported an increase in the engine BP and torque as tobacco oil biodiesel content increased in the fuel blends. The improved power produced by the engine while running on pure biodiesel could reach 70% relative to diesel fuel [132]. Ghobadian et al. [118] studied the performance and exhaust emission analysis of a diesel engine using WCO biodiesel and diesel blends at different engine speeds. The results show that the combustion of WCO biodiesel blends produced better engine performance and cleaner emissions. Also, the combustion of lower blends (B5) of castor oil biodiesel in a diesel engine increased the break thermal efficiency and reduced the fuel consumption. The exhaust gas temperature also increased with increasing biodiesel concentration [99]. Additionally, the combustion of canola biodiesel blends under different load conditions revealed that heat release rate decreased gradually with the reduction of premixed combustion fractions and caused increase in the combustion proportions when canola biodiesel ratio was increased [105]. There were higher NOx emissions, reduced smoke, CO, THC and higher CO_2 emissions for all loads. The oxygenated nature of biodiesel influences its complete combustion in engines, and thus lower CO and HC emissions are often released from biodiesel combustion in engines [134], [135].

The BSFC of IC engine increases with increase in biodiesel volume in fuel blends [136]–[138]. A higher biodiesel consumption by the engine is based on the difference in the energy content per gallon compared to diesel fuel. Demirbas [3] reported that biodiesels have relatively LHVs. The values, which range from 39 to 41 MJ/kg, are slightly lower when compared those of gasoline (46 MJ/kg), petrol-diesel (43 MJ/kg), or petroleum (42 MJ/kg), but greater than coal (32–37 MJ/kg). As engine delivers fuel on volumetric basis, more biodiesel is supplied for combustion to compensate the LHV [120]. The exhaust gas temperature increases just as biodiesel volumes increases in the fuel blends [24], [116]. This has majorly been the reason for the increased NOx emissions from biodiesel combustion. High gas temperature reacts with atmospheric air which in turns forms oxides of Nitrogen from the combustion of atmospheric Nitrogen. The BTE of diesel engines is lower when run on biodiesel than diesel fuel. The low calorific value, high volatility and poor spray properties of biodiesel are found to be responsible for the increased BTE efficiency Bhaskar [139], [140].

Summarily, it was found that the blending of biodiesel with diesel increases both the cetane number and oxygenated chemical compounds of the fuel which improves the overall combustion and reduces the gaseous emissions which increase global warming level and are also hazardous to health [141]. A summary of current researches which report reductions in the gaseous emissions compared to petrol-diesel is presented in Table 2.2.

Table 2.2: Summary of current findings on emissions from diesel engines fueled with biodiesel blends

Feedstock	Fuel blends	Engine condition	Emissions reduction compared to petrol diesel (%)				Author
			CO_2	CO	HC	NO_x	
Jatropha	B100	1500 and 2000 rpm	–	–20 to –25	–17 to -23	– 0.3 to –4.5	[142]
Soybean	B100	250 bar at 2400 rpm	–	–33	–	20	[143]
Soybean	B5, B20, B50, B85	9.6–35.7kW	–0.89 to 1.48	28 to 48	–9 to 18	–	[144]
Soybean	B10, B20, B30, B40	Full load, 1400–2100 rpm	–	–27	–27	–5	[120]
E. sativa	B10	5.88 kW at 2600 rpm	160	–30	–	108	[145]
Waste oil	B20, B40, B80, B100	1500 rpm, 0–5 kW	–	–31	–57	18.33	[146]
Waste oil	B5, B10	0.12–0.48 MPa, 2200 rpm	3.3 to 5	–11.8 to –51	–2 to –29	6.4 to 8.7	[147]
Waste oil	B10, B30, B50	Full load, 1000–2000 rpm	8.7 to 38.5	–3,3 to –26.3	–	4.7 to 19.0	[148]
Waste oil	B5	Full load, 1000–2500 rpm	–	–8.5	–28	–24	[149]
Jatropha	B10, B20, B30, B50	Full load, 1500–2400 rpm	13.08	–16.3	–7.4	27.25	[150]
Jatropha	B10, B20, B40, B50	1900 rpm	–40 for B50	150 for B50	–	99.05 for B50	[151]
Jatropha	B5, B10, B20, B30	20% to full load	20 for B20	–19.6 for B20	–22.6 for B20	23 for B20	[152]
Waste oil	B25, B50, B75	0–25 kW	8.5 for B50	20.1 for B50	23.5 for B50	4.8 for B50	[153]
Chlorella protothecoides	B20, B50, B100	1700 to 2900 rpm	–0.7 to –4.2	–12.3 to –28	–	–2.4 to –7.4	[154]
Chlorella protothecoides	B100	1500 rpm, Varied load	–	–31	–27	–13	[155]
Chlorella vulgaris	B2	2200 rpm, 50% load	–	–0.34	–50.2	2	[156]

Chlorella vulgaris	B10, B20	–3.4 to –5.4	–41.8 to –47.4	–44.3 to –51.1	1.9 to 5.1	[157]

The United States Environmental Protection Agency (USEPA) 2018 reports [158] identified CO, PM, NO*x* and VOCs as the major transportation pollutants that contribute to smog formation and poor air quality. All these are emitted basically from combustion of fossil fuels and they have negative impacts on the health of US citizens. The good fortune is that biodiesel combustion reduces CO, unburned HC and PM even from older engines. High-level reduction of GHG emissions continue to happen as biodiesel fuel remains the best carbon footprint of any US produced fuel. The emissions reduction percentage indexes from the use of biodiesel fuels wholly or partly in diesel engines in the US in 2018 are recorded in Table 2.3. These values are based on how the fuel blends are used in the vehicle (tank-to-wheel). These are important reasons why perceptive customers are shifting toward using biodiesel. As stated in section 2.5, the performances of biodiesel can be improved in IC engines with the use of different fuel additives [109], [110], [112], [116], [159]. The addition of these fuel improvers in biodiesel is inherent for improving the fuel properties, engine performance and emission control [106]. Extensive use of this can be found in several literatures [107], [108], [112], [116], [160], [161].

Table 2.3: 2018 emissions reduction in biodiesel in US

Emissions type	**B100**	**B20**
Regulated emissions		
Unburned THC	-67%	-20%
CO	-48%	-12%
PM	-47%	-12%
NOx	+10%	+2% to -2%
Non-regulated emissions		
Sulfates	-100%	-20%[a]
PAH	-80%	-13%
nPAH	-90%	-50%[c]
Ozone potential of speciated HC	-50%	-10%

National Biodiesel Board [123].

2.7 Global status of biodiesel adoption as vehicular fuel

Many countries have introduced biodiesel production and commercial feasibility into their energy industries [162]. An early consideration of alternative fuels for future possibility previously took place during the 1980s [163]. These efforts were made to find alternative solutions to energy security and sustainability, as well as seek advantages of alternative fuels to improving engine efficiency and reducing harmful emissions. According to 2017 reports of The Outlook for Energy, a worldwide view of demand and supply for energy through 2040 shows that the demand for both diesel and gasoline will keep increasing, with the former taking the lead. However, as the demand for energy in the transportation sector keeps increasing in the shortest period, the ratio of biofuel blending to the total quantity of fuel is also expected to increase and eventually lead to substantial reduction of the net GHG emissions on a long-term viewpoint [164], [165]. From a practical perspective, the vast use of biodiesel in diesel engines would guarantee the dual possibility of ensuring the world has access to cheap and reliable energy supplies while reducing emissions to solve the problem of climate change. Biofuels represent around 3% of the total global transportation fuels by 2012 [166]. The global energy demand in the transportation sector is expected to rise steadily at an average rate of 1.3% per annum as shown in Figure 2.8.

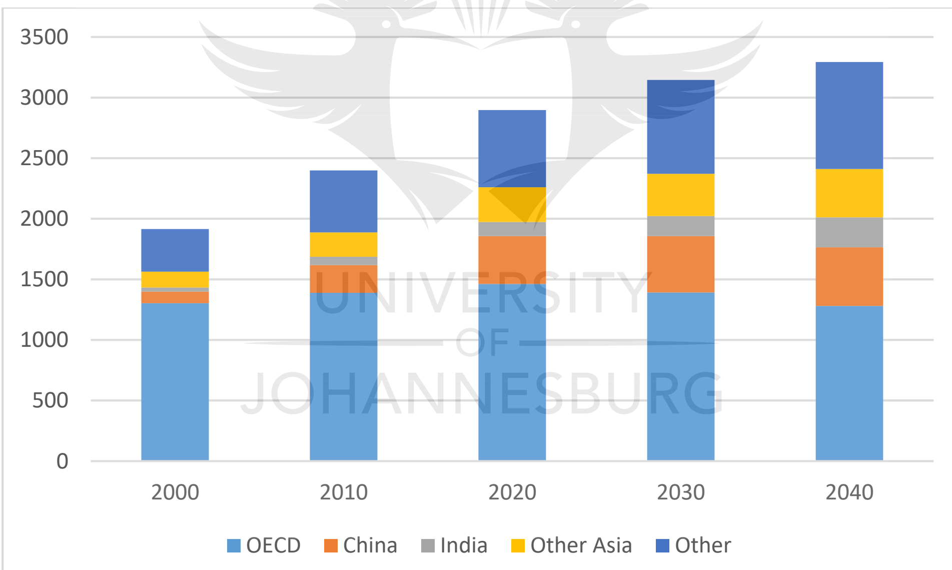

Figure 2.8: Global transportation demand by fuel

(Adapted by the author of this thesis from 2018 BP sustainability report)

A thorough review of the 2018 reports of World Energy Issues Monitor shows that there has been apparent constant advancement of the global energy sector towards a more transformed global energy blend penetration and shifting toward renewable energy technologies. World biofuels production has increased by an average of 11.4% in the last ten years. In 2017, an increase of 3.5% was recorded. Global ethanol production grew at a similar rate of 3.3% contributing over

60% to total biofuels growth [167]. The biodiesel production increased by 4% in 2018, driven mainly by growth in Argentina, Brazil and Spain [168]. Major supplying countries of biodiesel are notably Indonesia, India, China, Norway, Hong Kong, with Argentina taking the lead in production and supply of rapeseed biodiesel to the EU countries [169]. According to 2018 Biodiesel Market Report, the biodiesel market is expected to grow remarkably in the period between 2018 and 2023 [170].

Governmental support, favourable policy and public support are capable of playing an important role in the development of biodiesel industry in any country of the world [171], [172]. Important tools needed by the government include investment in research and development, price subsidies and renewable energy policy to promote biodiesel production and adoption by users [173]–[175]. Research and development have become a major driving force in the biodiesel industries by improving the technology of processing and production of biodiesel from individual feedstock [176]. The growth in the global biodiesel market can be associated to the enterprising implementation of biofuel policies in various nations including US, Argentina, Brazil, and Indonesia. For instance, the U.S. Renewable Fuel Standard (RFS) requires increased volumes of renewable fuels each year, with the current plan estimating companies to blend a total of 19.24 billion of renewable fuels in the country's fuel supply by 2019. The regulations regarding the formulation of fuel in these regions are expected to increase the share of biodiesel, thereby increasing the demand. So far, the Economic Impact Analysis has shown that biodiesel usage has supported a total of 64, 000 jobs in US and generated $11.42 Billion [158].

2.7.1 Biodiesel adoption policies by continent

2.7.1.1 North America

In North America, Diesel and Gasoline powertrains are envisaged to continue their influence on the commercial vehicle sector in the EIA forecasts through 2025. Diesel, HEV diesel and PHEV diesel powertrains together are estimated to make up nearly 62% of U.S. commercial vehicle registrations by 2025 [177]. The critical question that has arisen from this is: can those diesel engines be operated in a cleaner and more sustainable way without sacrificing the performance of the engines? The good news is yes; it can be done. Biodiesel blends, which are readily available in the marketplace of America, Asia and Europe, can be used in old and modern diesel engines without modification [178], [179]. The Canadian government has used production subsidies to promote excessive growth in biodiesel production. There is a mandate on fuel blends to support the policy reduction of GHG emissions. Half of the domestic biodiesel production comes canola oil [180]. The Canadian and US market share base case of commercial vehicle registration are shown in Figure 2.9 and Table 2.4 respectively.

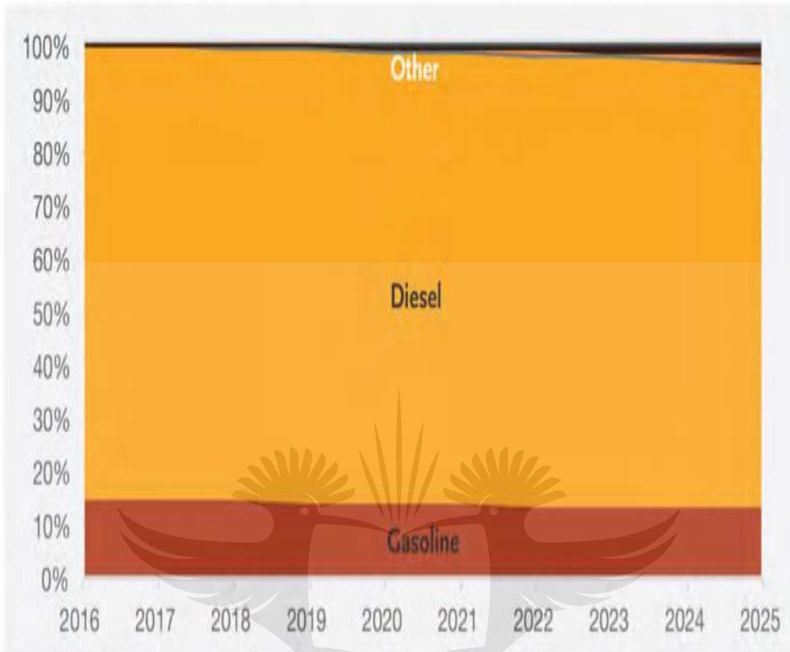

Figure 2.9: Canada market share base case of commercial vehicle registration
Source: EIA [181]

Table 2.4: US market share base case of commercial vehicle registration

	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025
Gasoline	35.10%	35.19%	35.29%	35.36%	35.41%	35.45%	35.46%	35.46%	35.45%	35.42%
Diesel	63.61%	63.34%	63.06%	63.78%	63.50%	63.21%	63.93%	63.64%	63.35%	63.07%
HEV Gasoline	0.06%	0.06%	0.07%	0.08%	0.10%	0.11%	0.13%	0.15%	0.17%	0.19%
HEV Diesel	0.13%	0.15%	0.18%	0.22%	0.27%	0.33%	0.39%	0.46%	0.53%	0.61%
PHEV Gasoline	0.01%	0.01%	0.01%	0.02%	0.03%	0.03%	0.04%	0.06%	0.07%	0.08%
PEH Diesel	0.01%	0.01%	0.02%	0.03%	0.05%	0.07%	0.09%	0.12%	0.15%	0.18%
BEV	0.02%	0.03%	0.05%	0.07%	0.09%	0.11%	0.14%	0.16%	0.19%	0.23%
FCV	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.01%	0.01%	0.01%
CNG	0.56%	0.64%	0.73%	0.81%	0.90%	0.98%	1.07%	1.15%	1.23%	1.32%
LNG	0.20%	0.21%	0.22%	0.23%	0.23%	0.24%	0.24%	0.24%	0.25%	0.25%
PAGV	0.31%	0.34%	0.37%	0.40%	0.44%	0.47%	0.51%	0.56%	0.60%	0.65%

Source: EIA [181]

According to the US National Biodiesel Board, 2.1 billion gallons of biodiesel was used by 3.8 million US consumers in 2015 which led to reduction of carbon emissions by a round figure of 18 million metric tons (about 78% less lifecycle greenhouse gas than petroleum diesel). Biodiesel has continued to succeed as America's first and only EPA-recommended biofuel, demonstrating its ability to attain large scale production. About 14.9 million acres of mature forests have been preserved while 466 million oil trees were planted. The USEPA has submitted that users are looking out for cleaner substitutes to petroleum products and they see biodiesel as a superior, cost-competitive alternative to petrol-diesel. As at 2014, domestic production of biodiesel was 1.47 billion gallons in 2014, while imports increased from 510 million gallons in 2014 to an estimated 670 million gallons in 2015, a pointer to biodiesel's rising popularity in the US. These numbers also prove that the biodiesel usage standard is absolutely working by introducing notable volumes of improved biofuel to the American people.

2.7.1.2 Latin America

Brazil is currently one of the world leading producers of bioethanol and biodiesel production [178], [179]. Biodiesel production in Brazil has increased from 736 million litres to approximately 2.7 billion litres between 2005 and 2011 [182]. The great extension of land and variety of climate and soil in Brazil favor cultivation and growth of different oilseeds that can be used for biodiesel production [183]. An adaptation (Figure 2.10) of the major feedstock used for biodiesel production in 2017 is taken from da Silva et al. [127]. An increase in biodiesel utilization was experienced in Brazil from January 2008 to November 2014 as blending level increased from 2% to 7% [183], [184].

Until 2012, Soybean biodiesel has accounted for more than 85% of the total biodiesel output in Brazil. The increase in biodiesel is borne out of the policy to promote renewable energy and efficient use of biodiesel. This has seen Brazil emerged as the third largest producer of biodiesel after the US and Germany [180]. There are indications that domestic demand will increase to 6 billion litres of B7 and 8.6 billion litres of B10 in the year 2023, as predicted by the Decennial Energy Extension Plan [185]. The reality of biodiesel in the Brazil has guaranteed the country a leading place in connection to the rest of the world.

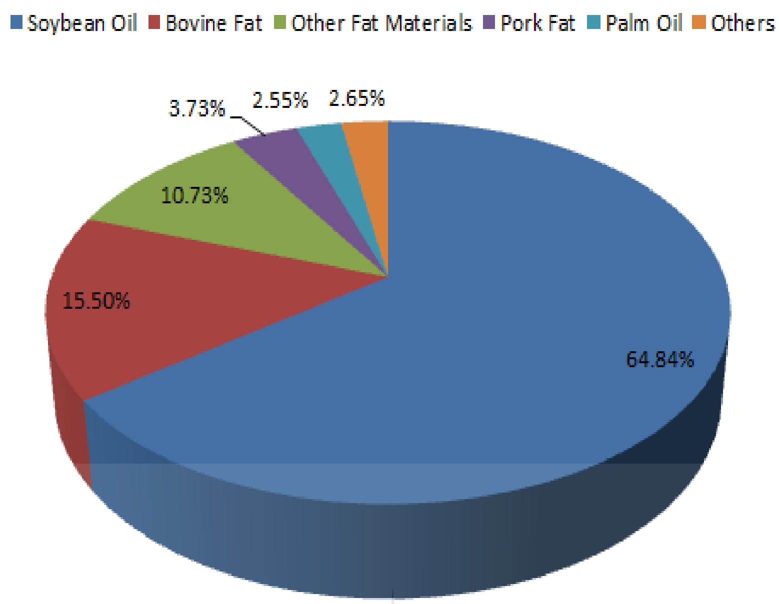

Figure 2.10: Raw materials utilized for biodiesel production in Brazil in 2017 (Compiled by the author of this thesis)

The level of biodiesel production and usage heighten the engagement of biofuels in the national energy market and portrays Brazil as a country that consider the variation of energy sources [127]. In 2017, it was legislated to add 8.0% biodiesel to the diesel fuel sold to the final consumer [186], and that content will be raised to 10% in March 2019 [187].

Argentina is another country well known for biodiesel production, promotion and exportation, with the bulk of their production coming from soybean, sunflower, safflower, rapeseed, and peanut vegetable oils [188]. Much of the biodiesel produced in Argentina is being exported. Sixty percent of 2.78 billion liters produced in 2012 was exported [189]. Seventy percent of their production between 2008 and 2014 was also exported [180]. The evolution of biodiesel of biodiesel industry in Peru has led to recognition of palm oil and jatropha as two major potential feedstocks for biodiesel production. Biodiesel fuel blends have increased from 2.0% in 2009 to 5.0% by 2011 as a result of increase in demand and usage of biofuel in diesel engines [190]. Such development has continued to strengthen biodiesel production in the Amazon up till present time. In encouraging biodiesel production and its commercial potential, the Colombian government has legislated policies mandating the use of blends of diesel and biodiesel with appropriate tax exemptions and subsidies provisions. Colombia has the potential for high biodiesel production as they are currently the fourth largest producer of palm oil in the world. The blending mandate, which was set by the Colombian government in 2015, endorsed B10 for remote rural areas while the industry regulated at approximately B8 [180].

2.7.1.3 Europe

The Europe marketplace has a big possibility in countries like India, UK, and China, because of the growing diesel costs and huge quantity of diesel cars. With the growing existing feedstock efficiency, the marketplace will probably have a pattern shift within the forecast range. In the upcoming years, the possibility of biodiesel production from new feedstocks like algae has been predicted. The Europe region is a noteworthy biodiesel producer with France and Germany serving as the pinnacle producers [191]. The policy framework for the development of a biofuels market in the European Union (EU) and the promotion of their use or other renewable fuels for transport is Directive 2003/30/EC [192]. For instance, the progressive use of biofuels as an alternative transport fuel has become mandatory for the partial substitution of diesel with biodiesel and bioethanol derived from agricultural sources. Furthermore, gaseous and liquid biofuels and other renewable fuels should substitute refined fossil fuels wholly or partially (blends) in their respective varieties.

The 28 member countries of the EU are increasingly covering its demand for energy with biodiesel imports, even though they remain as the world's biggest producer of biodiesel. Their production capacities have not been fully explored with their accomplishment of 3.9 billion gallons of biodiesel production including renewable diesel. However, more than 990 million gallons of biodiesel were imported from third world countries in 2018, a value three times more than a year earlier. The leading recipients of biodiesel imports remain the Netherlands, Spain and Belgium owing to the large storage magnitudes at their ports. Biodiesel products are transported to other EU countries from these places [169]. The index of EU imports of biodiesel and their major importers are shown in Figure 2.11.

The EU's plan to meet demand for low-carbon fuels has seen Targray, a leading international marketer of biodiesel, opened a trading desk in Geneva, Switzerland. This is part of the increasing plan to create sustainable value for customers in the EU countries Also, biodiesel production and usage in diesel engines in Germany have continued to project higher. The recent report of Germany’s biodiesel quality management association (AGQM) show that biodiesel imports to Germany increased more in 2018, reaching a quality mark of 1.2 million tons including

HVOs. The Netherlands, which are Germany's main supplier, have supplied in excess of 620,000 tons of biodiesel/HVO in 2018, more than twice the previous year's amount.

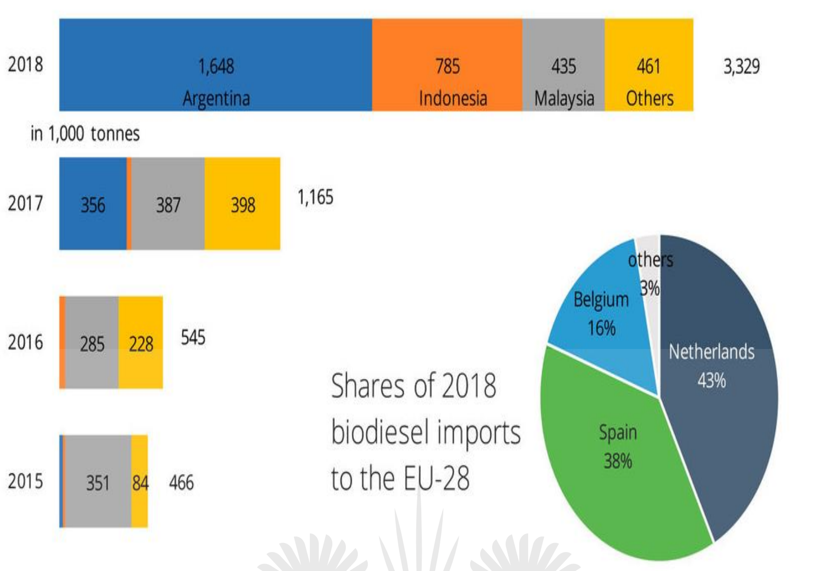

Figure 2.11: EU biodiesel imports index and their major importers
Eurostat [169]

2.7.1.4 Asia

The government of Thailand established a B7 mandate in 2012 which led to the formation of the Alternative and Renewable Energy Development Plan. Thailand has basically enlarged its biodiesel production sector mainly from palm oil, being the third largest producer after Indonesia and Malaysia [180]. Indonesia is gaining freedom from total independence on fossil fuels through the production and use of palm biodiesel [193]. Biodiesel production costs in Indonesia are the lowest compared to other countries because the fuels are being subsidized and this had led to rapid growth of the industry in Indonesia [189]. By 2025, the Indonesian Ministry of Energy and Mineral Resources (MEMR) seek to revolutionize domestic consumption of biodiesel by establishing a policy to substitute 15 and 20% of petrol-diesel fuels with bioethanol and biodiesel, respectively [193]. Malaysia as the second largest producer of palm oil after Indonesia has enough reasons and resources to promote biodiesel production on industrial scale. Currently, the country meets its B7 (7% biodiesel in fuel blend) biodiesel mandate [180] after the National Biofuel Policy introduced 5% biodiesel blend (B5) officially in 2009 [194]. Taiwan has surfaced on the list of countries which have decided to increase biodiesel production with a projection of 150 million liters per year by 2020 [195]. This was fostered by the consensus at the First National Energy Conference in 1998 to encourage the application of clean energy in Taiwan. Xu et al. [196] reported on the Chinese capacity to develop a brilliant biodiesel industry that will add more potential to the global trend of biodiesel development. The major raw materials that are currently used for biodiesel production in China are rapeseed oil, cottonseed oil and jatropha oil, with the expectation of replacing them with waste vegetable oil and microalgae in the future.

