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**COMBUSTION STUDIES OF HYBRID NANOADDITIVE
DOPED WASTE COOKING OIL BIODIESEL AND ITS
BLENDS IN COMPRESSION IGNITION ENGINE**

BY

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Dissertation submitted in fulfilment of the academic requirements for the degree
of Doctor of Philosophy in Mechanical Engineering

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December 2021

“As the candidate’s Supervisors we agree to the submission of this dissertation”.

Prof. Freddie Inambao

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DETAILS OF CONTRIBUTION TO PUBLICATIONS that form part and/or include research presented in this dissertation (include publications in preparation, submitted, in press and published and give details of the contributions of each author to the experimental work and writing of each publication).

1. H Maverengo and Freddie L. A Review on waste cooking oil biodiesel as a viable fuel for diesel engines, Existing concepts, and future prospect. *International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)* ISSN (P): 2249–6890; ISSN (E): 2249–8001 Vol. 11, Issue 5, Oct 2021, 11–32
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<http://www.tjprc.org/view-archives.php>

The author/candidate of this thesis is the main author of all the publications used in this thesis, whereas Professor Freddie L. Inambao is the Supervisor.

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ABSTRACT

South Africa, among the developing nations in sub-Saharan Africa lacks technologies for converting crude bio-oil into biodiesel to run fuel CI engines. The country has also struggled to identify a suitable feedstock that can be used for biodiesel production. This research was therefore aimed at analysing the suitability of mixed waste cooking oil (WCO) biodiesel doped with hybrid nano particles as a viable fuel for diesel engines. The utilization of WCO as feedstock for biodiesel is garnering attention since it does not impact on the food supply chain and provides a solution to the challenges associated with its disposal. Biodiesel acceptance has been hampered by three main issues. These are related to higher production costs linked to feedstock, higher nitrogen dioxide emissions, and a lack of economic evaluation of technologies incorporating different alcohols and catalysts. This research performed investigations to develop solutions to circumvent all these challenges. Regarding high feedstock cost, WCO was identified to present an easily available solution since it is acquired at a low cost and its usage helps to solve the disposal problem.

Manufacture, assessment, and engine testing of biodiesel from WCO was conducted to evaluate its viability as a potential feedstock for biodiesel. From the derived results, WCO oil has higher oil yields and excellent fuel properties and therefore is a viable feedstock to create biodiesel. Transesterification, a biodiesel creation measure, was performed utilizing methanol and NaOH or KOH as catalysts. This feedstock showed some favourable engine exhaust emission behaviour, but on engine performance considerable shortfalls were noted when evaluated against fossil diesel (FD) fuels. Lower brake thermal efficiency and higher fuel consumption were noted when the neat fuel blends with fossil diesel were tested in two-cylinder compression ignition engines. Higher NO_x emissions were also noted with WCO and its blends when evaluated against FD. Three options are available to deal with the above problems, namely, engine modification, exhaust after-treatment, and fuel reformulation. Fuel reformulation is the most promising due to its easy implementation and cheaper cost. The researcher's search for the most relevant solution resulted in identification of hybrid nanoparticles consisting of cerium oxide and aluminium oxide as the most appropriate solutions. WCO biodiesel and its blends were doped with nanoparticles and tested in two-cylinder compression ignition (CI) engines and results compared with those of FD. From the experimental analysis, addition of hybridized nano additives improved BTE by a maximum value of 6.22 % compared to FD fuel when evaluated against load. A maximum decrease in BSFC of 10.20 % was noted with hybrid nano fuel WCO20A50C50 compared to FD fuel. A significant reduction in NO_x of 25.62 % was found compared to FD. CO, unburnt hydrocarbons (UBHC) and smoke opacity were reduced by 36.8 %, 27.8 % and 17.68 % respectively compared to FD. WCO20A50C50 produced the most superior characteristics of all the fuels tested in this research. To understand the combined impact of hybrid nanoparticles and other engine conditions on performance and emissions, design of experiments (DOE) using the response surface method (RSM) was performed to model and optimize WCO20 performance and emissions parameters. This was accomplished by utilizing a variable compression engine and selecting three variables, namely, hybrid nanoparticle blends (fuel blend), compression ratio (CR) and load as input parameters, while the analyzed responses were brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), nitrogen oxides (NO_x), unburnt hydrocarbons

