Effects of Pyrolyzed Municipal Solid Waste Feedstocks as Energy Sources for Non-Road Diesel Engine, Combustion, Performance and Emissions Characteristics Using Biodiesel Blended Ratios

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As the candidate's supervisor, I agree to the submission of this Thesis.

Prof. F.L Inambao

Name of Supervisor Signature Date: 21ST MAY 2021

Declaration 1 -Plagiarism

I, **Maroa Samwel Semakula** declare that:

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Declaration 2 -Publications

This section presents the articles that form part of the research presented in this thesis.

ISI/DoHET Accredited Journals

Publication 1
Maroa, S., & Inambao, F. (2020). Waste to Energy Feedstock Sources for the Production of Biodiesel as Fuel Energy in Diesel Engine - A Review. *Advances in Science, Technology and Engineering Systems Journal*. DOI:10.25046/aj060147, https://www.astesj.com/publications/ASTESJ_060147.pdf
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Publication 2
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International and DoHET Accredited Conferences

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Maroa, S.S. and Inambao, F. L. (2019). Assessing the Effects of Engine load on Compression Ignition Engines Using Biodiesel Blends. Proceedings of the 17th Conference on the Industrial and Commercial Use of Energy, Riverclub, Observatory Cape Town South Africa: 25 & 26 November 2019: Proceedings available online. https://aiue.co.za/call-for-papers-congress/

The candidate is the main and corresponding author for all the publications and conference presentations while Prof. Freddie L. Inambao is the supervisor.

DEDICATION

This work is dedicated to my late mother Selina Sibora Marwa and my father Charles Marwa.

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ABSTRACT

Biodiesel oil blending is not a new concept in the study of biofuels and production. Blending is a chemical process of two or more different feedstocks comingled in varying proportions in the production of a new oil or fuel blend possessing different physico-chemical properties. Since fuel properties and the physico-chemical configuration of each feedstock vary from source to source, blending improves and enhances these properties. Therefore, the combination of different feedstocks enhances and improves properties of the initial parent feedstock, by adapting to improved and high-quality attributes. Worldwide, the sources of biodiesel production has been centred on edible and non-edible plants such as sunflower, canola, soybean, moringa, Jatropha, and so on. However, in the recent past, there has been a renewed shift into biomass and other recycled waste sources for biodiesel production and utilization. Waste to energy is a critical area of research and study in this present work as it intends to fill in these gaps by emphasising the shift to biodiesel production from non-plant-based sources. This shift will increase food security by discouraging the contribution of commercial farming for the production of biodiesel. This work contributes to improving environmental protection by reducing pollution from municipal solid waste found in landfills and other waste management sites. Waste resources such as waste cooking oil, waste engine oil, waste tyre oil and waste plastic oil converted into energy provide many alternatives in reducing wastage. By promoting use of these resources, this study aims at increasing environmental awareness and sustainability by using waste as an energy resource. This focus will open up socio-economic opportunities in recycling besides the academic and research impacts. By employing blending strategies using these waste feedstocks (engine oil, cooking oil, plastic oil and waste tyre oil using pyrolysis thermal processes), the study will improve the initial poor chemical properties which will confer improved engine performance with emissions reduction especially those dealing with sulfur and other contaminants from municipal solid waste streams. The production of pyrolyzed municipal solid waste (MSW) oil will be *ex-situ* and *in-situ* (the former means after production while the later means before production of biodiesel). This research work will assist in determining standard procedures and sequencing to obtain working ratios of the blending processes and techniques of biodiesel production.

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CHAPTER 1: INTRODUCTION

1.1 Introduction and Background

The history of biodiesel fuel goes back to the discovery of the diesel engine by German engineer Rudolf Diesel in the 1890s. The use of vegetable oil as a fuel was first introduced at the world exposition in Paris in 1900. This was at the request of the French government, which had an interest in development fuels of local origin for its African colonies for energy and power generation independence. There were a total of five engine models displayed and tested during the exposition [1]. In the next five years, after the Paris exhibition, Diesel improved his engine's efficiency from 26 % to 75 %. This culminated in the publishing of two articles in 1912 [2, 3]. In America, the demand for biofuels increased after the mass manufacture of the automobile by Henry Ford from 1890 to 1920.

In America Adolphus Busch and Clessie L. Cummins and other engine manufacturers led the way in pioneering work on the diesel engine models. In recognition of this effort, the Cummins engine is named in honour of Cummins's pioneering work in diesel engines. However, the discovery of "black gold" and its development by 1940s changed the course of biofuels. There were a number of forced design changes to accommodate petroleum fuels due to their low viscosity and fewer starting problems. This weakened the use and acceptability of biofuels in North America and Europe [4, 5]. After the Second World War, several studies reported the use of vegetable oil in diesel engines and some of the operational difficulties encountered with their application as combustion fuels [6-9]. These reports led to the Belgium patent 422877 in 1937 to Chavanne.

After the Second World War alternative fuel research was in a hiatus until the energy crisis of the 1970s when [10] came up with work on esters of vegetable oil. Using sunflower oil in a diesel engine, they reported that use of sunflower methyl esters eliminated the problems of viscosity and operational issues. Nevertheless fossil based fuel has qualities that readily appeal to users such as availability, good combustion properties and high heating values [11]. Therefore, fossil-based fuels have played a major role in the growth of industries, transportation and agricultural activities, with demand being stimulated by less-developed countries expanding urbanization and industrialization while catching up with the highly industrialized

countries. However, the future of fossil fuel as a primary source of energy is not sustainable due to depletion in relation to demand.

Energy estimates from the international energy agency puts the estimates of the growth of energy consumption at 53 % by the year 2030 [12, 13]. In the USA the energy information agency (EIA) projects liquid fuel consumption to increase from 86.1 million barrels per day to 110.6 MBD by the year 2035 [14]. The depletion of fossil fuel reserves has caused world energy forums and decision makers to seriously consider alternatives. Therefore, there has been a rapid development in research of green alternative fuel energy sources which are renewable, domestically available, environmentally friendly and technically feasible. Biodiesel therefore has become a viable technical choice for researchers as they contain characteristics and identical physical properties to fossil fuel especially diesel fuel.

Thus, biodiesel has a promising future as a source of alternative fuel energy especially in developing countries who carry a heavy burden of importation of liquid petroleum fuel for energy. This is besides the environmental impacts and effects of pollution on public health [15]. Fossil oils are facing erratic energy prices as well as uncertainty of future supplies due to unending internal conflicts, turmoil and war in major oil producing countries. These factors all combine to create a very compelling case for alternative renewable fuels [16].

Diesel engines are inherently lean burn engines and emit relatively low carbon dioxide emissions compared to petrol propelled internal combustion engines. Other advantages offered by diesel engines include high thermal efficiencies, durability and construction robustness [17]. However, there is pressure to phase them out, based on environmental and human health issues due to the high levels of NO_X, smoke and PM emissions. Diesel engines have been shown to run stably on most medium blended ratios of waste plastic oil, although they produce more NO_X, UHC and CO emissions. However, to stabilize them, for good performance for higher blend ratios, researchers have suggested modification of injection timing to achieve good engine performance. This improves stability without needing to upgrade engine fuel systems, engine component modification or fuel alteration through addition of additives [18].

In the literature, review of injection timing has been reported to affect performance. For example, using blends of WPPO and Jatropha ratios of 20 % tyre oil and 80 %. Jatropha ester oil produced lower fuel consumption, CO, UHC and PM. However it was observed that NO_X emissions increased significantly Kumar and Saravanan [20] found an increase in the BTE and

NO_X emissions, thus concurring with the findings of Sharma et al. (2013) on emissions of NOx, although on fuel consumption, CO, and UHC the authors reported decreased emission results.

Globally the fuel energy and transport sector has witnessed a continuous increase in stringent emission regulations enacted by global industrial powers such as the United States of America and the European Union environmental protection agencies and the G-7 and G-20. Though widely acknowledged as a primary transport engine, the diesel engine has withstood the worst accusation as a polluting engine. The diesel engine emits emissions, which contribute to environmental degradation, and air pollution from NO_X gases, and other exhaust emissions. Therefore, alternative fuels are critical in reducing energy consumption thus decelerating atmospheric carbon concentration globally. The rapid growth in the road transport sector and increase in global fossil oil consumption is an environmental concern, as their rapid expansion erodes all the technological developments and improvements thus so far achieved in the war against pollution from diesel-propelled engines.

Across the globe, significant resources have been mobilized to find alternative sources of energy. Different regions and countries have focused attention on source of supply and technical processes that give them comparative advantages. In sub-Saharan Africa, renewable energy alternatives for transportation have huge potential sources, one of which is biodiesel derived from municipal solid waste sites, waste tires, waste engine used oil and waste cooking oil. Considerable research has been conducted in this area but some gaps have not been addressed. There is a clear need to conduct evaluations that enable precise technical classification of the performance and emission of biodiesel derived from the waste sources mentioned above. This is one of the gaps this thesis intends to respond to by creating an alternative to the growing demands of energy needs.

The search for alternative sources of fuel energy and supply has been accompanied by a marked increase in food insecurity. This makes the use of biodiesel fuel from plant based feedstocks a less viable option due the fact that this can lead to higher food prices [21]. Therefore, waste plastic and waste biomass from municipal solid waste management sites is increasingly popular as an alternative source of fuel and energy. This is due to the widespread use of plastics in daily activities, besides the greater environmental effects of plastic waste and its disposal costs. There are two types of plastics widely used today, namely, PVC (poly vinyl chloride) and HPDE (high-density polyethylene), also known aspolyethylene high-density (PEHD) [22]. Plastic waste has wreaked havoc on the environment due to improper disposal and the fact that

plastics are petroleum based which makes them non-biodegradable [23]. Plastic waste accounts for between 8 % to 12 % of global waste with a projected increase of between 9 % to 13 % annually by the year 2025 [24, 25].

In South Africa 24,115,402 metric tonnes of general waste is produced annually. However, from the data obtained nationally it is evident that only 1,446,924 metric tonnes is recycled representing only 6 % of all solid waste generated. The growth of plastic waste nationally will average annual increment projection of 2 % to 3 % of waste plastic production [26] as shown in Figure 1. This makes a promising case for the sustainability of managing waste into energy by using modern technology to degrade waste plastic mass into energy. Techniques such as pyrolysis result in hydrocarbons similar in quality and characteristics to petroleum fuels [27, 28].

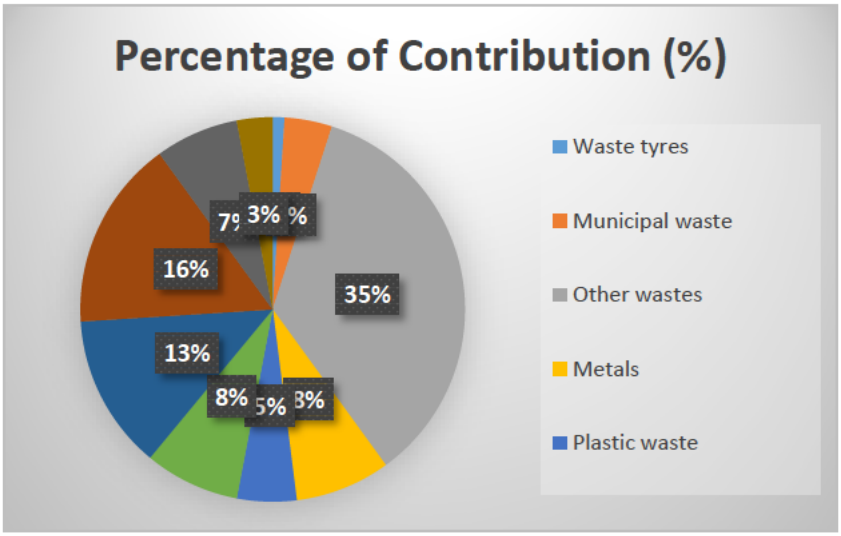

Figure 1.1Percentage contribution of each waste stream of general solids in municipal waste (South Africa, 2017) [29]

Coined originally from two Greek words 'pyro' which means fire and 'lysis' which means decomposition [30], pyrolysis is a chemical decomposition process of making fuel from plastic waste by heating. Geyer et al. [31] recommend this as one of the solutions to ending the menace of plastic waste and plastic littering. Pyrolysis is a process where assorted waste plastic is fed into a reactor where it is decomposed into other forms at high temperatures. Temperatures can range from 400 ºC to 600 ºC or sometimes 900 ºC at atmospheric pressure in the absence of oxygen for 3 to 4 hours [32]. The aim is to produce oil and other plastic waste by-products. In order to maintain and sustain such high temperatures during the pyrolysis reaction [33]

catalysts are employed, such as calcium oxide (CaO), silica dioxide (SiO_2), aluminium tri-oxide (Al_2O_3) and zeolite ($NaAlSi_2O_6$-H_2O) [34]. This process breaks down large molecules of plastic waste into minute molecules resulting in hydrocarbons with smaller molecular mass. For example, the addition of ethane enables the application of fractional distillation to obtain fuels, chemicals and by-products. The pyrolysis yield by weight is made up of liquid hydrocarbons in a mixture form of petrol, diesel and kerosene at 75 %, while residue coke and the remaining balance as liquidified petroleum gas (LPG), comprise 5 % to 6 % [35]. Pyrolysis is highly recommended by most researchers and commercial entities as a method for utilizing waste plastic and transforming it into biodiesel products and by-products. This is due to its cost effectiveness, high energy conversion rate and high yield compared to other methods of plastic waste extraction [36].

The wide acceptance and use of biodiesel has led to the adoption of NO_X reduction techniques and other processing techniques such as blending. NO_X reduction techniques are necessary due to the high oxygen content inherent in most biodiesel fuels which leads to high NO_X formation. This is due to reactions during high temperature combustion which increase the formation of NO_X [25]. Diesel fuels and biodiesel fuels both require fuel additives to improve engine lubricity, ignition qualities and better mixing. Oxygenates in biodiesels are providing a promising future to reduce PM emissions since the O_2 content aids in better combustion. However, there is a clear trade-off between PM and NO_X as suggested in the findings of [37, 38]. However, engine and component modifications such as thermal barrier coating have been investigated which improve engine efficiency with minimal increase in brake thermal efficiency, but with a drop in the fuel economy, NO_X and smoke density emissions [39].

1.2 Problem Statement

Fossil-based fuels have played a major role in the growth of industries, transportation and agricultural activities. However, the future of fossil fuel as a primary source of energy is not sustainable due to depletion, high demand, and high consumption of fuel energy. Fossil-based fuels have qualities that make them appealing to the user including availability, good combustion properties and high heating values ([11]. Energy estimates from the international energy are for growth of energy consumption at 53 % by the year 2030 [12, 13]. In the USA, the energy information agency (EIA) projects liquid fuel consumption will increase from 86.1 million barrels per day to 110.6 MBD by the year 2035 [14].

The depletion of fossil fuel reserves has occupied world energy forums and decision makers for a considerable time. This has led to rapid development of research in green alternative fuel energy that is renewable, domestically available, environmentally friendly and feasible technically. Technically biodiesel is a good choice for researchers because biodiesels contain identical characteristics and physical properties to fossil fuel especially diesel fuel. This makes the future of biodiesel more viable and more promising as sources of alternative fuel energy especially in developing countries [15].

The combination of different feedstocks (hybridization) enhances and improves the properties of the initial parent stock by adapting to improved and high properties. Worldwide the sources of biodiesel production have centred on edible and non-edible plants such as sunflower, canola, soybean, moringa and Jatropha. However, there has been a shift to recycled waste sources for biodiesel production and utilization as energy. This is an important area of research and study covered by this work as it intends to fill in these gaps by shifting the focus of biodiesel production to non-plant-based sources. This increases food security by discouraging use of commercial farming for the production of biodiesel and improves our environment by reducing pollution caused municipal solid waste management sites.

Through using waste cooking oil, waste engine oil, waste tire oil, waste plastic oil, and other waste biomass, this work intends to increase environmental awareness and sustainability, and to show that there are job opportunities in recycling besides the academic work. This work identifies waste plastic oil as a waste-to-energy resource intended to improve some of the poor properties of this fuel to offer improved engine performance and reduction in emissions. By blending, the oils produced from municipal solid waste ex-situ and in-situ (the former means after production while the later means before production of biodiesel). This work will evaluate the proper procedural sequence of extracting the product, obtaining the working ratios using sequential blending, then testing the fuel. The findings will be disseminated via publications in peer-reviewed journals, book publications and conferences.

This will enable us to filter the data by comparing it with local South African standards and regulations along with global standards and regulations. Through this, challenges can be identified and plans of action mapped out to tackle these challenges. It is necessary to identify and assemble the right set of tools and techniques to conduct studies on these biodiesel feedstock sources in a manner that optimizes them as available resources. The stated goal of this work was to extract, produce and test biodiesel from municipal solid waste plastics, waste

tires, waste engine oil and waste cooking oil using a commercial pyrolysis process, compare performance data with international standards and regulations while also identifying numerical pathways for further studies that could potentially lead to developing an optimal combustion strategy. If these goals are realized, they could secure a viable renewable energy source for sub-Saharan Africa.

1.3 Aims and Objectives

The main aim of this research was to produce, evaluate and test the viability of pyrolyzed plastic municipal solid waste feedstocks oil as energy fuel resources in diesel engines (compression ignition engine). Evaluation of waste plastic biodiesel blends included performance parameters as well as combustion and emissions characteristics. While doing this research it was prudent to identify the difficulties associated with the application of pyrolyzed municipal solid waste feedstocks blends in real time diesel engine environment applications. The following were the specific objectives of this study:

- To characterize the pyrolyzed plastic municipal solid waste oil and its diesel fuel blends in order to determine chemical and physical properties.
- To determine the effect of pyrolyzed plastic MSW oil blends with diesel fuel on the performance and emission characteristics of a diesel engine.
- To investigate if pyrolyzed plastic MSW oil blends can be used (B100) in a diesel engine without engine modification.
- To ascertain which of the pyrolyzed plastic MSW oil blend ratios are most suitable to replace diesel in CI engines and provide: 1. Hight thermal efficiency. 2. Minimum brake specific fuel consumption of the engine, 3. Minimum smoke density, 4. Low emissions.

1.4 Research Motivation and Significance of Study

Ever-increasing expenditure on energy and fuels is causing economic imbalance, price hikes and hardships for people. The issue of energy subsidies is causing an enormous burden on personal and national financial management and allocation of resources. Therefore, addressing this issue is one of the major challenges for our governments, especially in low-income and developing economies such as South Africa.

It is politically very difficult to reduce subsidies and hence there is need for a solution to reduce the fuel cost burden on the poor and taxpayers in many developing countries. Furthermore, an increase in biodiesel production and biodiesel fuel use will reduce over-dependency on coal

which provides 77 % of national energy needs in South Africa, for instance [40]. Overdependence on imported oil from countries producing oil has led to uncontrolled inflation due to the nature of price volatility in the world market, which requires us to rethink our energy priorities. The other major problem associated with the conventional fuels is emissions. The demand for conventional diesel and petrol is ever increasing due to rise in automobiles in South Africa and so is the air and environmental pollution along with it. Even stringent vehicle emissions and control norms and policies have not been able to reduce the level of emissions globally, including in South Africa.

This work provides the prospect of new economic opportunities in developing countries dealing with the endemic problem of waste management. Energy needs are increasing yet these countries have insufficient energy as populations surge with urbanization and the need to industrialize to meet needs and services. Biofuel development from renewable energy sources is expected to dominate the energy sector going forward as the world moves to more green energy. Shifting and embracing renewables will reduce dependency on imported petroleum which is associated with political and economic vulnerability, reduction of greenhouse gases (GHG) and other pollutants while stabilizing the economies of developing countries and stimulating their domestic demand for alternative energy. [41, 42].

It is becoming apparent that renewable resources such as virgin biomass, waste biomass like trees, agricultural waste, municipal solid waste, and microalgae, are increasing in appeal as sources of energy. These feedstock sources are attractive as potential and feasible renewable sources of energy. They are abundant and readily available at low or no cost [43-47].

1.5 Thesis Outline

This thesis work sought to achieve the aims and objectives presented above in ten chapters, as summarized below.

Chapter 1 presents an introduction and background to the study, outlining the need to study waste-to-energy in the production of biodiesel oil using blending as a technique for obtaining blended oil ratios and its improving performance. This chapter provides background on the main research question linked to the aims and objectives of this study. It also lays out the scope of study, research motivation and contribution to the field of science and technology especially regarding renewable energy.

Chapter 2 is the literature review. This chapter deals with previous work by various authors conducted in the same field of study. Various topics of importance in waste-to-energy for the production of biodiesel are discussed; development in alternative feedstocks and the shift from traditional feedstocks to non-edible feedstocks such as municipal solid waste are comprehensively reviewed and discussed. This chapter also reviews and discusses the factors, which affect biodiesel production, production and processing techniques of biodiesel, and biodiesel composition (properties). This review consists of proceedings from conferences, journal articles, published books, online articles and publications and dissertations from masters and theses from doctoral studies.

Chapter 3 is a research article publication entitled "Evaluation of Pyrolysis Oil from Plastic and Solid Waste Biomass". In this chapter, various topical issues dealing with design, fabrication and evaluation of small-scale pyrolytic systems reactor are discussed. This chapter highlights the design of a pyrolytic unit and its evaluation and performance in converting waste plastic and biomass into oil for biodiesel production. Key design components of the reactor unit included: the furnace housing assembly, the reactor assembly, the piping system, the heat exchange system (condenser) and the collection system.

Chapter 4 is a research article publication entitled "The Effect of Fuel Additives on Pyrorated Biodiesel Blends on the Performance of a Diesel Power Generator". This chapter discusses the role of fuel additives in improving the physicochemical qualities of biodiesel fuels. The chapter further discusses the growing influence of alcohols as cheap sources of alternative energy compared to other sources used as alternative additives. The chapter also discusses the role that additives play in reducing emission and improving diesel engine performance.

Chapter 5 is a research publication entitled "The Effect of Cetane Number and Oxygen Content in the Performance and Emissions Characteristics of a Diesel Engine Using Biodiesel Blends". This chapter discusses the critical role played by the cetane number and the oxygen content of biodiesel fuels. The chapter discusses the role of blend ratios and their influence on performance and emission characteristics of a diesel engine. This chapter highlights the relationship between the blend ratio as a function of brake specific fuel consumption and brake thermal efficiency.

Chapter 6 is a research publication entitled "Effects of Exhaust Gas Recirculation on Temperature, Using Biodiesel Blends". This chapter discusses the role of EGR on pyrorated

oil blends in diesel engines. The chapter further discusses and compares experimental results obtained from waste plastic oil using diesel blends and their influence on exhaust temperature. The role of the EGR trade-off with emission is discussed based on the results obtained under the influence of EGR percentage rate. The role and influence of the blend ratio in exhaust temperature is discussed critically especially in relation to diesel engine emissions.

Chapter 7 is a book chapter publication entitled "Effects of Biodiesel Blends Varied by Cetane Numbers and Oxygen Contents on Stationary Diesel Engine Performance and Exhaust Emissions". The chapter is contained in the book titled "Numerical and Experimental Studies on Combustion Engines and Vehicles". The chapter outlines in detail current international practice in using oxygenated fuel blends and other additives as renewables in diesel engines. This chapter examines the role of oxygenated fuel blends and their huge potential to reduce emissions of CO, CO_2, UHC, NO_X, and PM emissions. The chapter further discusses modern combustion and emission control strategies that have attained a global outreach.

Chapter 8 is a research publication entitled "Assessing the Effects of Engine load on Compression Ignition Engines Using Biodiesel Blends". This chapter evaluated the use of waste plastic pyrolysis oil biodiesel blends and their effect on engine load. It further discussed the effect of using waste plastic pyrolytic biodiesel blends on performance and emission characteristics of a diesel engine. The chapter also evaluated the influence of blend ratio on engine load and combustion characteristics in relation to brake specific fuel consumption, brake thermal efficiency and other parameters examined during experimentation.

Chapter 9 is a book publication entitled "Biodiesel, Combustion, Performance and Emissions Characteristics". The chapter discusses a number of topics critical to the use of biodiesel as an alternative fuel for combustion in diesel engines. These topics include biodiesel sources and types of feedstock families, production and processing technologies, physical and chemical properties and factors that influence emission when using biodiesel fuels. Other topics covered include the role of post-combustion NO_X reduction techniques when using biodiesel.

Chapter 10 discusses the conclusions and future recommendations from the literature review and experimental results contained in the nine chapters presented in this thesis and as laid out the aims and objectives. Chapter 10 summarizes the research findings in this work which have been published in DoHET accredited journals, including the literature review presented in Chapter 2. These recommendations are meant to produce future proposals that can move renewable energy research forward and particularly current knowledge trends in renewables.

1.6 References

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CHAPTER 2: WASTE TO ENERGY FEEDSTOCK SOURCES FOR THE PRODUCTION OF BIODIESEL AS FUEL ENERGY IN DIESEL ENGINE – A REVIEW

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Waste To Energy Feedstock Sources for the Production of Biodiesel as Fuel Energy in Diesel Engine - A Review

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ABSTRACT

In the recent past, there has been a renewed shift into biomass and other recycled waste sources for biodiesel production and utilization. This is a critical area of research and study in which this present work intends to review and identify gaps in literature by shifting the focus of review to non-plant based sources for biodiesel production. Traditional biodiesel feedstock sources have always presented a conflict of food security versus energy. This shift will be identified in literature to see if change to non-plant based feedstocks sources has increased food security by discouraging the contribution of commercial farming for the production of biodiesel. This work will identify biodiesel families, generations, traditional and non-traditional feedstocks for biodiesel production. It will also discuss the non-edible biodiesel feedstocks sources in relation to waste to energy recovery. The other factor this work will review is to study how the use of non-plant based feedstocks such as municipal solid waste has improved environmental protection by reducing pollution and landfilling. In other words, this work will review the impact of Using waste municipal solid biomass resources such as waste tyres and waste plastics and changing them into energy sources. This review study aims at increasing environmental awareness, sustainability and reporting the progress made in waste to energy policy shift in many countries globally. This review will look at socio-economic opportunities in recycling besides the academic and research impacts of waste to energy policies adopted in many countries. The review will climax with a conclusion and future trends in waste to energy in relation to municipal solid waste resources.

1. Introduction and Historical Background of Biodiesel

The history of biodiesel fuel has its route traced to the discovery of the diesel engine by the German engineer Rudolf Diesel in the 1890s. However, the first use of vegetable oil as a fuel was in the world exposition in Paris in 1900. This was at the request of the French government, which had an interest in development of fuels of local origin for its African colonies for energy and power generation independence. There were a total of 5 engine models displayed and tested during the exposition [1]. After the Second World War, several literatures report the use of vegetable oil in diesel engines and operational difficulties encountered with their application as combustion fuel [2-5].

These reports led to the award of the Belgium patent 422877 in 1937 to Chavanne. However, after the second world war the alternative fuel research took a lull until the energy crisis of the 1970s when [6] came up with work on esters of vegetable oil. Using sunflower oil in a diesel engine, they reported that use of sunflower methyl esters eliminated the problems of viscosity and operational issues. Although fossil-based fuels have been playing a major role in the growth of industries, transportation and agricultural activities, the future of fossil fuel as primary source of energy is not sustainable due to depletion, outstripped demand of fuel energy consumption and use. Fossil based fuel have more qualities that make them appeal to the user readily such as availability, good combustion properties and high heating values [7]. Energy estimates from the international energy agency puts

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the estimates of the growth of energy consumption at 53 % by the year 2030 [8, 9].

In the USA the energy information agency (EIA) projects liquid fuel consumption to increase from 86.1 million barrels per day to 110.6 MBD by the year 2035 [10]. The depletion of fossil fuel reserves has occupied world energy forums and decision makers. Therefore, there has been rapid research development in green alternative fuel energy, which is renewable, domestically available, environmentally friendly and feasible technically. Biodiesel therefore has become technically a better choice for researchers as they contain characteristics and identical physical properties to fossil fuel especially diesel fuel. This makes the future of biodiesel more tenable and more promising as sources of alternative fuel energy especially in developing countries. These countries experience a heavy burden on the importation of liquid petroleum fuel for energy, environmental impacts and effects of pollution on the public human health [11]. Table 1 showing a global production of biodiesel in 2015 and the unit cost of production.

Table 1: Worldwide production of biodiesel with cost [12]

Country	Estimated potential (Litres)	Production Cost($/l)
Brazil	2,567,000,000	0.62
Indonesia	7,595,000,000	0.49
Argentina	5,255,000,000	0.62
Malaysia	14,540,000,000	0.53
USA	3,212,000,000	0.85
Netherlands	2,496,000,000	0.75
Germany	2,024,000,000	0.79
Philippines	1,234,000,000	0.53
Belgium	1,213,000,000	0.78
Spain	1,073,000,000	1.71

The importance of modern-day transport systems cannot be gain said, especially the transportation of goods and services and people. The propulsion provided by internal combustion engines with diesel fuel as the primary source of energy, forms the bulk of commercial use and now personal transport, owing to their numerous advantages as compared to other forms or types of propulsion by internal combustion engines. Diesel engines are inherently lean burn engines, and emit relatively low carbon dioxide emissions as compared to petrol propelled internal combustion engines. Other advantages offered by diesel engines include high thermal efficiencies, durability and construction robustness [13]. This makes their continued increase and expansion as more countries move into urbanization, industrialization, and catching up with the highly industrialized countries. However, there has been a formidable challenge to phase them out, based on environmental and human health issues due to the high levels of NO_X, smoke and PM emissions.

Diesel engines have shown to run stably on most medium blended ratios of waste plastic oil, although they produce more NO_X, UHC and CO emissions. However to stabilize their performance for higher blend ratios, injection timing has been proposed as a method of achieving engine performance stability without upgrading of fuel, engine modification or fuel alteration through addition of additives as observed by [14]. Injection timing was seen to affect performance from WPPO Jatropa blends of 20% tyre oil and 80% Jatropa ester oil resulting into lower fuel consumption, CO, UHC and PM although NO_X emissions increased [15]. Nevertheless In a research study by [16] the authors report increased BTE and NO_X emissions, thus concurring with the findings of Sharma et al. (2015) on emissions of NOx, but decreased results on fuel consumption, CO, and UHC.

The continued increase in stringent emission regulations enacted by global industrial powers, United States of America and the European Union environmental protection agencies including the G-7 and G-20. Have since labelled the diesel engine as primary polluter in the transport sector. Hence the clamour for alternative fuels, which mitigate pollution, are sought in the interest of reducing energy consumption, environmental degradation and air pollution from NO_X gases, which diesel engines emit, thus decelerating atmospheric carbon concentration globally. The road transport sector is an environmental concern, since its rapid expansion is fast eroding all the technological developments and improvements thus so far achieved in the war against pollution from diesel-propelled engines.

Across the globe, significant resources have been mobilized to find alternative sources of energy. Different regions and countries have focused attention at sources of supply and technical processes that give them comparative advantages. In sub-Saharan Africa, renewable energy alternatives for transportation have huge potential sources, one of which is biodiesel derived from municipal solid waste sites, waste tires, waste engine used oil and waste cooking oil. Considerable research has been ongoing in this area but some gaps have not been addressed. There is a clear need to conduct evaluations that enable precise technical classification of the performance and emission of biodiesel derived from the waste sources mentioned above. Figure 1 is showing available general waste data (from municipalities) in South Africa from 1997 to 2011.

This will enable us to filter the data, by comparing it with local South African standards and regulations with global standards and regulations. Through this, challenges can be identified and plans of action mapped out to tackle them. It is necessary to identify and assemble the right set of tools and technique needed to conduct studies on these municipal solid waste feedstock sources in a manner that optimizes them as available resources. The stated goal of this work is to extract, information on solid waste municipal sources for the production

of biodiesel using thermal processes. This information is contained in many published research articles and will be presented here as a review and future development.

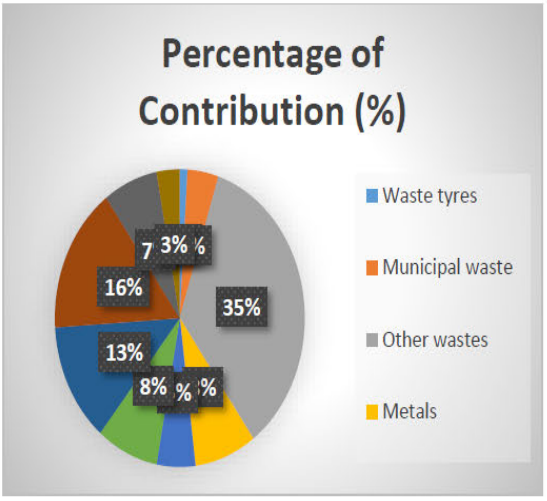

Figure 1: Percentage contribution of each waste stream of general solid Analysed from available data 2017 (from municipalities) in South Africa [17]

2. Biodiesel Families and Generations

Traditionally families come in generations defined by the length of time. As such, biofuels have lumped into families or generational categories. Production and use of biofuels has gained significant awareness and attention in academia, industry and government policy makers. Globally 28 countries including developing countries have been prominent in enacting biofuel mandated policies with substantial tax subsidies for biofuels [18]. Biofuels shift targets displacement of 20% of fossil fuels by biodiesel in the coming future [19].

This is driven in part by the potential of biofuels to create a new industry, raise farmer incomes restore degraded lands and promote independence from oil imports hence mitigating climate change [20]. For example, in literature, surveyed India is among the countries that have adopted Jatropa as a second-generation biofuel source of feedstock. However, in literature reviewed, there is no data on, water, pruning, and plant response to fertilizers hence varied planting management practices [21-23].

In biofuels, the main aim has been to identify methods of production by selecting appropriate feedstock, use of efficient conversion technologies and disposal of the product in this case the biofuels. The end product of any process in the world has become critical due to environmental issues and impact products bring, such biofuels production on the immediate environment [24]. One of the leading challenges in the energy sector is the promotion of biofuels compared to fossil fuels through arguments of sustainability i.e. economic environment and social aspects combined [25]. Sustainable development is a common term appearing in the global agenda of development since 1987. It is defined as development tailored to meet the needs of the present generations without compromising on the future generational needs in meeting today's needs [26, 27]. Sustainability requires that all environmental factors of impact be assessed in each of their phases of the biofuels chain such as (i) Production and collection of feedstock, (ii) Feedstock processing, (iii) Conversion to biofuels, and (iv) Distribution of the end product [28, 29].

The second point is sustainability, which according to literature surveyed is difficult to conduct and evaluate sustainably. For example due to a great number of competing interests interfacing factors are weighted different by stakeholders hence disagreements and lack of common approach [28, 29]. Measuring sustainability of the biofuels industry is a complex issue especially considering the diverse range of biofuel feedstock, pathways, variation in stakeholder's interests and competing interests. Literature surveyed thus advocates for establishment of other indicators, which will enable assessment of sustainability of bioenergy systems. This should apply to small, large and local infrastructure acceptable to all stakeholder and in diversity [30-32]. Figure 2 showing the interrelated pillars of sustainability between society, the environment and the economy.

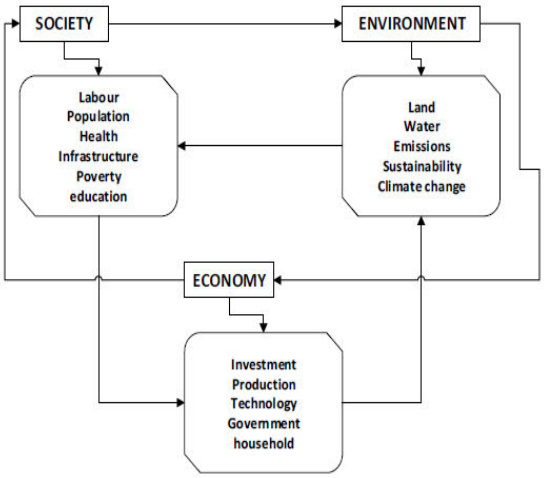

Figure 2: Interrelated pillars of sustainability adapted from [25]

2.1. *First Generation Biofuels*

First generation biofuels are derived from food crop feedstocks usually used as staple food. However, today this generation is vilified as the source of food insecurity and rising inflation in developing countries. Nevertheless, it is important to note even if it is alleged first generation cause increment in food prices and inflation its total influence is minimal [33]. First generation biofuels (otherwise called conventional biofuels) use three different technologies commercially for biodiesel, bioethanol and biogas [34, 35]. These commercial fuels are utilized as solid, gaseous or as liquid fuels. To add value these fuels are upgraded to high-density energy fuels such as charcoal, liquid fuels such as biodiesel, and bioethanol or gaseous fuels such as hydrogen, natural gas or biogas [33]. Table 2 shows the characteristics and demerits of first-generation biofuels.

As a first generation, conventional fuel biodiesel is produced through transesterification of vegetable oil, residual oils and animal fats as alternatives for petroleum diesel with slight engine modifications. In the processing triglycerides are chemically

reacted with alcohol in the presence of a catalyst or enzyme. This process generates biodiesel and glycerol [36, 37]. On the other hand, bioethanol are produced through a Biocatalytic fermentation of sugar or starch as ether (ETBE) which is used as a blend with gasoline. the gaseous category biogas a mixture of methane and carbon dioxide is processed through anaerobic digestion of organic materials [38, 39].

Table 2: Shows characteristics and demerits of first generation biofuels

Characteristic	First generation biofuel	References
Completion with food crops	Made from edible oil and starch feedstock	[40]
Land footprint	Requires arable land	[41]
Conversion to biofuels	Easy conversion	[42]
Water footprint	Potable water is required for cultivation	[43, 44]
Environmentally friendly	Using pesticides and chemical fertilizers	[45]
Commercialization	Commercially produced	[40]
Sustainability	Not sustainable in using natural resources such as water and land	[46-48]
Nutrient requirement	Chemical Fertilizers as main nutrients	[49]
Harvesting	Done by hand or machine	[50]
Regulation	Clear fair regulation	[40, 51]
Financial input	Low capital investment	[40]
Environmental condition	Temperature and humidity must be suitable	[52]

Despite their acceptance first generation, fuels have demerits, which have made their global appeal and wide commercial application difficult. For example, their overdependence on agricultural food crops initiates a heavy social debate on food vs fuel. Hence, their commercialization and adoption threaten food security while inflating food prices in developed countries. In semi-arid areas, production of biofuels would be too costly and limited with determined prices considered as non-competitive to conventional fuels. Figure 3 is showing different biofuel families and their available feedstocks sources.

2.2. *Second Generation Biofuels*

Second generation biofuels family is also called advanced biofuels. These fuels are also purported to be produced sustainably in a truly carbon neutral environment in terms of CO_2 concentration. The source of feedstocks of these fuels is lignocellulosic biomass, non-food crops, agricultural and forest residues and industrial wastes. The production of second generation is done by utilizing physical, thermochemical and biochemical technologies processing [55, 56]. Using these processes involves use of pre-treatment steps to facilitate the conversion process. Here properties of biomass are technically analysed such as size, moisture and density before treatment and processing is commenced [57].

In physical processing techniques in literature reviewed, the commonly applied techniques are briquetting, pelletizing and fibre extraction. These techniques enhance and convert loose biomass into high density solidified blocks of energy. Pelleting does the same thing pressure does to compact raw fibre particles of biomass into high density. On the other hand in fibre extraction fibre is removed from biomass residues and utilized as sources of energy fuel for heating [55, 58].

Under thermochemical processes for production of biofuels are found pyrolysis, gasification liquefaction and direct biomass combustion. Thermochemical liquid fuel processing uses thermal decomposition with chemical reformation. This involves heating biomass under the influence of different oxygen concentration leading to conversion of all organic components [39]. Pyrolysis is a slow or fast process depending on the existing operating conditions but in the absence of air [59, 60]. The former favours solid fuel production compared to the latter which is good for liquid fuel production (bio-oils) and gaseous biofuel production [61, 62].

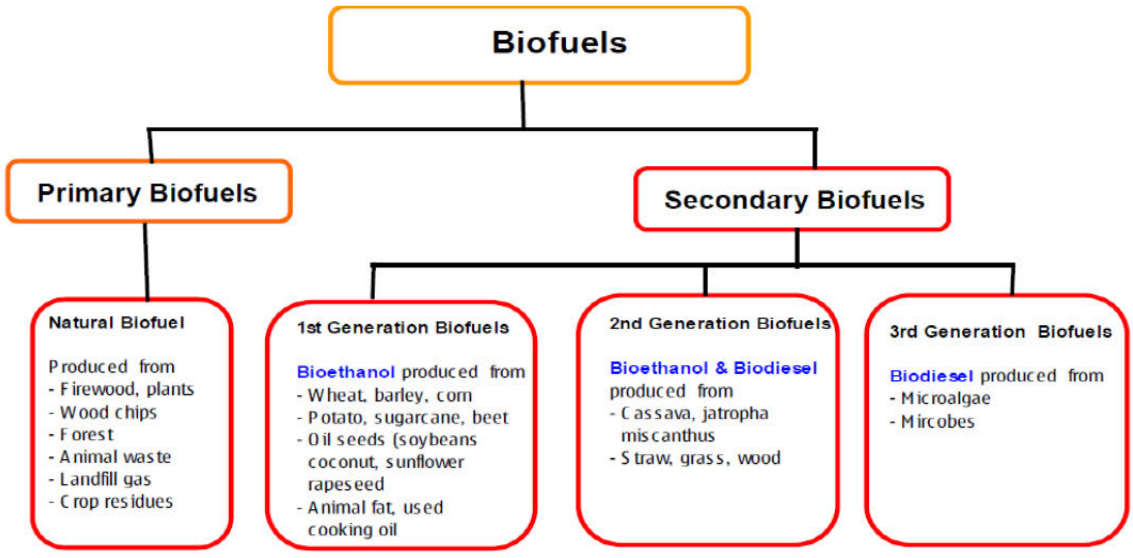

Figure 3. showing different biofuel families and their feedstocks [53, 54]

As a method in second-generation biofuels, gasification coverts biomass into combustible gaseous fuel mixtures also known as syngas. Through partial oxidation of biomass at elevated temperatures of 800 °C to 1400 °C syngas is produced. The medium for gasification can be air oxygen of steam [55, 60]. However gasification is still struggling with challenges of operational and downstream gas utilization problems [63]. The driver of gasification has been the versatility of the gases produced during the process. Reaction of the gasification and the feedstocks of solid carbon structure forms carbon dioxide or hydrocarbons. Nevertheless, as said earlier the gasfying agent has a very critical role in influencing the final product of the process. For example when steam is used as an agent of processing reaction temperatures are lowered to 600°C [39]. Table 3 is showing the principle components of a gasification process.

Table 3 is showing the principle components of a gasification process adapted from [63]

Target compounds	CO, H_2, CH_4, C_2H_x, C_3H_x
'Inert' (non-combustible) compounds	CO_2, H_2O, (N_2)
Trace contaminants	NH_3, HCN, other organic nitrogen compounds
	H_2S, COS, CS_2, other organic sulfur compounds
	HCl, NaCl, and KCl aerosols
Condensable fraction	Benzene, toluene, and xylene (BTX), tar, hetero-organics, (water)
Particles	Ash, mineral matter/salts, char, aerosols

During transformation (conversion) of solid fuel into gaseous components by gasification a number of reactions with intermediate reactions, take place. It is a complex network of reactions; influenced by feedstock sources, and properties, residence time, reactor design temperature gasifying agent and pressure. In this literature review, only a few examples of main reactions are presented in chemical equations 1 to 9. However, the references provided here would be useful to the reader for a detailed study and understanding [39, 64-66]. Table 4 is third generation biofuels characteristics and references.

Chemical reactions with molecular oxygen, which are exothermic in nature (combustion reactions).

$$C + O_2 \leftrightarrows CO_2 \qquad \Delta H = -110.62\text{kJ/mol} \tag{1}$$

$$2CO + O_2 \leftrightarrows 2CO_2 \quad \Delta H = -283.15kJ/mol \tag{2}$$

$$2H + O_2 \leftrightarrows 2H_2O \quad \Delta H = -242.15kJ/mol \tag{3}$$

Carbon dioxide and hydrocarbon/CO_2 reaction

Boudouard reaction:

$$C + C\,O_2 \leftrightarrows 2CO \qquad \Delta H = +172.54kJ/mol \tag{4}$$

Hydrocarbon/CO_2 reaction:

$$C_nH_m + nCO_2 \leftrightarrows 2nCO + m/2H_2 \tag{5}$$

Steam as the reaction agent

$$C + H_2O \leftrightarrows CO + H_2 \quad \Delta H = +131.38\,kJ/mol \tag{6}$$

Hydrocarbon and steam reaction:

$$C_nH_m + nH_2O \leftrightarrows nCO + (\frac{m}{2} + n)H_2 \tag{7}$$

Water gas-shift reaction (homogeneous water-gas shift conversion)

$$CO + H_2 \leftrightarrows CO_2 + H_2 \quad \Delta H = -41.16kJ/mol \tag{8}$$

Hydrogen reactions in gasification

$$C + 2H_2 \leftrightarrows CH_4 \;\; \Delta H = -75.00kJ/mol \tag{9}$$

2.3. *Third Generation Biofuels*

The third generation biofuel family comprises of fuels produced from microalgae feedstocks. This generation is currently under research and development as alternative renewable energy sources for biofuel processing and production. This family has been largely been fronted as a solution to overturning the demerits of the first generation and second generation biofuels [55, 68]. Majority of these fuels exist in laboratories under research and development with a few small scale enterprises producing algae oil [69]. The microalgae group of feedstock consists of microalgae, macroalgae (seaweed) cyanobacteria (blue-green algae) [70]. Microalgae consists of 72000 different species and as many as 800000 in fresh water or salty water [69, 71].

Table 4. Shows characteristics and references of third generation biofuels

Generational Characteristics	References
Eliminates food-energy conflict	[40]
Contaminated and Non-arable land used for cultivation	[41]
Easy conversion due to increased hydrolysis and/or fermentation efficiency	[42]
Waste, saline and non-potable water also can be used	
Merits (CO_2 fixation, waste water treatment, reduced cost of fertilizer) demerits (ecological concerns on marine eutrophication)	[43, 44]
Poor biomass production for commercialization	[45]
favorably poor economically	[40]
Large quantities of carbon and nitrogen required. Solar energy is only available at daytime. Nutrients recycling possible	[46-48]
Harvesting of microalgae is expensive, and complicated	[49]
Lack of regulation for marine cultivation	[50]
initial large scale cultivation costs too high	[40, 51]
cultivation in harsh environmental condition such high pH, salinity and light intensities possible	[52, 67]

The rise of algae as an alternative biodiesel feedstock is due to its rapid growth, increased harvest cycle in days compared to months or years. Microalgae need few nutrients for maximum growth and can thrive in severe poor conditions while giving high and increased output per acre ranging from 15 to 300 times more compared to food crops acreage [72, 73]. Algae oil can also be used as feedstock to provide high value products such as ethanol, butanol, biodiesel, jet fuel syngas, and bio-oil chemical feedstocks such as hydrogen and farm fertilizers [53, 70].

Another important factor with algal biofuel is the lack of competition with food crops or feed crops, yet algae is used to

reclaim agricultural wastelands. This seems to obviate and free land use while reducing energy versus food competition. This elevates this family against the first two-biofuel families. However a further research and study aimed at improving algae production methods especially the plant energy content yield and sustainability is required [54]. Table 5 shows different oil contents for a variety of microalgae species.

Table 5. Showing different Oil contents for a variety of microalgae adapted from [41]

Microalga Oil content	Percentage in dry weight (%)
Botryococcus braunii	25–75
Chlorella sp.	28–32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16–37
Dunaliella primolecta	23
Isochrysis sp.	25–33
Monallanthus salina	20
Nannochloris sp.	20–35
Nannochloropsis sp.	31–68
Neochloris oleoabundans	35–54
Nitzschia sp.	45–47
Phaeodactylum tricornutum	20–30
Schizochytrium sp.	50–77
Tetraselmis sueica	15–23

2.4. *Fourth Generation Biofuels Sources and Beyond*

The birth of fourth generation biofuel has been propagated by the need arising from environmental dilemmas. These dilemmas challenge our human capacity for sustainable solutions to protect nature for our own existence and posterity. For example, the need to protect water sources, agricultural lands for sustainable food production, reduction of GHG, the protection of atmospheric air and weaning overreliance from fossil fuels as the only sources of primary energy supply [74-79]. Table 6 Showing characteristics and references of fourth generation biofuels.

Table 6: Characteristics and references of fourth generation biofuels

Generational Characteristics	References
Eliminates the food-energy conflict	[40]
Contaminated and Non-arable land used for cultivation	[41]
Increased hydrolysis and/or fermentation efficiency	[42]
Waste, saline and non-potable water also can be used	[43, 44]
Offers Medium (CO2 fixation, waste water treatment) but releases GM organisms	[45]
Produces less biomass for commercialization	[40]
Leaking of GMO to environment pausing ecological risks	[46-48]
Large carbon and nitrogen required. (However, Solar energy is daytime). Requires Nutrients recycling in the process	[49]
Harvesting of microalgae is expensive, and complicated	[50]
No regulation for marine cultivation but strict regulation is required with GM algae	[40, 51]
Initial cost for large scale cultivation is expensive	[40]
Cultivation in harsh environmental condition possible (such as high pH, salinity high light intensities)	[52, 67]

Fourth generation biofuels are oils therefore produced from genetically modified feedstocks able to consume more CO_2 from the atmosphere than what they will produce during the combustion phase as fuels [80]. Therefore fourth generation fuel utilizes the existing platform technologies such as pyrolysis, gasification, solar to fuel and genetic manipulation of organism's genetic order. The fourth generation family is referred to as smart fuels based on the conversion of vegoil and biodiesel to biogasoline using advanced technology.

Despite large-scale production and efforts to try to commercialize this family progress has not been sufficient. This has been due to lack of sufficient biomass, increased production costs and set-up, environment and human health concerns as fewer feasibility studies have been completed [40]. Table 7 is showing health and environmental effects of fourth generation biofuels. While Figure 4 is showing main steps of algal biomass technologies in carbon fixation.

Table 7: The health- and environment-related risk of GM algae Human health [81, 82]

Topic Risk contribution	Risk contribution	Effect	References
Allergies	Human health	Dermal, ingestive, respiratory exposure	[82-86]
Antibiotic resistance	Human health	Reducing the effectiveness of medical treatments	[84-86]
Carcinogens	Human health	Carcinogenic residues	[82]
Pathogenicity or toxicity	Environment	Pathogenicity of some strain to human; toxic blooms; chemical transfer; toxic residues	[82, 87, 88]
Change or depletion of the environment	Environment	Removal of nutrients from ecosystem; reducing biodiversity of the flora and fauna	[89, 90]
Competition with native species	Environment	Outcompete native organisms; changing aquatic ecosystems	[91, 92]
Horizontal gene transfer	Environment	Transfer of genetic organisms	[93, 94]
Pathogenicity or toxicity	Environment	Pathogenicity of some strain to human; algal blooms; generating genetic–related toxins	[95]

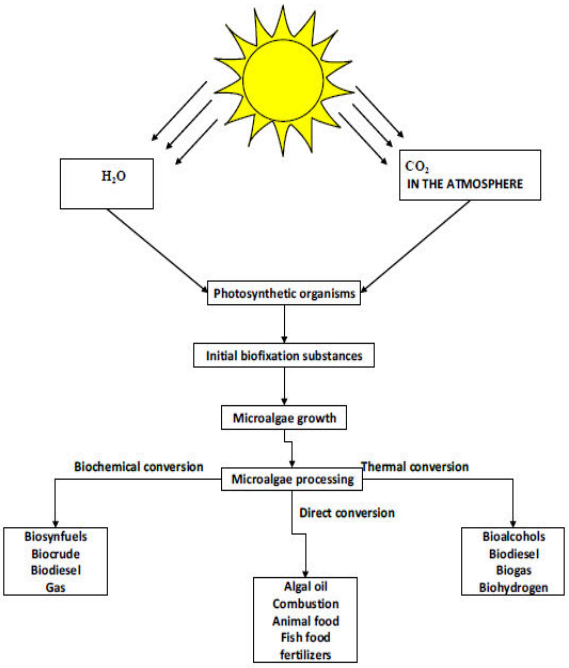

Figure 4: Carbon dioxide fixation and main steps of algal biomass technologies adapted [80]

GM crops have been with us since 1996 as sources of 3rd and 4th generation biofuels and have increased in their global acreage. For example soybeans, maize and rapeseed occupy 73.3×10^{13}, 46.8×10^{13}, and 7×10^{3}respectively of all global land mass area under cultivation [96, 97]. Nevertheless, in order to increase fourth generation biomass production of biofuels algae is heavily GM sourced. Which is achieved by improving areas of the micro-organism using genetic material engineering manipulation. For example, the following areas are mentioned in literature to engineer increased microalgal biofuel production. (i) Improvement of photosynthetic efficiency, (ii) Increasing light penetration by using the truncated chlorophyl antenna and (iii) Reduction of photo-inhibition.

Literature is averse with these developments in the literature reviewed and presented here such as [98-101]. The development in fourth generation biofuels also aims at providing new economic development opportunities in remote and suburban areas of developing countries. These opportunities include reduction of emission to zero for both air pollutants and GHG [102, 103].

Microalgae form a large group of eukaryotes and cyanobacteria and have a wide range of compositional characteristics which include; [104] Food reservation, Photosynthetic pigments, Cell wall chemistry and reproduction. However out of the many species of microalgae only Bacillanophyceae (diatoms), Eustigmatophyte, Chlorophyceae and Chrysophyceae are potential sources of biofuel production [105]. Microalgae have high adaptability in extreme environmental conditions such as high salinity, drought, photo oxidation, osmotic pressure, temperature, anaerobiosis and ultraviolet (UV) radiation [106]. Their main nutrients are nitrogen and phosphorous which accounts for 10% to 20% of its biomass [107, 108].

3. Biodiesel Feedstock Sources, Production, and Processing Techniques

3.1. *Introduction to Edible Vegetable Oil and traditional Feedstocks*

The production of biofuels such as biodiesel is becoming convenient as alternative energy. The use of biofuel such as biodiesel reduces GHG and provides opportunities for local and regional development in remote areas. This is made feasible considering the number of feedstocks sources. Biodiesel feedstock types differ from country to country depending on the geographical locations and their development [109, 110]. Globally more than 350 oil bearing crops have been identified [111] as possible biofuel feedstocks. However, there are many relevant candidates for biofuel production feedstocks adding to the list but are non-plant based. Figure 5 is showing the growth in vegetable oil production in China from 2003 to 2015.

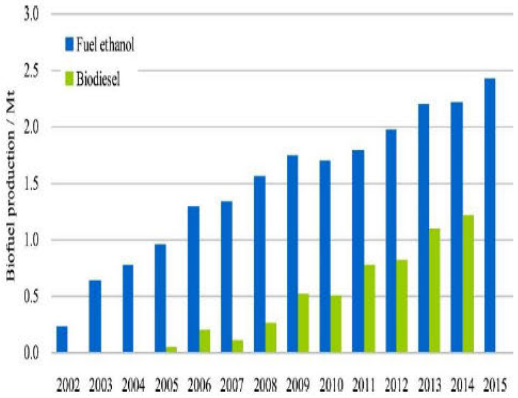

Figure 5: China's biofuel production over the past decade [112]

The advance in experimental biodiesel production from theses feedstocks has led to a waste to energy revolution. Biodiesel production from readily available feedstock considered waste candidates for dumping and landfill [113]. This has encouraged value addition and co-product markets while contributing to diversification of the biofuel industry [114]. Nevertheless, since each feedstock is different from the other the conversion and processing techniques vary but the basic process of production remains the same. The wide range of feedstocks availability plays a significant role in promoting the biofuel industry.

The availability of feedstocks is influenced by regional climate, geographical location, local soil characteristics and general agricultural practices of a region or country [115]. In sources of biofuel development production and processing, only sunflower, cottonseed, safflower, rapeseed and peanuts are considered compared to two, corn and sugarcane for bioethanol used in gasoline engines;. However, it is important to mention here that non-edible oil plants such as Karanja, rubber seed, tallow oil and microalgae, Jatropa and neem seeds are also gaining

acceptance as alternative sources of biofuel. In the last decade, non-edible feedstocks have been extensively studied in literature surveyed such as [77, 116-118].

Among plant-based feedstocks palm oil, soybean and rapeseed account for almost 80 % of global feedstock for biofuel production as shown in Table 8. To qualify as a feedstock for biodiesel production the oil percentage and yield are important factors for consideration [119-122]. Nevertheless quality, availability, physicochemical properties, composition and production costs are some of other critical factors of feedstock determination and acceptability [119]. Feedstock prices account for more than 80% of the cost hence selecting and quality feedstock is vital to ensure low production costs [120, 123]. Since feedstocks are impacted by oil percentage yield, these factors are critical and need consideration. Figure 6 is showing total global vegetable oil production and production contribution of each source from 2013 to 2018. While Table 8 shows major vegetable oil producers and their main sources of feedstock respectively. On the other hand, Figure 7 is showing, international vegetable oil prices from 2000 to 2014.

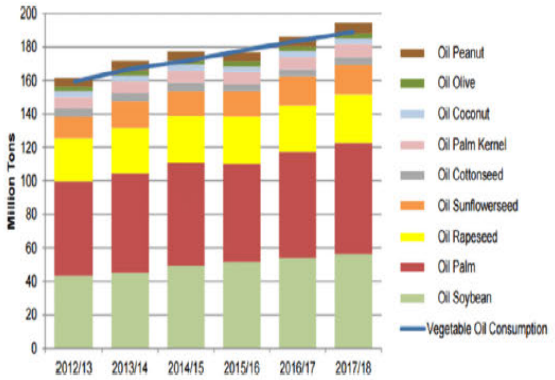

Figure 6. Global vegetable oil production and consumption [124]

3.2. *Soybean Biodiesel Feedstocks*

Soybean comes from the Glycinemax L. as a legume with an annual cycle from the Fabaceae family [130]. United states of America, Brazil and Argentina are the leading producers accounting for 80% of all global production [131]. However, china is increasing production and catching up, hence expanding its role in the near future considerably. It is important also to note that china imports almost 1/3 of the world's production of soybean. This accounts for 62% of all global soybean trade [132]. Soybean as a grain contains 14% to 17% oil, 33% to 40% protein [133]. In the period of 2013 to 2015 soybean was responsible for over 65% of the global supply of protein supplements and feeds [134]. Soybean meal is the extraction obtained from the oil extraction process and one of the most important source of human and animal protein [135-138].

Table 8. Shows major vegetable oil producers and their main source of feedstock [12, 125-129]

Country	Production (1000t)	Main feedstock
USA	4.150	Soybean (53%)
Brazil	3.000	Soybean (77%)
Germany	3.000	Rapeseed (>50%)
Indonesia	2.750	Palm oil (100%)
Argentina	2.550	Soybean (100%)
France	1.850	Rapeseed (>50%)
Thailand	1.050	Palm oil (77%)
Total Europe	10.200	-
Total world	26.150	-

In addition soybean extracts are used in the textile and plastic industry as molds, glue or adhesives for laminated paper and wood [139]. Soybean is also the main raw material in the vegetable oil industry, whose production by 2012 exceeded 40 million tonnes representing 25% of global production of vegetable oils [140]. Environmentally soybean compared to fossil energy consumption over the biofuel life ranges from 2 MJ/MJ^{-1} to 8.5 MJ/MJ^{-1} [141-143]. On the other hand, comparatively its GHG life cycle varies from 8 $gCO_2e\ MJ^{-1}$ to 42 $gCO_2e\ MJ^{-1}$ of biodiesel [143]. However, in the literature surveyed only one researcher reported higher values of 50 $gCO_2e\ MJ^{-1}$ [142]. This was attributed to the assumption adopted during life cycle analysis hence the difference in the values of the findings [114].

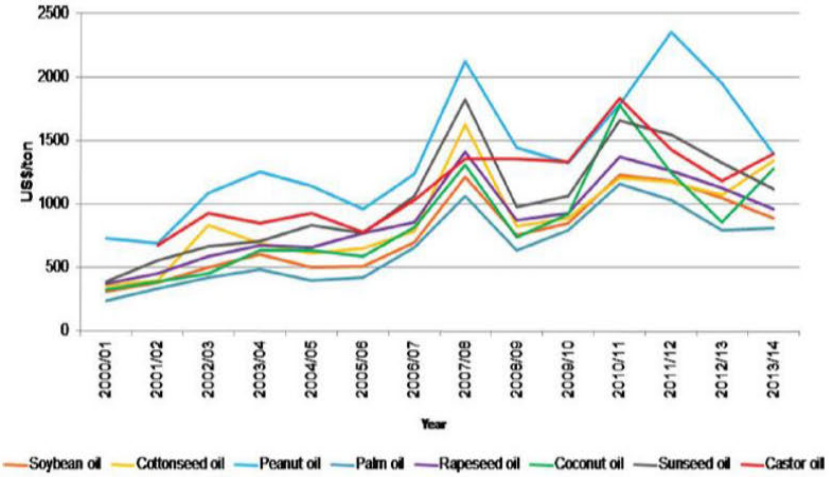

Figure 7: International prices of vegetable oils from 2000 to 2014

3.3. *Rapeseed Feedstocks for Biodiesel Production*

Known scientifically as Brassica hapus L., rapeseed is also known as colza and one of the most cultivated crops globally only beaten in acreage by soybean [140]. Its main geographical origin is the Mediterranean area and northern Europe. Among the leading global producers of rapeseed include China, Germany Canada, India and France accounting for 65% of global production [140]. Table 9 shows Oil yield for major non-edible and edible oil sources and feedstocks.

In Europe rapeseed is the main plant biofuel source accounting for 55% of the total European production of biofuel feedstocks and 68% of global feedstock production in 2016. However, its market share has been slowly decreasing as more recycled oil and alternative feedstocks eat away its market share since 2016 [144]. Other usefulness of rapeseed is in the protein range and food supplements, rapeseed can be used as an animal feed for pigs, cattle, sheep and poultry [145, 146].

Table 9: Oil yield for major non-edible and edible oil sources

Type of oil source (feedstock	(kg oil/ha)	Oil yield (Wt %)	Prices (USD/ton)	Literature references
Jatropha	1590	Seed:35–40 kernel:50–60	370	[5,6]
Rubber seed	80–120	40–50	1250	[7][147]
Castor	1188	53	1600	[5,9][148]
Pongamia pinnata	225–2250	30–40	286	[8],[149], [150]
Sea mango	N/A	54	N/A	[9]
Edible oil Soybean	375	20	684	[5,11]
Palm	5000	20	600	[5,12
Rapeseed	1000	37–50	683	[5,13

Rapeseed meal is known to contain 34% to 38% protein with an oil range of 34% to 40% [151]. However rapeseed has an unpleasant flavor due to glucosinolates which sometimes lead to toxicity in combination with the enicic acid [152]. This is one of the major drawbacks especially on cost reduction in related industries even though utilization can be undertaken by processing [153]. As a source of feedstock rapeseed has low levels of saturated fats coupled to high levels of monosaturated fats with omega 3 and 6 making it a healthy source for human consumption [96]. As a plant feedstock rapeseed ensures a steady acreage yield at stable production over a range of time [154] while allowing intercropping. Compared to soybean, and palm oil, rapeseed performs well in emission studies for example it reduces smoke, PM, and UHC [155]. Environmentally, life cycle studies report a wide range of mixed results. Nevertheless it reduces GHG emissions from 85% to 40% and fossil energy use from 83% to 43% compared to petroleum fuels [156].

3.4. *Palm Oil Feed Stocks*

Palm originate in West Africa and is used as the main feedstock for palm oil production. Palm oil plant has a life cycle of 26 years [157]. Palm plant as a feedstock generates co-products of 20% to 21% oil, 17% kernel oil, 3.5% palm kernel cake, 22% to 23% empty fruit bunches, 12% to 15% fiber, 5% to 7% shells and 50% liquid POME [158]. Palm oil plants are natural in Central America, north and south. Palm oil is rarely planted commercially due to its low oil content. As such attempts have been made to breed Elaeis OLEIFERA and Elaeis guineensis species to improve disease resistance, palm tree height and increase unsaturated fatty acid [159].

Palm oil as a biofuel feedstock is one of the leading vegetable oils with over 50 million metric tonnes accounting for 30% of global palm oil production in 2013 alone. However, by 2017 the production of palm oil rose to 37.6% (70.3 million metric tonnes) [124]. Nevertheless, as a feedstock only 10% of its global production goes to bioenergy and biofuels [160]. The leading producers of palm oil are Indonesia and Malaysia which control 85% of global production [130]. Palm oil in south east Asia was introduced in Malaysia in 1870 from Singapore [161]. As a feedstock, palm oil has a number of uses considering its byproducts. For example palm oil is used in the food industry as butter, solid fats, cooking oil, industrial oil, baking oil or as a substitute for trans-fat [159, 162].

Additionally, palm oil is applicable in the cleaning, cosmetic, and soap and detergent production. In the chemical industry palm oil is used as a lubricant and in oil production [162]. In waste to energy reform, palm oil shells and fiber can be used in chain production of steam for electricity in co-generation systems. For example, in literature surveyed it was reported that for a palm tree bunch the energy is 300 kWh and 600kg of steam [163, 164]. In literature-surveyed palm oil as a biofuel feedstock has limitations which include; (i) Low supply of seeds, hence poor production [165], (ii) Lack of research in co-product industries and comprehensive economic data due to logistical issues [166], (iii)The long cycle of the palm tree growth [130].

3.5. *Cotton Seed Feedstocks*

Cotton which is known scientifically as Gosypium hirsutum L., comes from the family of Malvaceae and is grown globally for the production of fiber used in the textile industry [167]. Cotton comprises of 65% seed and 35% fiber [168], oleic acid 15% to 20%, stearic acid 2% to 5% [167], with major fatty acid being palmitic acid at 27.76% while linoleic acid stands at 42.84% [169]. Nevertheless cotton as a feedstock for biofuels has a low oil content at 16% to 23% but with breeding and selection researchers have observed an improvement of 5% in crop oil yield [170].

However, what is of great interest is the cotton meal, which is heavily rich in protein second only to soybean after oil, has been extracted. The cotton meal is mainly used as an animal feed although it has other vital uses such as being a fertilizer, food flour or as a dye in the textile industry and as a biodiesel feedstock [171-174]. Globally cotton is the ninth highest oil producing plant [175]. Despite its low oil content cotton is advanced as a biofuel feedstock due to lower smoke and particulate emissions compared to other feedstocks such as palm oil discussed in earlier subsection

[155]. Nevertheless it has limitation which include poor quality oil requiring pre-treatment hence increased cost of biodiesel production when used as a feedstock [114]. Figure 8 is showing a cottonseed oil sample after extraction from cotton seed.

Figure 8: A sample of cottonseed biodiesel layer of cottonseed oil [167]

3.6. *Sunflower*

Known as Helianthus annuus L and a dicotyledon, Its oil content varies from 38% to 50% based on the species of variety employed [176, 177]. Russia is the world leading producer of the sunflower crop with a 21% of the total global landmass, others include Ukraine at 12.97%, Argentina at 11.83%, China at 7.17%, Romania at 6.56%, France at 5.56% India at 4.77%, USA at 4.14% and Spain at 3.09% [178]. Globally sunflower covers an area of 23.7 million hectares with an annual production of 1322 kg/ha on an expected production of 2.3 tonnes to 2.5 tonnes/ha [179].

Beside its potential for oil, sunflower grain produces 250 kgs to 350 kgs of meal shell and 45% to 50% crude protein per tonne of grain [180]. The co-products of sunflower can be utilized for other uses such as in packaging materials, animal feeds, forage silage or as green manure or as a biofuel feedstock [181, 182]. Sunflower in the last decade has gained prominence as a feedstock, for example in Brazil 62000 tonnes were realized in the 2015 to 2016 season. However this was a decrease compared to the previous seasons due to a drop in the acreage under cultivation [183]. The introduction of new crops such as corn saw farmers shift to corn due to low cost of production of inputs and processing [184].

Sunflower is a good feedstock for biofuel due to its drought resistance to cold and heat conditions besides being less likely to be influenced by latitude, longitude or photoperiods [185]. As a feedstock sunflower can be grown in rotation with other plants (intercropping), which offers higher returns to farmers and producers [186]. The main limitations of sunflower as biofuel feedstock include High international market prices [134], besides a cloudy nature as temperatures drop due to its high wax content [187]. Additionally Sunflower contains linoleic, oleic and linoleic acids, which account for almost 70% hindering oxidative properties, which offer stability, hence rapid lipid oxidation of its oil [188-190].

3.7. *Jatropa Curcas*

This is a plant cultivated almost globally for the production of biofuel although it is a non-edible plant. Jatropa seeds are composed of 37 % shell, and 63% kernel (dry matter) with a protein content of 35% and a 15% of oil [191]. Jatropa has been on the radar of biofuel developers and producers due to a number of factors. These include low production cost, Water stress tolerance, High oil content and yield, Resistance to pests and diseases; Resistance to drought, Good adaptability to semi-arid wastelands, hence reduces competition with food crops for arable land [36, 192].

Other uses of Jatropa as a feedstock include as a cooking fuel, insecticide, soap making, and for medicinal purposes [191]). Additionally Jatropa can be used as an organic fertilizer, livestock feed and a biogas feedstock [193, 194]. On the other hand, the limitations of Jatropa arises: From uncertainties around its seed yield range which is 2 to 12 Mg/ha leading to poor economies of scale for a feedstock [36]. Secondly, even when it seems adaptable to drought during flowering studies have shown it needs watering otherwise the yield drops significantly.

In other words, Jatropa capabilities are not exploitable and applicable simultaneously. This is evidenced by the moisture and nutrients influence on yield [195]. The third limitation is due to its vulnerability to viral infection [36, 196, 197]. The fourth limitation is due to lack of scientific validation regarding the basic ecological and agronomical properties. For example, yield, potential production and costs, and breeding programs have not been identified in the literature reviewed.

4. Introduction to Non-Edible Vegetable Oil and Emerging Feedstocks

The use of non-edible feedstocks for biodiesel production is an answer to the challenges of edible oil as biofuel feedstocks. Non-edible feedstocks are gaining attention, as they are easily available globally in wastelands in unsuited for food crops. This eliminates competition for food, reduction in deforestation rate and co-products. Although there is no direct competition for food versus fuel, Nevertheless, there is indirect competition for land. Among the non-edible plants used for biofuel production include; Cotton (Gosypium hirsutum), Castor (Ricinus curcas), Jatropa (Jatropa curcas), Rubber (Hevea brasiciensis), Mahua (Madhuka indica), Ethiopian mustard (Brassica carinata), Castannola (Terminalia catappa) [198-202]. Figure 9 is showing Waste cooking oil production based on country and global contribution.

In India, there are two major species of the genus, Madhuka longifolia and Madhuka indica, on the other hand rubber seed tree is mainly in Indonesia, Malaysia, Liberia, India, Sri-lanka, Sarawak and Thailand. Rubber as feedstock contains seed kernels of 40 % to 50% brown oil [203]. Another non-edible oil biofuel source is neem (Azadirachta Indica) a natural plant of the Indian subcontinent and commercially grown in India, Bharma,

and surrounding regions. Jojoba oil is another non-edible oil a shrub in southern Arizona. Therefore, in Literature reviewed non-edible oil studies as alternative biofuel feedstocks fill many researcher reports such as [44, 201, 204-207].

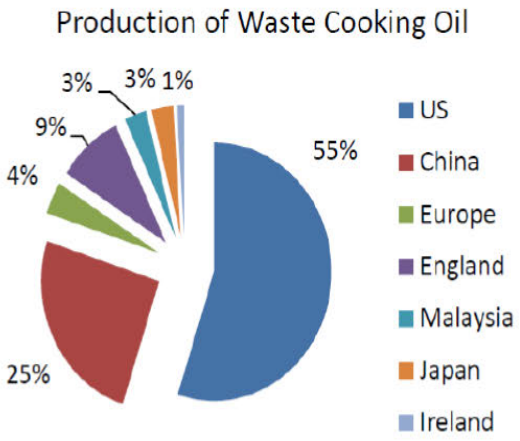

Figure 9: Waste cooking oil production based on country [10, 14-15]

4.1. *Waste Cooking Oil Feedstocks*

Waste cooking oil is also known as yellow grease due to the fact that most waste cooking oil FFA content is 8% to 12% wt. Waste cooking oil offers a high potential as a feedstock to biofuel production due to low cost. As modernization grows and more people shift to urban lifestyles the total quantity of waste cooking oil has been growing since 2008. Waste cooking oil can be collected from households and hotels and restaurants, fast food outlets with heavy use of frying activities [208]. The disposal oil from these activities is problematic as it contaminates ground water. However, their cooking oil sources differ greatly since their base material are plant lipids like corn, margarine, coconut oil, palm oil, olive oil, soybean oil, grape seed oil and canola oil. The most commonly used material for vegetable oil is palm oil [209].

The use of WCO as a biofuel feedstock does not come at the expense food versus energy or land resources. Instead it's a sustainable use of resources which reduces adverse effects of water pollution and blockage of water and drainage sewage system [210]. Presently WCO has been heavily utilized in soap manufacturing, although the soap produced is of poor quality hence its utilization has been low [211]. The main objective of using WCO is to transform it by reducing its viscosity to values close to diesel oil. Globally over 15 million tonnes of waste cooking oil are produced annually and if converted it can meet and satisfy the world demand of a biofuel feedstock [212]. Production of WCO oil as a biodiesel can contribute to a saving 21% in crude and a 96% energy saving [213]

Non-edible vegetable have potential to substitute a global fraction of petroleum diesel [214]. Plant oil feedstock when processed to biodiesel reduce particulate and sulfur emission and aromatic compounds [215] compared to petroleum diesel [216]. In 2009, the production of FAME waste oil was 11 tonnes with a demand increase of 3.5 metric tonnes/year. However, the production of waste oil in Europe, north America and in selected Asian countries such as China combined had a production of 16.6 metric tonnes [217, 218].

For example in 2014, China alone had a total WCO production of 1.8Mtonnes [112], pushing China to 3.4 Mtoe hence accounting for 2.9 % of global biofuel production, distributed in 50 plants. In other words, currently, the main leading feedstock of biofuel production in China is waste oil. However its main limitation is waste oil increased prices due to rapid development of the biofuel industry in the last decade [219].

The use of waste cooking oil has a number of challenges due to FFA and presence of high moisture, which make it hard for transesterification. Although chemical and physical properties of waste cooking oil are similar to fresh edible oil they differ from source to source [217]. For example, the water content and FFA in WCO compared to fresh edible is higher due to the frying process. During frying edible oil undergoes higher heating temperatures of 160 °C to 200°C for a long and a sustained period.

As a result, increased viscosity specific, specific heat, surface tension, colour and fat formation occur. Hence reactions of thermolytic oxidative and hydrolytic nature are observed [220]. Nevertheless, current research centres in operation and management of waste to energy with the focus on the following two key areas. (i) The supply chain incentive, and (ii) regulation policies for WCO to energy.

There is a growing importance on the use of subsidies as a measure of addressing issues of waste to energy based on the model dynamics [221-229]. Regulation policies of waste cooking oil to energy report illegal transaction in waste cooking oil utilized as barriers to expanding WCO utilization. This need increases a requirement of standard inspection and regulations with dedicated infrastructure to help in recycling [223, 230, 231]. For example, in America in south California and north western Mexico [232].

4.2. *Animal Fats Feedstocks*

Tallow is the most common commercially available feedstock from animals for the production of biofuels [233]. The production of meat in the last decade increased significantly to 237.7 million tonnes in 2010 represented by 42.7%, 33.4% and 23.9% for pork, poultry and beef. Nevertheless, the projected growth of these resources increased steadily and now stand at 266909000 million tonnes annually [124]. This corresponds to a representation of 39.76%, 37.3% and 22.97% for pork, chicken and beef. However lard and chicken fat [234] are also commonly used in addition to insects and all other high fat containing animals.

The main reason for use of animal fats as feedstock source is due to their cheap and low prices, hence providing an economical option for biodiesel production [201, 233]. For example, since 2013 the prices of animals based fats has been $ 0.4 to $ 0.5/litre compared to vegetable oil at $0.6 to $0.8 [201]. In the world today 90% of feedstocks for biodiesel production originate from animal

fats and greases compared to the USA at 8% to 10% [235]. In other words from this report there is an observed dynamic animal protein and being expressive especially in the poultry production which shows an annual growth of 4% to 5% in the last decade [236].

Animal fats are characterized by a high content of saturated fatty acids and as biological lipid materials they are composed of TAGs and less of di (DAGs), and mono-acylglycerols (MAGs). Animal fats and greases tend to be solid at room temperature compared to liquid oil of plant origin. This is due to their high content of SFAs [233]. Tallow is a waste final product generated in slaughterhouses and meat processing facilities, whose major composition is myristic, palmitic and stearic acids with tallow and pork lard composition of 40% SFA.

However in the literature surveyed the composition figure is higher for tallow at 45.6%, mutton tallow at 61.1%, lard at 39.3% and chicken fat at 32% [207]. Saturated fatty acids present increased demerits on the physical and chemical properties of biofuels. For example fatty acids cause poor cold properties while unsaturated animal fat content offers advantages of high cetane number, oxidation stability and high calorific value [234]. Thus considering the composition of animals fats as a source of biofuel requires synthesis at elevated temperatures compared to processing vegetable oil [237]. Animal fat greases are classified into two types as reported in literature. This classification is based on the level of FFAs,[207] such as Yellow greases with FFAs of ≤15% w/w and Brown greases with FFAs >15%w/w.

In theory animal fats are thought to contribute to oxidative stability for biodiesel, due to the lack of polysaturated fatty acids such as linoleic and linolenic commonly found in vegetable oil [238]. However comparatively in real-life, animal fats are unstable due to lack of anti-oxidants in their structure. Hence use of animal fats and greases eliminates the need for disposal and result in utilization to the supply of biofuels [239]. Like all feedstock, animal fats have limitations, for example, animal fats contain phospholipid or gums, which are insoluble in water.

These precipitates can plug fuel filters and render them ineffective. Secondly animal fats oil biodiesel deactivates exhaust pre-treatment devices in diesel vehicles [238]. Thirdly is the problem of the presence of high sulfur content mainly from sulfur containing amino acids traced from animal feeds [240]. Since animal fats are highly viscous and solid at ambient temperatures due to unsaturated fatty acids. This leads to poor atomization properties, hence incomplete combustion, while increases emissions of pollutants and particulate matter [241]

4.3. *Algae Oil Feedstocks*

The microalgae family contains more than 100000 species which can be utilized for biodiesel production [242]. However the most one with the highest probability of development in literature surveyed are green algae, diatoms and cyanobacteria (blue algae) [243]. Microalgae content is projected to hit 70% of dry matter and a yield of 90 tonnes/ha of cultivation [244].

Algae grow rapidly in different environmental conditions, while utilizing efficient use of water CO_2 and nutrients on the water surface [245, 246]. This requires if planted in a pond stirring becomes a necessity to ensure accessibility to CO_2 [247]. In addition to their faster growth and high yield content per acre, microalgae oil contains properties identical to petroleum fossil fuel. This is especially true for viscosity, density, flash point and the hydrogen carbon ratio [248].

Use of microalgae as an alternative fuel is being advanced as the fourth-generation biofuel as technology for producing and processing biofuels increases. This will enable its production as a biofuel to be cost effective for large-scale production in the near future. Microalgae compared to land-based plant feedstocks have efficient photosynthetic process in converting and utilizing solar energy into biomass [249]. The main algae, which can be utilized for the production of biofuel, are cyanobacteria as micro or macro algae.

Their sizes determine and influence the production process techniques. For example microalgae produce high oil content but their harvesting is costly due to low efficiency, cell size and low biomass concentration [250, 251]. On the other hand compared to cyanobacteria which are macroalgae the conversion rate into biomass is good but with a complex membrane rapture [252].

In the literature surveyed to produce algae it requires cell growing, separation, and lipid extraction [246]. The main microalgae growing technologies available vary but open pond and closed photobioreactors are commonly utilized [253]. In harvesting microalgae to extract oil physical chemical and enzymatic techniques are employed [254]. Processing of microalgae oil for biofuel production commonly takes the same route of processing and technologies used in vegetable oil and animal fats. It is important to note that fourth generation technologies for production of algal biofuels are still under research and development.

A number of questions remain unanswered. For example, in literature surveyed on algal feedstocks advantages and disadvantages of growing microalgae in fresh and salty water is not available in literature for all types of algae marked for biofuel production. Another factor noticed from literature surveyed is lack of feasibility studies whose data for biofuel microalgae is unavailable. For example, the cost of production for algae is projected at $0.9/kg to $2.55/kg in open pond systems compared to $1.5/kg to $5.5/kg using photobioreactors.

This is despite development in more realistic and appropriate technologies used for algae on commercial scale [243]. The methods utilized in the farming, harvesting and oil extraction for biofuel production still face surmountable difficulties. Nevertheless, microalgal diseases such as contamination are still not clear, although biofuel especially in chain and value addition offer high returns compared to other feedstocks [255]. If

technologies are developed for value addition such as on pharmaceutical, nutraceuticals, biodiesel commercialization etc. could increase economic viability of algal feedstocks for production [256].

4.4. *Waste Biomass Feedstocks*

A number of waste resources arise in line with the diverse human economic and social activities. However, utilization of natural resources such as water, air, soil etc. are being threatened. This solid biomass wastes take many forms either as solids. Although classified as waste they can be reused and turned into energy resources for industrial and domestic purposes [257]. In the current world energy scenario, a number of waste to energy, technologies have emerged. These technologies convert waste biomass into various forms of fuel before utilization as biodiesel [258].

Bio-waste feedstocks differ greatly from primary sources such as coal, in both energy content and physical properties. However compared to coal bio-waste comprise low carbon, high oxygen content, high silica and potassium, less aluminium and iron, low heating values, high moisture, low density per unit of mass and friability [259]. Figure 10 shows the Main waste to energy (WTE) technologies available currently for the utilization of biomass waste.

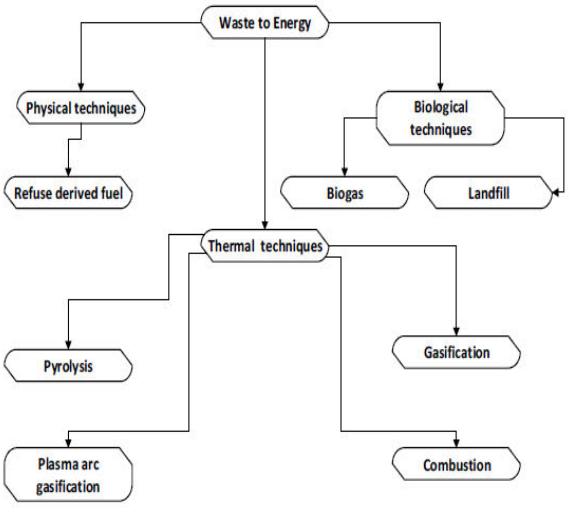

Figure 10: Main waste to energy (WTE) technologies adapted from [259].

However, utilization of natural resources such as water, air soil etc. is being threatened and takes many forms either as solids and can be utilized and reused to become energy resources for industrial and domestic use [260]. In the current world energy scenario, a number of wastes to energy technologies have emerged. These technologies convert waste biomass into various forms of fuel before utilization as a biofuel or biodiesel [259]. Depending on the use of the technology so is, the name derived.

For example in the literature surveyed technologies for fuel production are referred as waste to energy technologies (WFT) [259].The waste technologies include the following categories of utilization; Physical methods, Thermal methods and Biological methods. Globally these technologies have grown to nearly 750 facilities with a capacity to process 140 million tonnes of waste annually [261]. Energy from waste can be treated and compressed to solid fuel or converted into biogas, syngas, or combusted to produce heating for steam production in power generation. The gases produced in such cases include methane, CO_2, hydrogen, and H_3CO or liquid fuels such as ethanol and biodiesel [262].

Biomass to energy has potential feedstocks, which form its main potential line. These include wood, short rotation wood, crop waste, agricultural wastes, short rotation herbaceous crops and animal waste [263]. It is important to note that biomass accounts for 35 % of all energy consumption in developing countries [264, 265]. Nevertheless, biomass utilization carries a huge untapped potential for environmental and energy production, especially agricultural based plants absorbs CO_2 during growth and emit it during combustion.

This helps in the recycling of CO_2 in the atmosphere hence climate change mitigation [266]. Since biomass feedstocks contain lignocellulosic materials, they inherently produce high content of polymers such as cellulose $(C_6H_{10}O_5)x$, hemicellulose (xylas) $(C_5H_8O_4)m$, lignin $(C_9H_{1[267]0}O_3(OCH_3)_{0.9\text{-}1.7]n}$ and sometimes protein. This contributes to renewable energy sources, which are natural, sustainable, inexpensive and eco-friendly feedstocks [260]. Wood biomass thus forms the bulk of waste biomass accounting for 64%, municipal solid waste 24%, agricultural waste 5 % and landfill gases accounting for 5% [268, 269].

4.5. *Bioethanol Feedstocks*

Bioethanol is one of the leading clean and renewable energy sources in the transportation industry today. Globally bioethanol has seen a growth from 4.8 billion gallons in 2000 to 16 billion gallons in 2007 [270], representing a 30 % increase within the mentioned period. However, current statistic trends paint encouraging prospects, indicating for example that since 2007 with global production of 60 billion litres of bioethanol, by 2017 the figures stood at 143 billion litres annually [271].