The government has encouraged the use of biodiesel in Turkey by legislating that marketable diesel fuel should contain 1.0% MEFA from January 1, 2014. This figure has however increased to 2.0% in 2015 and 3.0% in 2016. Turkey, which have great production capacity for cotton and sunflower, produced 17,729 tons and 21,876 tons of biodiesel in 2012 and 2013 respectively [197]. Biodiesel production has become an essential commodity in Iran as energy demand was expected to increase from 2003 to 2030 by an average of 2.6% yearly. Oilseed yields for possible biodiesel production in Iran were seen to be 3,678,540.43 tons from 2007 to 2008. Feedstocks such as canola, cotton and soybeans, are the promising sources of biodiesel in Iran while olive, sesame, safflower, sunflower, corn, almond and coconut remain potential sources of oil [198].

2.7.1.5 Africa

Biodiesel production in Africa is emerging as a good prospect in the last ten years. The future of biodiesel production in Africa looks promising as it is one of the fastest growing continents in the world. Africa is endowed with a land mass of over 30 million km^2 which is equivalent to combined land masses of the United States of America, Brazil and Japan [199]. Africa appears to have the capacity to become the single largest producer of bioenergy crops for the global production of biodiesel [200]. Africa with the fastest growing population according to 2019 United Nations reports on global issues, biodiesel production and usage along with abundant fossil fuel reserves will offer Africa some prospect of energy sufficiency and environmental protection based on the comparative advantages. Estimated reports from the World Bank [201] and Muller et al. [202] show that biodiesel will constitute 60 - 80% transport fuel in Africa by 2030. Scientific researchers have therefore shifted their attention to exploring several non-edible oil seeds, which are abundant in African rain forests, in order to overcome the food security problems associated with the use of edible oils. The authors have been able to work on some inedible oils seeds [17], [18], [23], [77], while exploring other promising ones for sustainable production of biodiesel.

African countries, such as Ghana, Zambia, Liberia, Tanzania, Ethiopia, Nigeria, Senegal, Kenya and South Africa, are emerging as commercial producers of biodiesel with large-scale investment projects. Africa is blessed with vast number of inedible oil plants which are widespread in many parts of the continent. The common feedstocks which present adequate properties for biodiesel production include jojoba, mahua, castor, and karanja [199]. The most populous non-edible feedstock for biodiesel production in Africa is jatropha. There are searches for other relative seeds with high oil yields as jatropha cannot encourage biodiesel production for Africa's future energy security [203]. Biodiesel production in Africa has led to the discovery of abundant oil seeds with good potential for biodiesel production. The biodiesel potentials of different non-edible feedstocks in selected African countries are recorded in Table 2.5.

Table 2.5: Biofuel potential of promising non-edible feedstocks in selected African countries

Country	**Raw material**	**Biodiesel**		**Bioethanol**	
		Megalitres (ML)	**Mega Joules (MJ)**	**Megalitres (ML)**	**Mega Joules (MJ)**
Benin	Jatropha	30	1.3×10^4	20	8.4×10^7
Burkina Faso	Sugarcane	-	-	20	8.4×10^7
Ivory Coast	Molasses	-	-	20	8.4×10^7
Ghana	Jatropha	50	2.1×10^4	-	-
Guinea Bissau	Cashew	-	-	10	4.2×10^7
Mali	Molasses	-	-	20	8.4×10^7
Malawi	Molasses	-	-	146	6.1×10^8
Kenya	Jatropha/Molasses	40	1.7×10^4	413	1.7×10^9
Ethiopia	Jatropha/Molasses	-	-	80	3.3×10^8
Niger	Jatropha	10	4.2×10^7	-	-
Nigeria	Jatropha/Molasses	-	-	70	2.9×10^8
Sudan	Molasses	-	-	408	1.7×10^9
Swaziland	Molasses	-	-	480	2.0×10^9
Senegal	Molasses	-	-	15	6.3×10^7
Tanzania	Jatropha/Molasses	-	-	254	1.1×10^9
Togo	Jatropha	10	4.2×10^7	-	-
Uganda	Molasses	-	-	119	5.0×10^8

Jumbe et al. [204]

Several factors, among which are prices of crude oil, price instability, environmental impacts caused by fossil fuels, obligatory legislation from developed countries (UK, Germany, Japan, USA, etc) on the use of biodiesel blends in the transport sector, creation of jobs, advances in research and technological, and the need to meet the increasing demand for fuel, contribute to the increasing production level of biodiesel in Africa [200], [205], [206].

2.7.1.6 Oceania

Beauty leaf oil and Castor oil have been identified as the two major on-edible oil prospects in production of biodiesel in Australia [171]. The Australian Biofuel Research Institute (ABRI) was established in 2010 to center on production of second and third generation of biodiesel [207]. This project is focused on capturing atmospheric carbon and also neutralize it when biodiesel is burned in engines. The Australian Government is solely responsible for funding ABRI through the Australian Renewable Energy Agency (ARENA). A sum of $20 million AUD was set aside for funding renewable energy projects with $5.0 million for supporting algal biodiesel production and research proposals from across Australia [207].

Collaborative research works were found between the institute and some universities in Australia [171]. The Australian Government has recently revised her position on use of biodiesel in the transport sector as part of "Clean Energy Initiative" and progress into new renewable energy technologies [208]. For instance, State governments in New South Wales and Queensland have enacted mandates for B4 (4% biodiesel in fuel blends) and E5 (5% ethanol in fuel blends) [209]. Some considerable measures have been taken concerning generation of clean energy through Australian renewable energy policy. The main objective of the Australian clean energy council is to produce 20% of national grid supply from renewable resources by 2020. Reports from Puri et al. [210] showed that the Australian government has been able to increase researches focused on production of biofuel by investing AUD $5.1 billion over the coming decade [208].

2.7.2 Projected progress and use of biodiesel

From a global perspective, biodiesel is anticipated to form 70% of transport fuel to be demanded for by the year 2040 [164], [180]. The development of biodiesel industry in many countries has been largely influenced by their goal to mitigate climate change because biodiesel produced from biomass have the carbon-neutral potential [211]. The size of biodiesel produced from 2002 to 2013 grew by a factor of 15% [185]. There is a projected shift of biodiesel demand from 86.1 million barrels/day, to 110.6 million barrels/day by 2035 [181]. The highest 14 biodiesel producing countries in 2017 as adapted from Renewable Energy Network is shown in Figure 2.12

[209]. The top major countries with expected high biodiesel production by the year 2030 and the fraction of biodiesel blends expected to be used in vehicle engines are recorded in Table 2.6.

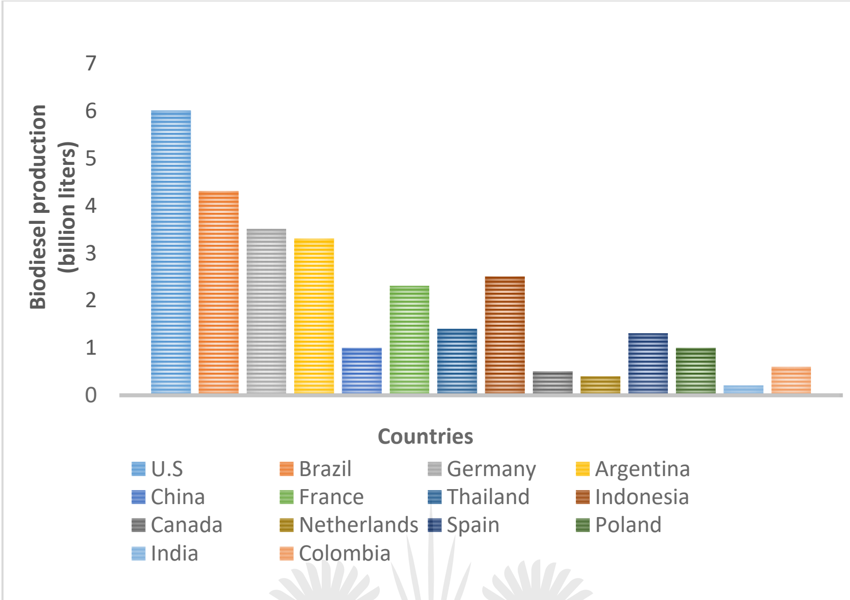

Figure 2.12: Highest 14 biodiesel producing countries in 2017

Table 2.6: Top major countries with expected high biodiesel production

Country	Growth index, %	Expected production (2030), billion litres	Projected use, billion litres	Blending ratio (2030), %
United States	6	8	6.9	15
Canada	8	5	5	10
EU	8	22	14	20
India	11	32.1	31.1	10-20
Brazil	6	5	5.6	25
Argentina	5	11	1.9	30
China	17	5	5	10
ASEAN	8	13	4.1	20

If the development trend achieved by established biodiesel producers can be followed by other developing countries, biodiesel production and adoption in vehicle engines will continue to increase in meeting up the sustainable goal of eradicating fossil fuel combustion. According to 2030 projections of Energy Outlook review, increase in energy consumption can only be brought by increased production of energy and industrialization in the developing world. A higher level of biodiesel blending with fossil diesel, B30, is expected to be promoted as alternative fuel in the transport sector by the year 2030. This can be supported by successful existing research studies on engine performance using higher blends of biodiesel-diesel fuel [36], [66], [104], [151], [212]–

[220]. The fraction ratio can also be expected to increase based on evolving research studies demonstrating improved use of higher biodiesel blends without any major engine modification.

One of the strongest arguments for biodiesel usage, aside the environmental benefits and good engine performance, is the current production rate relative to its demand. Most of the current world biodiesel producers have increased at an average index of 15% compared to previous years. However, biodiesel consumption could experience a shortfall if higher blending rates is not encouraged in the transportation sector. Most biofuel consumption in many of these countries take place at low level of blending with fossil fuels. Higher blending ratio is expected to meet SDS demand in 2030. Another degree of constraint that could limit the replacement is the commercialization of biofuel. The industrial production of biodiesel in US and EU comes majorly from palm oil which is limited in supply because it is required for consumption in many countries. The commercialization of inedible seed oils needs to be established in order to explore seed oil-derived biodiesel and BtL synthetic fuels. The study has also shown that domestic production of biodiesel is still falling behind as well. The increasing population growth can also be a factor contributing to the production and demand for biodiesel fuel [221]. As population increases, the demand for transportation increases, and there comes the need for provision of promising fuels. This must however be sustainable enough in order to meet up with up with increasing demand. With the current industrialization and commercialization of biodiesel production from limited feedstocks, the scenario will worsen if prompt attention is not shifted to commercialization of vast organic plant oil seeds which have large abundance in the natural forests. More research facts are nevertheless needed progressively to furnish the scientific world with important processing details and quality of biofuels synthesized from oil rich oil seeds.

2.8 Assessment of *Parinari polyandra* seed oil as promising feedstock for biodiesel production

Parinari polyandra is an inedible perennial plant found in the grassland of Tropical Africa. It belongs to the *rosaceae* family that are predominantly found in West African countries [222]. It has been traditionally observed that *Parinari polyandra* has been unusually underutilized owing to its inedible nature and unavailability of sufficient scientific data as a result of inadequate extensive investigations on the properties of its fruits and seeds [223]. *Parinari polyandra* consists of about 115 genera and 3200 species. The *Parinari polyandra* tree has a thick vegetation form with smooth bark and twisted stem with a varying height between 10m and 12 m. The branches are moderately hairy with fleshy flowers, about 1.3 – 2 cm long [224]. The leaves are rounded and shortly petiolate, broadly ovate, shining, and varying from glabrous to grey. About 8 – 9 pairs of the primary veins are usually plainly able to be seen on both sides of the leaves. The plants blossom between January and August and fruit between March and October. The fruits are fleshy and round in shape with the colour of mature ones varying from red to blackish purple or greenish pink [224], [225]. The reproductive structure is yellowish white having a thick seed coat containing the oily content. Considerable amount of oil, varying between 31 and 60% oil can be released from the fresh kernels depending on the specie and the period of harvest [226]. With the quantity of oil yield from *Parinari polyandra*, it is a cheap feedstock that still remains one of the underused oil for both small and large scale production of biodiesel [223], [227]. A picture of *Parinari polyandra* leaves, fresh fruits and dried seeds is presented in Figure 1.2.

Figure 2.13: The leaves, fresh fruits and dried nuts of *Parinari polyandra*

(Compiled by the author this thesis)

The fatty acid variation in *Parinari polyandra* oil was studied by Motojesi *et al*. [228]. The compositions and usability of *Parinari polyandra* seeds harvested in two seasons, April and November, were studied. Oil was extracted from crushed seeds of *Parinari polyandra* using a soxhlet extractor and n-hexane as the extracting solvent. For April Harvested Seed (AHS) and November Harvested Seed (NHS), the total saturated and unsaturated fatty acid compositions were found to be 46.25%, 20.65% and 4.69% and 58.69% respectively. They concluded from the fatty acid profiles that AHS oil would be grouped as palmitic oil (saturated fat) while NHS would be categorized as arachidonic oil (unsaturated fat). Amos et al. [229] reported a yield of 57% from a 4 hr Soxhlet extraction of oil from *Parinari polyandra* seeds using n-Hexane as extraction solvent. With acid values of 2.620 mg KOH/g and 1.683 mg KOH/g from the crude and refined oil, the authors further suggested that biodiesel production from the oil is desirable.

An oil extraction optimization study was carried out by Afolabi et al. [226] using RSM to evaluate the effect of four sets of parameters (residence time (A), temperature (B), solid/solvent ratio (C) and solvent types (D)) corresponding to optimum oil yield. The highest oil yield was found to be 61.7% under reaction variables of 6 hr time, 70 ºC temperature, and 0.03 solid/solvent ratio while using petroleum ether as the extraction solvent. An average of 60.4% oil yield was obtained from further validation experiments. The authors recommended the oil as a prospective raw material for application in the paints industry because of its high iodine value (one of the major properties of drying oils).

Currently, the global production rate of *Parinari polyandra* has not been documented in any literature, but this present study has been able to show that it is a promising industrial crop which can be produced on a large scale. With the high level of oil yield obtained from the seeds, it is an indication that improved yield can be obtained if intensive agricultural efforts are inputted into artificial production of the trees. This research is also a pointer that necessitates further study on sustainable production of the plant and evaluation of the oil yields per hectare of a natural or artificial grown *Parinari polyandra* forest.

To the best knowledge of the author, researchers have only attempted to extract the oil content from *Parinari polyandra* seeds using different extraction techniques. The oil contents were tested and verified for different applications based on their chemical properties. Up until now, no researcher has been able to successfully produce biodiesel from the oil and also experimentally tested the performance and emission characteristics in a diesel engine. This gap was identified and research studies were carried out on sustainable biodiesel production from *Parinari polyandra*, starting from oil extraction from the seeds to optimized biodiesel production and experimental analysis of its performance and emission properties from combustion in a diesel engine. Optimizing the biodiesel production process from the plant and evaluating the performance and exhaust emissions of biofuel in a diesel engine will provide useful information for enhancing its economic and industrial relevance.

2.9 Conclusions

This paper presents a review of current global production and adoption of biodiesel as a vehicle engine fuel based on research findings and essential descriptive statistics garnered from available literatures on the subject matter. It can be concluded that reliance on petroleum-based fuel in the future can no longer hold because the desire for energy security and concern for reducing GHG emissions have led to increased usage of biodiesel fuel. From the studies reviewed, the following conclusions can be made:

1. The high demand for diesel fuel has necessitated the need for renewable biodiesel from cheap sources which can meet the demand without depleting in the near future. From a realistic point of view, the extensive use of renewable biodiesel can directly give rise to improvements in engine performances and emission characteristics.
2. The improved state of things in achieving an effective power conversion from biodiesel combustion with minimal emission impact on the environment has been documented in this work. This has been able to show the global utilization of biodiesel in diesel engines most especially in the transportation sector.
3. An increasing trend is foreseen in the use of biodiesel in diesel engines considering its relative advantages. The worldwide usage adoption was captured according to the rate of production, usage and legislation favouring the economic feasibility of biodiesel products that are compatible and fit for diesel engines without any modification. With the establishment of biodiesel production and major biofuels market all around the globe, the adoption of biodiesel wholly or in blends has been fostered through policies that promote its marketability and use.
4. New jobs are being created to meet up with labour force for expanding industry, and viable foreign exchange earnings keep increasing for importers and exporters of biodiesel fuel.
5. GHG emissions are being reduced using biodiesel in diesel engines, and more can be achieved through the projected increase in biodiesel production and its combustion as fuel.
6. With the advantages offered by biodiesel, its renewable availability and better engine performance characteristics, there is no doubt that manufacturers of diesel engines can go

on making good transactions in the automobile market and more end users are expected to acquire these engines with reliability and satisfaction of using biodiesel as the running fuel. Overtime, switching to diesel engines can be expected to revolutionize the future of liquid fuel and power engines in automobile vehicles.

7. Attention is shifting to production of biodiesel from novel inedible feedstock with high oil yield. An appraisal of many inedible seed plants, including, *Parinari polyandra*, was done to provide comprehensive update on the work done so far.

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CHAPTER 3

RESPONSE SURFACE ANALYSIS FOR OPTIMIZATION OF REACTION PARAMETERS OF BIODIESEL PRODUCTION FROM ALCOHOLYSIS OF *PARINARI POLYANDRA* SEED OIL

It is reproduced from Ogunkunle, O. and Ahmed, N.A. (2019): Response Surface Analysis for Optimization of Reaction Parameters of Biodiesel Production from Alcoholysis of *Parinari polyandra* Seed Oil. International Journal of Sustainable Energy, 38(7): 630 – 648.

This chapter presents the optimization of biodiesel production from *Parinari polyandra* seed oil. The seed oil was identified as a promising feedstock suitable for biodiesel production relative to its high oil yield and lower free fatty acid value.

Availability of information on the efficiency of applied conditions to biodiesel synthesis from diverse seed oil can establish optimal biodiesel yield from favourable reaction variables. The effect of reaction parameters, temperature, time, and catalyst amount, were varied on biodiesel yield from alcoholysis of *Parinari polyandra* oil using potassium hydroxide as catalyst. Maximum biodiesel yield of 95.62% was obtained from the experimental results. Analysis of Variance revealed that the reaction variables had significant effects on biodiesel yield. Data analysis predicted an optimal biodiesel yield of 92.75% at reaction conditions of 61.20 ^{o}C temperature, 60 minutes, and 1 wt.% of catalyst amount. Validation experiments of the optimal conditions gave an average biodiesel yield of 91.72%. The study established optimal conditions of temperature, time, and catalyst amount for biodiesel production from *Parinari polyandra* oil. The fuel properties of the biodiesel fell within the standards of the American Society for Testing and Materials D6751.

3.1 Introduction

Over the past decade, human demand for energy has reached a revolutionary stage. Accelerated development of social civilization in terms of transportation and industrialization, has been a major boost in the demand for energy consumption [1]. The modern man cannot live without petroleum owing to his complete dependence on its products for transportation, heating, lighting, and industrial production. Owing to the accelerated development of social civilization since the industrial revolution in the late 18th and 19th centuries, energy has become a crucial determinant for continued economic growth and improved standard of living [2]. The International Energy Agency (IEA) report estimated that the world will require 50% more energy in 2030 than today of which 45% will be consumed by China and India [3], [4].

The growing demand for power has been a significant justification for utilization of renewable energy. The production of biofuels is highly region-specific and is affected by the production of agricultural products [5]. Global biofuels production has reached 135 billion litres having increased about 2% compared to 2015 [6]. This increase was due mostly to a comeback in biodiesel production after a fall in 2015. The power generated from renewable sources increased to 112 GW by an estimated 6% in 2016 [7]. United States, with an output of 68 TWh, was the leading country for electricity generation from biomass, followed by China (54 TWh), Germany (52 TWh), Brazil (51 TWh), Japan (38 TWh), India and the United Kingdom (both 30 TWh) [8]. At the end of 2016, 70% of all biofuel production came from the United States and Brazil, followed by Germany, Argentina, China and Indonesia [9]. Estimated production of ethanol, biodiesel, and hydrotreated vegetable oil, in terms of total energy percentage are 72%, 23%, and 4%, respectively.

The first quarterly report of Statistical Review of World Energy [10] indicated that global primary energy consumption grew strongly in 2017. As of present, the energy demand in Asia–Pacific emerging economies still grows rapidly. The report stated that primary energy consumption growth averaged 2.2% in 2017, up from 1.2 % in the previous year and the fastest since 2013. This compares with the 10-year average of 1.7% per year. Natural gas accounted for the largest increment in energy consumption which was followed by renewables and then oil. China remains the largest growth market for energy for the 17th consecutive year as energy consumption rose by 3.1% in China. The future of renewable energy such as biodiesel lies in sourcing for oil rich inedible seeds and optimization of the production to achieve a major energy boost.

Biodiesel is produced by alcoholysis of vegetable oils, animal fats or recycled cooking oils. It consists of long-chain alkyl esters, which contain two oxygen atoms per molecule. The reversible reaction proceeds with a catalyst (usually KOH or NaOH). The fats and oils, which are made up of glycerol-based tri-esters, are converted into monoesters in a reversible reaction in the presence of an alcohol and a catalyst (usually KOH or NaOH) yielding glycerol as a byproduct [11]. The advantages of burning biodiesel as fuel cannot be overemphasized: it is renewable, non-toxic, biodegradable, no sulfur content and a better lubricant [12]. Biodiesel can replace diesel fuel in many different applications such as in boilers and internal combustion engines without any engine modification. The gaseous emissions, sulphates, CO_2, and nitrogen oxides are very low in concentrations when compared to that of fossil diesel [13].

A number of recent studies on use of non-edible oils have increased the worldwide availability of feedstocks for biodiesel production locally and industrially. Most of the biodiesel is currently made from soybean, rapeseed, and palm oils. New plant oils that are under consideration include mustard seed, peanut, sunflower, and cotton seed [14]. There are many examples for non-edible oilseed crops such as jatropha tree (*Jatropha curcas*), karanja (*Pongamia pinnata*), mahua (*Madhuca indica*), castor bean seed (*Ricinus communis*), neem (*Azadirachta indica*), rubber seed tree (*Hevea brasiliensis*), tobacco seed (*Nicotiana tabacum*), rice bran, milk bush (*Thevetia peruviana*) etc. [15]–[19]. The production of biodiesel from different non-edible oilseed crops has been extensively investigated over the last few years. Biodiesel produced from extracted oil from *Parinari polyandra*, jojoba, *Ailanthus altissima*, have been used as engine fuel in blended forms with no modification to the engine [20]–[23].

The efficiency of biodiesel synthesis depends on the applied reaction conditions, and it is of great importance to investigate their influence on the biodiesel yield in order to determine the optimal reaction conditions. Statistical methods, such as the Response Surface Methodology (RSM) [24], Factorial design [25], Box–Behnken factorial design [26], Taguchi technique [27], Generic Algorithm (GA) coupled with Artificial Neural Network (ANN) [28] are frequently being used as tools for the optimization process.

The RSM based on central composite design was used by Su et al. [29] to investigate the influence of five important reaction variables for FAME production from jatropha oil using diethyl carbonate as acyl acceptor and Novozym 435 lipase as a catalyst. Ajala et al. [30] optimized the production of shea biodiesel (SBD) process using RSM and achieved the maximum conversion rate of 92.16%. Various reaction variables including temperature, agitation speed, methanol to oil molar ratio and catalyst amount were studied. Muthukumaran et al. [31] also optimized the variable factors in the production of biodiesel from *Madhuca indica* oil using the response surface methodology. The results obtained indicated that in optimal conditions of 1.5 wt% catalyst amounts, 90 minutes reaction time, reaction temperature of 60 ^{o}C and 0.32% v/v of methanol content would give a biodiesel yield of 88.71%. Hasni et al. [32] studied the effect of reaction variables on the alcoholysis of *Brucea javanica* seeds oil using RSM. The results showed that biodiesel yield of 94.34% would be obtained from optimal conditions; 6:1 methanol to oil ratio, 65 ^{o}C reaction temperature and 1 wt% catalyst amount. All the chemical and physical characteristics of biodiesel produced from these seeds oil showed they are consistent with requirements of ASTM D6751 and EN 14214 standards.