Bioethanol has many advantages compared to fossil fuels such as high octane, which prevents knocking in internal combustion engines and high oxygen content, which helps to produce less greenhouse gas effects [272-274]. This advantages Allows direct use of ethanol in the automotive industry for internal combustion SI engines without modification and bioethanol works with other oils as a blending agent.

Currently the USA and Brazil are the leading global bioethanol producers with the two countries combined contributing 75 % to 80 % of the total global production [270, 273]. Using corn grain the USA has 187 bioethanol plants spread across different states to produce ethanol [275]. On the other hand, Brazil produces bioethanol from sugar cane based feedstocks only, compared to the European Union who use wheat and sugar beets. In 2013, Brazil produced 37 billion litres compared to European

Union production of 5.785 billion litres of bioethanol and is expected to double its production in the near future.

Due to the reservation on plant-based feedstocks, in future renewable and sustainable feedstocks will dominate energy sources, hence replacing fossil fuels. Bioethanol has been a dominant feature of biofuels, nevertheless technology is moving to microalgae carbohydrates as potential feedstock [276-278]. Microalgae biomass feedstocks contain high contents of carbohydrates, (glycogen, starch, and cellulose) that through fermentation can be converted to sugars for production bioethanol [279, 280].

5. Factors Affecting Biodiesel Production

5.1. *Biodiesel Quality*

The quality of biodiesel of the feedstock used to produce a biodiesel determines the type of catalyst and process applied to produce FFA for the biodiesel production. Nevertheless, the biodiesel feedstock selection and determination are an important factor, inconsistence in the selection of feedstocks can lead to problems of quality and over-budget production. Suffice to mention that biodiesel fuels have standards recommended for their production such as ASTM D675 and EN14214. For example, feedstocks with more than FFA>3wt% cannot use homogeneous catalysts like NaOH, KOH or methoxide due to unwanted side reaction.

In order to produce biodiesel commercially the commonly used basic catalysts such as NaOH, KOH, or Methoxide are utilized. In addition, as a general rule acid catalyst are more appropriate for high FFA content feedstocks. On the other hand, homogeneous catalysts require less alcohol; have a shorter reaction time even though they result into complex products. This leads to required product purification compared to heterogeneous catalysed transesterification process. Development in catalysts has ensured use of a wide range of catalysts for biodiesel production such as heterogeneous and homogeneous acids, bases, sugars, lipases ion exchanges resins, zeolites etc. A number of researchers in the literature reviewed mention biodiesel quality as a factor influencing production include [135, 281-286].

5.2. *Cost of Biodiesel Feedstocks, Investment and Material*

Another factor that influences biodiesel fuel production is the higher cost of production arising from erratic feedstock prices as biodiesels gain widespread application. This is increased by the chemical composition due to their relatively low energy content increased NOx emissions compared to fossil fuels such petroleum diesel [287]. Price determination is an important factor of biodiesel production system and processing.

In every production system of biodiesel, a 50% feedstock price should be the guiding principle of all cost of production. Another factor to consider and is proposed in literature reviewed is price fluctuation especially when promoted through government policy shifts in relation to subsidies and tax incentives [8, 288, 289]. In other words when alternative sources are promoted there is diversification and stock piling to create demand and stabilize stabilization [287].

A number of researchers have reviewed and reported on this concept and can be read in some references provided here such as [239, 290-295]. In all the literature surveyed there is agreement that the higher cost of biofuel production is a major barrier for acceptability and use of biodiesel as an alternative fuel [296, 297].

In literature surveyed, a number of suggestions thus come forward to address this issue. For example, use of cheaper alternatives catalysts Coupled to conversion technologies with lower energy input and faster transesterification reaction [201, 296, 298-301]. Another commonly suggested solution in literature surveyed is the diversification of feedstock by increasingly moving to material materials, not formerly considered as feedstock [302-304]. Figure 11 shows the effect of government policy and promotion to create demand and stabilize prices on palm compared to petroleum diesel.

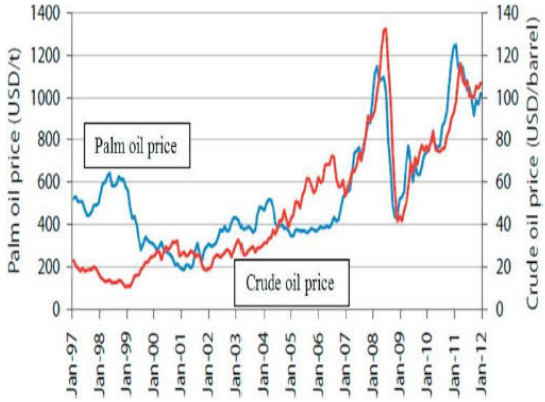

Figure 11: Effect of government promotion on price of feedstock price fluctuation 1997-2012 [305]

5.3. *Effect of Tax Policy Subsidy and Regulation*

In order to empower biofuels and bring them into mainstream economy as usable fuels there is need to implement laws and regulation. These laws should include taxes, policies and subsidies from government as incentives to develop this sector. Particularly in the area of enforcement which mostly needs guidance in order to improve the basic economics of biodiesel.

In the literature surveyed for example, European Union has proposed a renewable energy policy for transport fuels to ensure a viable expansion of the biofuel industry in the near future. As a result, the European Union introduced a blending target in their range of biofuels, which involved hitting a target of 5.75% to 10 % by 2020. Additionally, an amendment to the fuel quality service brought into service a mandatory 6% reduction of GHG by 2020 for transport fuels and non-road and transport engines [306].

Between 2000-2013 biofuels such as ethanol and biodiesel grew exponentially in terms of output from 64 million to 23 billion litters and 0.8 to 14.7 billion litres respectively [307]. For example the USA also crafted a renewable fuel standard program to increase the share of biofuels by 10 % by 2017 and beyond

since 2005 [308]. This increment in biofuel production is purely driven by government policy interventions. This is particularly so in the USA where financial incentives are almost guaranteed for producers [309].

Due to policy shift and incentives, a larger share of global biofuel market has been taken from ethanol to biodiesel in the market [310]. In other words, appropriate policies, tax, mandates and incentives can successfully drive growth of biodiesel. However, it is important to note that biodiesel incentives are distortionary in nature as biofuel use uniquely food crops and multiple feedstocks [311].

In other words, in 2006 for example 20 % of all USA corn production went to biofuels compared to ethanol. Although indicating a positive development in the growth of biofuel, this led to increased producer prices between 2003 to 2008 [312-315]. On the issue of regulation and GHG emission studies in literature reviewed, indicate a negative impact in reduction for specific types of crop feedstocks and their processing techniques. For example, this is revealed in studies conducted by researchers such as [316-318].

5.4. *Competition with the Food Industry Chain*

The increased biofuels production supported by the government policies interferes with food industry chain such as the oleo chemical industry. These industries use the same feedstocks as biofuels hence the rapid growth in the biofuel, which threatens their growth in the future. This is true considering the level of increased feedstock prices yearly. In other words, resource availability will be constrained hence causing a negative impact on the economic value of the food chain [288, 319, 320]. As the Competition for feedstock resources increases with greater incentives to encourage producers meet the demand. This leads to increased demand for resources and with it increased prices for land resources and prices for food [321].

In order to implement a sustainable biodiesel production strategy. The focus should not only be on reduction of GHG emissions but rather a complete package of policies, which support economic and environmental sustainability. However, one notes that the increased biofuel production from land resources and plant feedstocks is the leading cause of deforestation.

In recent trends governments defend their guidelines on implementation of sustainable policies on deforestation as is the case in brazil though it is not sustainable [288]. The second issue on sustainability is related to animal habitat destruction when deforestation is carried in large scale with some of these animals facing extinction [322]. This is due to replacement of virgin forests with plantations of plants such as palm oil. This can led to global warming especially in lower latitude areas while causing overcooling in high latitudes [323]. Use of biofuel in the transport industry when fully running is hoped to stabilize the global carbon cycle although deforestation will negate it. A practical example is in Malaysia where as a consequence GHG emissions increased to about 40 million tonnes of CO_2 up from 5 years earlier at 20 million tonnes of CO_2 [324, 325].

Another area that is often ignored in literature surveyed is change in land use, even with sustainable programs and policies. This problem is acute and severe in America, Mexico, and brazil where abuse of power forces farmers to sell land and move out leading to large population displacement and demographic changes [320]. However the European union seems to contain the problem by putting requirements for types of land to be used for biofuel production plantations as pointed in a number of literature surveyed such as [326, 327].

5.5. *Biomass composition*

In biomass composition, the most influencing factor is the carbon to hydrogen ratio. In other words, due to the differences in decomposition temperature for each of the constituents of biomass. These constituents thus undergo decomposition hence varying product yield. For example, in literature surveyed the following are the temperatures of the three main ligno-cellulosic biomasses [328-330]. This include Hemicellulose with a range of 150°C to 350°C, Cellulose with a range of 275°C to 350°C and Lignin with a range of 250°C to 500°C.

5.6. *Particle Size*

The particle size and composition, the physical structure and shape have a greater influence on the pyrolysis process products when exposed to heating [331]. For example, fine particles offer less resistance to escaping non-condensate gases and vice versa. This behaviour affects product yield [332]. In other words, size reduction of biomass before product extraction offers greater surface area for mass transfer. This enhances diffusion of the active components within the feedstock [333]. In literature surveyed, most scholars report these factors as variables in optimizing bio-oil production. Among the scholars who take this position, include the following researchers [334-337].

5.7. *Effects of Temperature on Pyrolytic Process*

Temperature is an essential factor of influence on pyrolytic product yield. Pyrolytic temperature defines the rate of increase from ambient to maximum until the completion of the process. Pyrolysis temperature thus influence composition and product yield and release rate of the constituent gases. Besides these components, the char produced depends on the pyrolysis temperature [336, 338, 339].

In other words, as the temperature of the reactor increases, the carbon content of the pyrolytic char products increases. This is due to the increase in surface area of the char. However beyond 1173k the temperature decreases slightly due to structural ordering and micropore coalescence with increasing temperature for char above 1073k [340, 341]. Increased heating rate results into a decrease in the carbon content while increasing hydrogen and oxygen content of the char [342].

In literature, surveyed pyrolysis takes many forms of processing but four forms of the criteria are critical namely: Slow

pyrolysis, which is a carbonization pyrolytic process with a primary goal of producing charcoal and char. This is the oldest form of pyrolysis operating at below <400°C over an extended period. Fast pyrolysis is tailored for liquid or bio-oils where biomass is subjected to rapid high temperature heating before decomposition begins. The rate of temperature increase can range from 1000°C/s to 10000°C/s. Nevertheless, the peak temperature is maintained between 650°C to 1000°C. The main features of fast pyrolysis are high heating rate, reaction temperatures of 425°C to 600°C, short residence time (<3s) and rapid cooling of the gas product.

Flash pyrolysis where rapid heating of biomass occurs in the absence of oxygen at moderate temperatures of 450°C to 600°C. In other words, the products of both condensable and non-condensable gas leave the reactor unit faster (short residence time) of 30ms to 1500ms [331]. Ultra-rapid pyrolysis, which borders on the extreme fast mixing of biomass with heating and a carrier solid leading into high transfer of heat and rate of heating. Ultra-rapid pyrolysis utilizes temperatures of 1000°C for gas components compared to 650°C for liquids in order to minimize product yield [343, 344]

5.8. *Effect of Heating Rate Change*

It is important to note that the heating rate of biomass particles from rapid to moderate 400°C to 600°C leads to high volatile yields by producing more char [345]. Owing to fast volatile material release which causes internal pressure and coalescence of smaller pores leading to increased surface area [346]. A number of scholars have studied this phenomenon and reported on it widely such as [347-349]. Nevertheless in literature surveyed it is widely reported that high heating rates of 900°C, a lower surface area is produced and vice versa [350]. In other words higher heating rates cause high char yield interior temperatures, partial graphitization and curtails development of large surface areas [351].

5.9. *Effects of Residence Time*

Residence time Space is inversely proportional to space velocity of the reactants in a pyrolytic reactor [352]. In other words, residence time has a greater impact on conversion and product yield in the pyrolysis process. Studies conducted on biomass gasification from kinetic models report positively on this influence of residence time. For example, the following researchers report how conversion increases in the first 20s and their after the chemical reaction slows down as reflected in a number of studies such as [353-356].

6. Biodiesel Production and Processing Techniques

6.1. *Introduction to Production and Processing Techniques*

Biofuels have increased in demand as the global energy demand grows significantly, although with a requirement for clean fuels [297]. Biofuels are degradable and promising fuels compatible with environment preservation and biodegradable [297]. Although biodiesel is advantageous as a biofuel, its major hindrances are high cost of production, processing and raw materials (feedstock). These costs account for 80% of the total cost of production, making biodiesel more expensive than fossil fuels which it is intended to replace [357]. However, one of the most glaring advantage of biodiesel is its use without modification for diesel-powered engines. Biodiesel use reduces emissions of PM, sulfur, UHC, and carbon monoxide due to a high oxygen content and carbon to hydrogen ratio [358, 359].

In literature surveyed a number of researchers have used many production and processing techniques. However, it is clear from the studies that feedstocks dictate and influence these techniques of production and processing. For example, thermal cracking (pyrolysis), catalytic cracking, Nano-catalytic processing, catalytic hydrocracking, micro-emulsion using solvents and surfactants, transesterification, bio-catalysis processing supercritical production processing.

The following literature references shows extensive work that has been done and reported in modern production techniques as knowledge and skills increase in biofuels; [205, 222, 360-365]. Nevertheless, the number of production methods has been increasing as the material science and biochemical-engineering sections grow. This has brought new and novel concepts as will be seen in the preceding sections of this review.

6.2. *Biodiesel Thermal Cracking (pyrolysis)*

Thermal cracking's main role is to decompose, rearrange and combine hydrocarbon molecules through application of heat. In other words, thermal cracking decomposes high molecules-weight hydrocarbon components into lower molecules weight. This makes the products more valuable hydrocarbon derivatives with lower boiling point species [366], such as gas liquids and char. Pyrolysis as a thermochemical decomposition process has similarities or overlaps with other processes such as carbonization, dry distillation, devolatilization, destructive distillation and thermolysis.

Nevertheless thermal cracking (pyrolysis) is similar and identical to gasification process [332]. Gasification is more external with chemical reactions compared to pyrolysis, carried out in low temperature settings of 300°C to 650°C or higher temperatures of 800°C to 1000°C. The main factors, which influence the process of thermal cracking, include feedstock type, residence time, operating temperatures and pressure. Many of this factors in literature reviewed are discussed and their influence on thermal cracking processes. However, these factors are discussed here briefly but further reading can be done from the references provided here in this section. The process of cracking alternative oils mainly vegetable or animal oils takes two main forms as mentioned in the following references [367-369].

Primary cracking where decomposition of triglycerides molecules occurs, forming acid species by breaking C-O bonds of the glycerides and triacyglycerides chain. Secondary cracking which involves degradation of the produced acids in the primary stage while forming hydrocarbons with properties identical or

similar to petroleum derivatives. The initial products of pyrolysis are condensable gases and solid char. However, further classification of the gases brings a non-condensable class such as CO, CO_2, H_2 and CH_4, liquid and char. In other words, this processes go through gas phase homogeneous reactions, partly gas solid phases heterogeneous reactions [332].

6.3. *Chemical Catalysis Production Technologies*

Chemical catalysis is the science of materials, which accelerate chemical reactions without affecting the equilibrium position of the thermodynamic reaction. Under this method which mostly describes use of catalysts both alkali and acid in the transesterification process. Transesterification has become a more popular method due to its versatility and ease of use [370]. This scheme utilizes triglycerides by reacting them with alcohol in the presence of a catalysts to produce biodiesel (FAME) which is a type of biofuel [371]. Once transesterification process is completed it produces glycerol by products of the process [372].

Transesterification process comprises of sequent reversible reactions. The first step is the conversion of triglycerides to form diglycerides. Followed by the conversion of the diglycerides to monocerides and glycerol and producing one methyl, ester molecule. It is important to note that the transesterification process is heavily dependent on external catalysts to perform reactions. For activation catalysts in transesterification takes two main forms either biological or chemical.

The chemical catalysts comprise of both alkali and acid catalysts as homogeneous agents [373, 374]. Namely, Heterogeneous agents' solid acid or solid alkali, Heterogeneous Nano-catalysts, Supercritical fluids (catalysts). On the other hand, biological catalysts come up through genetic engineering and are mostly preferred. This type of transesterification packs an environmental advantage over all other methods as reported by researchers such as [375-377]. However since it is still under research and development, the cost is prohibitive for commercialization and laboratory use [378].

6.4. *Transesterification Biodiesel Production Techniques*

Transesterification is a process in which none edible oil chemically react with alcohol. It is an imperative process for the production of biodiesel as it reduces biodiesel viscosity of feedstock oil closer to petroleum diesel viscosity [379]. The catalysts used during transesterification are either acidic (sulphuric acid, hydrochloric acid or phosphoric acid) or could be base catalysts such as NaOH, KOH, carbonates and Alkoxides [380]. Base catalysts (alkaline bases) are suitable for oils with FFAs below 3-wt % [381, 382].

Due to their less damage to equipment and efficiency in production, alkaline catalysts are preferred to acidic catalysts in transesterification [383]. During processing in transesterification, it is assumed that 100kg of glycerol will form a cubic meter of biodiesel [166]. This means a large portion of the by-products of the production of biodiesel causes concern to environmentalists. Hence, a number of studies in literature surveyed have studied on how to utilize glycerol, which is a major by-product of this process. For example, a number of researchers have proposed use of glycerol in the hydrogen reaction reforming processes as aqueous or vapour [384-386].

Utilization of glycerol is hailed as a breakthrough in lowering production costs which make biodiesel fuels expensive [387]. In the production of biodiesel 10 %, w/w is glycerol, which translates to every gallon of biodiesel, produces approximately 1.05 pounds of glycerol. For example in a 30 million gallon production plant per year, glycerol is 11500 tonnes. Therefore presenting an opportunity for new application and value addition processes in the commercial and chemical industry. Nevertheless, this area in research is aging behind in terms of data and experimental work, with few researchers having published reviews. Other uses of glycerol identified in literature surveyed include: Glycerol can be used in the production of animal feeds [388]. Glycerol feedstocks are good for chemicals production for example poly-hydroxyalkanoates (PHA), and docosahexaenoic acid (DHA) [389-391]. Glycerol can be used in the production of lipids for sustainable biodiesel feedstock production [392, 393], and in the manufacture of citric acid through biosynthesis [394, 395].

The commonly used alcohols in transesterification reactions include methanol and ethanol due to their low cost and availability. This reaction of alcoholysis reduces viscosity of nonedible oil converting it into triglycerides esters [396]. In other words, transesterification converts the carboxylic acid esters into carboxylic esters. The critical lipid in transesterification include non-polar lipids, triacylglycerols (TAGs) and free fatty acids (FFAs) [397]. There are two main forms of executing transesterification, either through catalytic transesterification or through non-catalytic transesterification [204, 398].

Nevertheless there are two main challenges in literature surveyed related with these two techniques. For example it takes longer time to process biodiesel and there arises a need for separation of the oil alcohol catalyst and the impurities from saponification in the mixture [399]. Therefore, a number of factors, which affect the transesterification process according to literature, surveyed. This factors include such as Reaction temperature, Ratio of alcohol to vegetable reaction, Catalyst used, the mixing speed (intensity of mixing) and Purity of reactants.

6.5. *Emulsion and Microemulsion Biodiesel Production Techniques*

Emulsion or micro-emulsion processes upgrade commodity fossil fuels by forming emulsion and micro-emulsion fuels. Micro emulsion also upgrades oil from other sources or feedstocks such as bio-oil without the help of a surfactant [400, 401]. Emulsion also helps in reducing problems associated with stand-alone bio-oils, hence reduced pollutants in emissions [402]. Emulsion as an upgrading of fuel method ensures that all the components of emulsion are utilized as fuel resources compared to other techniques discussed in other sections in this review.

Emulsion is among the key techniques that solves the problem of performance and emissions prevalent in internal

combustion engines especially diesel propelled ones. This technique is a solution that relies heavily on modification of fuel so that it reduces or eliminates engine modification and redesign. Globally many countries have fuel mandates specifying quantity and type of biofuel to use although the percentages may vary from country to country [403, 404]. For example water emulsion in diesel fuel is regarded as the most economical and effective method to reduce PM and NO_X emissions [405]. Emulsion in diesel fuel extends the combustible limit compared to using non-emulsified diesel fuel. This is due to the reduction of combustion temperature as the water in the mixture has a higher specific heat capacity resulting into secondary atomization as the water droplets explode in the combustion chamber [406-408]. Table 12 showing the properties, droplet size, stability, visual appearance, composition components of emulsion and micro-emulsion.

6.6. *Blending and Hybridization*

Blending in biodiesel production refers to mixing or combining two or more feedstocks into a final product with superior quality and desired characteristics. The blending process has a significant influence on the product homogeneity, as the biodiesel product is denser than petro-diesel besides their differences in cold flow properties. Blending of fuels depends largely on ambient temperature because in cold weather blending may present with challenges or fail in its objectives. There are two basic methods of blending (i) splash blending (either in a tank or in a truck), (ii) in-line blending which includes sequential blending, ratio blending, hybrid blending or side stream blending [409, 410].

Biodiesel hybridization is a new concept that has come up in the study of biofuels. Hybridization is a chemical process of two or more different feedstocks comingled in varying proportions in the production of a new hybrid fuel possessing different physico-chemical properties. Since fuel properties and the physico-chemical configuration of each feedstock vary from source to source, hybridization improves and enhances these properties.

Therefore, the combination of different feedstocks' (hybridization) enhances and improves properties of the initial parent stock, by adapting to improved and high attributes. It is important to mention here that both blending and hybridization cab be *ex-situ* or *in-situ* (the former means after production while the later means before production of biodiesel). Secondly both hybridization and blending produce fuel blends with intermediate properties able to improve combustion and emission characteristics when applied in internal combustion engines [411]

Table 12: Comparisons between emulsion and Microemulsion

Properties	Droplet size	Stability	Visual appearance	Composition	Production	Interfacial tension	Energy input	Chemical reagent Cost
Emulsion	1 µm - 10µm	Kinetically stable, thermodynamically unstable	Translucent, anisotropic	Water, oil, small amount of surfactant , no co-surfactant	Mechanical agitation, ultrasound	Low	High	Low
Microemulsion	1nm - 100nm	Thermodynamically stable	Transparent, isotropic	Water, oil, large amount of surfactant, and sometimes co-surfactant	Produced spontaneously without extra energy	Ultralow	Low	High

Table 13. Potential biodiesel yield from triglyceride feedstocks

Source	Annual yield, gallons/Acre	Reference
Corn	18-20	[416, 417]
Cotton	35-45	[152, 418-421]
Soybean	40-55	[152, 415, 418, 420, 422]
Mustard	60-140	[415, 423]
Camelina	60-65	[423-425]
Safflower	80-85	[420, 426, 427]
Sunflower	75-105	[428-430]
Canola	110-145	[431-433]
Rapeseed	110-130	[235, 434, 435]
Jatropa	140-200	[436-439].
Coconut	250-300	[434, 440, 441]
Palm oil	400-650	[294, 442-444]
Algae	>5000[a]	[445-447]

7. Biodiesel Composition and Physicochemical Properties

7.1, *Introduction*

There is a renewed and continuous increase in the use of biodiesel globally. The composition of biodiesel plays a critical role in dictating physical and chemical profiles of biodiesel FAME materials. A number of researchers such as [215, 412] have investigated this phenomenon. Greenhouse gases, (GHG), have accelerated this global warming, which has caused climate change. The other factor is due to a growing demand and desire to go green by using sustainable energy sources (renewable).

Another important factor fueling biodiesel research and development is energy security domestically as the demand for liquid fuels and supply grows in a fast-changing landscape. In the last decade, a number of countries have embarked on legislative and regulatory pathways to encourage production and use of biodiesel fuels. For example, in the USA using both prescriptive volumetric requirements and incentives.

The energy independence and security Act (EISA of 2007) required 0.5 million gallons/year for biomass-based biofuels to be increased to 1 billion gallons/year by 2012 a target, which has been surpassed [413]. Although biodiesel fuels have a wide variety of feedstocks depending on the geographical location, however the dominant feedstocks are soybean in the USA, rapeseed in Europe and palm oil in South East Asia [414, 415].

Nevertheless, the list of feedstocks is growing to include non-traditional feedstocks such animal fats and lard, used cooking oil, used engine oil, microalgae, municipal solid biomass, canola, coconut, Jatropa, sunflower, safflower, camelina. Table 13 showing Potential biodiesel yield in gallons per acre from triglyceride feedstocks and their references.

In literature, surveyed biodiesel fuel produced contains different varieties of individual FAME species. Nevertheless, a particular feedstock in the literature surveyed could dominate within a FAME species. FAME and FA are classified according to two categories; the first naming uses the number of carbon atoms in the FA chain. The second naming uses the number of carbon double bonds in the chain [414]. Among the 13 commonly found species in literature surveyed, there are 5 species which are dominant and are majorly derived from vegetable and animal fats and include the following; Palmitic acid (16:0), Stearic acid (18:0), Oleic acid (18:1), Linoleic acid (18:2), Linolenic acid (18:3). Table14 is showing the most commonly found fatty acids in the literature surveyed, their common names, formal names, molecular formula and molecular weight.

In biodiesel, composition FAME produced through transesterification is composed of exclusively of even numbered FA chains. It is important to mention here that FAME composition is not limited to vegetable and animal oil feedstocks but includes also algal derived lipids [448]. However, using the hydro-processing on biodiesel alters the FA chain irrespective of feedstock source to odd numbered FA chains. This is due to the removal of one carbon molecule during production of the biodiesel and has been reported in literature significantly by researchers such as [414, 449].

Table 14: Typical fatty acid (FA) groups in biodiesel

Common name	Formal name	Abbreviation	Molecular formula	Molecular weight
Lauric acid	Dodecanoic acid	12:0	$C_{12}H_{24}O_2$	200.32
Myristic acid	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$	228.38
Myristoleic acid	cis-9-tetradecenoic acid	14:1	$C_{14}H_{26}O_2$	226.26
Palmitic acid	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$	256.43
Palmitoleic acid	cis-9-hexadecanoic acid	16:1	$C_{16}H_{30}O_2$	254.42
Stearic acid	Octadeconoic acid	18:0	$C_{18}H_{36}O_2$	284.48
Oleic acid	cis-9-octadecenoic acid	18:1	$C_{18}H_{34}O_2$	282.47
Linoleic acid	cis-9,12-octadecadienoic acid	18:2	$C_{18}H_{32}O_2$	280.46
Linolenic acid	cis-9,12,15-octadecatrienoic	18:3	$C_{18}H_{30}O_2$	278.44
Arachidic acid	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$	312.54
Gondoic acid	cis-11-eicosanoic	20:1	$C_{20}H_{38}O_2$	310.53
Behenic acid	Docosanoic acid	22:0	$C_{22}H_{44}O_2$	340.60
Erucic acid	cis-13-docosenoic acid	22:1	$C_{22}H_{42}O_2$	338.58

Among the commonly found FAME majority are dominated by C18 compounds although a few have lighter compounds C12 such as coconut and palm oil with C16. Feedstocks dominated by C18 have their relative saturation at 18:0, mono-saturated at 18:1 and di-saturated at 18:2. Plant based feedstocks such as rapeseed and canola contain 18:1. Corn and safflower, soybean and sunflower 18:2, Jatropa and yellow grease have similar values 18:1 and 18:2. However, Camelina in literature surveyed contains the highest level at (18:3) while Jatropa has lignocenic acid level of (24:0).

The physicochemical properties of biodiesel are determined by the compositional profile. The physicochemical properties of biodiesel vary substantially as with feedstock source [450, 451]. Due to higher oxygen, content (11% or more) biodiesel fuels have a low carbon to hydrogen content compared to fossil diesel. This gives biodiesel a 10% lower mass to energy content, but due to high density the biodiesel volumetric energy content drops about 5-6% compared to fossil diesel.

In other words, biodiesel has increased molecular weight compared to fossil diesel, reflected in the high distinction temperature (T90). Another important property exhibited by biodiesel fuel is good and excellent cetane number due to the straight chain esters compared to NO_2 fossil diesel octane 93. Biodiesel fuels also especially renewable contain paraffinic hydrocarbons, dominated by odd carbon numbers [452-454]. Lastly comparing biodiesel viscosities with fossil diesel show higher values by a factor of 2 when compared to fossil diesel [455].

7.2. *Kinematic Viscosity*

Viscosity of a biodiesel fuel is a critical property. Viscosity plays a key role in the spray quality, mixture formation and ultimately influences the entire combustion process. In other words high kinematic viscosity interferes with the entire injection process thus leading to insufficient fuel atomization hence poor engine combustion and performance. The mean diameter of the atomized fuel droplets sprayed by the injector and their penetration increases as viscosity increases [456, 457]. Additionally high viscosity leads to rapid pressure rise in injection pumping system thus leading to advanced injection timing [458-462].

Among the leading problems associated with viscosity of fuel, include: Inefficient mixing of fuel which results into incomplete combustion [463]. Early injection due to the high line of pressure thus moving the start of combustion (SOC) closer to the top dead centre (TDC). This increases the maximum mean effective pressure leading to combustion chamber elevated temperature hence increased NO_X emissions in biodiesel blends and fuels [464, 465]. As a property of fuel, viscosity is directly linked to the chemical structure of the fuel composition.

For example viscosity has been reported to increase as the carbon length increases and decreases with increased saturation (number of double bonds) of the biodiesel [214, 466]. Another important fuel property linked to the chemical structure via viscosity is the heat content (also known as the calorific value of a fuel) for both the feedstock and the biodiesel. For both the feedstock and biodiesel, the values increase together, in other words the heat content and viscosity increase or decrease together [214, 467].

Viscosity also is connected to the type of feedstock, for example, the viscosity of fats and greases is higher compared to vegetable oil sources. This is due to different saturation levels of the feedstock, which has been reported by a number of researchers such as [235, 468, 469]. Viscosity values for vegetable oil based feedstocks vary from between 27.2 mm^2/s to 53.6 mm^2/s compared to vegetable oil methyl esters at 3.6 mm^2/s to 4.6 mm^2/s. This phenomenon is due to the process of transesterification [470]. Nevertheless, despite this variation in viscosity due to feedstocks, biodiesel fuels have values relatively within specifications of prescribed standards.

7.3. *Biodiesel Density*

Density is described as the unit of mass per unit area. The density of a biodiesel causes the break-up of fuel injected into the engine cylinder. In other words, as the density of a fuel sample increases the mass of fuel-injected increases. However, regardless of the feedstock used to produce biodiesel oil all biodiesel are high in density compared to fossil diesel [215, 471-473]. The density of a fuel and its compressibility hold a very high influence in diesel engine fuel injection systems. Density thus influences the injected mass injection timing and the injection spray pattern.

These are critical parameters in biodiesel fuel and engine combustion behaviour [464, 474]. In other words, increasing the density increases the diameter of the droplets injected and considering the high inertia of heavier fuel droplets, this increases their penetration as denser fuel requires a shorter injection duration [456]. The speed at which the injected fuel spray penetrates across the combustion chamber determines air utilization and fuel /air ratio mixing rate [475].

Low-density fuel paired with low viscosity fuel when injected provides better and improved atomization and diffusion of the spray, which is an important factor in emission reduction and control. Atomization of the injected liquid fuel mass in the combustion chamber is important. Its importance is in the number of droplets, which are necessary for creating a large surface are for the liquid fuel to evaporate. This is governed by injection parameters and the air/fuel properties [475]. Density is also linked to the calorific value (heating content) of a fuel [214]. For example in literature reviewed density is shown to correlate to PM and NO_X emissions and reported by many researchers in different experimental works such as [476-478].

The carbon chain and the level of saturation affect the density of fuel. In other words, these two factors can increase or lower density considerably depending on their interplaying factors. For example, biodiesel produced from fats and greases tend to be more saturated compared to vegetable oil. An increase in density for example from 860 kg/m^3 for vegetable oil methyl ester (biodiesel) increases the viscosity from 3.59 mm^2/s to 4.63 mm^2/s [470] Hence, fats and greases produce high-density oil compared to vegetable based feedstocks. Nevertheless as alluded earlier this increase in density due to the difference in feedstock falls within acceptable standards a factor that has been reported in literature reviewed for example [479, 480].

7.4. *Cetane Number*

A cetane number in any given fuel is a primer indicator of the fuel ignition quality, which is the same as octane rating in SI fuel. The cetane number measures the knock tendency of a diesel fuel of biodiesel as a function of ignition delay. Although the cetane number is dimensionless, it is generally understood that ignition in compression ignition engines depends on self-ignition of the fuel.

Cetane number has been included as a fuel quality in biodiesel standard and placed at 47 as the minimum for neat biodiesel using ASTM standard. The cetane number also measures the readiness of a particular fuel to auto ignite when introduced into the combustion chamber for combustion. Hence the cetane number is a parameter that is directly proportional to ignition delay in IC engines [481].

Another general assumption made with cetane number is the conceptual generality of the octane scale for gasoline with petrodiesel cetane scale. For example high iso-octane as a primary reference fuel (PRF) has an octane rating of 100 compared to n-heptane at 0 [482]. On the other hand, the cetane scale the long

straight chain hydrocarbon hexadecane ($C_{16}H_{34}$) is used as a PRF with an assigned CN of 100 compared to the highly branched hepta-methylnonane ($C_{16}H_{34}$) at 15. This confirms that branching and length of the carbon chain influence the CN [481]. In other words, increasing branching decreases the chain length hence the CN number also decreases or becomes smaller.

Ignition delay is a period between SOI and SOC. Ignition delay is heavily influenced by engine design parameters such as compression ratio, injection rate, injection time, inlet air temperature and fuel composition and fuel properties. As the cetane number increases, it directly decreases the ignition delay while increasing the phase combustion in diffusion-controlled combustion. Higher cetane numbers result into shorter ignition time. In other words, high cetane numbers reduce injection time, SOC and rapid pressure rise in diesel engine combustion ignition quality varies depending on the density, thus causing trouble during cold start and low load engine operating conditions. Other effects include long ignition delay, leading to increased and rapid pressure rise and high maximum combustion pressure factors, which are not desirable leading to rough engine operation.

In diesel engines, ignition knock is not desirable as it causes engine knock. Among influential effects of cetane number, cold flow and cold starting properties is the increase in smoke and engine noise emissions if found to be low. On the other hand, high cetane number causes SOC close to the injector nozzles hence overheating and nozzle premature failure. Secondly, it increases heat, and traps solid coated particles hence plugging the injector nozzles [472]. Because of this behaviour, a number of literature surveyed, limit the cetane number to below 65 [475]. Additionally a number of studies in literature surveyed on the effect of high cetane number report a correlation with reduced emissions [483-485]. For example smoke, UHC, NO_X emissions reduce, with high CN. This has led to increased efforts to improve biodiesel fuel cetane numbers using additives or cetane improvers [463].

7.5. *The Bulk Modulus of Compressibility*

The bulk modulus of compressibility of a biodiesel explains and provides critical information on the number of spaces in biodiesel fuel molecules. The bulk modulus of compressibility also measures how much the biodiesel oil molecules can be compressed [486]. Although its measurement is difficult in liquids such as biodiesel, the measurement is obtained from the speed of sound and density of a biodiesel using the Newton-Laplace equation. This model utilizes estimates from a number of carbon and double bond of FAME in their chemical structures [487-489]. This is represented in Gibbs free energy (as shown in equations 10 and 11.

$$lnk_s = lnA' + \frac{\Delta G k_s}{RT} \tag{10}$$

where

$$k_s = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right) s \text{ or } u^2 = \frac{1}{k_s \rho} \tag{11}$$

In other words, the bulk modulus of a biodiesel fuel is the reciprocal of its compressibility. This is the fractional change in volume per unit change in pressure P.

where

K_s is the isentropic compressibility (Pa^{-1})

u is the speed of sound ($m.s^{-1}$)

P is the density in kg.m-3

The bulk modulus of compressibility is a critical property in hydraulics such as biodiesel as it affects the hydraulic behaviour of fuels during injection hence its dilation [490]. The bulk modulus of compressibility is associated with the increase in NO_X emissions in diesel and biodiesel variants. High NOx emissions produced by neat and blended biodiesel are linked to low Ks compared to fossil diesel. This has been reported in a number of literature surveyed such as [491-495]. In Studies by [496], the authors established a linear relationship between isentropic compressibility of blends of biodiesel and NOx emission characteristics.

Therefore, the bulk modulus variation within the fuel composition and molecular structure is critical especially in biofuels, which are alternatives to fossil diesel. For example in literature surveyed, a number of experimental studies have been conducted in bulk modulus on biodiesel as alternative fuels and ULSD (Fisher Tropsch) [458, 497, 498]. This studies report advances in injection timing with use of biodiesel and ULSD fuels mainly due to the bulk modulus of compressibility and increased speed of sound. This leads to an earlier needle lift for in-line pump delivery systems [460, 499-502]. It is important to note that advanced injection timing in biodiesel and retarded timing in ULSD increases NO_X as the blend ratio increases with the blend sample and vice versa [503, 504].

In the literature surveyed on the bulk modulus of compressibility there are a number of models used by different authors to estimate the speed of sound in biodiesel. Nevertheless, only two models are commonly used an Example of these authors who have conducted experimental work include [505-509].

7.6. *The Calorific Value*

The calorific value otherwise known as the energy content is energy per unit mass or the volume consumed during the process off combustion to give maximum energy output. The calorific value is also known as the heat of combustion and is numerically equal to the enthalpy of reaction [510]. The calorific value is measured using a bomb calorimeter under ASTM 2015. It is interesting to note that high-density fuels have greater energy content compared to low density fuels. Nevertheless they pack high energy content per unit mass in comparison [295]. In other words, when different fuels with different energy balances are used for performance testing and evaluation the same engine experiences different power outputs.

Biodiesel fuels as hydrocarbon compounds comprise n-saturated, unsaturated, branched cyclics. Vegetable oil, which form a bulk of biodiesel, contain three fatty acids called triglycerides. These fatty acids have a carbon chain length formed in a number of double bonds [511]. Most biodiesel oil contain 74.5 wt % to 78.4 wt%, hydrogen content of 10.6 wt% to 12.4 wt% and an oxygen content of 10.8 wt% to 12 wt % [463]

In other words, the elemental composition of fatty acids is important because it defines the energy content, through provision of weight percentage of carbon, hydrogen and oxygen components within a given sample of biodiesel. For example, the heating values of vegetable oil range from 24.29 MJ/kg to 41.20 MJ/kg. Vegetable source feedstocks have greater differences in heating values, but in surveyed literature, camelina has the highest HHV at 45.2MJ/kg in one study[414]. Others include corn and safflower with 43.1MJ/kg and 42.2MJ/kg respectively. It is also important to note in literature surveyed and data reported in literature there is confusion between this two terms LHV and HHV, which is confirmed in a number of studies such as [414, 448, 449].

Another observation found in the literature surveyed for commonly used biodiesel heating values indicates that they are few. Nevertheless, few researchers have managed to research and put some values for heating values together such as [512-514]. Hence, experimental determination of HHV of biodiesel fuels and other pure fatty acids is not exhaustive. Nevertheless a variety of correlations for predicting different HHV of fatty acids exist such as in (12 and 13 [513].

$$HHV = 49.43 - 0.015IV - 0.041SV \quad (12)$$

$$HHV = 30.84Exp(0.0013MW) \quad (13)$$

where

HHV, IV, SV and MW are high heating value, iodine value, saponification value and molecular weight of the fatty acids

Due to the high oxygen content biodiesel fuels have lower mass to energy, ratio values compared to fossil diesel fuels. Hence, it is generally accepted that biodiesel has 10% less mass energy content MJ/kg [462, 515]. The reduction in calorific value is mainly due to the presence of high oxygen content in the molecular structure of biodiesel fuels. These findings corroborate to a number of studies such as [463, 516, 517].

There are mainly two properties of biodiesel, which influence the calorific value, namely the saponification number and iodine values[518]. In other words, the decrease in saponification value reduces its molecular weight, which is similar to the effect of increased carbon and oxygen percentages in an oil sample. It is also important to note that in a given oil sample the calorific value is greatly affected by the iodine value [470]. The iodine value measures fuel properties of unsaturation.

The ASTM65751 nevertheless excludes it while the EN14214 specifies 120 $mgI_2/100g$. On the other hand, the saponification value of biodiesel sample refers to a hydration reaction to break ester bonds using free hydroxide between fatty acid and glycerol of the triglycerides. The result forms free fatty acids and glycerol components soluble in aqueous solutions in (14.

$$HHV = 0.0303(C) + 1.423(H) \quad (14)$$

As observed from (12 the HHV can be determined using C, H, and O contents of the chemical structure as a function of percentage of these three components. However, (14 is a combination, of oxidative heat, values of C and H and the reduction heat of O with an assumption that the oxygen content effect on the fatty acid fuel has negative HHV. The determined values obtained by equations 12 and 13 and show the hydrogen content as the most decisive factor for unsaturated fatty acids [514]. Nevertheless, (13 shows HHV to be a functional component of the carbon percentage.

7.7. *Oxidative Stability of Biodiesel*

Biodiesel fuels degrade after storage for a long time due to oxidation. Hence, biodiesel stability refers to the ability of the biodiesel to resist degradation to form undesirable species and properties [519, 520]. This makes it possible for a biodiesel to resist physical and chemical changes caused by environmental factors. Nevertheless biodiesel fuels are none resistant to oxidation when exposed to air and moisture, this ultimately affects the biodiesel quality and storage. The existing time from initiation of oxidation to increased rate of oxidation is called induction period [521, 522]. During induction period, the concentration of ROOH is very low although this situation reverses as the reaction progresses.

In literature surveyed biodiesel fuel can degrade through a number of mechanisms [523] such as; Oxidation or autoxidation which occurs as a result of contact with ambient oxygen. The second mechanisms of oxidation is due to thermal oxidative decomposition due to exposure to excessive storage heat or direct light UV rays. The third mechanism comes from hydrolysis or accumulation of moisture or contact with water in storage tanks, fuel lines or moisture due to condensation. The fourth mechanism of biodiesel degradation is due to microbial or biodegradation contamination due to dust particles or water and moisture which contain bacteria or fungi into the storage tank or system. Metal contamination [524] and the Presence or absence of additives [525].

Besides these mechanisms biodiesel fuel itself is susceptible to oxidation and contamination through interaction with light and temperature. This is due to the presence of fatty acids, which interact with oxygen thus making biodiesel unstable. Besides nature and interaction, there are inherent chemical reactions such as alkenes, dienes and compounds of nitrogen, sulfur and oxygen, which hasten and play a dominant role on oxidation. The initial biodiesel products of oxidation are peroxides and hydro-peroxides, which when further degraded produce short chain hydrocarbons such as aldehydes, alcohols, ketones and low molecular compounds [520, 526, 527].

Among the visible physical changes to the naked eye is change in biodiesel physical colour, deposit formation that reduces biodiesel clarity and cleanliness [523, 528]. The degradation of biodiesel correlated to the process of transesterification, which either uses methanol or ethanol as each of them produces different esters. In other words during transesterification the fatty acid chain remains unchanged hence retaining the oxidation chemistry of the feedstock.

This is one of the leading explanation and cause of instability in biodiesel oil [519]. There are three types of oxidative stability identified with biodiesel fuels, which include oxidative stability [529, 530]. Storage stability which involves degradation due to interaction with light, air, metals, moisture and other storage related conditions [531, 532]. And Thermal stability which deals with oxidation at high temperature causing increased oil and fat [533, 534].

Nevertheless primary oxidation is further classified into three main reactions according to [519]. The first one is the initiation reaction where carbon free radicals are formed and produced [531, 535]. In other words, the diatomic oxygen present within the free radicals to form peroxy and further reaction leads to carbon free radical hydro-peroxide (ROOH). This is an extraction of the hydrogen atom from the carbon atom of the chain. The second reaction is the propagation reaction, which reacts the free carbon with atomic oxygen forming stable reaction products of two carbon free radicals, hence termination of the reaction. Vividly captured in equations 15 and 16 either through thermal dissociation of hydrogen peroxide.

$$RH + 1^{*} = R^{*} + 1H \quad (15)$$

$$ROOH \rightarrow RO^{*} + OH^{*} \quad (16)$$

Alternatively, it takes a metal catalysed decomposition of the hydrogen peroxide as in equations 17, 18, 19 and 20.

$$ROOH + M^{2+} \rightarrow RO^{*} + OH^{*} + M^{3+} \quad (17)$$

$$ROOH + M^{3+} \rightarrow ROO^{*} + H^{+} + M^{2+} \quad (18)$$

$$R^{*} + O_2 \rightarrow ROO^{*} \quad (19)$$

$$ROO^{*} + RH \rightarrow ROOH + R^{*} \quad (20)$$

In the secondary oxidation reactions, the hydrogen-peroxide breaks down to form aldehydes of propanol, hexanals and heptanol while forming formic acid, aliphatic alcohol and formate esters. Additionally there is formation of short chain fatty acids, which lead to increased acid biodiesel value [536, 537].

7.8. *Biodiesel Lubricity Properties*

The lubricity of biodiesel refers to the reduction of friction between solid surfaces relative to their motion [538]. Lubricity in biodiesel takes two main mechanisms namely; Hydrodynamic lubrication where a layer of a liquid such as blended biodiesel within the injection system prevents direct contact between opposing moving sides. The second is Boundary lubrication, which refers to compounds formulated to adhere to metallic surfaces while forming a thin protective layer that prevents wear.

These two forms of lubrication alternate with each other to provide lubrication especially boundary lubrication when hydrodynamic lubrication seizes to work or is removed from opposing surfaces. In other words, biodiesel oil should have good lubricity qualities, as this is critical in protecting moving parts in the modern injection systems. Modern day increased operational demands for injection systems is a critical factor and includes high and sustained pressure, injection rate shaping, multiple injection and engine injection cycles. Nevertheless, suffice to say that despite increased need for lubricity, natural lubricity from petroleum fuels has been decreasing with the advent of ULSD. This technology uses high level of hydrotreatment, which removes all heteroatom molecules of O, N and S which are key in improved lubricity[481, 539].

Generally, biodiesel is regarded with high and excellent lubricating properties a reason why blending with ULSD is recommended. This natural lubricity of biodiesel causes biodiesel to have no specification within ASTM and EN standards for B100. However blends B5 to B20 in ASTM7467 includes lubricity specifications[481]. Biodiesels excellent properties of lubricity traced to the esters group within its FAME molecules and other trace impure compounds. For example, free fatty acids and monoglycerides are effective in lubrication [540, 541]. In a number of studies reported in literature surveyed the authors note that the purification process by distillation decreases its lubricity as it removes impurities which are necessary to lubricity [539].

In literature surveyed, the effect of unsaturation on lubricity is inadequately covered and needs further study, as there is no comprehensive data. It is not clear from literature surveyed the role of unsaturation on lubricity and in the few available literatures, the results are mixed. For example, in a number of research work positive and negative effects of carbon-carbon double bonds is reported [215, 481, 542]. It is important to note that this impurities in biodiesel impact lubricity positively although they increase operational problems such as cold starting. Trying to reduce these impurities to improve cold flow properties of biodiesel has worsened the consequence of poor lubricity [414].

7.9. *Cold Flow Biodiesel Properties (Flash Point, Pour Point and Cloud Point)*

The cold flow properties of biodiesel indicate the ability of a biodiesel during cold weather and engine cold starting and is dependent on the long chain saturated factor [204]. Biodiesel fuels have similar and comparable physicochemical features as fossil diesel although their cold flow properties of the two fuels are dissimilar. All biodiesel fuels have very poor cold starting properties irrespective of the source of feedstock and blends without additives.

In biodiesel clod flow properties relate to the melting points of individual fuel components and their solubility in blends [543]. In other words, a high MP causes crystallization and precipitates

once its blend goes beyond its solubility. Due to long chain saturated fatty acids, biodiesel fuel components exhibit higher MP compared to fossil diesel. However, when unsaturated fatty acid components are present the MP decreases. Table 15 shows CP for different feedstocks.

Table 15. Selected biodiesel feedstocks cloud points [544]

Oil /Fat	Methyl ester composition (wt %)						Cloud point	
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	Others	K	°C
Beef tallow	23.9	17.5	43.9	2.3	0.1	12.3	286	13
Palm	39.5	4.1	43.2	10.6	0.2	2.4	283	10
Sunflower	6.1	4.2	24	63.5	0.4	1.8	274	1
Soybean	10.7	3.2	25	53.3	5.4	2.5	272	-1
Linseed	6.7	3.7	21.7	15.8	52.1	0	268	-5
Olive	10.7	2.6	78.7	5.8	0.7	1.5	268	-5
Safflower	6.4	2.2	13.9	76	0.2	1.3	267	-6
Rapeseed	4.3	1.9	61.5	20.6	8.3	3.1	267	-6

Nevertheless the flash point of biodiesel differs and refers to a safety measure of biodiesel storage as it's a point at which a biodiesel fuel spontaneously becomes flammable [545]. On the other hand, the fire point of a hydrocarbon is a point at which a sample of fuel will continue to burn at its highest temperature and remains burning. The difference between the flash point and the fire point is 50 °F to 70 °F. For example, fossil diesel has a flash point of 60 °C to 140°F while the fire point is 93°C to 200 °F $(32°F - 32) \times \frac{5}{9} = °C)$.

Table 16: Flash point and fire point of biodiesel and its blends

Type of fuel	Flash point (°C)	Fire point (°C)
Diesel	60	65
Mahua oil	286	295
MME	175	186
Ethanol	40	47
Kerosene	72	77
MME 20 % ethanol	50	55
MME 10 % ethanol	52	57
MME 10 % ethanol 10% diesel	54	59
MME 20 % kerosene	90	97
MME 10 % kerosene	95	101

The average flashpoint for biodiesel fuel is 150°C compared to fossil diesel at 55°C to 66°C [546]. This difference is primarily due to the difference in their physicochemical properties. For example diesel fuel has low molecular weight molecules with branched compounds hence low flash point compared to biodiesel with trace of alcohol which reduces its flash point [450]. Due to the relationship between the biodiesel flashpoint and alcohol content, the flashpoint sets the limit of residual alcohol in a biodiesel or biofuel.

This means therefore that the flashpoint is an empirical measurement but not a fundamental physical biodiesel parameter and is inversely proportional to fuel volatility [547]. Higher ethanol blends are a fire hazard and as such should be discouraged as they reduce flashpoint and firepoints of biodiesel. Table 16 shows the Flash point and fire point of different biodiesel and their blends.

The pour point of biodiesel is defines as the lowest temperature point which a biodiesel fuel will still manage to flow before turning jelly and waxy [548]. The difference in CFPP value in biodiesel oil samples depend on the feedstock but relies more on the carbon chain length of the saturated oil fatty acids. For example palmitic acid ($C_{16:0}$) in palm oil and ($C_{12:0}$) and ($C_{14:0}$) for coconut and Babassu respectively. In other words, carbon chains produce higher CFPP values [215, 414].

7.10. *Acid Number Biodiesel Properties*

The acid number of biodiesels is defined as the quantity of potassium hydroxide (KOH) which neutralizes fatty acids in a 1g sample. This is expressed in (form as follows in (21.

$$RCOOH + KOH \rightarrow RCOOK + H_2 \quad (21)$$

The acid value is an important biodiesel property as it determines the amount of free fatty acids in a sample of fat; this is elaborated further in (8 [549]:

$$Acid\ Value = \frac{(S-B)\times N\times 56.1}{W} \quad (22)$$

where

S is the standard alkali used during titration of the sample in ml

B is the blank sample used during titration in ml

N is the normal standard alkali

W is the weight of the sample in grams

The biodiesel acid number also shows the sum total of all acid chemicals comprising the following: Phenols, Acids, Sugars, biodiesel oil extracts. Since biodiesel oil have high content of oxygen there is a high association with acidity linked to it [550]. This means the acid number measures the quantity of carboxylic acid groups in a chemical compound like fatty acid or as a mixture of compounds [551]. The acid number of biodiesel is contained in ASTM D 6751 using method ASTM D664 and EN14214 using method EN14104 [481]. Acid numbers quantify the acid values in a sample of biodiesel. Nevertheless Higher acid values cause a number of problems in injection systems by causing severe corrosion of internal component parts [551].

8. Conclusion and Future Recommendation

- Families and family generation are defined by the length of time, likewise the biodiesel families are defined by the length of time.

- Use of non-edible feedstocks is an answer to the challenges paused by edible oil feedstocks. The use of non-edible feedstocks in the production of biodiesel eliminates competition for food, reduction in deforestation rate and co-products waste.
- Besides chemical and physical factors, which affect biodiesel production tax and policy subsidy, completion with food industry, cost of feedstock and investment affect production of biodiesel.
- Although biodiesel is advantageous in many aspects, high cost of production, processing and raw materials (feedstock) which account for 80% make it expensive as an alternative.
- Viscosity plays a key role in the spray quality, mixture formation and ultimately influences the entire combustion process. In other words high kinematic viscosity interferes with the entire injection process thus leading to insufficient fuel atomization hence poor engine combustion and performance.
- The density of fuel is a prime role in the injected mass timing and the injection spray pattern. It is also important to remember that as the density of a fuel sample increases the mass of fuel-injected increases too.
- The cetane number in any given fuel is a primer indicator of the fuel ignition quality, which is the same as octane rating in SI fuel. The cetane number measures the knock tendency of a diesel fuel of biodiesel as a function of ignition delay.
- The elemental composition of fatty acids is important because it defines the energy content within a given sample of biodiesel. Through provision of weight percentage of carbon, hydrogen and oxygen components with a given sample of biodiesel it makes easy to determine the energy content.
- Biodiesel fuel is susceptible to oxidation and contamination through interaction with light and temperature due to the presence of fatty acids, which interact with oxygen. Visible physical changes to the naked eye to show this change in biodiesel include physical colour change of oil, deposit formation that reduces biodiesel clarity and cleanliness.
- Generally biodiesel is regarded with high and excellent lubricating properties a reason why blending with ULSD is recommended.
- Due to the relationship between the biodiesel flashpoint and alcohol content, the flashpoint sets the limit of residual alcohol in a biodiesel or biofuel. In other words although flashpoint is an empirical measurement but not a fundamental physical biodiesel parameter and is inversely proportional to fuel volatility.
- The feedstock type influences difference in the CFPP value in biodiesel oil samples although it relies more on the carbon chain length of the saturated oil fatty acids.
- The acid value has a significant impact on system component s life and performance. Higher acid values contribute to a number of problems in the injection systems sometimes resulting into severe corrosion of internal component parts for injection.

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CHAPTER 3: EVALUATION OF PYROLYSIS OIL FROM PLASTIC AND SOLID WASTE BIOMASS

Journal article

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EVALUATION OF PYROLYSIS OIL FROM PLASTIC AND SOLID WASTE BIOMASS

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ABSTRACT

The main aim of this work was to design, fabricate and evaluate the performance of a small-scale solid waste pyrolysis waste converter reactor. The system's main components were the furnace housing assembly, the reactor assembly, the piping system, the heat exchanger assembly (cooling condenser) and the collection system. The entire system is stainless steel due to its stability at high temperatures, with the reactor holding a capacity of 440.48 kg/weight of waste solids. After design and fabrication, the reactor equipment was subjected to extensive practical performance testing each waste plastic and other solid biomass feedstock three times. The furnace and reactor temperature were controlled at 200 ℃ to 700 ℃ depending on the feedstock for 2 hrs at a constant rate increase of 20 ℃. The results obtained with the equipment showed a functional experimental conversion efficiency of 83.6 %, waste reduction efficiency of 86.6 %, and an oil recovery level of 845 ml/kg of waste.

Keywords: Waste converter reactor, Heat exchanger, Practical performance, Reactor temperature

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1. INTRODUCTION AND BACKGROUND

Due to the increase in energy consumption of fossil fuels as shown in Figure 1 [1], and the continued depletion of natural energy sources in recent years, the research community has focused on energy usage with the objective of improving efficiency and co-combustion and developing renewable energy sources which this research and work is focused on. One such source is waste biomass such as plastic waste, waste tyres, wood and other solid waste which can produce fuel as a result of pyrolysis.

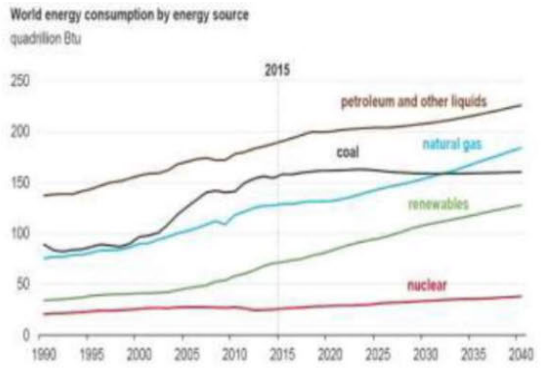

Figure 1 World energy consumption sorted by fuel source [1]

Originally coined from two Greek words *pyro* "fire "and *lysis* "decomposition", pyrolysis is one of the most reliable, efficient and effective thermochemical techniques used in the world today [2] for the recovery of energy from various solid waste resources. For example, the practice of carbonizing wood to make char has existed as long as human history has been recorded [3-6]. Char was the first synthetic material produced by humankind [7, 8]. As civilization progressed with technology, new wood products like acetic acid, methanol and acetone emerged. History records that the Egyptian civilization used pyrolytic fluids from wood such as wood tar and pyroligneous acid to embalm their dead [9].

Pyrolysis is a process where heated feedstock in an oxygen free environment produces pyrolytic oil, char and syngas [10, 11]. Although pyrolysis is an old method, torrefaction is a new concept. This is a new research area in renewable energy which aims at increasing the energy content of biomass through heating biomass for a given time (residence time) in the absence of air at a constant temperature (residence temperature) of between 200 ℃ to 350 ℃ [12].

The process produces oil that can be used as a biodiesel and char for the production of activated carbon [13]. Pyrolysis and now torrefaction is preferred over other methods due to simple operation and low operational costs for the production and recovery of energy from a variety of feedstock [14]. Additionally, the products obtained during pyrolysis can feed the system to generate electricity. Pyrolysis also reduces wastage of land resources by reducing the number of engineered landfill and dumpsites thus freeing a lot of land for agricultural purposes and other developmental planning. Pyrolysis further helps to reduce the carbon footprint penalty as it reduces feedstock and biomass contributing to a carbon neutral environment.

There are five commonly used types of pyrolysis reactors, namely: (i) fluidized-bed [15, 16], (ii) fixed bed [17-20], (iii) rotary kiln [21], (iv) vacuum [22], and (v) free fall [23]. Plastic waste has become an environmental hazard and menace because plastic products are petroleum based which means they are not biodegradable [24].

Disposal and management of waste as a resource has become a dominant problem for both developed, developing and emerging economies. This is because hourly and daily the quantity of waste generated increases proportionately compared to measures to manage and control waste effectively. As a resource, waste mismanagement is a major challenge and a major factor contributing to serious environmental problems such as water sources contamination, frequent flooding, air pollution and, ultimately, to climate change [25].

Plastics have disadvantages such as toxic chemical substances, which affect human health and other living organisms [26]. Worldwide there are about 20 types of plastic types [27]. In a

typical plastic bottle, there are many chemicals present, which can pose a negative impact on human health, for example, bisphenol A (BPA), thalates, anti-minitroxide, brominated flame-retardants and poly-fluorinated chemicals [28]. There are mainly two types of plastics commonly used today, namely, poly-vinyl chloride (PVC) and the high-density polyethylene (HPDE) also known as polyethylene high density (PEHD). Discarded plastics contaminate a wide range of natural terrestrial, fresh water and marine habitats [29] in addition to producing litter in our major urban centres, towns and cities.

Fischer [30] reports that poor plastic disposal leads to poor human health because some of the plastics contaminate humans through drinking water, cooking and the normal food chain. Research has shown that some of the compounds in plastic waste can alter hormones in humans and animals leading to serious negative health complications [29, 31, 32]. Plastics play an important role in our everyday lives. This is due to inherent characteristics such as being inert, durability, flexibility, inexpensive packaging material, and versatility. However, the management of plastic waste and plastic debris has not been anticipated correctly since their invention by Alexander Parkes in 1860 and their widespread use since the 1940s [33].

Globally, plastic waste accounts for between 8 % to 12 % of the total waste produced with a projected global annual increase of 9 % to 13 % by the year 2025 [34, 35]. In South Africa 24 115 402 metric tonnes of waste is generated annually of which 6 % (1 446 924 metric tonnes) is plastic waste with a projected growth rate of 2 % to 3 % since 2008 [36].

The above statistics make the case for integrated waste management approaches to municipal solid waste management. Such an approach requires allocation of more resources to recycling of waste especially plastic waste as an energy resource instead of continuation of landfills and dumpsites, which encourage pollution and are a waste of land, which requires deliberate policy change [37]. Recycling of plastic waste is gaining momentum and increasing in importance globally, with a particular emphasis on waste disposal options with high-energy recovery value, which are sensitive to the environment.

In this work, a pyrolysis unit was designed and fabricated to convert waste plastic waste into oil and other valuable energy sources and energy. The performance of this unit was evaluated and its results are tabulated and shown through equations, figures, tables and graphs.

2. THE METHODOLOGY AND EXPERIMENTAL SET-UP

2.1. Design of Furnace and Development

There is a temperature controlling electric heater employed to maintain the temperature of the system between 400 ℃ and 600 ℃ with a safety feature, which prevents the furnace from overheating or burning out which would lead to malfunction and premature failure. The heating elements are arranged around the housing and the bottom of the furnace housing. In order to provide insulation, prevent heat loss, and conserve heat, two different insulating layers of material are used. Glass wool and a brick wall made of refractory bricks of magnesium oxide act as insulators, and provide resistance from thermal heat losses and shocks. This is expressed in a mathematical relationship in Equations 1, 2, 3 and 4 as:

$$Heat\ Current = \frac{temperature\ difference}{heating\ resistance} \tag{1}$$

$$R = \int_{r}^{r+t} \frac{dx}{2\pi kH} \tag{2}$$

For the furnace cross-section,

$$R = log \frac{[1+\frac{t}{r}]}{2\pi kH} \tag{3}$$

$$HC = \frac{2\pi kH\,(T-T_0)}{log[1+\frac{t}{r}]} \quad (4)$$

Where:

R = heating resistance

r = inner radius of the furnace

t = thickness of the refractory bricks

H = the total height of the furnace

T = final temperature of the furnace

T_0 = initial furnace temperature

HC = heat current

It should be noted that an increase in the thickness of the refractory materials and the glass wool helps to increase small pockets of air between the glass, thus providing thermal insulation, causing the heat current to decrease and thus reduce the heat loss. However, it is important to remember that the weight of the entire unit directly affects the parameters of heat loss reduction. Figure 2 is a schematic diagram of the experimental set-up of the pyrolysis unit.

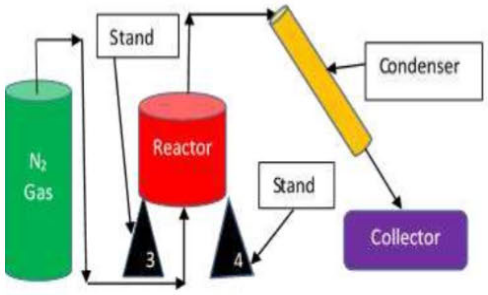

Figure 2 Assembled view of the pyrolysis unit experimental setup

This pyrolysis unit was designed at the University Of KwaZulu Natal School Of Mechanical Engineering by the author who is a member of the Green Energy Group, Howard campus, Durban, South Africa. The final product was fabricated at the university laboratory workshop. The pyrolysis unit comprises the heating system and its control, the reactor tank, pipes, the heat exchanger and the collector, which all culminate in the pyrolysis unit and the process of pyrolysis. The energy requirements for each step are according to Basu [38] and Nhuchhen et al. [39].

The choice of type of reactor and furnace is dependent on several controlling factors such as capacity of plant, type of plant design, cost of the plant, yield, type of feedstock, and the volume and bulk density of the materials used. In the present study, a fixed batch type of reactor was used. This is one of the oldest pyrolysis plant designs, where heat is supplied externally which then allows for combustion or decomposition of the biomass in the reactor. Nitrogen gas is used to ensure the absence of air in the reactor. The main reasons this gas is preferred is due to the fact that it does not react with the biomass and its products

The methodology is divided into the following subtopics:

i. Design of the furnace
ii. Design of the reactor
iii. Design of the heat exchange
iv. Instrumentation and measurement v. Evaluation and performance

2.2. Design Approach and Size of Reactor

The size of reactor was determined by and based on the heat transfer from the furnace housing heating coil to the stainless steel body by heat of conduction and determined by Equation 5 as:

$$Area = Length \times Width \quad (5)$$

2.3. Residence Time

This is defined as the amount of time the plastic biomass takes in the reactor volume in which it is flowing. Residence time is represented by three constants (i) the turnover time, which is a ratio of the biomass material in the volume compared to the rate it passes through the volume, (ii) mean age time, which is the mean length of time biomass material will spend in the volume it was occupying in the reactor, (iii) mean transit time, which is the mean length of time biomass material will spend in the reservoir as it transiting through the thermos-process [40].

2.4. Design Assumption

Table 1 lists the design assumptions.

Table 1 Design assumptions

Insulation material (Glass wool)	(ρ = 64 kg/m³ k = 0.23 W/
Temperature sensing element	m°k k-type
Length of heat exchanger	1000 mm
Inner diameter of heat exchanger	25 mm
Thickness of critical insulation	45 mm
Thickness of stainless steel material	2 mm
Perforated pipe diameter	50 mm
Outer diameter of heat exchanger	10 mm
Inner diameter of furnace	900 mm

2.5. Heat Transfer in the Reactor

The heat transfer equation also known as the heat of conduction is given by the following formulae and expressions in Equations 6, 7 and 8:

$$\text{Conduction} = Q_{cond} \quad (6)$$

$$Q \qquad — \quad (7)$$

Where:

$$— \quad (8)$$

Ah = the area of heating coils

Q_1 = wattage of the heating coils

Q_2 = heat transfer from the heating coil to the reactor in Kw

K_1 = thermal conductivity of stainless steel in W/mK

K_2 = thermal conductivity of the biomass residue in W/mK

X_1= thickness of the heating coils in m

X_2 = thickness of the stainless steel in m

D_t = temperature difference

r_R = internal radius of the reactor in m

D_p= diameter of the pipe in m

r_p = radius of the pipe in m

h = height of the reactor

2.6. The Calculation of the Total Height of the Reactor

The total height of the reactor is calculated from Equation 9 as:

$$h = \frac{V}{\pi r^2} \tag{9}$$

Where:

h = height of the specified zone

V = volume of specified zone

r = internal radius of the reactor

The volume of the reactor can be determined and given by the volume of material in the reactor minus the volume of the pipe as expressed in Equations 10, 11 and 12:

$$volume = V_R \tag{10}$$

$$V_R = \pi r^2 h \tag{11}$$

$$V_p = \pi r^2 h \tag{12}$$

2.7. Reactor Holding Capacity

Figure 3 shows the assembly of the designed reactor that was used to pyrolysis the plastic waste for this work. Since the reactor, tank and cover are of known dimensions, the reactor holding capacity can be determined by means of Equation 13:

$$V = \frac{\pi d^2 h}{4} \tag{13}$$

Where:

V = holding capacity volume

π = 3.14 d = inner diameter of the reactor

h = height of the reactor

d = inner diameter of the reactor

Figure 3 The reactor assembly unit

The reactor capacity was controlled by three factors and expressed in Equations 13, 14, 15, 16 and 17 as:

(i)The bulk mass density

$$\text{Bulk density} = \frac{\text{mass}}{\text{volume}} \tag{14}$$

But:

$$mass = bulk\ density \times volume \tag{15}$$

(ii) Thickness of the insulation

$$r_c = \frac{thermal\ conductivity\ of\ glasswool}{heat\ of\ transfer\ coefficient} \tag{16}$$

$$r_c = \frac{k}{h_c} \tag{17}$$

(iii) Reactor outer diameter

$$D_o = r_c + D_r + r_{critical} \tag{18}$$

2.8. The Heat Exchanger (Condenser)

There are two types of condensers, namely, contact and surface, which are called shell and tube heat exchangers. In the former the gas stream and coolant are physically mixed together, while in the latter the coolant and gas stream or condensed vapour leave the heat exchanger by separate exits [41]. This work uses the surface condenser as a heat exchanger. The length of the tube was designed by the method recommended by Cengel [42] and Demirbas [43] in order to determine the heat capacity rate of the hot fluid. Figure 4 shows a surface heat exchanger designed for this work.

Figure 4 Showing the surface condenser unit

Equations 19 and 20 were used for the hot fluid flow as:

$$C_h = m_h Cp_h \tag{19}$$

Where:

C_h = heat capacity rate

M_h = mass flow rate of the hot fluid in kg/s

Cp_h = specific heat of the hot fluid in kg/s

However, for the cold fluid the equation becomes as follows:

$$C_c = m_c Cp_c \tag{20}$$

Where:

C_c = heat capacity rate of the cold fluid

m_c = mass flow rate of cold fluid in kg/s

Cp_c = specific heat of cold fluid in kJ/kg

C_{min} = minimum heat capacity rate value in W/K

2.9. The Capacity Ratio

The unit's capacity ratio is determined by Equations 21 through 28 as:

$$C = \frac{C_{min}}{C_{max}} \tag{21}$$

Nevertheless, the maximum heat has to be determined from the following mathematical expression:

$$Q_{max} = C_{min}(T_h in - T_c in) \tag{22}$$

Where:

$T_h out$ = temperature of the hot fluid gases going out

$T_c out$ = temperature of the cold fluid gases out

$T_h in$ = the temperature of the hot fluid (water) in

$T_c in$ = the temperature of the cold fluid (water) in

Q_{max} = maximum heat transfer rate in kW

Equation 23 is the actual heat transfer rate as:

$$Q = [mCp(T_{out} - T_{in})] \tag{23}$$

The effectiveness of the heat exchanger is given by:

$$\in = \frac{Q}{Q_{max}} \tag{24}$$

The number of the transfer units (NTU) can be determined if the effectiveness of the heat exchanger for the parallel flow is derived from the following equation:

$$NTU = ln\frac{[1-\in(1+c)]}{1+c} \tag{25}$$

However, the heat transfer surface area A_s (m^2) is determined by the following equation

$$NTU = \frac{UA_s}{C_{min}} \tag{26}$$

But:

$$A_s = \frac{NTU \times C_{min}}{U} \tag{27}$$

Therefore, this equation determines the length of our tube as follows:

$$A_s = \pi DL \tag{28}$$

But:

$$L = \frac{A_s}{\pi D} \tag{29}$$

2.10. Assembling of the Pyrolysis Unit and System

This was the final preparation stage to actualize and commission the unit for performance and evaluation. The system (furnace housing, reactor housing, and heat exchanger) was assembled with thermocouples. Since the temperature of the furnace is crucial for delivery of good results, it is controlled via PID controller by use of probes in the form of thermocouples. The thermocouples are k-type T_1, T_2, T_3, T_4, T_5, T_6, T_7, and T_8.

These were fitted at various points of the unit to help monitor the temperatures of incoming fluids and outgoing fluids and furnace and reactor and the heat exchanger. To eliminate the presence of air in the reactor housing, nitrogen was introduced as an inert gas from the lower side of the reactor. A gasket is utilized between the mating surfaces to provide mechanical sealing and prevent leakage of gases from the reactor. Figure 5 shows the pyrolysis furnace heating system housing assembly.

Figure 5 Showing the pyrolysis furnace unit housing

3. PERFORMANCE AND EVALUATION OF THE PYROLYSIS UNIT

3.1. Fixed Carbon Content

This is the value of carbon that is obtained after subtracting the value of all moisture content, volatile matter and ash content from 100 % in order to balance the carbon value. This is expressed in Equation 30 as:

$$F.C = 100 - (m.c + v.m + a.c) \tag{30}$$

3.2. Ash Content

This is the residual material that remains in the crucible. The material sample is heated again in a muffle furnace at 750 ℃ for an hour and cooled in air i.e. natural cooling and the desiccators are weighed repeatedly until a constant weight is achieved irrespective of more heat. After completion of this test Equation 30 is used to determine the ash content:

$$\%\ of\ ash\ content = \frac{weight\ of\ ash\ left}{weight\ of\ the\ initial\ sample} \tag{31}$$

3.3. Bulk Density of Biomass

The ASTM D1895B standard is applied to determine the bulk density of biomass. Using a cylindrical container of known volume. The first weighing of the container is done when empty to determine its mass, then it is filled with the test sample material and weighed five times in order to establish an average. Table 2 shows the bulk densities for different biomasses, calculated by means of Equation 31 as:

$$Bulk\ density = \frac{average\ mass\ of\ material\ sample}{volume\ of\ the\ container} \tag{32}$$

Table 2 Showing different bulk densities for different biomasses [44-47]

Material	Bulk density (kg/m^3)
Timber	178
Gypsum plasterboard	207.7
Plaster gypsum	593.3
Masonry (brick)	830.6
plastics	13
Metals	900
Glass	2500
CDW mix (general)	830.6

3.4. Volatile Matter

In order to determine the volatile matter in a sample to be tested a muffle furnace is utilized to heat the sample at a constant temperature of 900°C in a covered crucible for 5 min to 7 min. After heating the sample is allowed to cool in air naturally, and reweighed. The volatile matter from the sample is calculated as in Equation 33 as:

$$\% \text{ of V.M} = \text{Weight in volatile matter divided by Weight of initial sample} \quad (33)$$

3.5. The Moisture Content

The moisture content plays a major role in the calculation of biomass, although it varies considerably. For this work, the oven dry method was applied at 110 °C for 24 hours after which the sample was weighed [48-50]. The final moisture content was then calculated and determined using Equation 34:

$$Mc = (W1-W2)/W1 \times 100 \quad (34)$$

Where:

W_1 = the weight of sample before drying

W_2 = the weight of sample after drying

3.6. The Biodiesel Oil Produced, Properties and Analysis

Table 4 shows the parameters that were considered for analysis and evaluation to determine the quality and chemical composition of the waste plastic pyrolysis oil (WPPO) produced from the unit.

Table 4 The test fuel properties, their units of measurement, standard methods of testing and the values for conventional diesel (CD) in comparison to the values of waste plastic pyrolysis oil (WPPO)

Property	Unit	CD	WPPO	STANDARD
Appearance	-	Clear/brown	Clear/amber	Visual
Density @20	kg/m^3	838.8	788.9	ASTM D1298
Kinematic viscosity @ 40 °C	cSt	2.32	2.17	ASTM D445
Flash point	°C	56.0	20.0	ASTM D93
Cetane index	-	46	65	ASTM D4737
Hydrogen	%	12.38	11.77	ASTM D7171
Cu corrosion	3hrs @ 100 °C	-	1B	ASTM D130
Carbon	%	74.99	79.60	ASTM D7662
Oxygen	%	12.45	7.83	ASTM D5622
Sulphur content	%	<0.0124	0.15	ASTM D4294
IBP temperature	°C	160	119	ASTM D86
FBP temperature	°C	353.5	353.5	ASTM D86
Recovery	%	-	98	-
Residue and loss	%	-	2.0	-
GCV	kJ/kg	44.84	40.15	ASTM D4868

3.7. Instrumentation and Measurement

Below are samples of the instruments that were used during this study and their names (Figure 6, Figure 7, Figure 8).

Figure 6 Redwood viscometer

Figure 7 Bomb calorimeter

Figure 8 Flashpoint machine

3.8. Output Products of the Unit

Figure 9 and Figure 10 show some of the sample output products from the pyrolysis unit that were produced during the performance testing.

Figure 9 Oil as an output of the equipment

Figure 10 Char as an output of the equipment

3.9 Performance and Evaluation Results

Table 4 and Table 5 show performance evaluation data and pyrolysis unit output data.

Table 5 Showing performance evaluation test trials data

Parameters	No of Test Trials						
	1	2	3	4	5	Total	Total/5=Average
Weight of Sample (kg)	100	100	100	100	100	500	100
Resident Time (hrs)	2	2	2	2	2	10	2
Recovered oil (ml/kg)	785	815	865	885	875	4225	845
Weight of oil recovered (g)	775	802	848	855	860	4140	828
Weight of Char Recovered (g)	15.5	14	13.5	12	11	66	13.2

Table 6 Pyrolysis unit output

Parameters	No. of Test Trials						
	1	2	3	4	5	Total	Total/5=Average
Conversion Efficiency (wt. %)	79	82	85	83.5	88.5	418	83.6
Waste Reduction Efficiency (wt. %)	81	82.5	87	90.5	92	433	86.6
Oil Recovery in (ml)/kg of plastic waste	785	815	865	885	875	4225	845

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CHAPTER 4: THE EFFECT OF FUEL ADDITIVES ON PYRORATED BIODIESEL BLENDS ON THE PERFORMANCE OF A DIESEL POWER GENERATOR

Journal article

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The Effect of Fuel Additives on Pyrorated Biodiesel Blends on the Performance of a Diesel Power Generator

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ABSTRACT

The demand for renewable energy sources such as waste pyrolysis plastic oil (WPPO), ethanol biofuel with high oxygen content is increasing globally. This study used blending of conventional diesel oil, waste plastic pyrolysis oil, ethanol and 2-ethyl hexyl nitrate (EHN) as additive. The purpose was to improve combustion, the ignition quality, and performance and emission characteristics of WPPO as an alternative source of energy. As an additive EHN reduces emissions of CO, CO_2, UHC, NO_X, and PM. On the other hand, the inclusion of ethanol purposed to improve the viscosity, increase the oxygen content of the blends, and increase miscibility of WPPO. The study utilized the following ratios, 50/WPPO25/E25, 60/WPPO20/E20, 70/WPPO15/E15, 80/WPPO10/E10 and 90/WPPO5/E5 for conventional diesel (CD), WPPO and ethanol and EHN respectively. The ratio of the additive was determined by the percentage method based on the total quantity of the blended fuel and was calculated as 0.001 %. A complete Miscibility was observed to avoid phase separation during the study and experimentation, for the blended ratios of WPPO. The testing for performance and emission characteristics was conducted on a fixed bed, water-cooled, single cylinder diesel generator engine. The results were compared to ASTM standards and discussed using tables and figures. The results conclusively show very close densities of 792 kg/m^3, 963 kg/m^3, 825 kg/m^3 for WPPO, ethanol, EHN respectively, which are close to CD fuel at 845 kg/m^3. Increased blend ratio decreased BSFC, 50 % engine load blend 80/WPPO10/E10 had values of 0.043 g/kW.h compared to full load with 0.041 g/kW.h. The highest brake thermal efficiency was by blend 90/WPPO5/E5 at 25 % engine load with a value of 26.5 % compared to 19 % at full engine load. Increase in the blend ratio and engine load decreased CO emissions up to 75 % engine load. For example, blend 90/WPPO5/E5 had a value of 0.035 % carbon emissions compared to 0.055 % at 25 % engine load. Therefore, conclusively WPPO blends can be alternative fuel with or without major engine modification.

1. Introduction

The demand for energy due to the increasing world population energy needs has placed tremendous pressure on the primary sources of energy, which are oil-based fossil fuels, in the last decade [1-3]. Although economically good on the other hand, widespread use and burning of fossil fuels is responsible for long-term environment problem in climatic changes. Secondly, fossil fuels are non-renewable and as such, their depletion is a global energy security threat. Besides depletion, the burning of fossil fuels decreases air quality leading to large-scale increase in cardiovascular diseases and cancer cases [4-6].

Globally fossil fuel still commands 80 % of the total energy requirements of the world which is consumed mostly by the transport industry alone [7]. The largest fossil fuel brand is diesel, which is a primary in diesel engines used for commercial and private transportation. Since their discovery in 1893 by Rudolph Diesel, diesel engine are efficient and good in fuel economy over power [8, 9]. Diesel engines are gaining more popularity in agricultural transport and applications, power generation and heating systems. This is due to their high thermal efficiency

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resulting into energy saving overload and safety aspects due to low volatility [10, 11].

However, diesel engines are responsible of high smoke and NOx emissions [12, 13]. Leading Diesel exhaust to be classified as carcinogenic [14] to humans which link it to increased risk of lung cancer and other cardiovascular ailments [15]. The diesel exhaust is now one of the primary sources of ground ozone [16], the sick building syndrome [17], acid rain [18], and smog [19]. Other disadvantages of fossil fuels include erratic fuel prices in the world market, potential turmoil in oil producing countries and the ever-increasing emission control requirements by governments. Therefore, finding an alternative renewable fuel that can mitigate the negative impact of fossil fuels cannot be emphasized [20].

The earliest development in alternative fuels utilized food crop-based feedstocks. As a result, this increased food insecurity in low middle-income countries and the developing countries. Hence, human rights campaigners including United Nations Food and Agriculture Organization (FAO) and the UN Security Council on human rights rejected these feedstocks. The rejection was based on Commercialization of large swathes of land for biodiesel feedstock cultivation, hence suppression of edible food crop acreage. Consequently, food prices increased and prices of essential commodities increased too [21]. Early this year a palm oil has been removed as a biodiesel feedstock by United Nations agencies like FAO due to the continued environmental hazards food security challenges in Malaysia and Indonesia.

In recent years, research has awakened focus and interest in higher alcohols due to their high levels of energy, higher cetane number (CN); better blend stability, less hygroscopic tendencies, increased carbon chain length and improved ignition quality by the alcohol fuel molecules [22]. However, lower level of alcohols methanol and ethanol, still have high qualities oxygenates. The availability of high-oxygen content with a hydroxyl (OH) group is one of the major advantages of alcohols, it reduces smoke emissions and opacity during high engine load [23, 24]. Other advantages of ethanol which make it preferable as an additive for waste plastic pyrolysis oil (WPPO) biodiesel blends include (i) ethanol is made from sources of plant origin, making it renewable, (ii) improvement in modern fermentation processes in biotechnology engineering.

This has led to improved yields in ethanol by synthesizing cellulose, for example *Clostridium species* [25], biosynthesis from glucose using genetically engineered micro-organisms like *Escherichia* coli [26], *cyanobacteria* [27] and *Saccharomyces cerevisiae* [28]. The third reason why ethanol is important as additive in WPPO due to its inherent physicochemical composition properties. These characteristics include the presence of high oxygen content, high solubility and miscibility in WPPO blends [29-34].

Extracting liquid fuel from plastic waste material using thermal decomposition in viable and sustainable technologies has been reported in research in the last decade. Plastic waste decomposition is not only through thermal processes but also through catalytic pyrolysis. The catalytic technique uses low levels of temperature to cause plastic decomposition compared to thermal decomposition, which employs very high temperatures to produce greater yield of liquid oil. This has increased developments in turning plastic waste into energy a development that has captivated and motivated researchers such as [35-37]. A number of researchers have studied additives in their work on performance and emission impacts using biodiesel blends such as [38-53]. Especially when the final product is used with fuel additives with characteristics focusing on reducing NO_X, CO, CO_2, unburnt hydrocarbon (UHC) and particulate matter (PM) emissions [20].

A number of studies have been conducted on the reduction of NO_X and PM emissions using additives and biodiesel blends in diesel engines such as: [54] the authors used ethanol, selective catalytic reduction (SCR) catalyst Ag/Al_2O_3, and blends of biodiesel-ethanol fuel (BE). The results were mixed for emissions of UHC, CO, and PM, with an increase of 14% respectively. The authors attributed it to the presence and increase in SOFs in the PM emissions. However, a decrease in the Bosch smoke by 60 % to 80 % was reported using the European stationary cycle (ESC) standard. The NO_X emissions reduced by a margin of 73 % leading to a conclusion that a combination of BE and SCR catalyst arrangement provides a platform for the reduction and control of PM and NO_X emissions.

In another study by [55] wanted to determine cold flow features using ethanol-biodiesel blends by characterization. In this study a relationship between blend and torque, brake thermal efficiency, brake specific fuel consumption and emission characteristics. The findings of this study have led developed and developing countries to adopt and make fuel blending a mandatory requirement in Europe, USA and Brazil. For example, In the United States of America, the renewable fuel standard (RFS) program requires blending of fuels in increasing measure with fossil transportation fuel. This is targeting an annual growth rate escalation of 36 billion gallons by 2022 [56].

As an additive in blends, an increase in the ethanol fraction decreases auto-ignition properties of the blends, due to ethanol's low propensity [57-64]. These findings report a decrease in the CN value of the blends as the fraction of ethanol increases as the main cause. Reduced CN values prolong ignition delay and is undesirable in the combustion of the blends. Ignition delay is responsible for increased engine peak combustion pressure [65, 66]. This increases wear, combustion noises besides increasing NO_X emissions in diesel engines. The effect of CN alteration on combustion values in relation to blend characteristics is not a new research area. For example, researchers such [67-74] have covered this area and one can read the findings and conclusions.