Parinari polyandra oil can be used as a cheaper biodiesel feedstock owing to its relative high oil yield content. *Parinari polyandra* seed, which is commonly found in West Africa regions of African continent, belongs to the family of *Rosaceae* that grow mostly in tropical savanna region. These areas include Nigeria, Ghana, Senegal, Ivory Coast, Mali, Cameroon and Sudan [33]. *Parinari polyandra* is an evergreen tree plant which is about 10 - 12 m tall. It has a low and bushy profile with smooth bark. The flowers are fleshy, about 1.3 – 2 cm long. The leaves are shortly petiolate, broadly ovate or ovate-elliptic, shining and green or brownish-green above, and varying from glabrous to grey-tomentose beneath. The leaves are rounded (sometimes emarginate) or more rarely obtuse, basally broadly cuneate to subcordate. The nerves are usually clearly visible on both sides having about 8 – 9 pairs of the primary veins. The fruits are drupe and oblong ovoid in shape. They are greenish-pink and turn black when harvested [34]. The endosperm has a yellowish white appearance with a thick seed coat containing the oily mass. The fresh seed kernel contains between 31 and 60% oil depending on the variety and the season of harvest [35]. However, *Parinari polyandra* seed has been noted to be generally underutilized either because of its non-edibility or non-availability of information and extensive research on its fruit and seed properties. The *Parinari polyandra* seed oil, on the other hand, has been found to have high oil yield content for production of biofuel and alkyd resin [36].

The extracted oil from *Parinari polyandra* Benth fruits was evaluated by Motojesi et al. [37] to check the variations in the composition of the seed oil. According to the reports, the major constituents of *Parinari polyandra* Benth seed oil are n-hexadecanoic acid (46.3%), 9,12-

octadecadienoic acid (18.10%), phytol (26.80%) for fruits harvested in April while n-hexadecanoic acid (4.69%), 9,12 Octadecadieonic acid (8.31%), arachidonic acid (43.38%), stigmasterol (13.41%) were obtained from fatty acid analysis for fruits harvested in November. As a result of the variation in the fatty acid compositions found in *Parinari polyandra* Benth seed oil, the study suggested that the oil extracted from seeds harvested in April month of the year may be appropriate for biodiesel production while that of November month will be good raw material for alkyd resin production. This reported study therefore influenced the harvest time of the *Parinari polyandra* seeds that were used for this work.

This work presents the production of biodiesel from *Parinari polyandra* oil through statistical optimization of the process parameters. Statistical optimization of the process parameters was done to establish optimum conditions for biodiesel production via alkali-catalyzed alcoholysis. A regression analysis which predicted the input values and the yield response of biodiesel was developed. This study established a biodiesel production method from *Parinari polyandra* oil via alcoholysis. The reports of the study showed that alcoholysis of *Parinari polyandra* oil proceeded to form biodiesel at an excess stoichiometric molar ratio of 6:1 ethanol to oil in the presence of potassium hydroxide (KOH) catalyst. The determined physical and chemical properties of the biodiesel fell within the acceptable standards of American Society for Testing and Materials (ASTM) D6751.

3.2 Experimental procedure

A soxhlet extraction system was used for oil extraction from the *Parinari polyandra* seeds and biodiesel was produced from the extracted oil through alcoholysis reaction. Standard procedures were used to determine the physicochemical properties of the oil and biodiesel at the Chemical Engineering departmental laboratory of Ladoke Akintola University of Technology Ogbomoso, Nigeria.

3.2.1 Materials and equipment

Sigma Aldrich supplied chemicals; potassium hydroxide, ethanol and N-hexane were used in this research. These reagents were all of analytical grade. A magnetic stirrer thermostat hot plate was used for biodiesel production.

3.2.1.1 Collection and preparation of feedstock

The feedstock used in this research is *Parinari polyandra* seeds. The *Parinari polyandra* fruits were harvested fresh from the research farm of National Centre for Agricultural Mechanization, Ilorin Nigeria. Owing to the thick pericarp of the fruits, they were cut open into halves at the harvest stage to extract the seeds. The seeds were dried under atmospheric temperature for three weeks to prevent bacterial degradation of the feedstock which comprised of moisture. The seeds were milled thereafter to particle sizes and kept in a dry container.

3.2.1.2 Oil extraction from *Parinari polyandra* seeds

A soxhlet system was used for extracting oil from the milled *Parinari polyandra* seeds. A round bottom flask placed on a heating mantle was fitted to the soxhlet extractor. The extracting solvent, N-hexane was placed in the round bottom flask and filter paper containing milled *Parinari polyandra* seed was placed in the soxhlet extraction system. Optimized extraction conditions of 0.06 g/ml seed/solvent (g/ml), 70 ^oC extraction temperature and extraction time of 5 hrs were employed in the extraction technique [38]. A constant weight of 20g of milled *Parinari polyandra* seed was placed inside the soxhlet extractor at each extraction run. The filter paper containing *Parinari polyandra* was removed from the extractor after 5 hrs and left to dry for 24 hrs at ambient temperature. The extracted oil was measured, and the recovered solvent was decanted to be used for another run. The oil yield was measured using Equation 3.1.

$$oil\ yield\ (\%) = \frac{(w_1 - w_2)}{w} \qquad (3.1)$$

Where w_1 is the weight of the filter paper containing *Parinari polyandra* milled seed before extraction; w_2 is the weight of the filter paper and the content after drying; and *w* is the weight of the milled *Parinari polyandra* seed. The soxhlet extraction system for oil extraction from *Parinari polyandra* seed is shown in Figure 3.1.

3.2.1.3 Determination of physico-chemical properties of *Parinari polyandra* oil

The properties of the extracted *Parinari polyandra* oil were determined using standard test methods of the Association of Official Analytical Chemists. The viscosity was determined using Oswald viscometer while the density was measured using density bottle. The moisture content was determined by the rotary evaporator oven.

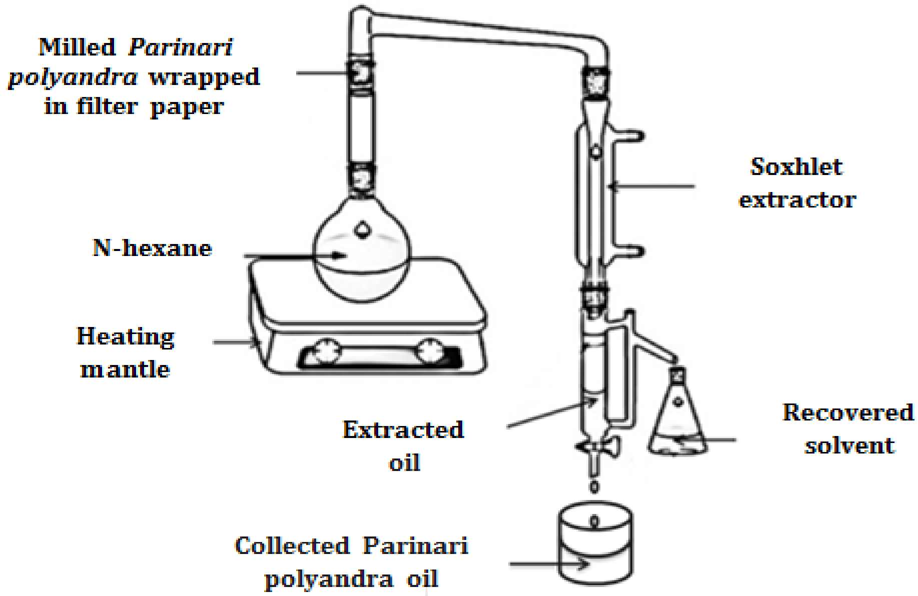

Figure 3.1: Soxhlet extraction system of oil from *Parinari polyandra* seed

The saponification, iodine, and acid values were determined by AOAC 920:160, AOAC 920:158, and AOAC Ca5a-40, respectively. The total free fatty acid content was estimated by titration of free fatty acids with KOH solution in the presence of phenolphthalein indicator. The mg KOH required to neutralize the free fatty acids present in 1g of oil was used to obtain the acid value, and the free fatty acid was calculated as the equivalent of oleic acid using Equation 3.2.

$$1\, mL\ N/10\ KOH = 0.028g\ oleic\ acid \tag{3.2}$$

3.2.2 Biodiesel production from *Parinari polyandra* oil

The oil extracted via solvent method was used for biodiesel production. The biodiesel production was carried out using the recommended alkaline alcoholysis of seed oil by Yarkasuwa, Wilson, and Michael [39]. Because of the reversibility of the reaction, an excess of 6:1 of alcohol to oil molar ration was used in order to push the reaction to the forward side. This was expected to ensure more solubility of the oil in the alcohol for efficient reduction of the viscosity. The Free Fatty Acid (FFA) content and the acid value of the oil, which were found to be 1.3 wt. % and less than 1% respectively, showed that there was no need for acid catalyzed esterification step.

The oil was preheated at 80 ^oC for 30 minutes to remove any moisture and solvent content in it. The catalyst was prepared by adding the calculated experimental weight of catalyst amount to measured ethanol and stirred for about five minutes at 150 rpm until it dissolved completely.

The solution formed was sodium ethoxide. A measured amount of oil was poured into a flat bottom flask and heated to the desired experimental temperature; the sodium ethoxide was then poured into the flask containing the oil and was immediately covered. The reaction mixture was then agitated at 400 rpm by switching on the stirrer. Both the temperature and stirring rate were maintained throughout the preset experimental reaction time. The alcoholysis setup of biodiesel production from *Parinari polyandra* seed oil is shown in Figure 3.2.

Figure 3.2: Transesterification setup of alcoholysis of *Parinari polyandra* seed oil

After the reaction, the mixture was transferred into a separating funnel and left for 24 hrs to allow separation by gravity. A two-phase product was formed after 24 hrs, the upper phase was biodiesel and lower phase glycerol. The products were separated into different bottles. The biodiesel was purified by washing with warm distilled water of 50 ^oC to remove unreacted alcohol and catalyst. Warm distilled water of about 20% volume of the biodiesel was added to the biodiesel and shaken vigorously. The mixture was transferred into a separating funnel and allowed to settle; after which the water was drained through the bottom of the funnel. The washing was done until a clear biodiesel product was obtained. The biodiesel was heated at 100 ^oC to remove moisture from the fuel and stored in a sample bottle. The yield of the biodiesel obtained was measured using Equation 3.3.

$$Y = \left(\frac{V_b}{V_r}\right) \times 100\ \% \tag{3.3}$$

Where:

Y = Yield of the methyl esters, %

V_b = Volume of methyl esters produced, ml.

V_r = Volume of raw oil used, ml.

The physicochemical characterization of the synthesized biodiesel was done using American Society for Testing and Materials (ASTM) standards for biofuel. The higher heating value, kinematic viscosity, cloud point, pour point, flash point, acid value, cetane number and water content were determined using the ASTM D2015, D445, D2500, D97, D93, D664, D613 and D2709 methods respectively. The specific gravity was determined using the method adopted by Coronado et al. [40]. The pH value was measured using a digital pH meter. The spectrum of the ester functional group of the biodiesel was determined using Proton Nuclear Magnetic Resonance (^{1}H NMR).

3.2.3 Experimental design and statistical analysis

The study type used in the experimental design for the statistical optimization of reaction parameters of biodiesel production from *Parinari polyandra* oil using potassium hydroxide as catalyst was Response Surface Methodology (RSM). A three-factor two-level Box-Behnken design was chosen because of its requirements for fewer design points which gives room to work around extreme factor combinations. Independent variables, temperature, time and catalyst amount, were designated as factor A, B, and C, respectively while the response, Y, was the biodiesel yield. Seventeen (17) experimental runs were generated and a linear quadratic model was chosen. The summary of the coded design factors and their levels are shown in Table 3.1.

Table 3.1: Design summary for factors and their levels for the biodiesel production

Factor	Name	Units	Type	Coded Low	Coded High	Mean	Std. Dev.
A	Temperature	Deg. C	Numeric	-1 ↔ 60.00	+1 ↔ 75.00	67.50	5.30
B	Time	minutes	Numeric	-1 ↔ 60.00	+1 ↔ 180.00	120.00	42.43
C	Catalyst amount	wt%	Numeric	-1 ↔ 1.00	+1 ↔ 3.00	2.00	0.7071

It is important to note that the factors chosen for this optimization study were based on preliminary experiments carried out in the laboratory. It is of note that preliminary experiments were carried out in the laboratory to determine the low and high levels to be chosen for the variables range. The low-level factors chosen were within the range at which biodiesel was formed, and the high-level values are those that are meant to show the effect of extreme reaction conditions on biodiesel yields. To predict the response and determine the input value at which an optimized yield will be obtained, Equation 3.4 was used as the linear regression model.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} {X_i}^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{3.4}$$

Where Y is the predicted response, β_0 is the intercept term, β_i is the linear effect, β_{ii} is the square effect, and β_{ij} is the interaction effect; X_i and X_j are the variables, i and j are the index numbers for the design, and ε is the error. The second order polynomial equation was gained to explain the biodiesel production process. The response was predicted with these parameters to get the best model for maximizing biodiesel production. The multiple regression analysis was used to investigate the significance effect of the three reaction variables on biodiesel production. The goodness of the fit of the model was evaluated using Analysis of Variance (ANOVA).

3.3 Results and Discussion

3.3.1 Extracted oil from *Parinari polyandra* seed

The percentage yield of *Parinari polyandra* oil obtained from solvent extraction method was 57.75%. This value fell within 31.7% – 64%, a range which was reported as oil yield from optimized extraction of oil from *Parinari polyandra* oil by Afolabi et al. [41]. The measured physiochemical properties of the *Parinari polyandra* oil are presented in Table 3.2.

Table 3.2: Physicochemical properties of *Parinari polyandra* oil

Properties	Unit	Average
Specific gravity	-	0.926
Kinematic viscosity	mPas	62
Cloud point	^oC	2.58
Pour point (^oC)	^oC	3.18
Flash point (^oC)	^oC	192
Heating value	MJL^{-1}	43.10
Moisture content	%	0.45
Saponification value	mg KOH/g	176.4
Iodine value	g/ 100 g	93.94
Acid value	mg KOH/g	0.94

3.3.2 Biodiesel yield from *Parinari polyandra* oil alcoholysis

The result of biodiesel yield obtained from the alcoholysis of *Parinari polyandra* oil under different temperature, time and catalyst amount is presented in Table 3.3 for the seventeen (17) experimental runs.

Table 3.3: Experimental biodiesel yield from sand apple oil

Runs	Experimental factors			Response	
	Temperature	Time	Catalyst amount	Experimental yield	Predicted yield
	(Deg C)	(Minutes)	(wt%)	(%)	(%)
1	75	60	2	81.46	80.75
2	60	120	3	79.58	78.72
3	67.5	60	3	82.84	83.76
4	67.5	120	2	93.62	93.98
5	67.5	180	3	81.86	82.01
6	67.5	120	2	94.12	93.98
7	67.5	60	1	95.62	95.47
8	75	120	3	72.49	72.28
9	67.5	120	2	94.42	93.98
10	67.5	120	2	93.16	93.98
11	60	60	2	88.54	88.48
12	67.5	180	1	91.27	90.35
13	60	180	2	84.36	85.07
14	67.5	120	2	94.58	93.98
15	60	120	1	89.85	90.06
16	75	180	2	77.23	77.29
17	75	120	1	80.14	81.00

The lowest and highest biodiesel yields were obtained at reaction conditions of 75 ^{o}C, 120 minutes, 3 wt% and 67.5 ^{o}C, 60 minutes, 1 wt%; of temperature, time and catalyst amount respectively. The biodiesel yields obtained ranged from 72.49 to 95.62%. It was observed that high biodiesel yields were obtained at medium reaction parameters which were chemically active enough to cause the breaking of triglyceride bonds. A reduction in biodiesel yields was noticed at high reaction variables. At high reaction conditions, a prolonged uncontrolled heating of the reaction mixtures led to evaporation of the alcohol and reversibility of the whole reaction.

Prafulla and Shuguang [42] established an optimum biodiesel yield of about 90 - 95% from popular biodiesel feedstock, *Jatropha curcas* oil, within similar range of optimum conditions at which highest biodiesel yields were obtained in this study. Meher et al. [43] obtained an average high biodiesel yield of 97-98% from similar optimization of transesterification parameters of *Pongamia pinnaata* oil using alkaline catalyst.

It can be observed from the results obtained that biodiesel yields reduced drastically at reaction conditions above 120 minutes. A justification for this is the reversibility nature of alcoholysis reaction at both reaction and product sides. According to Aworanti [44], higher alcohol to oil molar ratio could also reduce the activity of the catalyst on the triglycerides molecules and thus decrease the catalyst activity. These higher reaction conditions actually generated more production of glycerol and favoured backward reactions which led to reduction of biodiesel yield. The varying biodiesel yields are indications that the reaction parameters considerably affected the alcoholysis of *Parinari polyandra* oil.

3.3.3 Response surface analysis

3.3.3.1 Regression model

The regression coefficient estimates of β_0 to β_9 after simulation were;

$\beta_0 = +93.98$, $\beta_1 = -3.88$, $\beta_2 = -1.72$, $\beta_3 = -5.01$, $\beta_4 = -9.23$, $\beta_5 = -1.83$, $\beta_6 = -4.23$, $\beta_7 = -0.012$, $\beta_8 = +0.65$, $\beta_9 = +0.84$, $R^2 = 0.9932$.

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The final empirical model in terms of coded factors (reaction parameters) for the biodiesel yield is given in Equation 3.5. The equation in terms of coded factors can be used to make predictions about the biodiesel yield for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$Y = +93.98 - 3.88A - 1.72B - 5.01C - 9.23A^2 - 1.83B^2 - 4.23C^2 - 0.012AB + 0.65AC + 0.84BC \quad (3.5)$$

Where *Y* is the predicted value for biodiesel yield from *Parinari polyandra* oil alcoholysis and *A*, *B* and *C* are model terms of the independent variables for reaction temperature, reaction time and catalyst amount, respectively. The predicted conversion yields from different projects were determined by Equation 3.5 as shown in Table 3.3. It can be seen that the predicted values are in good agreement with the experimental values. It indicates that the biodiesel yield from *Parinari polyandra* alcoholysis is related to the selected variables in this study. The model equation in terms of original factors is presented in Equation 3.6. This can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. The correlated results with the residual values are shown in Table 3.4.

$$Biodiesel\ yield = -614.89975 + 21.46983 * Temperature + 0.068500 * Time + 4.33625 * Catalyst\ amount - 0.164133 * Temperature^2 - 0.000514 * Time^2 - 4.23250 * Catalyst\ amount^2 \quad (3.6)$$

Table 3.4: Correlated results of the residual values

Run Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residuals	Externally Studentized Residuals
1	81.46	80.75	0.7087	0.750	1.574	1.813
2	79.58	78.72	0.8575	0.750	1.904	2.539
3	82.84	83.76	-0.9188	0.750	-2.040	-2.966
4	93.62	93.98	-0.3600	0.200	-0.447	-0.420
5	81.86	82.01	-0.1488	0.750	-0.330	-0.308
6	94.12	93.98	0.1400	0.200	0.174	0.161
7	95.62	95.47	0.1487	0.750	0.330	0.308
8	72.49	72.28	0.2100	0.750	0.466	0.439
9	94.42	93.98	0.4400	0.200	0.546	0.517
10	93.16	93.98	-0.8200	0.200	-1.018	-1.021
11	88.54	88.48	0.0612	0.750	0.136	0.126
12	91.27	90.35	0.9187	0.750	2.040	2.966
13	84.36	85.07	-0.7087	0.750	-1.574	-1.813
14	94.58	93.98	0.6000	0.200	0.745	0.719
15	89.85	90.06	-0.2100	0.750	-0.466	-0.439
16	77.23	77.29	-0.0613	0.750	-0.136	-0.126
17	80.14	81.00	-0.8575	0.750	-1.904	-2.539

The ANOVA model values for biodiesel production from *Parinari polyandra* oil are presented in Table 3.5. The Model F-Value of 113.81 implies the model is significant. Significance of model terms are accepted at values of "Prob > F" less than 0.0500. In this case A, B, C, A^2, B^2, C^2 are significant model terms.

Table 3.5: ANOVA for response surface model of biodiesel yield

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Comment
Model	830.95	9	92.33	113.81	<0.0001	*significant*
A	120.20	1	120.20	148.17	<0.0001	*significant*
B	23.60	1	23.60	29.09	0.0010	*significant*
C	201.10	1	201.10	247.90	<0.0001	*significant*
A^2	358.90	1	358.90	442.42	<0.0001	*significant*
B^2	14.41	1	14.41	17.76	0.0040	*significant*
C^2	75.43	1	75.43	92.98	<0.0001	*significant*
AB	6.250E-004	1	6.250E-004	7.704E-004	0.9786	*not significant*
AC	1.72	1	1.72	2.12	0.1891	*not significant*
BC	2.84	1	2.84	3.50	0.1036	*not significant*
Residual	5.68	7	0.81			
Lack of Fit	4.30	3	1.43	4.17	0.1006	*not significant*
Pure Error	1.38	4	0.34			
Cor Total	836.63	16				

Values greater than 0.1000 indicate the model terms are not significant. There is no need for model reduction to improve the model since the insignificant model terms are few. The "Lack of Fit F-value" of 4.17 implies the Lack of Fit is not significant relative to the pure error. Non-significant lack of fit is good for the model to fit. Model values of 0.90, 86.77, 1.04, and 0.9932, were obtained for standard deviation, mean, C.V. and R-Squared values, respectively. The "Pred R-Squared" of 0.9151 is in reasonable agreement with the "Adj R-Squared" of 0.9845. The difference is less than 0.2. Adequate precision ratio greater than 4 is desirable. A ratio of 33.572 indicates an adequate signal. Thus, the response yield of the *Parinari polyandra* biodiesel model can be used to navigate the design space.

According to statistics studies, a high R-square of above 60% (0.60) is required for studies in the 'pure science' field because the behaviour of molecules and/or particles can be reasonably predicted to some degree of accuracy in science research. A higher R-square value than 0.80 is an indicator of more desirable goodness of fit for regression models. In this case, the R^2 value of 0.9932 indicated that the sample variation of 99.32% for the biodiesel production is attributed to the independent factors, and only 0.68% of the total variations are not explained by the model. The reliability of the model is described by the normal plots of residuals and comparison of the actual and predicted values are described in Figure 3.3. The response yields and experimental yields of fit are good. The space points concentrated around the diagonal line because of the closeness of the R^2 value to Adjusted R^2. The goodness match between the predicted and experimental values is a good indication of the excellent stability of the regression models.

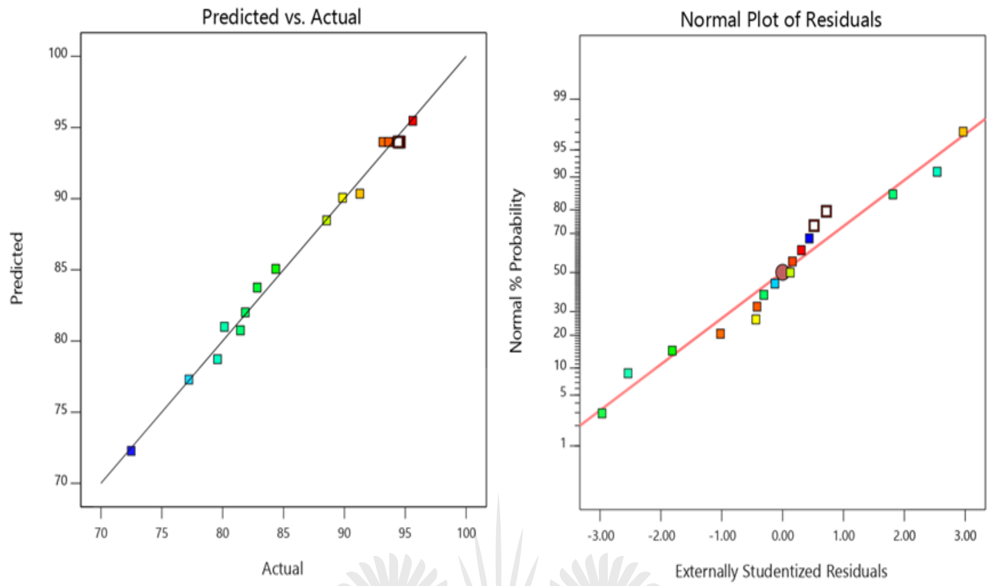

Figure 3.3: (a) The predicted and true values, (b) normal plot of residuals.

3.3.3.2 Effect of reaction variables on the biodiesel yield

The one factor plots of the effect of temperature, time and catalyst amount are shown in Figure 3.4, 3.5 and 3.6 respectively. The reddish dots at the center of the plot represent the design points at which high biodiesel yields were obtained. The whitish dots represent the highlighted point of the experimental variables at which the highest biodiesel yield from the experimental results. The maximum biodiesel yield was obtained at a temperature of 67.5 ^oC. A steady increase was observed from temperature of 60 ^oC upward until it got to about 67.5 ^oC. At 75 ^oC, there was decrease which is related to evaporation of alcohol (boiling point of ethanol is 78.37 ^oC). The effect of temperature plot on biodiesel is shown in Figure 3.4.

As shown on the red design points in Figure 3.4, the maximum biodiesel yield was obtained at experimental run 7 when the actual factors were 60 minutes reaction time and catalyst amount of 1.00 wt%. According to Lin et al. [45], higher temperatures can bring about negative effect on the biodiesel yield as it may damage organic molecules such as triglycerides which are cleaved to Free Fatty Acid (FFA). The highest biodiesel yields recorded were obtained at experimental runs with reaction time of 60 minutes and 120 minutes. The yields of biodiesel increased from 60 – 120 minutes as recorded in Table 3.3.