Plastics contain a high potential of stored energy from hydrocarbon inherent in their makeup and molecular structure. Plastics are daily used in our lives and are readily available as waste in municipal solid waste sites. Plastics have become a health hazard as they litter everywhere while pausing an environmental danger to humans and animals. Therefore, altering them through modern processing methods into liquid oils for transportation fuels is a novel idea whose time has come. [75]. This study aims at utilizing and developing feedstocks from waste streams of plastics and converting them through pyrolysis into energy. This will provide a framework for creating alternative fuels to reduce dependency on petroleum fuels, which are primary transport fuels. The third aspect of this work is to show the importance of blending WPPO or any other new alternative feedstocks to improve their

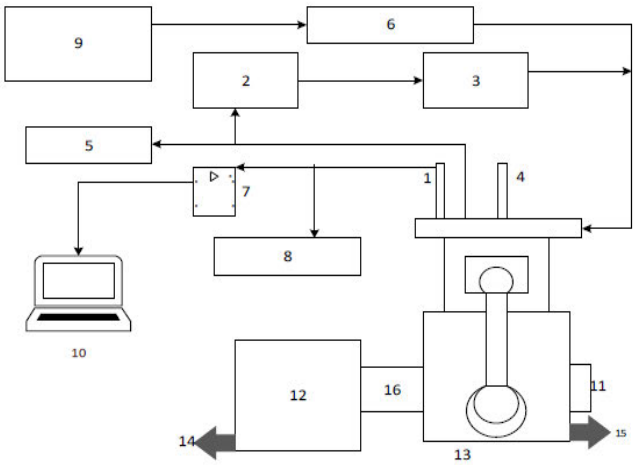

Figure 1: Schematic diagram of the test engine rig

Key: 1 Cylinder pressure sensor; 2 EGR control valve; 3 EGR cooler; 4 Injection control unit; 5 Exhaust gas exit; 6 Air box; 7 Signal amplifier; 8 Gas analyser; 9 Air flow meter; 10 Data acquisition system; 11 Crank position sensor; 12 Dynamometer; 13 Engine; 14 Cooling water exit from the dynamometer to the cooling tower; 15 Cooling water exit from engine to the cooling tower; 16 Dynamometer drive coupling

qualities. The focus is to reduce emission and enhance performance of transportation fuel while creating jobs in recycling but protecting our environment.

2. Methodology

2.1. Methodology and Experimental Set-Up

This experiment is making a case for blending of WPPO whose n-alkenes are very low by 25 % in auto-ignition, compared to diesel fuel whose n-alkenes are good for auto-ignition. The aromatics, which affect PM emissions, are very low in WPPO blends. WPPO consists of iso-alkanes, n-alkanes, and olefins in the areas of 27 %, 25 %, and 9 % respectively, the remaining 30 % content is undefined due to complicated chemical bond structures [76, 77]. However, aromatics cyclo-alkanes (naphthalene) and other poor in auto-ignition were also found to be 40 % by [78]. Blending was preferred to improve the low pour point of WPPO to improve its cold starting characteristics. Secondly blending improves the fuel spray characteristics. Blending using ethanol, which is soluble and miscible in WPPO blends, also improves physicochemical properties of blends. Thirdly blending helped this experiment to reduce the viscosity of WPPO biodiesel, thus aiding and improving spray characteristics. The blends used in this experiment are broken into five ratios namely: 50/WPPO25/E25, 60/WPPO20/E20, 70/WPPO15/E15, 80/WPPO10/E10 and 90/WPPO5/E5 respectively. For example, to define a blend sample such as 90/WPPO5/E5 is composed of 90 % conventional diesel (CD) fuel by volume 5 % WPPO and 5 % additive 2-Ethyhexyl Nitrate (EHN) respectively for all the replicates.

2.2. Engine Tests

The experiment used a naturally aspirated single-cylinder diesel engine power generator, water cooled, direct injection, Kirloskar TV1, in the Mechanical Engineering Department Laboratory, the University of KwaZulu Natal in Durban, South Africa. The details of the engine and specifications are in Table 1. Figure 1 shows a schematic of the engine test setup.

Table 1: Experimental engine specification

Parameters	Position value
Ignition Type	4 (Stroke)DICI
Number Of Cylinders	1
Model	TV 1
Cooling Medium	Water
Manufacturer	Kirloskar
Revolutions Per Minute	1500
Brake Power	3.5 kW
Cylinder Bore	87.5 mm
Piston Stroke	110 mm
Compression Ratio	18.5:1
Connecting-Rod Length	234
Engine Capacity	661cc
Dynamometer Make	234
Injection Timing	23.4˚bTDC
Maximum Torque	28 Nm @1500
Injection Pressure	250 Bar

2.3. Physicochemical Property Analysis

The WPPO pyrolysis unit was designed at the University of KwaZulu Natal School of mechanical engineering GPS (29°52'09.9"S 30°58'37.9"E), by the author who is from the Green Energy Group, Howard campus, Durban, South Africa. Lucien engineering Company fabricated the final product in their premises in Durban. The pyrolysis unit comprised of the heating system and its control, the reactor tank, pipes, the heat exchanger and the collector, which all culminate into the pyrolysis unit. The energy requirements for each step is according to the references [79, 80], and the plant's production chart is shown in Figure 3. Ethanol, conventional diesel and EHN in local outlets and blended using a homogenizer for 5 min at 3000 rpm. Sampling and testing for properties was in the Department of Chemical Engineering Laboratory, at the University of KwaZulu Natal in Durban, South Africa. Table 2 shows some important physicochemical properties of the fuels oils before blending.

Table 2: Properties of Diesel, WPPO, and ethanol before blending and the addition of EHN

Properties	Unit	CD	WPPO	Ethanol
Density @ 20°C	kg/m^3	845	825	792
Visc.@ 40°C	cSt	3.04	2.538	1.05
Cetane Number	_	55	_	8.5
Flash Point	° C	50	43	16
Fire Point	° C	56	45	53
Carbon residue	%	22	0.015	_
Sulfur content	%	<0.028	0.248	_
Gross Calories	kJ/kg	46500	43340	29700
Cetane index	_	46	65	_

Table 3: Properties of blended ratio mixtures of diesel, ethanol, WPPO with EHN

Property	Unit	CD	90/5/5	80/10/10	70/15/15	60/20/20	50/25/25	STANDARD
Density	Kg/m^3	842	838.5	834	830	825	823	ASTM D1298
KViscosity@40	cST	3.452	2.38	2.37	2.365	2.340	2.325	ASTM D445
Cetane Number	-	48	58	60	62	63	65	ASTM D4737
GCV	kJ/kg	44840	40125	39985	38700	36800	34500	ASTM D4868
Sulfur Content	%	<0.0124	0.0248	0.0249	0.0251	0.0253	0.0257	ASTM D4294
Oxygen	%	12.35	11.80	10.75	10.15	10.25	10.35	ASTM D5622
Carbon Residue	%	74.85	75.35	76.40	77.55	78.25	79.65	ASTM D7662
Flashpoint	°C	56.5	38.5	37.55	37.35	37.15	36.85	ASTM D93
Hydrogen	%	12.38	7.5	7.55	7.65	7.75	7.95	ASTM D7171

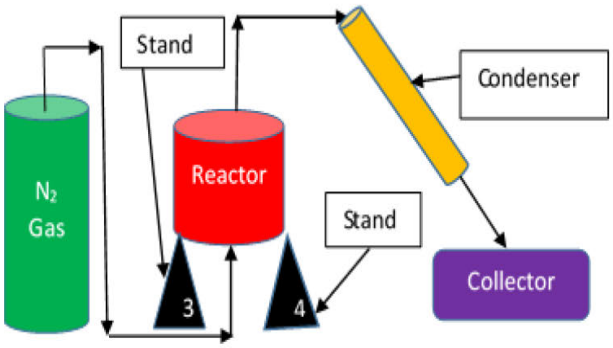

Figure 2: Assembled view of the pyrolysis unit experimental set-up

Table 3 shows the physicochemical properties of blended mixtures fuels and their determined fuel properties after blending in relation to American Standard of Testing and Measurements (ASTM).

3. Results and Discussion

3.1. Brake Specific Fuel Consumption

Figure 3 is a variation of brake specific fuel consumption (BSFC) with engine load. The BSFC compared to the engine load in Fig. 3 shows that as the load increases there is an equal increase for fuel consumed by the test engine. The values obtained at full engine load for the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 and CD were 0.04 g/kW.h, 0.041 g/kW.h, 0.042 g/kW.h, 0.043 g/kW.h and 0.035 g/kW.h respectively.

At high engine loads the conversion of heat energy to mechanical energy increases with increase in combustion temperature, leading to increased BSFC for the biodiesel. This increase is proportional to the difference in their heating values which is identical to the findings of [81]. Additionally, WPPO blends have high densities, therefore suffer high mass injection pressure, hence the increase in BSFC which is identical to studies by [82, 83]. These blends of WPPO compare well to conventional diesel fuel and sometimes-other biodiesel blends with comparative differences in the heating values.

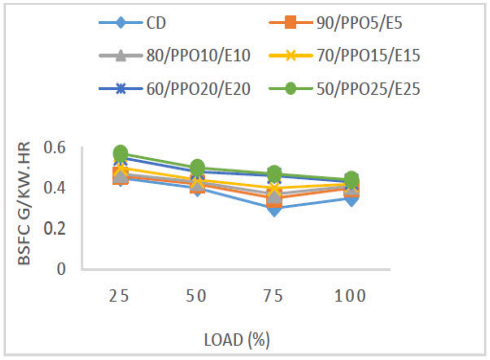

Figure 3: Brake specific fuel consumption versus load

As the blend ratio increased there was a decrease in the BSFC across all the test fuels. However, the values for all WPPO blends increased compared to CD test fuel. This is due to the lower calorific values of the blends as the percentage of the blend ratio

increased. In other words, by increasing the ratio of WPPO in the diesel test fuel, the engine fuel consumption increased, this is identical to the studies of [84-86]. The closeness of the values and the packed graph reveal a close resemblance and identical BSFC characteristics of WPPO, ethanol, and EHN compared to CD fuel. For example, at 50 % engine load the blend of 80/WPPO10/E10 had a value of 0.043 g/kW.h compared to full engine load with 0.041 g/kW.h. This value is higher than CD test fuel with 0.04g/kW.h at 50 % engine load and 0.035 g/kW.h at full engine load.

3.2. Brake Thermal Efficiency

The brake thermal efficiency (BTE) variations with engine load is as shown in Figure 4. The graphs show that, as the load increased there was an increase in the BTE across all the test fuel blends of WPPO and CD. The result of this experiment shows that the BTE increased as the load increased, explained by the reduction in the heat loss as the engine power (more fuel) increased with load. At 50 % engine load the values for blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 and CD were 22 %, 21 %, 20 %, 18 %, 16.5 % and 22.5 % respectively. As the blend ratio and engine load increased, there was an increase in BTE across the blends of WPPO but with a decrease in the BTE within the blends. For example, at 25 % engine load, 90/WPPO5/E5 had values of 14 %, 22 %, 26.5 % and 25 % compared to 70/WPPO15/E15 with 12.5 %, 20 %, 22.5 % and 23 % respectively.

The highest BTE value was by blend 90/WPPO5/E5 at 25 % engine load compared to any other blend of WPPO. For example, Fig. 4 shows values of 24.8 %, 23 %, 21 % and 19 % respectively for blends 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25. However, blend 50/WPPO25/E25 reported the lowest values compared to the other blends. At 25 % engine load the BTE value was 9.5 % compared with 19 % at full load, these two are the lowest values of BTE.

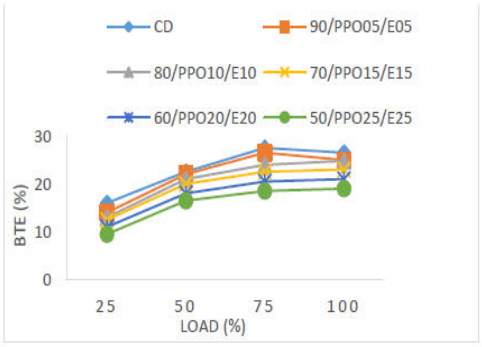

Figure 4: Brake thermal efficiency versus load

3.3. Exhaust Gas Temperature

Figure 5 is a variation of exhaust gas temperature (EGT) and engine load. The graph reveals that as the load increases the value of the EGT increased significantly and linearly especially for the blends. At 25 % engine load the blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20; 50/WPPO25/E25 reported values of 165 ºC, 195 ºC, 226 ºC and 256 ºC compared to CD with 155 ºC, 175 ºC, 205 ºC and 240 ºC for all engine load conditions. What explains this increase in engine temperatures is the increase in the required fuel to compensate increased load. However, observed also is temperature increase becomes pronounced with increased blend ratio of WPPO compared to CD test fuel as in Figure 5. The second reason for increased EGT temperature increase is the BTE heat loss factor for high blend ratios compared to CD test fuel.

The experiment also showed another interesting observation, as the engine load increased from 25 % to full load (100 %) the graph curves tend toward unitary, adopting almost identical and similar values to CD test fuel. This concludes that the blends of WPPO, ethanol, and fuel additives have identical temperature characteristics to those of CD test fuel especially as the engine load hits 75 % heading to 100 % (full load). This is due to the presence of ethanol, which decreased ignition delay thus lowering the combustion temperature. The equations are an exception to the prescribed specifications of this template. You will need to determine whether or not your equation should be typed using either the Times New Roman or the Symbol font (please no other font). To create multi-levelled equations, it may be necessary to treat the equation as a graphic and insert it into the text after your paper is styled.

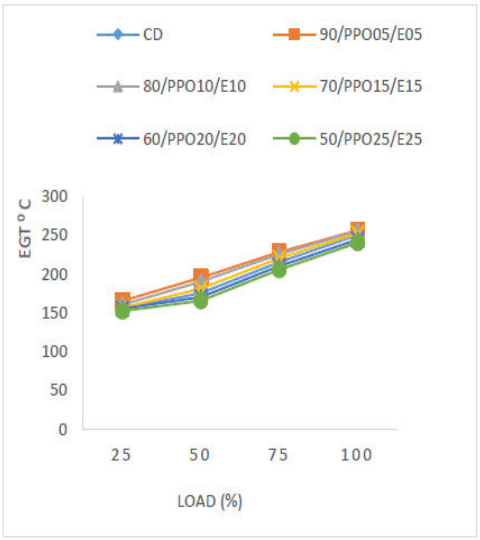

Figure 5: Exhaust gas temperature versus load

3.4. Carbon Monoxide

Figure 6 is a variation of carbon monoxide (CO) with engine load. The graph reveals that as the engine load and the blend ratio increased CO emissions decreased up to 75 % of engine load. This was for all blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25. The highest value in Figure 6 of CO emission reported was 0.0625 % for blend 50/WPPO25/E25 and the lowest value reported was by blend 90/WPPO5/E5 at 0.055 %. Another observation is that as the engine was approaching full load, all the test fuels showed increased CO emissions with blends 90/WPPO5/E5 and 80/WPPO10/E10 reporting the lowest emissions among the test blends across all the engine load conditions.

For example, at 25 % engine load the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 reported values of 0.055 %, 0.0565 %, 0.06 %, 0.0615 % and 0.0625 %. However, as the load increased for

example, from 25 % to 75 % the values reported are 0.035 %, 0.0375 %, 0.0445 % and 0.0.0475 respectively.

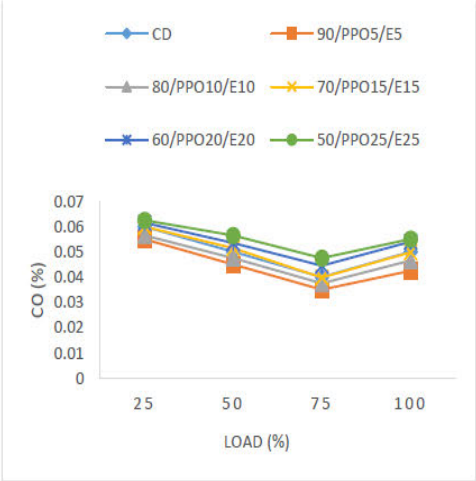

Figure 6: Carbon monoxide versus load

There are a number of factors, which explain the decrease in CO emissions as the engine load is increasing. The decrease can be attributed to increased unburnt or partially burnt hydrocarbons due to incomplete combustion, which is identical to the study by [87]. This phenomenon is linked to the increased load and the presence of ethanol, which shortened ignition delay, hence increasing CO emissions. Additionally, the decrease in CO emissions could also be due to the conversion of CO to CO_2 taking up this reaction from the high oxygen content of the fuel additive ethanol.

3.5. Carbon Dioxide

Figure 7 is the variation of carbon dioxide (CO_2) with engine load. The graph shows that as the blend ratio and engine load increased CO_2 emissions increased but compared to CD their emission levels are still lower and almost identical. At 50 % engine load the values of CD, and the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 were 3.58 %, 3.35 %, 2.95 %, 2.6 %, 2.55 % and 2.25 % respectively.

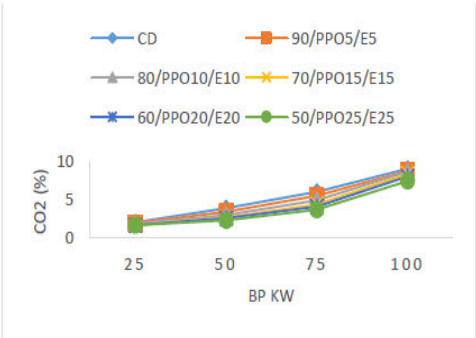

Figure 7: Carbon dioxide versus load

3.6. Oxides of Nitrogen

Figure 8 is a variation of engine load with oxides of nitrogen (NO_X) emissions. The graph plot shows that as the engine load was increased there was an increase in the NO_X emissions irrespective of fuel, blend ratio or EHN. However, the value of NO_X emissions from the blends 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 reported lower values compared to CD fuel. For example, at 50 % the values of the blends, was 385 ppm, 396 ppm, and 415 ppm, compared to CD fuel at 425 ppm.

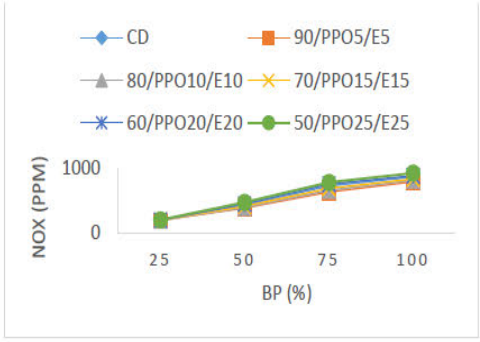

Figure 8: Oxides of nitrogen versus load

Blend 60/WPPO20/E20 and 50/WPPO25/E25 had the highest NO_X emissions compared to the other blends of 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 across all the engine load conditions tested. In Figure 8 at 25 % engine load, the two blends had values of 205 ppm and 200 ppm respectively. However, at full engine load the NO_X emissions values increased to 925 ppm and 885 ppm compared to blend 90/WPPO5/E5 at the same load with 197 ppm and at full load at 792 ppm.

From the graph plot in Figure 8, as the blend ratio increased there was a direct increase in emissions of NO_X across all the blended test fuels. However, blend 90/WPPO5/E5 reported the lowest values of NO_X emissions compared to all the other tested blends experimented. The formation of NO_X in biodiesel fuel combustion strongly depends on the combustion temperatures and the oxygen concentration in the combustion zone. The low blend ratios of 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25, show a shortened combustion process. Hence, a poor cooling effect and failure to decrease peak combustion temperatures leading to increased NO_X.

These findings show a correlation between the alcohol content in the fuel and peak flame temperatures, the content of nitrogen, and oxygen availability. this study findings are identical to the findings of [88]. The increased NO_X emissions are a result of the presence of nitrogen from the CN improver ENH and other contaminants from the WPPO impurities. Additionally, it could be due to the generation of radicals of hydrocarbon through molecular unsaturation in the blends being identical to the findings of [89, 90]. The final factor is due to increased EGT temperatures, linked to the high oxygen content and the air fuel ratio.

3.7. Unburnt Hydrocarbons

Figure 9 is a variation of unburnt hydrocarbons (UHC) emission with engine load. As the engine load was increased, the UHC emissions increased too. The higher hydrocarbon emissions may be due to hydrogen radicals in the diesel-ethanol-WPPO-EHN blends. The high fraction of ethanol in blends 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 contributes to increase in the emissions of UHC which is identical to the findings of [62, 91]. Who observed it in an SI engine cylinder walls, crevices, and quenched cylinder walls with richer air-alcohol mixtures.

However, the increase is more significant as the engine load was in intermediate loads of 75 % moving to or approaching full

load. For example, at 50 % engine load, the values of blends were 22 ppm, 21 ppm, 20 ppm, 18 ppm, and 15 ppm respectively compared to full load with 35 ppm, 34 ppm, 32 ppm, 29 ppm, and 26 ppm (for blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25). This leads to the conclusion that at high engine loads the values of UHC emissions are significantly high for all the blends of WPPO, ethanol and EHN, although comparatively low compared to CD fuel.

The UHC emissions from the blends 90/WPPO5/E5 and 80/WPPO10/E10 report higher values. Although, the graph plot in Figure 9 shows low values compared to the values of CD test fuel. However, the general trend by the graph in Figure 9 shows that increased blend ratio significantly reduced UHC emissions, across all the test fuels irrespective of the engine load condition. This reduction is due to the high oxygen content of ethanol and the effect of the fuel additive EHN, factors that helped in complete combustion.

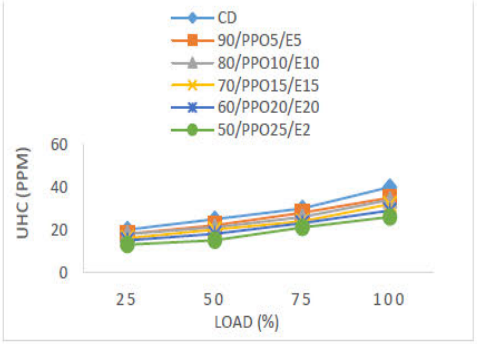

Figure 9: Unburnt hydrocarbons versus load

4. Conclusion

- The variation of BSFC with engine load shows that, as the load increases there is an increase in the fuel consumed by the test engine as in the graph as shown in Fig.1. However, the lower blend ratios 90/WPPO5/E5 and 80/WPPO10/E10 exhibit identical BSFC values to conventional diesel test fuel compared to the other blends. These blends show the lowest BSFC values compared to the other WPPO blends.
- The BTE of blend 90/WPPO5/E5 report values close to the values of conventional diesel fuel values. This is due to the close blend density values and the gross calorific values of WPPO blends, which showed very small and marginal differences. This is the case condition at lower blend ratios for WPPO blends tested.
- There is a reduction of UHC emissions with the use of WPPO blends, ethanol and EHN, with a notable reduction in NOX emissions, especially for the blend 90/WPPO5/E. This is a clear indication that this blend performed well when compared to petroleum conventional diesel.
- Although there is an indicated increase in the emissions of CO, CO_2 NOX and UHC, for all the blends of WPPO, ethanol, and EHN. There is a clear indication in the graph plots discussed that blended fuels have low emission levels compared to conventional petroleum diesel in relation to the ASTM standards during experimentation.
- During experimentation, the blends of WPPO, ethanol, and EHN report identical temperature characteristics to CD test fuel as the engine load hits 75 % heading to 100 % (full load). This is due to the presence of ethanol responsible for decreased ignition delay.

Conflict of Interest

The authors declare no conflict of interest.

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CHAPTER 5: THE EFFECT OF CETANE NUMBER AND OXYGEN CONTENT IN THE PERFORMANCE AND EMISSIONS CHARACTERISTICS OF A DIESEL ENGINE USING BIODIESEL BLENDS

Journal article

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The effect of cetane number and oxygen content in the performance and emissions characteristics of a diesel engine using biodiesel blends

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Abstract

The growth in demand for power generation and energy from alternative fuels at low cost and friendly to the natural environment is increasing. This study used waste plastic pyrolysis oil (WPPO) and ethanol to apply direct blending of conventional diesel, WPPO and ethanol with 2-ethyl hexyl nitrate (EHN). The purpose was to improve the combustion and performance characteristics of the WPPO blends. The EHN has the potential to reduce emissions of carbon dioxide, carbon monoxide, unburnt hydrocarbon, oxides of nitrogen and particulate matter. Ethanol improves viscosity, miscibility, and the oxygen content of WPPO. Five mixing ratios were selected. The mixing ratio with EHN was based on total quantity of blended fuel at 0.01%. At 50% engine load, the brake specific fuel consumption was 0.043 g/kWh compared with CD at 0.04 g/kWh. The blend 90/WPPO5/E5 had the highest value of 14% for brake thermal efficiency, while on NO_X emissions three blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, had the lowest values of 384 ppm, 395 ppm, 414 ppm, compared with CD fuel at 424 ppm. The implication was that ethanol and WPPO blends can be used in diesel engine power generators as an alternative fuel with modification, as their respective densities of 792 kg/m^3 and 825 kg/m^3 are close to CD fuel's at 845 kg/m^3. Additionally, these combinations with EHN reduced emissions more than earlier thought and improved engine performance, equalling that of conventional diesel fuel.

Keywords: *2-ethyl hexyl nitrate; ethanol; oxygen content; ignition quality; waste plastic pyrolysis oil; cetane index*

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1. Introduction

The increased use of private automobiles has significantly increased the demand for energy, especially primary sources of energy. Alternative solutions to meeting this increasing energy demand associated with modern day developmental needs must, therefore, be increased. Diesel engines, since their discovery by Rudolph Diesel in 1893, have proved superior, more power efficient and more economic with fuel than gasoline engines (Shrinivasa, 2012). Diesel engines, however, emit high levels of carbon dioxide, unburnt hydrocarbon, oxides of nitrogen and particulate matter and smoke. These emissions have been shown to affect human health and environment (Börjesson et al., 2014). Diesel exhaust is now classified as carcinogenic to humans (Benbrahim-Tallaa et al., 2012), with exposure linked to increased risk of lung cancer and cardiovascular diseases (Giles et al., 2012). Diesel exhaust emissions are considered the primary source of providing ground-level ozone (Innes, 1981), sick building syndrome (Hester and Harrison, 2009), acid rain (Mills and Elouali, 2015) and smog (Ou et al., 2016). The need to find alternative sources of fuel energies with the more desirable characteristics of petroleum-based fossil fuels can, therefore, not be overemphasised (Damodharan et al., 2018).

In the last two decades there has been a growing interest in higher-level alcohols because of their high energy levels, higher cetane numbers, better blend stability, less hygroscopic tendencies, increased carbon chain length and improved ignition quality of the alcohol fuel molecules (Koivisto et al., 2015), compared with the lower alcohols such as ethanol and methanol. Alcohols are classified under oxygenated fuels with a hydroxyl group. This inherent oxygen in their molecular structure enables alcohols to reduce smoke emissions during combustion in diesel engines, particularly during high engine loads as reported by (Lapuerta et al., 2010b). The reduction in smoke emissions and opacity is directly linked to the oxygen content of the blends of diesel and alcohol produced (Ren et al., 2008). Through research collaborations with various biotechnology research groups, there have been improvements in the yield of higher-level alcohols through processing cellulose by modern fermentation processes such as using clostridium species (Gaida et al., 2016); and biosynthesis from glucose using genetically-engineered micro-organisms like Escherichia coli (Desai et al., 2015), cyanobacteria (Formighieri, 2015) and saccharomyces cerevisiae (Ofuonye et al., 2013).

The research community has been constrained by the growing concern over fossil fuel depletion, oil price fluctuations, escalating energy demands and stringent emission regulation and control to continuously search for better alternative renewable energy resources to serve as replacements and sources of primary energy (Kumar and Saravanan, 2016b). Early developments of alternatives in fuel energy studies utilised food-based sources as alternatives to petroleum fuels, but this faced opposition and arguments from all sectors, including bodies such as the Food and Agriculture Organization and the United Nations Commission on Human Rights because of poor food security in low- and middle-income countries. The first-generation food-based biodiesels lead to cultivation of large swathes of land for commercial purposes, eventually supressing the edible food crop acreage. This increased food insecurity leads to increased food prices and economic inflation (Kumar and Saravanan, 2016b).

Research on waste plastic pyrolysis oil (WPPO) showed that using the pyrolysis technique to extract liquid fuel from plastic waste material is a viable alternative to diesel fuel production and is sustainable (Demirbas, 2004; Scheirs, 2006; Xue, 2015; Mani, 2009). This is true especially when waste plastic oil is used with fuel additives (Damodharan et al., 2017). Statistics show that, as of 2016, only a paltry 9% world wide of waste plastic has been recycled with almost 80% going to landfills to continue degrading the natural environment, since plastics are non-biodegradable (Geyer et al., 2017). This is poor response and alarming as the gap between generation and recycling continues to increase, thus requiring bridging. Plastic pyrolysis can also be done using catalytic pyrolysis and other thermal processes. The catalytic method uses low levels of temperature to cause plastic degradation and decomposition than the thermal technique, which requires high temperature to produce high and greater liquid fuel. This has helped in recycling waste into energy, a development that captivated and motivated associated research (Zhang et al., 2008; Cann and Liao, 2010; Dekishima et al., 2011).

Extensive research has used fuel-additives on WPPO biodiesel and other biodiesels (Rakopoulos et al., 2010; Li et al., 2015; Campos-Fernández et al., 2012; Lapuerta et al., 2010b; Jin et al., 2011; Zhu et al., 2011; Mani et al., 2011; Zhang et al., 2012; Park et al., 2012; Wang et al., 2012; Chen et al., 2013a; Campos-Fernandez et al., 2013; Soloiu et al., 2013; Chen et al., 2013b; Wei et al., 2014; Kumar et al., 2013; Saravanan, 2015; Devaraj et al., 2015; Kumar and Sankaranarayanan, 2016; Kumar and Saravanan, 2016a). (Xiaoyan et al., 2008) studied the use of biodiesel-ethanol (BE) blends to reduce the emissions of nitrogen oxides (NO_X) and particulate matter (PM) in a diesel engine utilising both ethanol and selective catalytic reduction over catalyst Ag/Al_2O_3. This study found increased unburnt hydrocarbons (UHC), carbon monoxide (CO) and PM emissions of 14% caused by an increase in the soluble organic fractions in the PM emissions, as well as a 60 % to 80% reduction

in Bosch smoke number, based on the European Steady-state Cycle standard. The NO_X emissions were, consequently, reduced significantly, by 73%, leading to a conclusion that a combination of BE and a selective catalytic reduction arrangement could provide a good platform for NO_X and PM reduction and control.

In another study by (Aydın and Öğüt, 2017) the authors presented the relationship of these fuels to torque, brake thermal efficiency, brake-specific fuel consumption (BSFC) and emission characteristics in diesel engines. Because of this research work in the last decade, new rules and regulation have emerged. For example, developed and emerging countries in Europe and America require fuel manufacturers and distributors to add 1–5% biofuel to most commercially available diesel fuels. In the United States of America, the renewable fuel standard programme now requires blending of advanced biofuels in an increasing amount. This rule is in line with the quantity of fossil fuel used in transportation. The government has been targeting to achieve an annual projection growth escalation of 136 billion litres by 2022 (Lawyer et al., 2013).

There are two reasons ethanol is considered as an additive to WPPO blends. Firstly, ethanol is produced from raw material of plant or plant waste origin, qualifying as alternative renewable source of energy and, secondly, its high oxygen content and solubility in WPPO blends (Lapuerta et al., 2008; Shahir et al., 2014; Kwanchareon et al., 2007; Fernando and Hanna, 2004; Li et al., 2005). Several studies have, however, shown that an increase in the ethanol fraction decreases the auto-ignition properties of diesel because of its low propensity to auto-ignite (Chacartegui et al., 2007; Tutak et al., 2015; Hansen et al., 2005; Kwanchareon et al., 2007; Kim and Choi, 2008; Moon et al., 2013; Can et al., 2004; Rakopoulos et al., 2008; Yilmaz et al., 2014; Kuszewski et al., 2017). The cetane number-value of the blends with diesel decreases as the fraction of ethanol increases (Chacartegui et al., 2007; Hansen et al., 2005; Can et al., 2004; Kuszewski et al., 2017). Reduced cetane numbers (CN) fuel values are undesirable because of their nature to prolong ignition delay, which causes increased engine peak cylinder combustion pressures (Baczewski et al., 2015; Yanowitz et al., 2017), increased engine combustion noise and wear in addition to increased NO_X emissions. This impact resulting from alteration of CN has been extensively studied (Kidoguchi et al., 2000; Içıngür and Altiparmak, 2003; Takahashi et al., 2011; Szybist and Bunting, 2005; Kurtz and Polonowski, 2017; Watanabe et al., 1998; Cataluña and Da Silva, 2012; Chaichan and Ahmed, 2012; Chukwuezie et al., 2017; Reijnders et al., 2016; Tat, 2011). Plastics have substantial stored potential energy of hydrocarbons inherent in their molecular structure (Mani et al., 2011). They are readily available as waste in municipal solid waste management sites where they threaten the environment (Geyer et al., 2017). Altering them through modern methods of decomposition, plastic waste can be converted to liquid fuels and used as biodiesels (Zhou, 2014).

The present study examines fuels that are derived from renewable feedstock sources such as municipal solid waste (MSW) disposed plastics through blending. Waste was converted into energy to contribute to energy sustainability studies through the use of ethanol to increase the oxygen content and 2-ethyhexyl nitrate, which improves the cetane number and reduces emissions of CO, CO_2 and NO_X.

2. Experimental setup

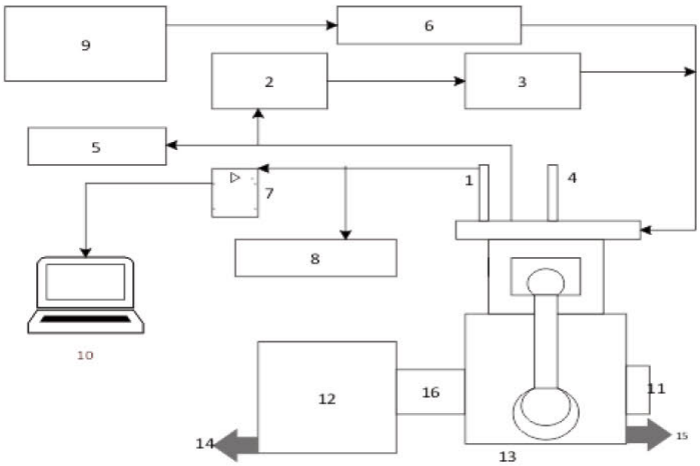
The blending of WPPO, whose n-alkenes are 25% lower for auto-ignition, was compared with diesel fuel, which contains adequate n-alkenes for auto-ignition. The aromatics, which affect PM emissions, are low in WPPO blends. The WPPO consists of about 27%, 25% and 9% iso-alkanes, n-alkanes and olefins respectively, with over 30% content being undefined because of complicated and complex chemical bond structures (API, 2010), (Harley and Kean, 2004). However, aromatics cyclo-alkanes (naphthalene) and others poor in auto-ignition were also found to be 40% by (Ghosh et al., 2006). Blending was, firstly, preferred to improve the low pour point of WPPO to improve cold starting characteristics. Secondly, blending was used to improve the fuel spray characteristics by using ethanol, which is soluble and miscible in WPPO blends. Thirdly, blending contributed in the reduction of the viscosity of WPPO biodiesel, thus aiding and improving spray characteristics.

2.1 Engine tests

The experiment was conducted at the at the Mechanical Engineering Department Laboratory (29°52'09.9"S 30°58'37.9"E), University of KwaZulu-Natal, Durban, South Africa. The experiment used a test rig of a naturally aspirated single-cylinder diesel engine power generator, water cooled, direct injection and Kirloskar TV1. Figure 1 shows a schematic of the engine test setup and Table 1 presents the details of the engine and specifications.

2.2 Physicochemical property analysis

The WPPO by pyrolysis was obtained from a commercial plant whose flow chart is shown in Figure 3. Ethanol, conventional diesel and 2-ethyl hexyl nitrate (EHN) were purchased from local outlets. Blending used a homogeniser for five minutes at 3000 rpm. The properties of all samples were measured in the Chemical Engineering Laboratory, University of KwaZulu-Natal, and Durban. Table 2



1. Cylinder pressure sensor. 2. Exhaust gas recirculation control valve. 3. EGR cooler. 4. Injection control unit. 5. Exhaust gas exit. 6. Air box. 7. Signal amplifier. 8. Gas analyser. 9. Air flow meter. 10. Data acquisition system. 11. Crank position sensor. 12. Dynamometer. 13. Engine. 14. Cooling water exit from the dynamometer to the cooling tower. 15. Cooling water exit from engine to the cooling tower. 16. Dynamometer drive coupling.

Figure 1: Schematics diagram of equipment to set up the test engine.

Table 1: Experimental engine specifications.

Parameters	*Position value*
Ignition type	4 (stroke)DICI
Number of cylinders	1
Model	TV 1
Cooling medium	Water
Manufacturer	Kirloskar
Revolutions per minute	1500
Brake power	3.5 kW
Cylinder bore	87.5 mm
Piston stroke	110 mm
Compression ratio	18.5:1
Connecting rod length	234 mm
Engine capacity	661cc
Dynamometer make	234
Injection timing	23.4 ° bTDC
Maximum torque	28 Nm @1500
Injection pressure	250 bar

Figure 2: The distillate samples from the waste plastic pyrolysis oil samples.

shows the physicochemical properties of the fuels before blending and Table 3 shows physicochemical properties of blended mixture-fuels and their determined fuel properties after blending. Figure 2 is a photograph of the sample distillates of WPPO obtained from pyrolysis.

3. Results and discussion

3.1 Brake specific fuel consumption

Figure 4 shows a variation of BSFC with engine load. The BSFC is compared to engine load in Figure 1. This graph reveals that, as the load increases, there is an equal increase for fuel consumed by the test engine. The values obtained at full engine load for the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 and CD were 0.04g/kW.h, 0.041g/kW.h, 0.042 g/kW.h, 0.043 g/kW.h and 0.035g/kW.h respectively.

At high engine loads, the conversion of heat energy to mechanical energy increases with increase in combustion temperature. This leads to increased BSFC for the biodiesel, the increase proportional to the difference in their heating values (GVC) in Tables 2 and 3, which is identical to the findings of (Lapuerta et al., 2010a). These blends of WPPO compare well to conventional diesel fuel and other biodiesel blends with comparative differences in the heating values.

As the blend ratio increased, there was a decrease in the BSFC across all the test fuels, although the values for all WPPO blends were higher than the conventional diesel (CD) test-fuel. The closeness of the values and the packed graph reveal a close resemblance and identical BSFC characteristics of WPPO, ethanol and EHN compared to CD

Table 2: Properties of diesel, WPPO and ethanol before blending and addition of EHN.

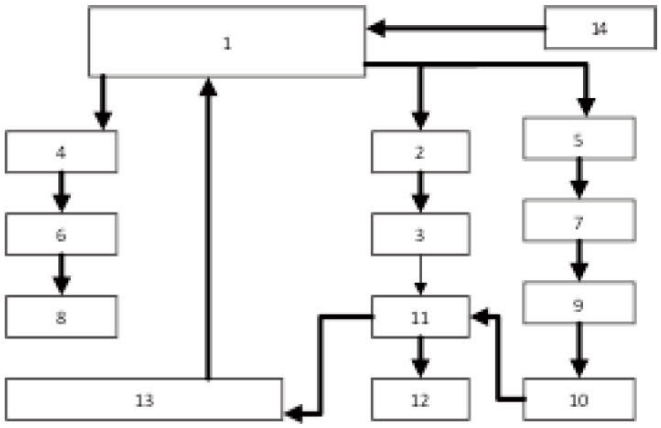
Properties	*Unit*	*CD*	*WPPO*	*Ethanol*
Density @ 20 °C	kg/m^3	845	825	792
Visc.@ 40 °C	cSt	3.04	2.538	1.05
Cetane number	_	55	_	8.5
Flash point	°C	50	43	16
Fire point	°C	56	45	53
Carbon residue	%	22	0.015	_
Sulphur content	%	<0.028	0.248	_
Gross calories	kJ/kg	46500	43340	29700
Cetane index	_	46	65	_

WPPO = waste plastic pyrolysis oil, EHN = 2-ethyl hexyl nitrate, Visc. = viscosity, CD = conventional diesel

Table 3. Properties of blended ratio mixtures of diesel, ethanol, WPPO with EHN.

Property	*Unit*	*CD*	*90/5/5*	*80/10/10*	*70/15/15*	*60/20/20*	*50/25/25*	*STANDARD*
Density	Kg/m^3	842	838.5	834	830	825	823	ASTM D1298
KViscosity@40	cST	3.452	2.38	2.37	2.365	2.340	2.325	ASTM D445
Cetane number	-	45	59	62	64	65	69	ASTM D4737
GCV	kJ/kg	44840	40125	39985	38700	36800	34500	ASTM D4868
Sulphur content	%	<0.0124	0.0248	0.0249	0.0251	0.0253	0.0257	ASTM D4294
Oxygen	%	12.35	13.80	14.75	15.15	16.25	17.35	ASTM D5622
Carbon residue	%	74.85	75.35	76.40	77.55	78.25	79.65	ASTM D 7662
Flash point	°C	56.5	38.5	37.55	37.35	37.15	36.85	ASTM D93
Hydrogen	%	12.38	7.5	7.55	7.65	7.75	7.95	ASTM D7171

WPPO = waste plastic pyrolysis oil, EHN = 2-ethyl hexyl nitrate, Visc. = viscosity, CD = conventional diesel, ASTM = American society for testing and materials standards, GCV = gross calorific value



1. Pyrolysis reactor, 2. Carbon black discharge, 3. Carbon black deep processing, 4. Exhaust smoke discharge, 5. Gas separator, 6. Smoke scrubber to take out colour and odour, 7. Condenser, 8. Chimney, 9. Oil tank, 10. Synchronized gas purification, 11. Synchronised gas-recycling system, 12. Extra gas burning, 13. Heating furnace during operation, 14. Loading of material.

Figure 3: Waste plastic pyrolysis oil processing plant flow chart.

fuel. For example, at 50% engine load the blend of 80/WPPO10/E10 had a value of 0.043 g/kW.h compared to the full engine load with 0.041g/kW.h; this value being higher than the CD test-fuel, with 0.04g/kW.h at 50 % engine load and 0.035g/kW.h at full engine load.

3.2 Brake thermal efficiency

The brake thermal efficiency (BTE) variations with engine load are shown in Figure 5. The graphs show that, as the load increased, there was increase in the BTE across all the test-fuel blends of WPPO and CD. At 50% engine load the values for blends

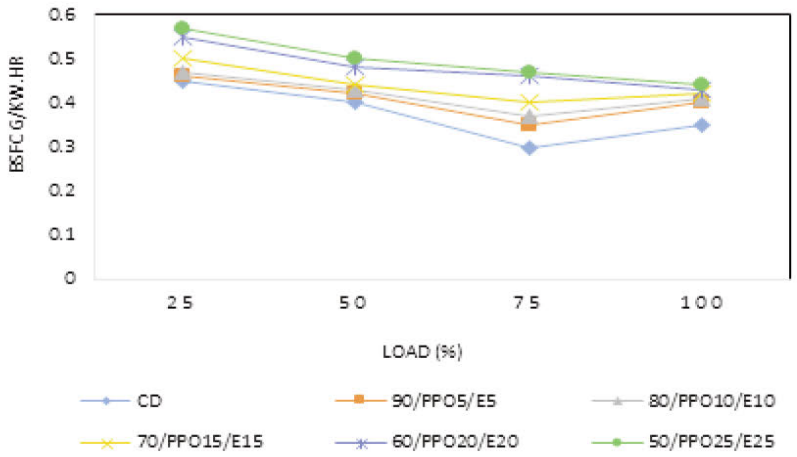


Figure 4: Brake specific fuel consumption (BSFC) versus load (CD = conventional diesel).

90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 and CD were 22%, 21%, 20%, 18%, 16.5% and 22.5% respectively. As the blend ratio and engine load increased, there was increase in BTE across the blends of WPPO but with a decrease in the BTE within the blends. At 25% engine load, 90/WPPO5/E5 had values of 14%, 22%, 26.5% and 25% compared with 70/WPPO15/E15 with 12.5%, 20.0%, 22.5% and 23.0% respectively.

The highest BTE value was recorded by blend 90/WPPO5/E5 at 25% engine load compared with any other blend of WPPO, ethanol and addition of EHN. The density, which is closer to CD and the effect of blending, which improved this blends physicochemical properties, could cause this. Figure 5 shows values of 24.8%, 23%, 21% and 19% respectively for blends 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20 and 50/WPPO25/E25. Blend 50/WPPO25/E25, however, reported the lowest values than other blends. At 25%, engine load the BTE value was 9.5% compared with full load at 19%, this being the lowest values of BTE as shown in Figure 5 for all the blends tested.

3.3 Carbon monoxide

Figure 6 shows a variation of carbon monoxide with engine load. As the engine load and the blend ratio increased, the values of blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 gave carbon monoxide emissions decreases of up to 75% of engine load. The blends subsequently recorded a continuous increase as the engine load approached full load. At 25% engine load, the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 recorded values of 0.0550%, 0.0565%, 0.0600%, 0.0615% and 0.0625% respectively.

As the load is increased to 75%, the values were 0.035%, 0.0375%, 0.0445% and 0.0475% respectively. At full load, all the test fuels showed increased CO emissions, with blends 90/WPPO5/E5 and 80/WPPO10/E10 reporting the lowest emissions among the test blends across all the engine load conditions. At 50%, the blends recorded values of 0.0445% and 0.0475% compared to full load at 0.0425% and 0.0465% respectively. The increased CO emissions, though lower as compared to diesel fuel, can be attributed to partial combustion

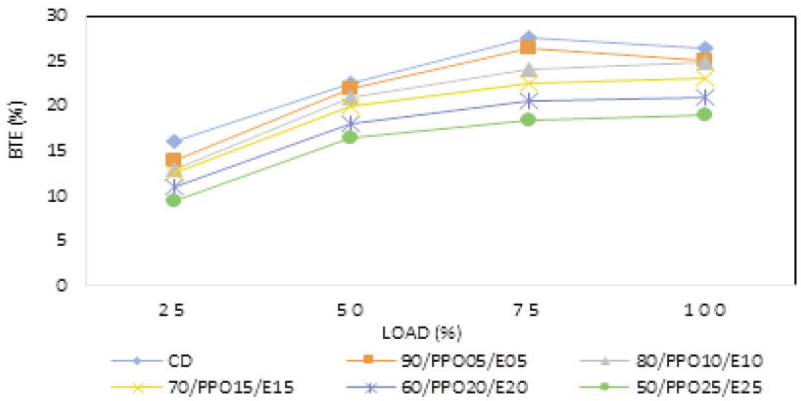


Figure 5: Brake thermal efficiency (BTE) versus load (CD = conventional diesel).

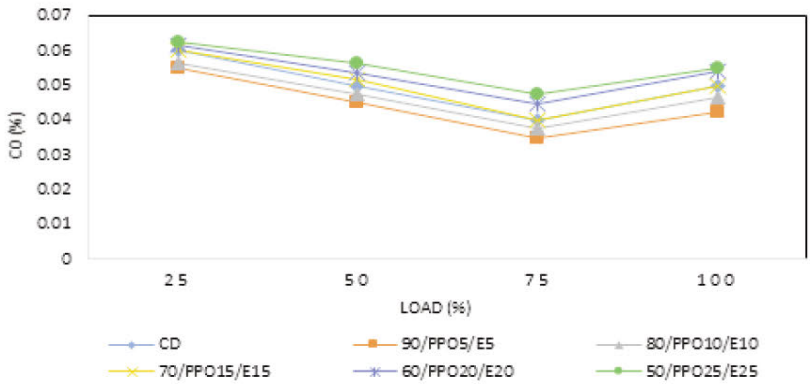


Figure 6: Carbon monoxide (CO) versus load (CD = conventional diesel).

(Rahman et al., 2014), as the load increased and the presence of ethanol shortened ignition delay, thus increasing CO emissions.

As the engine load and the blend ratio increased, an increase in the carbon monoxide emission across all engine loads and within the blends and CD, test-fuel was experienced. At 50% engine load, the values of the blends and CD recorded 0.045%, 0.0475%, 0.0515%, 0.0535%, 0.0565% and 0.05% for 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 and CD respectively. These values from Figure 4 imply a reduction of CO emissions across all test fuels, irrespective of blend ratio and type of fuel, except at high engine loads exceeding 75% and up to to full engine load. This was followed by a steady increase in the emissions of CO.

The CO emissions are a direct result of poor oxidation of the hydrocarbon fuels in the combustion chamber and are determined by the local fuel/air equivalence ratio. Compared with CD, all the biodiesels tested showed decreased CO emissions, because of the high oxygen content in the test biodiesels and the addition of EHN, which greatly increased the CN, corroborating the results of Içıngür et al. (2003) and Wu et al. (2009). However, as the engine load increased from 75% towards full load, there was an observed increase in CO emissions, despite the oxygen content of the biodiesel and increased CN of the blends of WPPO, ethanol and EHN. This deviation of results was attributed to differences in CN for the different biodiesel test fuel blends used. The increment in CN as the blend ratio increased, led to an increase in fuel quantity burnt during diffusive combustion, hence increased CO emissions as the quality of combustion decreased.

3.4 Exhaust gas temperature

The trend of exhaust gas temperature (EGT) and the engine load in Figure 7 increased significantly, as the load increased, especially for the blends. At 25% engine load, the blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25 recorded values of 165 °C, 195 °C, 226 °C and 256 °C than the CD with 155 °C, 175 °C, 205 °C and 240 °C for all engine load conditions.

As the engine load increased from 25% to full load, the graph curves tended toward unitary and similar to the values of CD. The blends of WPPO, ethanol and fuel additives, consequently, have

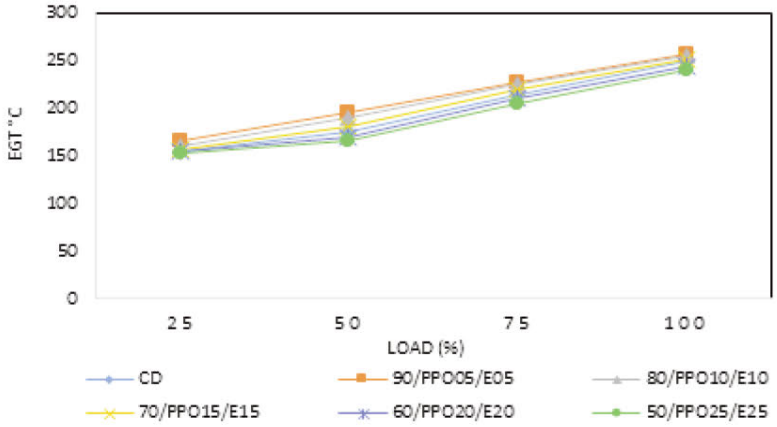


Figure 7: Exhaust gas temperature (EGT) versus load (CD = conventional diesel)

identical temperature characteristics to those of the CD test-fuel, especially as the engine load reaches 75% heading to 100% (full load). This was attributed to the presence of ethanol, which decreased ignition delay, thus lowering the combustion temperature.

3.5 Oxides of nitrogen

The variation of engine load with NO_X emissions is given in Figure 8, showing that NO_X emissions increased with increasing engine load, irrespective of fuel, blend ratio or EHN. However, the value of NO_X emissions from the blends 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 recorded lower values compared with CD fuel. For example, at 50% the value of the blends were 385 ppm, 396 ppm and 415 ppm, compared with CD fuel at 425 ppm.

Blend 60/WPPO20/E20 and 50/WPPO25/E25 yielded the highest NO_X emissions compared with the other blends of 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 across all the engine load conditions tested. At 25% engine load, the two blends emitted 205 ppm and 200 ppm NO_x respectively. However, at full engine load the NO_X emissions increased to 925 ppm and 885 ppm compared with blend 90/WPPO5/E5 at the same load with 197 ppm and at full load at 792 ppm. Figure 8 shows that, as the blend ratio increased the NO_X increased in direct proportion across all the blended test-fuels. However, blend 90/WPPO5/E5 registered the lowest values of NO_X of all the experimental blends.

The formation of NO_X in biodiesel combustion strongly depends on the combustion temperatures and oxygen concentration in the combustion zone. However, with high blend ratios of 70/WPPO15/E15, 60/WPPO20/E20 and 50/WPPO25/E25, the combustion process contracted, subsequently failing to provide enough cooling effect to decrease peak combustion temperatures, leading to increased NO_X. These findings imply that there is a correlation between the alcohol content in the fuel and peak flame temperatures, nitrogen content and oxygen availability (Heywood, 1988). Increased NO_X emissions can be attributed to the presence of nitrogen from the cetane number-improver ENH and other contaminants from the WPPO composition, as well as to the generation of hydrocarbon radicals through molecular unsaturation (Benjumea et al., 2010; Altun, 2014). The NO_X levels are still low, however, which is attributed to high CN numbers of the tested biodiesels (see Table 3) and increase in the CN and blend ratios (i.e., oxygen content). These findings are identical to the findings of Zhu et al. (2016).

3.6 Unburnt hydrocarbons

Figure 9 shows a variation of UHC emission with engine load, where emissions increased with an increase in engine load. The increase was specifically substantial at engine loads ranging from intermediate (75%) to full. For an example, a 50% engine load yielded respectively 22 ppm, 21 ppm, 20 ppm, 18 ppm and 15 ppm UHC from blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20 and 50/WPPO25/E25, compared with full load that yielded 35 ppm, 34 ppm, 32 ppm, 29 ppm and 26 ppm UHC. An inference here is that at high engine loads the values of UHC emissions are significantly high for all the blends of WPPO, ethanol and EHN, although lower than for the CD fuel.

Figure 9 shows that higher UHC emissions from blends 90/WPPO5/E5 and 80/WPPO10/E10 were recorded, but still lower than the values of the CD test-fuel. The general trend shown in the graph in Figure 9, however, was that as the blend ratio increased, there was significant reduction in the UHC emissions, observed across all the test-fuels irrespective of the engine load condition, for all the blends tested, when compared with CD fuel.

Hydrogen radicals in the diesel-ethanol-WPPO-EHN blends likely caused the higher hydrocarbon

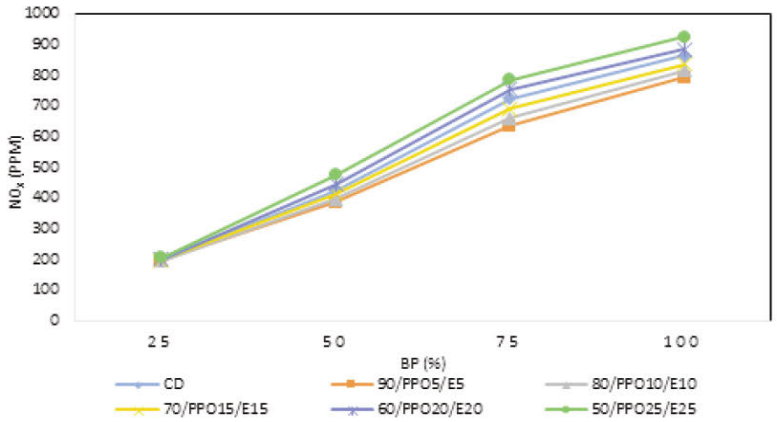


Figure 8: Oxides of nitrogen (NO_x) versus load (CD = conventional diesel)

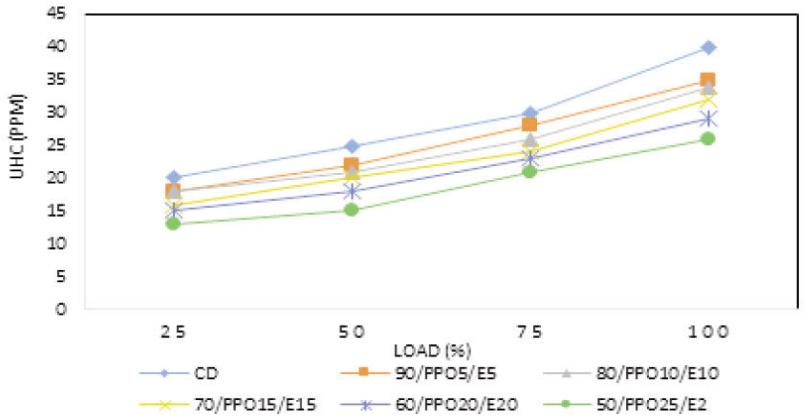


Figure 9: Unburnt hydrocarbons (UHC) versus load (CD = conventional diesel).

emissions. The high fraction of ethanol in blends 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 contributed to increase in the emissions of UHC. This compared well with Tutak et al. (2015) and Lujaji et al. (2011), and results in SI engine cylinder walls, crevices and quenched cylinder walls, especially when richer air-alcohol mixtures were introduced.

3.5 Carbon dioxide

Figure 10 represents the variation of CO_2 with engine load, where CO_2 emissions increased as the blend ratio and engine load increased, but these emissions remained lower and almost identical when compared with CD. At 50% engine load, the values of CD; and the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20 and 50/WPPO25/E25 emitted 3.58%, 3.35%, and 2.95%, 2.6%, 2.55% and 2.25% respectively.

Figure 10 also reveals that, as the load increased there was a significant increase in the CO_2 emissions across all test fuels, although with lower values as the blend ratio increased. For example, CD fuel corresponded with 2%, 3.85%, 5.95% and 8.95% CO_2 for respective engine loads of 25%, 50%, 75% and 100%, while blend 80/WPPO10/E10 corresponded with 1.8%, 2.95%, 4.85% and 8.55% for similar loads. The blend with the lowest CO_2 emissions was 50/WPPO25/E25, with values of 1.62%, 2.25%, 3.65% and 7.35% for engine loads of 25 %, 50 %, 75 % and 100 % respectively.

4. Conclusions

- Lower blend ratios 90/WPPO5/E5 and 80/WPPO10/E10 exhibit identical brake-specific fuel consumption (BSFC) of conventional diesel test fuel compared to the other blends. This blends show lowest BSFC values compared to the others.
- The brake thermal efficiency of blend 90/WPPO5/E5 (90 % conventional diesel, waste plastic pyrolysis oil 5 % an ethanol 5 % by volume) showed values, which were very close to the values of conventional diesel fuel values. This was attributed to close density values and the gross calorific values of waste plastic pyrolysis oil (WPPO) blends, which showed marginal differences. This case was apparent especially at lower blend ratios of all the mixtures and blends tested.

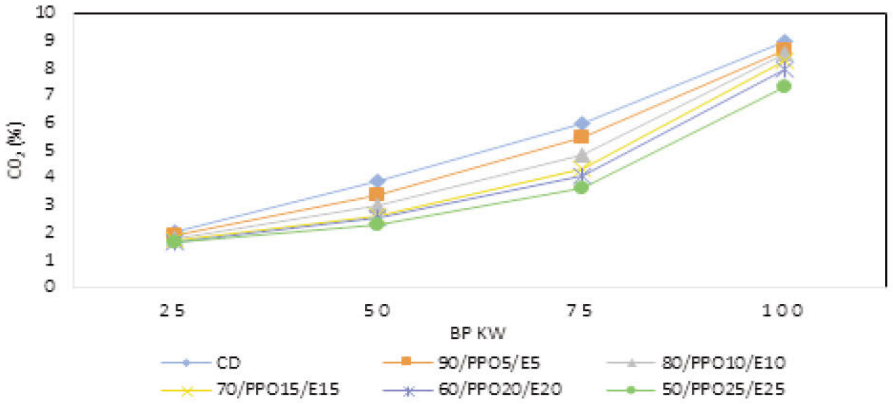


Figure 10: Carbon dioxide (CO_2) versus load (CD = conventional diesel, BP = brake power)

- There was a reduction of unburnt hydrocarbons (UHC) emissions with the use of WPPO blends, ethanol and 2-ethyl hexyl nitrate (EHN), with a notable reduction in oxides of nitrogen emissions especially for the blend 90/WPPO5/E (90% conventional diesel, waste plastic pyrolysis oil 5%, and ethanol 5 % by volume). This was a clear indication that this blend performed well when compared with petroleum conventional diesel.
- Although there was indicated increase in the emissions of CO, CO_2 NO_X and UHC, for all the blends of WPPO, ethanol and EHN. There was a clear indication that the emission levels were notably lower than the emission levels of conventional petroleum diesel, based on the ASTM measurements used in this study. However, when the overall value of emissions is compared with other emissions standards, the WPPO blend performed well on emission level tested.
- The blends of WPPO, ethanol and EHN have identical temperature characteristics to those of the conventional diesel test fuel especially as the engine load hits 75% heading to full load. This was attributed to the presence of ethanol responsible for decreased ignition delay. The presence of high oxygen enrichment was a factor of decreased CO emission for the tested biodiesels compared with conventional diesel fuel, although there was increase in CO emissions as fuel CN and blend ratio was increased. This was attributed to deterioration of the combustion characteristics, as the cetane numbers (CN) and the alcohol blend ratio increases. The biodiesels with extremely high CN in the tested fuel need further investigation as a fuel improver.

This study thus makes a strong case for alternative fuels to replace petroleum-based fossil fuels like diesel commonly used as the primary propulsion fuel in transport and power generation.

Author roles

Semakula Maroa: data collection, concept write-up, research formulation and all the analytical discussions pertaining to this research paper.

Freddie Inambao: editing, supervision and technical support.

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CHAPTER 6: EFFECTS OF EXHAUST GAS RECIRCULATION ON TEMPERATURE, USING BIODIESEL BLENDS

Journal article

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EFFECTS OF EXHAUST GAS RECIRCULATION ON TEMPERATURE, USING BIODIESEL BLENDS

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ABSTRACT

This experimental work compared the effects of temperature and emissions produced using waste plastic pyrolysis oil (WPPO) biodiesel blends under the influence of exhaust gas recirculation (EGR). The mixtures were prepared in the ratios of 10 %, 20 %, 30 %, 40 % and 100 % for 90WPPO10, 80WPPO20, 70WPPO30, 60WPPO40 and WPPO100 respectively. The EGR flow rate was 5 %, 10 %, 15 %, 20 %, 25 % and 30 % respectively. Testing and performance was on a Kirloskar engine, water cooled, direct injection operating at 1500 rpm and a torque of 28 Nm. The EGR system was modified with an addition of the EGR and valve in the exhaust system. The study had three objectives: (i) to investigate the effect of temperature on the emission characteristics of a diesel engine using WPPO biodiesel blends compared to conventional diesel (CD) baseline fuel. (ii) To find the effect of EGR on WPPO biodiesel ratio on the exhaust gas temperature (EGT) compared to baseline CD fuel. (iii) To find the trade-off point for EGR percentage flow rate in relation to WPPO biodiesel blends and exhaust gas temperatures (EGTs). Following testing and evaluation, the highest EGT obtained for CD was 456 ºC compared to 490 ºC for WPPOB100 blend both at 0 % EGR flow rate. However, the other WPPO blends showed trends of decreasing temperatures with the application of EGR percentage flow rate. Other results showed that increasing the blend ratio and the EGR percentage flow rate increased smoke emissions across all the WPPO blends tested. This study confirms that WPPO biodiesel blends can produce lower EGT temperatures with application of the EGR technique of NO_X control, but with higher emissions of UHC for WPPO100 blend.

Keywords: Biodiesel blend ratio, EGR flow rate, Exhaust gas temperature, Waste plastic pyrolysis oil.

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1. INTRODUCTION

In order to reduce dependency on fossil fuel especially diesel fuel there has been increased research on the biofuels classified as alternative or renewable fuels. Internationally government policies are focusing on alternative energy, especially renewable energy, and the use of and conversion of waste to energy. Despite years of research and improvement in petroleum fossil fuels and their combustion and emission characteristics, emissions from these fuels remains a divisive issue in the automotive manufacturing and transport sectors. The problem of fossil fuels is acute considering their limited supply, unpredicted price increments, and the turmoil in oil producing regions in the world. This creates the need for utilization of alternative fuels and blends as sources of fuel energy. This should be done in a sustainable manner, while meeting stringent production and emission standards now and in the immediate future.

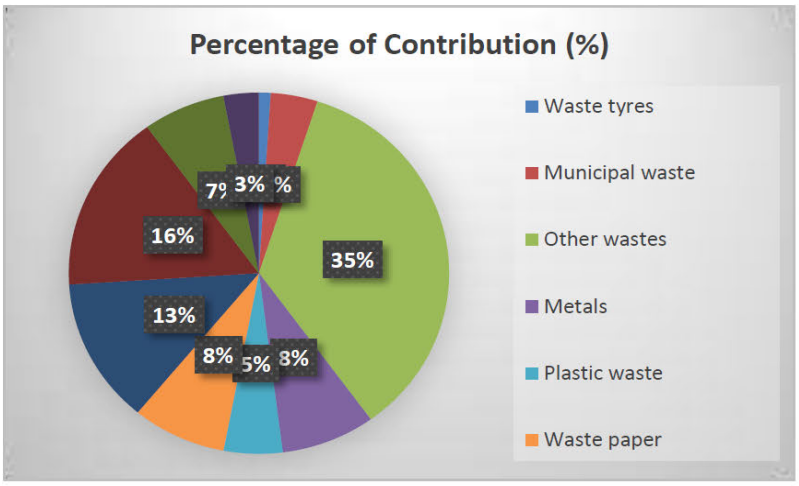

Figure 1 Percentage contribution of each waste stream of general solid. Analysed from available data 2017 (from municipalities) in South Africa [1]

Governments are putting in motion strategic plans to decrease dependency on the primary fossil fuels. Through policy shifts, governments are removing carbon from current classes of fuels in use [2-4]. However, the problem of municipal solid waste disposal is a technical problem which requires solutions that are environmentally acceptable and hygienically prudent. How can waste disposal be prudent and environmentally acceptable? World-wide over 1 billon waste tyres are generated annually [5] which includes industrial and domestic waste as shown in Figure 1 for South Africa. Municipal solid waste that contains high carbon value such as plastic, waste cooking oil and waste lubricating oil are becoming increasingly efficient feedstocks for alternative energy production in the management of waste to energy [6, 7].

Plastics are part of our daily life activities with a wide range of applications in domestic and industrial areas. This is due to their durability, light weight, energy efficiency in their production, cost, and their design elasticity [8]. Plastics are petroleum derivatives composed of hydrocarbons containing oxidants, colorants and other stabilizers as additives in their morphology [9, 10]. The most commonly used plastics are high-density polyethylene

(HDPE), followed by the polyvinyl chloride (PVC) and the polypropylene (PP) [11, 12]. The conversion of waste plastic is done through the pyrolysis process which transforms the polymers into basic monomers or hydrocarbons as a chemical way of recycling of plastic waste [13]. The pyrolysis process as a technique is effective and is a promising option for conversion of mass to energy.

This pyrolysis process yields hydrocarbons with almost identical qualities and characteristics of petroleum-based fossil fuels [14, 15]. The process cracks plastic materials by heating them into low molecular weight products able to be utilized as energy sources [16, 17]. Pyrolysis involves the thermal decomposition of long-chained hydrocarbon structures into small components at high temperatures [9, 18]. The required temperature range for the pyrolysis process is normally between 500 ºC to 700 ºC. This temperature range is not easy to achieve and maintain during reaction in a pyrolysis reactor [19], which has led to the inclusion of temperature catalysts such as SiO_2, Al_2O_3, CaO and zeolite. The inclusion of these catalysts enables reactors to reduce the temperature requirements to lower temperatures that can be sustained and maintained for the pyrolysis process [20].

Plastics in municipal solid waste management sites account for 7 % to 8 % of the entire weight of the waste generated. However, this translates to 20 % to 30 % of the total volume of waste generated. Therefore, separation of other waste needs to be carried out through sorting through mechanical and other forms [21, 22]. Municipal solid waste is divided into three main categories: (1) combustibles like paper, textiles, wood and kitchen waste, (2) incombustibles such as metals, glass and ceramics, and (3) plastics [23, 24]. Figure 1 shows the waste stream percentage contributions to waste production in South Africa.

A number of studies have been conducted to study the interaction of waste plastic pyrolysis oil blends with diesel engines. These researchers include such as: [25-36]. All the studies reported that waste plastic pyrolysis oil diesel blends can run basic diesel engines, with or without prior modification of the engines.

Rakopoulos et al. [37] investigated the effects of additives in diesel alcohol blends using ratios of 8 %, 16 % and 24 % and reported significant reduction in the NO_X, exhaust gas temperature, smoke density (opacity) and carbon monoxide (CO). However, unburned hydrocarbon (UHC) emissions, brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) reportedly increased compared to CD fuel levels. This study is identical to other studies that have been conducted by other researchers [37, 38-44].

However, it was further observed that WPPO blends have lower BTE coupled with high exhaust emissions of CO, UHC and NO_X. The maximum heat release rate of WPPO blends was also reported to be higher compared to CD fuel. This was due to the effect of longer ignition delay associated with WPPO blends. However, regarding emissions, the authors reported low smoke emissions, which reduced significantly by 40 % to 50 %, with soot emissions also observed to be low. Additionally, Soloiu et al. [45] reported that the higher viscosity of the waste plastic pyrolysis oil blends increased the injection duration compared to diesel fuel [45, 46]. This created a gradual in-cylinder pressure increase and low peak pressure rise.

There has been additional research in other areas of engine performance notably the effects of advanced injection timing (AIT) on diesel engines, especially on biodiesels that are derived from plastic waste by the process of pyrolysis. Researchers such as Gnanasekaran et al. [47], and Mani and Nagarajan[48] have reported increased carbon dioxide CO_2 with the use of WPPO blends. Further, these authors report a reduction in emissions of CO, UHC and NO_X with application of AIT technique and use of WPPO diesel blends. This has led to improved fuel utilization during combustion hence increased BTE. However, in other research using the AIT technique with 20 % tyre pyrolysis oil and 80 % Jatropha ester oil Sharma and

Murugan [49] reported increased NO_X with lower BSFC, CO, UHC and PM respectively Wamankar and Murugan [50] conducted a follow up experiment using a ratio of 90 % diesel and 10 % waste tyre pyrolysis oil and reported a high BTE and increased NO_X emissions, but decreased values for BSFC and emissions of CO and UHC.

2. EXPERIMENTAL SET-UP

2.1. Experimental Apparatus and Equipment

The engine experimental set up is shown on Figure 2 followed by its position names.

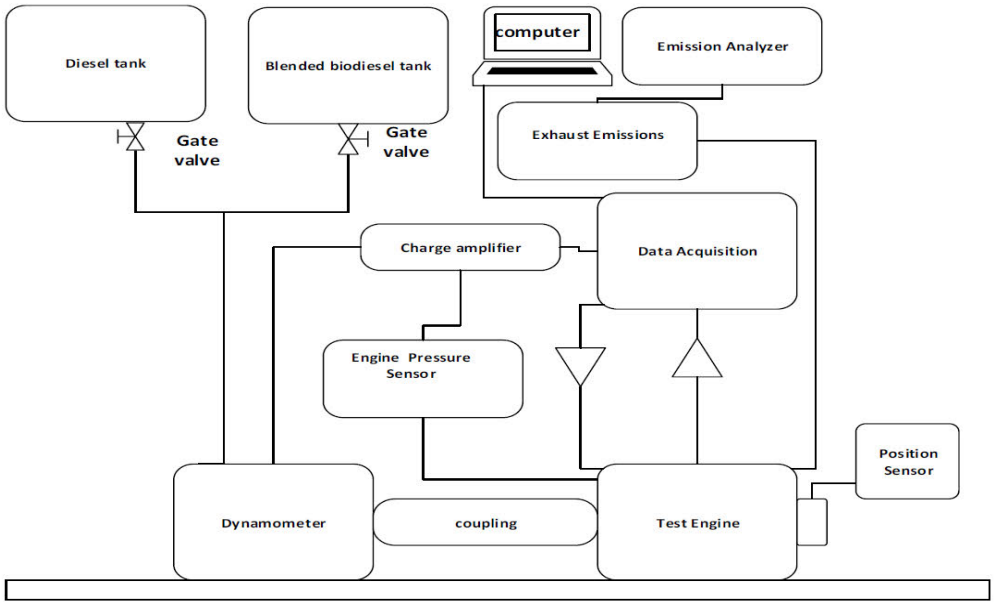

Figure 2 Experimental test engine schematic set-up diagram

1. Cylinder pressure sensor, 2. EGR control valve, 3. EGR cooler, 4. Injection Control Unit, 5. Exhaust gas exit, 6. Air box, 7. Signal amplifier, 8. Gas analyser, 9. Air flow meter, 10. Data acquisition system, 11. Crank position sensor, 12. Dynamometer, 13. Engine, 14. Airflow rate meter, 15. Cooling water exit to the cooling tower, 16. Dynamometer drive coupling

Figure 3 Photo of the lab set-up of the additional fabricated and modified exhaust recirculation mechanism to conform to the engine experimental set-up shown in Figure 2

Table 1 The engine specifications, position value and their type

Parameters	Position value
Ignition type	4 (Stroke) DICI
Number of cylinders	1
Model	TV 1
Cooling medium	Water
Manufacturer	Kirloskar
Revolutions per minute	1500
Brake power	3.75 kW
Cylinder bore	87.5 mm
Piston stroke	110 mm
Compression ratio	18.5:1
Connecting-rod length	234
Engine capacity	0.661 L
Dynamometer make	234
Injection timing	23.4° bTDC
Maximum torque	28 N-m @ 1500
Injection pressure	250 Bar

2.2. Waste Plastic Preparation and the Conversion Process

The plastic waste used in this study was obtained from a municipal solid waste management site. The waste was taken to a sorting area and dust and other unwanted particles were removed. The sorted and cleaned plastics were shredded into appropriate sizes of 25 mm to 50 mm. This prepared them for the reactor after which they were loaded onto the reactor loader. Using an electrical control panel, the system was activated, with the processes from then on running automatically as shown in Figure 4. After the completion of the pyrolysis process, the reactor system requires a cooling time of 4 h to 5 h. This can take two forms: natural cooling and the gas cooling which shortens the cooling time by almost half. The gases recommended as cooling agents are nitrogen and CO_2.

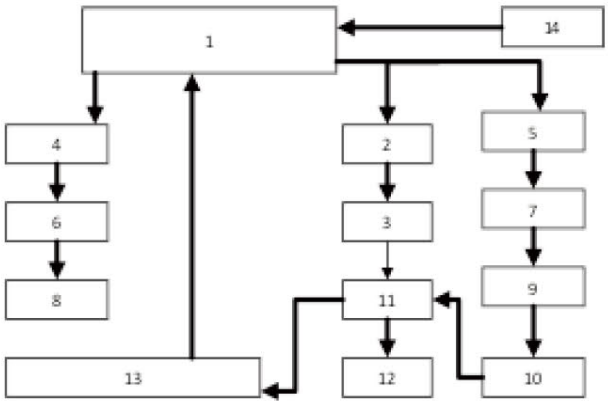

Figure 4 The waste plastic pyrolysis oil processing plant flow chart

1. Pyrolysis reactor, 2. Carbon black discharge, 3. Carbon black deep processing, 4. Exhaust smoke discharge, 5. Gas separator, 6. Smoke scrubber to take out colour and odour, 7. Condenser, 8. Chimney, 9. Oil tank, 10. Synchronized gas purification, 11. Synchronised gas-recycling system, 12. Extra gas burning, 13. Heating furnace during operation, 14. Loading of material.

2.3. Physical Properties of Waste Plastic Pyrolysis Oil (WPPO) Sample

Table 2 shows the results of the physical properties of the waste plastic pyrolysis oil obtained through the pyrolysis process of the waste plastics from municipal solid waste (MSW) management sites, at optimized conditions and compared to the properties of CD fuel oil.

Table 2 The test fuel properties, their units of measurement, standard methods of testing and the values for CD in comparison to the values of waste plastic pyrolysis oil

Property	Unit	CD	WPPO	STANDARD
Appearance	-	Clear/brown	Clear/amber	Visual
Density @ 20	kg/m^3	838.8	788.9	ASTM D1298
Kinematic viscosity @ 40 °C	cSt	2.32	2.17	ASTM D445
Flash point	°C	56.0	20.0	ASTM D93
Cetane index	-	46	65	ASTM D4737
Hydrogen	%	12.38	11.77	ASTM D7171
Cu corrosion	3hrs @ 100 °C	-	1B	ASTM D130
Carbon	%	74.99	79.60	ASTM D 7662
Oxygen	%	12.45	7.83	ASTM D5622
Sulphur content	%	< 0.0124	0.15	ASTM D4294
IBP temperature	°C	160	119	ASTM D86
FBP temperature	°C	353.5	353.5	ASTM D86
Recovery	%		98	-
Residue and loss	%		2.0	-
Gross calorific value	kJ/kg	44.84	42.15	ASTM D4868

The appearance of the oil is was yellowish in colour as shown in Figure 5. The liquid distillate was free of visible particulate sediments with a flash point of 20 °C, and a gross calorific value (GCV) of 42.15 KJ/kg. This result compares well to the indicated calorific value of petroleum fuels. Hence, WPPO has the capacity to perform well as a fuel in internal combustion engines.

Figure 5 The distillate samples from the waste plastic pyrolysis oil samples

The distillation report analysis showed the waste plastic pyrolysis oil (WPPO) had an initial boiling point (IBP) of 119 °C to 353.5 °C. This indicated the presence of other fuel oil components like kerosene, gasoline and to some extent diesel oil in the tested samples. Therefore, the conclusion can be drawn that this oil can function as a future feedstock if upgraded into a lighter compound as diesel fuel or any liquid fuel in the near future. Table 3 is a GC-MS analysis report of the WPPO oil.

Table 3 GC-MS laboratory analysis report with chemical compositions, carbon chains, and percentage compositions of the pyrolytic waste plastic oil

Molecular formula	Percentage composition
C_{10}	66.32
C_{10}-C_{15}	4.38
C_{15}-C_{20}	12.66
C_{20}-C_{25}	8.22
C_{25}-C_{30}	8.42

2.4. Experimental Procedure

a. The engine employed for this work was a Kirloskar experimental variable compression engine, four-stroke single cylinder, water-cooled developing 3.75 kW of power at 1500 rpm. The schematic is presented in Figure 2.

b. The technical specifications of the experimental variable compression engine are indicated in Table 1. A dynamometer provided the engine with load during the experimentation. Measurements for the engine intake airflow was through an air box fitted to the engine intake manifold system modified to use a standard orifice mechanism.

c. The fuel flow rate to the experimental engine was measured using a digital fuel gauge with a stopwatch mounted to measure time taken for the fuel to be consumed.

d. The exhaust gas temperatures were measured using mounted temperature thermocouples of k-2 type, including the EGR temperature, which was measured before it mixed with the intake air fresh charge and the constituents of the combustion chamber, through the same k-2 thermocouples.

e. A cylinder pressure transducer was mounted on the engine cylinder head to monitor cylinder combustion pressure and collect data values through a system charge amplifier connected to a data acquisition machine.

f. The crankshaft position or the crank angle was monitored through a mounted encoder near the crankshaft pulley area.

g. The emission gases during the experiment were monitored through a five-gas exhaust gas analyser, and an AVL 437C smoke meter was employed to measure the smoke intensity.

h. Since the engine developed maximum power at 1500 rpm and it being a variable compression engine, all the experiments were conducted based on this nominal engine speed at part load and full load. Part engine load was described as 50 % of engine load and full engine load was described as engine running at 100 % load, with a fixed compression ratio of 18.5:1.

i. The EGR system and the experimental engine were modified to enable data to be collected so that the study could be conducted. The exhaust gases were tapped from the exhaust pipe and brought to the intake manifold air intake system via the air flow meter box. Through a manually controlled gate valve, the mixing of EGR gases and the fresh air intake was possible.

j. The EGR quantity was determined as per Eq. 1. The EGR percentage rate flow was divided into the following flow rates 0 %, 5 %, 10 %, 15 %, 20 %, 25 %, and 30 %, at intervals of 5 %.

$$EGR\ \% = \frac{Mass\ of\ EGR}{Mass\ of\ total\ inlet\ intake} \times 100 \qquad \text{Equation 1}$$

k. The waste plastic pyrolysis oil fuel blends were prepared in percentages and blended with diesel fuel in ratios of 10 %, 20 %, 30 %, 40 % and 100 %, where WPPO10 blend was 90 % CD fuel and 10 % waste plastic pyrolysis oil (WPPO) fuel in that order respectively for the remaining blends. Therefore, throughout this experiment blends were referred to as 90WPPOB10 with 10 denoting the percentage blend of plastic oil by volume supplied.

l. To avoid experimental fuel from contamination each test was conducted after a thorough evacuation procedure. The previous preceding experiment fuel lines and the fuel injection system mechanism of the test engine were evacuated before the next trial. This made it possible to collect good data and measurements with inputs from the test mode only, without fear of contamination and poor results from error.

2.5. The Analysis of Error and Percentage Uncertainties

This process was carried out for the purpose of performing and identifying the accuracy and precision of the measuring tools and instruments used in this experiment work. Errors can occur due to conditions outside of the experiment itself, for example, from calibration of the instruments, observational errors, manufacturing errors, experimental set-up and planning, and environmental conditions during the experiment (Senthilkumar & Sankaranarayanan, 2015)[51]. The instruments used and their percentage error of analysis are listed in Table 4 with the uncertainties of CO, CO_2, UHC, NO_X, exhaust gas temperature (EGT) and smoke opacity. These percentages of error analysis were derived from the following formula, the root sum square method and expressed in equation form [27] as:

$$R = \sqrt{\sum_{i=1}^{n} X_i^2} \qquad \text{Equation 2}$$

Where R is the total uncertainty percentage, X_i is the individual uncertainty of all the calculated operating parameters, n is the total number of the parameters in the experiment and i is the i^{th} term of the computed parameters.

Table 4 Instruments used for measurements and data collection, their measuring range, accuracies and percentages of inaccuracies, as calculated from Eq. 3

Instrument	Accuracy	Measuring Range	Percentage inaccuracies
AVL 437C (Smoke meter) Smoke intensity	± 1 %	0 % to 100 %	± 1
AVL pressure transducer GH14D	± 0.01 bar	0 bar to 250 bar	± 0.01
AVL 365C Angle encoder	± 1°	-	± 0.2
AVL digas 444 (five gas analyser)			
CO	± 0.03 % to ± 5 %	0 % to 10 % by vol	± 0.3
CO_2	± 0.5 % to ± 5 % by vol	0 % to 20 % vol	± 0.2
O_2	± 5 % by vol	0 % to 22 % by vol	± 0.3
HC	± 0.1 % to ± 5 %	0 ppm to 20000 ppm by vol	± 0.2
NOx	± 10 %	0 ppm to 5000 ppm by vol	± 0.2

K-2 Thermocouple	± 1°C	0 °C to 1250 °C	± 0.2
Digital stopwatch	± 0.2 s		± 0.2
Digital fuel gauge	± 1 mm		± 2
Burette	± 0.2 cc	1 cc to 30 cc	± 1.5

The total percentage of the uncertainty for the instruments was calculated based on Eq. 3 as follows:

$$R = \sqrt{X_1^2 + X_2^2 + X_3^2} + \cdots X_i^2 \qquad \text{Equation 3}$$

3. RESULTS AND DISCUSSION

3.1. Brake Specific Fuel Consumption (BSFC)

Figure 6 is the variation of brake specific fuel consumption with full load under the effects of EGR percentage flow rate. BSFC is a measure of total engine efficiency and is considered to be inversely proportional to thermal efficiency of an engine [52]. In other words, a lower BSFC translates into an efficient engine and vice versa. Lower ratio blends of 90WPPOB10 and 80WPPOB20 show minimal reduction in the BSFC compared to high blend ratios. At 0% (EGR) flow rate as illustrated in Figure 6, the values of CD and WPPOB100 showed significantly high BSFC values. For example, at 0 % EGR flow rate CD had a BSFC value of 0.4 g/kW.hr compared to WPPOB100 with a value of 0.4751 g/kW.hr. This indicated that the fuel blend WPPOB100 had a higher BSFC compared to diesel and the other blends of WPPO at 0.3225 g/kW.hr, 0.3615 g/kW.hr, 0.3645 g/kW.hr and 0.3715 g/kW.hr, for 90WPPOB10, 80WPPOB20, 70WPPOB30 and 60WPPOB40 respectively.

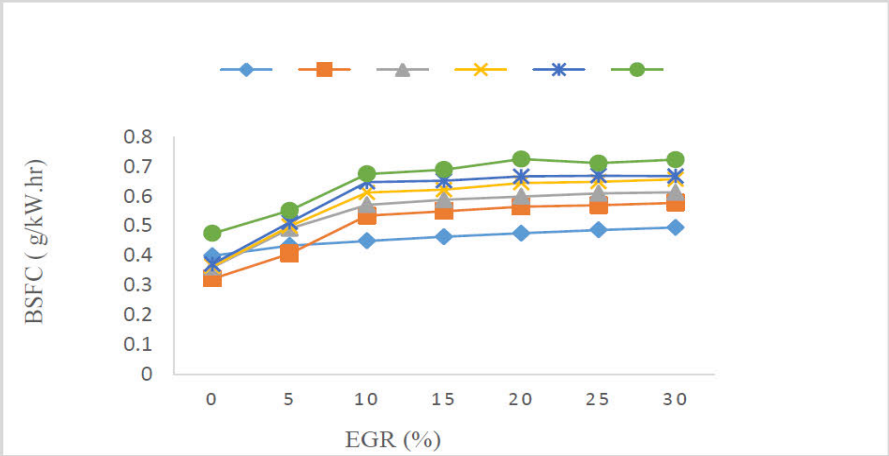

Figure 6 Brake specific fuel consumption (BSFC) versus EGR percentage flow rate under engine full load conditions

Under the influence of EGR percentage flow rate a similar trend was observed where for example at 20 % to 25 % EGR flow rate, the BSFC showed increased tendencies. These findings concur with the findings of other researchers [53, 54]. The effects of dilution of the fresh air intake explains this phenomenon as it mixes with exhaust gases that recirculate through the EGR system leading to incomplete combustion of the inducted mixture. This phenomenon leads to a drop-in power and engine torque as observed in the findings of [55, 56]. This scenario forces the engine to increase its fuel consumption in order to maintain

constant speed and its increased load hence the increase in BSFC (S. Maroa, Inambao, Freddie,, 2018)[57].