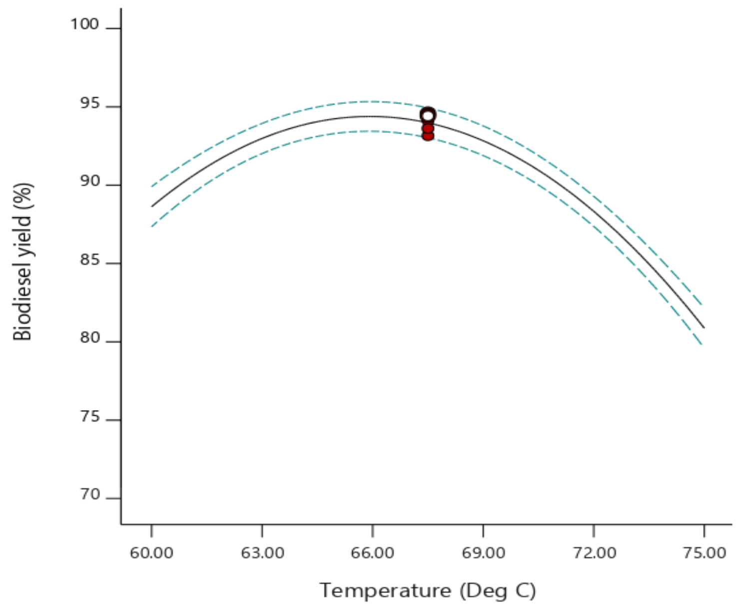

Figure 3.4: Temperature plot against the biodiesel yield

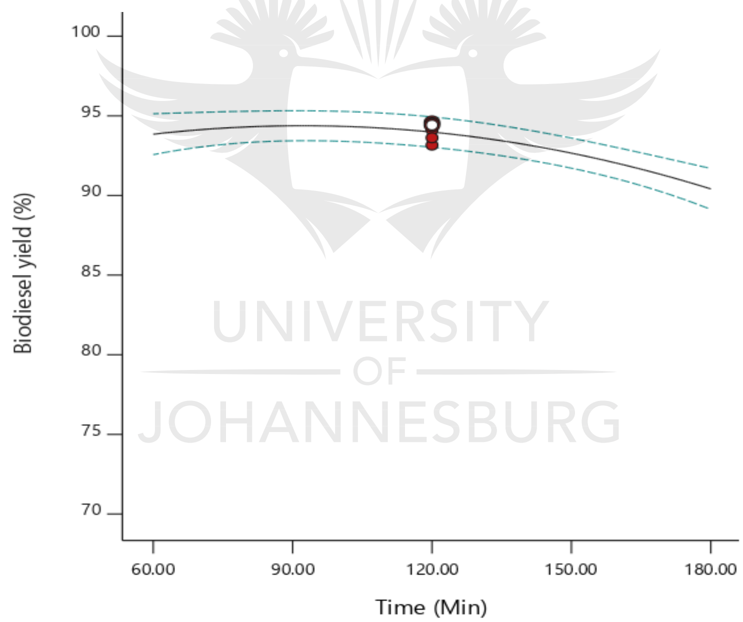

Figure 3.5: Time plot against the biodiesel yield

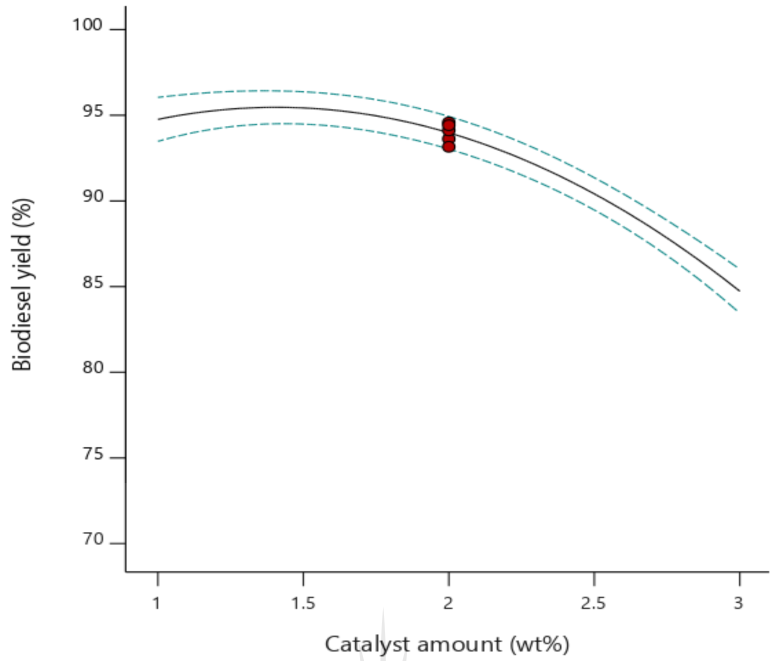

Figure 3.6: Catalyst amount plot against the biodiesel yield

Reaction time of 60 minutes was seen to be sufficient for the complete alcoholysis reaction. With increase in reaction time from 60 minutes to 120 minutes, there was no significant increase in biodiesel yields as shown in Figure 3.5. Increase in reaction time above 120 minutes was seen to have led to decrease in the biodiesel yields. Encinar et al. [46] reported, from his study of variables affecting biodiesel yields from used frying oil, that yield of biodiesel decreases with increase in the alcoholysis reaction time. They observed that the reaction may shift towards reactants side as a result of the reversibility of the process, and thereby lead to increase in viscosity of biodiesel. An optimization study based on this report confirmed that highest biodiesel yield was obtained at 120 minutes reaction time.

The catalyst effect on biodiesel yield is shown in Figure 3.6. The results obtained have shown that moderate amount of catalyst up to 2 wt% is required for complete alcoholysis and conversion of triglycerides to biodiesel. Catalyst amount showed signs of decreased biodiesel yields at values above 2 wt%. The highest biodiesel yields recorded was within a range of 93.16% – 94.58% for a catalyst amount up to 2 wt%. The biodiesel was seen to decrease at increasing amount of catalyst beyond this reference point. Alkali-catalysed alcoholysis has been reported to be very sensitive to water whereby leading to ester saponification [47]. High amounts of catalyst can also induce the formation of gel from the formation of emulsion [42].

The interaction between the variables and responses are shown in Figures 3.7, 3.8, and 3.9. The 3D response surfaces were plotted on the basis of the model equation to facilitate a better understanding of the interactive effects of the reaction variables and to determine the optimum condition of each factor for transesterification for biodiesel production.

The effect of interaction of temperature and time on biodiesel yield can be seen in the 3D response surface plot shown in Figure 3.7. The elliptical nature of the contour plots indicated that interaction between these reaction variables simultaneously had a positive significant effect on the yield of biodiesel. They were observed to have similar effects on biodiesel yields as the reaction progresses. Prolonged heating of the reactants will definitely lead to drying of the ethanol will hamper biodiesel formation. It was noticed that highest biodiesel yields from *Parinari polyandra* oil was obtained at middle levels of reaction time and temperature. A decline in biodiesel yield was noticed when the reaction temperature increased beyond 70 ^oC. The biodiesel yields initially increased from low levels of reaction temperature and time and then began to flatten as both variables neared their high-level values.

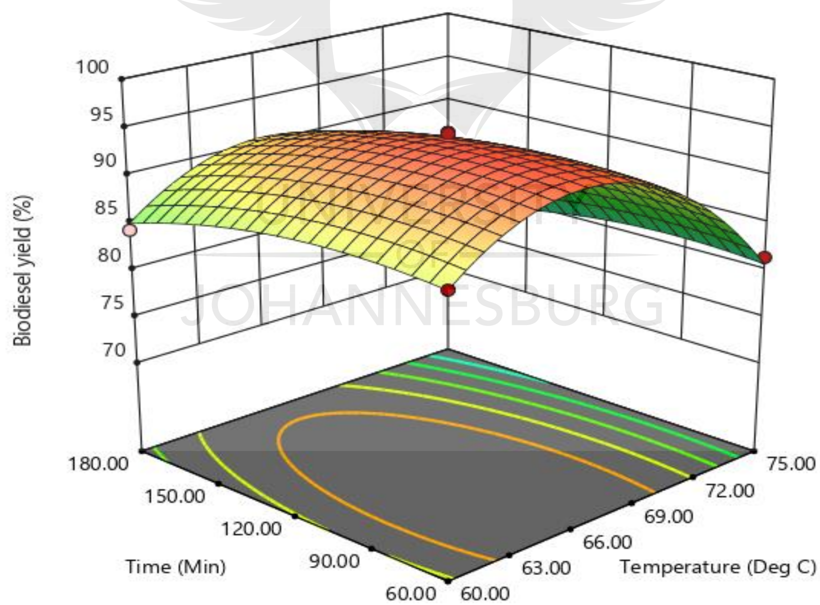

Figure 3.7: 3D plot of temperature and time interactive effect on biodiesel yield

The interactive effect of temperature and catalyst amount on biodiesel yield is shown in Figure 3.8. Biodiesel yields increased steadily from low level to high level until it began to drop at the close of high-level reaction variables. Temperature is necessary to cause interphase reaction between the reactants (alcohol, triglycerides and catalyst). In this case, temperature was seen to have more effect than catalyst amount on biodiesel yield. Higher temperatures close to high level values were seen to decrease biodiesel production. From the experimental results, high biodiesel yields were recorded from reactions that have catalyst amounts between 1 – 2 wt%. The amount of catalyst in any alcoholysis reaction is a critical factor. Low amount of catalyst can result in incomplete conversion of the triglycerides to biodiesel. However, the reaction rate can be slowed down as a result of resistance in mass transfer when the catalyst amount is high [48].

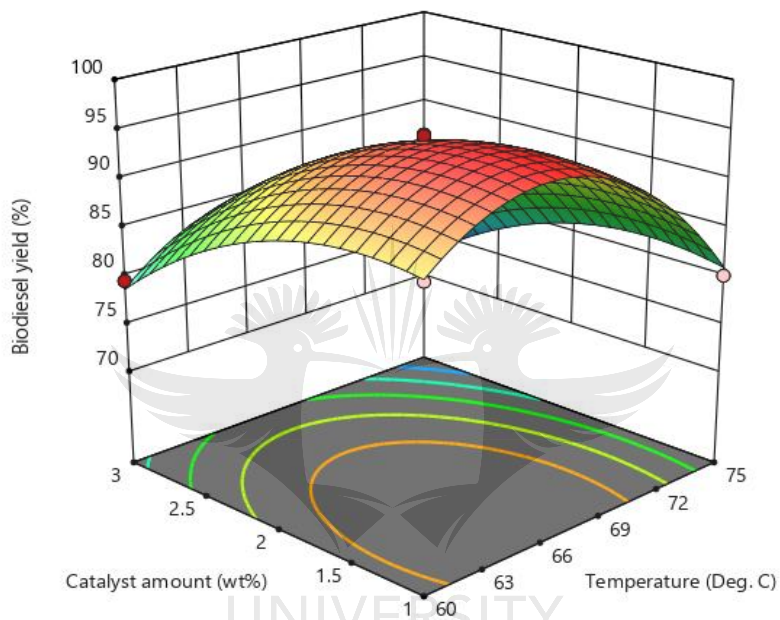

Figure 3.8: 3D plot of temperature and catalyst amount interactive effect on biodiesel yield

The interaction of the reaction time and catalyst on the biodiesel yield is shown in Figure 3.9 based on the results of the ANOVA model. Their effects are nearly the same on the biodiesel yield with the curvature plot showing that catalyst amount have less effect than reaction time. A careful observation of the experimental results showed that biodiesel yields decreased drastically at reaction beyond 120 minutes. Though there wasn’t much significant difference in the biodiesel yields from 60 to 120 minutes, there were variations showing that highest biodiesel yields were achieved between these time intervals.

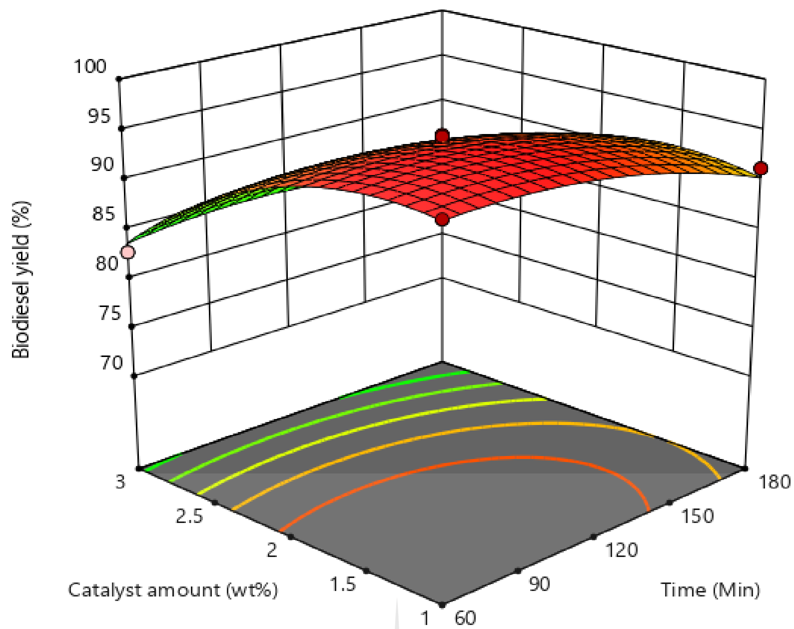

Figure 3.9: 3D plot of time and catalyst amount interactive effect on biodiesel yield

The interactive effect of time and catalyst amount was not favourable at high reaction levels because of the instability of alcoholysis reaction. An uncontrolled reaction time will lead to dissociation of the alcohol from the reaction mixture leading to formation of soap as a result of the resulting reaction between the triglyceride and catalyst. In this effect, the dissociation of the alcohol was brought about by evaporation of the alcohol as a result of continuous stirring of the reaction mixtures, especially at high temperatures. Leung and Guo (2006) carried out an alkaline catalysis alcoholysis of neat and used frying oil using optimization technique and found out that the biodiesel yield, in general, decreased with an increase in the KOH catalyst concentration which caused the form of soap.

3.3.3 Optimization and model verification of biodiesel production from *Parinari polyandra* oil

Statistical analysis of the experimental data was done to obtain the optimum reaction conditions for biodiesel production from *Parinari polyandra* oil. Using the optimization tool, numerical optimization technique based on desirability function was carried out to determine the workable optimum conditions for the production of biodiesel. In order to provide an ideal case for biodiesel production, the reaction temperature, reaction time and catalyst amount were set to minimum requirement levels and biodiesel yield was set on maximum level.

The predicted optimum values of reaction temperature, reaction time and catalyst amount were found to be 61.19 °C, 60 minutes and 1 wt% respectively, to achieve 92.74 % maximum *Parinari polyandra* biodiesel yield with a desirability of 0.947. This optimal solution chosen for biodiesel yield are based on economic considerations (reduced temperature and reaction time and catalyst amount which corresponds to reduced operating costs of the alcoholysis reaction) and not necessarily the highest biodiesel yield value. It can be seen that the optimized conditions fell within the design space of the reaction parameters. The points on the ramps denote the optimized conditions. From the predicted optimum and highest experimental yield of 92.74% and 95.62%, the analysis results clearly indicated the close effectiveness of process variables optimization in the biodiesel production.

Validation experiments were conducted at the predicted optimum reaction parameters to verify the effectiveness of the model and confirm the agreement between the results obtained. Three set experiments conducted gave an average biodiesel yield of 93.18% which was in reasonable agreement with the predicted optimal yield. The matching and good agreement confirmed the validity of the models for simulating the biodiesel production from *Parinari polyandra* oil under the three tested reaction variables (temperature, time and catalyst amount).

3.4 Fuel properties of biodiesel

The fuel properties of the biodiesel obtained from the experimental runs are contained in Table 3.6. All the fuel properties were found to be within the acceptable standards for biodiesel and petrol diesel. The good fuel properties and reduction in the kinematic viscosity values are evidences of the effectiveness of reaction parameters on the alcoholysis of the *Parinari polyandra* oil. The recommendation of *Parinari polyandra* Benth as a good feedstock for biodiesel production by Motojesi et al. [37] serves as a reliable ground for the good fuel properties obtained. The cetane number, cloud and pour points, and higher heating value were within the standards for diesel fuel; an evidence that transesterification reaction has completely taken place to convert the triglycerides to methyl esters. This can be seen in the reduced value of kinematic viscosity of the oil from 62 mPas to the range of 3.69 – 4.66 mPas.

Table 3.6: Fuel related properties of the experimental biodiesel samples

Run	Specific gravity	Kinematic viscosity @ 40ºC, mm^2/s	Cloud point, ºC	Pour point, ºC	Flash point, ºC	Higher heating value, MJ/kg	Cetane number	Acid value, mgKOH/g	pH	Water (% v/v)
1	0.881	4.66	-1	-6	142	44.9	65.2	0.33	7.43	<0.01
2	0.883	3.69	-2	-5	144	45.2	65.3	0.29	7.33	<0.01
3	0.886	3.71	1	-5	158	45.9	65.3	0.52	7.2	<0.01
4	0.888	3.84	0	-6	156	46.1	65.5	0.48	7.24	<0.01
5	0.886	3.81	-1	-7	168	45.9	65.5	0.51	7.18	<0.01
6	0.885	3.79	-1	-7	152	45.8	65.4	0.48	7.24	<0.01
7	0.888	3.84	1	-6	161	46.2	65.5	0.45	7.18	<0.01
8	0.882	4.33	-1	-5	148	44.8	65.2	0.31	7.21	<0.01
9	0.887	3.89	-2	-7	167	46.0	65.5	0.5	7.14	<0.01
10	0.886	3.78	-3	-7	149`	45.7	65.5	0.42	7.32	<0.01
11	0.883	4.22	-3	-8	142	45.8	65.4	0.37	7.25	<0.01
12	0.885	3.9	-3	-8	172	45.8	65.3	0.43	7.28	<0.01
13	0.881	4.53	-2	-4	148	45.2	65.4	0.28	7.37	<0.01
14	0.885	3.77	-2	-4	160	46.1	65.5	0.49	7.19	<0.01
15	0.881	4.12	-1	-4	145	45.7	65.4	0.28	7.42	<0.01
16	0.882	3.94	-1	-5	148	46.1	65.4	0.33	7.23	<0.01
17	0.881	3.88	-2	-6	152	44.8	65.2	0.31	7.42	<0.01

The major reason why vegetable oils are transesterified using alcohols is to reduce the high viscosity of vegetable oils and produce biodiesel with lower viscosity in order to prevent operational problems when combusted in diesel engines [49]. High viscosity leads to poor fuel atomization and may cause too much pump resistance, filter damage, poor combustion, and increased exhaust emissions [50], [51]. Kinematic viscosity is a necessary property any fuel derived from fatty acid compounds would need to meet [52]. Kinematic viscosity, determined at 40 ºC, is an important parameter required by biodiesel and petrol diesel standards for its use as an engine fuel [53], [54].

The saturation level of biodiesel is determined by the Fatty Acid (FA) composition of the feedstock. The degree of saturation increases with the FA composition. This implies that the level of saturated molecules is determined by the length of the FA carbon chains. Biodiesel reportedly has a higher cetane number than petroleum diesel since it is made from feedstock that is largely composed of long-chain hydrocarbon groups [55].

Flow properties, Pour Point (PP) and Cloud Point (CP) are important parameters of fuel flow system. They are both functional properties of the viscosity parameter. Viscosity has been generally reported to increase with the degree of saturation. The lower viscosity values obtained are good and these show that the biodiesel products have lower resistance to flow and can thus be used as diesel engine fuel owing to their similarity to that of petrol diesel. Operating a diesel engine at low temperatures especially in cold climate regions can be difficult because of high viscosities [56].

The Higher Heating Values (HHVs) of the biodiesel fuels are very good because they are very close to that of petrol diesel (49.65 MJ/kg). The HHV is an important parameter used to quantify the energy content and combustion efficiency of fuels [57]. The standard measure of the energy content of a fuel is its HHV. The Higher Heating Values (HHVs) of biodiesels are relatively high as a result of high oxygen content but slightly lower than that of diesel. The oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. The oxygen content of a fuel improves its combustion efficiency due to a rise in the uniformity of oxygen with the fuel during combustion [57]. The oxygen content of biodiesel generally varies between 10 wt% to 12 %wt depending on the degree of oxygenation of the feedstock [58]. Highly saturated oil, like *Parinari polyandra*, is more oxygenated and burns cleaner and stable when used as feedstock for biodiesel production.

The ^{1}H NMR spectrum of biodiesel from *Parinari polyandra* seed oil is shown in Figure 3.10. The NMR spectra showed a very neat and clearer signal separation of the functional alcohol group, the carboxylic and fatty acid ester. The chemical shift from δ 5.255 – 5.371 ppm represents the olefinic protons. The ethoxy protons of the ester of the biodiesel are represented in the double signals between δ 4.054 and 4.107 ppm. The fatty and carboxylic acid functional groups of the biodiesel are accumulated in the multiplet between δ 0.834 and 2.745 ppm.

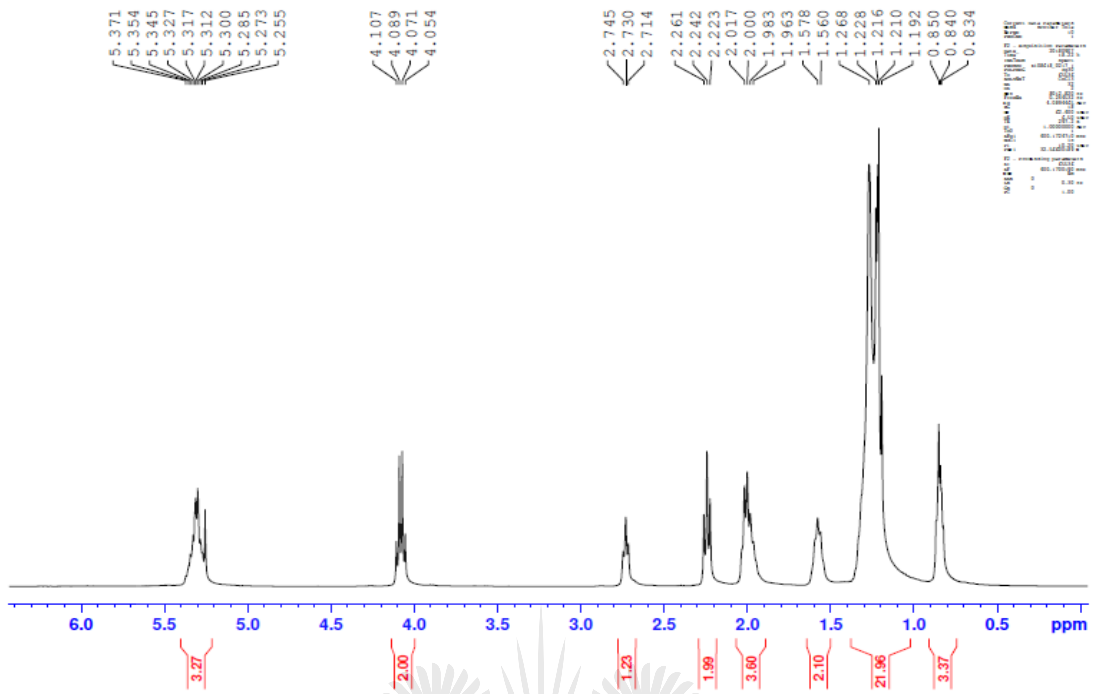

Figure 3.10: ^{1}H NMR spectrum of *Parinari polyandra* seed oil biodiesel

3.5 Conclusions

The substantial oil content obtained from *Parinari polyandra* seed has helped to establish the seed oil as a sustainable and renewable feedstock for biodiesel production. Also, the percentage biodiesel yield from the optimized low reaction factors after alcoholysis of the oil suggest that the utilization of this seed oil for biodiesel production on large industrial scale will be viable.

The RSM was efficient in the model prediction for optimized biodiesel yield from alcoholysis of *Parinari polyandra* oil with a high probability level and significance of reaction parameters. The properties of *Parinari polyandra* biodiesel met the ASTM D6751 standard for biodiesel usage as fuel.

The model applied in this study has generated a simple and reliable time saving approach for approximation of biodiesel yield from *Parinari polyandra* oil. Owing to the close agreement between the optimized and validated yields, the prediction by RSM has shown faster efficiency than the conventional duplication methods of using lengthy iteration methods of calculation to solve differential equations.

The optimization was validated at reaction conditions of temperature of 61 ^{o}C, 60 minutes reaction time and catalyst amount of 1 wt% to give a biodiesel yield of 93.18%.

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CHAPTER 4

PERFORMANCE EVALUATION OF A DIESEL ENGINE USING BLENDS OF OPTIMIZED YIELDS OF *PARINARI POLYANDRA* OIL BIODIESEL

It is reproduced from Ogunkunle, O. and Ahmed, N.A. (2019): Performance Evaluation of a Diesel Engine Using Blends of Optimized Yields of Sand Apple (*Parinari polyandra*) Oil Biodiesel. Renewable Energy, 134: 1320 – 1331.

This chapter covers the evaluation of a diesel engine fueled with *Parinari polyandra* biodiesel blends. The performance characteristics of the engine showed that the biodiesel had similar performance characteristics with that of fossil fuel without any engine modification.