The WPPO biodiesel blends with EGR percentage flow rate showed a better fuel economy especially the lower blend ratios of 90WPPOB10 and 80WPPOB20 compared to CD test fuels. However, as the EGR percentage flow rate was increased there was a noticeable increase in the BSFC across all the test fuels used. At 0 % EGR flow rate CD was 0.4 g/kW.hr compared to 30% EGR flow rate which was 0.495 g/kW.hr, while the WPPO biodiesel blends 90WPPOB10 was 0.3225 g/kW.hr at 0 % compared to 0.5780 g/kW.hr at 30 % EGR flow rate. From Figure 6 it is evident that the test fuel that showed the highest BSFC among the blends of diesel and CD test fuel was WPPOB100, which at 0 % EGR flow rate had a value of 0.4751 g/kW.hr compared to 0.7235 g/kW.hr at 30 % EGR percentage flow rate.

An interesting observation was that after the 10 % EGR flow rate the values for the BSFC across all the test fuels seemed to show and pick a lineal increment trend as seen in Figure 6 with the flattening of the graph curves and close packed value trends.

3.2. Brake Thermal Efficiency (BTE)

Figure 7 is the variation of the BTE under load with different blends of WPPO without application of EGR flow percentage. BTE studies specifically help us to know the ability of the combustion system, and to know if the system will accept the fuel provided, and is a means of assessing how efficiently fuel conversion is carried out to turn the sample fuel into mechanical output [46, 58].

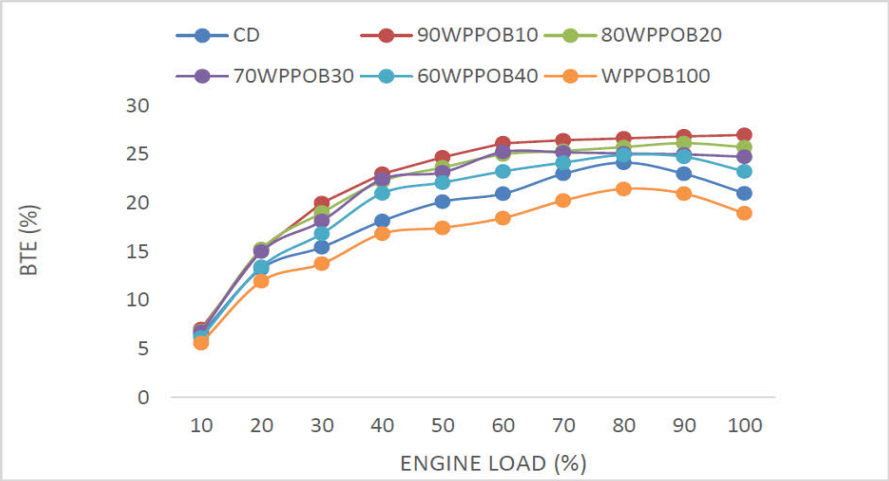

Figure 7 Brake thermal efficiency (BTE) versus engine load percentage

There is a noticeable increase in the BTE evident in Figure 7 especially with all low ratio fuel blends of 90WPPOB10 and 80WPPOB20 compared to CD fuel. The result of this experiment shows that the BTE increased as the load increased, explained by the reduction in the heat loss as the engine power (more fuel) increased with load. This observation was identical to the work reported by [57].

The high BTE values observed for WPPO blends in Figure 7 may be due to the high viscosity of the WPPO blends as compared to CD during the combustion pre-mixing phase. The second reason may be due to the presence of high oxygen content in the higher blends, which improves combustion [59]. The third factor explaining decreased thermal efficiencies may be because of decreased calorific value as the blend ratio increases, which is identical to studies by [60]. At high engine load the thermal efficiency for CD was 21.0 % compared to

the WPPO blends at 27 %, 25.75 %, 24.75 %, 23.25 % and 18.95 % for 90WPPOB10, 80WPPOB20, 70WPPOB30, 60WPPOB40 and WPPOB100 respectively.

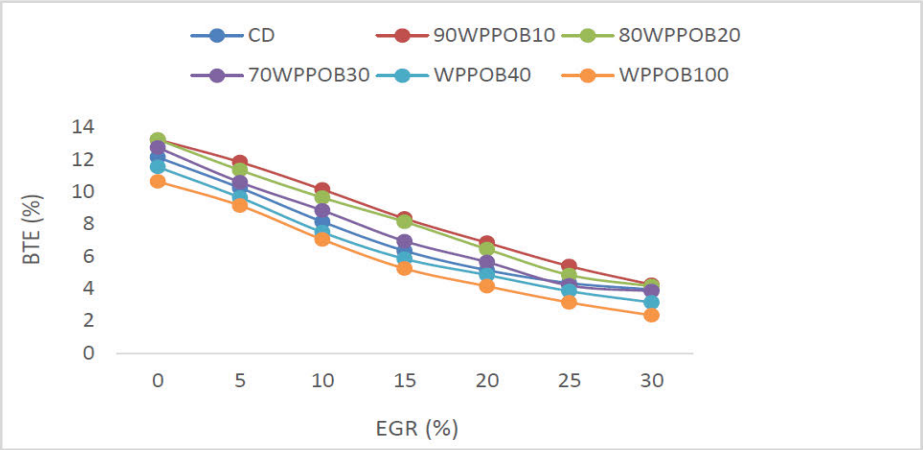

Figure 8 Brake thermal efficiency (BTE) percentage versus EGR percentage flow rate

However, in comparison to other WPPO blends WPPOB100 obtained the lowest increment of BTE with a value of 5.6 % at 10 % engine load and a maximum increment of 18.95 % at 100 % engine load. The other blends of WPPO as aforementioned exhibited higher BTE values, especially for the low ratio blends as compared to the high ratio blends, for example at 10 % engine load, the value for BTE for 90WPPOB10 was 7.05 % while blends 70WPPOB30 and 60WPPO40 were 6.75 % and 6.15 % respectively. The other blends of WPPO showed this same trend because at 100 % engine load the value for 90WPPOB10 was 27.0 % compared to 70WPPOB30 and 60WPPOB40 which were 24.75 % and 23.35 % respectively.

Although there is a reduction in BTE due to the application of EGR percentage flow rate as shown in Figure 8, the trends of decreased brake thermal efficiency are observed throughout. For example, at 0 % EGR flow rate, the BTE for CD was 10.25 % compared to 90WPPOB10 and 80WPPOB20 which were 11.85 % and 11.35 % respectively. The WPPOB100 blend had the lowest value for thermal efficiency for all EGR rate flow modes compared to the other test fuels. At EGR flow rate of 5% WPPOB100 blend had a maximum value of 9.50 % compared to 2.35 % for an EGR flow rate of 30% which was the minimum value obtained.

3.3. Brake Power (BP)

Figure 9 shows the brake power (BP) variations with different blends of WPPO and CD fuel at varying engine load to full load (100%). The results obtained showed that there was a linear increase in the BP for all the test fuels utilized with an increase in the engine load. CD fuel had the highest increase in BP values compared to the blended fuels of WPPO. At 20 % engine load 90WPPOB10 had a value of 1.350 kW compared to CD at 1.45 Kw representing a 6.8 % difference when the two fuels were compared.

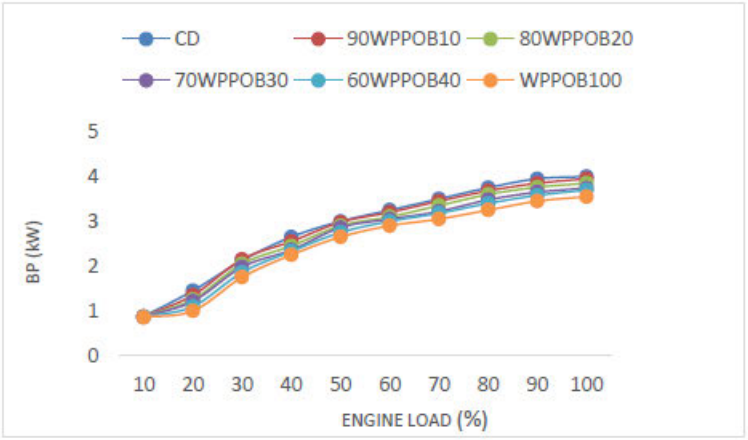

Figure 9 Engine brake power versus varying engine load percentage

The blended fuels in Figure 9 also showed marginal increments with an increase in engine load conditions, and a decrease in BP with an increase in the blend ratio for all the blended fuels tested. The increase in blend ratio showed a direct decrease in BP in a linearly incremented relationship. For example, at 20 % engine load 90WPPOB10, 80WPPOB20, 70WPPOB30 and 60WPPOB40 had values 1.255 kW, 1.215 kW, 1.1 kW and 1.0 kW respectively showing a decrease in the value of the engine BP throughout the experimentation period. These findings concur with the findings of [33] in relation to WPPO blends.

During experimentation, the WPPOB100 blend showed the lowest values for the engine BP compared to the blends of 90WPPOB10, 80WPPOB20, 70WPPOB30 and 60WPPOB40. At 30% engine load, WPPOB100 had a value of 1.75 kW compared to 90WPPOB10 at 2.15 kW, 80WPPOB20 at 2.05 kW, 70WPPOB30 at 1.98 kW and 60WPPOB40 at 1.86 kW respectively. From this result and observation, all the blends of WPPO produced less engine power compared to the power produced with the use of CD test fuel.

The application of EGR percentage flow rate was observed to cause no significant change in BP. However, there was a negligible drop in the engine BP with the influence of EGR flow rate except for the blend WPPOB10 that had almost identical values to CD as the curve of the two fuels indicate in Figure 9.

3.4. Exhaust Gas Temperature (EGT)

Figure 10 shows the variation of EGT under different types of WPPO blends and CD test fuel with application of EGR percentage flow rate. Temperature is one of the key factors in determining the formation of engine exhaust emissions, besides helping in the analysis and study of combustion processes in relation to fuel [61].

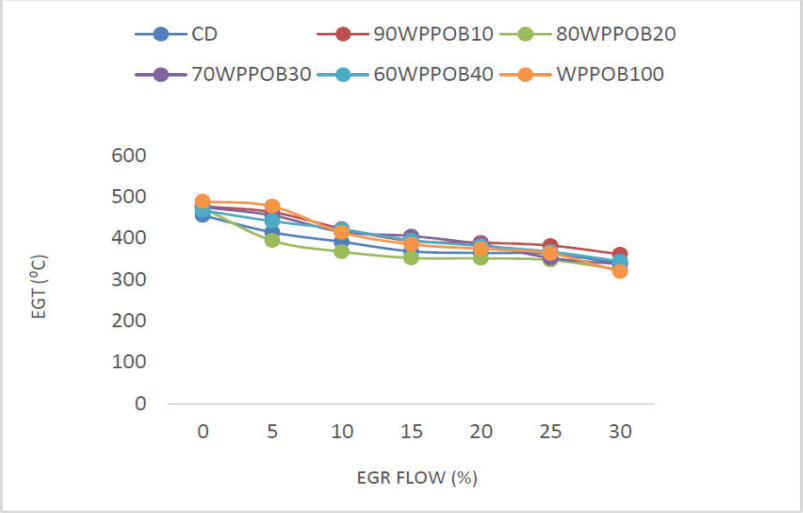

Figure 10 Exhaust gas temperature (EGT ºC) versus EGR percentage flow rate

Figure 10 shows the variation in exhaust gas temperature (EGT) with different WPPO fuel blends and CD under EGR percentage flow rates. The results indicate that EGT decreased with different blends of WPPO compared the CD test fuel. WPPO blends had higher temperature increases in all the test conditions compared to CD fuel during combustion. However, as the blend ratio increased with EGR percentage flow rate the EGT reduced marginally for WPPO blends of 70WPPOB30 and 60WPPOB40. The highest temperature value obtained for CD at 0 % EGR flow rate was 456 ºC compared to WPPOB100 blend which was 490 ºC.

The application of EGR percentage flow rate in increasing modes further reduced EGT with the CD test fuel measuring 440 ºC at EGR flow rate of 5 %. The minimum value was 340 ºC at 30 % EGR flow rate. The WPPO blends also showed a similar trend with decreasing temperatures with the application of EGR flow rate. For example, the highest temperature value for blend 90WPPOB10 was 467 ºC and the lowest was 362 ºC at 5 % and 30 % EGR flow rates respectively. However, increases in blend ratio increased temperature. For example, blend 60WPPOB40 showed its highest value to be 472 ºC and the lowest was 330 ºC at 5 % and 30 % EGR flow rates respectively. Nevertheless, at 30 % EGR flow rate WPPOB100 had the greatest reduction in temperature compared to the other WPPO blends.

The reduction in the EGT can be attributed to several factors. The reduction in EFT among the blends of WPPO could be attributed to the low calorific value of the blends and the low exhaust loss which concurs with the findings of [62, 63]. WPPO had a calorific value of 42.15 kJ/kg compared to the calorific value of CD which was 44.84 kJ/kg as shown in Table 2. The third cause can be directly linked to the effects of EGR rate flow, i.e. dilution effects, chemical effects and thermal effects [54, 64].

3.5. Unburnt Hydrocarbon Emissions (UHC)

Figure 11 shows the variation of UHC emissions in parts per million under full engine load with the application of various EGR percentage flow rates, and different blends of WPPO and (CD). The UHC emissions were significantly higher across all the blended test fuels of WPPO, especially with higher engine load conditions as indicated by the values shown in Figure 11. The cause of increased UHC emissions was due to the increased blend ratio. Increased blend ratios lower viscosity making it easier for the fuel to evaporate easily especially at lower engine loads and during the expansion stroke, hence slipping into the

cylinder [57, 65]. The second factor is due to the increased 'lean outer flame zone' [66]. This is where blended fuels are in a zone where their spray boundary is beyond the flammability limit due to overmixing [67].

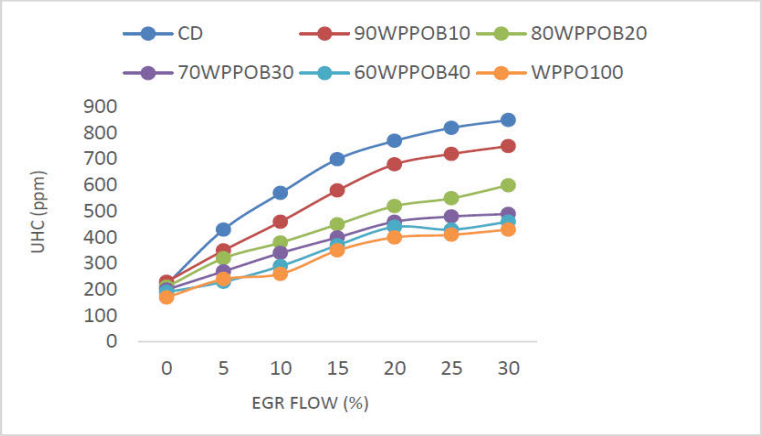

Figure 11 UHC emissions versus EGR percentage flow rate

For example, when the EGR percentage flow rate was 0%, in other words, no application effect, Figure 11 shows there was less UHC emissions for all the test fuels applied in this experiment, compared to 20 % or 30 % EGR percentage flow rates. The value for CD test fuel was 220 ppm at 0 % EGR flow rate and for the blend fuels the values were 230 ppm, 210 ppm, 200 ppm, and 170 ppm for 90WPPOB10, 80WPPOB20, 70WPPOB30, 60WPPOB40 and WPPOB100 respectively. Although the application of EGR percentage flow rate reduced the amount of UHC emissions of all test fuels across the board, CD fuel still produced higher UHC emissions from the test engine compared to all the WPPO blends. For example, at flow rates of 5 % and 15 % the values were 430 ppm and 700 ppm compared to blend WPPO10 with 320 ppm and 580 ppm.

3.6. NO_X Emissions

NO_X emission formation is highly dependent on in-cylinder temperature, the concentration of oxygen and the residence time of the fuel-air mixture in the combustion chamber during the pre-mixing phase [68]. All tested fuels indicated a reduction in NO_X emissions with EGR percentage flow rate for all load conditions. This can be attributed to the rise in the total heat capacity of the working gases with increasing EGR percentage flow rate. This finding concurs with the studies and findings of [30, 69, 70].

The NO_X emissions value for CD as shown in Figure 12 at full load was 432 ppm with 30 % EGR percentage flow rate, compared to blend WPPOB100 at 536 ppm. This represents a decrease in NO_X emissions by CD from a high of 536 ppm at 0 % to 432 ppm, which is a 19.4 % reduction.

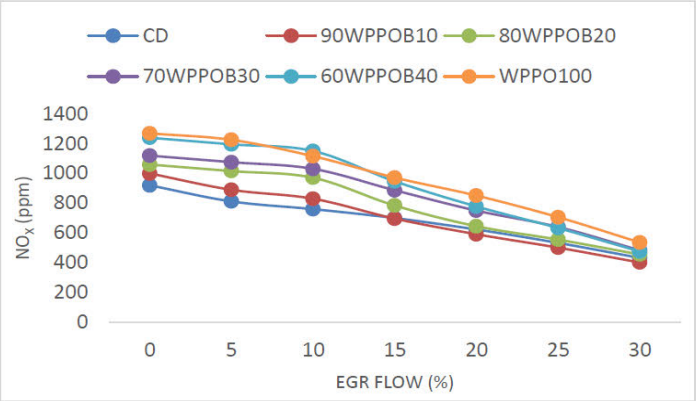

Figure 12 Variations of NO_X emissions (ppm) versus EGR percentage flow rate

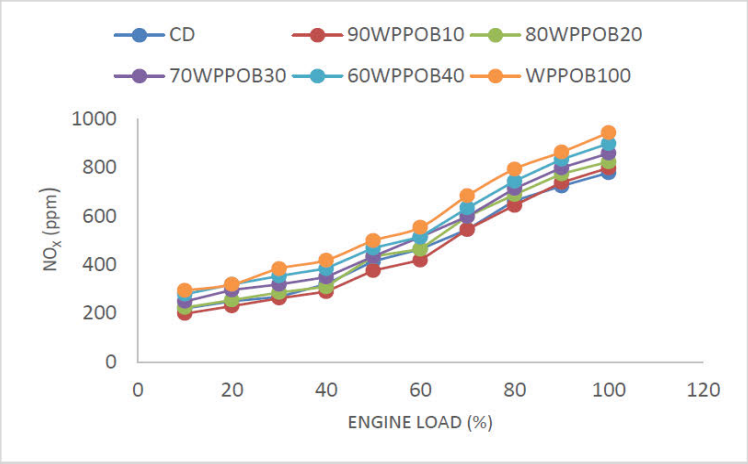

Figure 13 Variations of NO_X emissions versus load percentage without EGR percentage flow rate

However, during experimentation at engine part load (as shown in Figure 12), the values for NO_X emissions for the same fuels were high towards full load engine conditions. For example, at part load (50 %) the CD fuel value was 415 ppm compared to full load at 780 ppm, whereas blend WPPOB100 at engine part load (50 %) was 500 ppm as compared to 945 ppm at full engine load. This seems to indicate a concurrence that at part engine load (50 %) the values of NO_X emissions emitted by all the blends of WPPO except WPPO100 were lower compared to the values at full engine load conditions.

3.7. Carbon Monoxide (CO) Emission

Figure 14 shows variations of CO emission percentage with varying load under the effects of EGR percentage flow rate, with different fuel blends of WPPO and CD fuel. CO is a toxic gas that requires substantial control to maintain acceptable levels. CO is caused by poor combustion of hydrocarbon fuels due to dependency on the air-fuel ratio relative to the stoichiometric proportions (Mani et al., 2010)[30].

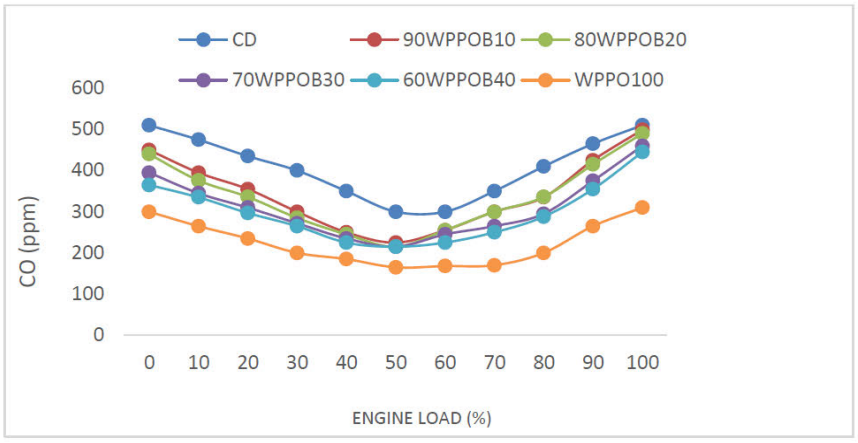

Figure 14 CO emissions percentage versus varying engine load

For all the test fuels the amount of CO emissions seemed to decrease at lower engine loads up to part load percentages or intermediate loads of (50 %), thereafter the CO emissions continued to increase marginally as shown in Figure 14. For example, at 0 % engine load the value of CD was 510 ppm compared to at 50 % engine load when the value reduced to 300 ppm.

However, as the engine load increased from 50 % there was a continuous marginal increase in the percentage of carbon emissions as the load increased across all the test fuels irrespective of the EGR percentage flow rate. For example, at 80 % engine load the value for WPPOB100 was 200 ppm up from 165 ppm at 50 % engine load, which represented a marginal increase of 17.5%. On the other hand, the value of CD was 499 ppm compared to 300 ppm at 50 % engine load. The WPPO blends also showed similar trends and concurrency. For example, blend 80WPPOB20 at 50 % engine load had a value of 215 ppm compared to 336 ppm at 80 % engine load.

3.8. Carbon Dioxide (CO_2) Emissions

CO_2 is the principal composition of the EGR gases, which indicates the quality of combustion and temperatures within the combustion chamber [71]. CO_2 gas produces high heat capacity making a thermal heat sink during the combustion process, hence reducing peak cylinder temperatures and reducing NO_X emissions.

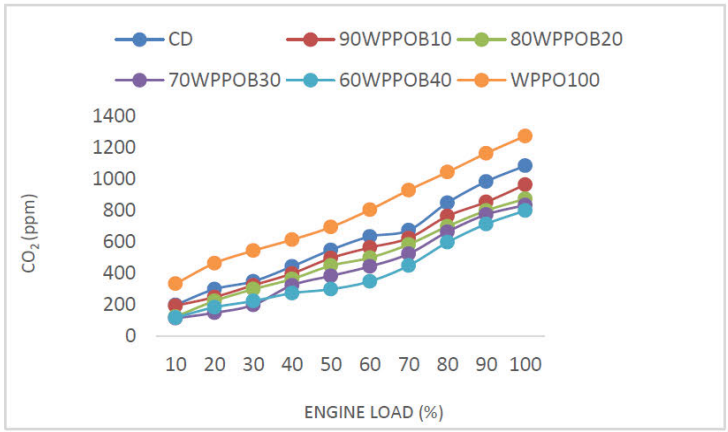

Figure 15 Variation of CO_2 versus engine Load, with blends of WPPO and CD fuel

Without EGR percentage flow rate and at lower engine loads, the value of CO_2 was high for all the test fuels used. For example, at 20 % engine load WPPOB100 had the highest carbon emissions of 465 ppm compared to all the other test fuels used. CO_2 emission values for CD fuel was 300 ppm compared to 60WPPOB40 at 225 ppm as shown in Figure 15.

However, the amount of CO_2 increased with increase in the engine load. For example, at 40 % engine load blend 60WPPOB40 was 275 ppm compared to WPPOB30 at 325 ppm. Nevertheless, at 70 % engine load the value for 60WPPOB40 was 450 ppm while WPPOB30 was 525 ppm respectively. In other words, as the engine load increased with the blend ratios, more CO_2 emissions were emitted. At full engine load, the value of CO_2 emissions was highest for all the test fuels, as shown in Figure 15. For example, CD was 1085 ppm compared to the blend WPPOB100 at 1275 ppm, 90WPPOB10 at 965 ppm, 80WPPOB20 at 875 ppm, 70WPPOB30 at 835 ppm and 60WPPOB40 at 800 ppm respectively.

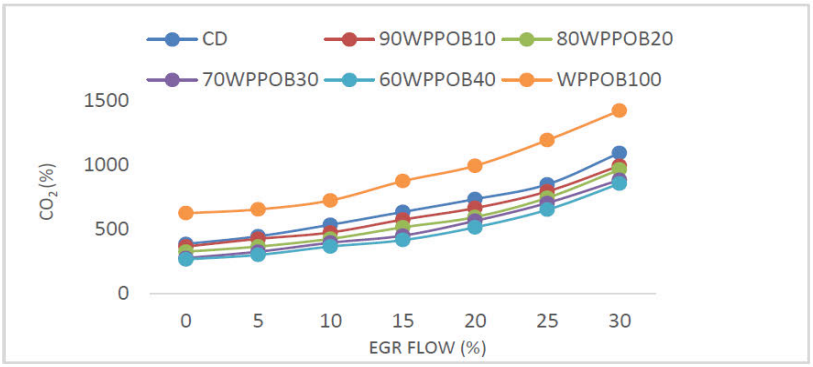

Figure 16 Variations of CO_2 percentage versus EGR percentage flow rate, with WPPO fuel blends and CD

The application of EGR percentage flow rate increased the CO_2 emissions exponentially by almost doubling the values as shown in Figure 16. For example, at 10 % EGR flow rate the value of CD was 585 ppm compared to WPPOB100 at 725 ppm, 90WPPOB10 at 475 ppm, 80WPPOB20 at 425 ppm, 70WPPOB30 at 395 ppm, and 60WPPOB40 at 365 ppm respectively. These results reinforce the earlier observation made regarding CO_2 emissions under load, that under EGR percentage flow rate the lower the blend ratio the higher the emission values and vice versa.

3.9. Smoke Emissions (Opacity)

These are solid hydrocarbon soot particles that are found in exhaust system gases [72] which are directly linked to smoke emission formation. For all the blends of WPPO there was a noted increase in the level of smoke emissions, although compared to CD the levels and values were considerably lower.

The application of EGR percentage flow rate show there was a significant increase in the values of smoke emissions and particulate matter emissions across all the test fuels. Smoke emissions of the WPPOB10 blend were 7.2 % lower compared to CD at 0 % EGR flow rate, although CD was 11.5 % higher than WPPOB100 blend fuel at 30 % EGR flow rate. This result seems to concur with the study findings of (Bridjesh, Periyasamy, Chaitanya, & Geetha, 2018)[73].

The 90WPPOB10 and 80WPPOB20 blends emitted the highest smoke emissions compared to the other WPPO fuel blends. However, as the blend ratio and the EGR percentage flow rate increased there was a steady increase in the smoke emissions across all the test fuels compared to 0 % EGR flow rate.

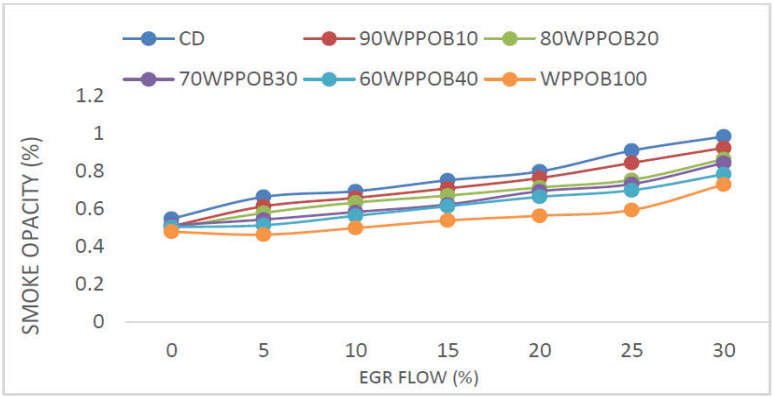

Figure 17 Variation of smoke opacity versus EGR percentage flow rate, with different WPPO blends

Figure 17 shows the variation of smoke emissions under the influence of EGR percentage flow rate with different WPPO blends and CD. The steady increase in smoke emissions can be explained by the fact that WPPO blends of fuel have a high kinematic of viscosity compared to the CD test fuel, besides the low volatility values of the WPPO tested blends. Other possible explanations for this phenomenon could be the poor injection and spray characteristics observed with WPPO blends of fuels as compared to the spray and injection characteristics of CD fuel, which has better spray qualities. Another likely cause was the presence of a high aromatic compounds found in WPPO blends of fuel compared to CD test fuel.

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CHAPTER 7: EFFECTS OF BIODIESEL BLENDS VARIED BY CETANE NUMBERS AND OXYGEN CONTENTS ON STATIONARY DIESEL ENGINE PERFORMANCE AND EXHAUST EMISSIONS

Book chapter

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Chapter 3

Effects of Biodiesel Blends Varied by Cetane Numbers and Oxygen Contents on Stationary Diesel Engine Performance and Exhaust Emissions

Semakula Maroa and Freddie Inambao

Abstract

This work investigated waste plastic pyrolysis oil (WPPO), 2-ethyl hexyl nitrate (EHN), and ethanol as sources of renewable energy, blending conventional diesel (CD), WPPO, and ethanol with EHN was to improve the combustion and performance characteristics of the WPPO blends. EHN has the potential to reduce emissions of CO, CO_2, UHC, NO_X, and PM. Ethanol improves viscosity, miscibility, and the oxygen content of WPPO. Mixing ratios were 50/WPPO25/E25, 60/WPPO20/E20, 70/WPPO15/E15, 80/WPPO10/E10, and 90/WPPO5/E5 for CD, waste plastic pyrolysis oil, and ethanol, respectively. The mixing ratio of EHN (0.01%) was based on the total quantity of blended fuel. Performance and emission characteristics of a stationary 4-cylinder water-cooled diesel Iveco power generator were evaluated with ASTM standards. At 1000 rpm, the BSFC was 0.043 kg/kWh compared to CD at 0.04 kg/kWh. Blend 90/WPPO5/E5 had the highest value of 14% for BTE, while the NO_X emissions for 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 were 384, 395, and 414 ppm, respectively, compared to CD fuel at 424 ppm. This is due to their densities of 792 kg/m^3, 825 kg/m^3 which are close to CD fuel at 845 kg/m^3 and the additive EHN. These results show blends of WPPO, ethanol and EHN reduce emissions, and improve engine performance, mimicking CD fuel.

Keywords: 2-ethyl hexyl nitrate, ethanol, oxygen content, ignition quality, waste plastic pyrolysis oil, cetane index

1. Introduction

Diesel engines the world over are the major power source in the automobile transport industry and nonroad powered engines. However, because of the issue of pollution associated with diesel exhaust, particularly particulate matter (PM) and nitrogen oxide (NO_X), there has been increasingly stringent regulation to control the manufacture and use of diesel engines. This has led to extensive research on improving diesel engines and fuel [1, 2]. The use of alternative fuels tops the list of measures to control diesel exhaust emissions as recommended by researcher [3]. Besides the use of alternative fuel to control and reduce emissions, other control

strategies such as exhaust gas recirculation (EGR), diesel particulate filters (DPF), selective catalytic reduction (SCR), and catalytic converter combinations have been recommended but not as stand-alone technologies [4, 5].

The transport industry and nonroad diesel engines are major contributors to global gross domestic product. Nevertheless, their use affects human health and degrades the environment. The transport industry is responsible for one third of all environmental emissions of volatile organic compounds (VOCs), including two thirds of carbon monoxide (CO) emissions [6]. Carbon dioxide (CO_2) is a primary cause of global warming with 34 billion tons per year or 22% of all the global emissions per year [7], with a projected increase in 3% annually since 2011. This is projected to rise to 41 billion tons of CO_2 emissions by the year 2020 [8, 9]. Diesel engines release emissions, which lead to poor air quality, acid rain, smog, haze, and climate change. These factors increase the global disease burden due to respiratory system diseases and cancer [10].

The soluble organic fraction (SOF) and volatile organic fraction (VOF) are mainly due to exhaust dilution and the cooling process from fuel or evaporating lubricating oil, due to the process of oxidation. The control of VOC emissions is with high-pressure injection system catalytic converters and positive crankcase ventilation systems. The PM emissions of VOCs arising from evaporating lubrication oil and incomplete combustion have a combined emission rate of 0.06–2.2 g/bkWh for light diesel (LD) engines compared to heavy diesel (HD) engines at 0.5–1.5 g/bkWh [11, 12]. The condensation of oxidized and pyrolyzed products of fuel molecules is the leading cause for the formation of PM emissions composed of the nucleation and accumulation modes [13]. In emerging economies, air pollution is the leading cause of thousands of premature deaths estimated at 2.4 million annually by 2009 estimates [14]. Besides the usual toxics emitted by stationary and nonroad engines, diesel engines emit toxics such as formaldehyde, acrolein, acetaldehyde, and methanol. Exposure to these toxic emissions causes eye, skin, and mucous membrane irritation, besides affecting the nervous system. Therefore, the need for environmental protection has played a role in bringing together relevant stakeholders and government agencies. These agencies include the WHO, the Organization of Economic Cooperation and Development (OECD), the Inter-Governmental Panel on Climate Change (IPCC), the Environmental Protection Agency (EPA), the European Environmental Agency (EEA), and the International Energy Agency (IEA). For example, the USA government through the EPA has established the Reciprocating Internal Combustion Engine (RICE) rules, which cover stationary and nonroad engine emission regulations [15]. These rules are out of the scope of this chapter, but future work will discuss them in line with other European Union rules [16] and other global adopted emission regulations.

In order to meet modern requirements, diesel engines are designed with complex contrary goals to operate optimally in stationary and mobile operations. This requires high torque, low emissions, and high efficiency engines. For this reason, auxiliary diesel engine components such as turbochargers, EGR, and high-pressure injection systems are utilized today. These auxiliary parts are grouped into engine operating subsystems such as air, combustion, injection, and mechanical units to meet these operating demands. Since fuel is a major determinant in engine combustion and emission characteristics, the use of alternative fuel is being encouraged as a strategy to reduce emissions. The combustion of alternative fuel is different from the combustion of diesel, which is a fossil fuel, but they too cause emission problems as has been reported in a number of studies [17, 18]. To mitigate these problems, researchers have come up with combustion control strategies such as:

- homogeneous charge compression ignition (HCCI) [19, 20];
- pre-mixed charge compression ignition (PCCI) [21, 22];

- reactivity charge compression ignition (RCCI) [23]; and
- variant strategies to deal with emissions [24–30].

Modern day passenger vehicles and stationary engines are now evaluated using driving cycles such as the New European Driving Test Cycle (NEDC) and the Federal Test Procedure (FTP) mostly as bench operated chassis dynamometer tests [31]. However, it should be remembered that at engine start conditions, after-treatment techniques report poor performance as most of them operate with catalysts that are light-off temperature dependent. At ambient temperature, most catalysts cannot attain the light-off temperature when engines are started and operated. Since the year 2000 when EURO III was implemented, the NEDC procedure has been modified to eliminate the 40 s warm up before emission sampling can take place [32]. The new development initiative for diesel exhaust emission has already been established in the United States and Japan. The last decade has seen the European Union implementing similar standards and procedures, with the rest of the world expected to also implement changes as globalization and interdependency grows. A number of requirement have been implemented in the United States to nominally reduce 85–90% of NO_X, while for the Euro VI (2014), an additional reduction 65–70% of NO_X to match the US standards has been accepted as shown in **Figures 1** and **2** [33].

The combustion of diesel fuel depends on several factors that affect engine geometry, fuel properties, compression temperatures (especially of the combustion mixture), injection strategy applied, and the existing condition of the ambient temperatures as reported by the authors of Refs. [34, 35]. High cetane number additives together with the development of high volatility fuels [36, 37] have boosted diesel engine performance. The oxygenated additives in biodiesel blend components improve the combustion process, especially the octane rating. Additionally, oxygenated additives enhance and increase the cetane number. In other words, the oxygen in the additives supports the combustion of the fuel while at the same time reducing inert material such as NO_X formation in CI engines. These changes deal with the complexities of cold start, which impede engine starting at lower or subzero engine temperatures. Warm engines have a starting time delay of 1–2 s at ambient temperature conditions, compared to a low ambient temperature start-up time of 10 s [38, 39].

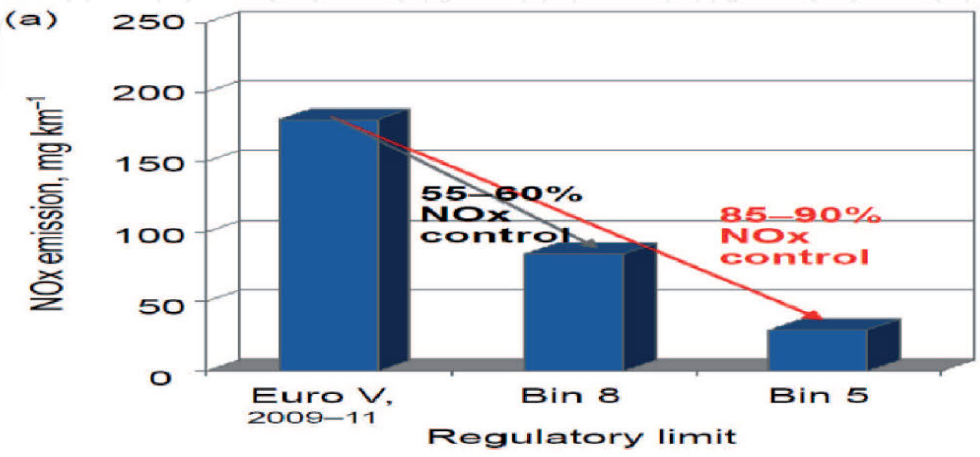

Figure 1.
Requirement to reduce about 55–60% of NO_X emissions for Euro V (2009) diesel to match the US Bin 8 maximum allowable emission in 45 US states [33].

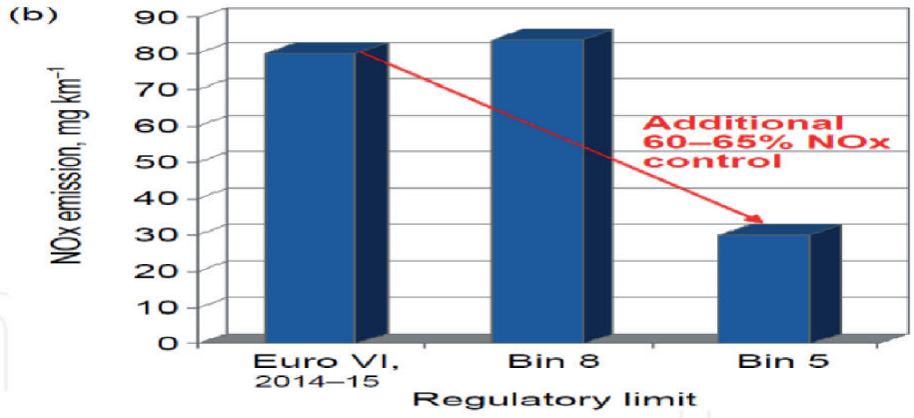

Figure 2.
Variation of NOx emission with the regulatory limit for 45 US states [33].

2. Regulatory development in diesel engine emission

Stringent diesel exhaust emission regulatory policies have been in operation in the United States and Japan since 2005. The European Union has also responded with additional emission regulatory standards called the EURO VI since 2014. Apart from these regulatory controls, there are market and political pressures on automobile manufacturers to continue to improve on efficiency while reducing emissions. These factors have been the driving force behind the significant technological progress in engine research and the transport industry in the past two decades.

2.1 Heavy duty diesel regulatory developments

The European Union commission on emissions in 2014 stipulated that the nominal NO_X emission limit must be 0.20 g/kWh^{-1} and the PM emission level must be 0.010 g/kWh^{-1}. This matched the US 2010 emission regulation, which put the emission limits at 0.26 g/kWh^{-1} for NO_X and 0.013 g/kWh^{-1} for PM emissions. The Japanese emissions regulation of 2009 stipulates 0.7 g/kWh^{-1} for NO_X emissions and 0.010 g/kWh^{-1} for PM emissions. However, it must be mentioned here that each of these countries propose a different transient testing cycle.

The European Union commission on pollution and emission has adopted a new world harmonized transient cycle (WHTC) that uses higher load and speed than the Japanese and American standards. Additionally, the European commission on emissions has set standards related to number-based PM standards with heavier in-use compliance measures as illustrated in **Figure 3**, by 2012. These measures are aimed at improving fuel economy and durability and lowering the cost of manufacturing and maintenance. The development in this segment is muted, mixed with conservatism and pragmatism. For example, the development in HD since 2004 has seen the US regulations matched and addressed through advanced EGR and intake charge boosting measures. However, later development starting from 2005 in Japan and 2007 in the United States has seen additional technologies added to cater for increased regulation. These two markets introduced diesel particulate filters (DPFs) to match the change in policy and regulation in the European Union with implementation of EURO V-VI emission regulations. This policy shift and regulation change has witnessed conventional engine technology adding the selective catalytic

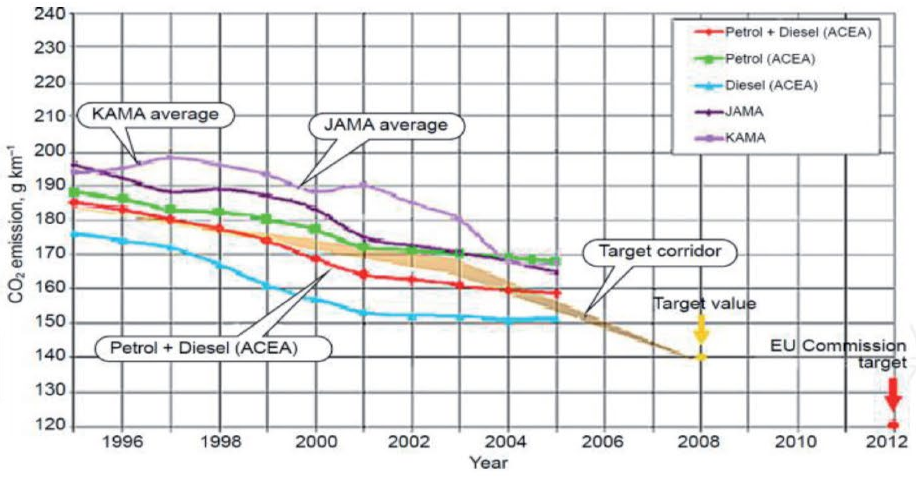

Figure 3.
Progress toward meeting the European Union voluntary CO_2 limits of the European Automobile Manufacturers Association (ACEA), Japan Automobile Manufacturers Association (JAMA), and Korea Automobile Manufacturers Association (KAMA) (courtesy of Daimler Chrysler) [40].

reduction (SCR) system in the fight against emission. Since 2009 and 2010, respectively, Japan and the United States have added significant incremental advances in emission compliant technologies, especially technologies that target low load emissions in HD engines. Researchers working on the traditional diesel combustion hardware and strategies are directing more effort to reduce LD engine category emissions with the future looking bright.

2.2 Light duty diesel regulatory development

Modern diesel engine development is driven by regulatory, market, and fuel efficiency demand. In addition, developments in spark ignition (SI) gasoline engines, electric vehicles, and new concepts in hybrid vehicles have had tremendous competitive pressure on diesel engine development, especially in the LD category. Diesel engine manufacturers are responding with the introduction of advanced fuel injection technology, exhaust gas recirculation (EGR) techniques,

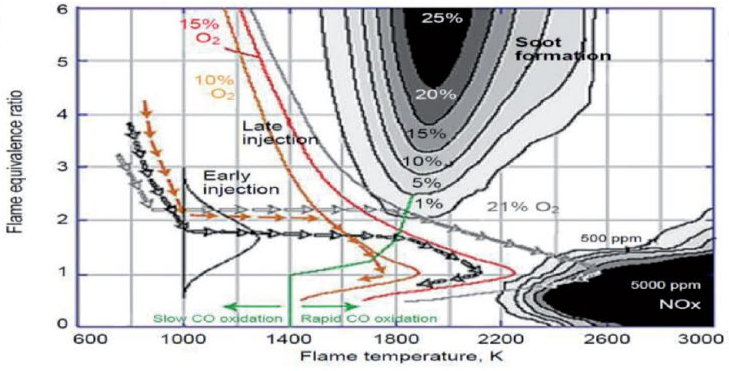

Figure 4.
Variation of flame equivalence ratio, temperature, and injection strategies and principles of advanced combustion (courtesy of Sandia National Laboratory) [44, 45].

two-stage turbocharging, variable valve actuation, closed loop combustion control, and advanced model-based controls. Development in advanced diesel engines has now achieved a specific output of 70 kW^{-1} and a brake mean effective pressure (BMEP) of 24 bars [41], hence meeting EURO VI emission standards [42, 43] as shown in **Figure 4**.

3. Control strategies for emissions in diesel engine

The world is now aware of the environmental and human health costs of pollution from diesel engines, which form the bulk of commercial and personal public transport systems. **Table 1** shows that there is an increase in the regulatory measures on toxic gas emissions. These regulations oblige vehicle manufacturers and transport industry service providers to be motivated to work harder to meet the appropriate standards and regulations. Among the techniques that have been employed to cut down on emissions are EGR, LNT, DOC, DPF, and SCR [46, 47]. However, there is no single method that meets emission standards by the regulatory bodies on vehicular emission.

3.1 Exhaust gas recirculation (EGR)

This is one of the most useful and successful techniques in the control of and fight against diesel exhaust emissions. EGR allows the recirculation of part of the diesel exhaust into the combustion chamber, to reburn together with the fresh intake charge [49] as shown in **Figure 5**.

This technology has been able to reduce NO_X emissions, but it causes an increase in UHC and CO emissions as compression temperatures decrease. It also affects engine thermal efficiency as shown in **Figure 6**. This technique has two methods for quantification of EGR flow rate, although there is no single method that is universally accepted. The two methods are the mass method and the gas concentration method [5]. These two methods are demonstrated in **Figure 5** and expressed in Eqs. (1) and (2):

$$r_{EGR} = \frac{\dot{m}_{EGR}}{\dot{m}_{air} + \dot{m}_f + \dot{m}_{EGR}} \tag{1}$$

$$\frac{[CO_2]_{int} - [CO_2]_{amb}}{[CO_2]_{exh} - [CO_2]_{amb}} \approx \frac{[CO_2]_{int}}{[CO_2]_{exh}} \tag{2}$$

where the $\dot{m}_{EGR}$ is the mass flow rate of the gas recirculated, $\dot{m}_{air}$ is the mass flow rate of fresh air, $\dot{m}_f$ is the mass flow rate of the injected fuel, and r_{EGR} is the mass fraction of the recirculated exhaust gases. $[CO_2]_{int}$ is the carbon dioxide at the intake side, $[CO_2]_{amb}$ is the ambient carbon dioxide, $[CO_2]_{exh}$ is the exhaust carbon dioxide (exit carbon dioxide).

3.2 The low NO_X trap (LNT)

This system is also known as NO_X storage reduction (NSR) and NO_X absorber catalyst (NAC). It has three main components, namely, the oxidation catalyst with platinum (Pt), the NO_X storage with barium (Ba), and the reduction catalyst with rhodium (Rh). The platinum catalyst is preferred as it reduces NO_X emissions at very low temperatures while offering a stable reaction in the presence of sulfur and H_2O [51, 52]. **Figure 7** shows the LNT three-stage catalytic process.

STD type	CO g/kWh	HC g/kWh	NO_X g/kWh	PM g/kWh
Euro I	4.5	1.1	8.0	0.61
Euro II	4	1.1	7.0	0.15
Euro III	2.1	0.66	5.0	0.13
Euro IV	1.5	0.46	3.5	0.02
Euro V	1.5	0.46	2.0	0.02
Euro VI	1.5	0.13	0.4	0.01

Table 1.
EURO standards for heavy-duty vehicles according to Delphi 2016–2017 as per Ref. [48]

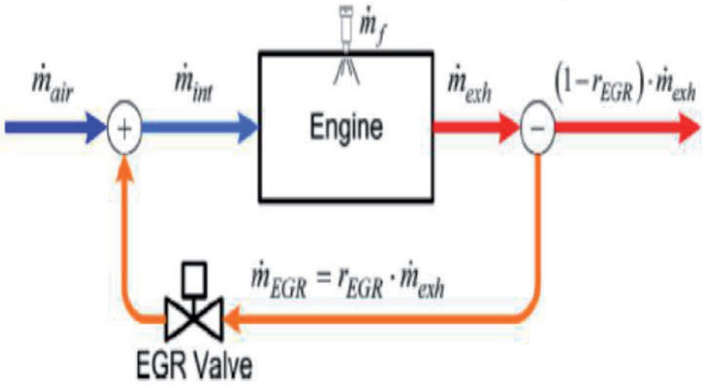

Figure 5.
EGR system nomenclature and control design for the EGR valve [4].

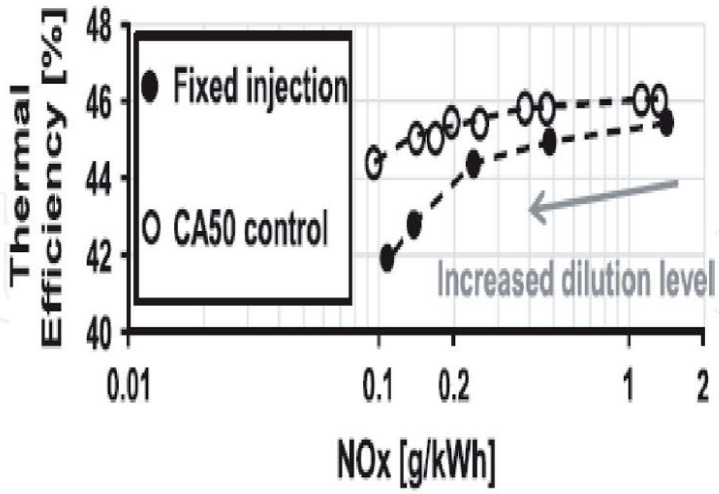

Figure 6.
Variation of engine thermal efficiency and NO_X with the influence of EGR dilution [50].

3.3 The selective catalyst reduction (SCR)

This is one of the most recent technology developments introduced for the control of diesel exhaust emissions. This system was originally introduced to cater for HD engines [53], but Audi and Volkswagen have also adopted it for their

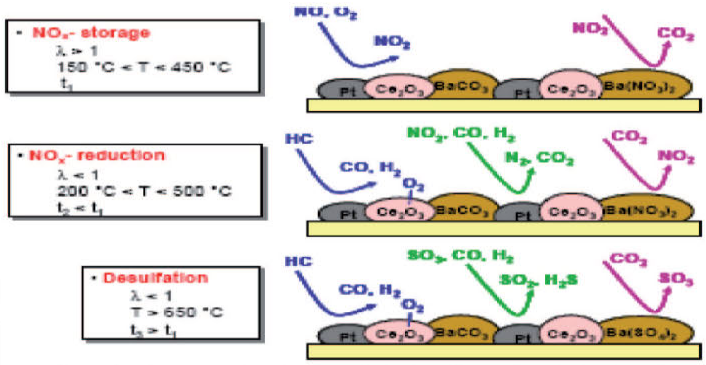

Figure 7.
The low NO_X trap (LNT) with three of its operating modes [53].

passenger vehicle and LD segments. The SCR system works by utilizing ammonia as a reductant in order to minimize NO_X emissions in the diesel exhaust by releasing N_2 and H_2O. This system therefore undergoes two processes during the working cycle, namely, hydrolysis and thermolysis as in Eqs. (3) and (4) for hydrolysis and thermolysis, respectively [54, 55].

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{3}$$

$$(NH_2)_2CO \rightarrow NH_3 + HNCO \tag{4}$$

In addition to the two processes of hydrolysis and thermolysis, SCR undergoes other chemical reactions to complete its normal cycle, thus reducing the emissions of NO_X further as in Eqs. (5)–(7). **Figure 8** shows a schematic diagram of an SCR system showing the oxidation catalyst, wall flow particulate filter, and the flow through the SCR catalyst. **Figure 8** also includes key components of a urea solution tank, a spray module, a static mixer, temperature, and NO_X sensor, courtesy of Robert Bosch GmbH [46].

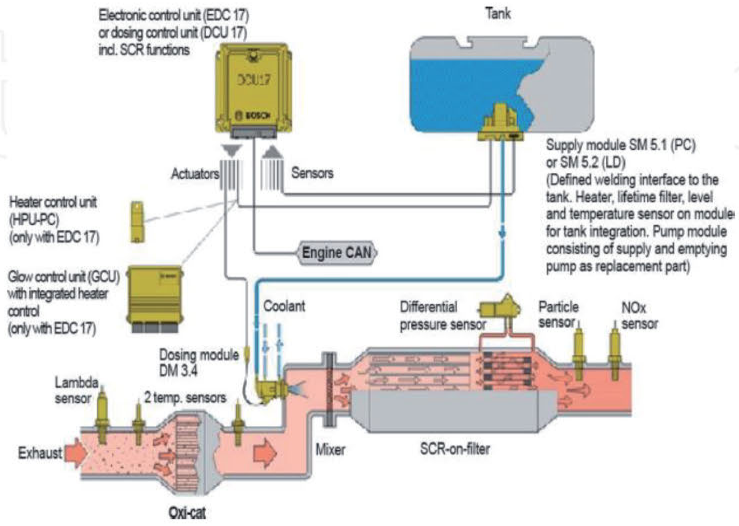

Figure 8.
Schematic diagram of the SCR NO_X control system as used in a standard production vehicle [46].

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (5)$$

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \quad (6)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (7)$$

3.4 Diesel particulate filter (DPF)

The DPF filter requires care to avoid excessive saturation and build-up of backpressure, both of which are harmful for engine operation and durability and increase fuel consumption and engine stress levels leading to premature failure of the filter and engine. DPF systems have been in operation in diesel exhaust emission control since the year 2000, primarily for removing PM emissions through physical filtration. DPFs are like a honeycomb with silicone carbide or cordierite written chemically as $2MgO - 2Al_2O_2 - 5SiO_2$. Both ends of the structure are blocked to force the particulate matter through the porous substrate walls, thus acting as a mechanical filtering system. These walls are made such that they offer little or no resistance to flow of exhaust gases while maintaining the power to collect particles [56] as shown in **Figure 9**.

3.5 Diesel oxidation catalyst (DOC)

The DOC is manufactured with the sole purpose of reducing CO and UHC emissions through oxidation of the hydrocarbons that are absorbed into the carbon particles. The DOC consists of a metal or a ceramic structure with an oxide mixture also called the wash coat that contains aluminum oxide (Al_2O_3), cerium oxide (CeO_2), zirconium oxide (ZrO_2), and an active metal catalyst of either platinum, palladium, or rhodium [54], as shown in **Figure 10**. For HD and LD vehicles in Europe, the United States, and Japan, the DOC is the after-treatment emission control systems of choice. The DOC with a platinum metal catalyst is the most popular among manufacturers and consumers. However, the DOC has the disadvantage of reacting with sulfur oxide and sulfur trioxide producing sulfates and sulfuric acid,

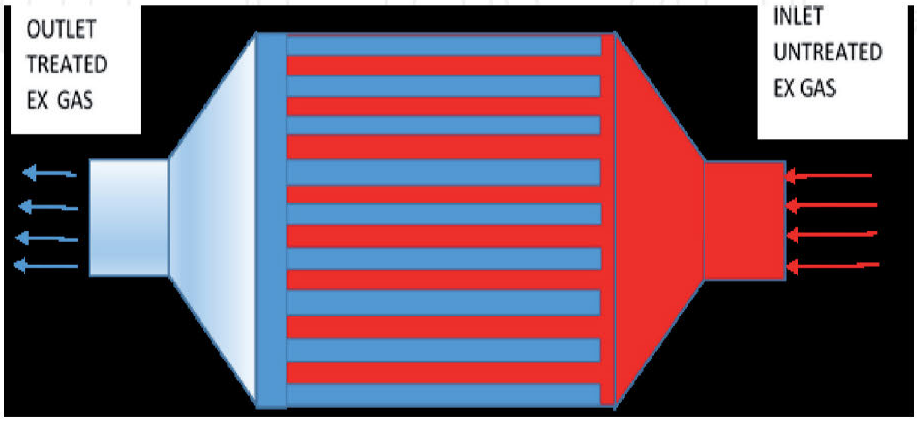

Figure 9.
Schematic of the working mechanism of a diesel particulate filter (DPF) [6].

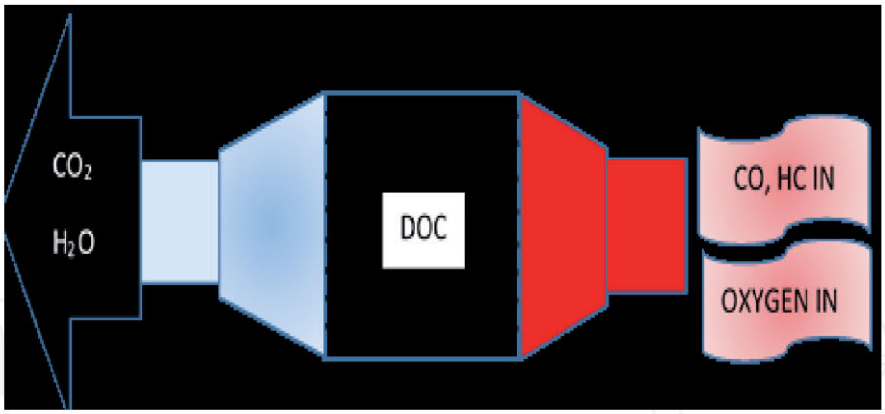

Figure 10.
Schematic diagram of a DOC and its operation in reducing emissions of CO and UHC through the process of oxidation [6].

which shortens the service life of the emission control system besides the additional effects on the natural environment and human health.

Six factors affect and influence the choice of a DOC filter:

- conversion factor;
- temperature stability;
- light-off temperature;
- tolerance to poisoning;
- cost of manufacturing the filter; and
- parametrical factors, including the density of the DOC filter measured in channels per square inch, the cross-sectional area, the channel wall thickness, and the length of the channels using the external dimensions [57, 58].

4. Methodology and experimental set-up

This experiment is making a case for blending of WPPO whose n-alkenes are lower by 25% in auto-ignition, compared to diesel fuel whose n-alkenes are good for auto-ignition. The aromatics, which affect PM emissions, are very low in WPPO blends. According to Refs. [59, 60], WPPO consists of iso-alkanes, n-alkanes, and olefins in the region of 27, 25, and 9%, respectively, with over 30% content being undefined due to complicated and complex chemical bond structures. However, aromatic cyclo-alkanes (naphthalene) and aromatics poor in auto-ignition were also found to be 40% by volume [61]. Blending was preferred to improve the low pour point to improve the cold starting characteristics of WPPO. Second, blending with ethanol was introduced to improve the fuel spray characteristics; ethanol is soluble and miscible in WPPO blends. Third, blending contributed to the reduction of the viscosity of WPPO biodiesel, thus further improving spray characteristics.

4.1 Engine tests

The experiment used a naturally aspirated four-cylinder diesel engine power generator, water cooled, direct injection, Iveco engine, in the Mechanical Engineering Department Laboratory, University of Kwazulu-Natal in Durban, South Africa. Using a defined flow rate of particles, PM emissions were detected by photoelectric measurement. Both the mass flow of the PM particles and the fuel were calculated as the sum of inlet air and fuel mass flow rate, and the result expressed in gram per kWh. To help in the analysis of the engine, pressure sensors and crankshaft position sensors and encoders were used. The aim of these sensors was to provide the in-cylinder pressure in relation to the crankshaft position variation.

Parameters	Position value
Ignition type	4 (Stroke)DICI
Number of cylinders	4 in-line
Cooling medium	Water
Manufacturer	Iveco
Revolutions per minute	2000
Brake power	43.40 kW @ 2000
Cylinder bore	104 mm
Piston stroke	115 mm
Compression ratio	17:1
Connecting-rod length	234
Engine capacity	2500 cc
Dynamometer make	DW234
Injection timing	12° bTDC
Maximum torque	206.9 Nm @ 1500
Injection pressure	250–272 Bar

Table 2.
Experimental engine specifications.

Property	Equipment	Standard
Kinematic viscosity	SVM 4000 (Anton Paar, UK)	ASTM D445
Flash point	NPM 550 (Norma lab, France)	ASTM D93
Oxidation stability	900 Rancimat (Metrohm, Switzerland)	ASTM D14112
CP/PP	NTE 500 (Norma lab, France)	ASTM D2500
Carbon residue	NMC 440 (Norma lab, France)	ASTM D4530
Total sulfur	5000 MULTI-EA (AJ Germany)	ASTM D5433
Calorific value	C 2500 basic calorimeter (IKA, UK)	ASTM D240
Density	SVM 3500 (Anton Paar, UK)	ASTM D1298
PM	AVL smoke meter	—
Gaseous emissions	Gas analyzer (MEXA 7000) Germany	—

Table 3.
List of equipment used in the experiment.

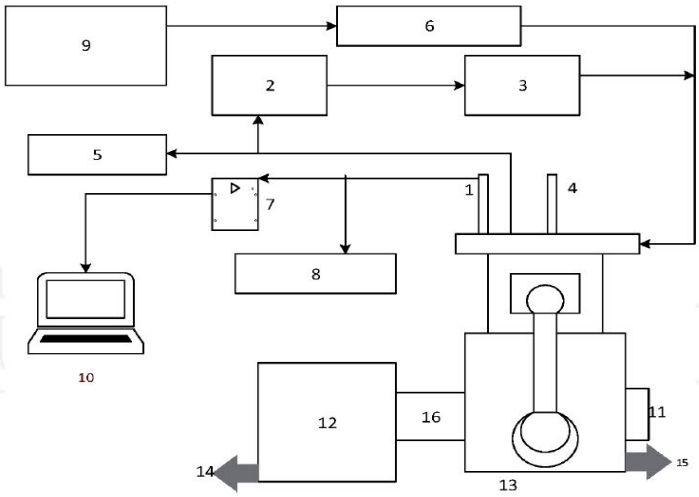

Figure 11.
Schematics of the test engine set up rig: (1) cylinder pressure sensor; (2) EGR control valve; (3) EGR cooler; (4) injection control unit; (5) exhaust gas exit; (6) air box; (7) signal amplifier; (8) gas analyzer; (9) air flow meter; (10) data acquisition system; (11) crank position sensor; (12) dynamometer; (13) engine; (14) cooling water exit from the dynamometer to the cooling tower; (15) cooling water exit from the engine to the cooling tower; and (16) dynamometer drive coupling.

The engine was coupled to a mechanical dynamometer with engine idling positions divided into two engine speed modes. The two speed modes were set at 500 and 1000 rpm as Mode 1, and Mode 2 as 1500 rpm and full load at 2000 rpm. The details of the engine and specifications and equipment are described in **Tables 2** and **3**. **Figure 11** shows a schematic of the engine test setup.

4.2 Physicochemical property analysis

WPPO by pyrolysis was obtained from a commercial plant whose production chart is shown in **Figure 12**. Ethanol, conventional diesel, and EHN were purchased

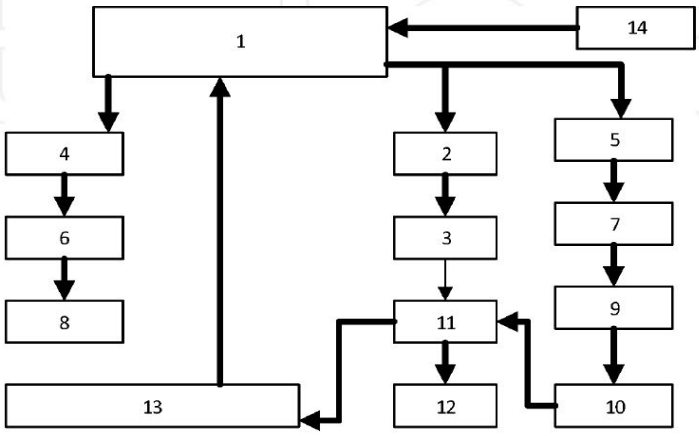

Figure 12.
Pyrolysis plant flow chart and its nomenclature: (1) pyrolysis reactor; (2) carbon black discharge; (3) carbon black deep processing; (4) exhaust smoke discharge; (5) gas separator; (6) smoke scrubber to take out color and odor; (7) condenser; (8) chimney; (9) oil tank; (10) synchronized gas purification; (11) synchronized gas-recycling system; (12) extra gas burning; (13) heating furnace during operation; and (14) loading of material.

Properties	Unit	CD	WPPO	Ethanol
Density @ 20°C	kg/m^3	845	825	792
Visc.@ 40°C	cSt	3.04	2.538	1.05
Cetane number	—	55	—	8.5
Flash point	°C	50	43	16
Fire point	°C	56	45	53
Carbon residue	%	22	0.015	—
Sulfur content	%	<0.028	0.248	—
Gross calories	kJ/kg	46500	43340	29700
Cetane index	–	46	65	—

Table 4.
Properties of diesel, WPPO, and ethanol before blending and addition of EHN.

Figure 13.
The distillate samples from the waste plastic pyrolysis oil samples.

Property	Unit	CD	90/5/5	80/10/10	70/15/15	60/20/20	50/25/25	STANDARD
Density	Kg/m^3	845	838.5	834	830	825	823	ASTM D1298
Viscosity @ 40	cST	3.452	2.38	2.37	2.365	2.340	2.325	ASTM D445
Cetane number	-	45	59	62	64	65	69	ASTM D4737
GCV	kJ/kg	44840	41245	39985	38700	36800	34500	ASTM D4868
Sulfur content	%	<0.0124	0.0248	0.0249	0.0251	0.0253	0.0257	ASTM D4294
Oxygen	%	12.35	13.80	14.75	15.15	16.25	17.35	ASTM D5622
Carbon residue	%	74.85	75.35	76.40	77.55	78.25	79.65	ASTM D 7662
Flash point	°C	56.5	38.5	37.55	37.35	37.15	36.85	ASTM D93
Hydrogen	%	12.38	7.5	7.55	7.65	7.75	7.95	ASTM D7171

Table 5.
Properties of blended ratio mixtures of diesel, ethanol, WPPO with EHN.

from local outlets and blended using a homogenizer for 5 min at 3000 rpm. The properties of all samples were measured in the Chemical Engineering Laboratory of the University of Kwazulu-Natal in Durban, South Africa. **Table 3** shows some important physicochemical properties of the fuels before blending. **Table 4** shows physicochemical properties of fuels and their determined fuel properties after blending. **Figure 13** is a photograph of the sample distillates of WPPO obtained from pyrolysis. **Table 5** is showing properties of blended ratio mixtures of diesel, ethanol, WPPO with EHN.

5. Experimental results and discussion of diesel engine emissions

5.1 Brake-specific fuel consumption (BSFC)

Figure 14 is a variation in brake-specific fuel consumption (BSFC) with engine speed. The BSFC compared to the engine speed in **Figure 14** shows that as the speed increased, there is an equal increase of fuel consumed by the test engine. The values obtained at full engine speed (2000 rpm) for the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25, and CD were 0.04 kg/kWh, 0.041 g/kWh, 0.042 kg/kWh, 0.043 kg/kWh, and 0.035 kg/kWh, respectively.

At high engine speeds, the conversion of heat energy to mechanical energy increases with the increase in combustion temperature, leading to increased BSFC for the biodiesel; this increase is proportional to the difference in their heating values, which is identical to the findings of Ref. [62]. These blends of WPPO compare well to CD fuel and other biodiesel blends with comparative differences in the heating values.

However, from the graph, it is evident that as the blend ratio increases, there is a decrease in the BSFC across all the test fuels. Nevertheless, the values for all WPPO blends were slightly higher than the CD test fuel. The closeness of the values and the packed graph reveals a close resemblance and identical BSFC characteristics of WPPO, ethanol, and EHN compared to CD fuel. For example, at 500 rpm engine speed, the blend of 80/WPPO10/E10 had a value of 0.043 g/kWh compared to full engine speed (2000 rpm) with 0.041 kg/kWh, which is higher than CD test fuel with 0.04 kg/kWh at 1000-rpm engine speed and 0.035 kg/kWh at full engine speed (2000 rpm).

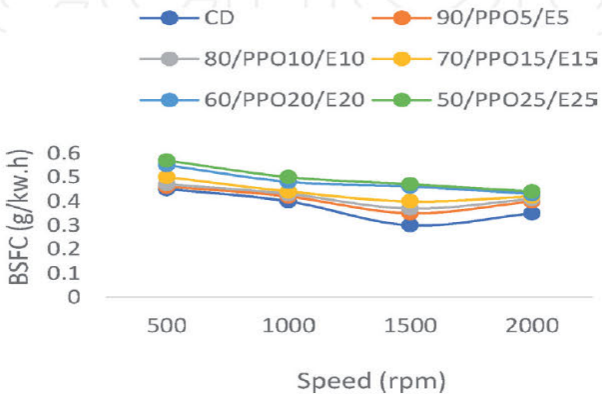

Figure 14.
BSFC versus engine speed.

5.2 Brake thermal efficiency (BTE)

The brake thermal efficiency (BTE) variations with engine speed are shown in **Figure 15**. The graphs show that as the speed increased, there was an increase in the BTE across all the test fuel blends of WPPO and CD up to 1500 rpm. At 1000 rpm engine speed, the values for blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25, and CD were 22, 21, 20, 18, 16.5, and 22.5%, respectively. As the blend ratio and engine speed increased, there was a decrease in the BTE within the WPPO blends but an increase in BTE across the blends. For example, at 500 rpm engine speed, 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 had values of 14, 13, 12.5, 11, and 9.5% compared to at 1000 rpm with values of 22, 21, 20, 18, and 16.5%, respectively.

The highest BTE value was 24% by blend 90/WPPO5/E5 at 1500-rpm engine speed compared to any other blend of WPPO, ethanol, and/or EHN. This could be due to the density, which is closer to CD, and the effect of blending, which improved this blend's physico-chemical properties. **Figure 15** shows values of 24.8, 23, 21, and 19%, respectively, for blends 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25. Blend 50/WPPO25/E25 reported the lowest values compared to the other blends. At 500 rpm engine speed, the BTE value was 9.5% compared with full engine speed (2000 rpm) at 19%.

As the engine speed increased above 1500 rpm, the BTE suddenly dropped as the engine approached full engine speed (2000 rpm), as seen in **Figure 15**. There are a number of factors explaining the above results. For example, at this speed, there is a sudden drop of the air fuel ratio as the mixture becomes richer. This leads to incomplete combustion and heat release energy as more carbon molecules escape the combustion process. These increase the dissociation heat losses by the engine, hence a fall in BTE. Additionally, decreased BTE with biodiesel blends could be due to their low calorific value, higher viscosity, high volatility, and poor spray characteristics. These findings are consistent with other studies by the authors of Refs. [63–65].

5.3 Unburnt hydrocarbon (UHC) concentration

Unburnt hydrocarbon (UHC) concentrations largely indicate the quality of the combustion in an internal combustion engine. UHC concentrations are formed from vaporized unburnt hydrocarbon fuel and partially burnt fuel by-products exiting the combustion chamber diesel exhaust system. UHC concentrations are inherently independent of the air fuel ratio of any working engine [6].

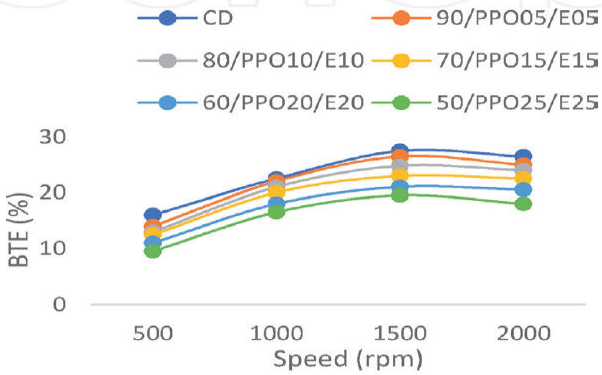

Figure 15.
Brake thermal efficiency versus engine speed.

In compression ignition (CI) engines, UHC concentrations are due to insufficient temperature, especially around the cylinder walls or in pockets. UHC concentrations are also formed through system malfunction, especially in input data failure in modern fuel injection systems. The higher hydrocarbon concentrations may be due to hydrogen radicals in the diesel-ethanol-WPPO-EHN blends. Principally, these concentrations are prevalent during light loads, when the combustion mixture is lean. This period is marked by a lower fuel ratio making the lean fuel-air mixture the primary source of the light load concentrations because of the lack of completion of the combustion during normal engine operating cycles. Hydrocarbon concentrations are not limited to vehicle exhaust systems but can occur in the entire vehicle fuel system from vapors during dispensing and distribution of fuel, which accounts for 15–20%, with the crankcase providing 20–30%. However, diesel exhaust remains the main culprit in engine emissions accounting for 50–60% of all the UHC concentration [66, 67].

Figure 16 shows the variation of UHC emission with engine speed in the stationary diesel power generator using blends of biodiesel. As the engine speed was increased, the UHC concentration increased too. However, the increase was more significant as the engine speed was in intermediate speeds of 1500 rpm moving to or approaching full engine speed (2000 rpm). For example, at 1000 rpm, the values of blends 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 were 22, 21, 20, 18, and 15 ppm, respectively, compared to full engine speed (2000 rpm) with 35, 34, 32, 29, and 26 ppm. This leads to the conclusion that at high engine speeds, the values of UHC concentration is significantly high for all the blends of WPPO, ethanol, and EHN, although still comparatively low compared to CD fuel.

The UHC concentration from the blends 90/WPPO5/E5 and 80/WPPO10/E10 had higher values although from the graph plot in **Figure 16**, the values are still low compared to the values of CD test fuel. However, the general trend reported by the graph in **Figure 16** shows that as the blend ratio increased, there was a significant reduction in the UHC concentration, observed across all the test fuels irrespective of the engine speed condition, for all the blends tested compared to CD fuel. The reduction in UHC concentration is attributed to the high oxygen content and cetane number of the blends. The high oxygen content supports combustion, while the high cetane number reduces ignition delay. This is identical to other studies by other researchers [68–72].

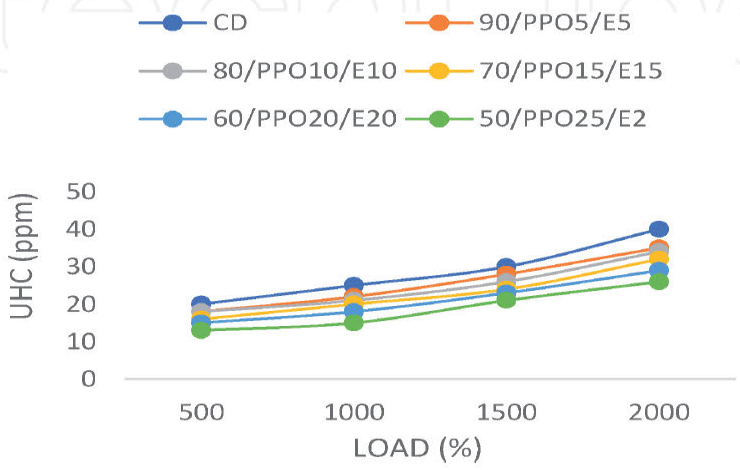

Figure 16.
Unburnt hydrocarbons versus engine speed.

The high fraction of ethanol in blends 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 contributed to the increase in the concentration of UHC, which is identical to the findings of Refs. [73, 74] who observed it in SI engine cylinder walls, crevices, and quenched cylinder walls, especially when richer air-alcohol mixtures were introduced. This type of UHC depends on the following factors: engine adjustments, engine design, and the type of fuel used in an engine. However, the engine-operating environment can sometimes contribute to the type of UHC concentration produced. This is observed especially when the temperature range is 400–600°C in the combustion chamber. At this temperature range, the hydrocarbons continue to experience reaction in the diesel exhaust pipe, thus lowering or increasing the concentration of the UHC in the exiting exhaust gas [75, 76].

5.4 Carbon monoxide (CO) formation

CO concentrations are a direct result of incomplete combustion, which results from hydrocarbons due to the failure of oxidation in the combustion process in diesel engines. This is true especially where the excess air factor λ meets the conditions $\lambda < 1$ for SI engines. Carbon monoxide is a colorless, tasteless, and odorless toxic gas, which is primarily a product of incomplete combustion of carbon containing fuels [6]. The United States is the single largest producer of carbon monoxide from anthropogenic sources as shown in **Figure 17** [77]. Carbon oxidation mechanisms are mostly determined by the equivalence ratio. Carbon monoxide concentrations mainly form in the areas of heavy traffic, parking garages, and under buildings, overheads, and overhangs. CO health effects include headaches and dizziness, but extreme exposure can lead to death.

Figure 18 is the variation of CO with engine speed in a stationary diesel power generator. The graph reveals that as the engine speed and the blend ratio increased 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25, the CO concentration decreased up to 1500 rpm of engine speed. Thereafter, the blends reported a continuous increase as the engine speed was approaching full engine speed (2000 rpm). At 500-rpm engine speed, the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 reported values of 0.055, 0.0565, 0.06, 0.0615, and 0.0625%.

However, as the speed is increased to 1500 rpm, the values were 0.035, 0.0375, 0.0445, and 0.0475%, respectively. At full engine speed (2000 rpm), all the test fuels showed increased CO concentration with blends 90/WPPO5/E5 and 80/

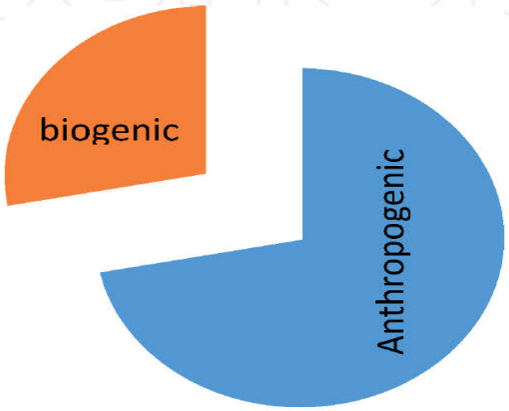

Figure 17.
Carbon monoxide (CO) concentrations by anthropogenic and biogenic sources in the United States [77].

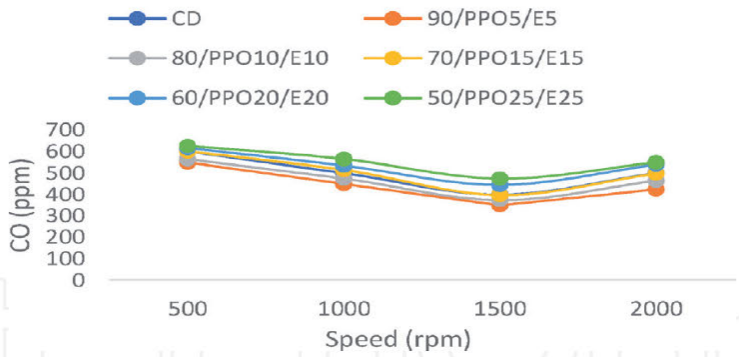

Figure 18.
Carbon monoxide versus engine speed.

WPPO10/E10 reporting the lowest concentration among the test blends across all the engine speed conditions. At 1000 rpm, the blends reported values of 0.0445 and 0.0475% compared to full engine speed (2000 rpm) with 0.0425 and 0.0465%, respectively. The increased CO concentration, although lower than diesel fuel, can be attributed to partial combustion [78] as the speed increased and the presence of ethanol, which shortened ignition delay, thus increasing CO concentration.

As the engine speed and the blend ratio increased, there was an increase in the CO emission across all the engine speeds and within the blends and CD test fuel. At 1000 rpm engine speed, the values of the blends and CD were 0.045, 0.0475, 0.0515, 0.0535, 0.0565, and 0.05% for 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, 50/WPPO25/E25, and CD, respectively. The above values obtained from **Figure 18** suggest that there was a reduction in CO concentration across all test fuels irrespective of blend ratio and type of fuel except at high engine speeds exceeding 1500 rpm to full engine speed (2000 rpm). After this point, there was a steady increase in the concentration of CO.

CO concentration is a direct result of poor oxidation of the hydrocarbon fuels in the combustion chamber but is determined by the local fuel/air equivalence ratio. The above scenario is due to the air/fuel ratio becoming richer as the speed increased, leading to insufficient mixing of oxygen and fuel molecules. Compared to CD, all the biodiesels tested showed decreased CO concentration due to the high oxygen content in the test biodiesels and the addition of EHN, which greatly increased the cetane number (CN). This is identical to the studies by the authors of Refs. [79, 80]. The initial concentrations were greater at the starting engine speed of 500 rpm due to low temperature and emission instability processes at lower engine speeds, which are identical to the studies of Ref. [81]. However, as the engine speed increased from 1500 rpm toward full engine speed (2000 rpm), there was an observed increase in CO concentration, despite the oxygen content of the biodiesel and increased CN of the blends of WPPO, ethanol, and EHN. This disagreement in experimental results is due to differences in CN for the different biodiesel test fuel blends used. The increment in CN as the blend ratio increased led to increases in fuel quantity burnt during diffusive combustion, hence increasing CO concentration as the quality of combustion decreased.

5.5 Particulate matter (PM) formation

PM is agglomerates of small particle phase compounds resulting from the combustion of partially burned lubrication oil, the ash content from the fuel, sulfates from the engine cylinder wall, lubrication oil, and water from condensation and the

combustion process [82]. These emitted compounds comprise elemental carbon (EC), organic carbon (OC) trace, and unknown compounds. Both EC and OC contribute to the toxicity of PM, regional haze, and climate change; therefore, PM concentration negatively affects the environment and human health [83]. The Global Burden of Disease Index reports that these types of emission are now responsible for 3.2 million deaths due to $PM_{2.5}$ ambient pollution [84]. Besides this, PM concentration causes deposit formation in the combustion chamber, fouling of emission control systems such as EGR and DPF and increased engine wear and premature failure.

PM concentration is primarily controlled by factors such as fuel quality (sulfur and ash content in fuel), engine lubrication oil quality, fuel consumption per combustion cycle of the engine, exhaust cooling rate, and the combustion process or strategy applied [85]. A number of PM characterization research works have been conducted categorizing PM concentration as 41% carbon, 7% unburned fuel, 25% unburned oil, 14% sulfates, water, 13% ash, and other concentrations [83]. However, an earlier study conducted by Agrawal et al. [86] reported that particulate concentration contains ≅31% elemental carbon, ≅14% sulfates and moisture, ≅7% unburnt fuel, and ≅40% unburnt lubricating oil. A study by Thiruvengadam et al. [87] yielded a similar outcome in terms of PM concentration except that the study was based on natural gas engine technology.

PM concentration is divided into three main components: SOF, soot, and inorganic fraction (IF), 50% of which is released as soot in the diesel exhaust pipe. SOF emissions are made up of condensed hydrocarbons embedded within the soot emissions in the form of very fine particles. The size distribution of PM concentration has three peaks: the nucleation peak, which includes all volatile hydrocarbons (D_p<~30 nm), the accumulation mode (~30 nm< D_p<~500 nm), and the coarse mode (~500 nm<D_p<~10 μm) [88]. These emissions are more pronounced during starting and engine idling when engine temperatures are reportedly very low [89].

Studies on OC/EC in PM samples show that their ratio is elevated in biodiesel combustion as the biodiesel blend ratio increases. This is mainly due to the high oxygen content in biodiesel and plays a major role in the generation of soot particles and final oxidation. For example, in a study by Chuepeng et al. [90], the authors reported that the OC fraction for B30 was greater than ULSD regardless of the engine speed and operating conditions. In another study by Williams et al. [91], a similar pattern was established for OC and EC as B100 > B20 > Diesel. This is identical to the studies of Ref. [90], which suggested an increased OC content with increased biodiesel fraction in a blend.

Cheung et al. [92] used soy methyl esters in an LD engine and found that the EC fraction was lower than during diesel operation. Nevertheless, the OC fraction in the PM concentration sample became identical for both LD and HD engines with the New European Driving Cycle (NEDC). However, a study by Song et al. [10] differs with this finding. Using cottonseed biodiesel, the authors reported decreased OC and EC driving conditions. This was mainly due to engine operating conditions, test methods, and test fuel chemical properties [83]. However, these studies have been inconsistent and inconclusive in the literature surveyed. For example, this is revealed in the studies of Refs. [90, 92–96].

DPF filters have now become part of virtually all diesel vehicles in the leading industrialized countries in the world (Europe, the United States, and Japan). DPF filters have had a high market penetration in Japanese and American LD and HD trucks since 2007. For smaller vehicle applications, subsequent developments have incorporated the diesel oxidation catalyst (DOC) function into the filter as reported by the authors of Refs. [10, 97]. It should be noted that for PM emission control in medium engines, the methods and approaches used are similar to the LD engines. However, in the US market, auxiliary fuel injectors and burners are incorporated into the

diesel exhaust to regenerate DPFs. This method has concerns over oil dilution in the crankcase and requires a separation with the engine management system demands, so it has become more complex in the manner of its development and use [98, 99].

Advances in the science of materials have greatly increased and therefore influenced the development in filter materials for LD and HD engines. LD vehicles have seen silicon carbide types of filters becoming standard installation, although the alternative use of aluminum titanate is gradually replacing it [97]. However, aided by better engine controls, the industry has now moved to cordierite filters [101, 102]. **Figure 19** shows new hybrid developments in DPF filtering technology, which reduces 95% of NO_X that comes from the DPF filter.

As shown in **Figure 20**, speed affects particle emission of blends. Nevertheless, differences in engine operating conditions, particulate formation, in-cylinder combustion processes, and engine type give mixed results and conclusions in PM emission studies. In **Figure 20**, it is evident that as speed increases, combustion time (residence time) is reduced, which reduces the reoxidation and combustion of the constituents of the process. This aptly explains the reason behind increased PM particle size and concentration as the speed tends toward full engine speed (2000 rpm), as typified in the graph in **Figure 20**. For example, PM concentration at 500 rpm is 0.15, 0.11, 0.094, 0.086, 0.063, and 0.051 kg/kWh, respectively, for CD, 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25.

However, as the speed increases from 500 to 1500 rpm, which is an intermediate speed, the PM emission increases and almost doubles to 0.29, 0.25, 0.235, 0.213, 0.183, and 0.57 g/kWh. These are for CD, 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25, respectively. These findings are identical to the studies of Refs. [103, 104]. In other words, these blends, when combusting, produce low heat loss to the wall resulting in increased soot oxidation, which is also reported conclusively in a study by Di Iorio et al. [105] and is identical to the findings of this work in **Figure 20**.

Since PM concentrations are influenced by engine operating conditions at 1500–2000 rpm, PM concentration decreases with increased blend fraction. The reduction is more with higher blend ratios 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 at 2000 rpm. However, there is a reversed reduction in CD fuel compared to the blends of WPPO as shown in **Figure 20**. This is due to diffusive combustion as the blend ratio increases (tends to B100) and the oxygen content of the blends increases. These findings are identical to the findings of a study by Di Iorio et al. [105].

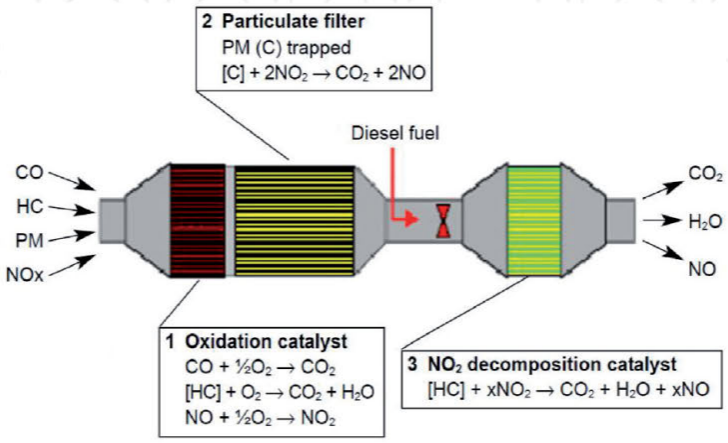

Figure 19.
A new NO_2 remediation system reduces 95% of the NO_2 emissions from catalyzed filter systems (courtesy of Technical University Dresden and Johnson Matthey) [100].

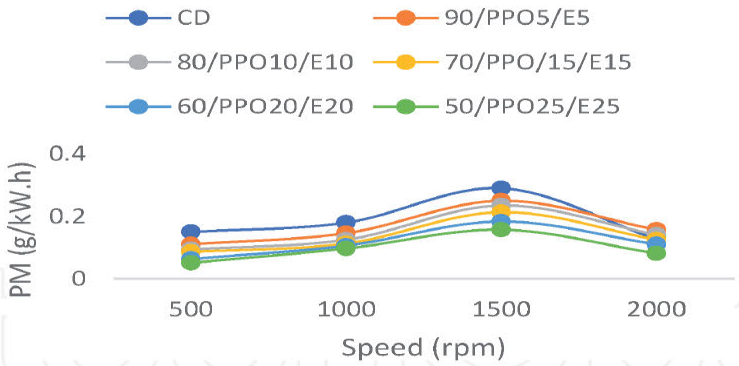

Figure 20.
PM emission for different blends of WPPO biodiesel fuel from 500 rpm to full engine speed (2000 rpm).

5.6 Carbon dioxide (CO_2) concentration

CO_2 is one of the gases responsible for maintaining the earth's optimal ecosystem balance. It enriches plants through the photosynthesis process and provides other benefits for the environment. However, CO_2 has become a topical global issue in recent decades due to its increase from levels of 0.04% in the atmosphere. The increase in CO_2 causes an increase in global temperatures due to the effect of blanketing. There are generally two sources of CO_2 formation: human activities and naturally occurring sources such as the ocean-atmosphere exchange, plant and animal respiration, soil respiration, decomposition of waste and elements, and volcanic eruptions. The majority of the human sources are due to the burning of hydrocarbon fuels in transport and power generation, land activities such as mining and agriculture, and industrial processes and manufacturing. The main gas produced from human activity is greenhouse gas associated with activities such as combustion of fossil fuels, namely, coal, natural gas, and oil for commercial and transportation services [106].

Figure 21 shows the variation of CO_2 with engine speed. The graph shows that as the blend ratio and engine speed increased, CO_2 concentration increased, but compared to CD, their emission levels were still lower and almost identical. At 500 rpm engine speed, the values of CD and the blends of 90/WPPO5/E5, 80/WPPO10/E10, 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25 were 3.58, 3.35, 2.95, 2.6, 2.55, and 2.25%, respectively.

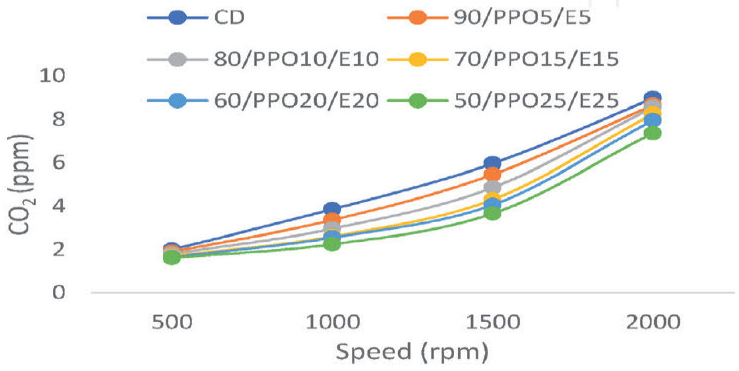

Figure 21.
CO_2 versus engine speed.

Figure 21 also shows that as the speed increased, there was a significant increase in the CO_2 concentration across all test fuels, although with lower values as the blend ratio increased. For example, CD fuel had values of 2, 3.85, 5.95, and 8.95% for engine speeds of 500, 1000, 1500, and 2000 rpm compared to blend 80/WPPO10/E10 with 1.8, 2.95, 4.85, and 8.55% for similar speeds. The blend with the lowest value of CO_2 emission was 50/WPPO25/E25 with values of 1.62, 2.25, 3.65, and 7.35%, respectively, for engine speeds of 500, 1000, 1500, and 2000 rpm, respectively. The increased carbon concentration in biodiesel blends is due to the reduction in the quantity of carbon relative to the increased oxygen ratio. However, the lower CO_2 concentration levels in comparison to CD fuel are due to factors explained under BTE and the equal energy balance generated by the addition of alcohol.

5.7 Nitrogen oxide (NO_X) concentration

NO_X concentration and its oxidized product NO_2 are the primary preserve of the diesel engine, constituting 85–95% of the total emission of a diesel engine. There are two fundamental differences between the two gases: whereas NO_X is odorless and colorless, NO_2 is reddish with a pungent smell [107]. It should be mentioned here that NO_2 is five times more toxic than NO_X gas and is a health hazard to the human respiratory system. It irritates the respiratory system and lowers the resistance to diseases such as the common cold and influenza [9, 108].

SCR is one of the leading NO_X emission control techniques for both LD and HD vehicles. This system entered the market in Japan and Europe for the HD category in 2005 compared to the US market in 2010. In the Japanese market and in Europe, zeolite and vanadium-based catalysts are utilized, respectively. The zeolite SCR catalyst combination performs better and has higher temperature tolerance levels. There is ongoing research to improve low temperature performance for more accurate NO_2 and NO_X concentration predictions [110–112].

The low NO_X trap (LNT) is a cheaper option for engines that are 2000–2500 cc [113, 114]. This type of emission control technique works better with mixed-mode engines to reduce low-load NO_X that is a persistent problem in SCR systems. This allows the LNT to focus on high temperature NO_X that is entering at temperatures over 300°C, thus eliminating between 60 and 70% of the platinum group metals (PGMs) [115]. This makes the LNT technology cheaper and economically appealing to the LD engine classification of 5000–6000 cc capacity [116, 117]. However, for medium- and heavy-duty vehicles, high temperature solutions have been developed to address the challenge of high load requirements of the US NTE regulatory condition as reported by the authors of Refs. [101, 118].

The LNT technique suffers due to contamination from sulfur, which shortens and affects its service life and durability. Earlier versions of LNT lost 50% filtration capacity, while the current generation of LNTs loses only 25% [119, 120]. Desulfication can be accomplished by passing a rich hot steam of diesel fuel at 700°C for 10 min at service intervals of 5000–10,000 km. **Figure 22** shows a new concept of combining the SCR emission control system with the LNT emission control system.

NO_X concentration is now known to be temperature dependent due to their equilibrium concentration presence in the combustion chamber. NO_X when mixed in high temperature adiabatically in the temperature range of 2000–3000 k forms NO_X concentration, which is then exited through the diesel exhaust system [121]. The NO_X concentration has four basic mechanisms of formation within the combustion chamber of a diesel engine: the Zeldovich mechanism also called the thermal NO_X route, the prompt mechanism, the fuel mechanism, and the NNH mechanism [122]. The variation of engine speed with NO_X concentration is shown in **Figure 23**. The graph shows that as the engine speed was increased, there was an increase in the

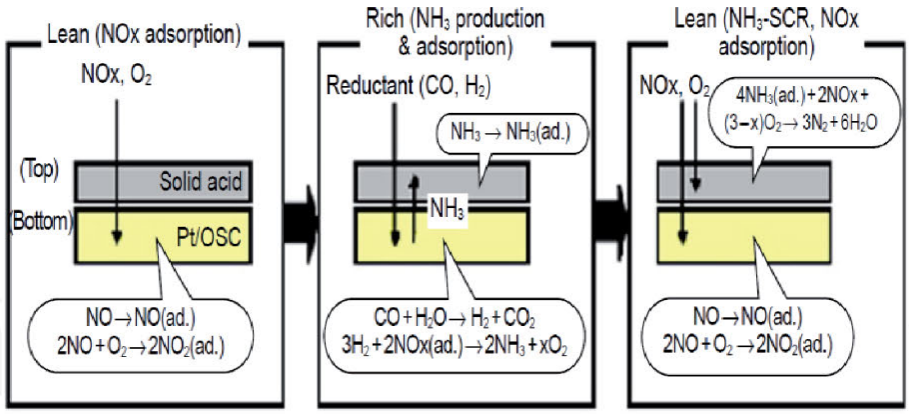

Figure 22.
The concept of employing a NO_X absorber with a double SCR layer configuration [109].

NO_X concentration irrespective of fuel, blend ratio, or additive. However, the value of NO_X concentration from the blends 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 reported lower values than CD fuel. For example, at 1000 rpm, the value of the blends was 385, 396, and 415 ppm, compared to CD fuel at 425 ppm.

Blends 60/WPPO20/E20 and 50/WPPO25/E25 had the highest NO_X concentration compared to the other blends of 90/WPPO5/E5, 80/WPPO10/E10, and 70/WPPO15/E15 across all the engine speed conditions tested. At 500 rpm engine speed, the two blends had values of 205 and 200 ppm, respectively. At full engine speed (2000 rpm), NO_X concentration values increased to 925 and 885 ppm compared to blend 90/WPPO5/E5 at 197 ppm and 792 ppm at full engine speed (2000 rpm). The graph in **Figure 23** shows that as the blend ratio increased, there was a direct increase in the concentration of NO_X across all the blended test fuels. However, blend 90/WPPO5/E5 reported the lowest values of NO_X concentration compared to all the other blends. The formation of NO_X in biodiesel combustion depends on the combustion temperatures and combustion zone oxygen concentration. With high blend ratios of 70/WPPO15/E15, 60/WPPO20/E20, and 50/WPPO25/E25, the combustion process is shortened, thus leading to failure to provide enough cooling effect to decrease peak combustion temperatures leading to increased NO_X.

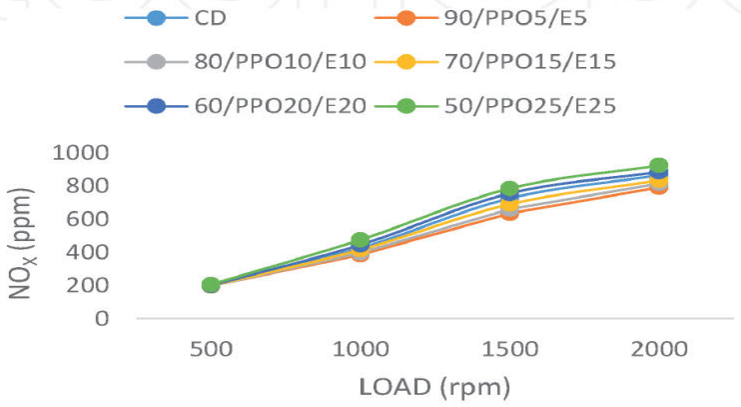

Figure 23.
Oxides of nitrogen versus engine speed.

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These findings seem to show that there is a correlation between the alcohol content in the fuel and peak flame temperatures, content of nitrogen, and oxygen availability [123]. Increased NO_X concentration is attributed to the presence of nitrogen from the cetane number improver ENH and other contaminants from the WPPO composition. Additionally, it could be due to the generation of radicals of hydrocarbon through molecular unsaturation being identical to the findings of Refs. [124, 125]. However, the NO_X levels are still low, attributed to high CNs of the tested biodiesels in **Table 3** and increased oxygen content due to the blend ratios. These findings are identical to the findings of Ref. [126].

6. Conclusion

- This study thus makes a strong case for alternative fuels to replace petroleum-based fossil fuels like diesel commonly used as the primary propulsion fuel in transport and power generation. This work looks at the concept of waste to energy and waste resource utilization in an era when environmental concerns and awareness are at the pick of development agenda across the globe.

- Lower blend ratios 90/WPPO5/E5 and 80/WPPO10/E10 exhibit identical brake-specific fuel consumption (BSFC) of conventional diesel test fuel compared to the other blends. These blends show the lowest BSFC values compared to the others.

- The brake thermal efficiency of blend 90/WPPO5/E5 (90% conventional diesel, waste plastic pyrolysis oil 5%, an ethanol 5% by volume) showed values, which were very close to the values of conventional diesel fuel values. This was attributed to close density values and the gross calorific values of waste plastic pyrolysis oil (WPPO) blends, which showed marginal differences. This case was apparent especially at lower blend ratios of all the mixtures and blends tested.

- There was a reduction in unburnt hydrocarbon (UHC) concentration with the use of WPPO blends, ethanol, and 2-ethyl hexyl nitrate (EHN), with a notable reduction in oxides of nitrogen concentration especially for the blend 90/WPPO5/E (90% conventional diesel, waste plastic pyrolysis oil 5%, and ethanol 5% by volume). This was a clear indication that this blend performed well when compared with petroleum conventional diesel.

- Although there was indicated increase in the concentration of CO, CO_2 NO_X and UHC, for all the blends of WPPO, ethanol and EHN. There was a clear indication that the emission levels were notably lower than the emission levels of conventional petroleum diesel, based on the ASTM measurements used in this study. However, when comparisons for overall values of concentration are compared to concentration standards, the WPPO blend performed well.

- The blends of WPPO, ethanol, and EHN have identical temperature characteristics to those of the conventional diesel test fuel especially as the engine speeds hit 75% heading to full engine speed. This was attributed to the presence of ethanol responsible for decreased ignition delay. The presence of high oxygen enrichment was a factor of decreased CO concentration for the tested biodiesels compared with conventional diesel fuel, although there was an increase in CO concentration as fuel CN and blend ratio increased. This is due to deterioration of the combustion characteristics, as the cetane numbers (CNs) and the

alcohol blend ratio increase. Nevertheless, this work proposes further study and further investigation on biodiesels with extremely high CN to meet the need for fuel improvers and additives.

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CHAPTER 8: ASSESSING THE EFFECTS OF ENGINE LOAD ON COMPRESSION IGNITION ENGINES USING BIODIESEL BLENDS

Journal article

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Assessing the Effects of Engine load on Compression Ignition Engines Using Biodiesel Blends

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Abstract

This study evaluated the performance of a diesel engine operated with waste plastic biodiesel fuel blends. From the experimental data and the results obtained, at all engine loads from idling to full load the emissions of carbon monoxide (CO), unburnt hydrocarbon (UHC) and carbon dioxide (CO_2) were low compared to conventional diesel (PD). However, the emissions of NO_X were high compared to PD. The brake specific fuel consumption (BSFC) for the blends dropped while the brake thermal efficiency (BTE) increased with load for all blends until intermediate load when it decreased. WPPO blends have a higher viscosity compared to PD fuel. Compared to PD fuel, CO emissions for blend 95/WPPO5 at all engine speed idling mode were 285 ppm, 298 ppm, 320 ppm, and 388 ppm while PD emissions were 270 ppm, 295 ppm, 315 ppm and 365 ppm respectively. The values for UHC for blend 95/WPPO5 at all engine speed idling modes were 35 ppm, 28 ppm, 22 ppm, and 18 ppm compared to PD fuel with 20 ppm, 25 ppm, 30 ppm, and 40 ppm respectively. The NOx emissions for PD fuel at all engine speed idling modes were 175 ppm, 225 ppm, 300 ppm and 375 ppm compared to blend 95/WPPO5 at 195 ppm, 245 ppm, 335 ppm, and 397 ppm. The BSFC values for blend 95/WPPO5 at all engine idling speed modes were 0.48 g/kW.h, 0.41 g/kW.h, 0.35 g/kW.h and 0.4 g/kW.h compared to PD at 0.45 g/kW.h, 0.39 g/kW.h, 0.33 g/kW.h and 035 g/kW.h respectively.

Keywords: Engine loads, Emissions, Higher viscosity, Spray characteristics

1. INTRODUCTION

The search for alternative and renewable energy has remained a persuasive concern in the last two decades with the aim of replacing depleting fossil oil. Fossil fuels have a detrimental environmental impact [1] when released to the atmosphere due to the combustion activities of fossil fuels. It is being projected that if no measures are put in place by 2030 the use of fossil fuel will raise emission levels by 39 % [2]. Besides environmental concerns, fossil fuels have erratic demand and supply which increases international market prices and other commodities hence aiding in inflation [3]. Figure 1 shows measures taken to combat environmental pollution from the transportation industry in the European Union by way of taxes.

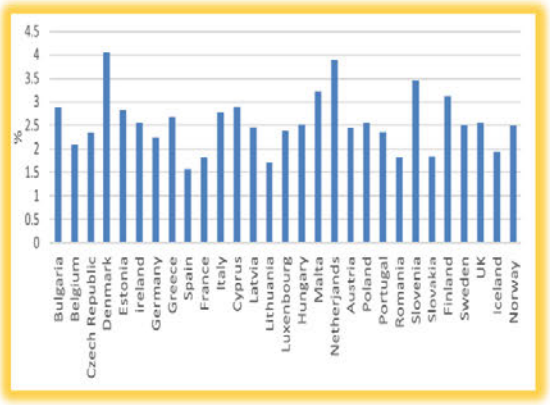

Fig. 1. Environmental taxes as % of GDP and as % of total taxes and social contributions [4]

Development of alternative fuel energy began in the 1900s when German engineer Rudolf Diesel invented the diesel engine using vegetable oil as fuel [5]. However, due to availability of petroleum at the time focus moved into fossil fuel to the disadvantage of bio-oil. Currently, many researchers such as [6-11] have focused on development of alternative fuel to petro-diesel. Most of this research is heavily biodiesel based as one of the solutions to replace fossil fuels while creating renewable and green fuels. Fossil fuels are non-renewable, hence depleting rapidly, which is a major reason for large-scale research to find alternative and renewable fuels. Alternative fuels must prove to be feasible, environmentally friendly and sustainable while meeting a large energy demand [12].

Biodiesel oil is known to contain physicochemical characteristics of functional petro-diesel fuel properties [13, 14]. Research has shown that biodiesel fuels have many advantages over petro-diesel fuels. For example, biodiesels are biodegradable, non-flammable, renewable, non-explosive, non-toxic and environmentally friendly [15, 16]. These qualities show biodiesel fuels as the best option to substitute fossil fuels. Biodiesel fuels have a variety of feedstocks such as used vegetable oil, waste plastics, waste biomass, animal fats (tallow) and currently microalgae all which can be processed into biodiesel [17]. These researches have a common finding that biodiesel has the ability to be utilized as a fuel with or

without engine modification which gives it high technical advantage [18, 19].

In order to determine the efficacy of biodiesel main line researchers in biodiesel fuels have evaluated engine performance using different feedstocks and different biodiesel blends [20-23]. However, few have been able to investigate the influence of load using plastic waste oil blends of biodiesel [24-26]. All these researchers have concentrated on performance and emission characteristics with little attention to low load and intermediate load compared to engine full load [12, 27, 28]. For example, all low load and intermediate engine idling speeds considered as high idling increases emission from trucks and vehicles in the transport industry.

High idling or low engine loads have been shown to increase NOx emissions on roads compared to high speed road driving by a factor of 1.5 [29, 30]. In other words, increasing low load increases NOX emissions [31-33]. During idling, which is low load, the fuel consumption, engine wear and maintenance increase. The average fuel consumption for example in trucks at idle is 0.8 g/hr to 1.5 g/hr based on the size of the engine, ambient temperature and the load of other systems such as HVAC and the vehicle's other electrical loads [34].

Driving cycle emissions of UHC are 1 to 5 times more than idling. During low, load other emissions such as CO rise to 295 g/hr [35-37]. The carbon emissions during the driving cycles are estimated at 45 % to 75 %, while UHC emissions during idling and low load can hit 86.4 g/hr [34, 38]. Most diesel engines typically spend a substantial amount of time in idling mode, either on traffic stops, checkpoints or in exchange periods in fuel stations. The idle time spent varies considerably with many varied reasons to maintain engines at idle. For long haulage trucks for example the common reason is climate control, loading and offloading transport cargo or service and maintenance [39, 40]. The other reason why trucks idle for a long time is use of the engines to heat and air condition cabs and to power amenities in the cab while on the road [41, 42].

The use of biodiesel and biodiesel blends affect diesel engine performance characteristics. Poor quality biodiesel fuel results in deposits and clogging [43, 44]. Besides these problems use of biodiesel results in corrosion, excessive engine wear and premature engine failure [45]. Biodiesel also causes deposits in the injector pump, which interferes with the spray pattern, an essential factor in mixing fuel during the combustion process, hence poor engine performance [46]. Other demerits, which are associated with biodiesel fuel use, include dilution of lubrication oil leading to high engine oil levels, followed by loss of engine oil pressure and increased engine-bearing wear. Thus, it is clear that the quality and testing of biodiesel is an important factor in ensuring proper rating, acceptance and durability of diesel engines.

The objective of this work was to use waste plastic pyrolysis oil (WPPO) to determine the effects of idling speed load-using blends of WPPO on a diesel engine. The second objective was to study the effect of BSFC of WPPO at low and intermediate engine conditions, also known as high idling conditions. The third objective was to find the effect of engine load at high idling on engine performance and emission characteristics using WPPO as an alternative fuel.

2. METHODOLOGY AND MATERIALS

2.1 Crude WPPO Oil Properties

In this study, WPPO is selected because of the recovery of waste into energy to reduce the environmental impact of waste plastic resources. The second factor that informed the use of waste plastic is sustainability as waste plastic is readily available in plentiful supply in municipal solid waste management sites. The plastics were collected from various holding facilities within the Durban metropolitan centre with a variety of composition of plastics.

The pyrolysis oil was obtained from the pyrolysis unit designed by the Green Energy Solutions Group laboratory in the Department of Mechanical Engineering, University of KwaZulu-Natal. The author in his previous work covered the design of the unit and its performance analysis published in the proceedings of the DUE 2019 conference in Cape Town [47]. The WPPO testing and measurements were conducted at InterTek, a private Laboratory in Durban, and the results are shown in Table 1.

Table. 1. Properties of diesel, WPPO and before processing into biodiesel

Properties	Unit	PD	WPPO
Density @ 20 °C	Kg/m^3	845	825
K. Viscosity @ 40 °C	mm^2/s	3.04	2.538
Cetane number	-	55	-
Flash point	°C	50	43
Fire point	°C	56	45
Carbon residue	%	22	0.015
Sulfur	%	< 0.028	0.248
Gross calories	MJ/kg	46.50	43.32

2.2 WPPO Biodiesel Processing

A two-step process was used to process the WPPO as its acid value is higher compared to petroleum diesel. Therefore, an acid catalysed process was used with the molar ratio maintained at 12:1 (50%v.v), 1 % of H_2SO_4 was added to the preheated oil at 70 °C for 3.5 hrs with a stirring speed of 400 rpm in a reactor of 5 litres.

Thereafter the products were put into a separating funnel and the excess alcohol, sulphuric acid and other impurities in the upper layer were drained.

To remove methanol and water from the esterified oil a rotary evaporator was employed at 100 °Cunder vacuum for 1 h 20 m.

To complete the process reaction an alkaline catalysed process was employed by reacting the esterified oil with methanol at 6:1 molar ratio and 1 % potassium hydroxide (KOH) at 80 °C for 2 h and a stirring speed of 400 rpm.

The final step to obtain a refined biodiesel oil was to leave the produced biodiesel in a separation funnel overnight, for the

reaction to end. This process needs 12 h to settle and finish reacting before the lower layer of impurities can be discarded.

2.3 WPPO Fatty Acid Composition

The double bond fatty acid (unsaturated), and the single bond fatty acid, (saturated), was tested using the FT-IR and confirmed by the GC-MS method. Table 2 shows the GC-MS operating conditions while Table 3 shows the FT-IR indicated compounds of pyrolysis biodiesel oil and their class compounds.

The biodiesel obtained was composed of more than 20 compounds of mixed proportion whose composition and GC-MS percentage areas spectrum are in Table 4. Table 5 is a list of the test equipment utilized in the experiment.

Table. 2. Showing GC-MS operating conditions during the experiment

Property	Specification
Carrier gas	Helium @ 23.8 psi
Linear velocity	44 cm/s @ 100 ℃
Flow rate	Air = 450 ml/min
	H2 = 40 ml/min
	He = 20 ml/min
Injector	Split injector, 50:1 ratio, 0.3 µL injection volume
Temperature ramp 1	100 ℃hold for 0 min
Temperature ramp 2	10 ℃/min to 250 ℃5 min hold
Detector temperature	250 ℃
Column head pressure	23.8

Table. 3. FT-IR WPPO indicated compounds of pyrolysis biodiesel oil (formulate table)

Frequency range (cm^{-1})	Group	Class compound
3750-3250	O-H stretching	Polymeric O-H, HO_2 impurities
3150-2950	C-H stretching	Alkanes
1950-1830	C=O stretching	Ketones, aldehydes, carboxylic acid
1830-1725	C≡C stretching	Alkenes
1725-1575	-NO_2 stretching	Nitrogenous compounds
1575-1475	C-H bending	Alkanes
1475-1375	C-O stretching	Primary/secondary alcohols
1325-1200	O-H bending	Esters, ethers, phenols
1175-1150	C-H bending	alkanes
1000-950	C≡C stretching	Alkynes
900-875	-	Aromatic compounds

Table. 4. Elemental fatty acid composition of WPPO

Composition	Chemical name	Percentage
C10	Aliphatic compounds	65
C10-C13	Doxosane	2.4
C13-C16	Isoparaffin	7.5
C16-C20	1-hexadecene	3.1
C20-C23	Eicosane	7.6
C23-C30	Docosane	15.4
C		81.5
H		11.3
O		7.2

Table 5. List of Equipment used in the experiment

Property	Equipment	Standard
Kinematic viscosity	SVM 4000 (Anton Paar, UK)	ASTM D445
Flash point	NPM 550 (Norma lab, France)	ASTM D93
Oxidation stability	900 Rancimat (Metrohm, Switzerland)	ASTM D14112
CP/PP	NTE 500 (Norma lab, France)	ASTM D2500
Carbon residue	NMC 440 (Norma lab, France)	ASTM D4530
Total sulfur	5000 MULTI-EA (AJ Germany)	ASTM D5433
Calorific value	C 2500 basic calorimeter(IKA, UK)	ASTM D240
Density	SVM 3500 (Anton Paar, UK)	ASTM D1298

Taking into account percentage areas of the spectrum, the highest pick areas of the total chromatography were the following: heptadecane, n-octadecane, n-hexadecane, nonadecane, pentadecane, eicosane, tetradecane and tridecane. Equation 1 shows the effect of linear velocity of the carrier gas in retention time which was used to determine the carrier gas linear velocity.

$$tr=(K+1)\mu\frac{(K+1)}{\mu} \qquad \text{Equation 1}$$

Where

t_r is the retention time

L is the column height

K is the retention factor (constant)

µ is the carrier gas linear velocity

The components present in the mixed waste plastics pyrolysis fuel ranged from carbon number C_{10} to C_{40}. A large percentage of these components were made of aliphatic compounds as shown by the results of the GC-MS spectrum analysis shown in Table 4.

2.4 WPPO Properties Analysis

In order to determine the physicochemical properties of the WPPO biodiesel, the characterization was based on the requirements and standards of ASTM D6751. Under this section, the following numbers were calculated using the fatty acid composition and empirical equations [48, 49]. These include the saponification number, the cetane number and the iodine number. The saponification value is as in Equation 2:

$$SN = \sum \frac{560 \times A_i}{MW_i} \quad \text{Equation 2}$$

The iodine value is as according to Equation 3:

$$IV = \sum \frac{254 \times D \times A_i}{MW_i} \quad \text{Equation 3}$$

The cetane index number is calculated based on Equation 4:

$$CN = 46.3 + \frac{5458}{SN} - (0.22 \times IV) \quad \text{Equation 4}$$

Where

A_i is the weight percentage of each fatty acid component

D is the number of double bonds in each fatty acid

MW_i is the molecular weight

To ensure proper mixing, blending and homogenization of the various ratios during the experiment, mixing equipment was used at speeds of 1800 rpm to 2000 rpm.

2.5 Engine Testing and Performance Analysis

The engine test was conducted on a four-cylinder Iveco diesel dual fuel engine. To help in the analysis of the engine, pressure sensors and crankshaft position sensors and encoders were used. The aim of these sensors was to provide the in-cylinder pressure in relation to the crankshaft position variation. LabVIEW software was used to obtain the combustion data and sketch the graphs.

The engine was coupled to a mechanical dynamometer with idling positions set at 500 rpm, 1000 rpm, as Mode 1, and Mode 2 1500 rpm and full load at 2000 rpm. Figure 2 shows the schematic of the test engine while Table 6 shows the engine specifications.

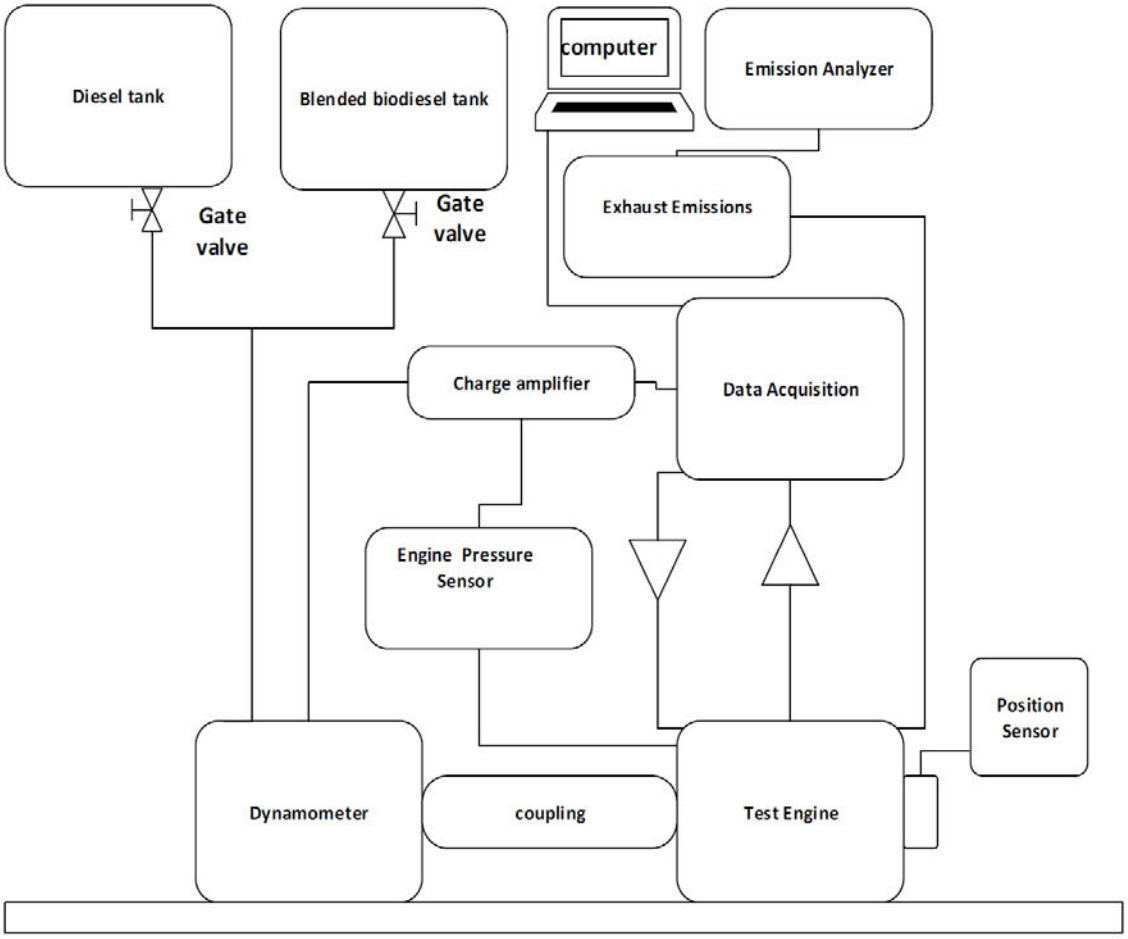

Fig. 2. Schematic diagram of the engine testing and equipment

Table 6. Experimental engine specifications

Parameters	Position value
Ignition type	4 (Stroke)DICI
Number of cylinders	4 in-line
Cooling medium	Water
Manufacturer	Iveco
Revolutions per minute	2000
Brake power	43.40 kW@2000
Cylinder bore	104 mm
Piston stroke	115 mm
Compression ratio	17:1
Connecting-rod length	234
Engine capacity	2500cc
Dynamometer make	234
Injection timing	12° bTDC
Maximum torque	206.9 Nm @1500
Injection pressure	250-272 Bar

3. RESULTS AND DISCUSSION

Table 7. Test fuel biodiesel properties, units of measurement, testing standard methods and the values for PD compared to WPPO

Property	Unit	PD	WPPO	STANDARD
Appearance	-	Clear/brown	Clear/amber	Visual
Density @ 20 °C	kg/m^3	838.8	788.9	ASTM D1298
Kinematic Visc @ 40 ° C	mm^2/s	2.32	2.17	ASTM D445
Flash point	° C	56.0	20.0	ASTM D93
Cetane index	-	46	65[a]	ASTM D4737
Hydrogen	%	12.38	11.77	ASTM D7171
Cu corrosion	3hrs @ 100 ° C	-	1B	ASTM D130
Carbon	%	74.99	79.60	ASTM D7662
Oxygen	%	12.45	7.83	ASTM D5622
Sulphur content	%	< 0.0124	0.15	ASTM D4294
IBP temperature	° C	160	119	ASTM D86
FBP temperature	° C	353.5	353.5	ASTM D86
Recovery	%		98	-
Residue and loss	%		2.0	-
Gross calorific value	MJ/kg	44.84	42.15[b]	ASTM D4868

a and b are calculated values

Blends 70/WPPO30 and 60/WPPO40 had the highest NO_X emissions compared to the other blends of 95/WPPO5, 90/WPPO10, and 80/WPPO20 across all the engine load conditions tested. At 500 rpm idling (Mode 1), the two blends (70/WPPO30, 60/WPPO40) had values of 235 ppm and 255 ppm respectively. However, at full speed (2000 rpm, Mode 2) the NO_X emissions for the two blends increased to 490 ppm and 525 ppm respectively compared to blends 95/WPPO5 for the same idling load (500 rpm, Mode 1) at 175 ppm and at full load (2000 rpm, Mode 2) at 345 ppm.

As the blend ratio in Fig. 5 increased, there was a direct increase in emissions of NO_X across all the blended fuels. However, blend 95/WPPO5 and 90/WPPO10 reported the lowest values of 175 ppm and 195 ppm of NO_X emissions compared to all the other blends tested. The formation of NO_X in biodiesel fuel combustion strongly depends on the combustion temperatures and the oxygen concentration in the combustion zone. The high blend ratios of 80/WPPO20, 70/WPPO30, and 60/WPPO40 showed a shortened combustion process hence a poor cooling effect and failure to decrease peak combustion temperatures leading to increased NO_X. WPPO blends emitted higher NOx due the higher cetane index compared to biodiesel. High cetane index number fuels have a shorter ignition delay which means longer residence time at elevated chamber temperatures, hence higher NO_X compared to PD.

The increased NO_X emissions could be a result of the presence of increased cetane index [52, 53] and other contaminants from the WPPO biodiesel impurities. Additionally, it could be due to the generation of radicals of hydrocarbon through molecular unsaturation in the blends being identical to the findings of [54, 55]. The final factor could be the increased chamber temperature, which improves combustion but increases NOx emissions, linked to the high oxygen content and the air fuel ratio [49].

3.4 Brake Thermal Efficiency (BTE)

The BTE variations with engine load were as shown in Fig. 6. The graphs show that, as the load increased there was an increase in the BTE across all the test fuel blends of WPPO and PD. The results of this experiment show that the BTE increased as the load increased, explained by the reduction in the heat loss as the engine power (more fuel) increased with load. At Mode 1 (1000 rpm, 50 % engine load) the values for blends 95/WPPO5, 90/WPPO10, 80/WPPO20, 70/WPPO30, 60/WPPO40 and PD were 22 %, 21 %, 20 %, 18 %, 16.5 % and 22.5 % respectively. As the blend ratio and engine idling load increased, there was an increase in BTE across the blends of WPPO but a decrease in the BTE within the blends. For example, at Mode 1 (500 rpm, 25 % engine load), 95/WPPO5 had values of 14 %, 22 %, 26.5 % and 25.7 % compared to 80/WPPO20 with 12.5 %, 20 %, 22.5 % and 23 % respectively.

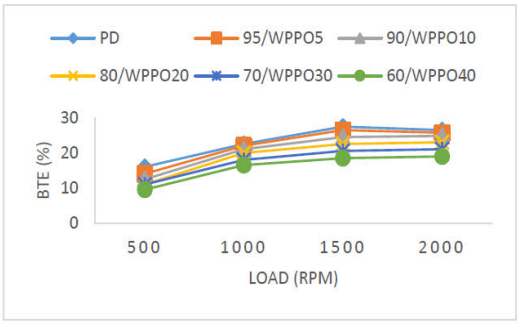

Fig. 6. Brake thermal efficiency versus load

The highest BTE value was 24. 5 % by blend 95/WPPO5 at 1500 rpm (Mode 2, 25 % engine load) compared to any other blend of WPPO. Fig. 6 shows values of 24.8 %, 23 %, 21 % and 19 % for full speed (2000 rpm, Mode 2) respectively for blends 90/WPPO10, 80/WPPO20, 70/WPPO30, and 60/WPPO40. However, blend 60/WPPO40/E25 reported the lowest values compared to the other blends. At 500 rpm (Mode 1, 25 % engine load), the BTE value was 9.5 % compared to 19 % at full load (2000 rpm, Mode 2), these two being the lowest values of BTE as shown in Fig. 6 for all the blends tested.

3.5 Brake Specific Fuel Consumption (BSFC)

Fig. 7 is a variation of BSFC with engine load. The BSFC compared to the engine load in Fig. 7 shows that, as the load increased there was an equal increase in the fuel consumed by the test engine. The values obtained at full engine load for the blends of 95/WPPO5, 90/WPPO10, and 80/WPPO20, 70/WPPO30, 60/WPPO40 and PD were 0.04g/kW.h, 0.041g/kW.h, 0.042 g/kW.h, 0.043 g/kW.h and 0.035g/kW.h respectively.

At high engine loads the conversion of heat energy to mechanical energy increases with increase in combustion temperature, leading to increased BSFC for the biodiesel. This increase was proportional to the difference in their heating values, which is identical to the findings of [56]. Additionally, the WPPO blends had high densities, therefore suffered high mass injection pressure, hence the increase in BSFC which is identical to studies by [57, 58]. WPPO blends compare well to conventional diesel fuel and sometimes other biodiesel blends with comparative differences in the heating values.

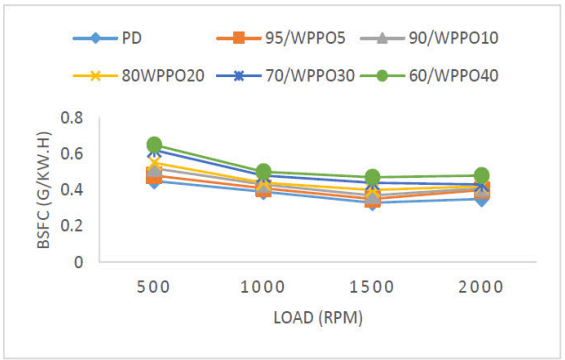

Fig.7. Brake specific fuel consumption versus load

3.1 Carbon Monoxide (CO)

Fig. 3 is a variation of CO with two engine load modes (Mode 1, and Mode 2) with a speed range of 500 rpm to 2000 rpm. The graph reveals that as the engine load and the blend ratio increased CO emissions decreased up to 1500 rpm (Mode 2, 75 % of engine idling load). This was for PD and all blends 95/WPPO5, 90/WPPO10, 80/WPPO20, 70/WPPO30, and 60/WPPO40; the values were 270 ppm, 285 ppm, 315 ppm, 345 ppm, 370 ppm, and 385 ppm respectively. The highest value of CO emission reported was 485 ppm for blend 60/WPPO40 and the lowest value reported was for blend 95/WPPO5 at 388 ppm.

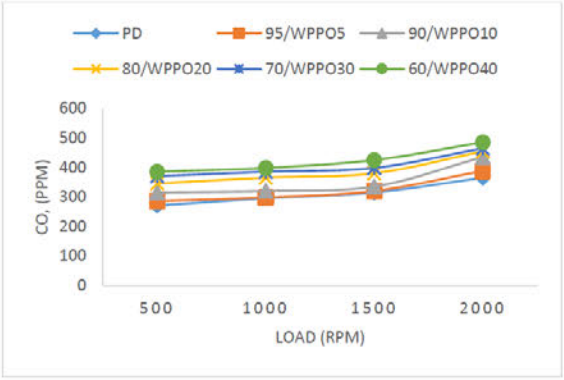

Fig. 3. Carbon monoxide versus load

Another observation is that as the engine was approaching full load (Mode 2, 2000 rpm), all the test fuels showed increased CO emissions with blends 95/WPPO5 and 90/WPPO10 reporting the lowest emissions value of 388 ppm and 435 ppm among the test blends across the entire engine load Modes 1 and 2 conditions. However, as the load increased from Mode 1 (25 % engine idling speed) to Mode 2 (75 % engine speed) the values reported were 320 ppm and 335 ppm respectively.

There are a number of factors, which explain the low CO emissions as the engine idling load increases. The reason the blends show decreasing and increasing trends in Modes 1 and 2 respectively is due to the high viscosity in WPPO. Viscosity affects the spray pattern hence resulting in poor fuel mixing hence incomplete combustion and increased emissions [50]. This phenomenon is linked to increased engine idling load and short ignition delay, hence increasing CO emissions. Additionally, the decrease in CO emissions could also be due to the conversion of CO to CO_2 taking up this reaction from the high oxygen content of biodiesel [51].

3.2 Unburnt Hydrocarbons (UHC)

Fig. 4 is a variation of UHC emission with engine load. As the engine load was increased, the UHC emissions increased too. The higher hydrocarbon emissions may have been due to hydrogen radicals in the PD-WPPO blends. However, the increase was more significant when the engine load was in intermediate loads Mode 2, 1500 rpm to 2000 rpm full load (75 % and 100 %).

For example, at Mode 1 (500 rpm -1000 rpm, 50 % engine load), the blend values were 22 ppm, 21 ppm, 20 ppm, 18 ppm, and 15 ppm respectively. Compared to full load Mode 2 (1500 rpm to 2000 rpm) with 35 ppm, 34 ppm, 32 ppm, 29 ppm, and 26 ppm (for blends 95/WPPO5, 90/WPPO10, 80/WPPO20, 70/WPPO30, and 60/WPPO40). This leads to the conclusion that at high engine loads the values of UHC emissions are significantly higher for all the blends of WPPO, although still comparatively low when compared to PD fuel.

The UHC emissions from the blends 95/WPPO5 and 90/WPPO10 reported higher values although the trends in Fig.4 show low values compared to the values of PD test fuel. However, the general trend in Fig. 4 shows that increased blend ratio significantly reduced UHC emissions across all the test fuels irrespective of the engine Mode 1 and 2 load conditions. This reduction is due to the high oxygen of WPPO, which has an oxygen content of 7.83 as seen in Table 7.

Fig. 4. Unburnt hydrocarbons versus load

3.3 Oxides of Nitrogen (NO_X)

Fig. 5 is a variation of engine idling load with NO_X emissions. The figure shows that as the engine idling load was increased there was an increase in the NO_X emissions irrespective of fuel blend ratio. The values of NO_X emissions for the blends 95/WPPO5, 90/WPPO10, and 80/WPPO20 reported higher values at Mode , (75 % load) compared to Mode 1. For example, at 1500 rpm the values of the blends were 335 ppm, 358 ppm, and 475 ppm, compared to PD fuel at 300 ppm.

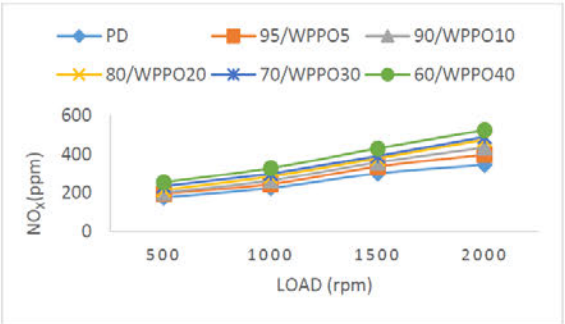

Fig. 5. Oxides of nitrogen emissions versus different engine idling speeds

As the blend ratio increased there was a decrease in the BSFC across all the test fuels. However, the values for all WPPO blends increased compared to PD test fuel. This is due to the lower calorific values of the blends as the percentage of the blend ratio increased. In other words, by increasing the ratio of WPPO in the diesel test fuel, the engine fuel consumption increased, which is identical to the studies of [59-61]. The closeness of the values and the packed graph reveal a close resemblance and identical BSFC characteristics of WPPO to PD properties. For example, at Mode 1 (500 rpm to 1000 rpm) 50 % engine idling load blend 90/WPPO10 had a value of 0.48 g/kW.h and 0.43 g/kW.h compared to full engine speed Mode 2 (2000 rpm) load with 0.37 g/kW.h and 0.41 g/kW.h. This value is higher than PD test fuel with 0.04 g/kW.h at 50 % engine load and 0.035 g/kW.h at full engine load.

4.0 WPPO COMBUSTION ANALYSIS

Due to the high cetane index of WPPO biodiesel the combustion, process starts early compared to PD, hence higher release than PD fuel combustion. This leads to a higher cylinder peak pressure for WPPO biodiesel fuel compared to PD fuel. Figure 8 shows a comparison of WPPO blends with PD in Mode 1 idling loads of speeds 500 rpm to 1000 rpm. Under this condition, WPPO blends in Mode 1 exhibited higher peak cylinder pressure compared to PDF, which is evident as the blend ratio increased as in Figure 8.

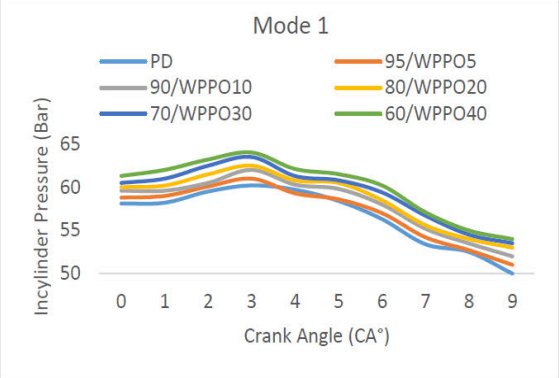

Fig. 8. In-cylinder pressure vs. crank angle variation compared to diesel and WPPO

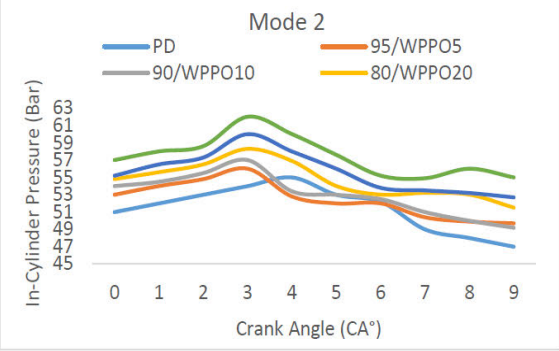

Fig. 9. In-cylinder pressure vs. crank angle variation compared to diesel and WPPO in Mode 2

Compared to when the engine is running at high speed (high load), low speed (low load idling) residual gas temperatures and engine wall temperatures are low [62]. In other words, injection pressure and fuel temperature are low hence the increased delay. This is the explanation of why diesel in the combustion analysis starts after 3° CA compared to WPPO biodiesel blends. This makes diesel fuel reach a peak cylinder pressure further after top dead center in the power stroke. On the other hand, biodiesel blends reaches peak cylinder pressure early before top dead center in the power stroke. For example, in Figure 9 Mode 2 speed, the values of peak cylinder pressure for PD fuel is 55 bar compared to 56 bar for WPPO blend 95/WPPO5. This is due to the enhanced combustion resulting from rapid combustion of the biodiesel blends at the pre-mixed phase. Of all the test fuels, PD fuel had the lowest peak cylinder pressure, which occurs slightly after top dead center [63].

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CHAPTER 9: BIODIESEL, COMBUSTION, PERFORMANCE AND EMISSIONS CHARACTERISTICS

Book publication

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Preface

Combustion technologies continue to evolve towards greater efficiency and reduced pollution. Therefore, their development requires a comprehensive understanding of the combustion behaviour of fuels, in this case, biodiesels. Biodiesel fuels are gaining prominence as alternative fuels to fossil fuels, and their combustion characteristics therefore need to be studied. In the past, many publications and reviews have been produced to discuss development and control strategies in biodiesel combustion but there is a gap in terms of bringing this large body of knowledge together and looking at it as a whole. This book is an attempt to bring together combustion studies by various researchers in the field of biodiesel combustion into a book format to help research students harness the synergy from a single resource in biodiesel combustion studies. For example, knowledge of chemical kinetics has facilitated strategies to mitigate problematic pressure rises during combustion. The development of homogeneous charge compression ignition engines has been able to maximize the use of different blends of fuels with different ignition and combustion characteristics. Such an application is an example of the type of knowledge that is advantageous in the development of combustors and the refinement of fuels by improving fuel efficiency and acceptability.

Although there has been progress in the defining of fuel specification and fuel quality assurance, biodiesel fuels have inherent differences in their fuel properties and composition compared to petro-diesel. Therefore, the effects of these differences in fuel properties and their interactions have to be carefully studied as well as their impact on the after-treatment system performance. The studies which are contained in this book are all highly researched on important and vital aspects of biodiesel operating systems such as particulate filters. Particular consideration is given in the long-term effects on the performance and service of these operating systems as some of their effects are irreversible such as diesel particulate filter (DPF) clogging which is due to ash accumulation. Therefore, this work will also seek to bring out development in technology in areas of after treatment and reduction in the demerits associated with the widespread use of biodiesel in the auto industry.

Biodiesel fuels have to fulfil a number of quality standards with specific minimum requirements. Density is a key fuel property as injection systems, pumps and injectors depend on it to deliver precise amounts of fuel for proper combustion to occur. Density also affects the amount of mass of fuel injected into the combustion cylinder and the manner in which operation units are designed in combustion reactors and other systems such as distillation units, separation processes, design of storage tanks and process piping. Density is greatly influenced by the type of raw material and the profile of the methyl esters in a particular biodiesel feedstock. In biodiesel production, this factor is critical due to the nature and composition of feedstock sources, of which there is a wide variety all with different character qualities. It is important that the impact of the differences in biodiesel fuels is understood, especially how these fuel properties affect spray behaviour characteristics in engine applications. As such, this work seeks to consolidate experimental and research work findings as reported in various literature on biodiesel combustion development. This is achieved by bringing together studies on various properties of feedstock and their profile. This enables research students to have a wider comparison tool from one source.

Durban, South Africa

Semakula Maroa
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Contents

Abbreviations and Acronyms

AC	Air conditioning
ASTM	American Society for Testing and Materials
BSFC	Brake-specific fuel consumption
bTDC	Before Top Dead Centre
BTE	Brake thermal efficiency
CA	Crank Angle
CFC	Chlorofluorocarbons
CI	Compression ignition
CN	Cetane number
CP	Cloud point
CR	Compression ratio
CS	Conventional surfactants
DI-DE	Direct injection diesel engine
DOC	Diesel oxidation catalysts
DPF	Diesel particulate filter
DTBP	Di-t-butyl peroxide
EGR	Exhaust gas recirculation
EOI	End of injection
EPA	Environmental Protection Agency
FAME	Fatty acid methyl esters
FFA	Free fatty acids
HC	Hydrocarbons
HCCI	Homogeneous charge compression ignition
HDD	Heavy duty diesel
HFRR	High-frequency reciprocating rig system
HSDI	High-speed direct injection
HVO	Hydrogenated vegetable oil
IID	Intercooler indirect injection
IT	Injection timing
JOME	Jatropha oil methyl esters

KOH	Potassium hydroxide
LDD	Light duty diesel
LMIC	Low middle income countries
LTC	Low-temperature mode of combustion
MTBE	Methyl tert-butyl ether
NAC	NO_X adsorber catalysts
NaOH	Sodium hydroxide
NO	Oxides of nitrogen
NREL	National Renewable Energy Laboratory
PCCI	Pre-mixed charge compressed ignition
PMBF	Pre-mixed burnt fraction
PP	Pour point
RCCI	Reactivity controlled compression ignition
SCR	Selective catalytic reduction
SMFAE	Single-molecule fatty acid esters
SNCR	Selective non-catalytic reduction
SOC	Start of injection
SOME	Soy oil methyl esters
TC	Turbocharged
TDC	Top dead centre
THC	Total hydrocarbons
UHC	Unburnt hydrocarbon
ULSD	Ultra low sulphur diesel
VNT/VGT	Variable nozzle turbine/Variable gas turbine
VOC	Volatile organic compounds
WC	Water cooled
WCOME	Waste cooking oil methyl esters

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Chapter 1
Introduction

1.1 Introduction and Historical Background

The history of biodiesel can be traced to the discovery of the diesel engine by the German engineer Rudolf Diesel in the 1890s. Vegetable oil was already being used as a fuel in the world exposition in Paris in 1900, where five engine models were displayed and tested during the exposition [14]. This was at the request of the French government, which had an interest in development of fuels of local origin for its African colonies for energy and power generation independence. After the Second World War, several literatures report the use of vegetable oil in diesel engines and operational difficulties encountered with biodiesel application as a combustion fuel [12, 13, 28, 48]. These reports led to the Belgium patent 422,877 awarded to Chavanne in 1937. However, alternative fuel research waned until the energy crisis of the 1970s created by the Arab–Israeli War, when Bruwer [8] came up with work on esters of vegetable oil. Using sunflower oil in a diesel engine, they reported that use of sunflower methyl esters eliminated the problems of viscosity and operational issues. Figure 1.1 presents statistics on biodiesel production by different countries from 2011 to 2016.

The commercial production of biodiesel in Europe began in the 1980s [52]. In the European Union (EU) biodiesel, production has greatly increased and doubled in consumption (Fig. 1.2). For example, in 2004 the estimated production figure was 1.9 million tonnes compared to 4.9 million tonnes in 2006, and has since increased 2.5 times more to stand at 6.1 million annually. Biodiesel is produced in more than 254 plants scattered across European countries such Germany, Italy, Austria, France and Sweden. This growth in biodiesel production represents a 60% increase since 2004 to date [15] using 2003–2018 statistics. The rapid growth in biodiesel production has not been demand driven but policy driven. For example, the European Parliament in 2003 adopted Directive 2003/30 creating indicative realistic targets for EU members to increase biodiesel penetration by 2% by December of 2005 and an annual growth projection of 5.75% by December of 2010 [15]. This is demonstrated by the statistical

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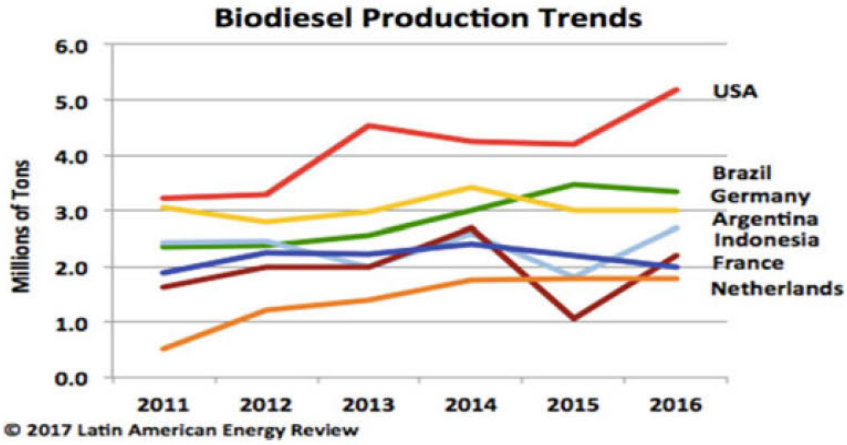

Fig. 1.1 Production of biodiesel from selected leading countries. *Source* James [24]

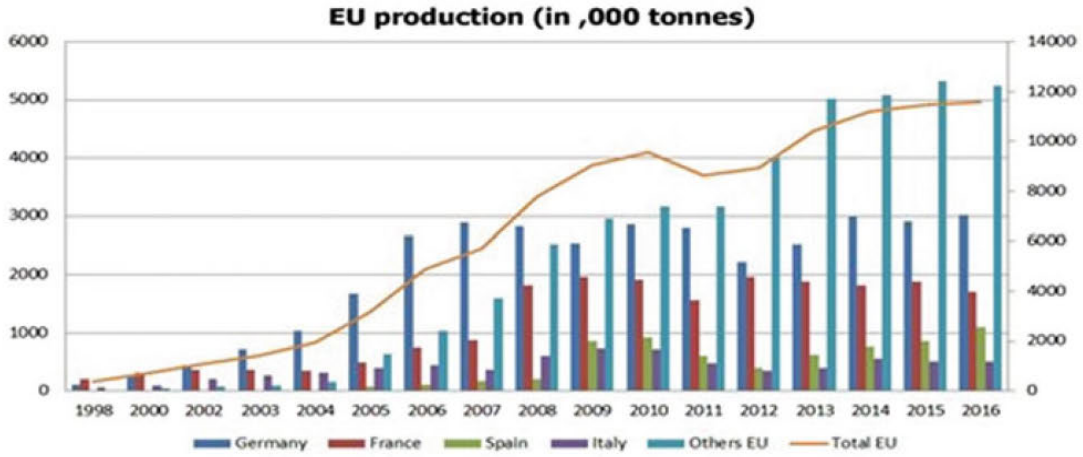

Fig. 1.2 European biodiesel production. *Source* EBB [15]

values projected in Fig. 1.2. The USA is the largest biodiesel producer with 5.2 billion litres in a global demand level of 9.7 billion litres as shown in Fig. 1.1.

Fossil-based fuels have played a major role in the growth of industries, transportation and agricultural activities, but fossil fuel, as a primary source of energy, is not sustainable in the long term due to depletion. Fossil-based fuels have qualities that are appealing such as availability, good combustion properties and high heating values [37]. Energy estimates from the International Energy Agency estimate the growth of energy consumption at 53% by the year 2030 [32, 35]. In the USA, the Energy Information Agency (EIA) projects that liquid fuel consumption will increase from 86.1 million barrels per day to 110.6 MBD by the year 2035 [10].

The depletion of fossil fuel reserves has occupied world energy forums policy and decision makers. As a result, there has been a rapid development of research in green alternative fuel energy, which is renewable, domestically available, environmentally friendly and feasible technically. Biodiesel contains characteristics and identical physical properties to fossil fuel, especially diesel fuel. This makes the future of

biodiesel promising as a source of alternative fuel energy, especially in developing countries which have a heavy burden of importation of liquid petroleum fuel for energy, as well as the environmental impacts and effects of pollution on public human health [31].

There are several sources of biodiesel feedstock such as edible vegetable oil, non-edible vegetable oil, recycled waste vegetable oil, recycled waste plastic and waste tires through pyrolysis, and from alcohols through alcoholysis [32]. Among these sources of biodiesel feedstock, edible oils are dominant at 95% of the world total biodiesel production, for example in USA canola and soybean, in Malaysia palm oil, while in Europe rapeseed oil has been the main source [40, 44]. However, the tide has been changing and shifting to renewables and recycled sources. It is important to mention here that the use of edible oil sources and plant-based biodiesel has had a negative impact in the low middle-income countries (LMICs) and developing countries. These sources have created a serious impact on food security in the developing world and LMICs leading to starvation and negative effects on the environment [4].

This is due to the commercialization and destruction of large forests for commercial oil production plantations instead of cultivation of food crops and has increased food price inflation. Research suggests elimination of these factors through adoption of non-edible, non-plant-based sources and other renewable and recycled sources such as algae and municipal waste solids. For example, algae have been shown to contain 80% oil content of its dry weight biomass [2]. Other measures include use of higher alcohols which can be produced from biological pathways such as natural microbial fermentation of engineered micro-organisms from lingo-cellulosic biomass which include rice straw, corn stock, wood pulp and sugar cane bagasse [51].

The main advantages of using biodiesel fuels in internal combustion engines include the non-toxicity of biodiesel, four times faster degradation compared to petro-diesel, pure biodiesel degrades 85%–88% in water, high flash points which make biodiesels safer to store, renewable energy supply, and maintenance of the CO_2 balance emissions and the carbon absorbed by plants. Thus, these fuels reduce CO_2 and greenhouse gases. Other merits associated with biodiesel are the relatively inexpensive cost of modification and redesign of engines when biodiesel fuel is applied in diesel and SI engines [6, 34].

Biodiesel fuels like any other fuel are affected by physicochemical properties, which have a direct impact on the combustion, performance and emission characteristics. Many fuel properties such as cetane number and the heating values are linked directly to fuel density. Fuel density influences the efficiency and atomization of fuel, hence the combustion characteristics [1, 36]. Density is a key in compression ignition engines due to the fuel metering system; in diesel engines, the system is volume-based. Moreover, such density influences engine output based on the mass of fuel injected. Kinematic viscosity is another key property in biodiesel fuels, influencing the operating conditions of injection systems, especially during cold start when fuel viscosity is high. Additionally, viscosity has been observed to affect fuel lubricating capacity [6] and the cooling and lubrication of fuel and injector pumps [19, 23].

Although biodiesels offer lower emissions of carbon monoxide (CO), unburnt hydrocarbons (UHCs) and particulate matter (PM), the production of NO_X emissions is excessive. This has been reported by researchers such as [3, 7, 9, 11, 17, 18, 22, 25–27, 29, 33, 38, 41–43, 45–47, 50].

NO_X emissions from internal combustion engines are the most harmful pollutant emissions to human health and the environment, with CO and NO being the two primary pollutants in the destruction of the ozone layer [20, 30]. Estimates from the Environmental Protection Agency (EPA) suggest that there is a 10% increase in NO_X emission for any pure 100% (neat) biodiesel fuel compared to conventional diesel [10, 16]. However, [49] found that exhaust emissions of PM, dry soot, UHC and CO were about 53–69%, 79–83%, 45–67% and 4–16%, respectively, while for NO_X they found 10–23% compared to petroleum diesel. Other researchers who have found and reported reduction of NO_X emissions with use of biodiesel fuel in exhaust emissions include [5, 21, 39]. Sun et al. [45] reported on the influence of injection timing on NO_X emissions from biodiesel which they linked to factors such as advanced injection timing, high adiabatic temperatures, less radiative heat transfer, increased ignition delay, higher degree of unsaturation and higher oxygen content.

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Chapter 2
The NO_X Formation Routes

2.1 Introduction

Oxides of nitrogen are NO and NO_2, but are given the formula NO_X [12]. However, it should be remembered that the main source of nitrogen during conventional combustion of petroleum and biodiesel fuels in internal combustion engines is atmospheric nitrogen (molecular nitrogen). It is imperative that the NO_X emissions kinematics behind the formation of these types of emissions are understood. This understanding helps in the development of strategies to reduce and control NO_X emissions. There are five main mechanisms, which control the formation routes of NO_X emissions, which will be discussed in this chapter and work. The main routes are Zeldovich (thermal NO_X), the Fenimore route (prompt NO_X), the N_2O route (nitrous oxide), fuel-bound route (fuel-bound nitrogen) and the diazanul (NNH) route [11, 29, 30]. However, the Zeldovich and Fenimore routes are considered the dominant mechanisms through which NO_X emissions are formed and produced [18, 48, 55].

2.2 Zeldovich NO_X Route

This is the NO_X that occurs at temperatures that are way above 1700 k [16, 24, 28, 39]. When the cylinder temperature hits this point, the molecular nitrogen and O_2 react following a series of chemical reaction steps called the Zeldovich mechanisms named after the Russian scientist who discovered this reaction and mechanism route. These reactions are shown in the following equations:

$$N_2 + O \overset{k_1}{\leftrightarrow} NO + N \tag{2.1}$$

$$N + O_2 \overset{k_2}{\leftrightarrow} NO + O \tag{2.2}$$

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$$N + OH \overset{k_3}{\leftrightarrow} NO + H \tag{2.3}$$

where k_1, k_2 and k_3 are reaction rate constants in terms of the Arrhenius law and the rate of NO concentration is given [25, 58, 59] as follows:

$$\begin{aligned} d\left(\frac{NO}{dt}\right) &= k_1 f + k_1 f[N][O] + k_2 f[N][O_2] + k_3 f[N][OH] \\ &\quad - K_{1b}[NO][N] - k_{2b}[NO][O] - K_{3b}[NO][H] \end{aligned} \tag{2.4}$$

The Zeldovich mechanism route takes the intermediate route especially in lean fuel where $\theta < 0.8$ and operating under low-temperature conditions as in Eqs. 2.5, 2.6 and 2.7 [13, 35] as follows:

$$O + N_2 + M \leftrightarrow N_2O + M \tag{2.5}$$

$$H + N_2O \leftrightarrow NO + NH \tag{2.6}$$

$$O + N_2 \leftrightarrow NO + NO \tag{2.7}$$

The first reaction in Eq. 2.1 is the rate-limiting phase or the rate-determining equation, which requires very high activation energy of 314 kJ/mole, coupled with very high instantaneous temperature [42]. However, the reaction in Eq. 2.3 (extended Zeldovich reaction) becomes significant only when the chemical reaction is reducing. The reduction is due to the fast-occurring reaction of Eq. 2.2, weakened by a lack of O_2. Zeldovich NO_X (thermal NO_X is affected by two factors; the residence time the combusting mixture takes in the combustion chamber [5, 29], and the concentration of the molecular nitrogen and oxygen [19, 54]. These findings have been corroborated theoretically by the findings and reports of [17, 47]. However, [27] suggest a third factor that affects NO_X emissions as the equivalence ratio and [6] suggest the fourth factor as being the atomic oxygen concentration within the combustion chamber. This leads to the conclusion that as the air–fuel ratio decreases so do NO_X emissions and vice versa.

2.3 The NNH Route Mechanism

The NNH route is a recent discovery on the NO_X reaction route by [3]. This reaction route has two major reaction mechanisms, especially in the combustion of hydrogen gas [21, 57] and hydrogen fuels with very large carbon to hydrogen ratios [45]. The following equations show this mechanism and its routes:

$$N + H \rightarrow NNH \tag{2.8}$$

$$NNH + O \rightarrow NO + NH \tag{2.9}$$

This NNH route mechanism to a large extent depends on the participation of the H atom forming NNH (diazanul) as observed by [53]. However, for its formation and reduction this mechanism depends on the thermal stability besides the reactant consumption channels as reported by [20]. The NNH route is one of the outstanding issues in the chemistry of combustion whose importance reported by Miller et al. (1981). However, there are other researchers who carried out subsequent work to confirm and collaborate that NNH is indeed in the reaction of $NH_2 + NO$ Atakan et al. [2], Bulatov et al. [4], Diau and Smith [7], Diau et al. [8], Fang et al. [10], Glarborg et al. [14], Miller [34], Miller and Klippenstein [36], Miller et al. [37], Park [40, 41], Song et al. [49], Stephens et al. [51], Walch and Dateo [56] and many others.

2.4 The N_2O Route Mechanism

This route has a reaction between N_2 and atomic oxygen to form N_2O through three reaction mechanisms. Molecule X executes these reactions by allowing N_2O formed from previous reactions to react with oxygen to form NO as in Eq. 2.10 [13, 35].

$$N_2O+ \leftrightarrow NO + NO \tag{2.10}$$

This reaction pathway contains mechanisms initiated by reverse rates of reaction [1, 32, 46] as shown from Eqs. 2.11, 2.12, 2.13, 2.14, 2.15, 2.16, 2.17, 2.18 and 2.19. The reverse rate reactions are shown in Eqs. 2.11 and 2.12 [33, 38, 50].

$$N_2O + X = N_2 + O + X \tag{2.11}$$

$$N_2O + X = N_2 + O(D) + X \tag{2.12}$$

$$N_2O + O = NO + NO \tag{2.13}$$

$$N_2O + O = N_2 + O_2 \tag{2.14}$$

$$N_2O + H = NO + OH \tag{2.15}$$

$$N_2O + H = NO + NH \tag{2.16}$$

$$N_2O + OH = N_2 + HO_2 \tag{2.17}$$

$$N_2O + CO = NO + NCO \tag{2.18}$$

$$N_2O + X = N + NO + X \tag{2.19}$$

After reverse reactions of Eqs. 2.11 and 2.12, the N_2O formed is oxidized into NO as shown in Eq. 2.13. Additionally, Eqs. 2.16, 2.18 and 2.19 are also because of N_2O oxidation. However, the reducing reactions mean that N_2O is reduced into N_2 as in Eqs. 2.11, 2.12, 2.14 and 2.17. It is important to note that the reactions in Eqs. 2.12 and 2.19 are kinematic mechanisms as reported by Michaud et al. [32].

2.5 The Fenimore Route (Prompt NO_X)

The prompt mechanism is also known as the Fenimore mechanism, named after Fenimore who discovered it in 1971 [13, 33]. It consists of reactions of fragmented hydrocarbons with molecular nitrogen under weak temperature. This mechanism accounts for a small percentage of the total hydrocarbon emissions as in Fig. 2.1 and Eqs. 2.20, 2.21 and 2.22.

$$O + N_2 + M \rightarrow N_2O + M \tag{2.20}$$

$$H + N_2O \leftrightarrow NO + NH \tag{2.21}$$

$$O + N_2 \leftrightarrow NO + NO \tag{2.22}$$

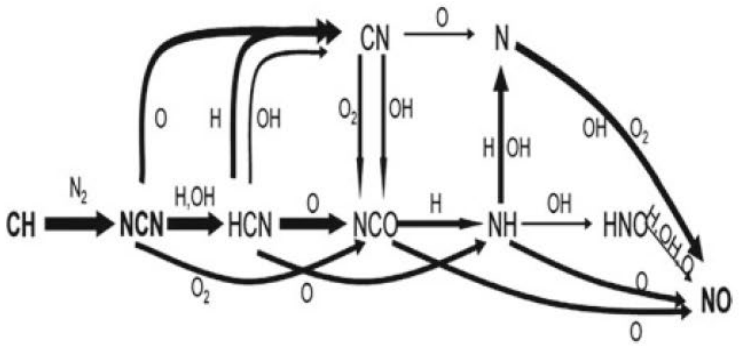

Fig. 2.1 Prompt-NO in the flame front of a rich CH_4–O_2–N_2–NCN mechanism. *Sources* Lamoureux et al. [22, 23]

2.6 The Fuel NO_X Mechanism

This is defined as the reaction of fuel-bound nitrogen from compounds of N–H or N–C leading to the formation of ammonia NH_3 and cyanhydric acid (HCN). Disassociation of these nitrogen compounds is credited with the formation of NO, in which two-thirds of the fuel-bound nitrogen from lean fuel–air mixtures are converted into molecular nitrogen N_2 [43, 44]. However, for high fuel to air ratios, i.e. rich mixtures, less NO_X is formed but more ammonia and cyanhydric acid are produced which, when they are released to the atmosphere and decompose, eventually form NO [15] as in Fig. 2.2. NO_X formed from this route cannot be controlled and optimized through the normal combustion process. Therefore, the amount of nitrogen in this process eventually depends on the nature of the combustion process [23]. Figure 2.3 shows the relationship between different types of NO_X formation under the influence of temperature with the reaction laid out in Eqs. 2.23, 2.24, 2.25 and 2.26.

$$NH_2 + \frac{1}{2}O \rightarrow NO + H_2 \tag{2.23}$$

$$NH_3 \rightarrow \frac{1}{2}N_2 + 1\frac{1}{2}H_2 \tag{2.24}$$

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2 \tag{2.25}$$

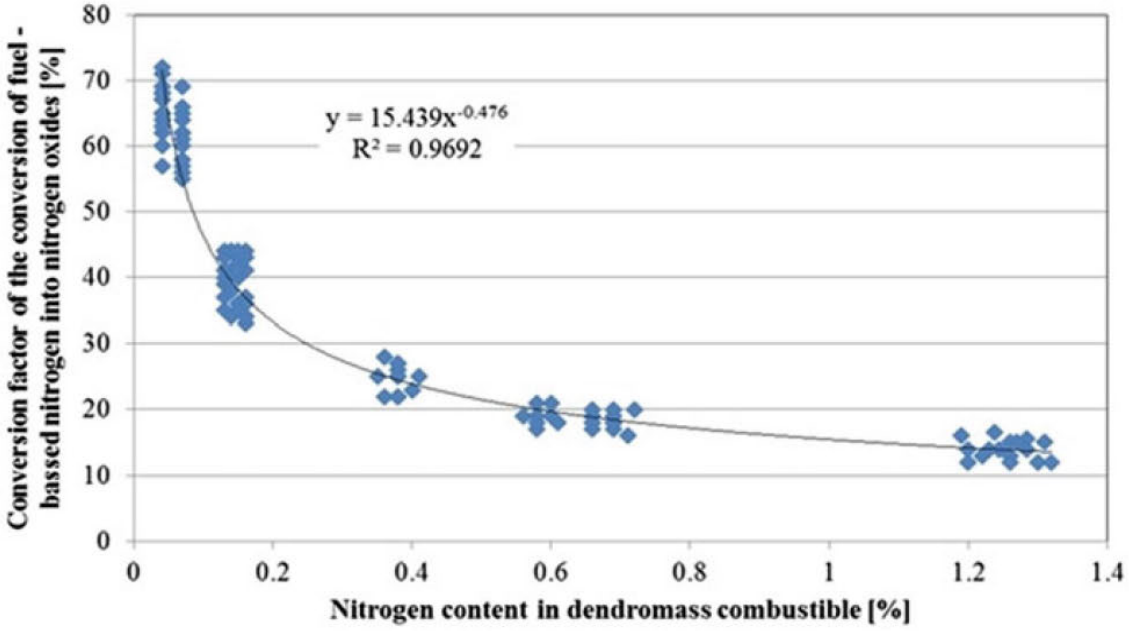

Fig. 2.2 Variation of the conversion factor of fuel-bound NO_X emissions in a dendromass wood biomass. *Source* Dzurenda et al. [9]

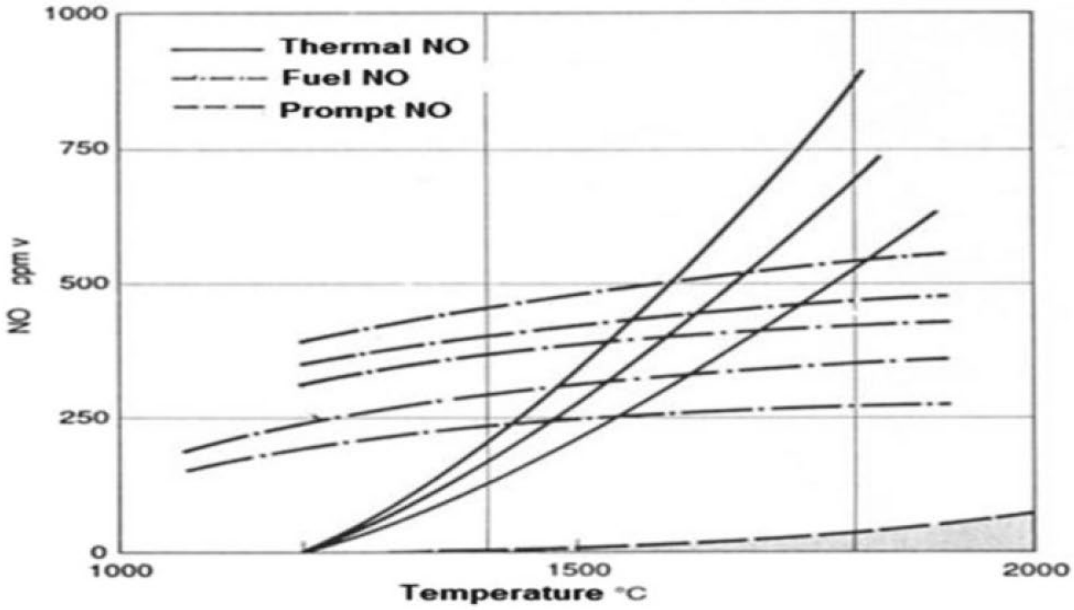

Fig. 2.3 Relationship of temperature and formations NO_X, thermal NO_X, fuel NO_X and prompt NO_X. *Source* Merryman and Levy [31]

$$HCN + 2NO \rightarrow 1\frac{1}{2}N_2 + CO_2 + \frac{1}{2}H_2 \tag{2.26}$$

Figure 2.3 is a variation of NO_X and formation temperature range, with different routes of formation mechanisms. This figure provides a correlation between fuel and prompt NO_X formation routes with varying temperature. The NO_X emissions continue to increase proportionally with increase in temperature. The areas with rich pockets of fuel show reduced availability of oxygen, and thus, least reaction with molecular nitrogen hence reduced fuel conversion and thermal NO_X [26, 52].

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Chapter 3
Biodiesels Production Proccesses and Technologies

3.1 Transesterification

This is the production of one ester from another ester. For example, mono-alkyl esters are produced from vegetable and plant oil consisting largely of triacylglycerol of long-chain fatty acids with a low molecular weight alcohol [34], the low molecular weight alcohol acting as a substrate. Both acids and bases catalyse transesterification. The base catalysis is more rapid compared to the acid catalysis [19, 53] and requires high temperature and pressure [15, 39, 68]. The most commonly used catalysts in transesterification are sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulphuric acid (H_2SO_4) [53]. The process involves heating and stirring together the starting oil and the methanol mixed with the catalyst or sometimes the catalyst dissolved first in methanol before mixing and heating. Figure 3.1 shows a transesterification reaction to produce esters.

Conventionally, KOH and alkoxides are the most well-known homogeneous base catalysts which produce high yields of methyl esters [80]. These are recommended even though their reaction rate is slow and requires high reaction temperatures [4, 5, 33, 43, 65]. However, due to its solubility in the medium of reaction, via saponification soap is formed. This leads to the reduction in the biodiesel yield, high consumption of the catalyst, besides difficulties in separation and purification of the final product [42]. Among the catalysts, the heterogeneous (solid) types are preferred due to benefits such as ease of separation from reaction medium, reusability [53], no recovery or treatment steps required, high purity of 98% glycerine production, exempt and free of salt contaminants [7, 71]. Figure 3.2 is schematic of the biodiesel production chain commonly practised in industry.

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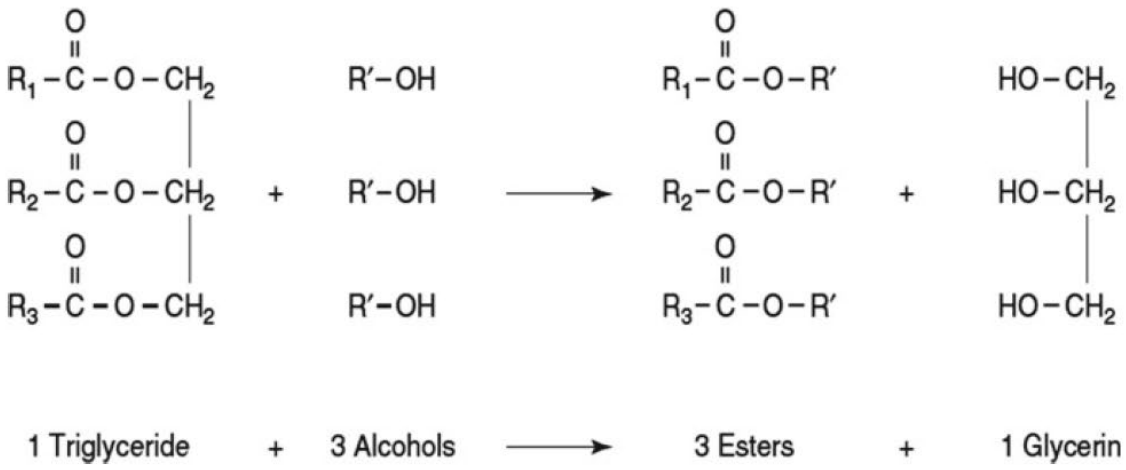

Fig. 3.1 Transesterification reaction used to produce biodiesel esters (the reaction typically employs a catalyst). *Source* [45]

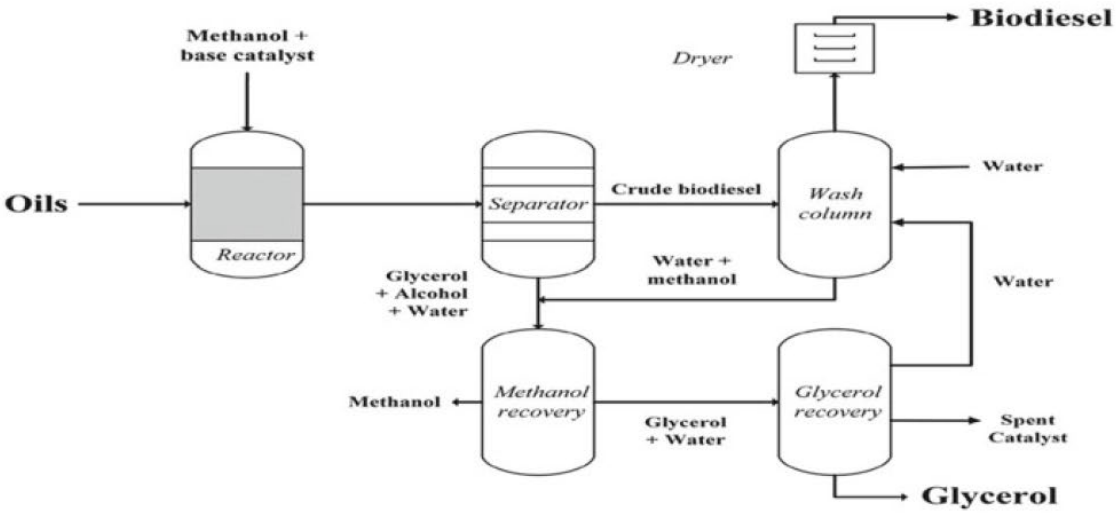

Fig. 3.2 Biodiesel production process, as commonly practised in industry. *Source* [34]

3.2 The Acid Catalyst Method

The acid catalyst technique is made up of five main methods, namely (i) methanolic [13, 22, 56, 60, 74] (ii) ferric sulphate [76], (iii) sulphonic acid [26], (iv) methanolic hydrogen chloride [11], (v) and methanolic boron trifluoride [58]. However, it is sulphuric acid, hydrochloric acid and sulphonic acid that are usually preferred as catalysts in transesterification. A catalyst is first dissolved in methanol (an alcohol) and mixed thoroughly by stirring in a reactor. Thereafter, the biodiesel, which is to be trans-esterified, is transferred into the reactor and the mixture (alcohol and catalyst) is added into the oil. Sulphonic and sulphuric acids provide a very high yield in alkyl esters, although the reaction rate is slow, commonly referred as to Bronsted acids. However, the amount of alcohol in the mixture influences the formation of

alkyl esters. The excessive quantities of alcohol during the transesterification process make the recovery of glycerol difficult. This leads to the conclusion that the ratio of the oil and alcohol has to be empirically established and determined for every transesterification process.