Sand apple oil seed that has relatively high oil yield is widely cultivated in Africa. Evaluation of the performance of sand apple ethyl ester is a missing link in establishing it as an alternative fuel for use in diesel engines. Performance evaluation of optimized yields of sand apple biodiesel was, therefore, conducted in a diesel engine at various loading rates. Oil was extracted from sand apple seeds via solvent extraction. A Central Composite Design was used to optimize biodiesel yields from sand apple oil transesterification using potassium hydroxide as catalyst. Engine tests were carried out to evaluate the performance of a stationary 5Hp diesel engine starting from 0% to 100% load conditions. The engine was run with diesel and four different blends of diesel/biodiesel. Values for speed, torque, fuel consumption rate and exhaust temperature were determined. The optimum biodiesel yield recorded was 94.6%. The torque, speed, fuel consumption rate and exhaust temperature recorded for best engine performance for all blends were 8.50 Nm, 2950 rpm, 2.925 x 10^{-6} kg/s, and 300^{o}C. The evaluated engine parameters showed sand apple biodiesel can be burned in diesel engines using appropriate blending ratio without any modification to the engine.

4.1 Introduction

Biodiesel refers to a non-petroleum based fuel consisting of alkyl ester derived from trans-esterification of triglyceride or by the esterification of Free Fatty Acid with low molecular weight alcohols [1]. In recent times, remarkable utilization of plant oil derived from inedible oil seeds has taken place [2], [3]. Biodiesel is considered as an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as ethanol [4]. Biodiesel comprises of alkyl fatty acid (chain length C_{14}–C_{22}) esters of short-chain alcohols, primarily, methanol or ethanol. A renewable fuel such as biodiesel, which produces lower exhaust emission is in high demand worldwide [5]. Oil prices have been volatile over the years. West Texas Intermediate (WTI) crude oil price is still hovering over $65 per barrel in the first quarter of 2018, a much higher figure of nearly $28 per barrel recorded in 2001 [6]. Such increases in price and consumption of petroleum products in developing countries are the reasons why alternative fuels particularly those that are renewable and have positive environmental benefit are required [7]. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs in these countries can provide an alternative fuel for diesel engine.

Biodiesels are mostly characterized by their density, viscosity, cloud and pour points, cetane number, distillation range, flash point, acid value, ash content, sulfur content, carbon residue, and higher heating value (HHV). Most researches on bio-renewable fuel have been highly focused on producing biodiesel from vegetable oils [5] using various biodiesel production methods amongst which transesterification using alkali catalyst which gives high level of conversion of triglycerides to their corresponding ethyl ester feature prominently [8].

Some of the important parameters affecting the ester yield during the transesterification reaction are the reaction time, molar ratio of alcohol to vegetable oil, stirring rate, catalyst concentration, and reaction temperature [9]. Biodiesel (B100) specifications are given in Table 4.1. These parameters conform to the biodiesel standard, The American Society for Testing and Materials (ASTM D 6751). This standard prescribes the parameters that pure biodiesel (B100) must meet before it can be used as a pure fuel or blended with petroleum-based diesel fuel. A comparative look at this table shows the closeness of kinematic viscosity, boiling point, flash point, water, carbon, hydrogen and sulphur contents and cetane number of biodiesel to those of diesel fuel as recommended by American Society for Testing and Materials. This is an indication that biodiesel and its blends can serve as alternative to conventional diesel in diesel engines [9].

Table 4.1: Biodiesel, B100, specifications (ASTM D 6751 requirements)

Property	Method	Limits	Units
Flash point	D 93	130 min	^oC
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 40 ^oC	D 445	1.9 – 6.0	Mm^2/s
Sulfated ash	D 874	0.020 max	wt%
Total sulfur	D 5453	0.05 max	wt%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	^oC
Carbon residue	D 4530	0.050 max	wt%
Acid number	D 664	0.80 max	Mg KOH/g
Free glycerine	D 6584	0.020	wt%
Total glycerine	D 6584	0.240	wt%
Phosphorus	D 4951	0.0010	wt%
Vacuum distillation end point	D 1160	360 ^oC max, at 90% distilled	^oC

Source: Ramadhas et al. [9]

Unlike petro diesel, biodiesel is capable of being decomposed by bacteria, and it significantly reduces toxic and other emissions when burned. The main advantage of biodiesel in this regard is that it is a derivative of natural products. As demand rises, the production of the required agricultural products can be increased to compensate accordingly [10]. A vast number of plant materials including energy crops and various agricultural residues are generally considered as oil feedstock for biodiesel production [11]–[13]. These seed oil such as soybean oil [14], waste cooking oil [15], sunflower oil [16].

Some of the common feedstocks for biodiesel production from non-edible oils also include tobacco seed (*Nicotiana tabacum L.*), rubber seed tree (*Hevea brasiliensis*), desert date (*Balanites aegyptiaca*), croton megalocarpus, rice bran, babassu tree, *Terminalia belerica*, *Euphorbia tirucalli*, neem (*Azadirachta indica*), koroch seed oil (*Pongamia glabra vent.*), mahua (*Madhuca indica and Madhuca longifolia*), chinese tallow, silk cotton tree (*Ceiba pentandra*), jojoba (*Simmondsia chinensis*), *Aleurites moluccana*, sea mango (*Cerbera odollam*), and jatropha (*Jatropha curcas*) [17]. Other inedible oil seeds include soapnut (*Sapindus mukorossi*), mahua (*Madhuca indica*) and karanja (*Pongamia pinnata*) [18]. A variety of biolipids can also be used to produce biodiesel. These include virgin vegetable oil feedstock such as rapeseed, mustard, palm oil, sunflower, hemp, and even algae show considerate promise [5].

The choice of oil that can be used for biodiesel production is determined by the available oil seeds in a particular region. To produce a certain percentage of biodiesel fuel as a part of every nation's economy using oil seeds would require a boost in utilization of the seeds that are abundant and have high oil yield content. However, sand apple, with its high oil yield content (31 - 60%) is one of the under-utilized oil for local and industrial production of biodiesel [19]. There is therefore a good case to explore sand apple oil as a potential feedstock sources for biodiesel production.

Sand apple (*Parinari polyandra* L.) is a savannah plant found in West Africa extending from Mali to Sudan. It belongs to the family of *rosaceae* that grow mostly in tropical savanna region that includes Nigeria, Ghana, Senegal, Ivory Coast, Mali, Cameroon and Sudan. In Nigeria, it is found in part of the Northern states, Middle belt region and part of Southern states. It is generally noted that the fruit has been grossly underutilized either because of its non-edibility or due to lack of extensive research or non-availability of information on its fruit and seed properties. The sand apple seed oil, on the other hand, although considered not edible, has been found to have the desirable properties that are suitable for alkyd resin preparation [20].

Although engine manufacturers may recommend biodiesel to be used in their engines, there are no long term field test results available that show the impact of biodiesel over the engine life in terms of its performance and wear and tear of its components [21]. In order to establish ethyl or methyl esters of inedible oils as potential biofuels for running diesel engines wholly or partially as required by American Society for Testing and Materials (ASTM), plans to evaluate the performance of the esters as a fuel in a diesel engine were formulated. First oil was extracted from sand apple seeds using solvent method. Next, transesterification reactions were carried out and biodiesel from sand apple oil was produced using a low-cost homogeneous catalyst potassium hydroxide (KOH). Sand apple biodiesel was thereafter blended with Automotive Gas Oil (AGO) and the physicochemical properties of sand apple oil, its ethyl ester and that of its blends with diesel were determined. Finally, engine tests were carried out to investigate the performance of the blended biofuel in a stationary 5Hp diesel engine attached to a hydraulic dynamometer.

4.2 Materials and Method

4.2.1 Collection and processing of feedstock

Sand apple seeds were harvested and collected from bushes around Ogbomoso South Local Government area, Oyo State, Nigeria. The fresh seed kernel had moisture content of 2.2% when determined on wet basis. The pericarps are fleshy but tough. The seeds were cut into two parts with a sharp knife to remove the whitish seeds. The seeds were sun dried for two weeks to reduce their moisture content and prevent microbial degradation. A picture of fresh fruits and dried seeds of sand apple can be seen in Figure 4.1.

Figure 4.1: Fresh fruits and dried nuts of sand apple

Source: Compiled by the author of this thesis

4.2.2 Extraction of Oil from Sand Apple kernel

Oil extraction was done via solvent extraction method according to the experimental method of [22] using petroleum ether as extraction solvent. The dried kernels were pounded using porcelain mortar and pestle to 2 mm fine particle size. The extraction of the oil was carried out using soxhlet apparatus of 500 cm^3 capacity. The extraction was conducted at 60 ^oC reaction temperature, residence time of 4 hours and solid/solvent ratio of 0.05 g/ml. Reaction parameters considered for the oil extraction were subjected to preliminary experiments to ascertain the best conditions that favoured oil extraction from sand apple seeds. Oil yield was computed using Equation 4.1.

$$\%\,Oil\ yield = \frac{weight\ of\ extracted\ oil}{weight\ of\ grinded\ seed} \times 100 \qquad (4.1)$$

4.2.3 Production of Biodiesel from Sand apple oil

Biodiesel was produced from sand apple oil via transesterification reaction. The reactants were the raw sand apple oil, anhydrous ethanol and KOH. Ethanol was chosen as the alcohol type because it carries more energy per gallon and owing to its lesser chemical toxicity than its substitute methanol. The reaction variables taken into consideration for the transesterification reactions were reaction temperature, reaction time and alcohol to oil molar ratio. The Free Fatty Acid (FFA) content of the oil predetermined to be 1.2 wt. % made a direct base catalyzed transesterification possible (see Table 5). Catalyst (KOH) was mixed vigorously with ethanol to form potassium ethoxide. The ethoxide was swiftly introduced into heated oil and stirred to produce biodiesel and glycerol as by product.

The experiments were conducted at temperatures (60 – 65 ^{o}C) which were below the boiling point of ethanol. High level temperature of 65 ^{o}C was adopted for the reaction temperature as recommended by [23]. The experiment was carried out between 60 minutes low level and 120 minutes high level reaction time. The reaction time was to ensure enough interaction between the reagents and the oil as the reaction mixture was continuously stirred at a constant rate. Also, for the reaction, 6:1 moles of alcohol to oil was used at high level while 3:1 moles of alcohol to oil was used at low level. Catalyst concentration used was 1 % by weight of oil.

A constant volume of 50 ml of sand apple oil was pre-heated and measured into the reactor and placed on electric magnetic stirrer to the desired experimental temperature. The required amount of catalyst was mixed with a required amount of ethanol and stirred vigorously. Thereafter, the formed product was quickly introduced into the oil in the reactor and stirred vigorously with the magnetic stirrer for the set experimental reaction time. After this, 10 ml of distilled water (20 % of initial volume of oil) was added to the mixture and stirred continuously for another 15 min to aid formulation and easy separation of biodiesel. The mixture was thereafter poured inside a separating funnel for 24 hours, glycerol which is a heavier liquid settled at the bottom and ethyl ester, which is lighter, was at the top (Figure 4.2). The glycerol was decanted in a container and biodiesel was collected and stored in a sample bottle.

Biodiesel product was washed with distilled water at 30% of the ester volume. The mixture was stirred vigorously with mechanical stirrer. The stirring was stopped after 10 min and unreacted ethanol and glycerol that were present were decanted. The washing was done three times to obtain a pure ethyl ester sample. After this procedure, the biodiesel was heated at 100 ^{o}C for 20 minutes to remove any water present and then stored for further analysis.

Figure 4.2: Settling phase of ethyl ester and glycerol

The percentage of ester yield by sand apple was computed using Equation 4.2 as recommended by [24]. A simplified process flow diagram for biodiesel production is shown in Figure 4.3.

$$Y = \frac{V_e}{V_r} \times 100\ \% \tag{4.2}$$

Where;

Y = yield of ethyl ester (%)
V_e = volume of ethyl ester produced (m^3)
V_r = volume of raw oil used (m^3)

The experimental design for biodiesel production from sand apple oil was carried out using a Central Composite Design (CCD) of Response Surface Methodology (RSM) to study the efficiency of ethyl ester (biodiesel) production in relation to the applied reaction conditions. Temperature (A), Time (B) and Alcohol to oil ratio (C) were the factors (reaction variables) considered while the response was Biodiesel yield (Y). The design generated twenty (20) experimental runs. The model obtained was quadratic. The data obtained from the sand apple oil transesterification experiments were analysed statistically using Analysis of Variance (ANOVA).

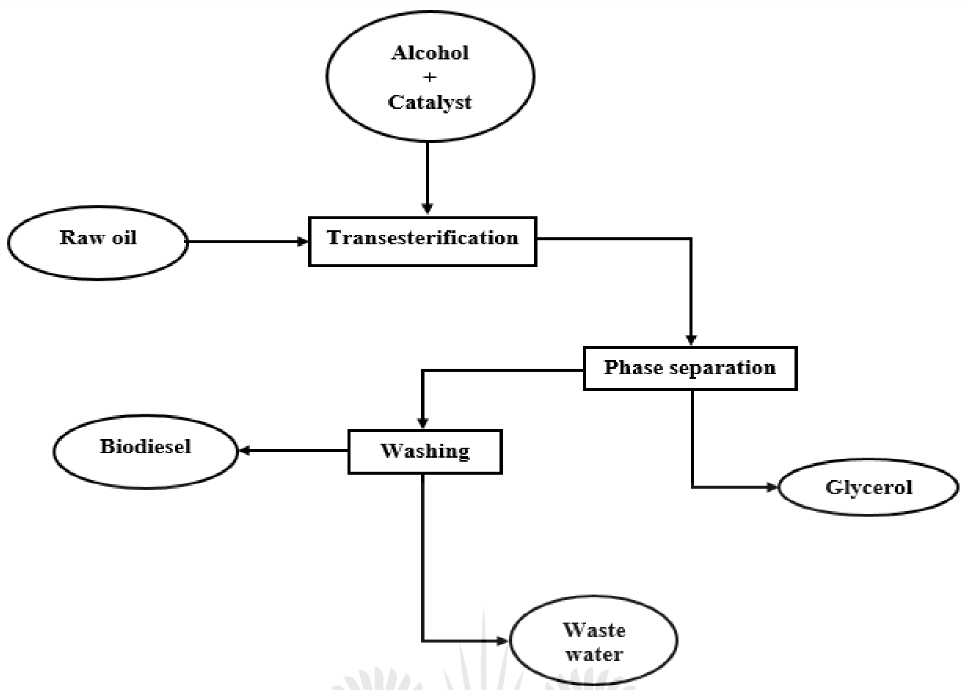

Figure 4.3: Simplified process flow diagram for biodiesel production

4.3 Testing Procedure of a Diesel Engine Using AGO and Biodiesel Blends

Engine tests results were obtained for the purpose of comparison of the combustion parameters of biodiesel to that of diesel in a diesel engine. A single cylinder, 5Hp diesel engine made by Kipor Machinery Company was used for the performance test. The engine specification is shown in Table 4.2. The diesel engine was coupled to a Hydraulic Dynamometer made by AL – Tech BK. An overhead water tank supported by a standing table was placed above the level of the dynamometer to cool it. A water flow rate was controlled by a needle valve mounted on the engine bed. The quantity of water in the dynamometer absorbed by the power from engine, depended on the settings of the needle valve and tap.

The 5Hp diesel engine shaft drove the paddle inside valve casing, churning up the water in the dynamometer. This casing was restricted from rotating at the same speed with the paddle by a spring-loaded nylon cord that passed round the casing. The tension of the two springs was always equal as the dynamometer casing rotated. The angular position taken up by the casing depended on the torque and stiffness of the two springs. Hence, the angular displacement of the casing was proportional to the torque which was measured by the calibration of the arm of the dynamometer by a rotary potentiometer that fed the output into the input of a torque meter.

Table 4.2: Specification of the test diesel engine

Engine parameter	Engine specification
Maker	Kipor Machinery Company
Model	KM 178 F (A)
Type	Air Cooled diesel Engine
Rated power	3.6 kW (3.3 Hp)
Rated speed	3000 rpm
Maximum power	3.68Kw (5Hp)
Number of cylinder	1
Valve clearance	-0.10 – 0.15
Cooling system	Air cooled
Lubricating No	SAE 10w – 30
Net weight	40 kg
Fuel capacity	3.5 litres

Automotive Gas Oil (AGO) (Diesel #1) was obtained and stored in a clean container. The engine test was carried out by operating the Compression Ignition Engine (CIE) with AGO as a baseline study. The engine was operated at wide open throttle (WOT) on no load condition for about five minutes. For each of the fuel blends tested, the engine was allowed to run for two minutes at half throttle and then increased gradually until it reached WOT. At every 2 minutes interval of engine operation the data was collected from no load to 100 % load with an increment of 25 % load.

The above method was used to obtain the value for torques, speed, fuel consumption rate and exhaust temperature at loads of 0% (no load), 25%, 50%, 75% and 100% load. Also, to determine the stable torque range of the engine, preliminary test was performed, where the water flow into the dynamometer was allowed for like two minutes during which the inlet valve control knob was used to regulate the inflow of water into dynamometer until a stable, desired torque was attained. The engine was operated in a similar manner using biofuel of sand apple and fossil diesel blends having 5, 10, 15 and 20 % ethyl ester on volume basis. The test for the blended biofuel was kept within 20 % of sand apple ethyl esters as recommended by Kumar and Dixit [25]. The torque, speed, fuel consumption rate and exhaust temperature were recorded for each test. Other parameters such as brake thermal efficiency, brake specific fuel consumption, brake power and fuel equivalent power of fuel sample were also computed using the formulae by Srivastava et al. [26].

4.3.1 Determination of fuel consumption rate

The fuel consumption rate was determined using the formula in Equation 4.3.

$$M_f = \frac{8\rho \; X \; 10^{-4}}{t} \quad (4.3)$$

Where:

M_f = Fuel consumption rate (kg/s)
ρ = Density of Fuel (kg/m^3)
t = Time taken (s)

4.3.2 Determination of fuel equivalent power

The equivalent power of fuel was determined using the formula in Equation 4.4.

$$P_f = H_g \times M_f \quad (4.4)$$

Where:

P_f = Fuel equivalent power (W)
H_g = Heating value (J/kg)
M_f = Fuel consumption rate (kg/s)

4.3.3 Determination of brake power

The output of brake power was determined using the formula stated in Equation 4.5.

$$P_B = \frac{2\pi NT}{60} \quad (4.5)$$

Where:

P_B = Brake power (kW)
N = Speed (rpm)
T = Torque (Nm)

Also, $P_B = T \times \omega$

Where:

$$\omega = \frac{2\pi N}{60} \quad (4.6)$$

ω = angular speed (rad/s).

4.3.4 Determination of brake specific fuel consumption

The brake specific consumption measures the efficiency of an engine using fuel supply to produce work. The formula used to calculate BSFC is stated in Equation 4.7.

$$BSFC = \frac{M_f}{P_B} \quad (4.7)$$

Where:

$BSFC$ = brake specific fuel consumption (kg/kwh)
M_f = fuel consumption rate (kg/s)
P_B = brake power (kW)

4.3.5 Determination of brake thermal efficiency

The brake thermal efficiency was also calculated using Equation 4.8.

$$\eta_{\mathrm{bth}} = \frac{P_B}{P_f} X\ 100 \quad (4.8)$$

Where:

η_{bth} = brake thermal efficiency (%)
P_B = Brake power (kW)
P_f = Fuel equivalent power (W)

4.4 Results and Discussion

4.4.1 Extracted oil from sand apple seeds

The total volume of the oil yield obtained from sand apple seeds using soxhlet extraction method was 1400 ml. 1400 ml (1260.6g) of oil was extracted from 2350 g of grounded sand apple seeds. The oil yield reflected a yield of 53.64 %. This value seems to slightly lower than 64 % reported by Afolabi et al. [22]. This slight difference in the oil yield of sand apple seeds may be caused by the type of fruit specie, the time of harvest and the experimental conditions.

4.4.2 Biodiesel yield from transeterification of sand apple oil

Results of biodiesel yields from transesterification of sand apple oil are presented in Table 4.3. Maximum biodiesel yield of 94.6 % was obtained at experimental run 8 with reaction conditions of 65 ^{o}C temperature, 120 minutes reaction time and 6:1 alcohol to oil molar ratio while the minimum biodiesel yield of 74.3% was obtained at experimental run 2 at temperature 60 ^{o}C, reaction time of 60 minutes and alcohol to oil molar ratio 3:1. Almost the same reaction conditions were obtained by [27]. Using KOH as catalyst for transesterification of milk bush oil, 97% of methyl ester was obtained at 60°C temperature, methanol/oil molar ratio 12:1, and reaction time

180 minutes. The percentage of biodiesel yield obtained from sand apple oil transesterification in this study showed that the sand apple oil is to be a promising feedstock for biodiesel production as compared with other vegetable plant oil such as soybean 20%, jatropha 99%, sunflower 43% and camola 40% [5]. The different biodiesel yields obtained are also indications that the reaction parameters affected the biodiesel yield considerably.

Table 4.3: Experimental biodiesel yields from transesterification of sand apple oil

Runs	Reaction variables			Response
	Temperature (°C)	Time (Minutes)	Alcohol to oil molar ratio (Mol)	Biodiesel yield (%)
1	62.5	90	4.5	85.8
2	60	60	3	74.3
3	62.5	90	7.02	90.02
4	62.5	90	4.5	84.6
5	58.3	90	4.5	79.5
6	65	120	6	94.6
7	62.5	90	4.5	86.4
8	62.5	39.55	4.5	66.8
9	65	60	6	81.8
10	65	120	3	87.3
11	60	120	6	83.4
12	60	120	3	89.4
13	62.5	90	4.5	85.6
14	62.5	90	4.5	86
15	60	60	6	76.5
16	62.5	140.45	4.5	88.7
17	62.5	90	4.5	89.2
18	62.5	90	1.98	82.7
19	66.7	90	4.5	86.7
20	65	60	3	80.7

The Analysis of Variance (ANOVA) of biodiesel yield from sand apple oil transesterification is shown in Table 4.4. Values of "Prob>F" less than 0.0500 indicate the model term are significant and values greater than 0.1000 indicate the model term are not significant. The model F-value of 12.93 implies the model is significant and there is only a 0.02% chance that a model "F-value" this large could be due to noise. The "lack of fit F-value" of 3.87 implies the lack of fit is not significant relative to the pure error.

Standard deviation of 2.43, mean of 84.01, C.V of 2.89, PRESS of 414.99, R-squared of 0.9209, adjusted R-square 0.8497, predicted R-squared of 0.4447, adequate precision of 14.237 were obtained. Guan and Yao [28] reported that an R^2 should be at least 0.80 for the good fit of a model.

Table 4.4: ANOVA for response surface model of biodiesel yield

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Comment
Model	688.27	9	76.47	12.93	0.0002	*Significant*
A	*79.30*	*1*	*79.30*	*13.41*	*0.0044*	*Significant*
B	*448.14*	*1*	*448.14*	*75.79*	*< 0.0001*	*Significant*
C	*21.70*	*1*	*21.70*	*3.67*	0.0844	*Not Significant*
A^2	*10.30*	*1*	*10.30*	*1.74*	0.2163	*Not Significant*
B^2	*107.95*	*1*	*107.95*	*18.26*	0.0016	*Significant*
C^2	*1.66*	*1*	*1.66*	*0.28*	*0.6082*	*Not Significant*
AB	*0.85*	*1*	*0.85*	*0.14*	*0.7133*	*Not Significant*
AC	*18.60*	*1*	*18.60*	*3.15*	*0.1065*	*Not Significant*
BC	*0.50*	*1*	*0.50*	*0.085*	*0.7772*	*Not Significant*
Residual	59.13	10	5.91			
Lack of Fit	*47.00*	*5*	*9.40*	*3.87*	*0.0818*	*not significant*
Pure Error	*12.13*	*5*	*2.43*			
Cor Total	747.40	19				

In this case, the R^2 value of 0.9209 indicated that the sample variation is 92.09% for the biodiesel production which can be attributed to the independent factors (temperature, time, and alcohol to oil molar ratio). The remaining 7.91% of the total variations are not explained by the model. A ratio of 14.237 obtained indicates an adequate signal. Adequate precision ratio greater than 4 is desirable. The final empirical model equation in term of coded factor for the yield is given by Equation 4.9.

$$Biodiesel\ yield = +86.22 + 2.41A + 5.73B + 1.26C - 0.85A^2 - 2.74B^2 + 0.34C^2 - 0.33AB + 1.52AC - 0.25BC \quad (4.9)$$

Where A, B, C were the coded values of the independent variables i.e. temperature, time and alcohol to oil molar ratio, respectively. The 3D response surface plots showing the interactive effects of reaction variables on biodiesel yield are shown in Figures 4.4, 4.5 and 4.6. The effect of interaction of temperature and time on biodiesel yield can be seen in the 3D surface plots (Figure

4.4). The elliptical curvature of the plot shows the interactive effect had positive effect on the increase in yield of biodiesel. The biodiesel yield increased with increase in temperature from 60 to 65 ^{o}C and time from 60 minutes to 120 minutes, respectively.