3.3 The Alkali Method

In this technique, the catalyst, which in this case is KOH or NaOH, is first dissolved into the alcohol (methanol) as in the earlier method by vigorous stirring in a reactor for 2 h at 340 k under ambient pressure. This process produces two levels of liquids in two phases—an ester and a glycerol—both in crude form. Alkali catalysed transesterification is faster than the acid reaction catalyst method. The first reaction of the base with the alcohol produces alkoxides and a protonate catalyst. This reaction forms an alkyl ester with corresponding diglycerides from the nucleophilic reaction on the alkoxides at the carbonyl group generated from the tetrahedral intermediate. The diglycerides and monoglycerides becoming alkyl esters and glycerol through the same reaction process discussed earlier. The alkoxides metal alkalis give very high yields of >98% as catalysts in a short reaction rate of 30 min [14]. This is especially so when applied in some lower molar concentrations of 0.5 mol %. It should be remembered that for them to effectively work, they need or require the absence of water [62].

3.4 Biocatalytic Transesterification

This is a method where transesterification is conducted chemically or enzymatically [27, 48, 49, 77]. There are currently about six commercial operating plants in the world: Lvming Co. Ltd. in Shanghai, China; Hainabaichuan Co. Ltd. China; Sunho Biodiesel Corporation, Taipei, in Taiwan, Trans-biodiesel; Shfar-Am in Israel, Purolite Bala Cynwyd in Pennsylvania, USA, and Piedmont Biofuel in Pittsboro, North Carolina, USA. Table 3.1 shows the comparisons of producing biodiesel using homogeneous base, acid catalysts and biocatalysis.

In recent studies for three different enzymes on Jatropha oil (*Chromobacterium viscosum*, *Candida rugosa* and *Porcine pancreas*), only lipase from *C. viscosum* gave good yield [63]. Biocatalysts are being touted as having the ability to outperform chemical catalysts [2]. Biocatalytic catalysts are natural occurring lipases with abilities to perform transesterification reactions necessary to produce biodiesel oil. These have been identified from isolated groups of bacterial species such as *Pseudomonas fluorescens, Pseudomonas cepacia, Rhizomucor miehei, Rhizopus oryzae, Candida rugosa, Thermomyces lanuginosus* and *Candida Antarctica* [73].

The biocatalytic method of transesterification has two major classifications: extracellular lipase and intracellular lipase. Extracellular lipase is from live producing

Table 3.1 Comparison of biodiesel production using homogeneous base, acid catalytic and biocatalytic processes

Factors affecting production	Homogeneous base catalytic process	Homogeneous acid catalytic process	Biocatalytic process
Reaction temperature	40–60° C	High temps of 60–100° C	Low-temps 30–40° C
FFA in feedstock	Saponified products (soap formation)	No influence (alkyl ester production)	No influence (alkyl ester production)
Water in raw materials	Inhibition of the reaction rate	Low water content, reaction not hindered	Low water, lipase shows maximum activity at oil–water interface
Yield of product	Normal	High	Depends on enzymes
Recovery of glycerol	Difficult	Comparatively easy	Easy
Purification of biodiesel	Repeated washing (soap emulsifier)	Easy to water wash for product separation	None
Catalyst cost	Cheap	Cheap	Expensive
Rate of reaction	Faster comparatively	Slower than catalytic process	Lower than base and acid catalytic process

microorganism broth and then purified and includes enzymes such as *Mucor miehei, R. Oryzae, C. antarctica, P. cepacia.* Intracellular lipase remains inside or in the cell producing walls due to immobilization of enzymes. Methods of enzyme or lipase immobilization include adsorption, covalent bonding, entrapment, encapsulation and cross-linking [1].

Biocatalytic transesterification has many advantages over the chemical transesterification method. For example, zero generation of by-products, and less difficulty in removing final products from a reactor. Transesterification with triglycerides releases glycerol as a by-product. In enzymatic reactions, glycerol produced with a high purity enables it to be used for renewable fuels and chemicals. Other advantages are the low processing temperature of 35–45° C and that it allows for recycling of the catalysts, thus reducing greatly the cost of production, which promotes sustainability.

3.5 Blending Method and Micro-Emulsion

Blending as a technique is used to mix petro-diesel and biodiesel fuels in suitable ratios under appropriate conditions. This leads to fuel blends with intermediate properties, which improve combustion performance and emission characteristics during usage in diesel engines. The differences in biodiesel physical properties such as atomization characteristics, spray characteristics and spray tip penetration need to be studied. The increase in spray tip penetration is influenced by the mixing ratio during

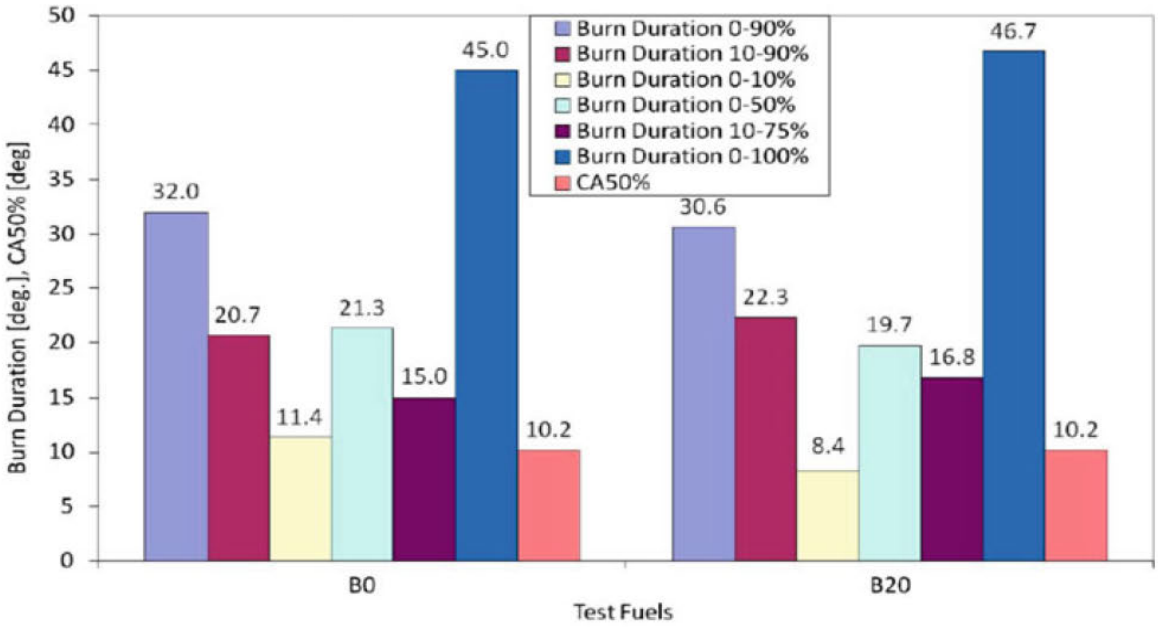

Fig. 3.3 Variation of the combustion intervals under the influence of blending ratio. *Source* [70]

blending. Figure 3.3 shows the variation of burn duration (combustion interval) and blending ratio.

Due to difficulties associated with using crude biodiesel feedstock oils, biodiesel oil is diluted or mixed to improve viscosity and allow application in diesel engines. Blending of biodiesel feedstock and petro-diesel has disadvantages and advantages. This blending yields fuels with intermediate properties [8] which improve performance, combustion and emission characteristics of biodiesel. Biodiesel fuel has been found to be a viable alternative fuel to petroleum diesel, with mixing ratios of 1:10 to 2:10 found to be good and successful [21].

3.6 Use of Biodiesel By-products and Treatment

As a means of reducing the costs of biodiesel, the use of low-cost carbon sources to make them competitive has been studied for some time [25, 46, 50]. For example, the bulk use of waste by-products such as glycerol for lipid production as they contain high sugar content. The conversion of glycerol as a biodiesel by-product for increasing the productivity of biodiesel plants will help to lower the cost of production hence adaptability as alternative fuel. Table 3.2 shows different biodiesel processed by-products characteristic use and references.

A synergistic relationship in all waste-handling situations offers economic opportunity for conversion of waste liabilities into revenue streams hence reduced costs of biodiesel production [66]. Biodiesel production produces three main waste by-products glycerine, methanol and water used to wash biodiesel [40]. For example,

Table 3.2 Lipid yields reported in the literature from different wastes and lignocellulosic biomass

Substrate	Microorganism	Lipid yields	References
High carbohydrate content			
Glucose derived from starch hydrolysate	*Mortierella alpina*	0.33–036	[83]
Molasses	*Candida lipolytica* *Candida tropicalis* *Rhodotorula mucilaginous*	0.16–0.60 0.12–0.46 0.39–069	[31]
Glycerol	*Mortierella alpina*	0.05–033	[12]
Crude glycerol	*Cryptococcus curvatus*	0.44–052	[41]
Lignocellulosic material			
Rice hull hydrolysate	*Mortierella isabellina*	0.64	[16]
Cassava starch hydrolysate	*Rhodosporidium toruloides*	0.63	[75]
Corncobs	*Trichosporon dermatis*	0.17	[28]
Corn stover	*Cryptococcus curvatus*	0.16	[23]
Rice straw hydrolysate	*Trichosporon fermentans*	0.4	[29]
Wheat straw	*Cryptococcus curvatus*	0.05	[79]
Complex substrates			
Distillery wastewater	*Rhodotorula glutinis*, *Cryptococcus curvatus*	0.25 0.27	[24]
Pre–treated sewage sludge (ultrasounds)	*Lipomyces starkeyi*	0.32–0.35	[3]
Waste cooking oil	*Yarrowia lipolytica*	0.17–0.55	[32]
Palm oil mill effluent	*Rhodotorula glutinis*	0.21–0.38	[59]

in every production of 10 parts of biodiesel produces 1 part of glycerine. Therefore, with increased production of biodiesel and falling of demand for crude glycerol, efficient and prudent options have to utilize biodiesel waste resources are critical.

The nature of these compounds and by-products is dependent on the type of raw material and the processing technique applied. Since the processing technology influences biodiesel production, it must also influence the characteristics of the by-products. In other words, new processing technologies, techniques and catalysts have greater roles in influencing the composition and utilization of glycerol [7]. Nevertheless, these by-products are suitable for anaerobic digestion and for biogas production. Crude glycerol contains 50–60% of glycerol, 12–16% alkalis' such as alkali soaps and hydroxides, 15–18% methyl esters, 8–12% methanol and 2–3% water [35, 69].

In Europe, there are 245 plants processing biodiesel with over 9 million metric tonnes of liquid biodiesel oil annually. In the European Union, the main producers and consumers of biodiesel are Germany, Italy, France and Sweden. However, other countries are rapidly catching up mainly the USA, Brazil, India, Argentina, Malaysia and Fiji [36]. As the production of biodiesel is exponentially increasing, so is the

crude glycerol generated. However, to improve economic feasibility of the biodiesel industry in the G-phase more studies have been undertaken to find possibilities. The following researchers have been involved in finding these possibilities in a wide range of studies such as [6, 9, 10, 17, 18, 20, 37, 38, 44, 54, 55, 64, 67, 72, 78, 81].

These possibilities include the use of biodiesel by-products for combustion, co-burning, compositing, animal feeds, thermochemical conversions and biological conversion for glycerol processing. Besides the aforementioned uses, biodiesel by-products are also utilized in industrial microbiology. This is achieved through the conversion of glycerol to various products such as 1, 3-propanedio [47, 52]. This by-product is considered the main component of glycerol fermentation [51] and is used as a monomer for poly-condensation. Among the products, it is used to make in plastics that include polyesters, polyether's and polyurethanes [61, 82]. However, as a monomer glycerol is used to produce polyglycol lubricants [30] and acts as a solvent [57]. Despite widespread application in the food, pharmaceutical, and cosmetic industries, the by-products refining process is high and expensive [51].

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Chapter 4
Biodiesel Feedstocks

4.1 Introduction

The increasing uncertainty on energy production, and supply is impacting on sustainability and environment [18]. This is coupled to volatile global prices of petroleum products. A number of biodiesel feedstocks currently exist mostly from vegetable oils prepared by various transesterification processes available. The feedstocks are of edible agricultural plant origin with a bigger chunk of agricultural land utilized for their production hence competition with food production. This leads to increased prices for land use and on essential food commodities. Feedstock prices is an important factor in managing the cost of production [91], as it contributes to 75–95% of the overall cost of biodiesel production.

Biodiesel feedstock offers hope as they have lower emission pollutants compared to petroleum fossil fuels. Biodiesel fuels have shown higher cetane numbers with no aromatics, or sulphur and contain more oxygen content of 10–12% by weight of dry mass [14]. Secondly, biodiesels are biodegradable and enhance lubricity in engine moving parts and injection systems [24]. Besides these advantages biodiesel have also contributed greatly to sustainability of energy resources [18]. For example, all fatty acids like animal fats and plant lipids with more than 300 sources can be used for biodiesel production [66, 84, 89, 115, 117].

Biodiesel feedstocks are classified into oil crops such as rapeseed, soybean and oil trees such as moringa, palm oil, animal fats and waste oil food. Waste biomass sources such as plastics, microorganisms sources such as microalgae are from non-edible primary feedstocks [59]. Examples of non-edible primary feedstocks include cottonseed, algae, neem orange, linseed, mahua, jojoba, kusum, rubber seed, sea mango and Deccan hemp. For non-plant sources, waste cooking oil, engine oils, pyrolytic oils and used oils are in various forms. Biodiesel feedstocks largely depend on climate and local soil condition, especially for crop-based feedstocks. For example, in the USA, the main sources are soybean and corn, Germany is rapeseed and in Brazil it is

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sugarcane bagasse [52]. However, these feedstocks can be summarized and classified in generational feedstocks as

- First generation comprising of all edible vege‘ oils such as sunflower and soybean [84].
- Second generation consisting of all non-edible sources like jojoba oil, waste oils, Jatropa and animal fats—tallow Third generation which are classified as biofuels from biomass of microalgae source [84, 117]. Table 4.1 shows a major achievement of biodiesel in the last decade.

In biodiesel production, many feedstocks have been experimented, thus from such advancements waste to wealth biodiesel was created [97]. To consider feedstock for biodiesel production, the determinant factors are oil content percentage and the yield per hectare. Estimated yields and oil of many biodiesel stocks can be found in [45, 63, 98, 108].

As such, cheap and readily available raw materials have been used such as waste cooking oil, yellow greases and animal fats to produce biodiesel. Another notable development is the breakthrough in using non-edible plants such as Jatropa (miracle plant) to produce biodiesel. This plant can be cultivated anywhere with minimal intensive care or irrigation, thus making it suitable for farmers in semi-arid areas in

Table 4.1 Major biodiesel achievement in the last two decades of research and development

Economic and social impact	Environmental impact	Energy security
Sustainability made from agricultural or waste resources	Reduced 78% GHG emissions	Reduced dependence on fossil fuels
Fuel diversity and improved fuel efficiency and economy	Reduced air pollution	Domestic targets
Improved rural economy	Biodegradability	Supply reliability
Increased income tax and trade balances	Improved water and land use	Readily available
International competitiveness	Carbon sequestration	Renewability
Increased investments on feedstocks and equipment	Lower sulphur content	Domestic distribution
Technological developments (R/D)	Lower aromatic content	Improved fuel economy
Higher cetane number (52 vs 48), lubricity and flash point	Lesser toxicity	Comparable energy content (92.19%)
Knowledge development and diffusion	Safer handling and storage	Strict quality requirements are met
Strong growth in demand and market formation	Sustainability and round economy	Viscosity 1.3–1.6 times that of diesel fuel
Improved engine performance	Less exhaust emissions	Good energy balance 3.24:1 vs 0.88:1

Source adopted from [5, 16, 25, 76, 110, 113]

rural Africa. This plant has sustained yield for 30–50 years of its life and can be intercropped with castor plantations to increase its economic viability [45].

4.2 Waste Cooking Oil

Waste cooking oil is made up of vegetable oil obtained from fried foods by repeated frying. Due to the high FFA repeated frying makes it no longer suitable for consumption, hence disposal. The amount of heat and water in the frying oil increases hydrolysis of the triglycerides and the percentage of FFAs in the oil [70]. The water and FFAs have a significant effect on the production of biodiesel [65]. Waste cooking oil and waste oil feedstocks around the world depend on the consumption by various countries. For example, UK 0.2 million tons of WCO, Canada 0.135 million tons of WCO, China 4.5 million tons and Japan 0.6 million tons [4, 26, 59]. Cindering growth and other factors, the USA market is projected to hit 2.1 billion gallons of biomass-based diesel by the end of 2019 [77].

Management of waste cooking oil and animal fats pose a significant challenge due to poor disposal and contamination of water and land resources. Despite use of waste oils in the soap manufacturing still a large part is released to the environment [18]. In the USA, the energy information administration estimates that 100 million gallons of waste cooking oil are produced per day alone [90]. Large amounts of WCO are illegally dumped into rivers and landfills to cause more pollution [116]. Therefore, its use as an alternative oil for biodiesel production offers significant advantages. Fats and oils are raw materials for liquid oils and are functional ingredients in the production of foods for homes, restaurants and the manufacturing industry [78].

The term fat and oil can be used interchangeably but their use is based on the physical state at ambient temperature. For example, oil appears liquid in ambient temperatures while fats are solid. However, the characteristics are determined by the chemical composition, which defines characteristics of fats and oil and sustainability for various industrial processes and applications [47, 78]. Fats and oil have unique properties, which add flavour, lubricity, texture and satiety to foods, besides their nutritional value. Fats and oils also provide the highest sources of energy for the three basic foods carbohydrates, proteins and fats. Fats also act as carriers of soluble vitamins essential for the human body. Oil and fats are insoluble in water and are predominantly made up of glycerol esters or triglycerides with traceable quantities of non-glycerides.

Waste cooking oil as a feedstock faces many drawbacks for biodiesel production [102] this includes:

- Separation of free fatty acids esters and glycerol is difficult
- Easily forms dermic polymeric acids and glycerol's
- The oils from WCO have high viscosity
- Due to saponification WCO oils suffer from decreased molecular mass and iodine values [70, 96, 104]

- WCO leads to pollution of water sources.

Besides these challenges in China, the government prohibits use of crops as feedstock. Thus, currently, the main feedstock in China is dominated by waste cooking oil. This has greatly increased the production cost, especially for small firms as prices of waste cooking oil go up.

Biodiesel feedstocks are classified on their free fatty acid as follows:

- Refined oil (soybean or canola) (FFA <1.5%)
- Low free fatty acid yellow grease (FFA <4)
- High free fatty acid greases and animal fats (FFA ≥20%).

it is important to note that there are other eases with free fatty acids (FFA ≥50%) such as trap and sewage greases [58]. However, proposed volumes by renewable fuel standard (RFS) would need an increase in biomass-based diesel from renewables. The proposed volumes are based on historical trends with key factors of impact on availability of fats oils and greases [77], these factors include;

- Increasing production of vegetable oils
- Increasing livestock production
- Increasing consumption of fats and oils in food as the population grows
- Increased consumption of lubricants and oils
- Constant production of yellow grease.

These factors sometimes interact to cause the other to decrease or increase. For example, soybean, canola and edible corn can be projected to increase as yields improve from developments in seed and improved agricultural practices or subsidies to farmers. Another projected increase related to livestock, which affects both supply and demand, is animal fats. Although animals produce tallow oil, they also consume oil and fats in feeds. Therefore, an overall increase will see also an increase on FOGs. Another very important thing to note in these factors is the fact that increased demand for biodegradable products in lubricants and oil industry will affect the supply and production of tallow. However, since the collection of waste oils from restaurants and hotels is a mature industry, this has not been replicated in households. Researchers and governments assume households have no contribution or production that is significant [77].

In using agricultural resources for food or fuel, little I still known, especially the economic and social impact. The issue of opportunity cost is still very unclear on land for biomass production to produce fuels [39, 94]. As the global population increases and the demand for energy increases. Agricultural production will have to be increased to meet this demand for food and energy by 60% [32]. However, it is important to note that land degradation is deepening as a long-term consequence of loss of biodiversity as climate changes [86]. Therefore, the additional impact of higher demand for crops as energy feedstocks will increase concerns and increased risk on land and water resources. What makes the scenario more threatening is the fact that although global energy demand has doubled the contribution from renewables, and alternative sources has remained constant at 13% for the last 35 years [54].

4.3 Animal Fats Biodiesel Feedstocks

This type of oil has been used on the production of biodiesel for some time. For example, beef tallow in Brazil accounts for 18.5% of all supply of raw oil in 2015 [101]. In total, the Brazilian cattle population is over 210 million heads of cattle, hence the justification and sustainability of this feedstock for biodiesel production [35]. This industry in Brazil produces 600,000 tonnes of tallow and is the second largest after USA with 3500, 000 tonnes of tallow [36]. The yield per head varies widely, but it ranges from 18 to 75 kg [20]. However, tallow oil fetches low prices compared to vegetable oils and is considered a major advantage as a feedstock. Nevertheless, competition from increased demand of biodiesel, animal feeds and soap manufacture, and cosmetic industry have increased prices and is a worrying situation. One of the major disadvantages of tallow oil is its physical conditions a room temperature [67]. Hence, proving to be a hindrance in using it's biodiesel blends in cold regions. This problem has been solved by blending and hybridization of feedstocks in situ and ex situ to avoid cold flow problems [30, 71, 103].

Another important aspect that needs consideration in animal fats is in the area of insects. Some insect species at larvae stage have shown to exceed 50% lipid content dry weight matter [69]. Insects' fat content variability is very large with a range of 2–50% of dry matter, with some insects' polyunsaturated fatty acid content hitting 70% of the total fatty acids. There is also a high level of C18 fatty acids including oleic, linoleic and unoleic acids in the fat of insects [105].

Therefore, it is a new area that requires further exploration as insects will not be competing with human's food but adding to food security after oil extraction. It is important to remember that insects are a greater source of protein varying from 20 to 70% of dry matter [61]. Besides being a greater value in proteins, insects also contain a reasonable amount of minerals such K, Na, Ca, Cu, Fe, Zn, Mn and P and such vitamins as the B-group, A, D, E, K and C [61].

4.4 Potential Feedstocks of Oil Plants

With a more than 300 oil bearing plants [7] with some species reaching a yield of more than 40% [28]. Plants provide the potential to supply biodiesel oil in the world today. For example, the Jatropa curcas is widely distributed in dry subtropical climates and tropical rain forests of the world. The Jatropa seed can produce 9.75 tons/ha with more than 40% oil on dry mass [28].

Plant-based biodiesel feedstock is the largest widely used feedstock. This section will endeavour to highlight plant feedstocks currently used for biodiesel production such as soybean, palm oil, rapeseed, cotton and sunflower. However, not all plant crops are feasible in biodiesel production and as such their FFA yield content are below 5% or have extremely high production cost.

4.4.1 Soybean

Soybean comes from the family of Fabaceae (*glycine max L.*) and is a legume with many different seasons for different countries. The USA, brazil and Argentina are the largest soybean producers accounting for 80% of all global production [33]. The soybean seeds contain 14 to 17% oil, and 33 to 40% protein and its production reached 40 million tonnes of oil accounting for 25% global production [34]. Rapeseed id the main feedstock for biodiesel in Europe accounting for 55% of all oil produced for biodiesel [101]. Rapeseed like soybean is a source of protein, although for animals such as pigs and in poultry, although now it is considered a biodiesel feedstock plant [10, 56]. Rapeseed contains 34–38% protein and its oil content range is 34–40% [13].

Due to the presence of glucosinolates rapeseed oil has one of the most unpleasant flavours and sometimes leads to high levels of toxicity from erucic acid [10]. Research has established that rapeseed contains low levels of saturated fats but high levels of monosaturated fats but high levels of monosaturated fat with omega 6 and 3 making it one of the beneficial oils for human consumption [93].

In terms of effect on the environment, as a biodiesel feedstock rapeseed present very low smoke emissions and greatly reduces PM and HC compared to soybean and palm oils [37]. However, rapeseed cultivation still offers difficulty which prevents expansion and profitability [62]. Life cycle studies for rapeseed have mixed results with suggestion that rapeseed biodiesel can reduce GHC emissions from 40 to 85% of fossil fuels depending on the scope of study [74].

4.4.2 Cotton Sources for Biodiesel Production

Cotton comes from the family of *Gossypium hirstutum L.*, for example, in 2015–2016 season alone brazil produced 3.2 million tonnes [101]. What makes cotton a biodiesel feedstock is its seeds which make 65% of the cotton bud and 35% fibre [64]. The cottonseed is rich in protein from its seedcake with extracts used in animal feed manufacturing [6, 27, 46]. Other uses of cotton seeds is in manufacturing of fertilizers, food flour and the dye industry [95, 109]. As one of the leading industries in countries such as Brazil and India and USA cotton seed oil is now a feedstock for biodiesel production [29, 85, 100].

Cotton seed oil produces low smoke levels and lower emissions of PM and hydrocarbons compared to soybean palm oil [37]. However, its main disadvantage is its high impurity and low-quality oil which requires pre-treatment. Another disadvantage of cotton seed is its low oil content in its seeds, cotton seed oil ranges between 16 and 23% per tonne [21], which can be improved by 5% though breeding and selection of cotton progenies [23].

4.4.2.1 Sunflowers Biodiesel Production

Sunflowers (*helianthus annuus L.*) has a very good oil content varying from 38% to 50% based on the variety [2, 119]. Sunflower has multiple advantages besides oil, each tonne of sunflowers produces 250 grams of shell, 350 kg of meal, 45.5–50% protein, use in the package and in the animal feed industries [15]. Sunflower is also used as a forage or green manure in the production of other plants [75].

Sunflower is resistant to drought, cold and heat resistant and adapts well to different climates and soil conditions. However, its yield is greatly influenced by latitude, longitude and photoperiod [31]. Sunflower can be intercropped or grown in rotation with other crops such as soybean and corn, hence higher profitability for growers [75]. However, sunflower oil prices in the world market make it an uneconomic option as a biodiesel feedstock [106]. The physicochemical properties of sunflower such high wax makes its biodiesel cloudy with cooling hence poor performance [42, 44].

4.4.3 Microalgal Biomass Feedstocks

Biofuels are now considered the fastest growing opportunity as a source of fuel and alternative energy, throughout the world. This has seen the development in biofuels like biodiesel and bioethanol commercially and replicated in so many developing and developed countries. Microalgae are increasingly becoming a biofuel raw material and in balancing and compensating the demand for biofuel, food, animal feeds and high value added products and chemicals [50, 83]. Other factors, which endear microalgae fuels, are the fact that microalgae do not compete with arable land and water resources of freshwater. This reduces competition for food production in developing countries, thus mitigating the human–animal conflict, hence sustainability. The other advantage of microalgae is that it defies seasons hence reduces dependence on natural cycles of growth and production [60, 82].

These fuels are produced from several sources of biomass such as food crops, crop waste or fruits, woody parts and plants, garbage and algae this have proved to have excellent qualities as alternative fuels [49]. The appealing characteristics of fuels created from microalgal biomass are renewable and reduce environmental pollution and global warming which is responsible for climate change. Global warming which increases by burning fossil fuels increases greenhouse gases mainly CO_2. The burning of fuels is responsible for releasing 29 gigatons of carbon dioxide annually into the atmosphere [83]. Fuels from microalgal biomass have shown oxygen levels of 10 to 45% with very low sulphur emission when combusted. This when compared to fossil fuels which have no oxygen content but when combusted release high sulphur emission and NO_X? It is important to note the importance of microalgal biomass as important because they can utilize SO_X and NO_X nutrients along with CO_2 in some species [41].

Therefore, making microalgal biomass one of the leading biofuels with non-polluting characteristics, available, sustainable and reliable. Microalgal-based biofuels are therefore eco-friendly, non-toxic and contain a high potential to correct CO_2 levels globally. For example, research is showing 1 kg of algal biomass can fix 1.83 of CO_2. However, it is imperative to remember that 50% of dry weight of algal biomass is made up of CO_2. Thus, manner in which these biofuels are developed and used is critical in order to adjust and optimize the energy structure and cost. If this is not done properly, it has the direct consequence of greenhouse gas emissions environmental and economic sustainability factors [40].

Microalgae grow rapidly photosynthetically while utilizing, 9–10% of the solar irradiance into biomass. This yields 77 g/biomass/m^2/day resulting into 280/ha/year [38]. However, in a large-scale production (cultivation), this yields decrease in the culture system both for outdoor and indoor modes. This is due to the loss of solar radiation and poor mixing of the microalgae culture for homogeneity [1, 9, 72, 92]. Figure 4.1 shows different species of microalgae feedstock, which produce bioethanol and heir carbohydrates compositions percentages.

In several ways, microalgae biomass feedstock has shown greater competency as a preferable feedstock to produce biofuels. However, the absence of lignocellulosic material in their cell walls makes it an advantage to reduce overall cost of production. This allows microalgae to feed on industrial waste, hence less cost in processing energy [80, 99, 118]. It is important to remember that biofuels as second-generation alternative fuels involve feedstock such as food crops. This is a very controversial issue as it affects food security. This makes this type of feedstock unsustainable and incompatible as future fuels [48].

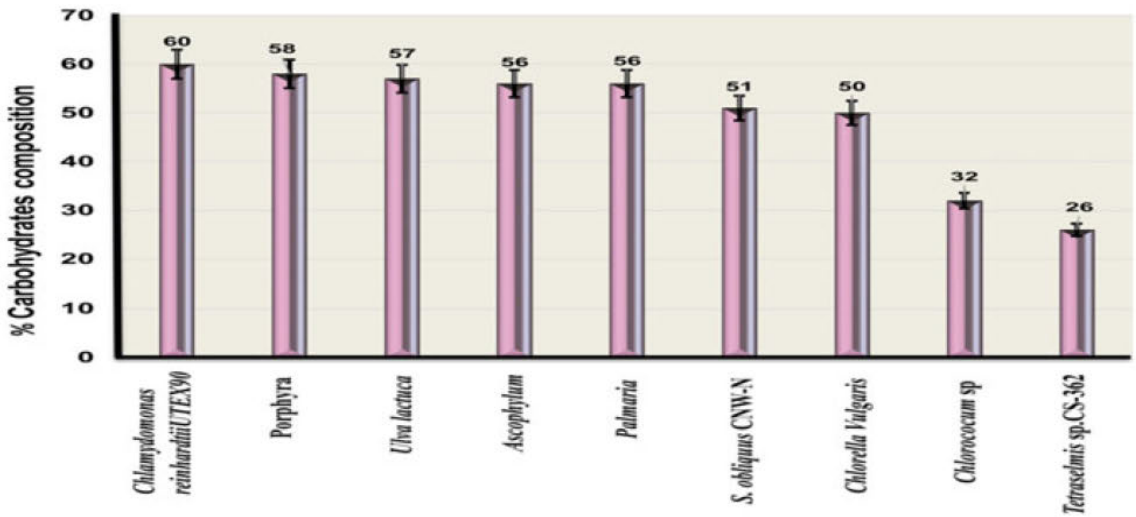

Fig. 4.1 Different species of carbohydrate-rich microalgae that compose feasible feedstock for bioethanol production [57]

4.5 Bioethanol Feedstocks

One of the leading and major clean and renewable energy sources in the transportation industry. Global bioethanol has grown from 4.8 billion gallons in 2000 to 16 billion gallons in 2007 [55]. This represents a growth rate of 30% within the mentioned period. However, current trends paint very encouraging statistics, for example, since 2007 when the global production stood at 60 billion litres of bioethanol by 2017 the figures stood at 143 billion litres annually [22]. Bioethanol has been widely developed as a biofuel due to its many advantages [4, 111, 112] compared to fossil fuels such as:

- High octane which prevents knocking in internal combustion engines
- High oxygen content which produces less greenhouse gas effects
- Allows direct use in the automotive industry for internal combustion SI engines without modification
- Bioethanol works with other oil as a blending agent.

Currently, the USA and Brazil are the world-leading producers of bioethanol. These two countries alone contribute 75 to 80% of the total global bioethanol production [55, 112]. The USA has 187 bioethanol plants spread across the states and produce ethanol mainly from corn grain [3]. However, Brazil produces its bioethanol from sugar cane feedstock compared to the European Union who use wheat and sugar beets. For example, in 2013, Brazil produced 37 billion litres of bioethanol compared to European Union production of 5.785 billion litres annually.

Considering the reservation expressed on biofuels from plant-based feedstocks, biofuels from renewable and sustainable feedstocks will dominate future energy sources and feedstocks hence replacing fossil fuels. Although bioethanol has been a dominant feature of biofuels, technology is moving to microalgae carbohydrates as a potential feedstock [8, 11, 43]. Microalgae biomass contains high contents of carbohydrates, such as glycogen, starch and cellulose that can be converted to fermentable sugars for bioethanol production [12, 17].

Removal of carbohydrates from microalgae cells largely depends on cell lysis. This is accomplished through enzymatic acidic solvent extraction methods. However, ethanol production yields depend largely on the method of extraction. In order to break the polymer molecules to monomeric forms, the sugars are preheated by fermentation to yield bioethanol. Bioethanol development from microalgae is one of the novel efforts in creating sustainable biofuels. However, there are challenges on large-scale cultivation, production and commercialization of microalgal biofuels. This is because ethanol yields depend on the species type of microalgae organisms used. The other factor is culture contamination, hence, the fermentation process needs to be carried in an aseptic environment to avoid poor culture yield [51, 114].

Therefore, for microalgae to sustainably produce bioethanol, it will require intensive and extensive efforts to overcome current limitation such as:

- Production of carbohydrates rich in biomass algal culture
- Dewatering and harvesting

- Pre-treatment of the biomass
- Ensuring there is maximum fermentation yield from the process.

These limitations once addressed will improve and optimize carbohydrate algal cells economically and sustainably [87]. For example, Chlorella vulgaris and Chlamydomonas reinhardtii are carbohydrates rich microalgae, which can be considered for bioethanol production suitably and profitably, with respect to investment and operational costs [68, 79, 107]. In other words to increase microalgae bioethanol production through fermentation requires proper study and evaluation, especially operation and maintenance costs [99]. This is two key factors in order for bioethanol to compete with fossil fuels in the energy market, which sometimes sell at 100 US dollars per barrel [19]. This compares well to biodiesel from algal biomass at 5 US dollars/gallon and bioethanol at 2.95 US dollars/gallon [53]. However, some studies suggest a price of 1 US dollar/litre [81] to other biofuels or 0.85 US dollar/litre [88].

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Chapter 5
Physicochemical Properties of Biodiesel

5.1 Introduction

This can be defined as biodiesel fuel properties in terms of physical and chemical properties such as viscosity, density, bulk modulus of compressibility, sound velocity, cetane number, iodine value, surface tension, thermal conductivity, chain length, heat capacity and fuel composition. The physicochemical properties of biodiesel have a significant impact on the formation of NO_X and other emissions due to the application of different types of fuel. Generally, the physicochemical properties of biodiesel and the performance of methyl esters and ethyl esters are comparable [32]. However, the viscosities of ethyl esters and their pour point are high compared to methyl esters. Therefore, engine tests conducted with methyl esters produce more torque and power compared to ethyl esters. This is despite their heat capacity values being identical and sometimes producing similar values [39]. Nettles-Anderson and Olsen [97] work studied NO_X emissions in biodiesel and found out that biodiesel viscosity plays a significant role in the emission of NO_X gases in diesel engines. Their studies analysed NO_X emissions as a function of viscosity and found that low-temperature biodiesel showed increased viscosity and therefore increased NO_X emissions when combusted in diesel engines.

Depending on the type of feedstock or biodiesel fuel used, the kinematic viscosity of biodiesel is normally higher compared to conventional diesel fuel (see Table 2), which reduces nozzle leakage during injection into the combustion chamber. High viscosity also increases injection pressure which allows the application of advanced timing as reported by Kegl and Hribernik [65]. Advanced injection timing increases the mass of fuel injected leading to increased NO_X emissions. However, Sukumaran et al. [115] and Yuan and Hansen [131] report reduced NO_X emissions by 3.52% with reduced viscosity in their experiment using soy methyl esters. The following sections in this chapter will discuss some of the vital physicochemical properties of biodiesel, the research work that has been done on them, and the findings.

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5.2 Kinematic of Viscosity

Viscosity is one of the key properties of biodiesel, and the main reason for the abandonment of vegetable oils as alternative fuels for diesel engines. Viscosity affects fuel flow in all the temperature ranges, besides affecting fuel injection equipment. The effect of temperature on the kinematic of viscosity has been investigated by many researchers for example Dunn [36] who found that viscosity increased with the oxidation temperatures of biodiesel, leading to the formation of dimers and polymers [62]. This is critical especially during the injection and atomization stage in the engine combustion chamber, when at low temperature increases in viscosity affect the fluidity of the biodiesel in use. Atomization is a determining factor in engine deposit size and formation, as it increases poor atomization and poor performance of fuel injectors and the fuel spray system and pattern. The kinematic viscosity of most biodiesel can be determined by ASTM standard D445 [6, 60]. Other scales of measurement include Redwood No. 1, Engler degrees, Saybolt seconds and many more.

The factors, which affect the kinematic of the viscosity of individual fatty acid alkyl esters, are chain length and the number and nature of the double carbon bonds. The relationship is that as the chain length increases (i.e. the number of carbon atoms increase) the saturation and viscosity increase. This is an important and vital factor and holds true for ethyl esters, as double bonds with cis configuration lower viscosity. However, trans-configured bonds or peptide bonds are formed between two molecules when the carboxyl group of one molecule reacts with the amino group releasing water (H_2O). The viscosity of trans-configured bonds takes the form of saturated compounds [34, 76]. It is important to mention here that branching in esters does not have a profound influence on the viscosity of a biodiesel. This is promising for future development, as it will help in the study of how to improve the cold flow properties of biodiesel, without affecting other fuel properties. Table 5.1 shows a comparison of temperature effects and viscosity between petro-diesel and biodiesel.

The kinematic viscosity of most biodiesel fuels at 40 °C conforms to the ASTM range. The kinematic viscosity of a biodiesel sample of biodiesel fatty esters can be derived from equations in which the kinematic viscosity is directly proportional to the viscosities of the individual components [79] as shown in Eq. 5.1.

$$V_{\text{mix}} = \sum A_c \times V_c \tag{5.1}$$

where

V_{mix} is the kinematic of viscosity of the biodiesel sample (fatty acids alkyl esters).
A_c is the relative amount (%/100) of the individual neat esters in the mixture.
V_c is the individual kinematic viscosity of individual esters.

Equation 5.1 is a simplification of the Grunberg–Nissan equations related to dynamic viscosity. There has not yet been a universal theory which can calculate

Table 5.1 Low-temperature kinematic viscosity range of biodiesel compared to petro-diesel

Temperature (°C)	Biodiesel	Petro-diesel
40	4.15	2.90
35	4.64	3.25
30	5.15	3.64
25	5.76	4.08
20	6.43	4.55
15	7.52	5.31
10	8.67	6.21
5	10.47	7.23
0	11.75	8.58
−5	nd[a]	10.81
−10	nd	nd
LTVR	2.83	2.96

[a]Not determined (ND)
Source Adopted from [77]

with an accuracy of the viscosity of a complex mixture from viscosities of individual components [56]. The majority of the theories used today limited on the ideal binary mixtures. Binary mixtures are where mixing of individual components does not produce any change in the volume in the individual components. In other words, the excess mixing volume should be zero thus obeying the Arrhenius equation [132] as shown in Eq. 5.2.

$$ln\eta_{1,2} = x\, ln\, \eta_1 + x\, ln\, \eta_2 \tag{5.2}$$

where x_i $(i = 1, 2)$ is the mole fraction of the ith component in the mixture.

This is to say, the dynamic viscosity $\eta_{1,2}$ of any ideal binary mixture with individual viscosity components η_1 and η_2 obeys the Arrhenius equation principle through the absolute reaction rate theory [46]. This theory states that the fluidity (inverse of viscosity) of a liquid is related to the flow of activation energy (this is a measure of intermolecular cohesion as in the equation for high energy corresponding to low fluidity and vice versa). However, we know that:

$$\frac{V_i}{h} = A(\text{constant}) \tag{5.3}$$

Implying that

$$ln\eta_i = \text{constant} + \frac{\Delta E_i^{\#}}{RT}(i = 1, 2) \tag{5.4}$$

$$\frac{1}{\eta_i} = \frac{V_i}{h} = \exp\left(-\frac{\Delta E\#}{RT}\right) \tag{5.5}$$

where

exp is the experimental data.
V_i is the kinematic of viscosity.
R is the universal gas constant.
T is the temperature.
η is the rate of coefficient of efficiency.
h is the oxidative stability.

Alternatively, the kinematic viscosity can be derived from the overall kinematic of viscosity mixture contribution through extrapolation, leading to a third-order polynomial equation. This is through the contribution of compounds with melting points >40 °C as prescribed in most biodiesel standards, and with hypothetical kinematic viscosity, which is greater than 40 °C as, expressed in Eq. 5.6.

$$V = 0.30487 + 0.0265 \times C + 0.0066 \times C^2 + 0.000491 \times C^3 \tag{5.6}$$

where

V is the kinematic viscosity as calculated viscosity contribution (CVC).
C is the number of carbon atoms.

5.3 The Cetane Number

Cetane number (CN) is one of the primary and important properties of biodiesel fuels. Combustion is the final stage of the life cycle in an engine. Therefore, the CN is one of the main properties that affects efficiency and other by-products of the engine combustion process. Although it is dimensionless, it is the primary indicator of fuel quality and ignition behaviour of any particular fuel. Fuels with higher CNs have been seen to provide shorter ignition delay time (time between injection and ignition onset) and vice versa. In combustion, studies and experimentation shorter ignition delay fuels are preferred compared to the fuels with longer ignition delays.

A number of CN scale standards developed internationally to assist in the unification of fuel CN numbers. For example, the ASTM D613 [10] has been developed in the USA, while the International Organization for Standardization (ISO) has developed ISO 5165. The ASTM D975 [1] was developed for petro-diesel and requires a CN of 40. The European CN standard EN 590 [24] requires a minimum CN of 51 while for biodiesels all the standard bodies prescribe a minimum CN of 47 in ASTM 6751 and a minimum of 51 for biodiesel in EN 14214. An interesting point in the CN scale is the fact that as the carbon chain length branching decreases and the carbon branching increases, the CN decreases too. For example, the long and

straight-chained hydrocarbon hexadecane ($C_{16}H_{34}$) has 100 as its CN on the scale as compared to the highly branched 2,2,4,4,6,8,8 heptamethylnonane with the same molecular formula $C_{16}H_{34}$. However, heptamethylnonane has poor ignition quality and a low CN of 15 [76, 80, 93].

Aromatic compounds found in petro-diesel all exhibit characteristics of low CN, although the low CNs increase as the size of the n-alkylside chain increases [29, 66, 104]. Wartime studies on 72 different additives (including 26 nitrates and 9 peroxides) on 10 different basic fuels [108] found that nitrates and peroxides caused substantial increase in CN compared to other types of additives. However, a general rule is that a given additive is not equally effective in all the fuels [29].

The determination of CN based on traditional standards ASTM 613 consumes significant amounts of testing fuel. However, there has been an ignition quality tester manufactured and developed. This tester forms the current basis of test standard ASTM 6890 [7], where a derived cetane number (DCN) correlates with a CN obtained by the traditional standard as in most of CN data presented in most journal tables [75]. Regarding the differing CN of hexadecane and HMN, structure elements become the defining factors of a compound. Chain branching reduces the CN as in these two compounds, while increasing unsaturation decreases the CN. The second role played by the double bonds arises from the position of the double bonds in relation to CN. If the double bonds are placed or positioned more towards one end than to the middle of the chain, the CN is higher and vice versa [52]. This study's insights on CN determination are confirmed by various researchers such as [43, 67, 70]. This is shown in Table 5.2.

Branched esters are of great interest as they exhibit and show improvement in low-temperature properties (cold start). Similar to the approach used to determine kinematic viscosity, the CN of most biodiesels can be determined and approximated by the equation in which the overall CN is proportional to the amount of CN of the individual components [52, 79] as in the following equation:

$$\mathrm{CN}_{\mathrm{mix}} = \sum A_c \times \mathrm{CN}_c \tag{5.7}$$

where

$\mathrm{CN}_{\mathrm{mix}}$ is the CN of the mixture.
A_c is the relative amount (vol%) of an individual neat ester in the mixture CN_c is the CN if individual neat ester.

5.4 Biodiesel Density

Density is another of the necessary properties of biodiesel and is defined as the mass per unit volume of a liquid at a given temperature. Density is the main property that influences the conversion of volume flow rate into mass flow rate [50]. Density is vital in diesel engine performance due to the fuel metering system in compression ignition

Table 5.2 Structural formula for fatty acids and their CN

Acid chain	C:N	Type	Structure
Caprylic	C8:0	S	$CH_3(CH_2)_6COOH$
Capric	C10:0	S	$CH_3(CH_2)_8COOH$
Lauric	C12:0	S	$CH_3(CH_2)_{10}COOH$
Myristic	C14:0	S	$CH_3(CH_2)_{12}COOH$
Palmitic	C16:0	S	$CH_3(CH_2)_{14}COOH$
Palmitoleic	C16:1	US	$CH(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic	C18:0	S	$CH_3(CH_2)_{16}COOH$
Oleic	C18:1	US	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	C18:2	US	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	C18:3	US	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Arachidic	C20:0	S	$CH_3(CH_2)_{18}COOH$
Eicosenoic	C20:1	US	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$
Behenic	C22:0	S	$CH_3(CH_2)_{20}COOH$
Erucic	C22:1	US	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$

Note C:N is the number of carbon atoms and double bonds in the fatty acid chain, US is the unsaturated fatty acids, S is the saturated fatty acids
Source Adopted from [49]

engines injection systems (which is volume-based) [112]. As the fuel injection system operates on volume, the high densities of biodiesel increase the delivery mass volume, which thus increases the overall biodiesel consumption. Additionally, the cetane index of a fuel is determined from the liquid product of the fuel, thus linking it to density [114].

Density influences injection systems, pumps and injector nozzles which have to deliver a precise amount of fuel for proper combustion to take place [103]. As an important influence on injected mass [14, 15, 18], density plays a major influence on the mass injected in biodiesel fuel. Besides the merits mentioned above, density also plays a pivotal role in providing data for the reactor design, distillation units, separation processes, storage tanks design construction and process piping [99, 123]. For biodiesel use and application, density has been shown to depend on the type of feedstock and methyl ester profile of the biodiesel [16].

5.5 Cloud and Pour Point

Cloud point (CP) and pour point (PP) are another two important properties of biodiesel, especially for low-temperature use of the fuel. The CP is the temperature at which crystal clouds appear which occur under conditions explained and described in

ASTM D2500-91. The biodiesel CP varies with the type of feedstock, ester composition and the presence of any additive [31, 106]. However, the CP is adjusted depending on the existing season, for example higher during winter compared to other seasons. The PP is defined as the temperature at which the amount of wax from a solution gels or mixes sufficiently and effectively [32]. The PP can also be at the temperature at which any oil sample is movable and is determined by international standard ASTM D97-96. The CP determines the biodiesel storage temperature and handling facilities equipment design. The CP and PP help in the determination of specifications of usability of a biodiesel in cold temperature conditions. In a study conducted by Prakash [101], they reported triglycerides to contain higher CP and PP compared to conventional diesel (CD) fuel.

5.6 The Bulk Modulus of Compressibility

This is defined as a measure of resistance to compressibility by a substance, to the pressure ratio of the infinitesimal pressure increase relative to the decrease in the volume [33]. The bulk modulus is important for biodiesel fuels as it affects hydraulic behaviour during the fuel injection process [81, 90]. The bulk modulus of compressibility is of particular importance during injection because it describes how the volume of the fuel reduces, in a process called 'dilatation'. This process of bulk modulus compressibility is vital in biodiesel fuels, as these fuels comprise different types of oil samples with different molecular structures compared to conventional petroleum–diesel, which is a single fuel. The bulk modulus can be measured through observation of dilatation directly in fuel under pressure or through measurement of the speed of sound in the biodiesel sample due to the isentropic bulk modulus which is related to the speed of sound in a fluid [81]. Figure 5.1 shows the variation of bulk modulus of linear hydrocarbons versus the carbon number.

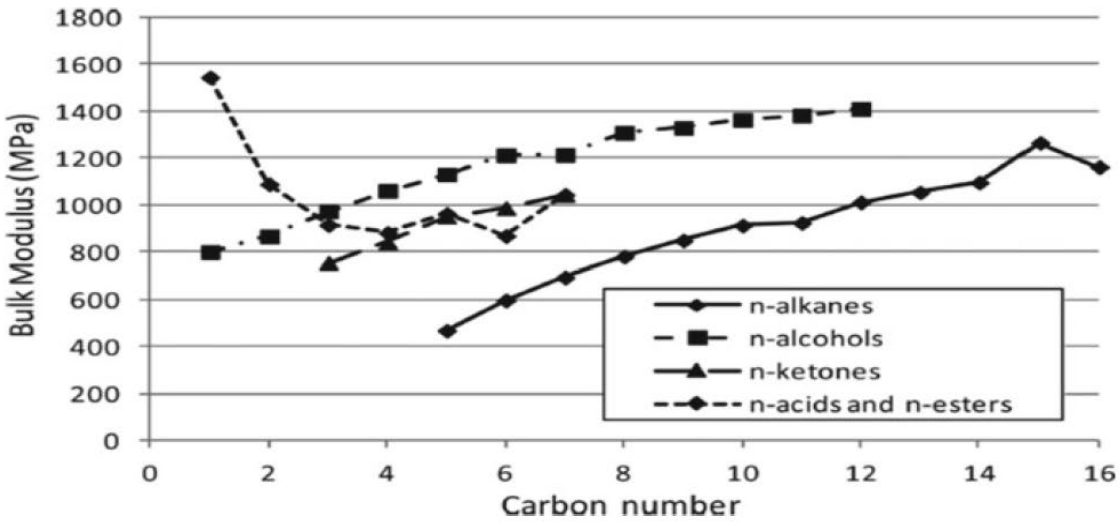

Fig. 5.1 Variation of bulk modulus of linear hydrocarbons against the carbon number. *Source* [88]

Studies in bulk modulus have reported increased advances in injection timing with the use of biodiesel fuels as compared to Fischer–Tropsch (synthetic fuels and oils) fuels [3, 25, 92, 95, 105, 116–119]. Through these studies, it has been identified that the bulk modulus of compressibility and increased speed of sound are the predominant factors in the increased advance injection timing that occurs with biodiesel fuel use. The advance in injection timing results from the early lifting of the pump-line nozzle-type injection system [25, 95, 116, 118, 119]. Although viscosity has already been shown to influence fuel injection, through rapid pressure build rise with the pump, further studies have shown that the bulk modulus of compressibility of a fuel is key and has greater influence on injection timing [3, 105]. Bridgman [19] is the person credited for reviewing methodologies for testing compressibility of fluids. He found that fluid compressibility at lower pressure is due to the consumption of the free space of the loosely packed molecules of the fluid tested. However, at high pressure the fluid compressibility is due to resistance from intermolecular repulsion.

5.7 The Speed of Sound

Biodiesel fuels are a product of transesterification of various feedstocks with short-chain alcohols, for example methanol, which form fatty acid methyl esters. Biodiesel feedstock contains glycerol esters of straight chain aliphatic carboxylic acids with carbon atoms, and even-numbered carbon chain lengths between 10 and 24. These chains might differ in their length and degree of unsaturation. These differences have great influence on the physical characteristics of biodiesels and on engine efficiency and performance.

Speed of sound, density and bulk modulus of compressibility impact operation of fuel injection system. It is imperative to know the speed of pressure wave propagation in liquids when smaller diameter pipes are used as is the case in fuel delivery and injection systems. The speed of propagation of the pressure is vital because it is equal to the speed of sound propagation through a fuel, in this case biodiesel [86, 127].

5.8 The Acid Number

The acid number in biodiesel is used to determine the level of free fatty acids (FFA) present in a particular sample of biodiesel as specified in standard ASTM D664, which is the same as for petroleum–diesel. The acid number has been lowered by the ASTM 6751 from a high from 0.8 to 0.50 [58], in order to be in harmony with the European standard of 0.25 wt% of FFA by content. The acid number is closely related to FFA content, as the higher the FFA number the higher the acid number [4, 102, 126]. The high acid in biodiesel increases corrosion and fuel system deposits and sedimentations. Additionally, a high acid number has a strong solvency effect on rubber seals and fuel hoses of the engine fuel system leading to premature failure.

Most acids in biodiesels come from two sources: the acid used during the production (even though it is removed during the production process); and from the degradation caused by oxidation of the biodiesel fuels in stored samples. Stored biodiesels have their acid numbers changed or affected over time due to the process of oxidation. Therefore, this requires frequent monitoring especially of those fuels that are not to be utilized immediately after production. High acid values in biodiesels can also possibly indicate poorly refined production or contamination. This is due to poor processing control when converting oil into FAME fuel as can be seen in Table 5.3.

5.9 The Biodiesel Ash Number

The ash number is a measure of the quantity of metals found and contained in a fuel sample specimen. The ash number is processed under standard ASTM D482 or its ISO equivalent standard ISO 6245-1993. The materials, which form ash, take three forms, namely (i) from residual biodiesel catalysts, (ii) from soluble metallic soaps and (iii) from abrasive solids. Biodiesel and abrasive catalysts contribute to rapid wear of the fuel system, the engine internal components exposed to biodiesel fuel during, and after the fuel injection, process is completed. In other words, the two sources contribute greatly to fuel pump, engine piston and piston ring wear besides the engine deposits in the fuel system. Although metallic soaps cause deposits in the fuel system, they have little effect on the wear of engine internal components. Additionally, ash in biodiesel contributes to early failure of the fuel filter due to clogging.

Due to the sensitivity of the DPF to the lubricant-derived ash, sulphated ash has been reduced and limited to not more than 1.0% of the quantity of lubricant [91]. These changes have been introduced due to the increased use of biodiesel as a blending agent with conventional diesel, which is petroleum, based. The typical blending ratios range from 5 to 20% by volume in commercial applications between biodiesel and conventional diesel.

5.10 The Calorific Value

The calorific value also known as the heat of combustion is numerically equal to the enthalpy of reaction [122]. It is a measure of heat obtained through combustion of a unit of mass (or volume of fuel) that produces the maximum possible output limit of power that can be obtained from a sample of fuel [112]. Understanding the calorific value helps us to understand the definition of 'fuel'. Fuel is defined a very widely, but generally includes the notion that fuel is a substance that undergoes physical and chemical change in return releasing large amounts of heat energy to do work. Fuels are divided into two categories:

Table 5.3 Calculated acid numbers using D974 Standard

Standard No.	Acid number by D974	Mean	SD	Repeatability[a] (%)	Real acid number[b]	Accuracy[c]
Solvent	0.057, 0.068, 0.057, 0.057, 0.063, 0.060, 0.060	0.060	0.0041	18.7	–	–
1	0.177, 0.205, 0.183, 0.194, 0.199, 0.0205	0.193	0.0116	16.6	0.198	98.0%
2	0.286, 0.302, 0.307, 0.313, 0.263, 0.287	0.293	0.0182	17.2	0.289	101.4%
3	0.371, 0.372, 0.349, 0.349, 0.333, 0.372	0.356	0.0158	12.3	0.363	98.1%
4	0.448, 0.448, 0.443, 0.464, 0.437, 0.441	0.447	0.0094	5.8	0.438	102.1%
5	0.585, 0.607, 0.601, 0.595, 0.608, 0.614, 0.583, 0.595, 0.572	0.595	0.0136	6.36	0.615	96.7%

(continued)

Table 5.3 (continued)

Standard No.	Acid number by D974	Mean	SD	Repeatability[a] (%)	Real acid number[b]	Accuracy[c]
6	0.774, 0.746, 0.782, 0.752, 0.787, 0.765	0.768	0.0164	4.1	0.757	101.5%
7	0.843, 0.841, 0.837, 0.866, 0.876, 0.846, 0.848, 0.876, 0.846	0.850	0.0126	4.1	0.865	98.3%
8	0.897, 0.899, 0.902, 0.900, 0.895, 0.891	0.897	0.0039	1.21	0.894	100.3%
9	1.142, 1.137, 1.136, 1.135, 1.137, 1.140, 1.157, 1.155, 1.141	1.142	0.0082	1.98	1.167	97.9%

[a]Repeatability expressed as a percentage of experimental mean
[b]Real acid numbers are based on the acid number of the solvent and the weight of the palmitic acid and soybean oil in the standards
[c]Accuracy = (experimental mean/real acid number) × 100
Source Adopted from [87]

- Natural fuels such as coal, petroleum, natural gas, peat, biomass and wood; and
- Synthetic fuel such as coke which is a direct result of chemical synthesis of high energy substances including nuclear energy.

However, moving from the traditional definition of fuel, we can use other criteria to distinguish and define fuel. This distinction is based on the state of matter (solid or fluid, liquid or gaseous), or depending on the source of origin (fossil or biofuel), or depending on the application of the fuel (heat production and transportation) or better still we can use the calorific value (high or low calorific value). The calorific

value is measured in a bomb calorimeter using standard ASTM D2015. Vegetable oil calorific value ranges between 37.27 and 40.48 MJ/kg [47]. Goering concluded that increased carbon chain length and reduction in the numbers of double bonds were the likely cause of increased viscosity and calorific value. However in another research by Sadrameli et al. [109], it was concluded that the calorific value of fatty acids increases with the molecular weight and carbon number bonds, but decreases with increased density. The analysis of biodiesel fuels provides the weight percentages of C, H and O contained in a sample of fuel by weight. Most vegetable oils have carbon content of 74.5–78.4 wt%, hydrogen content of 10.6–12.4 wt%, and oxygen content of 10.8–12.0 wt%.

There are two important properties of biodiesel that affect the calorific value, namely the saponification and iodine value. The decrease in the saponification value of an oil sample decreases its molecular weight. An increase in the carbon and oxygen percentages in an oil sample decreases its molecular weight. The iodine value in an oil sample affects the heat value of combustion by reducing the calorific value [32]. It is important to remember that the induction times of saturated fatty acid methyl esters are all >24 h.

5.11 The Water Content in Biodiesel

The main reason why the water content in biodiesel is measured is to accurately determine the net volume of actual fuel contained in a sample [114]. There are several methods that are used to determine the water content in a fuel sample, such as distillation, evaporation, xylene and the Karl Fischer titration methods. For example, the evaporation method relies on the measurement of the mass of water in a known mass sample before evaporation and after evaporation [32]. On the other hand, the distillation method employs direct measurement of the water that is removed from the sample by evaporation. The Karl Fischer method through titration is often used to determine the water content in low water and low-moisture oil samples.

The presence of water in biodiesel, which incorporates during the production process, transportation and storage [54, 110], presents many problems such as severe damage to the fuel injection equipment and corrosion to the storage tanks [44]. The water in biodiesel is classified into two main forms: soluble water, which is dependent on the temperature composition of the fuel, and free water, which promotes corrosion. However, considering that biodiesel fuels are largely hygroscopic in nature, longer periods of storage lead to an increase in soluble water content in a biodiesel sample [45, 100]. Free water in a biodiesel oil sample encourages and promotes the growth of biological elements in storage tank leading which exacerbates the problem of corrosion of metals such copper, iron, and steel, and formation of sludge and slime. These developments cause further fuel line blockages, fuel filter clogging, and damage to the fuel injection system [5, 20, 40, 113]. Although knowledge of water content in biodiesel is vital, it should be emphasized that the removal of water is a difficult

process in a given sample specimen. In the moisture content or water ASTM D6751 standard, the allowed water content should never exceed 500 ppm [5].

5.12 Cold Flow Biodiesel Properties

Flow properties are a concern to biodiesel producers and users, as this property affects biodiesel in its neat and blended forms of oil. Major operability problems have been shown to arise from solids and crystals, which rapidly agglomerate, plugging and clogging fuel filters and fuel lines and sometimes causing premature component failure. There are many researches which have been conducted on cold flow problems associated with cloud point (CP) [8] and pour point (PP) of biodiesel [9]. The CP normally occurs at high temperatures compared to PP, which begins occurring at lower temperatures where sample substance flow can be observed. Examples of melting points of fatty acids are shown in Table 5.4.

In mixtures, the fatty acid esters crystallize during high temperature compared to unsaturated methyl esters. Investigation for improving low-temperature (cold flow) problems of fatty acid methyl esters has suggested blending [17, 72, 89, 124] with petro-diesel, winterization [51, 83, 111]. Researchers who investigated additives [72,

Table 5.4 Melting points of fatty acid methyl esters

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Fatty acid Methyl esters	Melting point (°C)	Fatty acid Methyl esters	Melting point (°C)
8:0	−37.4	16:1 Δ9c	−34.1
10:0	−13.5	18:1 Δ6c	−1.0
12:0	4.3	18:1 Δ9c	−20.2
14:0	18.1	18:1 Δ9c	9.9
16:0	38.5	18:1 Δ11c	−24.3
18:0	37.7	18:2 Δ9c, Δ12c	−43.1
20:0	46.4	18:3 Δ9c, Δ12, Δ15c	<−50
22:0	53.3	20:1 Δ11c	−7.8
24:0	58.6	22:1 Δ13c	−3.0
Methyl dihydrosterculate	−4.4[a]	18:1 Δ9c 12-OH	−5.85
Iso-stearate (16-methylheptadecanoate)	26.8		
Methyl vernolate	0.5[b]		

[a]Methyl dihydrosterculate = C20H36O2, Methyl 9.10-methylene octadecanate calculated by Rashid et al. [107]
[b]Calculated by Knothe et al. [74]
Source Adopted from [74]

85], and esters with branching [38, 41, 82], while research in alcohol moiety or fatty acid chain includes [73, 94]. Compared to those on bulky substituent's chain such as [26–28], 55, 130].

Since the CP depends on the amount of saturated fatty acid compounds [59], biodiesel fuels of this nature naturally display high CPs and PPs. However, the general rule is that the CP is more critical than the PP in the improvement of a fuel's cold flow properties [35]. The cold flow properties of a fuel are tested using the low-temperature flow test (LTFT). This test is commonly used in North America [11]. The rest of the world and the European Union use the CEN standard [21]. In recent development, the cold soak filterability test is used to determine filtration time through a specific filter of biodiesel stored at 4.5 °C and warmed upwards to 25 °C.

5.13 Oxidative Stability of Biodiesel

This is one of the subjects that has developed considerable interest in research on biodiesel due to the technical issues surrounding it [37, 63, 64, 78, 128, 129]. Oxidation is a complex process that causes fuel to lose its stability and continually deteriorate. The oxidation process begins through the formation of hydro-peroxides with secondary reactions producing a variety of products such as aldehydes, carboxylic acids, hydrocarbons, ketones, polymers and many others [42]. Table 5.5 shows the oxidative stability of FAMEs.

The oxidative stability of biodiesel becomes an issue primarily during extended storage of biodiesel. Additionally, stability issues arise from the moisture content and microbial growth [54]. The propensity to gather water or moisture due to the hygroscopic nature of biodiesel promotes hydrolysis of fatty acids while enhancing oxidation and microbial growth [84]. These studies look at, the influence of heat, air and light, traces of metal, antioxidants and peroxide and nature of storage facilities. These studies have gone far to confirm the catalyzing influence of metals in oxidation with copper being observed as being among the most oxidative promoting

Table 5.5 Oxidative stability (induction times) of unsaturated fatty acid methyl esters

Fatty acid methyl ester	Oxidative stability (h)
16:1 Δ9c	2.11
18:1 Δ9c	2.79
18:2 Δ9c, Δ12c,	0.94
18:3 Δ9c, Δ12c, Δ15c	0
20:4 Δ5c, Δ8c, Δ11c, Δ14c	0.09
22:6 Δ4c, Δ7c, Δ10, Δ13c, Δ16c, Δ19c	0.07
18:1 Δ9c 12-OH	0.67

Source Adopted from [68, 69]

metals [71]. Additionally, the structural composition of the fatty esters especially the unsaturated esters play a prominent role in promoting oxidation of biodiesel stored oil [63].

Biodiesel oxidative stability evaluating methods have changed over time. Initially, the biodiesel oxidative this test was done by the Rancimat method, but it was changed to CEN standard [22] for neat biodiesel. However, a more recent version has been developed for investigating the blends of biodiesel and petro-diesel [23]. These two tests call for the oxidative stability times capped at 3 h and 8 h, respectively.

5.14 Biodiesel Lubricity

Lubrication can be defined as an indication of how much a fluid can protect two mating surfaces from wear through scarring caused by the friction motion between the moving surfaces [53, 96]. If fuel does not contain enough lubricating ingredients, it is considered a dry fuel [2, 121]. Lubricity gained prominence with the advent and increasing use of low sulphur fuels also known as synthetic fuels. This is mainly due to the hydro-desulphurization of the petro-diesel, which reduces the inherent lubricative properties of these petro-diesel fuels [30, 98, 120, 125]. Hydro-desulphurization not only reduces a fuel's sulphur content, but also oxygen and nitrogen-containing compounds responsible for inherent lubricative characteristic qualities [13, 30].

Lubricity is vital for the proper functioning of the engine components such as the fuel pump and injection nozzles, which are precision equipment. The failure of these components due to poor lubrication leads to poor fuel metering, poor fuel delivery and shortened service life. Lubricity is tested using the high-frequency reciprocating rig system (HFRR) as described in [12] standard or its European equivalent [61]. The most notable feature of this method of lubricity test is that the wear scars generated on the steel ball disc during testing have been shown to be directly proportional to the lubricating properties of the test sample specimen [68].

Numerous studies have been conducted on biodiesel lubricity fatty compounds and characteristics. The results show beneficial advantages on the low sulphur petro-diesel, known for poor lubricity qualities. Biodiesel compared to fuel additives contains inherent lubricative properties characteristics which are compatible with diesel fuel [57, 77]. The addition of biodiesel at low levels of 1–2% to low sulphur diesel increases lubricity of this petro-diesel. This is due to the presence of the OH group which is known to enhance lubricity in fatty acid chains [48, 77], and the presence of double bonds in the chain length. Therefore, what this concludes is there are other compounds in biodiesel besides methyl esters which are responsible for improved lubricity [77]. We can argue thus that the free fatty acids and the monoacyglycerol, viewed as undesirable due to their poor cold flow properties, could be responsible for this improved phenomenon in low sulphur petro-diesel when biodiesel is added. Therefore, more research is needed to unlock this observation conclusively.

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Chapter 6
Factors Influencing Formation of Emissions in Biodiesel

6.1 Introduction

The emission of pollutants to the environment takes two routes: the natural and anthropogenic routes. These pollutants take two forms adsorbed either as particulates or in the gaseous form. Emission particles emitted via these routes include from combustion processes, volcanic eruptions, forest fires, fumes from industrial activities, transport activities especially road transport, marine and biological materials [13]. Commonly found pollutants especially in the atmosphere are CO, NO_X, sulphate oxide (SO_X), PM, VOC, O_3 and greenhouse gases CO_2, methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbon (CFC) and nitric acid (HNO_3) [13], as in Table 6.1.

The transportation sector is one of the largest and leading sources of atmospheric pollution (especially from exhaust fumes of the engines used in propulsion) such as PM, UHC, CO, NO and O_3. This is in addition to the unregulated polycyclic aromatic hydrocarbons, which occur as a result of incomplete combustion. Studies conducted on polycyclic hydrocarbons show lower amounts of mutagenic compounds with the use of biodiesel fuels [22]. However, more needs to be done as there are still contradictory results that have been obtained pointing to need for more studies and research. As has been discussed in the previous sections, the reasons and factors for high NO_X with biodiesel fuel use are ubiquitous. There is no single reason that can be used to explain the increased NO_X emission in biodiesel [56]. Table 6.2 has some of the properties of commonly found biodiesel fuel types and their profiles.

The physicochemical properties of biodiesel could have the single most effect on the formation and production of emissions with the use of biodiesel fuels compared to petro-diesel fuel. These properties have been observed to change such combustion features such as combustion temperatures, combustion mixture residence time, position of injection, quantity of injection and NO_X emission values [56]. On the other hand, fuel properties such as bulk modulus, oxygen content, cetane number,

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https://doi.org/10.1007/978-3-030-51166-1_6

Table 6.1 Commonly found pollutants in the atmosphere and causes

Pollutants	Sources	Reactive causes
CO	Traffic and industry	Operating non-catalytic converter vehicles
NO_X	Traffic and general industry	From high- or low-temperature combustion
SO_X	Traffic	Vehicles using high sulphur content fuel
	Industry (chemical, paper, refineries and boilers)	Using high sulphur content fuels
PM	Traffic	Transportation agriculture and construction
	Industries (cement, refineries, steel, paper pulp, chemical industry	Construction and agricultural practices
Pb (Lead)	Traffic and industry	Leaded fuels and manufacturing industries raw materials containing lead
VOC	Chemical industry, traffic, fuel storage, car work-shops	Construction materials, and handling of solvents and other activities
O_3	NO_X, VOC or CO	Chemical reactions between the primary source pollutants, e.g. traffic, industries, landfills, paints and solvents (VOC), forests and other sources
CO_2	Fuels	Use of fossil fuels, deforestation and change in land use
CH_4	Commercial and economic activities	Production and consumption of energy, farming and livestock, landfills and wastewater
N_2O	Human economic activities	Fertilizer use, production of acids and burning of biomass and fossil fuels
CFC	Human economic activities	Industry, refrigeration, aerosols, propellants, expanded foams and solvents
HNO_3	Human economic activities	Combustion of wood, fossil fuels, chemical composition of fertilizers and microbes

Adopted from [13]

kinematic viscosity, density, heat capacity (calorific value), degree of saturation, surface tension and thermal conductivity can also contribute to emission and engine overall performance as can be deduced from Table 6.3.

Table 6.2 Fatty acid profiles of soybean, cottonseed, palm, Jatropha and sunflower

Fatty acid	Formula	Structure	Soybean	Cottonseed	Palm	Jatropha	Sunflower
Lauric	$C_{13}H_{26}O_2$	C_{12}:0	–	–	1.0	–	–
Myristic	$C_{15}H_{30}O_2$	C_{14}:0	0.2	0.8	2.1	0.1	–
Palmitic	$C_{17}H_{34}O_2$	C_{16}:0	10.2	22.9	44.3	14.2	–
Marganic	$C_{18}H_{36}O_2$	C_{17}:0	–	–	–	–	–
Stearic	$C_{19}H_{38}O_2$	C_{18}:0	4.6	3.1	2.2	7.0	–
Oleic	$C_{19}H_{36}O_2$	C_{18}:1	22.2	18.5	44.4	44.7	–
Linoleic	$C_{19}H_{34}O_2$	C_{18}:2	54.6	54.2	5.2	32.8	–
Linolenic	$C_{19}H_{32}O_2$	C_{18}:3	8.2	0.5	0.2	0.2	–
Arachidic	$C_{21}H_{42}O_2$	C_{20}:0	–	–	–	0.2	0.3
Gadoleic	$C_{21}H_{40}O_2$	C_{20}:1	–	–	–	–	–
Behenic	$C_{23}H_{46}O_2$	C_{22}:0	–	–	–	–	–
Lignoceric	$C_{25}H_{50}O_2$	C_{24}:0	–	–	–	–	–

Source Adopted from [28]

Table 6.3 Physical properties of biodiesel

Property	Unit	CD	WPPO	Standard
Appearance	–	Clear/brown	Clear/brown	Visual
Density @20 °C	kg/m^3	838.8	788.9	ASTM D1298
K.V@40 °C	cSt	2.32	2.17	ASTM D445
Flash point	°C	56.0	20.0	ASTM D93
Cetane index	–	46	65	ASTM D4737
Hydrogen	%	12.38	11.77	ASTM D7171
Cu corrosion 3 hr	100 °C	–	1B	ASTM D130
Carbon	%	74.99	79.60	ASTM D7662
Oxygen	%	12.45	7.83	ASTM D5622
Sulphur content	%	<0.0124	0.15	ASTM D4294
IBH temperature	°C	160	119	ASTM D86
FBP temperature	°C	353.5	353.5	ASTM D86
Recovery	%	–	98	–
Residue loss	%	–	2.0	–
Gross calorific value	kJ/kg	44.84	40.15	ASTM D4868

Source [31]

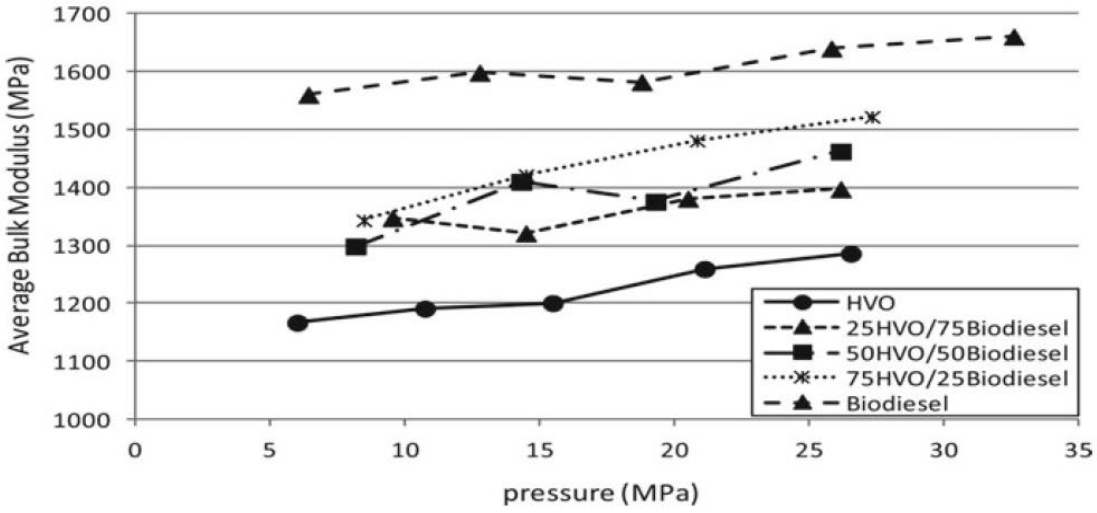


Fig. 6.1 Variation of average bulk modulus and pressure for HVO/biodiesel blends. *Source* [24]

6.2 Effects of Bulk of Modulus of Compressibility on Biodiesel Fuels

The bulk of modulus is as a measure of resistance to compressibility. The bulk modulus of compressibility increases with pressure but to decreases as the temperature increases. Figure 6.1 shows the variation of the bulk modulus and pressure of various biodiesel blend fuels and hydrogenated vegetable oil (HVO). However, the bulk modulus of biodiesel is affected by the speed (velocity) of sound and the density of the biodiesel fuel.

Higher bulk modulus of compressibility, for example, from vegetable oil and their methyl esters, is because of advanced injection timing. However, lower bulk modulus of compressibility causes retardation of injection with paraffinic fuels [58]. Yamane et al. [58] reported that density, speed (velocity) of sound and the isentropic bulk modulus of unsaturated methyl esters compared to saturated methyl esters is high. These findings were corroborated by the study conducted and reported by Tat et al. [52]. The bulk modulus of compressibility alters and modifies fuel behaviour for saturated fatty acid fuel, resulting in similar injection timing values to petrodiesel. Additionally, in another study related to bulk modulus, it was further reported that the isentropic bulk modulus, the density and speed (velocity) of sound had an approximate relationship with pressure especially within temperature ranges of between 20 and 40 °C [53].

6.3 Effect of Surface Tension on Biodiesel Fuels

Surface tension is the elastic tendency of a fluid surface to acquire the minimum surface area possible and measured in Newton per meter (N/m). In liquids, surface tension is regarded as one of the most fundamental properties that affects atomization

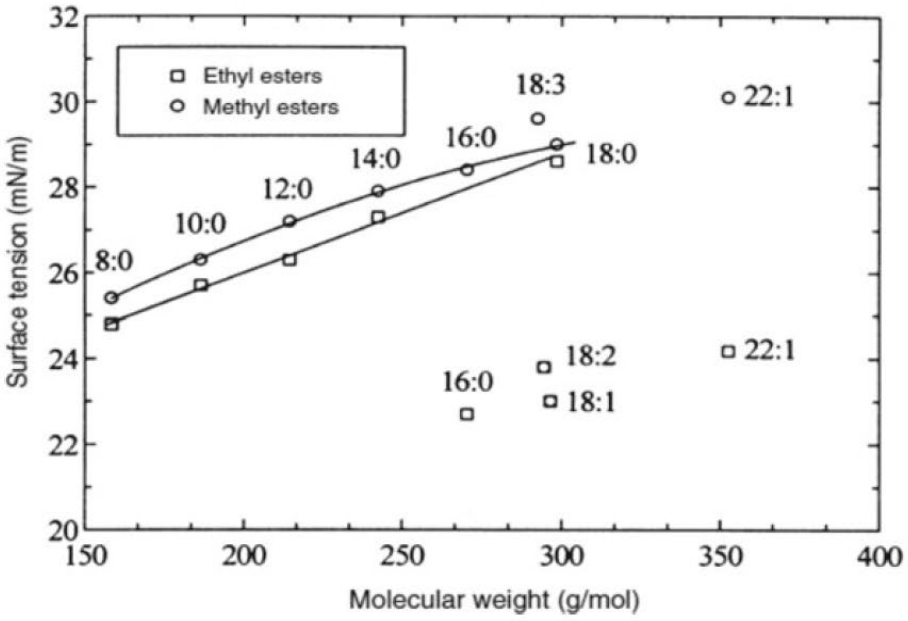
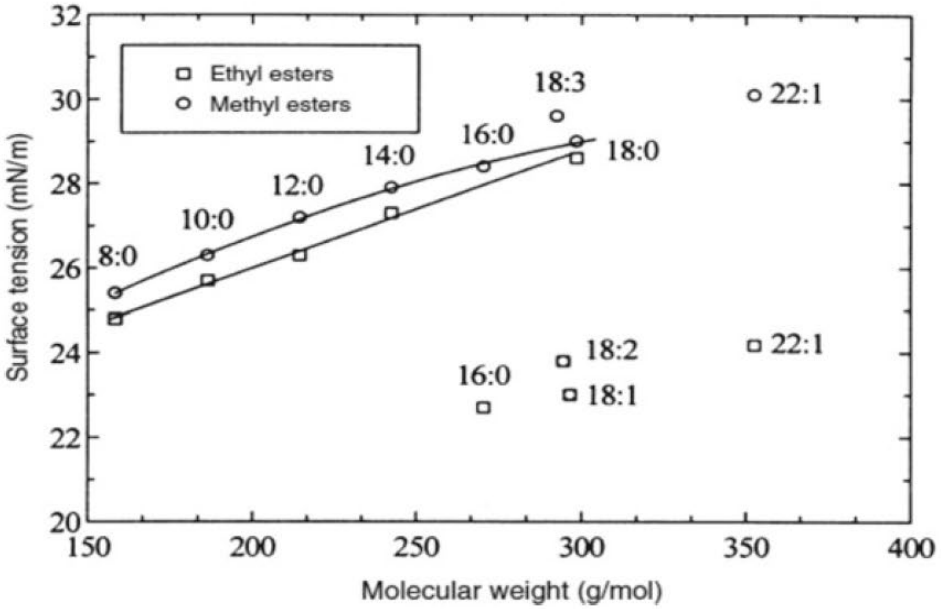


Fig. 6.2 Variation of surface tension trend and molecular weight lines for saturated methyl and ethyl ester gas chromatographic standards at 40 °C. *Source* [1]

and its characteristics in fuels in this case biodiesels [32]. Surface tension affects atomization, which is the primary factor in the first phase of combustion of biodiesel fuel. As such, the surface tension of fuel plays a pivotal role in the combustion phases of fuel in a diesel engine [1]. Although pressure does not affect surface tension extensively, it is important to remember that the operating engine injector nozzles are cooled by engine fuel during atomization. This lowers the fuel temperature, thus reducing the occurrence of vapour lock that would have been formed otherwise [43]. Figure 6.2 shows the variation of surface tension and molecular weight in g/mol for saturated methyl and ethyl esters.

Studies on biodiesel atomization, spray tip penetration and fuel droplet size have proved to be important in understanding the role of these factors in the performance and emission characteristics of a diesel engine. The research results obtained have concluded that spray tip penetration increases with the mixing ratio increase in biodiesel fuel blends. However, this causes difficulty in biodiesel fuel atomization due to the high surface tension of biodiesel fuels compared to petro-diesel fuels [26]. In studies conducted by Yuan et al. [59], it was reported that decreased surface tension of pure methyl esters did not seem to contribute to increased NO_X emissions. However, surface tension increases with unsaturation of methyl esters; in other words, increased viscosity and high surface tension in biodiesel fuels affect biodiesel fuel atomization. This is caused primarily due to the increase in the droplet sizes and the Weber number as a result of high surface tension [42]. The increase in droplet size directly increases the spray tip penetration. It should be remembered here that the biodiesel properties, droplet size and distribution and the Sauter mean diameter are greatly impacted by surface tension as a function of biodiesel blend ratio. This was corroborated in a study conducted by Lee et al. [27] using a common



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rail diesel engine. The study reported that higher blend biodiesel ratios and higher injection pressure associated with common rail designs are linked to high surface tension of biodiesel fuels. The authors concluded that high surface caused more shearing between biodiesel molecules leading to poor atomization and consequently increasing NO_X emissions with use of biodiesel blends and fuels.

6.4 The Effect of Kinematic of Viscosity on Biodiesel Fuel

Biodiesel fuels have been observed to contain high kinematic viscosity compared to petro-diesel, although they have shown inferior spray characteristics. The interaction of these factors results in a large mean diameter of biodiesel fuel droplets, thus increased ignition delay [15]. This has been confirmed in studies, which have shown reduced kinematic viscosity results in relation to reduced mass of injected fuel, therefore leading to reduced combustible quantity of the air–fuel mixture, hence reduced NO_X emissions. Research has shown that due to increased droplet mean diameter, there is also poor combustion and increased NO_X emissions. Poor atomization leads to larger biodiesel fuel mean diameter droplets, thus increasing the physical mixing time. This leads to increased peak pressure resulting in increased cylinder peak temperature, hence high emissions of NO_X [11]. Figure 6.3 shows the variation effect of kinematic of viscosity and temperature on different types of biodiesel profile properties.

Another factor regarding kinematic viscosity is its high jet penetration associated with increased injected mass volume ratio. The increase in penetration length introduces low velocity and slow mixing speed of the air–fuel near the nozzle spray tip, which results in formation of NO_X emissions [29]. The volumetric injection rate

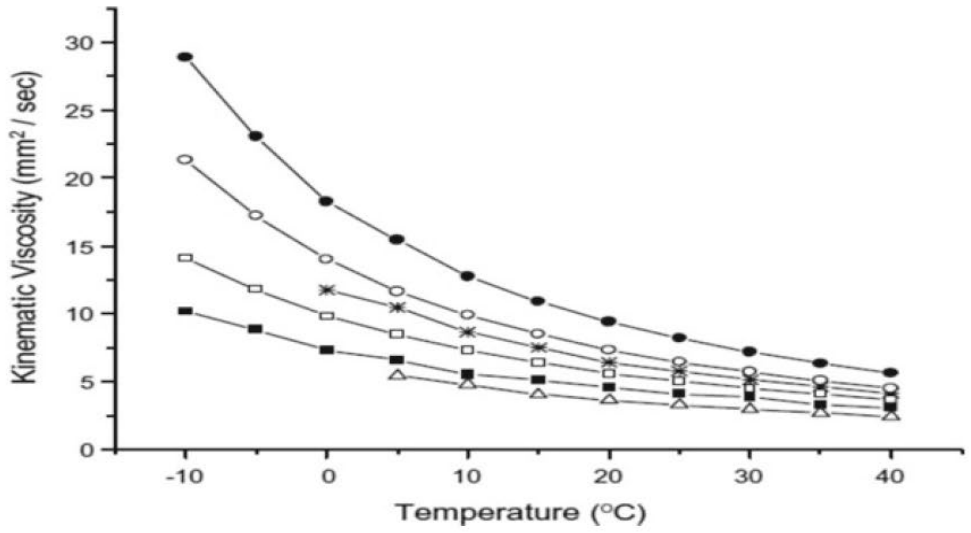


Fig. 6.3 Kinematic viscosity in the range from 40 to 10 °C for ∗ methyl soyate (biodiesel), △ methyl laurate, ○ methyl oleate, ● butyl oleate, □ methyl linoleate and ■ methyl linolenate. *Source* [20]

and velocity of biodiesel fuels are lower due to the high viscous resistance inside the injector passage [4]. As the quantity of biodiesel fuel increases, the spray tip velocity also increases, although this increase in velocity reduces the total spray volume [18, 49].