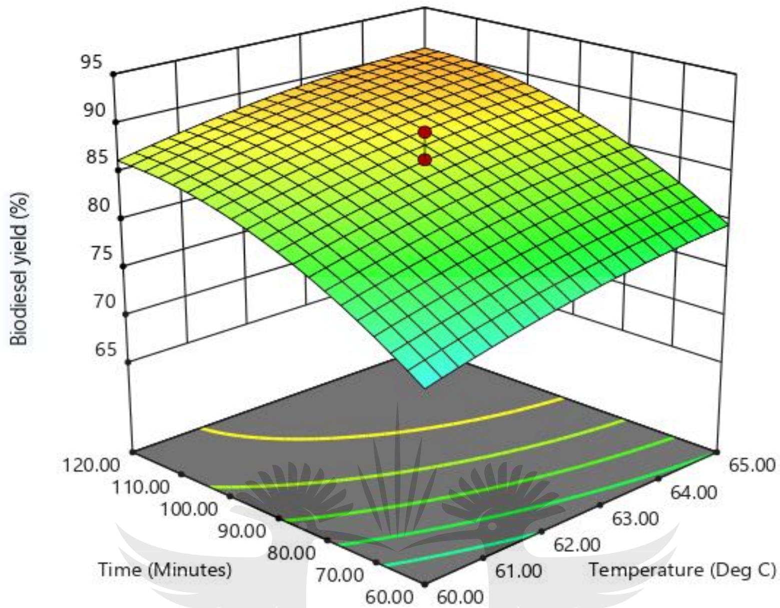

Figure 4.4: 3D response surface plots showing the interactive effect of temperature and time on biodiesel yield

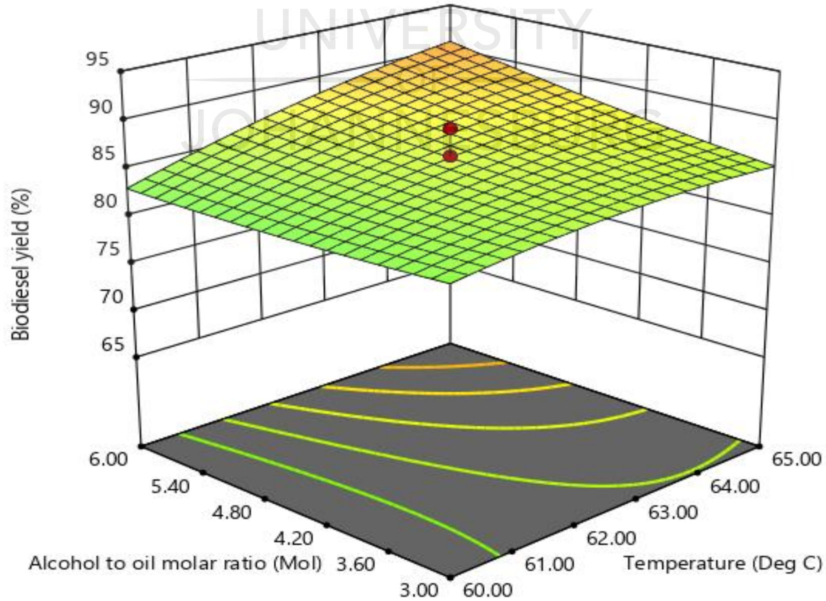

Figure 4.5: 3D response surface plots showing the interactive effect of temperature and alcohol to oil ratio on biodiesel yield

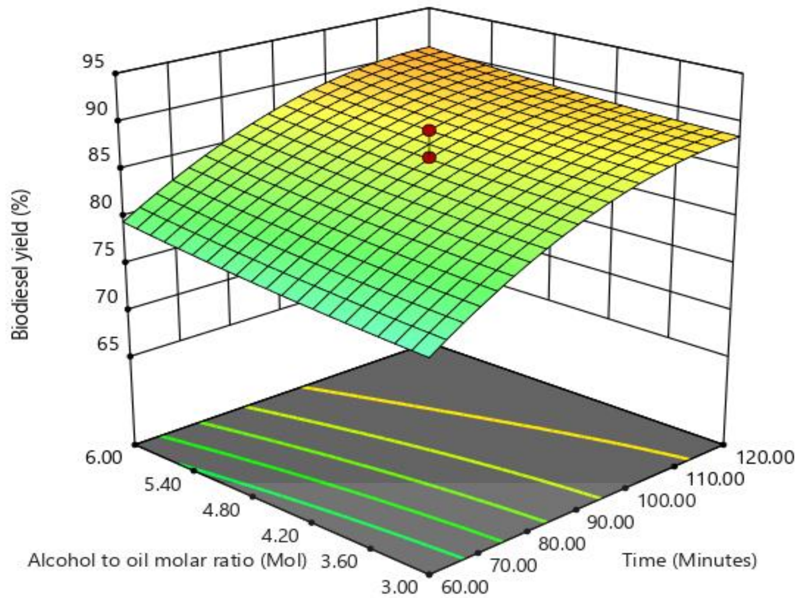

Figure 4.6: 3D response surface plots showing the interactive effect of time and alcohol to oil ratio on biodiesel yield

The interaction and 3D response surface plots of interactive effect of temperature and alcohol to oil ratio on biodiesel yield is presented in Figure 4.5. The biodiesel yield increased with increase in temperature from 60 to 65 ^{o}C and showed unstable yield response as alcohol to oil ratio was increased from 3:1 to 6:1. Increase in alcohol to oil molar ratio resulted in increased biodiesel yield but a noticeable decline in biodiesel production was noticed when alcohol to oil ratio was increased at higher temperatures. The interactive effect of time and alcohol to oil ratio on biodiesel yield is presented in the 3D response surface plots as shown in Figure 4.6. The effects of time and alcohol to oil ratio on biodiesel yield followed the same increasing trend. The biodiesel yield increased with increase in alcohol to oil molar ratio from 3:1 to 6:1 and also increased from 60 minutes progressively to 120 minutes with a declining curve at further increase in reaction time and alcohol to oil ratio beyond 120 minutes and 6:1.

4.4.3 Physicochemical properties of sand apple oil and ethyl ester

The results of selected physicochemical properties of sand apple oil are shown in Table 4.5 while those of sand apple biodiesel compared with that of ASTM D6751 standard is shown in Table 4.6. The specific gravity observed for raw sand apple oil was 0.936 which was slightly higher than 0.887 as reported by Afolabi et al. [22]. The pour point, cloud point and heating value were presented as 3.09, 4.63 and 42.625 respectively.

Table 4.5: Physicochemical properties of sand apple oil

Properties	**Values**
Specific gravity @ 40^{o}C	0.93
Kinematic viscosity @ 40^{o}C (Cst)	44.42
Pour point (^{o}C)	3.44
Cloud point (℃)	4.60
Pour point (^{o}C)	3.44
Acid Value (mgKOH/g)	2.50
Free fatty Acid	1.20 wt. %
Heating value (MJ/kg)	43.46
Refractive index (25℃)	1.65
pH	5.78

Table 4.6: Physicochemical properties of sand apple ethyl ester compared with ASTM D6751 standard

Fuel properties	Sand Apple Biodiesel	ASTM D6751
Specific gravity (40 ^{o}C)	0.899	0.87 to 0.98
Viscosity (40 ^{o}C)	3.905 (cSt)	1.90 to 6.0
Pour point	1.05 (^{o}C)	-15 to 13
Acid value	0.52 (mgKOH/g)	0.80 (max)
pH	7.42	7 to 9
Cloud point	4.78 (^{o}C)	-3.15 to 11.85
Flash point	165.5 (^{o}C)	>120
Cetane number	54.3	>45

These values were similar to the values reported by Alamu et al., (2007) for the properties of raw palm kernel oil. This suggested that raw sand apple oil is suitable for biodiesel production and can be used as an alternative fuel in diesel engines. The kinematic viscosity was reduced from 42 cSt of the sand apple oil to 3.94 cSt of the ethyl ester. This confirmed that transesterification had taken place. The flash point was also reduced from 183^{o}C to 163^{o}C. This reduction makes the fuel more suitable for compression ignition in the engine. The fuel properties were compared with ASTM standards and the selected properties that were determined from sand apple ethyl ester fell within the specifications of ASTM D6751. These properties are also consistent with those reported by Alamu et al. [23]. Furthermore, the flash, cloud and pour points were also comparable to the values obtained for jatropha ethyl ester, sunflower methyl ester and groundnut methyl ester [29].

The fuel properties of sand apple ethyl ester blends with diesel in percentage ratio is shown in Table 4.7. The cloud and pour points were seen to be higher than that of AGO. This may enhance some cold application for their use in diesel engine during cold weather. The results correspond with the findings of other researchers for biodiesel produced from mustard, rapeseed and sunflower oil [30]. The kinematic viscosity of sand apple ethyl ester – AGO blends range from 3.5 to 5.1 cSt. This is slightly higher than that of AGO but fell within the limit specified by ASTM D6751 standard for biodiesel usage as engine fuel. The specific gravity at 15 ^{o}C of sand apple ethyl ester blends with AGO range from 0.9039 to 0.9112 for B5D95 to B25D75. All these fell within the specification of ASTM D6751 and EN 14214 standards for biodiesel. This indicates that sand apple ethyl ester will have similar combustion properties to that of AGO in diesel engines. Similar specific gravity values of jatropha methyl ester as reported by Rao et al. [31]; Ramesh and Venkatachalam [32]; and Rahman et al. [33] were given as 0.86, 0.92 and 0.88 respectively.

Table 4.7: Fuel properties of sand apple ethyl ester - diesel blends

Fuel properties	**B5D95**	**B10D90**	**B15D85**	**B20D80**	**AGO**
Kinematic viscosity @ 40 ℃	3.5	4.3	5.1	4.7	2.95
Specific gravity @ 15 ℃	0.9064	0.9112	0.9102	0.9107	0.86
Heating value (MJ/kg)	44.09	43.79	43.46	43.17	44.41
Flash point(℃)	90	69	67	65	74
Cloud point (℃)	-4	-4.5	-5	-3	-11.9
Pour point (℃)	-7.5	-8	-9	-7	-15.4
Sulphur content (%)	0.006	0.009	0.014	0.016	< 0.01
Fire point (℃)	97	83	76	74	78
Cetane number	49.5	50.8	51.6	52.45	48

4.5 Performance evaluation of sand apple biofuel blends on 5hp diesel engine

The performance test results of a 5Hp diesel engine using AGO and various blends of ethyl ester and AGO under different loads are presented in Table 4.8, 4.9, 4.10, 4.11 and 4.12 respectively. The performance parameters which were tested and computed were torque, speed, fuel consumption rate, exhaust temperature, fuel equivalent power, brake specific fuel consumption, brake power and brake efficiency.

Table 4.8: Performance engine test results using AGO

Parameters	No load	25 % load	50 % load	75 % load	100 % load
Torque (Nm)	7.20	7.85	8.65	9.47	10.10
Speed (rpm)	3000	3000	2995	2995	2990
Exhaust Gas Temperature (^oC)	405	501	610	713	815
Fuel Consumption Rate (kg/s)	2.825×10^{-6}	2.875×10^{-6}	2.992×10^{-6}	3.058×10^{-6}	3.15×10^{-6}
Brake power (kW)	2.26	2.47	2.71	2.97	3.16
Brake Specific Fuel Consumption (g/kWh)	4.50	4.19	3.97	3.71	3.59
Fuel Equivalent Power (W)	125.46	127.68	132.87	135.80	139.89
Brake Thermal Efficiency (%)	18.01	19.34	20.39	21.87	22.59

Table 4.9: Performance engine test results using B5D95

Parameters	No load	25 % load	50 % load	75 % load	100 % load
Torque (Nm)	6.60	6.95	7.60	8.10	8.30
Speed (rpm)	2950	2950	2950	2945	2945
Exhaust Gas Temperature (^oC)	385	401	475	550	660
Fuel Consumption Rate (kg/s)	$2. 925 \times 10^{-6}$	2.998×10^{-6}	3.108×10^{-6}	3.258×10^{-6}	3.442×10^{-6}
Brake power (kW)	2.04	2.15	2.35	2.50	2.62
Brake Specific Fuel Consumption (g/kWh)	5.16	5.02	4.76	4.69	4.73
Fuel Equivalent Power (W)	128.96	132.18	137.03	143.64	151.76
Brake Thermal Efficiency (%)	15.81	16.26	17.15	17.40	17.26

Table 4.10: Performance engine test results using B10D90

Parameters	No load	25 % load	50 % load	75 % load	100 % load
Torque (Nm)	6.00	6.40	7.00	7.45	7.90
Speed (rpm)	2900	2900	2900	2895	2895
Exhaust Gas Temperature (°C)	350	390	440	510	600
Fuel Consumption Rate (kg/s)	3.092×10^{-6}	3.158×10^{-6}	3.258×10^{-6}	3.425×10^{-6}	3.583×10^{-6}
Brake power (kW)	1.82	1.94	2.13	2.26	2.4
Brake Specific Fuel Consumption (g/kWh)	6.12	5.86	5.51	5.46	5.38
Fuel Equivalent Power (W)	135.40	138.29	142.67	149.98	156.90
Brake Thermal Efficiency (%)	13.44	14.02	14.93	15.07	15.29

Table 4.11: Performance engine test results using B15D85

Parameters	No load	25 % load	50 % load	75 % load	100 % load
Torque (Nm)	5.70	6.20	6.90	7.15	7.50
Speed (rpm)	2850	2850	2850	2845	2845
Exhaust Gas Temperature (°C)	345	380	430	500	580
Fuel Consumption Rate (kg/s)	3.292×10^{-6}	3.425×10^{-6}	3.658×10^{-6}	3.758×10^{-6}	3.925×10^{-6}
Brake power (kW)	1.70	1.85	2.06	2.13	2.23
Brake Specific Fuel Consumption (g/kWh)	6.97	6.66	6.39	6.35	6.34
Fuel Equivalent Power (W)	143.07	148.85	158.97	163.32	170.58
Brake Thermal Efficiency (%)	11.88	12.43	12.96	13.04	13.07

Table 4.12: Performance engine test results using B20D80

Parameters	No load	25 % load	50 % load	75 % load	100 % load
Torque (Nm)	5.10	5.80	6.40	6.95	7.20
Speed (rpm)	2850	2850	2850	2845	2845
Exhaust Gas Temperature (^oC)	300	350	385	435	400
Fuel Consumption Rate (kg/s)	3.667×10^{-6}	3.767×10^{-6}	3.925×10^{-6}	4.0×10^{-6}	4.167×10^{-6}
Brake power (kW)	1.52	1.73	1.91	2.07	2.15
Brake Specific Fuel Consumption (g/kWh)	8.68	7.84	7.40	6.96	6.98
Fuel Equivalent Power (W)	158.30	162.62	169.44	172.68	179.89
Brake Thermal Efficiency (%)	9.60	10.64	11.27	11.99	11.95

The torque developed by the engine increased in the engine load for all the fuels. The highest torque value obtained from the running of the diesel engine on biodiesel blends was 8.50 Nm at 100% loading rate when 5% sand apple ester – AGO blend was used. The speed of the engine decreased uniformly with increase in engine load up till 100% load after which the speed remained constant with little or no further increase against the load. The highest speed value obtained was 2950 rev/min at 0% (no load), 25% and 50% loading conditions when 5% sand apple ester – AGO was used to run the engine. When AGO was used to run the engine, the engine developed the highest speed value of 3000 rev/min at no load condition and lowest speed value of 2990 rev/min at full load condition.

It is clear from the results presented in the tables that the exhaust gas temperature increased as the load increased. There was a constant steady increase in exhaust gas temperature from B5 except for slight decrease from 75% to 100% load condition when B20 was used. The maximum exhaust gas temperature of about 815 ^oC at full load was obtained when the engine was run on AGO (Table 8), whereas the maximum exhaust temperatures were 660, 600, 580 and 400 ^oC when the engine was run on 5, 10, 15 and 20% sand apple ester – AGO blend respectively. This is comparable to the results obtained by Prasad et al. [34] who reported that the exhaust temperature increased with increase in operating load for all the blends of neat castor oil with AGO. The fuel consumption rate increased as the loading rate increased. This corresponding increase could be as a result of the increasing mechanical and pumping losses as the speed increased too. This is similar to the report of Wail and Khaled [35] who found that the fuel consumption of a diesel engine fueled by waste cooking oil biodiesel blends increased as the loading condition and biodiesel content in the fuel increases.

Though, the BSFC at any loading condition was found to increase with a higher proportion of sand apple ester in the blend but there was a steady decrease in the value of BSFC at increased loading rate throughout the use of ester blends and AGO. This agreed with the reports of Saravanan et al. [36] who found that BSFC developed by a diesel engine fueled by rice bran ester blends with diesel increased as the percentage of rice bran ester increased in the blends. The BSFC of the biodiesel and its blends is higher compared to the diesel fuel as shown in Figure 4.7. The BSFC was observed to increase with biodiesel content in the blends. This was a result in the decrease in heating values of blends as biodiesel content increased. Lower BSFC of diesel may be attributed to its lower viscosity and higher heating value.

The BTE increased as the load on the engine increased for all the fuel samples. Enweremadu et al. [37] reported that, besides heating values, BTE is the inverse of BSFC which is more suitable to measure the performance of different fuels. Figure 4.8 shows the BTE of sand apple biodiesel and its blends with diesel fuel at different load conditions. The maximum and minimum BTE obtained when the engine was run on biodiesel blends were 17.40% (B5) at 75% of full load and 9.60% (B20) at no load condition respectively.

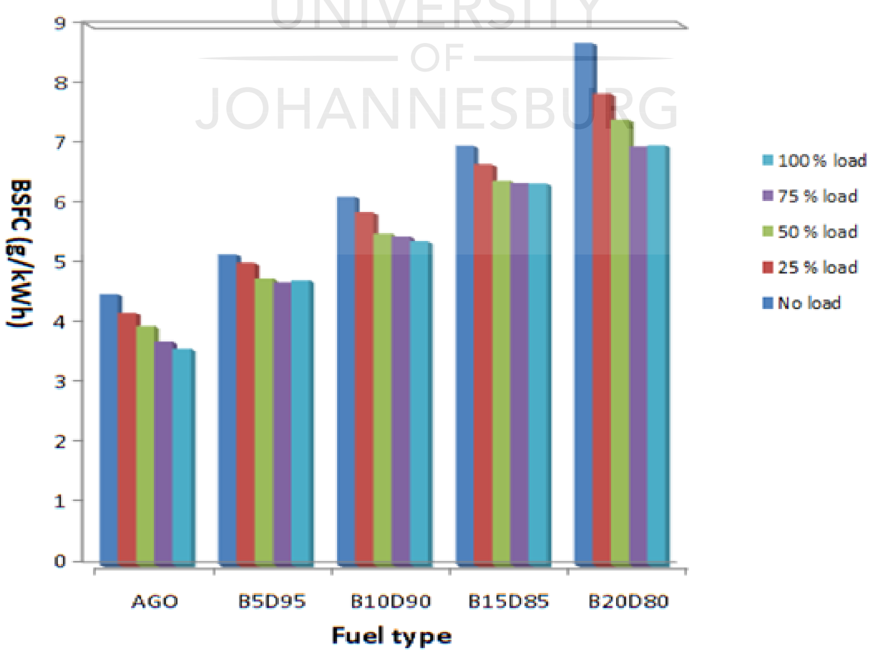

Figure 4.7: BSFC for diesel and biodiesel-diesel blends at different load conditions

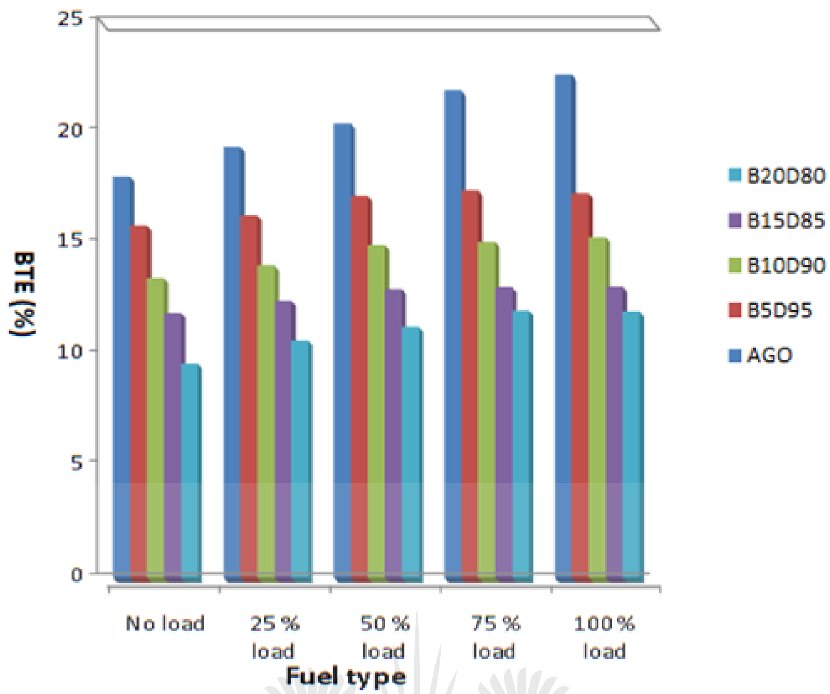

Figure 4.8: BTE for diesel and biodiesel-diesel blends at different load conditions

The BTE of the engine was higher when it was run on pure diesel than when biodiesel blends were used. High Cetane Number (CN) and high oxygenated nature of biodiesel can improve BTE compared to diesel fuel. Usta [38], in an engine performance test using tobacco oil biodiesel, reported that BTE of the diesel engine was enhanced. The maximum BTE (22.59%) was obtained when the engine was run on AGO at full load and was higher than those obtained for all the blends. The B5D95 fuel had close range BTE values with AGO. This was due to smoother lubricating quality of the blends as compared to diesel fuel. These results suggest that fuel blend consisting of 5% biodiesel on volumetric basis can improve the thermal efficiency of the diesel engine.

4.6 Conclusions

This study has dealt with the production of biodiesel from sand apple oil through the investigation of the physicochemical properties and performance evaluation of a 5Hp diesel engine run on blends of biodiesel at various loads.

The performance evaluation showed that the diesel engine produced lower brake thermal efficiency when biodiesel blends were used to run the engine compared to when diesel fuel was used. This has shown that the biodiesel blends are better in terms of the index of flammability because of its high cetane number and high oxygenated nature than that of diesel fuel.

The results obtained also showed that the flash point and fire point values of sand apple ester blends were very similar to that of the AGO. These blends when used in recommended percentages also exhibited combustion properties similar to conventional diesel demonstrating that biodiesel blends can be burned in diesel engines with little or no modification to the engines.

The sand apple seed is already cultivated widely in different parts of the world, particularly Africa. The adoption of efficient cultivation methods of this feedstock makes the production of the sand apple diesel blends either on small farms or on large industrial basis, a viable economic proposition.

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CHAPTER 5

EXHAUST EMISSIONS AND ENGINE PERFORMANCE ANALYSIS OF A MARINE DIESEL ENGINE FUELED WITH *PARINARI POLYANDRA* BIODIESEL-DIESEL BLENDS

It is reproduced from O. Ogunkunle and N.A. Ahmed. (2020): Exhaust emissions and engine performance analysis of a marine diesel engine fueled with Parinari polyandra biodiesel-diesel blends. Energy Reports, 6: 2999 – 3007.

This chapter presents the exhaust emissions analysis of a marine diesel engine fueled with *Parinari polyandra* biodiesel blends. The results show that the carbon emissions are quite low compared to those from the combustion of fossil fuels. The engine performance evaluation also demonstrate the effective performance of the engine while utilizing different blends of *Parinari polyandra*.

The sustainability of biodiesel adoption in diesel engines is dependent on its environmental friendliness relative to lower pollutant emissions. Biodiesel was produced from extracted *Parinari polyandra* oil via alkali catalyzed methanolysis. Performance and emission analysis of a diesel engine was conducted on a diesel engine, operated under different operating conditions, using varied *Parinari polyandra* biodiesel blends. Exhaust emissions, like unburnt hydrocarbons, carbon dioxide, carbon monoxide, sulphur dioxide, and nitrogen oxides were measured. The biodiesel properties were found to be similar to fossil diesel. B10 was found to be the optimal blend in improving the engine performance in terms of speed, power and thermal efficiency. B30 demonstrated stable performance characteristics without any modification of the diesel engine. The exhaust emissions from biodiesel blends combustion were lower than that of diesel, except for nitrogen oxides. High percentage reductions of greenhouse gases, carbon monoxide, and carbon dioxide were recorded at 81.7% and 65.7%, respectively. The utilization of *Parinari polyandra* biodiesel for engine application was found to be a viable means of heightening adoption of sustainable biofuels and minimizing pollutant emissions from the combustion of fossil fuels.

Nomenclature

Symbols

CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
NO_x	Nitrogen oxides
N_2O	Nitrogen dioxide

Abbreviations

ASTM	American society for testing and materials
BP	Brake power
BSEC	Brake specific energy consumption
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
CCD	Central composite design
CI	Compression ignition
FAME	Fatty acids methyl esters
FC	Fuel consumption
FEP	Fuel equivalent power
FFA	Free fatty acid
GHG	Greenhouse gas
HHV	Higher heating value
IC	Internal combustion
PM	Particulate matter
RSM	Response surface methodology

5.1 Introduction

A paradigm shift into complete utilization of biomass-derived biofuels in engine applications is inevitable as green energy policies have already begun in many countries to enforce abolition of products whose combustion have the capacity to pollute the environment. Many developed countries, as a result of global climate issues, have started to show constructive interests in environmental issues and conservation of natural resources [1]. The development of biodiesel industry in many countries has been majorly influenced by the objective to alleviate adverse climate change and environmental pollution. The combustion of biodiesel produced from seed plant oil are carbon-neutral as only the carbon dioxide taken in by the plants through photosynthesis returns to the atmosphere [2].