6.5 The Effect of Density on Biodiesel Fuels

Defined as the mass per unit volume of a substance, density draws a comparison with the amount of matter contained by an object in relation to its volume. Density is an important property of biodiesel, because injection systems, pumps and injectors depend on it to deliver precise amounts of fuel for proper combustion to take place [40]. In other words, density is the main factor that influences the volume and mass of fuel injected within a system [3, 5].

After looking at the definition, the next important question is how does density affect the performance of biodiesels and emission characteristics? Low density in biodiesels results in lower biodiesel NO_X emissions of 10–12% by the weight of the fuel-bound oxygen. The presence of high oxygen content of this magnitude lowers the energy density, resulting in a greater increase in the injected mass volume of fuel; this happens in order to achieve the same output from the engine [10]. Figure 6.4 shows the variation of density as a function of temperature for soybean blend samples.

Increased biodiesel density increases injection duration as well as advanced injection timing, factors whose interaction results in increased NO_X emissions as more fuel is injected and burnt, hence increased combustion chamber temperature [38].

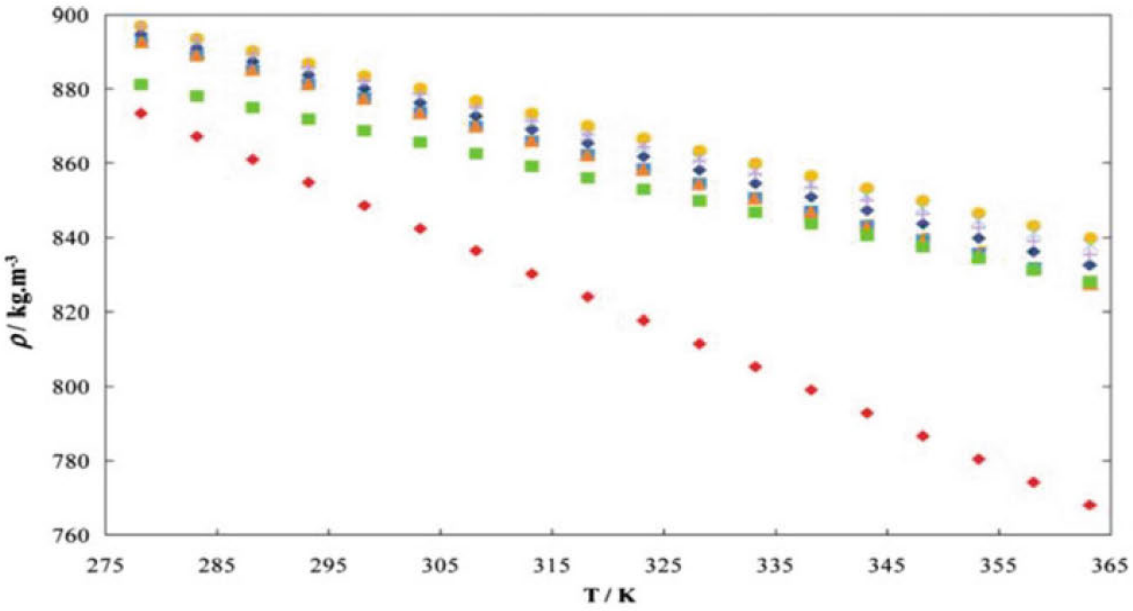


Fig. 6.4 Density values as a function of the temperature for different soybean biodiesel samples. *Source* [40]

Another interesting reporting with biodiesel density is ignition delay. In other words, earlier injection timing results in an earlier combustion phase. This case is made urgent by the introduction of electronic diesel fuel injection system, which computes fuel by volume. This seems to suggest that any change in biodiesel density will automatically affect the volume of fuel injected, hence influence NO_X emissions [2].

6.6 The Effect of Thermal Properties on Biodiesel Fuels

Thermal properties of biodiesel include thermal conductivity and thermal diffusivity. These are properties which characterize heat transfer behaviour in biodiesel fuels and quality of the produced biodiesel and thermal processing [6]. The knowledge of thermal properties is important because of the mechanical and thermal processes of biodiesel production whose feedstock is exposed to natural and unnatural changes of temperature [7]. Biodiesel blends have higher boiling points compared to petro-diesels. Expressively, increase in the biodiesel percentage ratio increases the boiling point causing incomplete combustion in the engine combustion chamber. This is the leading cause of particulate emissions and largely the increase in unburnt hydrocarbons with application of biodiesel fuels.

Liquid thermal conductivity and the vapour heat capacity have been reported by McCrady et al. [33, 34] to influence the heat transfer between the interior and exterior surfaces of the fuel droplets and the surrounding temperature distribution of the mixture biodiesel spray droplets and its fuel ratio. This is due to the lower heat capacity of biodiesel fuel compared to petro-diesel. This affects the energy balance and temperature distribution that surrounds the spray droplets from the injector nozzle into the combustion chamber [9]. However, the factor attributed for the increase in NO_X is the poor radiative heat, which is being transferred inside the combustion cylinder. This is due less soot being formed, a factor attributed to biodiesel spray droplets' temperature distribution, hence reduced NO_X [50]. It should be remembered that soot formation is a pre-cursor to the formation of NO_X.

In their study, Takeda et al. [51] concluded that the low-temperature mode of combustion (LTC) reduced NO_X and other emissions as this combustion model produces lower average cylinder temperature from the engine due to high thermal efficiency. In a thermo-gravimetric study conducted by Lujaji et al. [30] to find the relational changes in chemical and physical properties of biodiesel as a function of increasing temperature against time, the authors found a large and strong relationship between biodiesel thermal characteristics and cetane numbers. Thermo-gravimetric studies is a form of thermal analysis which measures changes in chemical and physical properties of a biodiesel fuel as a function of increasing temperature with increasing time [56].

6.7 The Effect of Cetane Number on Biodiesel Emissions

The cetane number is a dimensionless measurement of the ignition quality of any fuel used for propulsion purposes in an engine. Biodiesel fuels are multi-component mixtures of 5–6 methyl esters especially if methanol is used as a catalyst during the transesterification process [55]. As such, the major constituents of biodiesel fuels include methyl palminate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2) and methyl linoleate (C18:3) [19]. These esters contain their own effect on biodiesel properties due to the straight chain saturated and unsaturated compounds. A saturated fat is one that cannot chemically accept additional hydrogen and contains single carbon bonds [11], while unsaturated fats can accept addition of hydrogen and can contain more than one double bond [12].

Increased chain length for the saturated methyl esters, for example, leads to increased viscosity resulting in poor cold flow and cold start properties of biodiesel. However, this increased viscosity results in increased cetane number and improved engine performance [19, 21]. This was corroborated in a study conducted by [57] in which it was concluded that higher cetane number values in biodiesel fuels resulted into low NO_X emissions during combustion.

6.8 The Effect of Fuel-Bound Oxygen on Biodiesel Emissions

The presence of higher oxygen content in biodiesel helps with complete combustion and so reduction in emissions of UHC, CO, PM and other emissions. One of the key biodiesel characteristics distinct from fossil fuels is the amount of oxygen bound in the fuel [16]. Although there are two oxygen atoms in one fatty acid methyl ester (FAME), the oxygen content is dependent on FAME properties especially the carbon chain length and the degree of unsaturation [39]. However, it has been observed through study that this advantage of high combustion efficiency tends to increase the combustion reaction temperatures leading to high NO_X emissions formation. Figure 6.5 shows the variation of NO_X and CO emissions with oxygen content percentage at different engine speeds.

The oxygen content plays a pivotal role in the formation of NO_X emissions owing to the excess HC oxidation as reported by [41, 48]. Song et al. [48] further reported a relationship of intake oxygen and oxygenated fuels as factors responsible for increased NO_X emissions with the use of biodiesel. It is important to remember that the emissions of NO_X respond to the content of oxygen in a fuel, adiabatic temperatures and fuel spray characteristics.

In their study, Mueller et al. [36] reported that fuel-bound oxygen influences the stoichiometric mixture especially during lift-off length, thus increasing the NO_X emissions. The result of that study was confirmed by Kumar et al. [23] who reported that oxygenated fuels aid complete combustion compared to non-oxygenated fuels.

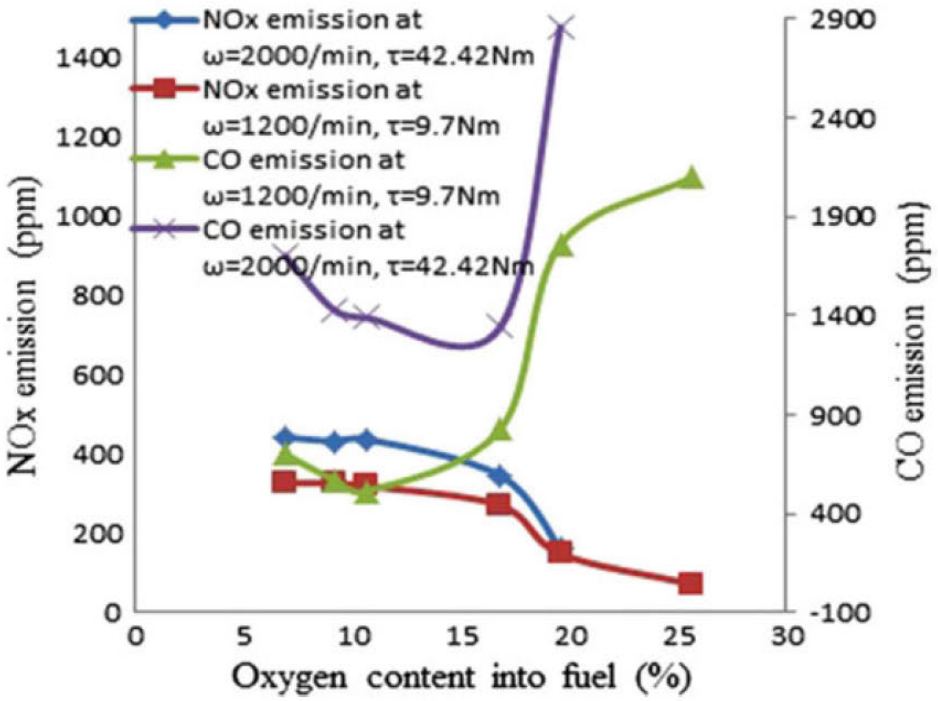


Fig. 6.5 Effect of fuel oxygen content on NO_X and CO emission. *Source* [44]

This implies more fuel for combustion, which directly interferes with the stoichiometric balance of the air–fuel ratio. In other words, a decrease in fuel-bound oxygen reduces soot formation, thus lessening the radiative heat transfer at elevated reaction temperatures leading to increased NO_X emissions. Therefore, it is important to point out here that reduction in fuel-bound oxygen does not reduce NO_X but is responsible for reducing other components that contribute to the overall reduction in NO_X emissions [45].

However in a parallel study conducted by Magin [25], it was reported that contrary to earlier findings on the role of the oxygen content, they found no link between oxygen content and the increase in NO_X emissions with application of biodiesel fuels in diesel engines. Instead, they point out that the increase in NO_X in biodiesel is caused by diffusion combustion mainly from regions with oxygen–fuel ratio around the stoichiometric level of 2.81 for biodiesel compared to 3.58 for petro-diesel fuels. However Moser et al. [35] reported that fuel-bound oxygen is the main factor responsible for the high NO_X emissions with the use of biodiesels. This is due to the generation of a permanent dipole moment in the molecule, which is stronger and increases the molecular affinity of oxygenated fuels. This chain of events tending to reduce the molecular space thus decreases the compressibility, hence increases NO_X emissions. The role of fuel-bound oxygen in biodiesel is still a very controversial subject, just as combustion is with differing points of view.

6.9 The Role of Fuel Composition in Biodiesel Emissions

The chemical composition of fuel plays a pivotal role in determining fuel properties, hence the quality and performance of a diesel engine and its emissions [36]. Historically, fuels have been refined from fossil fuels, which are recovered from the earth's surface. These liquid phase hydrocarbons (HCs) have been the main and primary fuels from transportation and non-road applications. However, due to the non-renewable nature of fossil fuels, the search for renewable fuels has intensified and gained traction. Currently, fuels are not limited to fossil sources only but can be created from biomass, solar energy, atmospheric CO_2, etc. Alternative fuel can play a major role in addressing the concerns leading to a carbon neutral economy and sustainability in the energy sector [17]. Hydrogen as a single fuel is an example of an alternative fuel, considering that hydrogen is a cleaner fuel which produces no CO_2, PM and UHC emission when combusted. However, as a single fuel hydrogen faces decreased cold starting ability especially at low temperatures besides causing unstable combustion. As a result, blending of hydrogen fuel with conventional fuels is preferred.

The double bonds and configuration positions play an important role in influencing the physical properties found in biodiesel fuels. In other words, unsaturated fatty acids become converted to form trans-configuration by isomerization, making the physical properties of unsaturated and saturated fatty acids to be equal. This was confirmed by Hess et al. [14] in a study which used reformulated biodiesel in order to reduce NO_X emissions. In their study, the authors reported that isomerized biodiesel was responsible for a 2.7% increase in NO_X emissions. Additionally, they noted that besides transesterification, the number of double bonds in unsaturated fatty acids was reduced by hydrogenation or during blending if saturated methyl esters were added to the biodiesel fuel.

High CP, high degrees of saturation and longer chain length of fatty acids cause fuel filtration system clogging. As a result, many approaches have been adopted to mitigate the higher CP in biodiesel, through blending, use of fuel additives and selection of quality feedstock. These approaches have been shown to reduce NO_X emissions in saturated and unsaturated fatty acid ratio by a factor of 5.7 [46]. Blending has shown very good results in biodiesel which have been corroborated in research findings and experimental work, for example, in a study conducted by Chapman et al. [8]. The authors in their study blended and tested caprylic acid methyl ester (C8:0) with capric acid methyl ester (C10:0) in B100. The results showed a reduction of 2.8% for blended biodiesel compared to petro-diesel. The authors thus concluded that saturated components in a biodiesel could be fraternized to produce higher NO_X even with the presence of unsaturated components in a biodiesel.

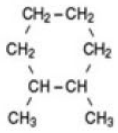
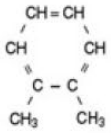
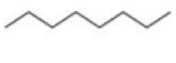
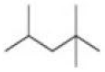
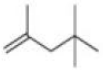
Hydrocarbon class	Unbranched alkane	Branched alkane	Olefin	Cyclic alkane	Aromatic
Representative compound	*n*-Octane	2,2,4-Trimethyl-pentane (*iso*-octane)	2,4,4-Trimethyl-1-pentene	Trans-1,2-dimethyl-cyclohexane	1,2-dimethyl-benzene (*ortho*-xylene)
Chemical formula	C_8H_{18}	C_8H_{18}	C_8H_{16}	C_8H_{16}	C_8H_{10}
Condensed or dash structural formula	$CH_3(CH_2)_6CH_3$	$CH_3-CH(CH_3)-CH_2-C(CH_3)_2-CH_3$	$CH_2=C(CH_3)-CH_2-C(CH_3)_2-CH_3$		
Bond-line structural formula					

Fig. 6.6 Representative molecules from the five HC classes with carbon number $n = 8$ Molecules. *Source* [37]

6.9.1 Hydrocarbons

Typically, petro-diesel and biodiesel fuels contain five classes of hydrocarbon compounds, namely branched alkanes, unbranched alkanes, cyclic alkanes, olefins and aromatics. These classes have concentrations that are a function of their processing and production. The number of the total carbon atoms in a compound is called the carbon number denoted with small (n) as in Fig. 6.6.

6.9.2 Branched Alkanes

Branched alkanes are commonly referred to as iso-alkanes or iso-paraffins. Like unbranched hydrocarbon alkanes, branched alkanes contain saturated hydrocarbons with a chemical formula in the order of C_2H_{2n+2}. However, the distinguishing feature is that their carbon atoms in their molecular structure are longer and arranged in a single linear chain. In other words, there are two extensions from the main hydrocarbon chain as shown in Fig. 6.7.

Fig. 6.7 Branched alkanes showing extension from the main HC chain

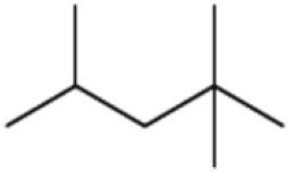


Fig. 6.8 Unbranched alkanes

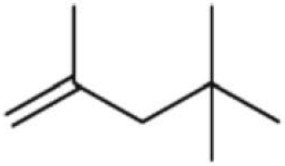


Fig. 6.9 Example of olefin showing a branched structure with double bonds between the first and second position

6.9.3 Unbranched Alkanes

The unbranched alkanes are known as the normal alkanes, n-alkanes or n-paraffins. Unbranched alkanes are also called saturated compounds due to their composition of the maximum number of hydrogen atoms in their molecular structure. This means chemically unbranched alkanes are saturated and are unable to accept any addition of hydrogen atoms. Unbranched alkanes contain straight chain hydrocarbons with only one single bond between their carbon atoms positioned in a zigzag linear chain as in Fig. 6.8.

6.9.3.1 Olefins

Referred to as alkenes, the olefins are types of hydrocarbon known to contain at least one carbon bond or one double carbon bond. They are low in concentration during production and refining of petroleum products; however, they are predominantly high in thermal cracking processes especially in pyrolysis production of biodiesel fuels.

Olefins include ethane, propene, butenes and butadiene. Ethylene and propylene are used in chemicals and plastic products, while butadiene is used in making synthetic rubber. Olefins can exist both as unbranched or branched or even cyclic structures as shown in Fig. 6.6. It should be remembered that an olefin is classified as an unsaturated compound due to the possible addition of a hydrogen atom without affecting the structural arrangement of the carbon atoms. For example, by adding two hydrogen atoms to the olefin in Fig. 6.9, it can be converted into an iso-octane.

6.9.3.2 Cyclic Alkanes

Known as the cyclo-alkanes or naphthenes, this type of alkanes is classified as saturated compounds. Their carbon atoms are arranged in one or more ring structure with 3–9 carbon atoms in each of the ring structure. The chemical formula is CnH2n, with most of the 5-6-membered ring structure being more stable due to low carbon bond strains. The 5-6-ringed structure is more abundant in petroleum-derived fuels. It is important to note that cyclo-alkanes are not coplanar. For example, in 5-ring carbon

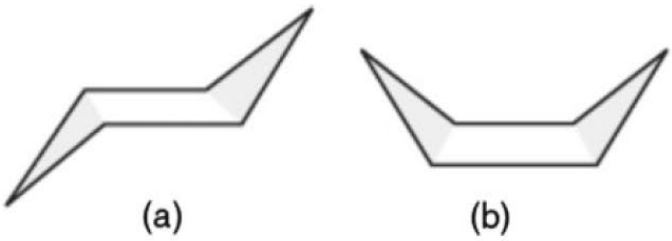


Fig. 6.10 Conformation in 6-ring carbon structure of a cyclohexane **a** chair **b** boat

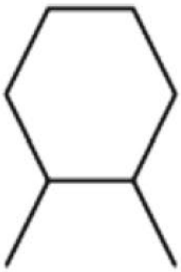


Fig. 6.11 Structural formation of a cyclo-alkane

ring structure, one carbon atom is raised above the plane of the four others, while in a 6-ring structure, several conformation configurations can be observed. The two most common conformations being the 'chair' and the 'boat' [37], as in Fig. 6.10a, b.

The molecules in these arrangements can change conformation (introvert) approximately one million times per second at standard conditions [47]. Additionally, conformational differences among molecules can result into stereoisomerism with molecules of the same chemical formula but different arrangement of their atoms in structural space. Cyclo-alkanes that one or more branched or unbranched chain sides (substituents) are predominantly common in stereoisomerism as in Fig. 6.10. However, when both the substituent project above the cyclohexane ring, the nominal plane becomes a cis isomer, while the reverse becomes a trans-isomer. For example, the trans-1, 2-dimethyl cyclohexane in Table 6.2 has methyl substituents that are bonded to the carbon atoms in the first and second position while projecting one above and one below the nominal plane (Fig. 6.11) [37].

6.9.3.3 Aromatics

Aromatics are unsaturated compounds whose carbon atoms are arranged in one or more ring structures; aromatic hydrocarbon benzene contains one or more alkyl substituents. For example, benzene which is a common hydrocarbon has chemical formula C_6H_6, with all the six carbon atoms lying in the same plane as shown in Fig. 6.12.

Fig. 6.12 Structural arrangement of the aromatics bond line

6.9.3.4 Fuel Oxygenates

Fuel oxygenates are the second-largest group of compounds contained in modern types of fuel and biodiesel fuels. Oxygenated fuels are composed not only of hydrogen and carbon but also contain oxygen hence the name. The most commonly found oxygenated fuels are alcohols, with a general formula R–O–H, where the R represents an HC radical from the ethyl alcohol radical C_2H_5, which is from ethanol (C_2H_5OH). Ethanol is the most commonly used and the leading additive in gasoline propelled SI engines in the USA and Brazil. The FAME methyl esters are the second group of fuel oxygenates and assume a structural formula R–(C=O) O–R′. The R and R′ represent the HC radicals. Esters enter fuels as FAMEs, but they can also be derived using chemical and biological processing techniques.

The third common group of oxygenated fuels comprises the ethers which have a general formula R–O–R′, where R and R′ represent HC radicals that are different from R–(C=O) O–R′ oxygenates. The most common known ether fuel is methyl tert-butyl ether (MTBE) which the USA EPA approved in 1980 for 15% volume use in SI engines but later banned it in 2004, although some countries still use it in gasoline. When MTBE is used as an additive in diesel fuel, it significantly reduces soot emissions as most ethers contain a CN > 60 [54].

The fourth component contained in fuel are the ketones, with a general formula structure R–(C=O)–R′. Among the commonly available ketones is the solvent acetone (dimethyl ketone) with chemical formula $CH_3(C=O)CH_3$, although it is not available in high concentrations in modern fuels. It can be produced using biological process synthesis, which is a promising venture in smart fuel and biodiesels in the near future.

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Chapter 7
The Factors Influencing Formation of NO_X Emissions in Biodiesel Fuels

7.1 Introduction

The cause for high NO_X emissions in biodiesel combustion is conflicting and disputable in research circles. The idea of vegetable oils as fuel for compression ignition (CI) engines is not a new concept. In the 80s, there was an increased effort to utilize biofuels as a replacement of fossil-derived fuel [34]. Many researchers have tried to explain the factors that influence the formation of NO_X emissions with the use of biodiesel in diesel engines. For example, [4, 14–16, 25, 31, 36–38, 41, 42, 45, 46, 57, 58, 63, 64, 73, 82, 84–86, 91, 95, 96, 103, 108, 110, 112]. However, other researchers [48, 67, 80, 86] have found high and reduced NO_X by use of biodiesel in compression ignition engines.

Although biodiesel as a fuel when used in diesel engine reduces emissions of PM, UHC and CO significantly, it increases NO_X emissions by 10–23% compared to petro-diesel fuel. The reasons for the increase in NO_X emissions have been linked to the physicochemical properties of biodiesel by researchers such [11, 109, 115]. Additionally, Lin et al. [63, 64] suggested that the high oxygen content could be the cause of increased NO_X. This is due to incomplete combustion, reduced UHC, and CO emissions, increased combustion temperatures hence NO_X formation.

Research in emissions has shown that there are many factors, which play a critical role in the formation of NO_X emissions. These studies have continued to report high isentropic bulk modulus and pump-line-nozzle injection systems as the cause of increased mass delivery of biodiesel and residence time leading to high reaction temperature hence NO_X [29]. However, when a common rail fuel injection system was used by McCormick et al. [72], the authors reported no increase in the NO_X emissions, although [118] also using a common rail fuel injection, reported an increase in NO_X emissions. This leads to the conclusion that the increase in NO_X cannot be attributed to advanced fuel injection timing only. In their study [8] attributed the high NO_X in biodiesel fuel as being due to the impact of three components of combustion, namely, adiabatic flame temperature, heat release rate and stoichiometric burning

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(burnt fraction mass). The adiabatic flame temperatures for biodiesel fuel have been observed to be higher compared to petro-diesel of the fuel-bound oxygen. However, in their study, [74] refuted this findings in their work and stated the contrary and opposite view.

In 2011, Kegl [45] reported that the high heat release of biodiesel could be responsible and a possible reason for increased NO_X. However, in another study conducted by Szybist et al. [100] that finding was disputed; the authors reported the heat release rate to be lower in biodiesel across all engine loads. These finding were confirmed by Bittle et al. [9] in an extensive work which liked increased NO_X to increased ignition delay. Increased ignition delay has been reported to cause increased pre-mixed burnt fraction, which is a predominant factor in NO_X formation [77, 111]. This study on ignition delay further shows that the lower calorific value of biodiesel fuels causes more quantity of injected biodiesel to be consumed. This in return increases combustion temperatures and hence the higher NO_X emissions [95].

Other researchers such as Allen et al. [3] state that the reasons for increased NO_X with use of biodiesel are related to the Sauter mean diameter. This group of researchers argue that the Sauter mean varies from 5 to 40% compared to the petro-diesel Sauter mean diameter. This phenomenon reduces the pre-mix phase of combustion, leading to increased diffusion of combustion hence high emissions of NO_X. The USA Natural Renewable Energy Laboratory has added its voice to this debate by pointing fingers at the prompt NO_X route and its mechanisms. This institution has suggested the use of antioxidants as a control strategy for prompt biodiesel NO_X emissions [71].

7.2 The Effect and Role Pre-mixed Burnt Fraction

The oxygen content reduces the quantity of the air that the injected fuel jet mixes with before combustion takes place. This reduced energy density necessitates greater fuel quantities to be pre-mixed to form a pre-mixed burnt fraction (PMBF) with equal proportions of the total energy [83]. The reduction in energy observed through increased injection duration, and hence, reduction in available energy (injected fuel) in the cylinder at any moment between start of injection (SOC) and end of injection (EOI) results in a diminished pre-mixing process. Large PMBFs have come to be associated and correlated with increased NO_X emissions [56, 76] due to the following correlation factors:

- Large PMBF for a given SOC releases more heat earlier in the combustion diffusion phase. This means that the earlier pressure and temperature rise increase, the less expansion cooling occurs (more compression heating occurs) before maximum pressure point hence high exhaust peak cylinder temperatures. This has been corroborated in studies by Ladommatos et al. and Musculus [50, 76].
- Lack of access to immediate cooling of the high temperature combustion products of the pre-mixed flame from the cooler regions of the in-cylinder gas compared

to the products of the diffusion flame. This leads to the combustion products of pre-mixed flame maintaining high temperatures for longer periods because of lack of quick diffusion into the cool surrounding gas areas [76].

- Due to less soot in the combustion chamber with use of biodiesel fuel, the radiative heat losses would naturally be reduced, leading to increased higher actual temperatures [77].
- Contributions from prompt NO_X via the NO route oxidation have been dealt with extensively in Chap. 2 and in literature in the subsections of this work and by researchers such as [5, 33, 66, 68]. It should be recalled that biodiesel generates higher prompt NO_X as a result of high hydrocarbon radicals in the flames, as a consequence of increased unsaturated molecule quantities in biodiesel fuels [28, 93].

Although biodiesels have shorter ignition delay which leads to advanced SOC, hence increased NO_X, it helps in the direct reduction of the pre-mixed burnt fraction thus explaining further the reduction in NO_X. At the point of ignition, the biodiesel jet length is approximately similar to that of petro-diesel [75]. This has been attributed to late spray break-up of the biodiesel jet which gives it greater penetration rate compared to petro-diesel as it contains large droplet diameter [10]. Additionally, it has been reported that the biodiesel jet is narrower thus entraps less air. These converging factors (late droplet break-up and large droplet diameter size) cause a number of complexities such as [10, 35, 49, 55, 65, 94].

- Poor atomization and a
- Shallower or narrow spray angle as well as
- Higher viscosity,
- High surface tension,
- High density values,
- High heat capacity and higher boiling points (slow evaporation) and
- Higher pre-mixed burnt fraction.

These challenges have been shown by this above-mentioned researcher to affect the PMBF.

7.3 The Effect of Hydrogen and Addition of Hydrogen

Hydrogen (H_2) is a zero carbon fuel which produces zero particulate matter emissions, total hydrocarbons (THC), CO and CO_2 when combusted [43]. However, as a fuel hydrogen suffers from a very low CN making it hard to be used in diesel engines as they depend on self-ignition of the fuel [102]. Therefore, hydrogen in diesel engines requires aspiration or injection into the cylinder, while the diesel fuel injected will act as a pilot ignition fuel [53, 59]. Although hydrogen requires a low amount of energy to ignite, it has a very high flame propagation rate compared to any hydrocarbon fuel, especially at lower temperature conditions. This is explained

by the fact that hydrogen is a fast and thermally neutral fuel with branching reaction chains compared to other hydrocarbon fuels which have slow endothermic chain reactions [43].

The heat release rate for H_2 is higher compared to petro-diesel fuel combustion thus leading to a short combustion duration with minimum heat loss to the surrounding environment. This leads to increased and improved thermal efficiency for H_2 compared to any other hydrocarbon fuel [19, 69, 87]. However, Christodoulou and Megaritis and Masood et al. [19, 69] reported a deterioration in the thermal efficiency when H_2 was used with diesel blend at low speed and engine load conditions. This was attributed to the incomplete combustion of all the H_2 aspirated into the combustion chamber of the diesel engine. In a follow up study conducted by Tsolakis et al. [105] on the effects of H_2 in a diesel engine without exhaust gas recirculation (EGR) using 20% ROME. The researchers reported and concluded that the addition of H_2 through the engine intake decreases NO_X and smoke emissions simultaneously. This was attributed to the hydrocarbon fuel replacement by hydrogen from the addition of H_2 and subsequent reduction of hydrocarbon fuel injection into the engine. The small ratio of H_2 increased ignition delay by 2°CA, although it increased the combustion duration by a further 5% compared to when B20 and ULSD were used without H_2. However, it is important to note that the engine efficiency and combustion quality remained unaffected.

7.4 The Effect of Adiabatic Flame Temperatures

The adiabatic temperature from unsaturated molecules is higher compared to saturated molecules [6]. Biodiesel fuels have been observed to give higher adiabatic flame temperatures compared to petro-diesel fuel due to their high concentration of unsaturated molecular structure. However, studies that have been conducted with calculation of adiabatic flame temperature for fuel surrogates reported that the stoichiometric adiabatic flame temperature for biodiesel could be lower [30, 75] or equal to petro-diesel [18, 32]. Despite this, there still exists a large difference in adiabatic flame temperatures between petro-diesel and biodiesel especially due to the local oxygen equivalence ratio [18]. The oxygen content in fuel-rich regions of the combustion chamber produces an equivalence ratio closer to unity [83], which leads to higher adiabatic flame temperature as compared to petro-diesel under similar fuel–air mixing conditions [1, 18, 75]. Figure 7.1 is a variation of adiabatic flame temperature and the oxygen content with NO_X emissions with addition of pentadecane.

This seems to explain the rapid increase in thermal NO_X formation with application of biodiesel as fuel. In a study conducted in gas turbines by Glaude [30] concerning adiabatic temperature with use of biodiesel and petro-diesel on NO_X emissions, the authors reported that biodiesel fuels emit less NO_X compared to petro-diesel due to low adiabatic temperature during biodiesel combustion as shown in Table 7.1 for sampled biodiesels.

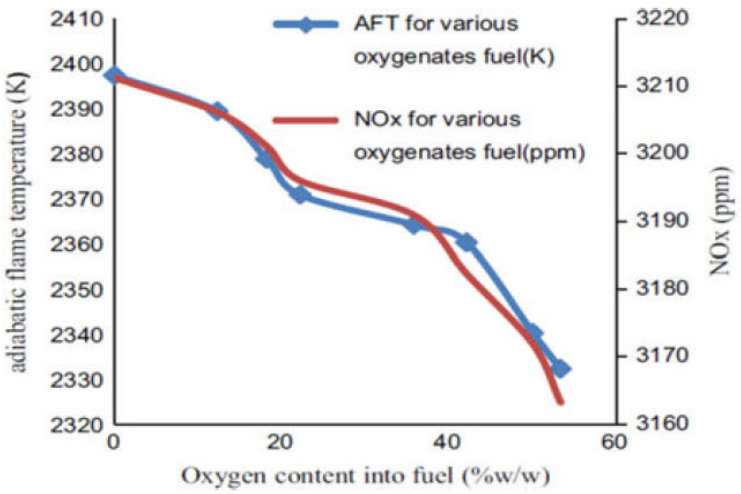

Fig. 7.1 Adiabatic flame temperature (T_{ad}) and NO_X emissions with pentadecane and differently oxygenated fuels ($\varphi = 1.0$). *Source* [78]

7.5 Chemical Kinetics of Biodiesel Fuels

Chemical kinetics is a study of how fast chemical reactions take place at a molecular level by the change in their concentration with time and reaction mechanisms. It is important to stress here that chemical kinetics is the final factor which controls combustion and other reactions. Mixing (decreasing bulk difference) requirements for combustion, and as a natural process, does not require expenditure of energy. If fuel and an oxidizer gas are allowed contact and enough time, a perfect mixing can take place within their energy level (temperature), relative speeds and chemical compositions. The factors which affect the speed of reactions are

- Reactant concentration
- The action of catalysts
- The surface area
- The pressure of the gaseous reactants of a product.

7.5.1 Elementary Reactions

The overall reactions of a mole of an oxidizer to form combustion products can be expressed using this example of a global reaction mechanism equation:

$$F + aO_x \rightarrow bPr \tag{7.1}$$

However, from experimental measurements, fuel is consumed as a function of time which can be expressed mathematically as

$$\frac{\mathrm{d}[X_F]}{\mathrm{d}t} = -k_G(T)[X_F]^n\left[x_{O_x}\right]^m \tag{7.2}$$

Table 7.1 T_{ad}, at constant pressure, stoichiometric mixture for the different fuel by using software GASEQ

Fuel condition	DF1 (C/H) 0.537	DF2 (C/H) 0.555	DF3 (C/H) 0.671	ROME –	SOME –	SME –	POME –	TOME –	Naphtas (C/H) 0.476	Naphtas (C/H) 0.515	NG Alaska	NG Libya
Case: 1	2291	2292	2309	2287	2291	2290	2279	2278	2281	2287	2227	2245
Case: 2	2560	2560	2578	2556	2559	2558	2547	2546	2548	2453	2449	2509
Case: 3	2523	2523	2541	2519	2522	2521	2510	2509	2511	2517	2454	2470

Adopted from [30]

Note Case 1: $T = 300$ K, $P = 1$ atm; Case 2: $T = 673$ K, $P = 13$ atm, Case 3: $T = 623$ K, $P = 115$ atm

where

O_x is the oxidizer,
x_i is the molar concentration (kmol/m^3) of the ith species in the mixture,
k_G is the constant of proportionality or the global rate coefficient as a function of temperature and is therefore never constant, with the –ve sign indicating the decreasing bulk of concentration with time,
n is the exponential reaction order with respect to fuel,
m is the exponent reaction with respect to the oxidizer with $n+m$ being the overall reaction order.

For example, let us consider the global reaction of hydrogen conversion and oxygen to become water and the intermediate species from sequential processes as

$$2H_2 + O \rightarrow 2H_2O \tag{7.3}$$

$$H_2 + O_2 \rightarrow HO_2 + H \tag{7.4}$$

$$H + O_2 \rightarrow OH + O \tag{7.5}$$

$$OH + H_2 \rightarrow H_2O + H \tag{7.6}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{7.7}$$

From Eq. 7.4, when oxygen and hydrogen molecules collide and react, it is important to note that no water is instantly formed, instead intermediate species of HO_2 (which is a hydroperoxy radical) are formed and a hydrogen atom H [106]. It is important to remember that radicals are reactive molecules or atoms with an unpaired electron. In other words, to form these radicals HO_2 from H_2 and O_2, there is chemically one bond, which was broken, and one bond, which formed. The hydrogen atom created in Eq. 7.4 thus reacts with O_2 to add two radicals OH and O in Eq. 7.5. However, what finally forms water is the reaction in Eq. 7.6 of the hydroxyl group OH with molecular hydrogen that finally combine to form water although there could be other reactions that could be considered from these chains [26, 27, 44].

7.5.2 *Bimolecular Reaction and the Collision Theory*

Reactions of interest in combustion studies are bimolecular reactions with two molecules colliding to form two different concentrations (kmol/m^3) as shown in Eq. 7.8.

$$A + B \rightarrow C + D \tag{7.8}$$

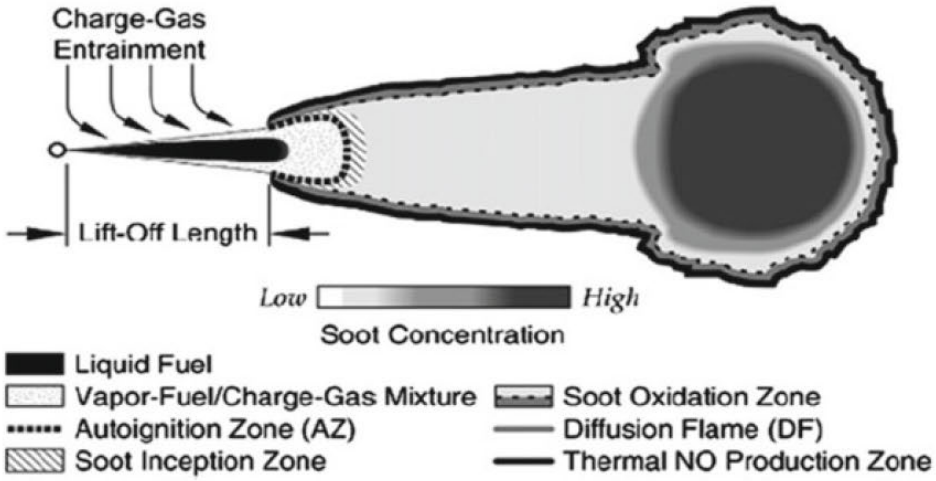

Fig. 7.2 Chemical kinetic of reacting DI biodiesel jet spray and combustion of biodiesel. *Source* [75]

Equations 7.5–7.9 are also exampling of bimolecular but elementary reactions their rate of reaction being directly proportional to the concentrations in kmol/m^3 of the two-reactant molecule species, which is expressed in equation form as

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k_{\text{bimolecular}}[A][B] \tag{7.9}$$

However, due to the complexity and the size of constituent molecules within the biodiesel fuels, direct modelling has never been attained. Instead, surrogate fuel molecules or blends with matching characteristics with lower computational requirements have been experimented and modelled by such researchers such as [24, 47, 51]. Chemical kinetics becomes important especially when tracing NO_X formation pathway with use of biodiesel fuels in diesel engines. This is critical, as chemical kinetics has now been identified as one of the leading factors that influences the increase of NO_X emissions with application of biodiesel fuels. This explanation is vividly captured in Fig. 7.2 on chemical kinetics during biodiesel jet spray and combustion.

7.6 The Engine Load and Age Conditions

Engine loads and variations affect the combustion temperature and diesel engine exhaust gas NO_X emissions, as the cycle load increases linearly [98]. Zhang and Boehman [118] investigated low and high load engine conditions, using three types of blended fuels ULSD BP15, B20 and B40. These authors reported low NO_X emissions under low load engine conditions compared to high engine load conditions as can be seen in Fig. 7.3 showing variation of brake specific NO_X and injection timing. These findings were corroborated in a study by Yoon and Lee [116], although lower

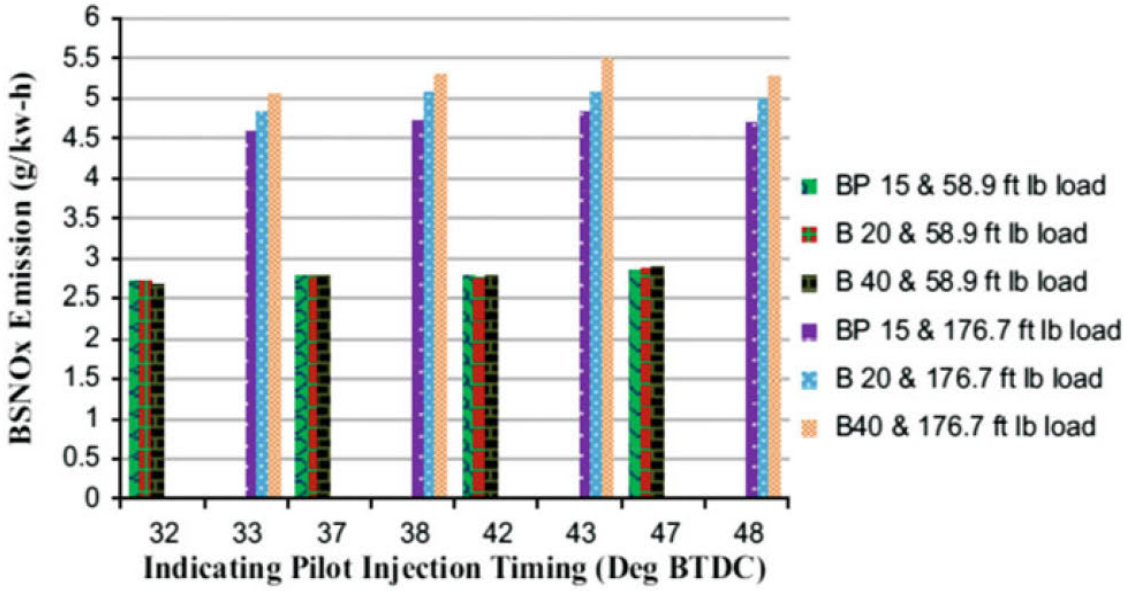

Fig. 7.3 Variation of brake specific NO_X emissions with respect double injection both high and low loads condition at 1600-rpm engine speed. *Source* Lapuerta [54]

NO_X emissions were reported under dual fuel mode operation (biogas diesel) for both cases of pilot fuel and single fuel mode at all engine load conditions. This was attributed to the phenomenon of advanced injection timing in biodiesel and early start of combustion, factors which are responsible for the high combustion temperature and pressure hence high NO_X emissions through the thermal NO_X route.

Another factor that influences emissions under engine conditions is engine age, which has been shown to impact negatively on both oil and fuel emissions of CO, HC and NO_X in both city or highway driving conditions [92]. An increase in tail pipe emissions is therefore not unexpected and has been reported on extensively by many researchers [7, 20–22, 40, 113]. When vehicle or engine age increases due to engine control deterioration, catalyst efficiency drops and particulate filters malfunction [17]. There are three factors which combine to increase tail pipe emissions in aged engines, namely internal engine changes to the engine itself, changes to the computer controlled parameters of operation and changes in catalyst efficiency in the tail pipe [92]. It is important to mention that catalyst efficiency is reduced by a combination of factors such as thermal degradation over time and the deposition of phosphorous as Zinc-di-alkyl di-thiophosphate. The latter is a reversible process through acid wash [22], compared to the former which is permanent.

Engine speed is also an important factor in the production of increased NO_X emissions with the use of biodiesel [60–64]. This phenomenon is due to reduced reactant mixture residence time in the combustion chamber as the volumetric efficiency is increased and flow velocity of the reactant mixture is increased at high engine speeds. However, other researchers in other studies such as Utlu and Koçak [107] reported increased NO_X which occurred between maximum torque and maximum power speeds. This was predominant for waste cooking oil methyl esters (WCOME)

and conventional diesel which to a large extent depended on the exhaust temperature and rise of volumetric efficiencies. Additionally, Eckerle et al. [23] in their modelling and experimental work reported a significant increase in NO_X linked to engine load conditions. They noted that under high engine load conditions, diffusion flame combustion is dominant. Engine control parameters played a significant role in the NO_X increase compared to low loads which are dominated by pre-mixed combustion and influenced by other factors. By engine control factors, they are referring to mean timing changes by low and light load advance mechanisms inherent in the fuel injector pumps.

7.7 The Effect of Ignition Delay

Ignition delay can be defined as the period between the onset of injection and the start of combustion. This delay period in diesel engines is classified into (i) physical delay during which vaporization, atomization and air/fuel mixing occur, (ii) there is a chemical delay primarily attributed to the pre-combustion reaction in the combustion chamber. However, it is important to note that these two factors do not overlap but occur simultaneously [52]. During this time, reactants become rapidly preheated due to ignition delay [6], leading to increased flame temperature hence high NO_X emissions. The resultant vaporization produces an apparent heat release curve that assumes negative values, making the SOC values to be read from where they begin changing to positive values only. The start of injection (SOI), on the other hand, is defined as the crank angle where the nozzle needle attains a 5% lift off. Therefore, the time difference between SOI and SOC is what is defined as the ignition delay and can be shown in Eq. 7.10 as

$$\tau_{\text{id}} = a\Phi^{-k^*} P^{-n^*} \exp\left[\frac{E_a}{R_u T_{\text{cyl}}}\right] \tag{7.10}$$

where

τ_{id}	is ignition delay.
Φ	is the equivalence ratio.
E_a	is the activation energy.
T_{cyl}	is the cylinder charge temperature.
R_u	is the universal gas constant.
A, k^* and n^*	are empirical constants.

This has been confirmed in biodiesel fuels with higher degrees of unsaturation which have longer ignition delay time hence higher adiabatic temperatures. Additionally, the molecular structure of biodiesel fuel has also been linked to increased NO_X and high adiabatic temperature, as in the study conducted by Schönborn et al. [89] on the molecular structure of natural biodiesel and single molecule fatty acid

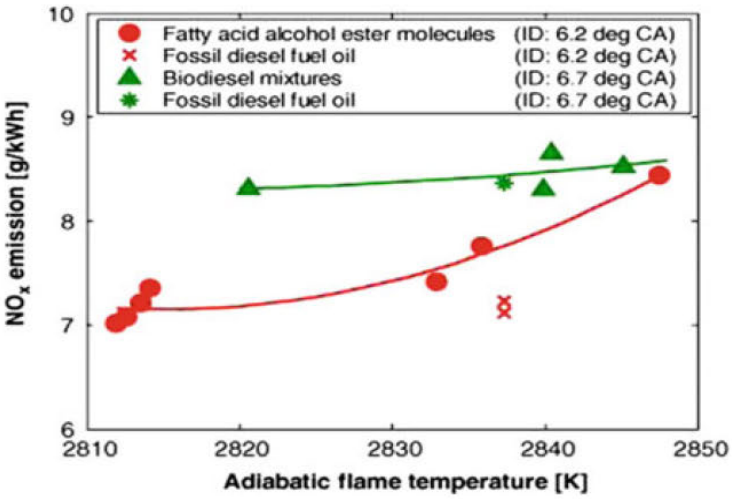

Fig. 7.4 Relationship between measured NO_X emission and calculated T_{ad} at P = C, $\Phi = 1$, with no dissociation; $T_{in} = 881$ K and $P_{in} = 4.5$ MPa. Engine running condition as 1200 rev/min, IMEP = 0.4 MPa; ignition delay equalized to 6.21°CA for all fatty acid monoalkyl molecules. *Source* [89]

esters (SMFAE) on combustion in a diesel engine. However, biodiesel fuel has generally been shown to have shorter ignition delay time at all engine load conditions as has been reported and confirmed by many researchers [2, 72, 79, 81, 89, 90, 95, 97]. Figure 7.4 shows the strong relationship reported between shorter ignition delay and high adiabatic temperature.

7.8 The Role of Injection Timing in NO_X Emissions

Injection timing in biodiesel is an important factor and parameter in combustion studies due to its greater effect on combustion temperature which is a vital component of increased NO_X in biodiesel fuels. Fuel injection factors such as duration, timing and pressure are key in order for good performance and low emissions to occur. Injection pressure can therefore be defined as the pressure before the injector holes open, whereas injection timing is the tie span between SOI and piston top dead centre (TDC) [39]. However, it is injection timing which influences injection pressure, combustion characteristics and engine exhaust emissions [12].

It is important to note that injection pressure is also affected by the type of injection system, injector nozzle, engine speed, engine load and the physicochemical properties of a fuel. In all types of fuel injection timing systems (rotary, inline or distributive types) for biodiesels, the SOI is normally advanced compared to petro-diesels [6, 13, 54, 70, 74, 81, 101, 104, 114, 117].

Their studies attributed the injection advance timing to several physicochemical properties such as high density, high bulk modulus of compressibility and greater speed of sound in biodiesel, which is corroborated in studies by Lapuerta et al. and Schönborn et al. [54, 89]. For example, Monyem and Van Gerpen [74] conducted an experiment and found that the settings of injection timing altered for B100 and B20 by 2.3° and 0.25°–1.5°, respectively, without changing the main engine injection timing. In other words, the higher bulk modulus and viscosity move the pressure wave

Table 7.2 Effect of advanced injection timing of biodiesel fuel compared to diesel fuel on NO_X emissions

References	Engine specifications	Fuel	SOI advance timing	NO_X emission comparison to diesel combustion
[74]	John Deer diesel	Veg-based B100 B20 B20	B100(23°CA) B20(0.25°CA) 0.75°CA	↑
[13]	John Deer 4276T, 4 Cyl, TC, 4, DI Diesel	Soy bean Biodiesel B100 B20	2.28 °CA 0.4–0.6 °CA CA	B100 (10–24.5%) ↑ B20 (0.62–16.6%) ↑
[100]	Yanmar L70 EE, AC, 4S, 1 Cyl, Max-power 5.8 HP @ 3600 rpm	Soy-derived biodiesel	1.1°CA	6–9% ↑
[88]	Lombardini 6LD4OO, 1 Cyl 20 Mpa, SOI 20°CAbtdc, CR: 18:1, Torque: 21 Nm @ 2200 rpm, Max-power: 8 kW @ 3600 rpm	COME + Diesel	5°CA	B5 (3.03) ↑ B20 (8.6%) ↑ B50 (9.14%) ↑ B100 (12.92) ↑

Note ↑ indicates increase

in the fuel injection lines forward, resulting in an earlier needle lift hence advanced injection. However, in another study by Szybist et al. [100] using soy-diesel blends and Fisher–Tropsch diesel (ULSD), an injection timing SOI of 1.1° was reported compared to petro-diesel (conventional diesel). This was attributed to high bulk of modulus of compressibility as shown in Table 7.2.

Other explanations which have been advanced for increased injection timing in biodiesel are that since the ignition delay lengthens ignition delay to injection timing (IT), the additional time allows for more pre-mixing of fuel and air. The increase in pre-mixing time period for the combustion of the mixture increases the diffusion reaction temperature hence causing high levels of NO_X formation [95, 99, 101], as can be seen in Fig. 7.5.

The molecular structure of biodiesel fuel has also been linked to increased NO_X and high adiabatic temperature. For example, Schönborn et al. [89] conducted a study on the molecular structure of natural biodiesel and single molecule fatty acid esters (SMFAE) on combustion in a diesel engine. They found a strong relationship between shorter ignition delay and high adiabatic temperature as shown in Fig. 7.6.

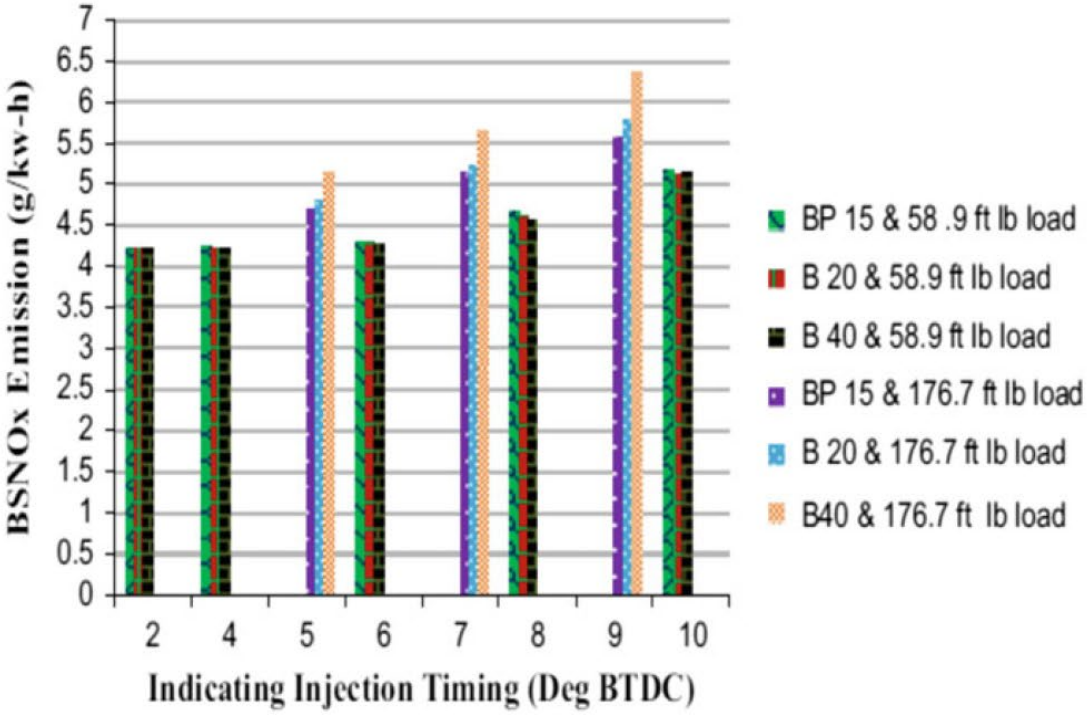

Fig. 7.5 Brake specific NO_X emission with respect single injection both high and low loads condition at 1600 rpm engine speed. *Source* [54]

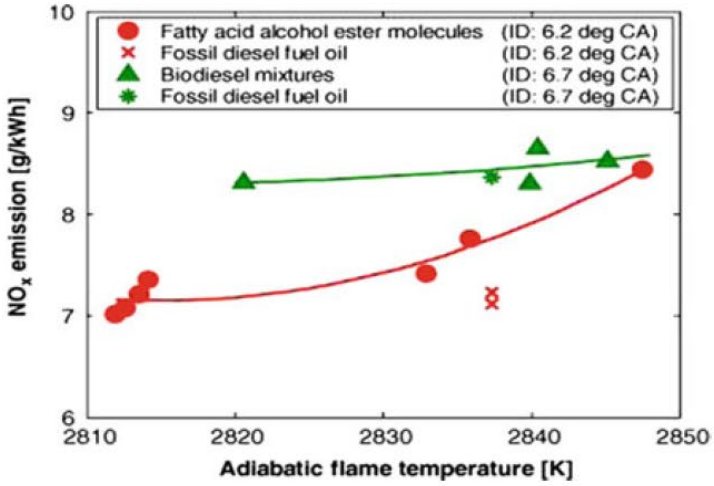

Fig. 7.6 Relationship between measured NO_X emission and calculated T_{ad} at P = C, $\Phi = 1$, with no dissociation $T_{in} = 881$ K and $P_{in} = 4.5$ MPa. Engine running condition as 1200 rev/min, IMEP = 0.4 MPa; ignition delay equalized to 6.21°CA for all fatty acid monoalkyl molecules. *Source* [89]

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Chapter 8
Reduction and Control Techniques in Biodiesel Emissions

8.1 Introduction

The world energy consumption demand is growing at a rate of 50% annually and in the next two years, it will hit 180,000 GW by 2020. This growth is predominantly fuelled by the transportation sector whose main propulsion fuel is fossil based [1]. Therefore, in order to meet this demand without compromising the environmental and human health is the main challenge [16]. There are several advantages to using biodiesel as an alternative fuel to conventional diesel. For example, biodiesels mix very well with conventional diesel, thereby reducing carbon monoxide, UHC and PM emissions [14]. Other advantages of biodiesel also include reduction of the net CO_2 especially when plant-based biodiesel which consume CO_2 from the atmosphere during growth (photosynthesis process) [24, 86]. Biodiesel fuels are also known to be oxygenated by approximately 11–12% by weight [104] which helps in aiding complete combustion, thus decrease in CO, UHC and PM emissions [57, 100]. However, in urban areas around the world today, more than 300 different types of chemical compound concentrations are released into the atmosphere by automobiles in organic form. This complex mixture of pollutants has direct impact on the environment and human health, thus, regulation and control is needed to identify, quantify and measure them [21].

The USA and the European Union have introduced stringent and rigid regulations for the control of hydrocarbon emissions from automobiles. For example, the rules in USA include two components: (i) emissions standards and (ii) diesel fuel regulation for the following emissions categories:

- PM, 0.01 g/bhp.h
- NO_X, 0.02/bhp.h
- NMHC, 0.14/bhp.h.

There are broadly two classification methods of NO_X reduction and control techniques with the use of biodiesel fuels. These are the (i) pre-combustion treatment

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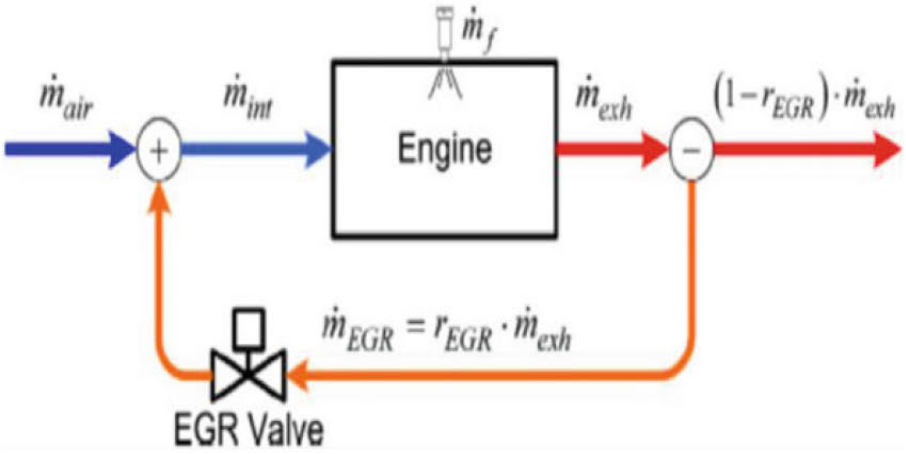

Fig. 8.1 Typical simplified schematic of an EGR system. *Source* [96]

techniques and (ii) the post-combustion treatment techniques. This classification has been adopted to meet stringent vehicular exhaust emissions norms worldwide. This chapter will endeavour to discuss these classifications and their application in biodiesel emission reduction and control. Figure 8.1 is a simplified schematic diagram of an EGR set-up which is an example of a pre-treatment technique, while Table 8.1 shows the effects of EGR as a control technique on emissions.

Table 8.1 Effect of EGR on NO_X and other emissions

References	Biodiesel blend	EGR % rate	NO_X condition	Other results
[8]	Soybean B20	5, 10, 15	↓	↓BTE, ↑BSFC, ↑HC, ↑CO, ↑Smoke
[103]		–	↓	↓BTE, ↑BSFC, ↑HC, ↑CO
[20]		10, 15, 20	↓	↑BTE, ↑BSFC, ↑CO, ↓Smoke
[52]		10, 20	↓	↓BTE, ↑BSFC, ↑HC, ↓CO, ↓Smoke
[71]		–	↓	↓BTE, ↑HC, ↑CO
[99]		10, 20	↓	↓BTE, ↓BSFC, ↑HC, ↑CO, ↑Smoke
[53]		5, 10, 15, 20	↓	↓BTE, ↓BSFC, ↑HC, ↑CO, ↑Smoke
[61]		–	↓	↓BTE, ↑HC, ↑CO
[30]		10	↓	↓BTE, ↑HC, ↑CO, ↑CO_2

Note ↑ indicates increase, ↓ indicates decrease

8.2 Pre-combustion Treatment Techniques

8.2.1 *Exhaust Gas Recirculation as a NO_X Reduction Technique*

Exhaust gas recirculation (EGR) is one of the leading methods used in the control and reduction of NO_X emissions in diesel engine combustion chambers. Since exhaust gas consists of CO_2, N_2 and water (H_2O) in the form of vapour, when part of the EGR is recirculated, it dilutes the combustion mixture. This leads to the reduction in the concentration of O_2 in the combustion chamber and increases the specific heat of the intake charge leading to depressed cylinder temperature for the same heat release in the combustion chamber. EGR can be defined mathematically in Eqs. 8.1 and 8.2 as:

$$\text{EGR}\% = \frac{\text{Volume of EGR}}{\text{Total intake charge into the cylinder}} \times 100 \tag{8.1}$$

Or

$$\text{EGR} = \frac{[CO_2]_{\text{intake}} - [CO_2]_{\text{ambient}}}{[CO_2]_{\text{exhaust}} - [CO_2]_{\text{ambient}}} \tag{8.2}$$

There are three main explanations for the effect of EGR on the reduction of NO_X, namely increased heat capacity, dilution of the intake charge with inert gases and increased ignition delay. However, at high engine load the application of EGR becomes difficult due to diffusion combustion deterioration resulting in increased and excessive smoke and particulate emissions. At low loads, unburnt hydrocarbons found in the exhaust gases are reburnt thus improving fuel efficiency, and, since EGR is hot, it raises intake charge temperature, thereby influencing combustion and exhaust emissions. The use of EGR as a technique of NO_X reduction introduces a trade-off between NO_X reduction and increased soot, CO and UHC emissions. This leads to recommendations for the use of particulate traps [58], since increase in EGR % ratio increases pm emissions. Table 8.2 shows the different effects of EGR application in the reduction of NO_X emissions.

Studies have reported that a change in the concentration of oxygen causes change in the flame temperature and the duration of combustion. From this, one can conclude that there is a link between reductions in NO_X is and flame temperature. Like any other system, there are problems that are associated with the application of EGR [36] such as:

- Introduction of the particulate matter into the combustion chamber;
- Increased soot emissions; and
- Increased CO and UHC emissions.

Table 8.2 Result of reduction NO_X emissions using the EGR method for petroleum and biodiesel blend fuels and explanation

Engine type	Fuel type	EGR condition	Result	Explanation	References
1C, DI-DE	Diesel	Cold start OEV (0,50,100) OCV (100,50,10)	↓NO_X, 60% @ 100% OCV/OEV	Stable combustion and less common rail pressure	[73]
6C, TC, Volvo-(D-12), 1C, DI-DE	Diesel	12%	↓NO_X, 65.2%, ↑BSFC-8.6%	No explanation	[9]
4S, 1C, CI-DE, HCCI-Mode	LPG + DEE	Full load with 20% EGR	↓NO_X-68% full-load, ↑BTE-2.5% Partial load	Low elevated peak temperatures	[35]
1C, vertical, DI-DE, 4S, HCCI-mode,	Diesel + H_2 (0.15 kg/h)	20% EGR @ 80% Engine load	↓NO_X-41.4, ↓Smoke-8.3%, ↓CO_2-29.1%, ↓HC-12.3%, ↑BTE-2% compared to neat diesel	Reduction of combustion peak temperatures due to EGR effect of inert gases	[6]
1C, DI-DE, 4S, WC	JOME	Hot EGR ratios, 5–25 at full load	↓NO_X-17.7%, @ 15% EGR, compared to CD at same EGR %	Significant NO_X reduction, minimum sufficient possible reduction in HC, CO, smoke and BTE	[74]
2C, 4S, WC, DI-DE	JOME	Optimum EGR rate@12% FL	↓NO_X-33%, ↑BSFC-11%	Due to reduction in O_2 density and a drop in in-cylinder maximum temperature	[81]
2C, vertical DI-DE, WC	B2 (20% SOME + 80% Diesel)	15% EGR	↓NO_X-25%, ↓HC-5%, ↓CO-10%, ↑smoke-but negligible	Less flame temperatures due to unavailability of O_2 in EGR gases	[78]
4C, WC, TC, IDI-DE	20% JOME	10% EGR	↓NO_X-36%, ↓Smoke-31%	Limited EGR rate of 5–25%, with minimal effects on performance	[20]

(continued)

Table 8.2 (continued)

Engine type	Fuel type	EGR condition	Result	Explanation	References
4C, 16 V, Mercedes	SOME 100	27% EGR with load @ 68 Nm	NO_X-87.7%, CO, CO_2-5.5		[39]

DI—Direct injection, DI-DE—Direct injection diesel engine, IDI—indirect injection, HCCI—Homogeneous charge ignition engine, WC—Water cooled, FL—Full load, TC—Turbocharged, ↑—Increase, ↓—Decrease

These problems lead to particulate abrasion besides sulphuric acid and condensed water in the EGR valve leading to corrosion of system components. The EGR system is classified into three main categories:

- Temperature group;
- Configuration group; and
- Pressure group.

8.2.2 *Classification by Temperature*

This is further classified into three classes namely:

1. Hot EGR which is generally characterized by increased intake charge temperatures.
2. Fully cooled EGR which uses a water-cooling exchanging unit. However, this presents a further problem of condensation which causes corrosion which has an undesirable effect on the engine cylinders and components.
3. Partially cooled EGR, where the temperature of the exhaust gas is kept above the dew point to avoid moisture condensing into water to cause corrosion.

8.2.3 *Classification by Configuration*

This is further classified also into three main groups namely:

1. Long-route (LR), where the exhaust gas velocity is responsible for creating stagnation pressure which combining with low pressure after the intake air rises the pressure difference, thus accomplishing EGR across the speed and torque range of the engine. In other words, the backup pressure P_3 is less or smaller than the intake pressure P_2, thus $P_3 - P_2 < 0$. This produces a longer route for residual exhaust gases as shown in Fig. 8.2.
2. Short route (SR), where the exhaust gas residuals flow out upstream of the turbine directly to the intake manifold. At this point, the backup pressure P_3 is greater

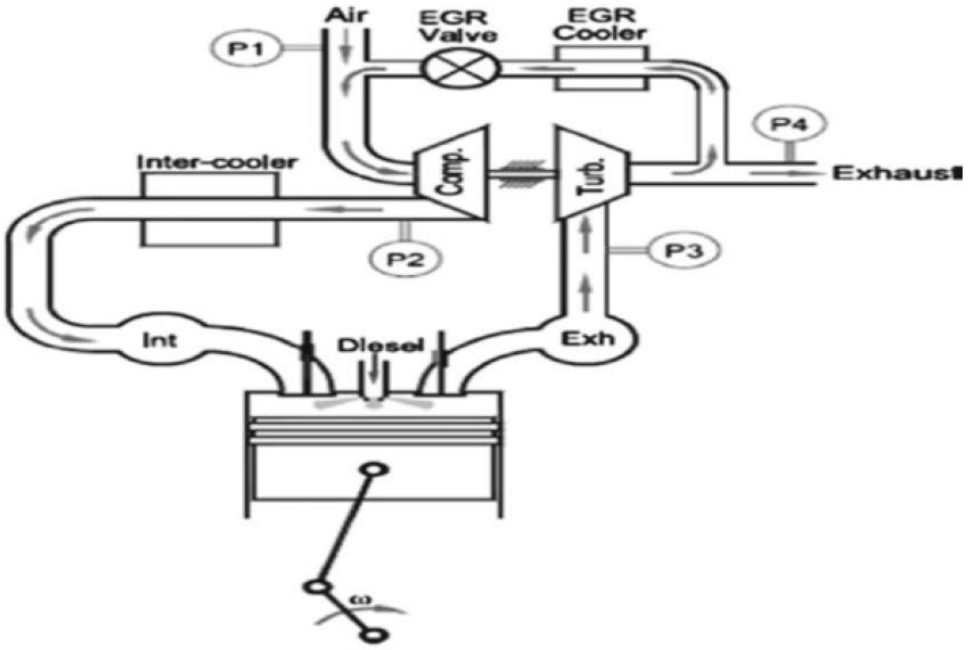

Fig. 8.2 EGR loop—low-pressure loop. *Source* [96]

than the intake pressure P_2 hence $P_3 - P_2 > 0$. This therefore produces a shorter pipe route with high pressure as shown in Fig. 8.3.

3. The variable nozzle turbine (VNT/VGT).

This system provides an effective desired EGR driving pressure without sacrificing performance of the turbocharged engine [108]. Through tying the EGR control to the VGT control [23, 29], the turbine nozzle is shrunk, thus increasing the upstream pressure P_3 and reducing the boost pressure P_2. The boost pressure is normally in the region of 1–2 bar of gauge pressure. This further requires that flow component (ducts and valves) is able to withstand the high boost pressures and high turbine temperatures, which are in the region from 100 to 600 °C. These components should be able also to tolerate and absorb thermal and mechanical vibrations.

8.2.4 Classification by Pressure

This method is divided into two main classes and uses low-pressure and high-pressure routes [44], as follows:

1. Low-pressure route where EGR is taken from downstream of the turbine compressor unit. This method helps in reducing NO_X emissions because EGR residual gases can be delivered up to very high loads. However, the low-pressure route has demerits such as high prohibitory compressor outlet temperatures, which lead to premature failure and clogging of the heat exchanger (intercooler) (Fig. 8.2).

2. High-pressure route where the EGR gases are passed from upstream of t compressor turbine to downstream of the compressor unit into the intake mar fold. This system helps the EGR during high loads by producing an exce air ratio reduction; however, this becomes its main demerit by increasing fu consumption. Figure 8.3 shows an EGR loop of high pressure (Fig. 8.4).

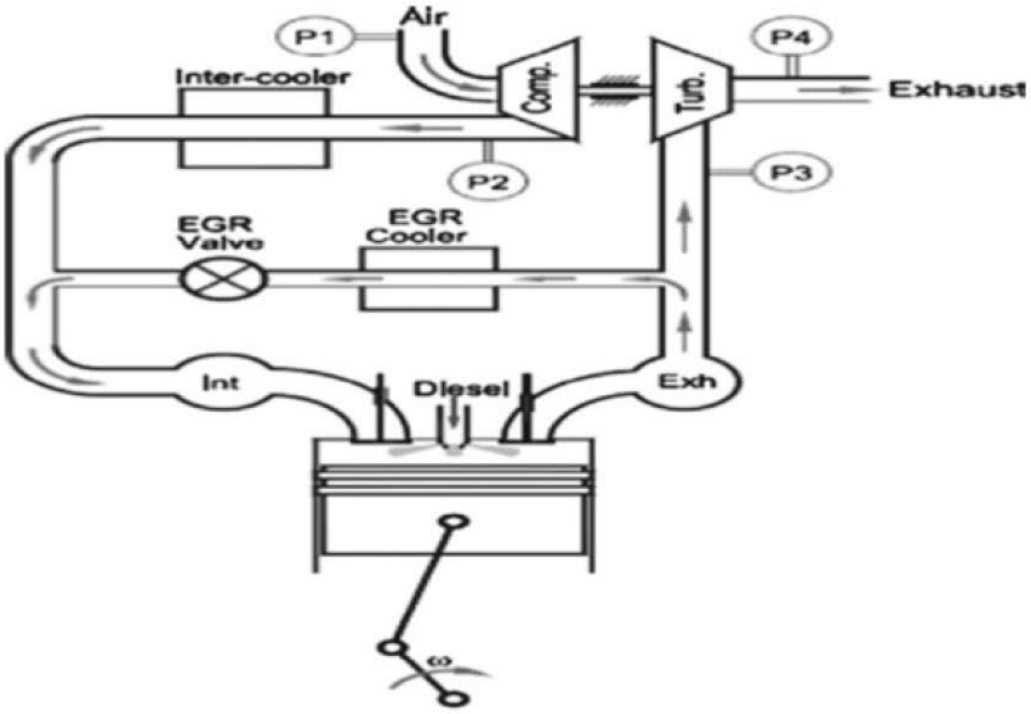

Fig. 8.3 EGR loop—high-pressure loop. *Source* [96]

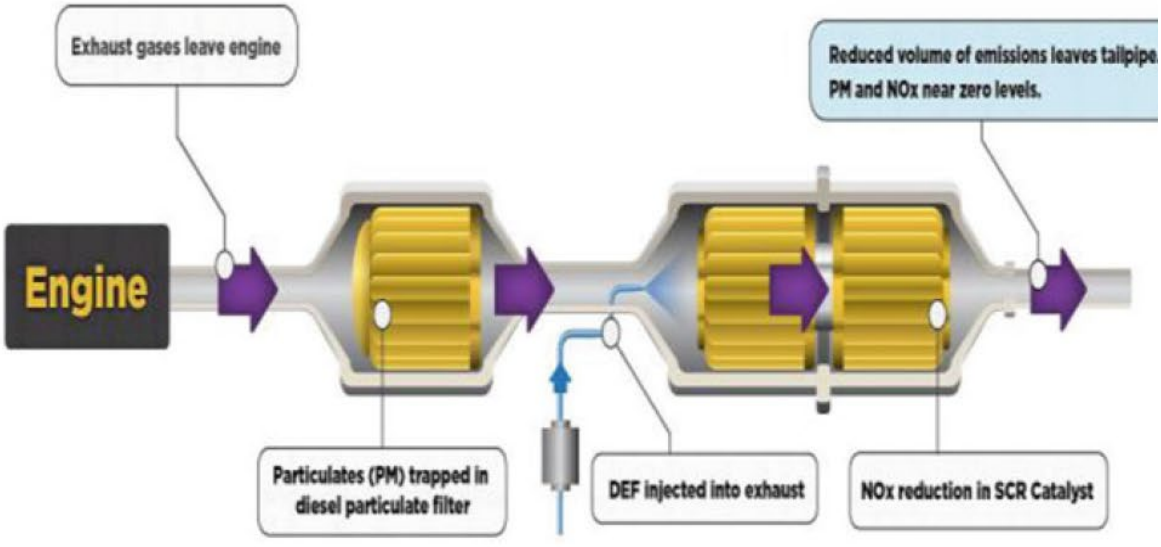

Fig. 8.4 Diesel engine control system process working steps. *Source* [13]

8.3 The Use of Biodiesel Fuel Additives

Biodiesel additives play an important part in meeting fuel standards, while at the same time solving the problem of emissions associated with use of biodiesel fuels, although the use of biodiesel is limited by demerits such as low heating value, high viscosity and high density. Additionally, biodiesel fuels also have poor cold flow properties, for example, CP, PP and cold filter plugging which cause poor atomization leading to injector nozzle clogging and narrow spray patterns. There are a number of studies which have confirmed the use of biodiesel additives in enhancing biodiesel fuel properties [12, 47, 62, 66, 77, 98, 106] as shown in Tables 8.3 and 8.4.

Fuel additives enhance fuel properties of pure biodiesel or biodiesel blends, thereby increasing performance while reducing tail pipe emissions from diesel engines. There are different types of biodiesel additives such as metal-based, oxygenated types (dimethyl ether, ethanol and methanol) diesel–vegetable oil blends, antioxidant and cetane improvers, which mainly are used to control NO_X emissions additives. Basically, the selection of the biodiesel additives is based on the different additive properties which enhance the primary feedstock such as flash point, fire point, viscosity, density, calorific value and improved solubility [87]. Additives should be able to help acceptability of biodiesel by eliminating the technical undesirable problems, which are a hindrance to wider commercial acceptance.

For example, most researchers concur that the addition of ethanol in small ratios in the blends of biodiesel enhances and increases the BTE, heat release rate, reduces viscosity and smoke emissions in the tail pipes of diesel engines. In other words, the addition of ethanol improves the physical and thermal properties of the ethanol and biodiesel blends aiding in complete combustion hence improved BTE efficiency [32, 85]. The second example to look at is diethyl ether, which is an oxygenated additive. Diethyl ether possesses qualities of high volatility and tends to respond even at very low temperatures, besides having a high cetane number. Table 8.4 is a summary of the effects of different additives on biodiesel fuels.

The addition of diethyl ether has been reported by many researchers as improving biodiesel blends solubility, which improves and enhances engine performance hence

Table 8.3 Properties of different bioadditives

References	Additive	K.V@40 °C (cST)	Density kg/m^3	C.V (kJ/g)	CN	FP (°C)
[27]	Ethanol	1.14[a]	791[a]	27.33	5–8	–
[27]	n-butanol	3.00	812	34.33	25	35
[27]	DEE	0.22	712	33.89	25	–
[76]	Methanol	0.59	790	19.62	5	11

[a]Measured @ 20 °C

Source Adopted from Madiwale [49]

Table 8.4 Results of NO_X reduction with use of fuel additives and their references

References	Test fuel	Additive	Engine condition	Test results
[55]	POME20	1% of ODA	IDI, 50 Nm load @2250 rpm	↓NO_X-22.69, ↓CO, ↓HC
[42]	TOME60	Mn/Ni	Unmodified, DI-DE@FL	NO_X reduction for (TOME60Ni > TOME60Mn), ↓CO-64.28%, ↓Smoke-30.91%
[43]	TOME60	Mg/Mo	1C, DI-DE@FL, with varying engine speed	Low NO_X recorded at (B60-8 Mg/B60-12 Mg) fuel, ↓CO-56.42%, ↓Smoke-30.43%
[92]	POME	DGMME/DGMBE	1C, Kirloskar AV-1	↓NO_X
[41]	TOME 60	Cobalt (Co)	1C, DI-DE@FL, with varying engine speed	Low NO_X for (T60-8Co), ↓CO-53.37, ↓Smoke-29.47
[22]	10% (CFB)	12 μ/mole Mg	4S, 1C, AC, DI-DE	↓CO-13%, ↓Smoke-9%, SFC-5.2%, ↑NO_X-5%
[4]	SOME 80	20% ethanol	1C, 4S, DI-DE	↓NO_X-12%, ↓CO-16.67%, ↓CO_2-18.75%, S↓O_2-52%
[97]	JME	p-phenylenediamine	1C, 4S, WC, 4.4 kW power	NO_X-43.55, but (CO/HC) compare to pure biodiesel
[75]	B30	BE-1 (5%DEE/B25) BE-2 (5%ethanol/B25)	1C, 4S, DI-DE @ 2000 rpm	The serial NO_X reduction rate is higher to lower (BE-1 > B30 > BE-2)

Note ↑ indicates increase, ↓ indicates decrease

reduction in emissions and other biodiesel pollutants [28]. Recently, n-butanol has become the preferred biodiesel additive due to its high oxygen content and its molecular structure with inclusion of the OH group, which has very low hydrophilic characteristics. Other qualities making n-butanol desirable with researchers are its high cetane number, good solubility and high heat content, although it suffers from poor cold flow properties especially in adverse weather conditions.

High cetane number improvers when used as additives have two main objectives: to reduce NO_X emissions and to decreasing ignition delay. Ignition delay is common with biodiesel fuels during premixed combustion thus burning less fuel during this phase [109]. This is due the reduction in peak maximum cylinder temperatures, hence

suppression of NO_X emissions. The commonly used cetane improvers in biodiesel are 2-ethylhexyl nitrate (EHN) and di-t-butyl peroxide (DTBP) [25, 56]. Antioxidants play a role in reducing the formation of free radicals using four methods [97], namely chelating transition metal catalysts, chain breaking reactions, scavenging initial radicals and corresponding prompt NO_X, reduction of the reactive radical concentration.

8.4 The Effects of Emulsified Biodiesel

This method causes some heat of combustion to be absorbed by water molecules in the combustion chamber, thus helping to lower the cylinder combustion temperatures, hence NO_X emissions. Emulsified biodiesel contains a mixture of two partially miscible liquids, namely biodiesel and water. The purpose of water is to increase expansion thus offering additional force which increases the BTE [2]. Senthil et al. [84] reported that B20 biodiesel (from diesel 20% thevetia Peruvian biodiesel) emulsified with water in the ratios of 5–7.5% reported a NO_X reduction of 8% and 10%, respectively. In a similar experiment and study but with increased water ratios of 5, 10 and 20%. Kannan and Marappan [38] reported an increase in BTE and a significant reduction in NO_X emissions, although CO and HC emissions increased. These authors attributed this occurrence to reduced combustion temperatures, but, in a parallel study using fuel with a high cetane number and a high oxygen content water–biofuel emulsion, this problem was countered by Sachuthananthan and Jeyachandran [80]. It is also important to note that emulsified biodiesel lacks fuel stability compared to petro-diesel. This is due to the miscibility of biodiesel in water. Tables 8.5 and 8.6 show the reduction of NO_X and other emissions resulting from using water emulsified in biodiesel.

Thus, emulsified biodiesel requires surfactants in the emulsion to reduce interfacial tension [31] to provide stability, though this makes it inferior to petro-diesel emulsions for the same mixture [46]. The other problem that is apparent with emulsification of biodiesel fuel is corrosion which is caused by the nature of the water content in the mixtures and the problem of condensation which has been experimentally solved and demonstrated by Parlak et al. [69]. The authors used engine exhaust to heat the water into superheated steam and introduced it through electronic injection into the combustion chamber, thereby eliminating corrosion as superheated steam prevents condensation.

Table 8.5 Reduction of NO_X by using a water injection method

References	Engine specification	Fuel used	Injection condition	Test results
[9]	6C, TC, Volvo-D12	Diesel	30% H2O	↓NO_X-42%, ↑BSFC-2.1%
[93]	2.0L, WC, HSDI-DE	Diesel	M_W = 60–65% Of the fuel	↓NO_X-50%, ↑CO, ↑BSFC, ↓BTE
[90]	Kirloskar TAF1, 1C, 4S, AC, CI-DE, CR:17.5:1 IT-23° bTDC, 6BHP@1500 rpm	Diesel, fuel + H_2O (1:0.4)	No data is available	↓NO_X-37.62%, ↑CO
[95]	4C, 4S, DI-DE, TC	ROME	FR-3 and 1.8 kg/h	↓NO_X-50% @ 3 kg/h ↓NO_X-30% @ 1.8 kg/h ↑CO-for both FR ↑BSFC-4% @ 3 kg/h ↓BTE-3% @ 3 kg/h

Note HSDI—High-speed direct injection, TC—Turbocharged, AC—Air cooled, WC—Water cooled, DE—Diesel engine, bTDC—before top dead centre, ↑—Increase, ↓—Decrease, FR—Flow-rate, M_W—Mass of water
Source Adopted from [67]

8.5 Low-Temperature Combustion Strategies

Low-temperature combustion involves limiting the combustion temperatures during combustion in the cylinder to below 1800 k which is considered as the lowest temperature of combustion [5, 45]. Low-temperature combustion schemes such as homogeneous charge ignition engine (HCCI), pre-mixed charge compressed ignition (PCCI) and reactivity controlled compression ignition (RCCI) have attracted a large degree of research attention as they offer hope in the reduction and elimination of NO_X and soot emissions [105]. In other words, combustion in LTC occurs at pre-determined air and fuel ratios and temperatures with the objective of reducing NO_X and soot emission simultaneously [72, 88, 89] as shown in Fig. 8.5 and Table 8.7.

The long ignition associated with LTC and the absence of fuel rich regions which promote thermal NO_X enhances combustion efficiencies and reduction of soot emission which are a pre-cursor to NO_X emissions [79]. Table 8.6 shows LTC on biodiesel results and effects, while Table 8.7 shows the operating conditions of the LTC combustion strategy. This is confirmed in a study by Fang et al. [15] on soy biodiesel B20, B50 and B100 under LTC mode. This study reported and concluded that NO_X emissions for the blends were 68.1, 66.7 and 64.4% lower compared to the petro-diesel NO_X emissions. Table 8.8 is a summary of LTC technique operating conditions.