The continuous rise in the total earth's atmospheric temperature is basically attributed to the greenhouse effects occasioned by increased levels of CO_2 and other air pollutants. Greenhouse gases, comprising CO_2, CH_4, and N_2O, are major gaseous emissions that bring about global anthropogenic air pollution [3]. The use of fossil fuels is one major cause of release of GHGs, which have the potentials to cause global warming. The ozone layer is depleting, glaciers are melting, and our environmental ambience is becoming polluted. As the population index increases over the years and industrial actions heighten to meet up with daily modern demands of people, the level of release of GHGs are higher than ever before [4], [5]. Thus, there is a present and continuous need for production and use of alternative and sustainable cleaner fuels which are renewable and also does not contribute to the release of GHGs into the atmosphere.

Owing to this pressing need, there is an imminent worldwide transformation from fossil hydrocarbons to clean energy sources with renewable energy increasing within the power sector with a 7.5% growth rate per annum, a figure that account for over 50% of the increase in power generation [6]. For several years, low-cost renewable energy sources that are environmentally friendly have been developed for different applications. Seed oil biodiesel, a cheap renewable biofuel with clean burning characteristics, has been found to have the production capacity to reduce the worldwide reliance on petroleum diesel fuels. Research studies continue to show that biodiesel products from several seed oils have fuel properties equivalent to those of diesel fuel, with lower harmful emissions, when used in unmodified diesel engines [7]–[9].

The utilization of *Parinari polyandra* as an industrial crop for renewable clean biofuel production and engine applications is still at its infancy and of little research interest. Relevant information is still very much needed on its utilization as an industrial crop. *Parinari polyandra* is a bioenergy crop whose potential has not been widely utilized. The utilization of the biodiesel produced from it has not been fully explored to fully demonstrate its engine performance and emission analysis. Experimental studies of performance and emission characteristics of *Parinari polyandra* biodiesel needs to be established on practical details of its application in a diesel engine, and that, to the best knowledge of the authors, is yet to be reported. However, experimental assessment of the performance and exhaust characteristics of this renewable biofuel is the pivot objective of this research for the purpose of providing more useful information to support its performance and environmental friendliness (reduction of carbon footprints).

Parinari polyandra is one of the untapped promising feedstocks for biodiesel production in Africa. *Parinari polyandra* is a feedstock with relative high oil yield suitable for biodiesel and oleochemical with an average oil yield between the range of 40% and 60%. The biodiesel produced from the oil was found to have similar properties to that of fossil diesel making it a quality clean fuel for engine applications. The production and utilization of this industrial crop can offer new prospects for agriculture and potential market for it. This will allow farmers to become part of a larger inductrial complex and expand beyond their traditional role of food production and evolve into skilled producers of oil rich crops. The full exploitation and utilization of this plant seed oil will help contribute immensely to the development of biodiesel industries in Africa and help reduce unemployment while providing income earner opportunities for farmers in the rural areas.

Experimental studies on the application of *Parinari polyandra* biodiesel as engine fuel are scarce, more particularly the emissions charatceristics of its combustion in diesel engines. The aim of this study is to determine the emission and performance rate of *Parinari polyandra* biodiesel blends combustion in a diesel engine. The experimental work was carried out on a marine diesel engine using varied blends of the biofuel. It was found that the engine performance improved while run on blended fuel with no modification of the engine. The performance characteristics of the diesel engine showed similar characteristics to the values obtained from running the engine on AGO. All the exhaust emissions, mostly especially the oxides of carbon, except NOx, were found to be lower than those released from diesel.

5.2 Experimental

Oil was extracted from *Parinari polyandra* seeds using solvent extraction method. Biodiesel was prepared from the oil using a validated optimized transesterification method for producing biodiesel from *Parinari polyandra* oil. Engine tests were conducted on a marine diesel engine using blends of *Parinari polyandra* biodiesel. The performance data were computed to assess the engine operational characteristics comparative to fossil diesel while the exhaust emissions were measured and recorded concurrently.

5.2.1 Oil extraction and biodiesel production

Oil was extracted from *Parinari polyandra* seeds using solvent extraction process used by Ogunkunle and Ahmed [10]. The experiment was carried out using a seed/solvent ratio of 0.06 g/ml, extraction temperature and time of 70°C and 5 hrs. N-hexane was used as the extraction solvent owing to its low-cost and relative high comparative performance against other types of solvents in extraction of oil from plant seeds [11]. The Free Fatty Acid (FFA) of the oil, which was measured to be approximately 1.05%, is a guarantee for a direct alkali catalysis of transesterification reaction required for conversion of the oil to biodiesel. Two step transesterification processes are recommended for biodiesel production from oils with acid values greater than 2.0 mg/KOH/g [12]. Transesterification is generally required for the lowering of the viscosity and improving the cetane number and heating values of biodiesels produced from plant oils. These are desirable properties suitable for plant oil-derived biodiesels in their applications as engine fuels.

Biodiesel was produced at optimized reaction conditions reported by Ogunkunle and Ahmed [10]. The transesterification reaction was done using reaction variables, viz, 61.19°C temperature, 60 minutes reaction time and catalyst concentration of 1 wt%. Methanol was chosen as the alcohol because of its shorter functional chain and fast reaction rate. These reactions were performed using potassium hydroxide as catalyst with excess alcohol to oil molar ratio of 6:1 for favourable forward reaction kinetics. Selected physicochemical properties of the biodiesel were determined using American Society for Testing and Materials (ASTM) standard procedures. The specific gravity of the samples was measured at room temperature using a specific gravity bottle (size 0.795-0.910, accuracy 0.001). The viscosity was determined using a calibrated glass capillary viscometer. The flash point was determined using a Pensky-Martens Closed Cup Tester. The cetane number was determined using ASTM D613 - 18a standard of injecting the fuel samples into a diesel engine with variable compression ratio using fuels of known CN as references. The acid value was determined using the ASTM D664 potentiometric titration standard. The cloud point was determined using the ASTM D2500 method of visually inspecting for a haze to become visible as the sample was cooled in a refrigerator. The pour point was determined using the ASTM D7346 - 15 standard of ascertaining the flow of the fuel at temperature between 1 °C or 3 °C intervals. The FAME contents of *Parinari polyandra* biodiesel were identified using GCMS by comparing the chromatogram peaks with retention times of standards available in the NIST libraries (NIST 14 Mass Spectral Library & Search Software – Version 2014) with a match acceptance criterion above a critical factor above 90%.

5.2.2 Engine tests using blended *Parinari polyandra* biodiesel

The engine tests were conducted on a 206 kW six-cylinder diesel engine integrated with a Froude hydraulic dynamometer with a maximum power of 283.5 kW. The engine specifications are provided in Table 5.1. The engine was instrumented with a thermocouple, load cells, a tachometer, a Froude hydraulic dynamometer, and a calibrated tank with an accuracy of ± 0.5 for measuring the fuel consumption. The fuel consumption was measured, based on volumetric measurement approach, as a measure of flow rate-mass per unit time [13]. The engine setup and instrumental devices are displayed in Figure 5.1. Performance evaluation of the engine was carried out using different fuel blends varied between zero percent (0%) and 30% of biodiesel volume with diesel. The automotive gas oil (AGO/Diesel #2) with specifications that conform to the regulations of the Department of Petroleum Resources (DPR) was obtained from a TOTAL fuel station. Higher percentage composition of biodiesel (B30) in diesel blends was allowed in this experiment to determine the influence on the engine performance and emission characteristics, and to ascertain if higher blends can be utilized in diesel engines without any major modification or negative impact on the engine. Even though ASTM standards allow fuel blends between 5% and 20%, more research works are evolving to test suitable biodiesel blends in diesel engine in order to establish their performance and emissions quality. According to Kousoulidou et al. [14], a maximum 30% biodiesel blend with fossil diesel can still be permitted as long as there is no cold-flow inhibition. In comparison with EN590, running diesel engines on higher blends containing about 30% of biodiesel still falls within legal limit of the European Standards [15].

Table 5.1: Diesel engine specifications

Parameters	Specifications
Model	407T
Manufacturer	ADE
Number of cylinders	6
Cycle	4-Stroke
Aspiration	Turbocharged
Max. engine output	206 kW @ 2200 rpm
Max. torque	1140 Nm @ 1200 rpm
Bore stroke	125/155 mm
Wet mass	815 kg
Total piston displacement	11,412 litres

Figure 5.1: Engine setup and instrumental devices

All the tests were conducted at constant torque operating condition from 20Nm to 100Nm in steps of 20Nm. The engine torque was varied through a controlled water flow into the dynamometer. The movement of water into the dynamometer was used to obtain different engine torques, which could be read directly from the instrumentation board. Preliminary tests were carried out to ensure a controlled water flow into the dyno and regulate well balanced torque needed for the engine. Torques ranging between 20 Nm and 100 Nm were used in the experiment as loading conditions for the engine. After each engine test, the corresponding speed, fuel consumption (FC), brake power (BP), brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC), fuel equivalent power (FEP) and brake thermal efficiency (BTE) were obtained and computed for each corresponding torque. After the collection of data, the whole step was repeated for all tested torques. All the performance parameters were determined using the method adopted by Ogunkunle and Ahmed [16]. The fuel consumption rate, equivalent power, brake power, brake specific fuel consumption, brake thermal efficiency were all determined using Equation 5.1, 5.2, 5.3, 5.4, 5.5, and 5.6.

$$M_f = \frac{m(kg)}{t(s)} = \frac{V\ (m^3) \times \rho(kg/m^3)}{t(s)} \qquad \text{Eqn. 5.1}$$

$$P_f = H_g \times M_f \qquad \text{Eqn. 5.2}$$

$$BP = \frac{NT}{14300} \qquad \text{Eqn. 5.3}$$

$$BSFC = \frac{M_f}{\mathrm{BP}} \qquad \text{Eqn. 5.4}$$

$$BSEC = BSFC \times H_g \qquad \text{Eqn. 5.5}$$

$$\eta_{\mathrm{bth}} = \frac{\mathrm{BP}}{FEP}\ X\ 100 \qquad \text{Eqn. 5.6}$$

Where:

M_f = *fuel consumption rate (kg/s)*

V = *volume of fuel used per time (m^3)*

ρ = *density of fuel (kg/m^3)*

t = time taken (s)

P_f = *fuel equivalent power (W)*

H_g = *heating value (MJ/kg)*

BP = brake power (kW)

N = speed (rpm)

T = torque (Nm)

BSFC = brake specific fuel consumption (kg/kwh)

BSEC = brake specific energy consumption (kJ/kWh)

η_{bth} = *brake thermal efficiency (%)*

5.2.3 Exhaust emissions analysis

The concentrations of gaseous emissions, such as total hydrocarbons (THC), carbon dioxide (CO_2), (CO), and nitrogen oxides (NOx), were detected and measured in percent of total volume (%) using a portable ULTRA TUNE 4 Gas Analyzer while that of sulphur dioxide (SO_2) was measured in Parts per Million (ppm) using a ToxiRae Pro SO_2 Toxic Gas Monitor. An Exhaust Gas Temperature Gauge Kit was used to measure the exhaust gas temperature.

5.3 Results and Discussion

The results of extracted oil, biodiesel yields, engine tests and emission analyses are discussed in the following sections.

5.3.1 Extracted *Parinari polandra* oil and biodiesel

The extraction of oil from crushed *Parinari polyandra* seeds produced a clean neat oil with relatively low FFA. Approximately 60% of neat *Parinari polyandra* oil was obtained after extraction. The properties of the raw oil are provided in Table 5.2. An average of 91% biodiesel yield was recovered from transesterification of *Parinari polyandra*. The biodiesel yield showed that *Parinari polyandra* oil is a promising raw material for production of biodiesel with comparable yields with biodiesel obtained from some promising African seed oil such as loofah 88% [17], jatropha 95.8% [18], *Hura crepitans* 93.97% [19], *Thevetia peruviana* 94.33% [20]. The average values determined for fuel properties of the biodiesel are recorded in Table 5.3. Also, the properties of blended fuel samples and diesel fuel are presented in Table 5.4.

Table 5.2: Physicochemical properties of *Parinari polyandra* oil

Property, unit	Value
Specific gravity @ 40^{o}C	0.903
Viscosity, cSt	51.67
Acid value, mgKOH/g	1.43
Moisture content, %	0.39
Free fatty acid, wt%	1.05
Saponification value, mgKOH/g	165.4
Iodine value, g/100g	89.72

Table 5.3: *Parinari polyandra* biodiesel properties

Fuel property, unit	Value
Specific gravity @ 40 ^{o}C	0.871
Viscosity @ 40 ^{o} C, cSt	3.87
Pour point, ^{o}C	1.00
Acid value, mgKOH/g	0.58
pH	7.62
Cloud point, ^{o}C	4.67
Flash point, ^{o}C	136
Heating value, MJ/kg	45.52
Cetane number	48.4

Table 5.4: Properties of *Parinari polyandra* biodiesel blends and diesel fuel

Fuel properties, units	Diesel	B10	B20	B30
Specific gravity @ 40 °C	0.866	0.889	0.926	0.933
Viscosity @ 40 °C, cSt	3.05	3.57	3.83	3.89
Flash point, °C	76	64	71	92
Cloud point, °C	-11.5	-7	-3.5	-1.5
Pour point, °C	-14.8	-7.4	-5.6	-2.4
Sulphur content, %	< 0.01	0.007	0.005	0.003
Cetane number	49	51.4	53.1	54.8
Heating value, MJ/kg	44.5	42.26	40.57	37.5

The properties of the blended fuel samples, as measured in conformity with ASTM and EN standards, were found within acceptable standards for use as an engine fuel. The chromatogram for *Parinari polyandra* biodiesel, which shows a neat FAME profile content, is presented in Figure 5.2. The major FAME compounds that were detected in the biodiesel samples from the GC chromatogram were majorly palmitic acid methyl ester (methyl palmitate), 9,12-Octadecadienoic acid methyl ester (methyl linoleate), 9-Octadecenoic acid methyl ester (methyl oleate) and Stearic acid methyl ester (methyl stearate). The retention time and m/z values for methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate were obtained to be 21.83, 23.60, 23.65, 23.88, and 74, 150, 152, 199, respectively. The percentage compositions of the biodiesel FAME profile are 10%, 62.5%, 45%, and 5%, for methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate, respectively.

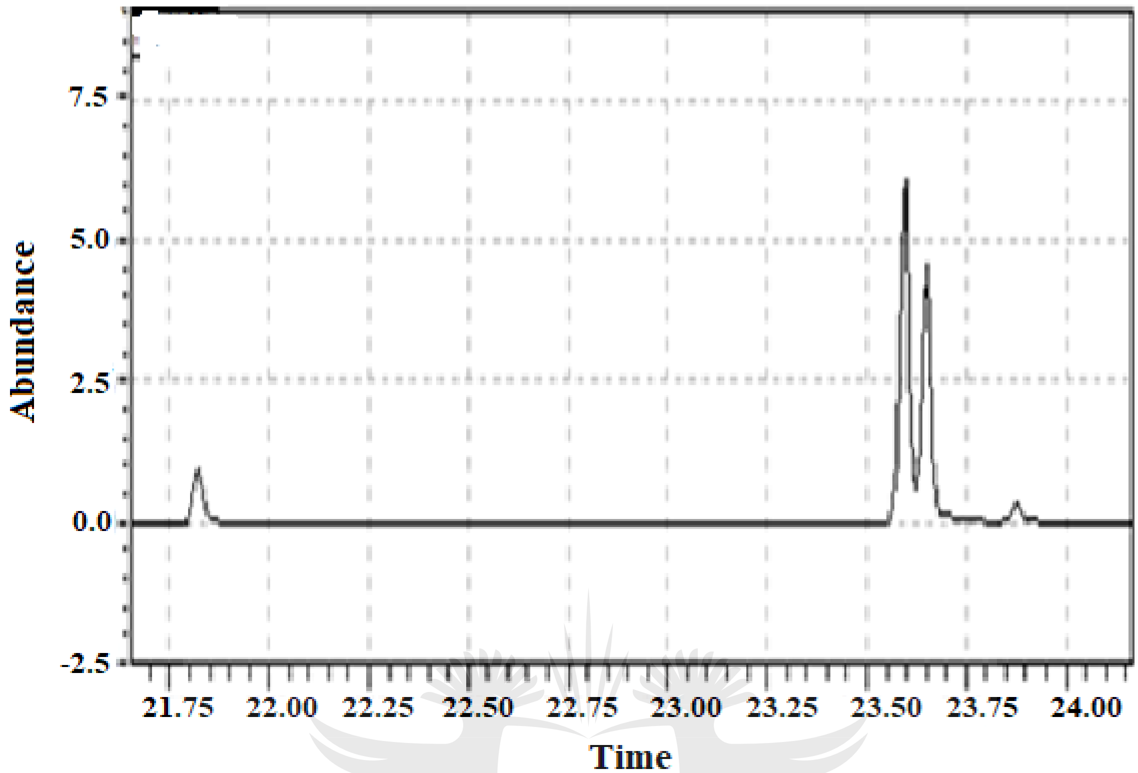

Figure 5.2: Chromatogram for *Parinari polyandra* biodiesel

5.3.2 Engine performance results

The diesel engine performance results for the different levels of applied torque are described in the following subsections. The relationships between applied torque and all the measure engine performance characteristics are presented in Figure 5.3.

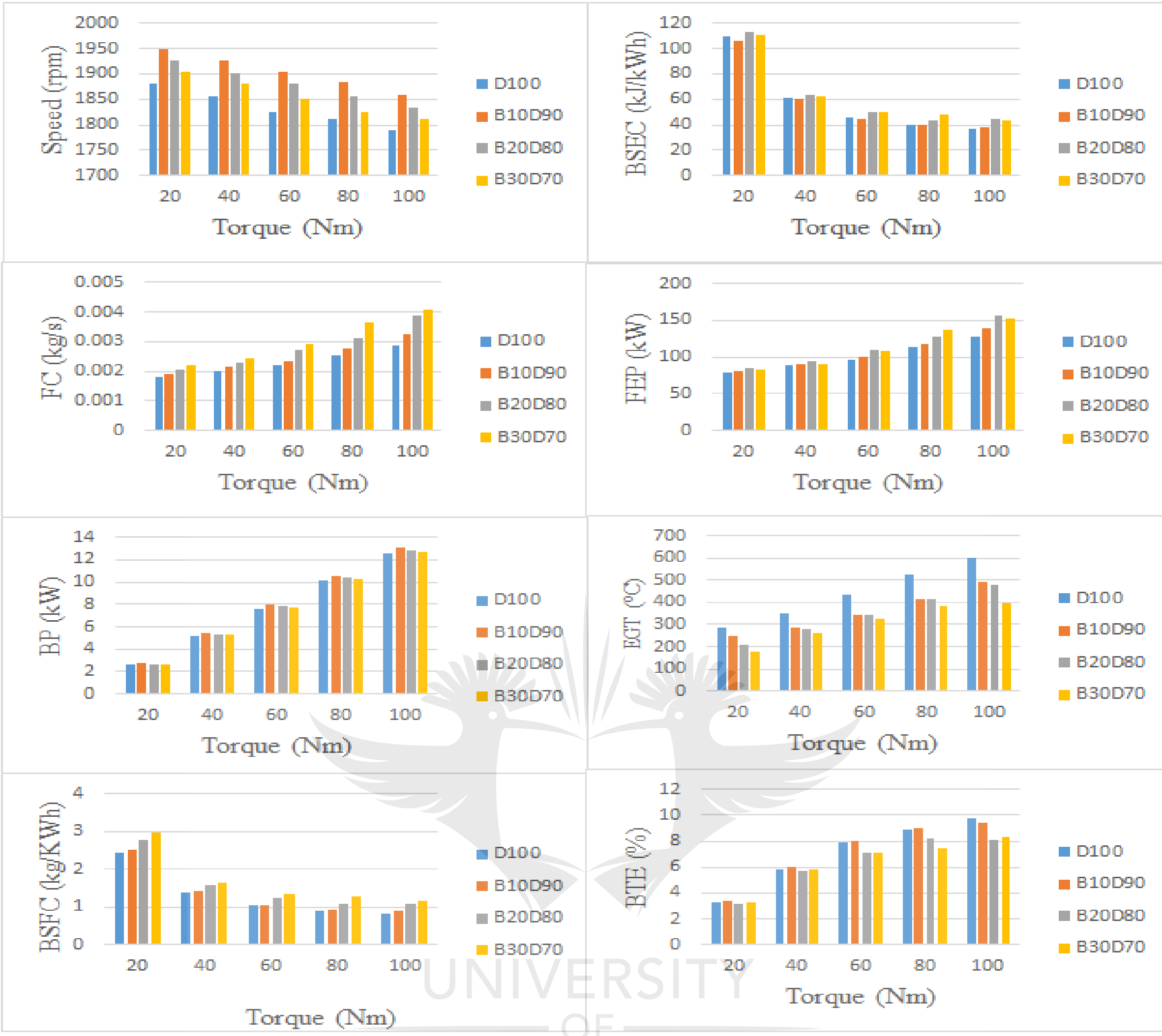

Figure 5.3: Engine performance data vs brake torque

5.3.2.1 Engine speed

A noticeable decline in the speed of the engine was observed as the torque increased. CI engines have been reported to reduce at maximum speed values as a result of volumetric efficiency and augmentations in mechanical losses owing to the increase in the equivalent engine speed [21]. The reduction in speed, which was more evident at higher torques, was due to the high resistance the engine shaft initially encountered [16]. At higher torques with more biodiesel content in the fuel, the effect of the resistance was negligible due to better air to fuel ratio and better efficiency existing at high load conditions. The engine had the highest speed when it was run on B10 as compared to diesel fuel and other fuel blends. A similar study performed on a six-cylinder direct injection diesel engine revealed that increase in the volume of biodiesel in fuel blends caused a slight decrease in both power and torque over the entire speed range of the engine test [22].

5.3.2.2 Fuel consumption

From the results obtained, the FC rate decreased as torque increased. At lower torque, the engine is invariably at its lower maximum power. High fuel volumetric efficiency is necessary to achieve high torque in engines. Better volumetric efficiency means more air; more air means more fuel can be burned; more fuel burned means bigger explosion; bigger explosion means more torque. Invariably, as the engine torque increased, the FC rate became less in order to achieve proper air-fuel mixture rate for improved and better combustion. It can be observed that biodiesel blend 30B had the highest FC rate. Similar results were observed for high fuel consumption as biodiesel content in fuel increases [16], [23], [24]. This can be further explained based on variance in heating values and energy densities of the fuels. The heating value of biodiesel is lower than that of diesel because of its higher oxygen content [25], [26]. As a result of this, more quantity of biodiesel is required to be burnt to release the amount of energy equivalent to the one released by diesel. Also, the densities of biodiesel blends and petroleum diesel vary as observed in the fuel properties test carried out. The higher the density of the fuel, the higher the viscosity [27]–[29]. The presence of biodiesel in the blended fuels suggests higher density value which in turn increases the viscosity and affects the fluidity of the fuel [30], [31]. High fuel viscosity has been reported to be a major factor causing poor fuel atomization which may lead to higher fuel consumption and gaseous emissions [32].

5.3.2.3 Brake power

The engine BP output can be seen to increase as the torque increased and cause slight decrease as the biodiesel percentage increases. The higher value for the power at higher torque is because more power is generated as the torque is being increased. The decrease in BP observed as fuel blends increased could be associated with lower heating value of biodiesel than diesel fuel. The engine had better brake power when it was run on B10 than the other fuel samples. Speed and power of the engine decrease slightly for the fuel blends because the output power reduces with respect to energy content [33].

5.3.2.4 Brake specific fuel consumption

In contrast to the FC efficiency getting better with respect to increasing torque of the engine, a falling trend was recorded in the values obtained for the BSFC. The BSFC decreased in values owing to more brake power being generated at higher torques than at lower torques. As the applied torque increases, the exerted load on the engine requires more engine power at a relatively lesser rate of fuel consumption [34]. There was a decreasing trend in the BSFC of all the fuel samples as torque values increased. Higher BSFC is required at low engine load conditions because the temperature of the cylinder is lesser when compared to engine loads which brings about incomplete combustion of fuel [35]. The results also showed that BSFC increased as biodiesel content increased in the blended fuel. As shown in Figure 5.3, lower BSFC was recorded from combustion of diesel at every applied torque. This was largely influenced by the higher heating value, lower viscosity, and high index of hydrogen efficiency of diesel [36].

5.3.2.5 Brake specific energy consumption

The BSEC can be seen to increase as fuel blends increased and decrease as the applied torque increased. Energy is consumed at lower torques because the energy stored in fuel is quickly released through combustion at lower speed [37]. Because biodiesel blends contain more carbon atoms than biodiesel, the blended fuel burns more quickly at lower torque and is more consumed, reducing the energy consumption efficiency as the torque increased. More energy is consumed as the fuel blends increased because of the lower heating values and higher viscosity than diesel fuel.