Table 8.6 Experimental result on the effect of water–biodiesel fuel emulsion on exhaust emissions

References	Emulsion	Engine test conditions	Results	T_{AD}/BTE/BSFC
[68]	Water-emulsified diesel	4cycle, WC, 6C, 121 kW, LS-1000 rpm, HS-1400 rpm	↓NO_X-9.5% @ LS/29% @ HS with ↑(W/O) (CO, HC, Smoke) ↑ with emulsion ratio ↑(W/O)	Small BSFC @ LS BSFC-2.6% @ HS
[65]	Water–diesel emulsified: 20% + EGR:16.7%	4C, DI-DE, Ford	↓NO_X-60%, ↑HC, ↑CO, ↓Smoke	BSFC/BTE no change
[3]	Water–oil emulsified	IID, TC, DI-DE, Speed-2087–3175 rpm	↓NO_X, ↓THC	↓T_{AD} about 26 K, Slight BTE↑
[63]	Diesel + GS/CS + 5–15% water	XLD418, DI-DE Ford, 4S, 4C, WC, Speed 1000–5000 rpm,	↓NO_X high @ GS (15%W), ↓CO compares to CD, ↓PM-68–72	↓T_{AD} about (15–25 K) ↑BSFC,
[90]	Water–diesel emulsion (0.4:1)	4S, AC, 1C, CI-DE, CS, 1500 rpm	↓NO_X-37.6%, ↑CO, ↑HC	↓BTE@LL ↑BTE@FL
[11]	94% D + 5% H_20 + 0.5%	Comet DE, 2C, Vertical WC, 7.5 kW@1500 rpm	↓NO_X-30–50%, ↓HC@LL/↑HC@HL, ↑CO with H2O emulsion	No data available
[102]	74% D + 10% H_2O + 11% additives	Toyota, 4C, 4S, DI-DE, Speed 1000-4000 rpm	↓NO_X-30.6%, (↓HC/↑CO) @ PL (↑HC/↓CO) @ FL	BTE-14.2%
[10]	10% CH_3OH + WCOME	4C, DIDE, Speed 1800 + 5 different loads	↓NO_X-6.2%	↑BTE@LL ↓BTE@HL
[37]	Biodiesel, diesel B70D10E20M Micro-emulsion fuel	1C, WC, DIDE, CS, Speed 1500 rpm	NO_X emissions less than diesel/BD (BD < MEF < CD), HC/Smoke (BD < B70D10E20M < CD)	↑BSFC, BTE compares to CD

(continued)

Table 8.6 (continued)

References	Emulsion	Engine test conditions	Results	T_{AD}/BTE/BSFC
[26]	H_2O-BD-diesel nano-emulsion	Diesel engine	↓NO_X, ↑CO	No data

Note AC—Air cooled, WC—Water cooled, HS—High speed, LS—Low speed, IID—Intercooler indirect injection, GS—Gemini surfactants, CS—Conventional surfactants, BSFC—Brake-specific fuel consumption, BTE—Brake thermal efficiency, HL—High load, LL—Low load, FL—Full load, ↑ indicates increase, ↓ indicates decrease

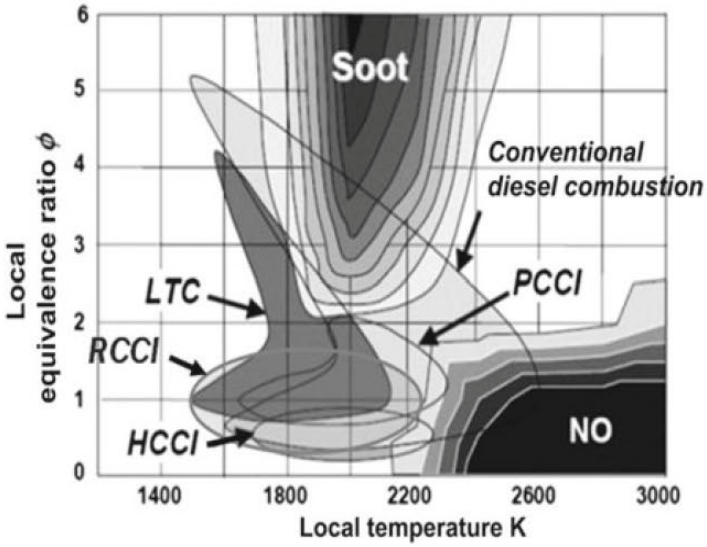

Fig. 8.5 Variation of equivalence ratio and temperature. *Source* [72, 88, 89]

Table 8.7 Effects of LTC on biodiesel

References	LTC MODE	Biodiesel fuel	Results and effects
[17]	HCCI	Jatropha oil	↓NO_X, ↑HC, ↑CO, ↓Smoke, ↑BSFC, ↓BTE
[18]	HCCI	Jatropha oil	↓NO_X, ↑HC, ↑CO, ↓ Smoke, ↑BSFC, ↓BTE
[33]	HCCI	Colza oil	↓NO_X, ↓PM, ↑HC, ↑CO
[107]	HCCI	Soy oil Canola oil Yellow grease	↓NO_X, ↓Soot, ↑HC, ↑CO
[94]	PCCI	Palm oil/gasoline	↓NO_X, ↑HC, ↑CO
[48]	PCCI	Soy oil/n-butanol	↓NO_X, ↑HC, ↑CO
[88, 89]	PCCI	Peanut oil/bioethanol	↓NO_X, ↓Soot, ↑HC, ↑CO
[50]	PCCI	Rapeseed oil/bioethanol	↓NO_X, ↓Smoke, ↓BTE
[89]	RCCI	Cottonseed oil/n-butanol	↓NO_X, ↓Soot
[19]	RCCI	Waste fish oil/CNG	↓NO_X, ↑HC, ↑CO

Note ↑ indicates increase, ↓ indicates decrease

8.6 The Effect of Injection Timing Retardation

A number of researchers [7, 34, 57, 60, 64, 82, 83, 91, 101] have reported increased reduction in NO_X emissions through adoption of this technique as shown in Table 8.9. Using this technique, Kegl [40] was able to demonstrate lower NO_X emissions with the use of biodiesel compared to petro-diesel if injection timing could be retarded. His studies have been corroborated by Sayin et al. [82] who did work on advancement and

Table 8.8 Operating conditions of the LTC control technique

Operating condition	HCCI	PCCI	RCCI
Intake environment	1.3 bar @ 50 °C	1.3 bar @ 70 °C	1.3 bar @ 50 °C
Pre-mixed charge %	100	79.1	92.6
Ignition type	CI	CI	CI
Fuel type	Liquid/gaseous	Liquid/gaseous	Fuel with high octane/CN
DI-DE timing	–	−65°CA	−45°CA
Combustion controlling mechanism	CK	CK/IT	CK/reactivity of fuels
Emission characteristics	Higher HC/CO, Lower NO_X, PM/CO	Higher HC/CO Lower NO_X, PM/CO	Very high HC/CO Ultra-low NO_X, PM/CO_2

Note CK—Chemical kinetics, IT—Injection timing, CA—Crank angle, CN Cetane number, CI—Compression ignition, DI-DE—Direct injection diesel engine
Source Adopted from [79]

retardation of diesel engines at the SOI using coconut methyl esters (COME) blends and conventional diesel. These authors concluded that advancing of SOI produced better results for CO and smoke emissions for B100 compared to retardation of SOI, which resulted in minimum results for NO_X emissions for B0 and B100. This was because injection timing retardation reduces the reaction time moving the SOC to advance or late onset, hence decreasing the overall gas cylinder temperatures. The continued retardation of SOI has been observed to significantly reduce NO_X emissions but incidentally increases other emissions such as HC and PM emissions [54]. Table 8.9 shows the effects of retarded injection timing in reducing the NO_X emissions, in studies by various authors and their references. These studies show a NO_X emission drop of between 8.2 and 40.95% compared to the original SOI with retardation. However, there was a reported increase in the emissions of CO and HC although in the studies of [40, 51] the increase of the two was not confirmed. However in very exceptional circumstances, some researchers have reported increased BSFC with retarded injection timing [7, 70].

Table 8.9 Effect of retarded injection timing on biodiesel blends and conventional diesel fuel compared to original injection timing on NO_X emissions

References	Engine specifications	Retarded SOI	Fuel type	Test results
[70]	Ricardo E6-MS/128/76, 1C	4°CA from ORG-38°CAbTDC	Diesel	↓NO_X- 40%
[83]	Super star 7710, 1C, 4S, DI	6°CA from ORG-27°CAbTDC	E5 + D95	↓NO_X-37.3, ↑CO, ↑HC
[7]	Ford 6.0L, TC, 6C, DI-DE	(2°–4°) CA from ORG-20°CAbTDC	Diesel	↓NO_X-11%
[59]	John Deere DI-DE	3°CA—retarded injection timing	Vegetable-derived B100, B20	↓NO_X-35– 43%
[91]	Diesel engine DI-DE	Retarded injection timing from ORG	POME	↑NO_X, ↑HC, ↑CO
[40]	MAN D2566MUM, 4S, AC, WC	4°CA from ORG-23°CAbTDC	ROME100 compared to CD	↓NO_X-25%, ↓CO-25%, ↓HC-30%
[51]	KirloskarTAF1, 1C, 4S, AC, DI-DE	9°, 6°, 3°CA from ORG-23°CAbTDC	Waste plastic oil	↓NO_X, C↓O-25%, ↓HC-30%
[34]	Small DI-DE	Retarded SOI	KOME	↓NO_X-8.2%
[82]	Lombardini 6LD 400, 1C, IOP-20 MPa, SOI-20°CAbTDC, CR-18:1, Max-Torque-21 Nm@2200 rpm, Max-power 8 kW@3600 rpm	5°CA from ORG-20°CAbTDC	CME + CD, fuel blends-B0, B5, B20, B50, B100	NO_X-↓B0 40.95%, ↓B5-30%, ↓B20-28%, ↓B50-15.59%, ↓B100-9.77% CO-↑B0-13.21%, ↑B5-11.39%, ↑B20-21.08%, ↑B50-31.25%, ↑B100-35.11% HC-↑B0-35.54%, ↑B5-9.1%, ↑B20-33.3%, ↑B50-27.03%, ↑B100-44.68%

Note ↑ indicates increase, ↓ indicates decrease

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Chapter 9
Post-combustion NO_X Reduction Techniques in Biodiesels

9.1 Introduction

The transport sector is a major source of environmental pollutants, even though it is a main artery of the economies of each country [1]. Due to their many advantages such as low operating costs, high durability and reliability, diesel engines have taken leadership role in the heavy-duty market in the auto-industry. In recent years, the diesel engines have taken also 60% of the light-duty vehicle segment [2]. However due to stringent and rigid automobile emission control requirements especially for diesel engines. Attention has been turned to design improvement and redesign of engine management control systems such as high-pressure fuel injection, small injection nozzle hole area. Additional focus is in high swirl ratio, large volume ratio of piston cavity, improved combustion chamber shape and geometry, high response and performance turbo-chargers, fuel pre-treatments, modifications of fuel formulation, better tuning and control of the engine combustion process. Other additional areas include increased use of blends and alternative non-fossil fuel like natural gas, alcohols, esters and use of additional filtering and non-filtering after-treatment devices [3]. Since reduction of regulated emissions cannot be achieved using one strategy alone, a multi-strategy approach is currently being employed by manufacturers and researchers to reduce diesel exhaust emissions [4].

Although biodiesel fuel possesses similarities, which mimic conventional diesel fuel, it also possesses many other unique properties and characteristics requiring consideration for application in the current diesel engine systems. For example, it has been observed that biodiesel increases NO_X emissions in engines which use in-line pump nozzle technologies, due to the high bulk modulus of compressibility [5]. However, even in diesel engines with common rail injection systems and initially thought to have low NO_X emissions, studies are showing and reporting a different picture, revealing also elevated values of NO_X emissions than earlier reported. What is interesting is the lack of link to the bulk modulus of compressibility, which has

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been associated with increased NO_X emissions, thus remaining one of the stic
points in emission studies.

Due to continued research in controlling biodiesel NO_X emissions, a numbe
commonly used post-treatment approaches have been adopted in the control
reduction of NO_X emissions in diesel engines. These methods include selective
catalytic reduction (SNCR), selective catalytic reduction (SCR), NO_X adsorber
lysts (NAC) and De NO_X (lean NO_X) catalysts. These are techniques, whic
combination with others, have the potential in meeting EU, and USA EPA emiss
standards for the protection of the atmospheric and natural environment.

9.2 The SCR

This is a more recent inclusion in heavy-duty vehicles [6]. However, it has been
in light-duty vehicles such as Audi and Volkswagen, where it has been adopte
the passenger vehicle categories. SCR has been the main emission controlling t
nique in stationary combustion installations for a long time using ammonia (N
However, in vehicular applications, the reducing agent is an aqueous urea solu
(NH_2CONH_2) [7] as shown in Figs. 9.1 and 9.2. It is important to note that one o
demerits of this system technique is the excess production of ammonia which l
to slip ammonia [8] emissions, although this is good for maximum NO_X reduc
and is overcome by an addition of an oxidation catalyst.

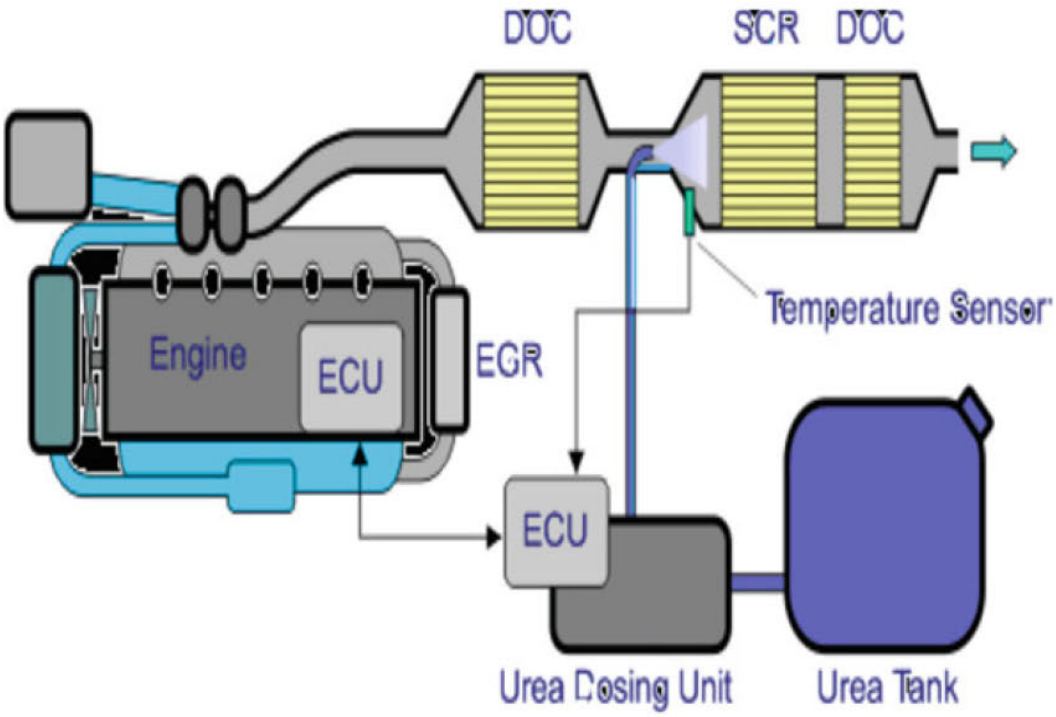

Fig. 9.1 SCR process schematic. *Source* [9]

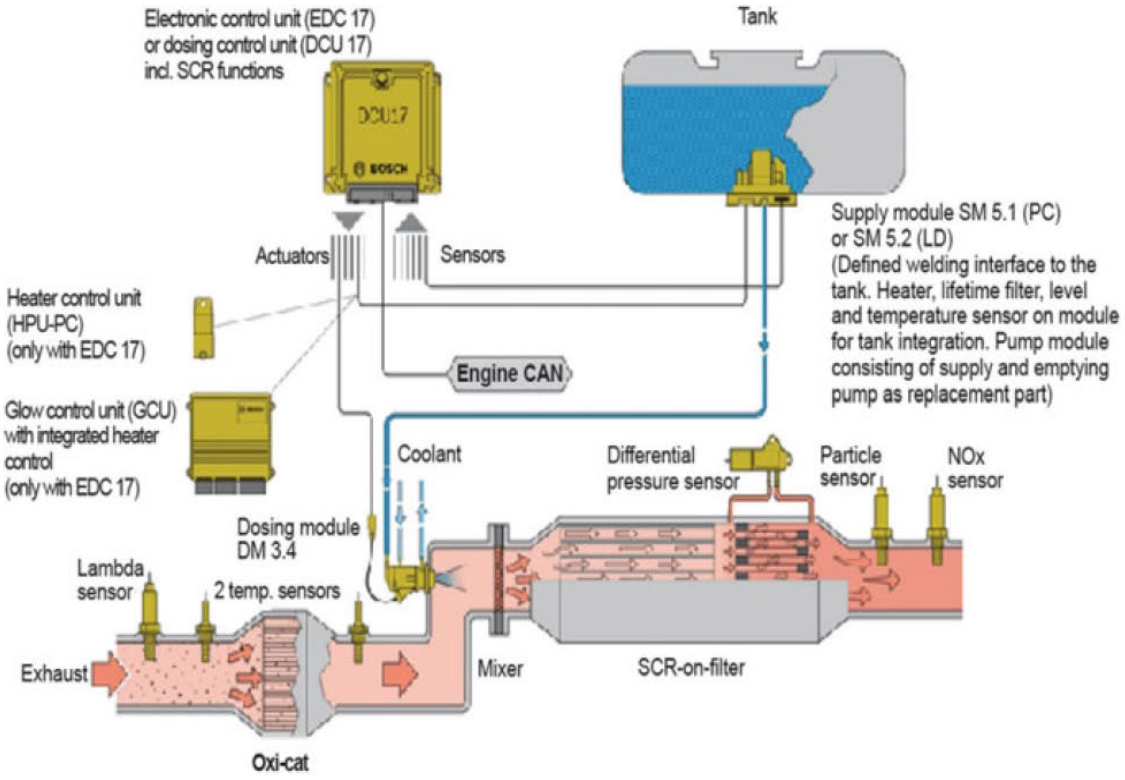

Fig. 9.2 Schematic diagram of the SCR NO_X control system in a standard production vehicle. *Source* [10]

The performance of the SCR system is affected by the following factors, namely (i) temperature, (ii) the NH_3/NO_X ratio, (iii) the oxygen concentration, (iv) catalyst loading and (v) the type of catalyst support used [11]. The most commonly used catalyst is vanadium pentoxide (V_2O_5) supported by titanium dioxide (TiO_2) although no catalyst has been reported to be active above temperatures of 873 K or below 523 K [12] as shown in Table 9.1.

The SCR system utilizes ammonia as a reductant which minimizes NO_X emissions within the emitted exhaust gases, while releasing N_2 and H_2O [24]. During its operation, the SCR system undergoes two processes, namely hydrolysis and thermolysis, as can be seen in Eqs. 9.1 and 9.2 for hydrolysis and thermolysis respectively [25, 26]. However, after thermolysis and hydrolysis, there are other chemical processes which take place as in Eqs. 9.11 to 9.13 [27, 26] as follows:

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{9.1}$$

$$(NH_2)_2CO \rightarrow NH_3 + HNCO \tag{9.2}$$

Further equations after the two chemical processes in the SCR:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{9.3}$$

Table 9.1 SCR literature conditions and results

References	Catalyst used/condition	Test results
[13]	F-doped vanadium/titania	Catalyst with F/Ti = 1.35% showed high rates of NO removal at low temperatures
[14]	Cr–Mn mixed oxide	Cr–(05)–MnO_X showed very high NO_X conversion, under relatively high space velocity
[15]	Ce/TiO_2	Catalyst with at least 5% Ce had a high activity at 275 to 400 °C
[16]	6% W/HZSM-5	89% reduction at 350 °C with C_2H_2
[17]	In/WZr	70% rate of conversion with 1% In/WZr catalyst at 450 °C
[18]	0.5% H_2 assisted Urea Ag/Al_2O_3	Over 84% conversion at 200 to 500 °C
[19]	Mg–CeO_2 supported by Pt (0.1 wt%)	At 200 °C almost 100% conversion of NO, with 85% N_2-selectivity for feed of 1000 rpm
[15]	Ce-supported on titania	Ce/TiO_2 catalyst is highly active and selective for the catalytic reduction of NO to N_2 by NH_3 at 275 °C—0 to 0 °C
[19]	Using Mg- CeO_2 supported by Pt (0.1 wt%) using H_2-SCR	100% conversion of NO and 85% $-N_2$ selectivity was obtained between 150 and 200 °C
[20]	V_2O_5/CNT @ 373–523 K	90% conversion at 463 K
[21]	Mn–Ce/ZSM-5 with NH_3	Within a temperature of window of 517 K to 823 K, NO conversions were between 75% and 100%
[22]	Mo-impregnated HZSM-5 Zeolite	83.9% NO removed at 350 °C
[23]	Monolith V_2O_5–WO_3–TiO_2 @ 250 and 350 °C in a biomass fired CHP	Chemical poisoning and physical blocking of active sites both contributed to loss in activity. Reactor temperature not important in determining deactivation rate

Note CHP = combined heat plant
Source adopted from [12]

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \tag{9.4}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{9.5}$$

9.3 The SNCR System

The SNCR system, also known as the thermal $DeNO_X$, was first used by Exxon in 1974 [28]. The SNCR technically operates by injection of ammonia or urea as a reducing agent into the hot exhaust system operating in temperatures of 760 to 870° C. Without a catalyst, the reducing agent ammonia breaks down the NO_X in the exhaust system turning it into water and molecular nitrogen. This involves the reduction of NO_X into N_2 in the presence of oxygen by reacting with an amine-based reagent ammonia or urea $CO(NH_2)_2$ at temperatures between 1073 K to 1273 K, especially when urea is the reagent as it requires very high temperatures. Table 9.2 shows aggregated results using three different fuels and two emission control strategies.

The SNCR system has been credited with reducing NO_X emissions by up to 70% [29], especially when proper reduction compounds are chosen for the system [30]. However, like any system, the SNCR has a demerit of amine solubility and increased cost of production and use, which makes it uneconomical to end users. The following are the reaction schemes with SNCR and ammonia as the reagent (Eqs. 9.6 to 9.8).

$$4NH_3 + 6NO/5N_2 + 6H_2O\ (R14 - a) \tag{9.6}$$

$$4NH_3 + 4NO + O2/4N_2 + 6H_2O\ (R14 - b) \tag{9.7}$$

$$8NH_3 + 6NO2/7N_2 + 12H_2O\ (R15) \tag{9.8}$$

Table 9.2 Aggregated results obtained on an entire route, using three different fuels and two technologies to control exhaust emissions

		EGR + DPF			SCR + Urea		
Emission	Deviation	Diesel	B20	B100	Diesel	B20	B100
CO (g/km)	Mean	0.250	0.154	0.069	1.716	1.477	1.041
	SD	0.056	0.065	0.064	0.158	0.125	0.074
CO_2 (g/km)	Mean	913.822	926.301	954.932	864.98	886.841	889.117
	SD	12.636	36.095	17.967	34.495	25.214	16.602
THC (g/km)	Mean	0.068	0.042	0.044	0.053	0.054	0.043
	SD	0.003	0.001	0.001	0.002	0.006	0.005
NO_X (g/km)	Mean	6.925	8.261	8.580	6.121	6.517	8.460
	SD	0.114	0.499	0.016	0.396	0.556	0.373
PM (g/km)	Mean	0.049	0.025	0.026	0.073	0.053	0.029
	SD	0.001	0.001	0.0003	0.004	0.003	0.002
Fuel (l/100 km)	Mean	34.042	35.401	38.522	32.308	33.896	35.868
	SD	0.469	1.346	0.672	1.291	0.945	0.622

Source adopted from [24]

Taking urea as the reagent, the reaction scheme is as follows:

$$H_2NCONH_2 + 2NO + {}^1/_2O_2/2N_2 + CO_2 + H_2O \text{ (R16)} \tag{9.9}$$

9.4 NO_X Adsorber Catalysts (NACs)

Because diesel engines run lean with excess oxygen and have excellent fuel economy, this makes the removal of NO_X under these conditions necessary. Besides, there has been stringent and increasing emission limit control standards in Europe and USA EPA. For example, for light-duty diesel (LDD), the 2005 NO_X emissions was 0.25 g/km compared to 2000 which was 0.5 g/km, a trend that is replicated in heavy-duty diesel (HDD). The NACs, due to inhibiting the presence of SO_2 from high sulphur content fuel, the commercialization of NACs was delayed until the late 1990s, when low sulphur content fuel arrived in the market [31, 32]. The fundamental reactions under lean engine conditions with this system are as indicated in Eqs. 9.10 to 9.11.

$$2NO + O \rightarrow 2NO_2 \tag{9.10}$$

$$2NO_2 + MCO_3 + \frac{1}{2}O_2 \rightarrow M(NO_3)_2 + CO_2 \tag{9.11}$$

The adsorption is according to Eqs. 9.17 and 9.18, with MCO_3 as the stable carbonate form of the adsorbing material, and MNO_3 is the stable NO_X containing compound that is formed (reduced). Because of studying chemical kinetics, it is understood that the rate-limiting step of the NO_X oxidation is due to the interaction between adsorbed atomic oxygen and the NO. The final phase of the reaction is catalyzed by rhodium through the reduction of NO_X to form N_2 as in Eqs. 9.12 and 9.13.

$$NO_2 + CO \rightarrow NO + CO_2 \tag{9.12}$$

$$NO + CO/HC \rightarrow \frac{1}{2}N_2 + CO_2/H_2O \tag{9.13}$$

While the regeneration equation takes place after a period due to saturation, with the engine shortly switched to rich fuel mode allowing the catalyst to promote decomposition of the nitrate phase and release the stored NO_X to regenerate the storage capacity as expressed in Eq. 9.14:

$$M(NO_3)_2 + 2CO \rightarrow MCO_3 + NO_3 + NO + CO_2 \tag{9.14}$$

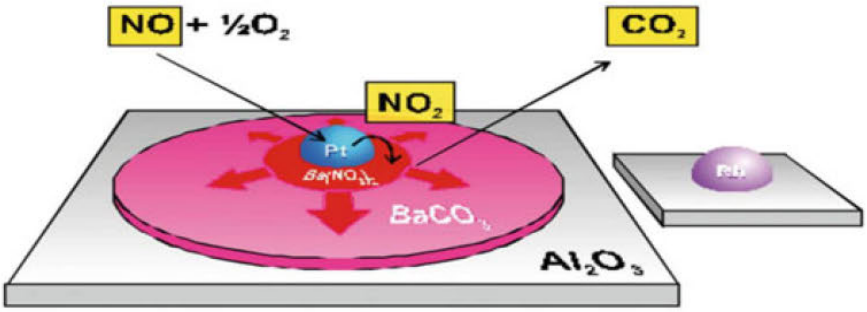

Fig. 9.3 Reactions during engine lean fuel conditions. *Source* [34]

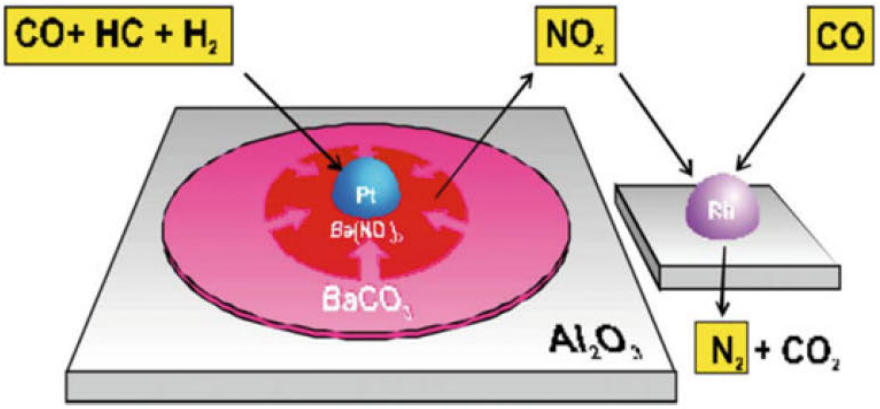

Fig. 9.4 Reactions during engine rich fuel conditions. *Source* [35]

For effective regeneration, it is important to remember that two factors are essential, the platinum (catalyst) and the reducing agent because regeneration is a catalyst-dependent process [33] as shown in Figs. 9.3 and 9.4 and is divided into two main areas, passive and active.

NACs are formulated using platinum as the oxygen catalyst, barium as the storage component and rhodium for the reduction of NO_X. NAC is one of the most fundamental NO_X reduction techniques, also known as low NO_X Trap (LNT). Its working principle is to store NO_X on a catalyst, especially during rich engine conditions. The NO_X is trapped in an organic substance (oxidation catalyst), in this case BaO, which then during rich engine operating conditions helps the nitrite to become unstable and decompose causing the release of the stored NO_2. This system is extremely sensitive to sulphur contamination. Sulphur reduces the system's performance gradually rendering it ineffective to reduce and control NO_X emissions.

In a study conducted to corroborate the effectiveness of this system with biodiesel use [36], using a light-duty diesel engine tier 2, found and reported that the exiting engine exhaust gas emission NO_X was higher for soy biodiesel (B20) compared to petro-diesel by 10%. However, the tail pipes out exhaust NO_X gas of B20 was lower after passing through NAC. This was explained by the higher temperature of petro-diesel combustion compared to B20; therefore, NAC was able to trap NO_X emissions from B20 more effectively compared to petro-diesel.

9.5 DeNO$_X$ (Lean NO$_X$) Catalysts

This is a relatively new approach for the control of NO_X from lean engines (diesel engines). Lean NO_X trap catalysis works by storing NO_X during O_2-rich conditions short of stoichiometric combustion. After periodic accumulation, the catalyst is exposed to reductant-rich exhaust, which reduces and releases the stored NO_X to N_2. The lean NO_X trap catalyst consists of a wash coat, which supports both the precious metal component and the sorbate component. The wash coats are from metal oxides applied on a monolithic cordierite structure. The precious metal plays a vital role in the regeneration and oxidation of pollutants and NO during the sorption phase besides facilitating the reduction of the stored NO_X to N_2. The sorbate is an alkali metal or alkaline earth material with the most commonly used being potassium and barium.

The general NO_X trap and NO_X sorption equations are shown in Eqs. 9.15 and 9.16:

$$K_2CO_3 + NO + \frac{1}{2}O_2 \rightarrow KNO_3 + CO_2 \tag{9.15}$$

$$K_2NO_3 + H_2 + CO_2 \rightarrow K_2CO_3 + H_2 \tag{9.16}$$

In a DeNO$_X$ catalyst, there are two catalyst methods for depleting the oxygen because oxygen must be combusted with natural gas fuel to obtain a rich mixture. These methods are:

- By operating the engine under rich conditions; and
- Injection of the fuel into the exhaust system upstream of the NO_X trap while catalytically combusting the fuel and oxygen.

Minimization of fuel use in catalyst regeneration is vital since it provides no useful energy for propulsion but is an additional cost on the end user or consumer. It should be noted that lean NO_X traps are not ideally designed for optimal methane combustion efficiency. Therefore, for optimization of methane combustion within the system, oxidation and reformer catalysts are placed upstream of the lean NO_X trap as mentioned earlier. This is in order to combust methane and generate the required rich exhaust that contains CO and H_2 for efficient regeneration of lean NO_X trap as in Figs. 9.5, 9.6 and 9.7 and some summarized chemical reactions in Eqs. 9.17 to 9.20.

The summarized equations are as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{9.17}$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \tag{9.18}$$

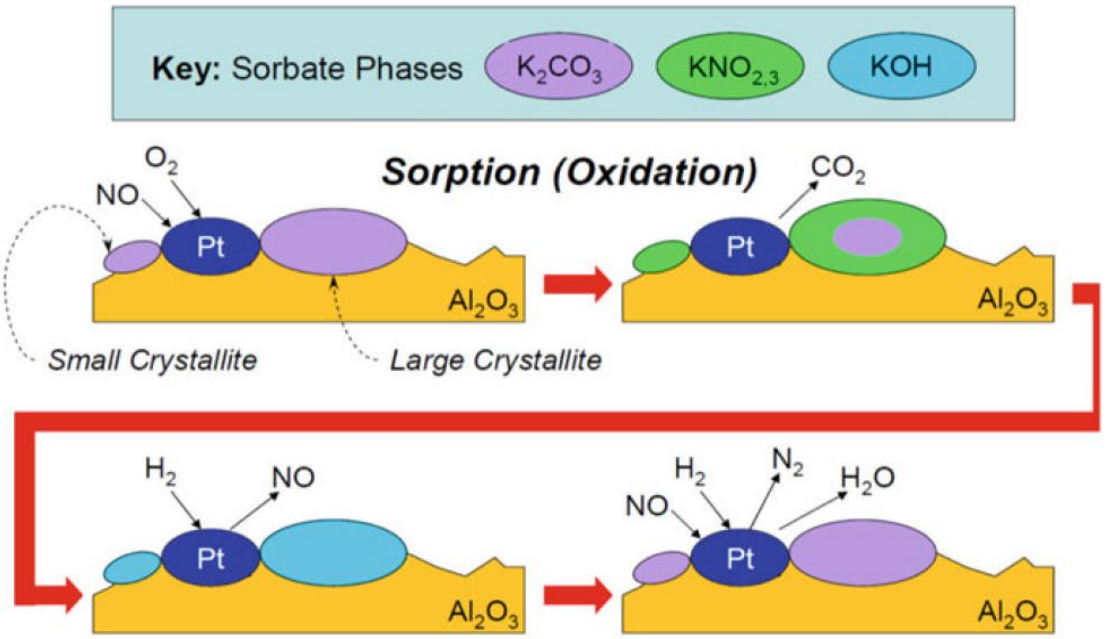

Fig. 9.5 Schematic of the finely dispersed catalyst components during adsorption–regeneration cycle. *Source* [37]

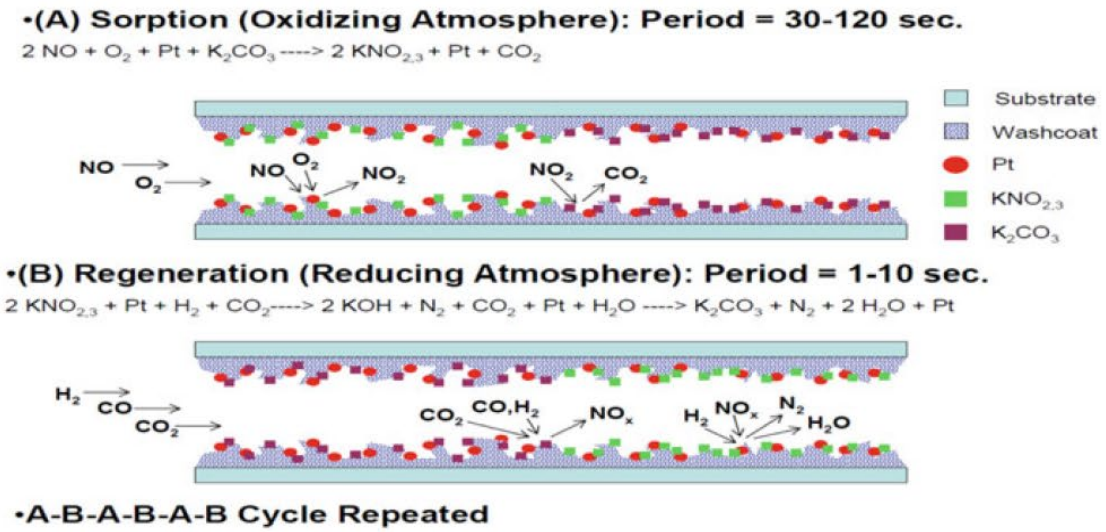

Fig. 9.6 Diagram of the lean NO$_X$ trap catalyst process along the flow axis of a monolithic cell. *Source* [37]

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{9.19}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{9.20}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{9.21}$$

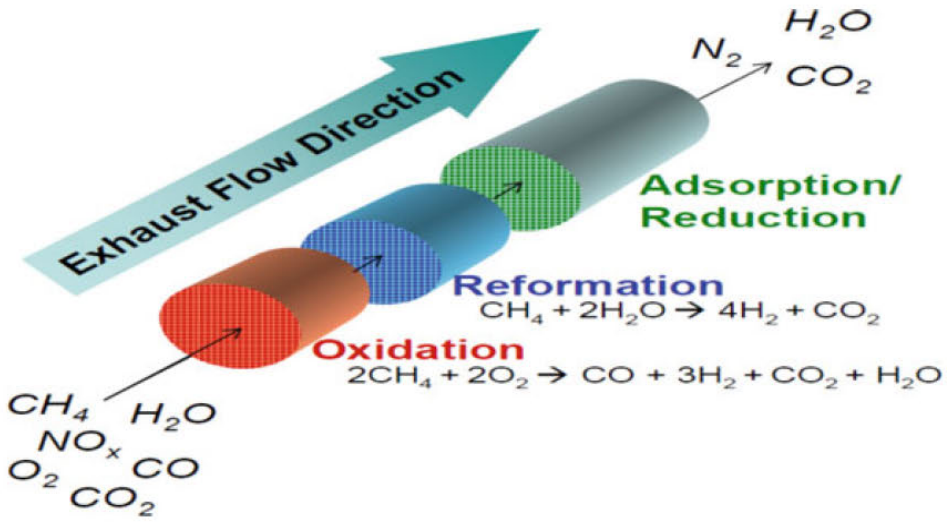

Fig. 9.7 Catalyst geometry in the lean NO_X trap catalyst system. *Source* [37]

From the oxidation processes, palladium (Pd) is commonly applied for the oxidation of methane while rhodium (Rh) is commonly used for the reforming processes. Therefore, Eqs. 9.17 and 9.18 represent the oxidation of CH_4 with Pd as the catalyst whereas Eqs. 9.19 and 9.20 are reforming reactions showing CO_2 and H_2O occurring on the Rh containing reformer catalyst, and Eq. 9.21 is the main oxidative objective equation and reforming process which produces H_2 and CO from methane through reactions of regeneration hence the lean NO_X trap [37].

9.6 Diesel Particulate Filter (DPF)

These types of filters are known to capture particle emissions through a combination of surface type and deep bed filtration mechanisms such as diffusion inertia deposition or flow-line interception [38]. Since the year, 2000 DPFs have been used in automotive manufacturing units. DPFs are made up of silicone carbide cordierite ($2\,Mg–2Al_2O_2–5SiO_2$) with both ends of the structure blocked to force PM through the porous substrate walls thus creating a mechanical filtration system. Figure 9.8 shows a schematic diagram of a DPF filter working principle.

Thus, DPFs physically capture biodiesel particulates so prevent atmospheric pollution by PM particles. Due to developments in material science, filtration materials that have been developed have shown impressive filtration qualities and efficiencies in excess of 90%, besides the high mechanical and thermal qualities of durability. However, traps may exhibit limited effectiveness in the control of non-solid PM fractions such as SOFs of the sulphate particulates. This calls for incorporation of additional functional components, which can, for example, target SOF emissions through use of oxidation catalysts and sulphate deposits of ultra-low sulphur fuels, which are currently in use.

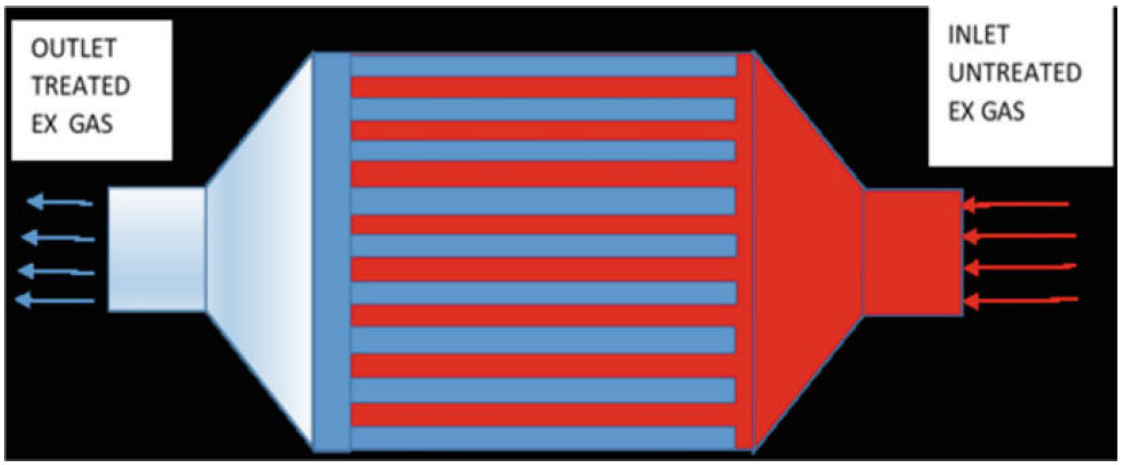

Fig. 9.8 Schematic of the working mechanism of a diesel particulate filter (DPF). *Source* [39]

9.7 Diesel Oxidation Catalysts (DOCs)

This is also a post-combustion after-treatment component designed to convert CO and HC into carbon dioxide and water. This is achieved through reduction of PM emissions through oxidation of the absorbed HC in the carbon particles [39]. Additionally, DOC can be used as a heating device during active regeneration of DPF filters. The DOC is made up of a metal or sometimes a ceramic structure with an oxide mixture (wash coat) comprising aluminium oxide (Al_2O_3), cerium oxide (CeO_2), zirconium oxide (ZrO_2) and an active catalytic metal such as platinum (Pt) or rhodium [39].

The DOC has been used in diesel engines exhaust systems since the introduction of emissions regulations standards and limits in diesel engines [40]. Emissions in diesel engines are formed in many ways and routes such as incomplete combustion, which primarily creates CO, UHC and soot emissions. Further reactions from the chemical kinetics of these hydrocarbons form polynuclear aromatic compound components and other volatile organic compounds (VOCs) which further react with NO_X in complex reaction chains. Therefore, the catalytic control of both NO_X and PM is more difficult to achieve in diesel engines, especially at low diesel temperatures of 200 to 300° C which are common with LDD or 300 to 450° C which are common with HDD [38]. Changes designed to lower either form of emission more often than not cause an increase in the other, which explains the increase in PM and low NO_X emissions. Figure 9.9 explains this phenomenon and some of the chemical reactions within the operation of the DOC filter.

The DOC system has the potential to regulate and control particulate mass concentration, particle number concentration and other unregulated emissions from biodiesel fuels as its conversion efficiency is different from fuel to fuel [42]. The particle number concentration attracts attention because biodiesel and petro-diesel particles are mainly submicron in size and can diffuse in ambient air into the human respiratory system [43]. This has been confirmed in studies by researchers such as [44–46].

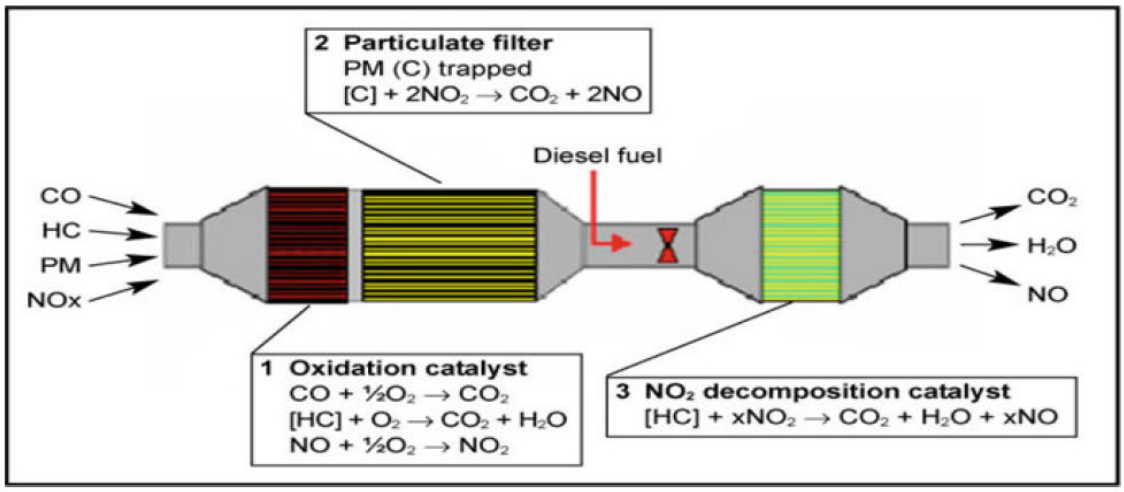

Fig. 9.9 Chemical reactions within a DOC system. *Source* [41]

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CHAPTER 10: CONCLUSION AND FUTURE RECOMMENDATIONS

Due to factors such as industrialization, population growth and increased standards of living, the level of global energy consumption, GHC emissions and vehicular engine dependence on fossil fuels will grow to 60 % compared to the current at 25% to 30%by 2030. The world is moving from traditional feedstock sources of edible plants to non-edible plants and waste by-products for the production of biodiesel. For example, the use of waste animal fats, lard, tallow, yellow grease and use of non-edible plant oils such as Jatropha, neem oil, castor oil, and tallow oil. Other sources include waste cooking oil, microbial and insect oil, tobacco seed oil, rice bran, and rubber seed oil.

The literature review shows that commercialization of non-edible oil for the production of biodiesel and application in diesel engines has not been addressed adequately and conclusively. Even with growth in the passenger and commercial segment of diesel vehicle manufacture in America and Europe there is no corresponding growth in policies in respect of improved engine performance using renewable fuels. Therefore, there is a need for further study in policy development and implementation in relation to biodiesel as applied in the transport industry.

As the demand for energy increases, there is an opportunity for growth in renewable energy to meet this demand in the transport industry. As technology to process biomass resources improves, sustainable production and utilization of biodiesel will see wider acceptance and application in the developing world. This will definitely come with new opportunities for investment and skills, creating the need for researchers, engineers, and manufacturers of engines, biodiesel producers, fuel suppliers and consumers of biodiesel to come together for sustainable production and utilization of biodiesel fuels. Technical collaborations and conferences to bring research findings from the scientific community to target industry players of biodiesel are required. These partnerships have the prospect of developing cost effective and efficient biodiesel production processes. On the other hand, these relationships can also aid all sides to formulate biodiesel blends with complete quality compliance to standards. This will lead to potential mutual benefits for the different parties within the biodiesel industry.

Biodiesel has become an important fuel and an integral part of energy supply. However, tests conducted and reported by many researchers using different blends of biodiesel show that ratios

above 20 % present maintenance problems and damage to internal engine components. On the other hand, some studies have shown that this ratio can be surpassed using vegetable oils without the mentioned consequences or engine modifications. This presents a 50/50 scenario, which calls for more research in the areas of characterization of chemical and physical properties of feedstocks, as feedstock sources expand. This will help to bring vehicle manufacturers on board from a warranty point of view regarding the application of biodiesel in the transport industry. Most warranties cover up to ratios of 5 % compared to the research-finding of satisfactory performance up to a ratio of 20 %, but for a long-time nothing concrete has come out to harmonize standards.

In the work reported in this thesis and reported in the literature reviewed herein using solid municipal waste plastics, lower blend ratios of biodiesel show increased BTE and good fuel economy and consumption for the compression ignition engines tested. However, due to the high oxygen content in biodiesel blended ratios there is increased NO_X emission with all tested blends compared to baseline diesel fuel, which is reported in many of the experimental work reported here and published in this thesis. However, smoke emissions decreased marginally with increasing blend ratios with higher oxygen content. Nevertheless, the NO_X emissions and exhaust temperatures seem to increase as the blend ratios continue to increase. This work clearly shows that waste municipal solids have high potential as a sustainable feedstock for the production of biodiesel for diesel engines. Nevertheless, there remain challenges regarding cold flow properties, thermal and oxidative stability which need solutions before commercialization. Therefore, more research is needed in order to reduce the effects of these demerits in engine applications.

The addition of additives has shown to improve the chemical and physical properties of pyrolyzed plastic waste blends by inhibiting oxidative and thermal degradation of biodiesel fuels while improving combustion. For example, oxygenated additives improve PM emissions but are more useful in power recovery. Metallic additives, oxide additives and emulsifiers improve NO_X emissions of biodiesel blends, show less improvement in HC and CO_2 emissions of biodiesel blends. Nevertheless, more assessment is needed to ascertain how fuel additives interact with other emissions in relation to engine performance. In the next decade fuel additives such as oxygenates, metal-based additives, anti-oxidants CN improvers and nano additives will grow and gain more interest in the energy market as they increase fuel economy and reduce emission as demonstrated in the some of the research undertaken and published work in this thesis.

Since the increase in demand for alternative fuels such as biodiesel for diesel propelled engines, there has been an increase in global acceptability and usage, increased production and processing, and growth in terms of policy and regulation. This has led to wide acceptance and compliance with regulation on quality of biodiesel fuel. For example, in 2015, 2.1 and 3.8 million gallons were consumed in Canada and USA respectively directly reducing carbon emissions by 18 million metric tons. This increase in demand for alternative fuels leads to creation of new jobs and skills to meet the expanding biodiesel industry, with viable foreign exchange earnings for producers and governments.

Many countries in the world use production subsidies to promote growth in biodiesel and alternative energy. Many of these countries have experienced growth such the USA, and Canada. In other words, the biodiesel industry supports jobs in other sectors through employees spending their income on food, clothing, real estate, restaurants, hotels and other consumer goods and services.

As the war to control emissions and climate change rages, there is a need to make diesel engines more efficient by modifying engine components in line with biodiesel end use and application as fuels. For example, modification of fluid flow in the intake manifold, fuel injection and delivery systems, combustion and heat transfer. It is also important to check out that these modifications do not lead to more complex emission issues but minimize emissions in combination with other combustion control strategies. This research has been lagging behind, hence the slow acceptability, usage and large-scale commercialization of biodiesel fuels.

Biodiesel fuels show low in-cylinder pressure and low heat release rate due to slow oxidation reaction rate when the temperature of combustion are low. This phenomenon has been reported in the literature reviewed and the research conducted and published in this thesis.

Although biodiesel fuel is a renewable resource, it cannot be produced in limitless quantities. Global energy needs far outpace abilities to grow or make biomass for biodiesel production. The balance between food and energy keeps feedstocks expensive compared to fuels of fossil origin, therefore making biodiesel production expensive. However, this can be mitigated by diversification of feedstocks through including non-traditional feedstocks and improving production and processing technologies. Although there are many production and processing technologies for biodiesel their full potential is lagging in terms of commercialization and utilization. Thus, innovations are needed to expand efficiency of production processes for biodiesel production especially reduction of cost of production and investment. In the wake of

corona virus pandemic and its depressing effect on global oil prices, investment in biodiesel and the renewable energy sector is expected to fall too.

In the last 30 years starch-based bioethanol has been viable commercially. Through research more hybrid crops with high yield and extractable fermentable starch have been developed. This has made it easier to obtain grains to meet specific and novel process constraints as the feedstock are specifically engineered.

Microalgae can now be used as a feedstock suitable for biohydrogen fermentation. Particular species of microalgae such as *Chlamydomonas reinhardtii, sp., Dunaliella spirulina, Nitzchia closterium, Phaeodactylum tricornutum*, and *Spirulina platensis* show high photosynthetic efficiency. The use of these algae as feedstock will accelerate traditional applications such as direct combustion and fermentation due to economic feasibility for domestic or industrial use.

Regulations in many countries treat biomass as a zero-carbon fuel and are using different pricing regimes for climate change targets. This leads to greater utilization of bioenergy or biodiesel from a climate standpoint. However, this exacerbates the climate impact even when use of biodiesel removes carbon, because the increase in demand for biodiesel has the potential to drive an increase in deforestation.

The use of waste biomass could offer a double advantage. It could be used as an energy source to substitute fossil fuel, and as an effective tool in mitigating GHG since decomposing waste material would be reduced. Nevertheless, there are many industries which compete for biomass such as the pulp and paper industry, the furniture industry, and bio-refineries. The use of biomass for the production of composite building materials can lead to long-term sequestration of the carbon hence offset of high GHG emissions from steel and the cement industry.

A direct positive environmental contribution is possible by using biodiesel because it displaces diesel fuel resulting in less carbon intensity, which reduces GHG emissions. Biodiesel production can contribute to energy security by reducing the use of imported oil in the production of transportation fuels in a country. Biodiesel produced from biomass and other solid residues do not have a land use issue as they are accumulated as a result of production of crops and waste hence provide a potential solution to disposal problems.

As the world grapples with the changing energy patterns of supply and demand, the biodiesel industry creates an exclusive role in climate policy on GHG emissions. These policies have created an emission trading system such as the cap-and-trade mechanism. A good example is

the Kyoto protocol of 1997 and the Paris climate agreement of 2015. Creation of a carbon dioxide price allows governments to offer incentives for the development of biodiesel to substitute fossil fuels. Therefore, there is a need to harmonize biofuel and biodiesel policies as policy uncertainty affects international opportunities as each government applies different policies and taxes in the biodiesel mandate. In other words, policy instead of system forces play a critical role in influencing production in all countries.

There is a need in the near future to develop innovative biofuels, lignocellulosic fuels and biodiesel fuels, which will need minimal resources such as water and land for production of energy. Lignocellulosic fuels use the whole plant instead of starch or the sugary part, or residue products from arable agriculture land such as straw. Algal biofuels constitute a diverse group of aquatic photosynthetic organisms (third generation biofuels).

Diesel emissions regulated and unregulated contribute to short and long-term human health problems such as cancer, minor eye and throat irritations and slow blood poisoning. The use of biodiesel helps to reduce these problems by reducing the quantity of particle emissions, because exhaust particles have an adverse effect on human health.

There is a need to gain understanding of waste production characteristics, capture and diversion, processing methods, transport requirements, available conversion technologies and return on energy investment. This will lead to accurate estimates on energy and co-product potential and better understanding of demand for other resources such as land, water, infrastructure and opportunities for co-product generation.

The role of technology is critical in the implementation of the biodiesel policy, especially production, processing and use. Therefore, intense research is a pre-requisite in biotechnology, plant agronomy, oil extraction technologies, transesterification and fermentation processes for the production of biodiesel of biofuels such as bioethanol. For successful implementation of biodiesel programs hard and soft infrastructural development is necessary, particularly in developing countries. In other words, relevant biodiesel and biofuels supply chain infrastructure is required to cater for all stakeholders in the industry such as producers, manufacturers, consumers and the supply network. For example, serious efforts are needed to design and build large-scale bio-refineries for biodiesel production as the world moves to this technology. This will prevent conflict between fossil fuels and biodiesel fuels as competing products. Another important infrastructural development would be building blending and

dispensing facilities in the same locations as conventional oil and gas refineries to minimize cost of transport.

There is a danger of future technologies wiping out demand for biodiesel if by-products are not developed. In other words, for a sustainable future, the by-product of the biodiesel or biofuel supply chain need to be developed by 2030 for the industry to remain relevant because of the rapid rise of electric cars. This means that more feedstock utilization is needed for biodiesel and biofuels to remain relevant and sustainable in future.

The question of arable land for the production of biodiesel feedstocks needs to be addressed because as the industry grows more land will be required for the cultivation of feedstocks. This will result into inflated food prices, as the demand for edible oil will outstrip supply. Therefore, cheaper alternatives and diversification of feedstocks is critical to the existing ones including development of efficient production and processing technologies. An example of a non-edible plant is Jatropha which can grow on non-arable land such as wasteland and uses little water with no fertilizers, growing rapidly with a lifespan of 26 to 30 years.

APPENDIX A: EDITING CERTIFICATES

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EDITING CERTIFICATE

Re: **Semakula Maroa**
PhD thesis: **Effects of Pyrolyzed Municipal Solid Waste Feedstocks as Energy Sources for Non-Road Diesel Engine, Combustion, Performance and Emissions Characteristics Using Biodiesel Blended Ratios**

I confirm that I have edited Chapter 1 and Chapter 10 of this thesis and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years.

Dr Richard Steele
30 January 2021
per email

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EDITING CERTIFICATE

Re: **Maroa, Semakula**
PhD Chapter 2: **Waste to Energy Feedstock Sources for the Production of Biodiesel as Fuel Energy in Diesel Engine - A Review**

I confirm that I have edited this chapter and the references for clarity, language and layout. I am a freelance editor specialising in proofreading and editing academic documents. I returned the document to the author with track changes so correct implementation of the changes in the text and references is the responsibility of the author. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). During my 13 years as a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology I supervised numerous Master's degree dissertations.

Dr Richard Steele
02 October 2020
per email

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EDITING CERTIFICATE

Re: **Maroa Semakula**
For editing journal article: **EVALUATION OF PYROLYSIS OIL FROM PLASTIC AND SOLID WASTE BIOMASS**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct

implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree

which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban

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supervised numerous Master's degree dissertations.

Dr Richard Steele
02 August 2019
per email

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EDITING CERTIFICATE

Re: **Semakula Maroa**
Journal article: **The Effect of Fuel Additives on Pyrorated Biodiesel Blends on the Performance of a Diesel Power Generator**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many masters degree dissertations during that period.

Dr Richard Steele
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EDITING CERTIFICATE

Re: **Maroa, Semakula**
Journal article: **THE EFFECT OF CETANE NUMBER AND OXYGEN CONTENT IN THE PERFORMANCE AND EEMISSIONS CHARACTERISTICS OF A DIESEL ENGINE USING BIODIESEL BLENDS**

I confirm that I have edited this article and the references for clarity, language and layout. I am a freelance editor specialising in proofreading and editing academic documents. I returned the document to the author with track changes so correct implementation of the changes in the text and references is the responsibility of the author. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). During my 13 years as a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology I supervised numerous Master's degree dissertations.

Dr Richard Steele
05 January 2019
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EDITING CERTIFICATE

Re: **Semakula Maroa**
For editing journal article: **Effects of Exhaust Gas Recirculation on Temperature, Using Biodiesel Blends**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years.

Dr Richard Steele
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EDITING CERTIFICATE

Re: **Semakula Maroa**
For editing book chapter: **Effects of Biodiesel Blends, Cetane Number and Oxygen Content on Stationary Diesel Engine**

I confirm that I have edited this chapter and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years.

Dr Richard Steele
2020-01-15
per email

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EDITING CERTIFICATE

Re: **Maroa Semakula**
Journal article: **Assessing the Effects of Engine load on Compression Ignition Engines Using Biodiesel Blends**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years.

Dr Richard Steele
07 December 2019
per email

APPENDIX B: ACCEPTANCE LETTERS

ACCEPTANCE: Chapter 2 Journal Article

ASTES

Advances in Science, Technology and Engineering Systems Journal

Journal Homepage: https://www.astesj.com/

Dated: 08-Dec-20

Letter of Acceptance

Dear Semakula Maroa c/o Prof F Inambao,

It's my pleasure to inform you that, after the peer review, your paper, **"Waste To Energy Feedstock Sources for the Production of Biodiesel as Fuel Energy in Diesel Engine - A Review"** has been **ACCEPTED** to be published in Advances in Science, Technology and Engineering Systems Journal under ISSN (Online) 2415-6698 and it will be available online at https://www.astesj.com/ in December 2020.

Thank you very much for submitting your article to the Advances in Science, Technology and Engineering Systems Journal. I believe that our collaboration will help to accelerate the global knowledge creation and sharing one step further.

Best Regards

[redacted]

Prof. Passerini Kazmerski
Editor in Chief
ASTES Journal
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www.astesj.com

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ACCEPTANCE LETTER: Chapter 3 journal Article

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INTERNATIONAL JOURNAL OF MECHANICAL ENGINEERING AND TECHNOLOGY (IJMET)

www.iaeme.com/ijmet/index.asp

Journal Impact Factor (2019): 10.6879 Calculated by GISI (www.jifactor.com)

ISSN Print: 0976 - 6340 **ISSN Online**: 0976 - 6359

Official Acceptance of Research Paper

Paper ID: IJMET/10/08/2019/IJMET_44350 **Date:** 31-August-2019

Dear **Maroa Semakula and Prof Freddie Inambao**

We would like to inform you that your paper titled **"EVALUATION OF PYROLYSIS OIL FROM PLASTIC AND SOLID WASTE BIOMASS"** has been accepted for publication in **International Journal of Mechanical Engineering and Technology (IJMET),** Volume 10, Issue 08, (August 2019) issue of the journal based on the Recommendation of the Editorial Board without any major corrections in the content submitted by the researcher.

This letter is the official confirmation of acceptance of your research paper.

Your research work is licensed under a Creative Commons Attribution 4.0 (International) License (CC BY-NC 4.0). Hence no need to submit the Copyright form.

Your research paper will be appearing in IJMET, Volume 10, Issue 08, August 2019.

International Journal of Mechanical Engineering and Technology (IJMET)
Journal Impact Factor (2019): 10.6879 Calculated by GISI
ISSN Print: 0976 – 6340
ISSN Online: 0976 – 6359

Review Comments are attached along with the mail.

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Type of Account	Current
Swift Code	KKBKINBBXXX
IFSC CODE	KKBK0000468
MICR CODE	600485008

Kindly acknowledge the Paper acceptance. Thanks and looking to receive the payment from your side at the earliest.

Thank you.
Yours Sincerely,

[redacted]

Prof. Dr. S. Balasubramanian, Ph.D, DSc
Chief Editor
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Website: www.iaeme.com

ACCEPTANCE LETTER: Chapter 4 journal Article

Dear Mr. Semakula Maroa,

Congratulations! We are pleased to inform your manuscript review result submitted to *Advances in Science, Technology and Engineering Systems Journal*.

Manuscript ID: 19M-06-199
Title: THE EFFECT OF FUEL ADDITIVES ON PYRORATED BIODIESEL BLENDS ON THE PERFORMANCE OF A DIESEL POWER GENERATOR
Author(s): Semakula Maroa, Freddie Inambao
Corresponding Author: Semakula Maroa
Affiliation of Corresponding Author: University of Kwazulu Natal
Date of Manuscript Submission: 22-Jul-2019 (UTC)

Overall review result: Accept with minor changes

The second half of this email contains important review comments that you must follow to ensure successful publication of your paper, and you can also find them in the following online system.

* Online System URL: https://www.manuscriptlink.com/journals/astesj

What you should do at the next step is to make your camera-ready paper for the above manuscript. When making your camera-ready paper, please take into consideration all review comments.

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The deadline for the camera-ready paper submission is 16-Aug-2019. We cannot guarantee to include your paper in final edition, in case of late submission of your camera-ready paper.

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Thank you for submitting your manuscript to *Advances in Science, Technology and Engineering Systems Journal*.

ACCEPTANCE LETTER: Chapter 5 journal Article

Gmail ssemakula maroa <ssemakulamaroa@gmail.com>

[JESA] Editor Decision

Dr Mokone J Roberts <mok.roberts@uct.ac.za> Thu, Feb 21, 2019 at 4:04 PM
To: Samwel Semakula Maroa <ssemakulamaroa@gmail.com>, Freddie Inambao <inambaof@ukzn.ac.za>

Samwel Semakula Maroa, Freddie Inambao:

We have reached a decision regarding your submission to Journal of Energy in Southern Africa, "THE THE INFLUENCE OF CETANE NUMBER AND OXYGEN CONTENT IN THE PERFORMANCE AND EMISSIONS CHARACTERISTICS OF A DIESEL ENGINE USING WASTE PLASTIC BIO-DIESEL BLENDS".

Our decision is to: Accept for publication subject to revisions and editing processes.

You are requested to revise your manuscript according to issues raised by Reviewer C. Due date is Tuesday 26 February 2019.

When you revise, also create a separate file (Change-log or Rebuttal File) where you restate all issues raised by the reviewer together with respective responses to them (clear, full and precise position in your revised submission). Add continuous line numbering in your submission (if not added in your original submission) to simplify and submit both the revised submission (clean with no mark-ups like track changes or comments) and Change-log File. Additional author comments/queries can be added in the system email when you notify editor.

Example for Change-log/Rebuttal File:

Title:

Reviewer A (or B, C or D)

Issue 1:

.....

Response:

..... addressed in line ...to...

Issue 2:

.....

Response:

..... line ...to...

This is unacceptable: 'corrected', 'edited to show this', 'done'.

Feel free to defend your views with reasons because you have first-hand understanding of your work.

When complete, upload your two files and notify editor.

Feel free to contact the editor for clarity.

Dr Mokone J. Roberts, Ph.D. Pr.Sci.Nat MSAIMM NSEF
https://orcid.org/0000-0002-3858-0077
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Tel.: +27 (0)21 650 3894
Website: https://journals.assaf.org.za/jesa

Twitter: @JournalEnergySA

The following message is being delivered on behalf of Journal of Energy in Southern Africa (JESA).

A-Review Annotated file Paper JESA.docx
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ACCEPTANCE LETTER: Chapter 6 Journal Article

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INTERNATIONAL JOURNAL OF MECHANICAL ENGINEERING AND TECHNOLOGY (IJMET)

www.iaeme.com/ijmet/index.asp

Journal Impact Factor (2020): 11.2184 Calculated by GISI (www.jifactor.com)

ISSN Print: 0976 - 6340 ISSN Online: 0976 - 6359

Official Acceptance of Research Paper

Paper ID: IJMET/11/01/2020/IJMET_45275 **Date:** 14-Jan-2020

Dear **Semakula Maroa and Freddie Inambao**

We would like to inform you that your paper titled **"EFFECTS OF EXHAUST GAS RECIRCULATION ON TEMPERATURE, USING BIODIESEL BLENDS"** has been accepted for publication in **International Journal of Mechanical Engineering and Technology (IJMET),** Volume 11, Issue 01, (January 2020) issue of the journal based on the Recommendation of the Editorial Board without any major corrections in the content submitted by the researcher.

This letter is the official confirmation of acceptance of your research paper.

Your research work is licensed under a Creative Commons Attribution 4.0 (International) License (CC BY-NC 4.0). Hence no need to submit the Copyright form.

Your research paper will be appearing in IJMET, Volume 11, Issue 01, January 2020.

International Journal of Mechanical Engineering and Technology (IJMET)
Journal Impact Factor (2020): 11.2184 Calculated by GISI
ISSN Print: 0976 – 6340
ISSN Online: 0976 – 6359

Review Comments are attached along with the mail.

Kindly send the Publication fee of **$ 450/- (Online only).** The Online Only mode includes online publication of paper, indexing of paper in more than 20 search engines and soft copy of the publication certificate.

You can transfer the money and send the scan copy of payment made evidence through e-mail.

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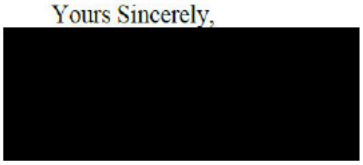
Branch	T. Nagar Branch
Address of the Bank	Ground Floor, Shree Essarar Towers, 41 Venkatnarayana Road, T.Nagar, Chennai - 600017, Tamil Nadu, India
Type of Account	Current
Swift Code	KKBKINBBXXX
IFSC CODE	KKBK0000468

Kindly acknowledge the Paper acceptance. Thanks and looking to receive the payment from your side at the earliest.

Thank you.
Yours Sincerely,



Prof. Dr. S. Balasubramanian, Ph.D, DSc
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ACCEPTANCE LETTER: Chapter 7 Book chapter

IntechOpen

NOTIFICATION OF CHAPTER ACCEPTANCE

April 16, 2020, London

Dear Mr. Maroa,

It is my pleasure to inform you that the manuscript titled "effects of biodeiesel blends, cetane number and oxygen content on stationary diesel engine" has been accepted for publication.

Your chapter will appear in the Open Access book, "Non-road Engines - Development, Current and Prospective Applications" edited by Ph.D. Paweł Woś

Congratulations on your achievement! I would like to thank you for your important contribution to the scientific community, and for ensuring your research is freely available to readers all over the world.

We wish you every success with your publication.

With my best wishes,

Anke Beck,
CEO, IntechOpen

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P: +44 (0) 20 3972 6202 / W: intechopen.com / M: info@intechopen.com

ACCEPTANCE LETTER: Chapter 8 Journal Article

Dear Semakula Maroa,

Paper Code: 18994-IJERT

We are very pleased to inform you that your paper **Assessing the Effects of Engine load on Compression Ignition Engines Using Biodiesel Blends**, is accepted by our Editor-in-chief for our journal, **International Journal of Engineering Research and Technology (IJERT) ISSN 09743154, Scopus indexed, active in 2019.**

Please find the attached copy right transfer form and page charge/Reprint form for your accepted paper. Please find below the details of no. of pages with cost of publication.

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APPENDIX C: PUBLISHING AGREEMENT

CHAPTER 9: Book Publication Agreement

Contract No.: 103374

Publishing Agreement

The following agreement has been approved by and entered into between

Maroa Semakula, University of KwaZulu-Natal, Mechanical Engineering, Mazisi Kunene Road, 4041 Durban, South Africa

Prof. Freddie Inambao, University of KwaZulu-Natal, Mechanical Engineering, Mazisi Kunene Road, 4041 Durban,

South Africa

(hereinafter called **Author**)

on the one part and

Springer Nature Switzerland AG, Gewerbestrasse 11, 6330 Cham, Switzerland

(hereinafter called **Publisher**)

on the other part.

When Author is more than one person, the expression "Author" as used in this agreement will apply collectively unless otherwise indicated.

§ 1 Rights Granted

1.1 Author undertakes to prepare for publication by Publisher a work provisionally entitled:

Biodiesel, Combustion, Performance and Emissions Characteristics

(hereinafter called **Work**)

comprising approximately 125 pages, including no illustrations, whereas the Publisher intends to publish the Work under the imprint Springer. The work may be published in the book series **Green Energy and Technology**.

The Work may contain or link to media, social or functional enhancements. If such enhancements are included in or linked to the Work it will be specified in Clause 9. To the extent Clause 9 specifies that enhancements are included in the Work, they are an integral part of the Work and, unless otherwise explicitly set forth in Clause 9, all rights, licences and obligations agreed to hereunder shall apply to such enhancements.

1.2 Author hereby grants and assigns to Publisher the exclusive, sole, permanent, world-wide, transferable, sub- licensable and unlimited right to reproduce, publish, distribute, transmit, make available or otherwise communicate to the public, translate, publicly perform, archive, store, lease or lend and sell the Work or parts thereof individually or together with other works in any language, in all revisions and versions (including soft cover, book club and collected editions, anthologies, advance printing, reprints or print to order, microfilm editions, audiograms and videograms), in all forms and media of expression including in electronic form (including offline and online use, push or pull technologies, use in databases and data networks (e.g. Internet) for display, print and storing on any and all stationary or portable end-user devices, e.g. text readers, audio,

video or interactive devices, and for use in multimedia or interactive versions as well as for the

display or transmission of the works or parts thereof in data networks or search engines, and posting the Work on social media accounts closely related to the Work, as well as using the Work for educational or training purposes,
e.g. but not limited to use in massive open online courses), in whole, in part or in abridged form, in each case as now known or developed in the future, including the right to grant further time-limited or permanent rights. Publisher especially has the right to permit others to use individual illustrations, tables or text quotations and may use the Work for advertising purposes. For the purposes of use in electronic forms, Publisher may adjust the Work to the respective form of use and include links (e.g. frames or inline-links) or otherwise combine it with other works and/or remove links or combinations with other works provided in the Work. For the avoidance of doubt, all provisions of this contract apply regardless of whether the Work itself constitutes a database under applicable copyright laws or not.

1.3 The copyright in the Work shall be vested in the name of Publisher. Author has asserted his/her right(s) to be identified as the originator of this Work in all editions and versions of the Work and parts thereof, published in all forms and media. Publisher may take, either in its own name or in that of Author, any necessary steps to protect the rights granted under this Agreement against infringement by third parties. It will have a copyright notice inserted into all editions of the Work according to the provisions of the Universal Copyright Convention (UCC}.
The parties acknowledge that there may be no basis for claim of copyright in the United States to a Work prepared by an officer or employee of the United States government as part of that person's official duties. If the Work was performed under a United States government contract, but Author is not a United States government employee, Publisher grants the United States government royalty-free
permission to reproduce all or part of the Work and to authorise others to do so for United States government purposes. If the Work was prepared or published by or under the direction or control of the Crown (i.e., the constitutional monarch of the Commonwealth realm) or any Crown government department, the copyright in the work shall, subject to any agreement with Author, belong to the Crown. If Author is an officer or employee of the United States government or of the Crown, reference will be made to this status on the signature page.

1.4 Author retains, in addition to uses permitted by law, the right to communicate the content of the Work to other research colleagues, to share the Work with them in manuscript form, to perform or present the Work or to use the content for non-commercial internal and educational purposes provided the original source of publication is cited according to current citation standards.

§ 2 Delivery and Acceptance of the Work

2.1 Author shall deliver the Work to Publisher on or before November 30, 2019 (hereinafter called **Delivery Date**) electronically in Microsoft Word format or in such form as may be agreed in writing with Publisher. The Work shall be in a form acceptable to the Publisher (acting reasonably) and in line with the instructions contained in the guidelines and Author shall provide at the same time, or earlier if the Publisher reasonably requests, any editorial, publicity or other form required by the Publisher. Publisher is entitled to have the Work peer- reviewed by external reviewers of its choice.

If Author fails to deliver the Work by the Delivery Date, or within any grace period given by Publisher, acting reasonably, then Publisher shall be entitled to:

(a) commission an appropriate and competent person (who, in the case of joint Authors, may be a person comprising the Author) to complete the Work and any fees payable to the competent person shall be deducted by Publisher, acting reasonably, from any sums due to Author under this Agreement; or

(bl terminate this Agreement by immediate written notice to Author, in which case all advance payments paid to Author under or in connection with this Agreement shall be repaid to Publisher within 28 days of said notice.

(c) If Author, or where Author consists of two or more persons, any of the persons comprising the Author, dies or becomes incapacitated or otherwise incapable of performing Author's obligations under this Agreement, Publisher shall be entitled to be given copies of all notes, manuscripts or other materials relating to the Work. Publisher may either terminate this Agreement with immediate effect (by written notice to Author or Author's estate) or elect to continue to publish the Work.

1.1 Publisher is entitled to carry out editorial changes on the manuscript within the usual limits. This is intended especially to enhance the uniform overall organisation and form of the Work. Any significant changes in content require the approval of the Author. Publisher is entitled to prepare and use summaries within the intended use of the Work and for the purposes of sales, distribution and advertising.

1.2 Author agrees, at the request of Publisher, to execute all documents and do all things reasonably required by Publisher in order to confirm to Publisher all rights intended to be granted under this Agreement. Author warrants and represents that the Work is original except for such excerpts from copyrighted works (including illustrations, tables, animations and text quotations) as may be included with the permission of the copyright holder thereof, in which case(s) Author is required to obtain written permission to the extent necessary and to indicate the precise sources of the excerpts in the manuscript. Author is also requested to store the signed permission forms and to make them available to Publisher if required.

Author warrants and represents that Author is entitled to grant the rights in accordance with Clause 1 "Rights Granted", that Author has not assigned such rights to third parties, that the Work has not heretofore been published in whole or in part, that the Work contains no libellous or defamatory statements and does not infringe on any copyright, trademark, patent, statutory right or proprietary right of others, including rights obtained through licences. Author agrees to amend the Work to remove any potential obscenity, defamation, libel, malicious falsehood or otherwise unlawful part(s) identified at any time. Any such removal or alteration shall not affect the warranties and representations given by Author in this Agreement.

§ **3 Publication of the Work**

3.1 Publisher will undertake the publication and distribution of the Work in print and electronic form at its own expense and risk within a reasonable time after it has given notice of its acceptance of the Work to Author in writing. The final determination of the electronic formats and the number of copies produced is at the discretion of Publisher. Publisher will, at its sole discretion, set or alter the list-price, allow for deviations from the list-price (if permitted under applicable jurisdiction) and promote the Work as it considers most appropriate to optimise sales, including a good and suitable presentation for all distribution channels. All right, title and interest in the typography, design and/or look-and-feel of the Work shall remain the property of and is reserved to Publisher. Illustrations and any other material or immaterial property prepared at the expense of Publisher remain, as between the parties, the exclusive property of Publisher.

Nothing in this Agreement shall constitute an undertaking on the part of Publisher to publish the Work unless and until: (i) Publisher has given notice of acceptance in writing of the final manuscript of the entire Work, and

(ii) any issues in relation to the Work (including all necessary consents and permissions) raised by the Publisher have been resolved to the Publisher's satisfaction.

In consideration of the above, if Publisher decides to not publish the Work, Author shall in no event be entitled to any compensation or remedy in respect of any expense or loss incurred.

3.2 Publisher is entitled, depending on the market and the demand, to publish and distribute the Work in instalments (including but not limited to individual chapters) or to order. In case the Work is stored in physical stock Publisher is also entitled to pulp the print run or any portion thereof without previously notifying Author. Publisher is required to continue promoting the Work and to retain a sufficient number of copies unless the Work is available in electronic form or on the basis of a print-to-order offer.

§ 4 Approval for Publishing

1.3 Author shall proofread the page proofs, check the illustrations as well as any media, social or functional enhancements, and give approval for publishing, if and when requested by Publisher. Author's approval for publishing is deemed to have been given if Author does not respond within a suitable period of time after receiving the proofs.

1.4 Proofs are sent to enable Author to check that the manuscript has been properly set in type and to allow Author to correct any typesetter's or illustrator's errors. No alterations or corrections may be made by Author other than for the purpose of correcting typographical errors without the Publisher's prior written consent. In case Author makes major changes that lead to additional costs for Publisher, and if such costs exceed 10% of the total cost of typesetting (or reproduction in the case of illustrations) they will be borne by Author.

§ 5 Complimentary Copies, Author's Discount for Books and Electronic Access

5.1 Author or, if "Author" comprises several individual authors, each of the co-authors who is party to this agreement is entitled to receive 3 printed copies free of charge and may obtain additional copies for personal use at a discount of 40% off the list-price if ordered directly from Publisher.

5.2 Furthermore, Author is entitled to purchase for Author's personal use (directly from Publisher) other books published by Publisher at a discount of 40% off the list-price for as long as there is a contractual arrangement between Author and Publisher and subject to applicable book price regulation.

Resale of such copies or of free copies is not permitted.

5.3 Publisher shall provide electronic access to the electronic final published version of the Work on Publisher's Internet portal, currently known as springer.com and/or palgrave.com, to Author, provided Author has included his/her email address in the manuscript of the Work. Furthermore, Author has the right to download and disseminate single contributions from the electronic final published version of the Work for his/her private and professional non-commercial research and classroom use (e.g. sharing the contribution by mail or in hard copy form with research colleagues for their professional non-commercial research and classroom use, or to use it for presentations or handouts for students). Author is also entitled to use single contributions for the further development of his/her scientific career (e.g. by copying and attaching contributions to an electronic or hard copy job or grant application).

When Author is more than one person each of the co-authors may share single contributions of the Work with other scientists or research colleagues as described above. In each case, Publisher grants the rights to Author under this clause provided that Author has obtained the prior consent of any co-author(s) of the respective contribution.

§ 6 Remuneration

6.1 Publisher shall pay to Author a remuneration of EUR 900 payable upon publication, publication being stipulated as the point in time when the Work is being distributed in print or electronic form, whichever occurs earlier.

1.5 If Publisher grants licenses to use the Work or derivative works thereof or parts of either in products published by other publishers (e.g. a licence to translate the Work and to distribute the translation, or a licence to distribute parts of the Work in a third-party publication), Author's sole payment for the respective licence and any related use will be a share of Publisher's Net Proceeds according to industry standards of 50%.

1.6 In the event that the Work contains or links (e.g. through frames or in-line links) to media, social or functional enhancements, the aforesaid remuneration, complimentary copies and/or access rights shall also cover the use of such material.

1.7 If "Author" comprises several individual authors, the aforesaid remuneration will be paid as a total to the joint group of authors. Each co-author will receive an equal share of any payment.

1.8 If there is a legal requirement for Publisher to withhold any taxes, the taxes will be deducted from the payments to Author. Authors are responsible for the taxation of their payments. Publisher is entitled to report related information (including personal and financial data) to the respective authorities.

1.9 Any publisher's proceeds from rights managed by national copyright organisations (collecting societies including but not limited to societies such as Copyright Clearance Center) are the sole property of Publisher. Any such author's proceeds are the sole property of Author, and if applicable, registration and taxation of such proceeds is Author's sole responsibility.

§ **7 Competing Works**

Author agrees not to contribute or to release with another publisher any publication that contains expression or subject matter substantially similar to the Work and which may compete with the Work. Any publication of substantial parts of the Work requires the prior written consent of Publisher, such consent not to be unreasonably withheld.

§ **8 New Editions**

5.4 Publisher has the sole right to determine the publication of any subsequent edition, such determination to be made only after consultation with the Author. In the event of subsequent editions, they shall be published by Publisher. Once notified by Publisher that a new edition is deemed necessary, Author agrees to deliver an updated manuscript according to the terms of Clause 2 "Delivery and Acceptance of the Work", together with the material for any new illustrations within 9 months of such notification. Substantial changes in the nature or size of the Work require the approval of Publisher. Upon publication of such new edition, Author shall receive a consideration equivalent to Clause 6 "Remuneration". The terms of this Agreement shall apply to any new edition that is published under this New Edition clause.

5.5 If Author, for whatever reason, is unwilling, unable or fails to submit an updated manuscript that meets the terms of this Agreement within the above stated period, then Publisher is entitled to revise, update and publish the content of the original edition or to designate one or more individuals (which, where Author comprises two or more persons, may be one or more of the persons comprising the Author) to prepare this and all future editions. In this case, Author does not participate in preparing any subsequent editions. Publisher is entitled to continue to use the name of Author on any new editions of the Work. Notwithstanding clause 8.2 (first sentence), Author or Author's beneficiaries shall receive 50% of the financial consideration

stipulated in Clause 6 "Remuneration" (if any) but shall have no right or claim from any further subsequent editions of the Work.

§ **9 Miscellaneous**

This clause is left blank intentionally.

§ **10 General Provisions**

1.1 If any difference shall arise between Author and Publisher concerning the meaning of this Agreement or the rights and liabilities of the parties, the parties shall engage in good faith discussions to attempt to seek a mutually satisfactory resolution of the dispute. This agreement shall be governed by, and shall be construed in accordance with, the laws of Switzerland. The courts of Zug, Switzerland shall have the exclusive jurisdiction.

1.2 Either party shall be entitled to terminate this Agreement forthwith by notice in writing to the other party if the other party commits a material breach of the terms of the Agreement which cannot be remedied or, if such breach can be remedied, fails to remedy such breach within 28 days of being given written notice to do so.

1.3 If Publisher, acting reasonably, decides that the Work is not suitable for publication in the intended market place, or that there is no substantial market for the Work, or the economic circumstances of publication have substantially changed (in each case other than due to the Work not being of a suitable quality to justify publication) then Publisher may at any time terminate this Agreement by giving one month's notice to Author in writing. In the event of such termination: (a) Author shall be entitled to retain all amounts received in respect of the Work previously paid to Author by Publisher at the date of termination, and (b) all rights granted by Author to Publisher under this Agreement shall revert to Author. Author will not in any event be entitled to any further payments due after the date of termination in respect to the Work.

1.4 Termination of this Agreement, howsoever caused, shall not affect:

- any subsisting rights of any third party under any licence or sub-licence validly granted by Publisher prior to termination and Publisher shall be entitled to retain its share of any sum payable by any third party under any such licence or sub-licence;
- the rights of Author to any payments due in respect of exploitation of the Work by a third party pursuant to any licence granted by Publisher prior to the date of termination;
- any claim which either party may have against the other for damages or otherwise in respect of any rights or liabilities arising prior to the date of termination; or
- any option granted by Author to Publisher in respect of future works.

1.5 On termination of this Agreement in accordance with its terms, all rights and obligations of Publisher and Author under this Agreement will cease immediately, except that any terms of this Agreement that expressly or by implication survive termination of this Agreement shall remain in full force and effect. On termination of this Agreement by Publisher for any reason, Publisher shall not be liable for any payment in respect of any part of the Work not delivered at the date of termination. On termination of this Agreement Publisher may continue to sell any copies of the Work which are in its power, possession or control as at the date of expiry or termination of this Agreement for a period of 6 months on a non-exclusive basis subject to the payment of royalties due hereunder.

2.2 This agreement and the documents referred to within constitute the entire agreement between the parties with respect to the subject matter hereof and supersede any previous agreements, warranties, representations, undertakings or understandings. It may be modified or amended only in writing. For purposes of this agreement, "in writing" requires either a written and signed document or an electronic confirmation with DocuSign or similar e-commerce solution.

2.3 The failure by either party to enforce any one or more of the terms of this Agreement at any time or for any period shall not constitute a waiver of such term or of that party's right to enforce any and all terms of the Agreement subsequently.

2.4 Author will not, without the prior written consent of Publisher, disclose the terms of this Agreement to any third party, except to Author's respective professional advisors or as required by a court, regulatory body or other authority of competent jurisdiction.

2.5 Nothing contained in this Agreement shall constitute or shall be construed as constituting a partnership, joint venture or contract of employment between Publisher and Author. Each author is jointly and severally liable for Author's obligations. Neither party may assign this agreement to third parties but Publisher may assign this agreement or the rights received hereunder to its affiliated companies.

To signify their agreement to the terms outlined herein, all parties have signed and exchanged this contract.

The Author(s) Springer Nature Switzerland AG, Cham

[redacted]

Maroa Semakula

Guido Zosimo-Landolfo

Editorial Director /Asset Manager

Date 18/09/2019

Date

[redacted]

Prof. Freddie Inambao

Physical Sciences and Engineering Vice President

Date September 2019

Date

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APPENDIX D: UNCERTAINITY ANALYSIS TABLE

The instruments used and their percentage error of analysis are listed in the table below with the uncertainties of CO, CO_2, UHC, NO_X, exhaust gas temperature (EGT) and smoke opacity. This table applies to chapters 3, 4 and 5. These percentages of error analysis were derived from the following formula, the root sum square method and expressed in two equations form as:

$$R = \sqrt{\sum_{i=1}^{n} X_i^2} \qquad \text{Equation 1}$$

$$R = \sqrt{X_1^2 + X_2^2 + X_3^2} + \cdots X_i^2 \qquad \text{Equation 2}$$

Instrument	Accuracy	Measuring Range	Percentage inaccuracies
AVL 437C			
(Smoke Meter)			
Smoke Intensity	±1%	0-100%	±1
AVL Pressure			
Transducer GH14D	±0.01 bar	0-250 bar	±0.01
AVL 365C Angle encoder			
	±1º	-	±0.2
AVL digas 444 (five gas analyzer)			
CO	±0.03% to ±5%	0-10% by vol	±0.3
CO_2	±0.5% to ±5% by vol		
		0-20% vol	±0.2
O_2	±5% by vol	0-22% by vol	±0.3

HC	±0.1% to ±5%	0-20000ppm by vol	±0.2
NOx	±10%	0-5000 ppm by vol	±0.2
K-2 Thermocouple			
	±1ºC	0-1250ºC	±0.2
Digital Stop Watch			
	±0.2s		±0.2
Digital Fuel Gauge			
	±1mm		±2
Burette	±0.2cc	1-30cc	±1.5