5.3.2.6 Fuel equivalent power

As the biodiesel amount increased in the blended fuel, the FEP increased because there is better combustion which enabled the engine to produce higher power stroke. High FEP is also supported by the increasing torque. Increasing the blends tend to increase the smoothness of the fuel and produced desirable lubrication.

5.3.2.7 Exhaust gas temperature

The exhaust gas temperature was directly proportional to the torque. The maximum and minimum EGT values were obtained at 100 Nm and 20 Nm when diesel fuel and 30% biodiesel blend was used to run the engine respectively. A general increase in EGT was noticed as the torque increases and decreases as biodiesel content increased in the blends. The increase is brought about by more brake power that is generated as the torque increases. The diesel fuel generated more EGT because it comprises of more energy per gallon than biodiesel, and the heating values are quite more than all the blended fuels.

5.3.2.8 Brake thermal efficiency

A continuous increase in the engine BTE for all the fuel samples was observed as the applied torque increased. From the results, the blended fuels have almost the same BTE as pure diesel fuel (D100). The efficiency of these fuels can be taken to have the same performance on the engine without any adverse effect. More of the heat energy stored in the blended fuel are being released as biodiesel blends increase in the combusted fuel. This implies that more of the heat energy from the blended fuel can be well converted to mechanical energy.

5.3.3 Emissions analysis results

The emissions analysis results are presented in the following subsections. Overall, it was noticed the emissions from the diesel engine vary owing to the differences in the fuel properties of the blended biodiesel. The average emissions from combustion of biodiesel blends compared with pure diesel is summarized in Figure 5.4. All the exhaust emissions were found to be lower than that of diesel except NO_x. Biodiesel obtained from *Parinari polyandra* oil transesterification has proved to be a viable and efficient fuel with comparative potential to reduce gaseous emissions except that of NO_x. Sundar and Udayakumar reported that an evaluation of recent works on biodiesel combustion in diesel engines generally decreased the emission without any negative effect on engine performance [38], [39]. Generally, blending of biodiesel with diesel can increase the cetane number, as well as the oxygenated chemical compounds responsible for the proper fuel combustion [12], [40]. The different emission values obtained from each fuel blends at different experimental torques are plotted in Figure 5.5.

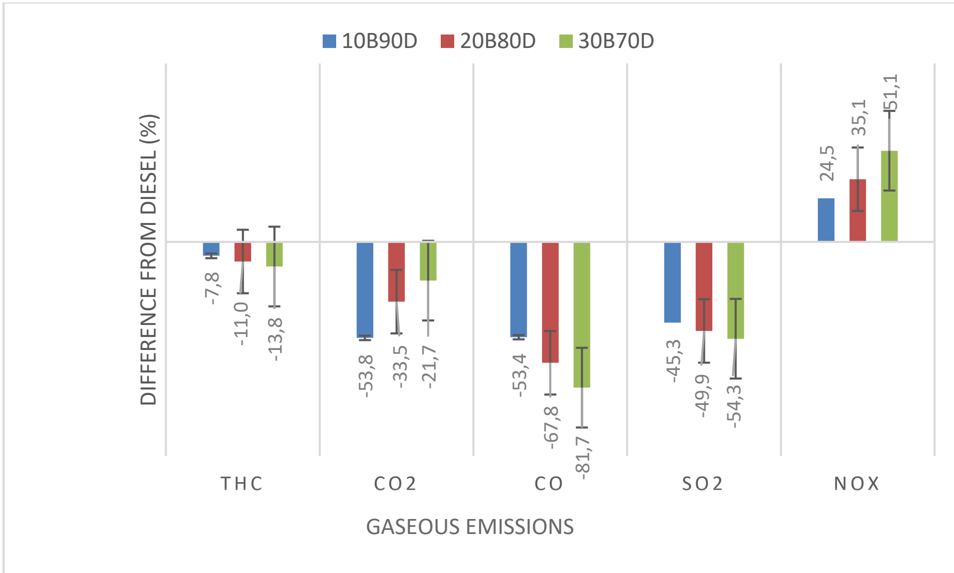

Figure 5.4: Averaged exhaust emissions of biodiesel blends compared with diesel

Figure 5.5: Engine exhaust emissions vs brake torque

5.3.3.1 THC emission

The THC emissions from biodiesel blends combustion were found to be generally lower than those released from diesel combustion. As the torque increases, the THC emissions generally decreases. More heat is generated at higher torque which was responsible for the combustion of the hydrocarbon contents of the blended fuel. As shown in the plot, the THC emissions reduced as the volume of *Parinari polyandra* biodiesel increased in the blended fuels. On average, the THC were found to reduce by 7.8%, 11.0%, and 13.8% while using B10, B20, and B30, respectively. The THC concentrations was found to decrease significantly when using 30B. These results are corroborated by the findings of Ulusoy et al. [41]. Ulusoy et al. [41] reported that increase in engine speed during the combustion of waste cooking oil biodiesel in a diesel engine has a thermo-chemical effect on THC emissions. The THC emissions is a function of oxygen and temperature of the combustion environment. Basically, higher oxygen and temperature are meant to ensure complete combustion of the fuel constituents thereby reducing THC emissions. The higher the content of biodiesel in the fuel, the more oxygen content available for combustion. Biodiesel contains about 11% oxygen which aids the combustion of the fuel resulting in lower THC emissions [42]. The degree of complete combustion of fuel is dependent on the oxygen content available in the combustion chamber and thereby reduces the amount of unburnt hydrocarbons present in the emissios [43].

5.3.3.2 CO_2 emission

The CO_2 emissions, which is mostly a common product of every combustion process, was observed to decrease generally as the torque increases. Based on the higher oxygen composition of biodiesel than diesel, the CO_2 emissions from the combustion of the blended fuels were lower than the diesel fuel [44]. On average, the CO_2 were found to reduce by 53.8%, 33.5%, and 21.7% while using B10, B20, and B30, respectively. The combustion of the higher biodiesel blends at higher torques tends to initiate higher heat release to favour complete fuel combustion in the engine as a result of the oxygenated nature of the blended fuel. The CO_2 emissions was found to be more than CO as biodiesel volume increased in the fuel blends. As a result of higher oxygen molecules bound to the chemical structure of biodiesel, excess oxygen in the fuel blends ensures complete combustion of the fuel components making carbon and oxygen react to form CO_2 [35], [45]. Lower oxygen content has been reported to be a major factor behind more production of CO in IC engines

[46]. From the plot, it is evident that CO_2 emission is highest in 100D while lower CO_2 emissions were observed in biodiesel blends with higher percentage (30B) of biodiesel. This is an evidence of the organic and oxygenated nature of the renewable fuel at increasing level of blending.

5.3.3.3 CO emission

The CO emission fluctuated as the torque increased in value. A noticeable decline was observed at first when the torque increased from 20 Nm to 40 Nm, and then increased afterwards for 100D, 10B and 20B, with the exception of 30B. Altogether, CO emission decreased as the volume of *Parinari polyandra* biodiesel increased in the blends and was significantly profound in 20BD and 30BD blends. On average, the CO were found to reduce by 53.4%, 67.8%, and 81.7% while using B10, B20, and B30, respectively. This can be explained by the excess air ratio of the combustion as biodiesel content increases [47], [48]. More oxygen is available for combustion in the cylinder and more carbon molecules will be oxidized compared to diesel. The CO concentrations was found to increase predominantly for 0B (100D) which was quite higher than emissions collected from other blended biodiesel fuels.

5.3.3.4 SO_2 emission

The SO_2 emissions was found to gradually decrease as torque increased. It was observed that SO_2 emissions from combustion of fossil diesel was higher compared to that from combustion of biodiesel blends. The increase in SO_2 emission while using diesel fuel is greater by about 5% than that of biodiesel blends at every increase in torque. On average, the SO_2 were found to reduce by 45.3%, 49.9%, and 54.3% while using B10, B20, and B30, respectively. Abdul Rahim [49] reported a percentage reduction of 14.45%, 14.62%, and 21.39% of SO_2 from engine combustion of 25% blend of methyl esters each of jatropha oil, palm oil, and coconut oil, respectively. SO_2 emission was noticeably higher in the exhaust from combustion of 30B than other blends. Since the feedstock oil for the biodiesel production does not contain sulphur, the reduction of SO_2 in the emissions from combustion of biodiesel blends is justified.

5.3.3.5 NO_x emission

A slight increase in NO*x* (a combination of nitric oxides, nitrogen dioxides and particulate matter) emissions was detected for all the blended fuels used in running the test engine. A progressive increase in NO*x* emissions was noticed from 0B to 30B as the torque increased in values, even though there was an insignificant difference in the NO*x* emissions at all levels of biodiesel blends (10B – 30B). On average, the NO*x* were found to increase by 24.5%, 35.1%, and 51.1% while using B10, B20, and B30, respectively. The formation of higher NO*x* is proportional to the amount of oxygen content in biodiesel. Based on the biological nature of biodiesel, it contains more oxygen than diesel. The NO*x* increase was brought by the increase in heat released by the combusted fuel at high torques when the combustion fuel temperature is high, making atmospheric nitrogen combust with oxygen at the exhaust pipe [46], [50]. The increase in NO*x* emissions is in agreement with recent scientific studies on emissions analysis from combustion of biodiesel in CI engine [46], [51]–[55]. However, more fuel treatment for quality combustion and eradication of NO*x* emissions from the diesel engine is necessary for efficient operation of diesel engines running on renewable biodiesel fuel. Examples of this fuel enhancement strategy are the addition of fuel additives such as CN improvers and oxygenates, and the use of emulsified fuels to make biodiesel-diesel fuel combustion occur at low temperatures [56], [57].

5.4 Conclusions

From the results obtained and the analysis carried out, the following conclusions can be drawn from the study:

- The study has shown that an alkali methanolysis was effective in production of biodiesel from *Parinari polyandra* oil, with the fuel properties conforming to the ASTM D6751 standards.
- B10 was found to be the optimal blend in improving the engine performance in terms of speed, power and thermal efficiency.
- B30 demonstrated stable performance characteristics without any modification of the diesel engine. This indicated that *Parinari polyandra* B30 does not have any negative impact on the engine and can be used in existing vehicular diesel engines without any major modification with the goal of mitigating offensive and harmful emissions from fossil diesel fuel.
- The engine had the highest speed when it was run on B10 as compared to diesel fuel and other fuel blends.
- It was observed that biodiesel blend 30B had the highest fuel consumption rate.

- The engine had better brake power when it was run on B10 than the other fuel samples.
- The BSFC increased as biodiesel content increased in the blended fuel. There was a decreasing trend in the BSFC of all the fuel samples as torque values increased.
- The BSEC and FEP were found to increase as fuel blends increased and decrease as the applied torque increased.
- A general increase in EGT was noticed as the torque increased and decreased as biodiesel content increased in the blends.
- An increase in the engine BTE for all the fuel samples was observed as the applied torque increased.
- The emissions from the diesel engine were found to vary owing to the differences in the fuel properties of the blended biodiesel.
- All the measured emissions were found to be lower than that of diesel except NO_x. Compared to diesel fuel, the THC, CO_2, CO, SO_2 emissions were found to reduce by 7.8%, 53.8%, 53.4%, 45.3%; 11.0%, 33.5%, 67.8%, 49.9%; and 13.8%, 21.7%, 81.7%, 54.3%; while biodiesel-diesel blends of B10; B20; and B30; were used respectively. The NO_x was found to increase by 24.5%, 35.1%, and 51.1% while biodiesel-diesel blends of B10; B20; and B30; were used respectively.
- The partial inclusion of *Parinari polyandra* in fuel blends for engine application was confirmed to be a potential sustainability for reduction of carbon footprints in our society.

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CHAPTER 6

CONCLUSION AND FUTURE WORK

6.1 Conclusions

In this thesis, optimized biodiesel production from *Parinari polyandra* seed oil and its application in diesel engine was carried out. This study has been carried out to provide adequate information on the oil yields from *Parinari polyandra* seeds, biodiesel production from the oil, and application as an engine fuel. Different regression models have been developed for the prediction of biodiesel production from *Parinari polyandra* seed oil. The optimization of biodiesel yields with validation experiments were carried out to achieve optimal biodiesel yields from the seed oil. The biodiesel produced was tested in engines with suitable properties similar to those of fossil diesel.

In line with the first objective of this work, the RSM was efficient in the model prediction for optimized biodiesel yield from *Parinari polyandra* oil owing to the close agreement between the optimized and validated results. The fuel properties of *Parinari polyandra* biodiesel were found to be within the ASTM D6751 standard.

In line with the second objective of this work, regression models for predicting *Parinari polyandra* biodiesel yields under different reaction conditions were developed. The model generated was simple and time saving. There was close agreement between the optimized and validated yields and RSM was found to show faster efficiency than the conventional duplication methods of using lengthy iteration methods of calculation to solve differential equations.

In line with the third objective of this work, the performance evaluation showed that the diesel engine could be run successfully on biodiesel blends without any modification of the engine. The results showed that the biodiesel blends are better in terms of the index of flammability because of its high cetane number and high oxygenated nature than diesel fuel.

In line with the fourth objective, the exhaust emissions of a diesel engine was analyzed while it was operated on *Parinari polyandra* biodiesel blends, which have suitable fuel properties conforming to the ASTM D6751 standards. The results revealed that biodiesel–diesel blends, up to B30, demonstrated similar performance characteristics with that of diesel in an unmodified diesel engine. B30 can be used as a possible substitute to diesel fuel for better fuel economy and engine efficiency. This showed that B30 does not negatively impact the engine and can be used in vehicular diesel engines without any significant modification coupled to mitigate offensive and harmful emissions from fossil diesel fuel. B10 has the highest heating value and was found to be the optimal blend with better performance output in speed, brake power, and thermal efficiency.

Conclusively, the production of biofuels has become one of the indispensable solutions to energy challenges facing humankind. Biodiesel is considered a good replacement for fossil fuels due to its suitable properties and ability to burn clean. The utilization of such biofuels can reduce the over-dependence on fossil fuels whose resources are limited, expensive, non-renewable, and associated with negative environmental impacts. However, one of the major problems facing its adoption globally is the high cost of production which primarily centers on the sourcing and preparation of the feedstock. Suppose the high energy costs associated with producing these biofuels are reduced via sourcing and utilization of novel feedstock and the development of low-cost, efficient methods. In that case, underutilized plant residues and oilseeds can be explored for production and brought to the fore. Also, their industrial relevance can be established for increased and quality biofuel production.

6.2 Future work

The future of biofuel production from inedible oil seeds looks very promising, considering the associated benefits. This work may be extended in various ways: 1) development of fast and energy-efficient synthetic pathways for higher oil extraction *Parinari polyandra* seeds and biodiesel yields via transesterification, 2) the development and use of novel heterogeneous catalysts with efficient, active sites in the oil-biodiesel conversion process, 3) the use of higher blends of the biodiesel in CI engines, 4) combined application of RSM and evolving AI algorithms in modeling the biodiesel production parameters, and 5) modeling the engine performance using design of experiment approach for determination and modeling of optimal performance characteristics.

APPENDIX A

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Review article

A review of global current scenario of biodiesel adoption and combustion in vehicular diesel engines

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A B S T R A C T

Delving into the current chronicles of research findings, explorations of biodiesel production and utilization in diesel engines have been at the forefront of sustainable and creative energy discovery. Far beyond the problems of energy crises, renewable biodiesel offers unlimited solutions to the associated issues of depleting reserves and harmful emissions with fossil fuels. In overcoming the increasing energy demand owing to the growing worldwide population, the emergence of biodiesel and its global adoption in the transportation sector has brought along a reliable fuel supply that can be used in diesel engines without any modification. This study explores the comprehensive utilization of biodiesel as engine fuel and shows the prevalent global current adoption in automobiles engines. The production rates are documented globally and promoting policies that are being mandated in many countries of the world are discussed as well. The improved state of things in achieving effective power conversion from biodiesel combustion with minimal emission impact on the environment has been documented. Worldwide technological adoption has been captured according to production rate, usage and legislation favouring the economic feasibility of diesel engines that are suitable for biodiesel with little or no modification. With the progress made so far by many researchers to establish biodiesel as a viable engine fuel, coupled with the ability to eradicate environmental issues like global warming and sustainability, it is evident that biodiesel is designed to make a future energy investment and significant addition to the domestic and industrial automobile economy.

Contents

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Appendix

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Response surface analysis for optimisation of reaction parameters of biodiesel production from alcoholysis of *Parinari polyandra* seed oil

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ABSTRACT

Availability of information on the efficiency of applied conditions to biodiesel synthesis from diverse seed oil can establish optimal biodiesel yield from favourable reaction variables. The effect of reaction parameters; temperature, time and catalyst amount, were varied on biodiesel yield from alcoholysis of *Parinari polyandra* oil using potassium hydroxide as catalyst. Maximum biodiesel yield of 95.62% was obtained from the experimental results. Analysis of Variance revealed that the reaction variables had significant effects on biodiesel yield. Data analysis predicted an optimal biodiesel yield of 92.75% at reaction conditions of 61.20°C temperature, 60 min, and 1 wt% of catalyst amount. Validation experiments of the optimal conditions gave an average biodiesel yield of 91.72%. The study established optimal conditions of temperature, time, and catalyst amount for biodiesel production from *P. polyandra* oil. The fuel properties of the biodiesel fell within the standards of the American Society for Testing and Materials D6751.

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Parinari polyandra oil; alcoholysis; reaction parameters; optimal; validation

1. Introduction

Over the past decade, human demand for energy has reached a revolutionary stage. Accelerated development of social civilisation in terms of transportation and industrialisation, has been a major boost in the demand for energy consumption (Zou et al. 2016). The modern man cannot live without petroleum owing to his complete dependence on its products for transportation, heating, lighting, and industrial production. Owing to the accelerated development of social civilisation since the industrial revolution in the late 18th and 19th centuries, energy has become a crucial determinant for continued economic growth and improved standard of living (International Energy Agency 2011). The International Energy Agency (IEA) report estimated that the world will require 50% more energy in 2030 than today of which 45% will be consumed by China and India (Shahid and Jama 2011; Atabani et al. 2012).

The growing demand for power has been a significant justification for utilisation of renewable energy. The production of biofuels is highly region-specific and is affected by the production of agricultural products (REN21 2015). Global biofuels production has reached 135 billion litres having increased about 2% compared to 2015 (Clean Energy Council 2016). This increase was due mostly to a comeback in biodiesel production after a fall in 2015. The power generated from renewable sources increased to 112 GW by an estimated 6% in 2016 (Kairies, Dirk, and Sauer 2015). United States, with an output of 68 TWh, was the leading country for electricity generation from biomass,

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Appendix

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Performance evaluation of a diesel engine using blends of optimized yields of sand apple (*Parinari polyandra*) oil biodiesel

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ABSTRACT

Sand apple oil seed that has relatively high oil yield is widely cultivated in Africa. Evaluation of the performance of sand apple ethyl ester is a missing link in establishing it as an alternative fuel for use in diesel engines. Performance evaluation of optimized yields of sand apple biodiesel was, therefore, conducted in a diesel engine at various loading rates. Oil was extracted from sand apple seeds via solvent extraction. A Central Composite Design was used to optimize biodiesel yields from sand apple oil transesterification using potassium hydroxide as catalyst. Engine tests were carried out to evaluate the performance of a stationary 5Hp diesel engine starting from 0% to 100% load conditions. The engine was run with diesel and four different blends of diesel/biodiesel. Values for speed, torque, fuel consumption rate and exhaust temperature were determined. The optimum biodiesel yield recorded was 94.6%. The torque, speed, fuel consumption rate and exhaust temperature recorded for best engine performance for all blends were 8.50 Nm, 2950 rpm, 2.925×10^{-6} kg/s, and 300 °C. The evaluated engine parameters showed sand apple biodiesel can be burned in diesel engines using appropriate blending ratio without any modification to the engine.

1. Introduction

Biodiesel refers to a non-petroleum based fuel consisting of alkyl ester derived from *trans*-esterification of triglyceride or by the esterification of Free Fatty Acid with low molecular weight alcohols [1]. In recent times, remarkable utilization of plant oil derived from inedible oil seeds has taken place [2]. Biodiesel is considered [3] as an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as ethanol. Biodiesel comprises of alkyl fatty acid (chain length C_{14}–C_{22}) esters of short-chain alcohols, primarily, methanol or ethanol. A renewable fuel such as biodiesel, which produces lower exhaust emission is in high demand worldwide [4].

Oil prices have been volatile over the years. West Texas Intermediate (WTI) crude oil price is still hovering over $65 per barrel in the first quarter of 2018, a much higher figure of nearly $28 per barrel recorded in 2001 (www.macrotendo.net/1369/crude-oil-price-history-chart). Such increases in price and consumption of petroleum products in developing countries are the reasons why alternative fuels particularly those that are renewable and have positive environmental benefit are required [5]. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs in these countries can provide an alternative fuel for diesel engine.

Biodiesels are mostly characterized by their density, viscosity, cloud and pour points, cetane number, distillation range, flash point, acid value, ash content, sulphur content, carbon residue, and higher heating value (HHV). Most researches on bio-renewable fuel have been highly focused on producing biodiesel from vegetable oils [4] using various biodiesel production methods amongst which transesterification using alkali catalyst which gives high level of conversion of triglycerides to their corresponding ethyl ester feature prominently [6].

Some of the important parameters affecting the ester yield during the transesterification reaction are the reaction time, molar ratio of alcohol to vegetable oil, stirring rate, catalyst concentration, and reaction temperature [7]. Biodiesel (B100) specifications are given in Table 1. These parameters conform to the biodiesel standard, The American Society for Testing and Materials (ASTM D 6751).

This standard prescribes the parameters that pure biodiesel (B100) must meet before it can be used as a pure fuel or blended

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Appendix

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Exhaust emissions and engine performance analysis of a marine diesel engine fuelled with *Parinari polyandra* biodiesel–diesel blends

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ABSTRACT

The sustainability of biodiesel adoption in diesel engines are dependent on its environmental friendliness relative to lower pollutant emissions. Biodiesel was produced from extracted *Parinari polyandra* oil via alkali catalyzed methanolysis. Performance and emission analysis of a diesel engine was conducted on a diesel engine, operated under different operating conditions, using varied *Parinari polyandra* biodiesel blends. Exhaust emissions, like total hydrocarbons, carbon dioxide, carbon monoxide, sulphur dioxide, and nitrogen oxides were measured. The biodiesel properties were found to be similar to fossil diesel. B10 was found to be the optimal blend in improving the engine performance in terms of speed, power and thermal efficiency. B30 demonstrated stable performance characteristics without any modification of the diesel engine. The exhaust emissions from biodiesel blends combustion were found to be lower than that of diesel, except nitrogen oxides. High percentage reduction of greenhouse gases, carbon monoxide and carbon dioxide, was recorded at 81.7% and 65.7%, respectively. The utilization of *Parinari polyandra* biodiesel for engine application was found to be a viable means of heightening adoption of sustainable biofuels and minimizing pollutant emissions from the combustion of fossil fuels.

1. Introduction

A paradigm shift into complete utilization of biomass-derived biofuels in engine applications is inevitable as green energy policies have already begun in many countries to enforce abolition of products whose combustion have the capacity to pollute the environment. Many developed countries, as a result of global climate issues, have started to show constructive interests in environmental issues and conservation of natural resources (San Miguel et al., 2013). The development of biodiesel industry in many countries has been majorly influenced by the objective to alleviate adverse climate change and environmental pollution. The combustion of biodiesel produced from seed plant oil are carbon-neutral as only the carbon dioxide taken in by the plants through photosynthesis returns to the atmosphere (Zhou and Thomson, 2009).

The continuous rise in the total earth's atmospheric temperature is basically attributed to the greenhouse effects occasioned by increased levels of CO_2 and other air pollutants. Greenhouse gases, comprising CO_2, CH_4, and N_2O, are major gaseous emissions that bring about global anthropogenic air pollution (US EPA, 2017). The use of fossil fuels is one major cause of release of GHGs, which have the potentials to cause global warming. The ozone layer is depleting, glaciers are melting, and our environmental ambience is becoming polluted. As the population index increases over the years and industrial actions heighten to meet up with daily modern demands of people, the level of release of GHGs are higher than ever before (McKenzie et al., 2011; Bais et al., 2018). Thus, there is a present and continuous need for production and use of alternative and sustainable cleaner fuels which are renewable and also does not contribute to the release of GHGs into the atmosphere.

Owing to this pressing need, there is an imminent worldwide transformation from fossil hydrocarbons to clean energy sources with renewable energy increasing within the power sector with a 7.5% growth rate per annum, a figure that account for over 50% of the increase in power generation (BP Energy, 2018). For several years, low-cost renewable energy sources that are environmentally friendly have been developed for different applications. Seed oil biodiesel, a cheap renewable biofuel with clean burning characteristics, has been found to have the production capacity to reduce the worldwide reliance on petroleum diesel fuels. Research studies continue to show that biodiesel products from several seed oils have fuel properties equivalent to those of diesel fuel, with lower harmful emissions, when used in unmodified

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