(UBHC), carbon monoxide (CO) and smoke. The outcomes from this investigation showed that RSM is a viable technique for improvement of the parameters of biodiesel blends doped with nanoparticles in diesel engines. Considering the intricacy of biodiesel production measures, process development, technical assessment, and advancement of biodiesel according to the entire chain, is fundamental for improving its performance and increasing its global adoption. A detailed biodiesel process flow design was developed and economic assessment incorporating material performed. The designed plant is expected to produce 16.88 tons per annum. The cost of biodiesel was evaluated based on researched cost variables and plant data which resulted in a biodiesel production cost of ZAR10.10 per kg giving a total production cost of ZAR10,100.00 (US\$673.33) per ton. A CaO ethanolsis catalysed process was shown to be the most appropriate process for WCO production – the reaction was faster and produced a high yield. South Africa, among the developing nations in sub-Saharan Africa, has a huge capacity to produce its own renewable fuels but at present there is an absence of localized and effective applicable techniques for converting crude bio-oil into biodiesel to run fuel CI engines. Therefore, the discoveries of the present doctoral study are important because they demonstrate that it is viable to convert WCO to biodiesel and that its properties can be enhanced with the addition of nano particles, thereby demonstrating that its performance is even better than that of FD. Furthermore, a more sustainable CaO catalysed ethanolsis, with superior yields and locally produced in comparison to methanolsis, has been effectively developed and evaluated, as per the objectives of the thesis.

Key words; modelling and optimization, waste cooking oil biodiesel, nanoparticles, performance, and emissions

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SYMBOLS AND ABBREVIATIONS

ASTM	American Society for Testing and Materials
CI	Compression Ignition
CaO	Calcium Oxide
EN	European Committee for Standardization
FD	Fossil Diesel
GHG	Green House Gases
IEA	International Energy Agency
WCO	Waste Cooking Oil
UN	United Nations

CHAPTER 1 INTRODUCTION

1.1 Background and Motivation for the Study

Energy is the most fundamental and central resource that promotes economic development and advancement in quality of life for humans. The improvement in energy generation has resulted in development in several sectors such as the economy, transport, and agriculture. All these developments have influenced population growth. Figure 1-1 shows the increase in world population averaging around 1.06 % per annum between 1950 and 2030 (Hachimi 2019). The International Energy Outlook 2016 (UN 2015) reports that a global population increment of 50 % was anticipated between 2014 and 2040. This scenario, together with economic development being experienced globally, are the key drivers for increased energy demand of which most is being satisfied by fossil fuels (UN 2015). Estimated energy consumption and its sources up to 2040 are shown in Figure 1-2.

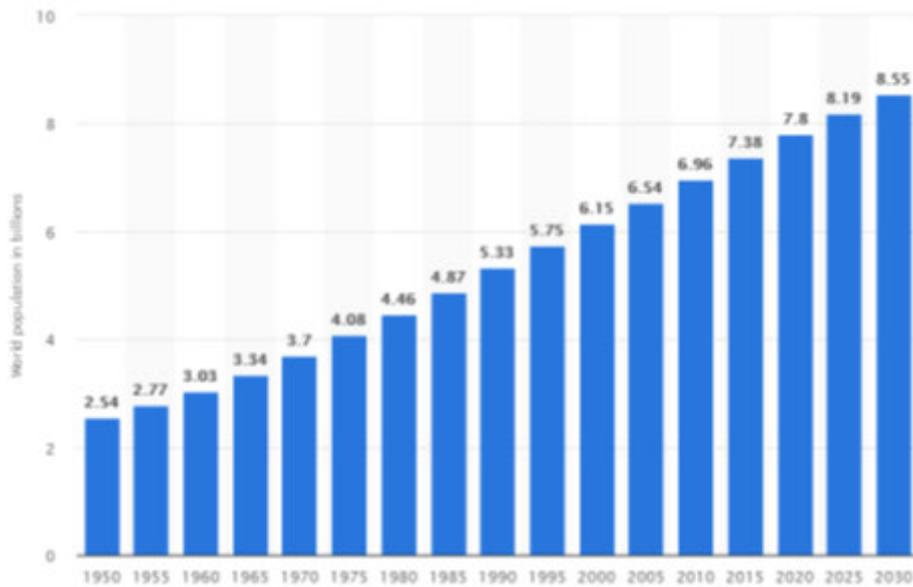


Figure 1-1 : Global population growth up to 2030 (Hachimi 2019)

This scenario has brought about threats to the ecosystem due to climate change and pollution. The Intergovernmental Panel on Climate Change (IPCC) report predicted that a million species would be eradicated if the normal worldwide temperature increases beyond 1.5 °C (Samaras 2019). Greenhouse gases (GHG) occur as a result of combustion of fossil fuels to meet the ever increasing demand for energy and have been identified as the major driver of climate change. Masson-Delmotte, Zhai et al. (2018) state that in order for the increase in global temperatures to be maintained below 1.5 °C, there must be a 50 % decrease in GHG emissions. This is highly unlikely, because, as shown in Figure 1-2, demand for petroleum resources is expected to continue rising unless more strategic and meaningful alternative sources can be found and implemented. Almost 80 % of present energy supply is derived from petroleum products (Carrington and Stephenson 2018), hence, the danger of ecosystem and climate change is going to continue unabated unless research on alternative energy resources are undertaken now.

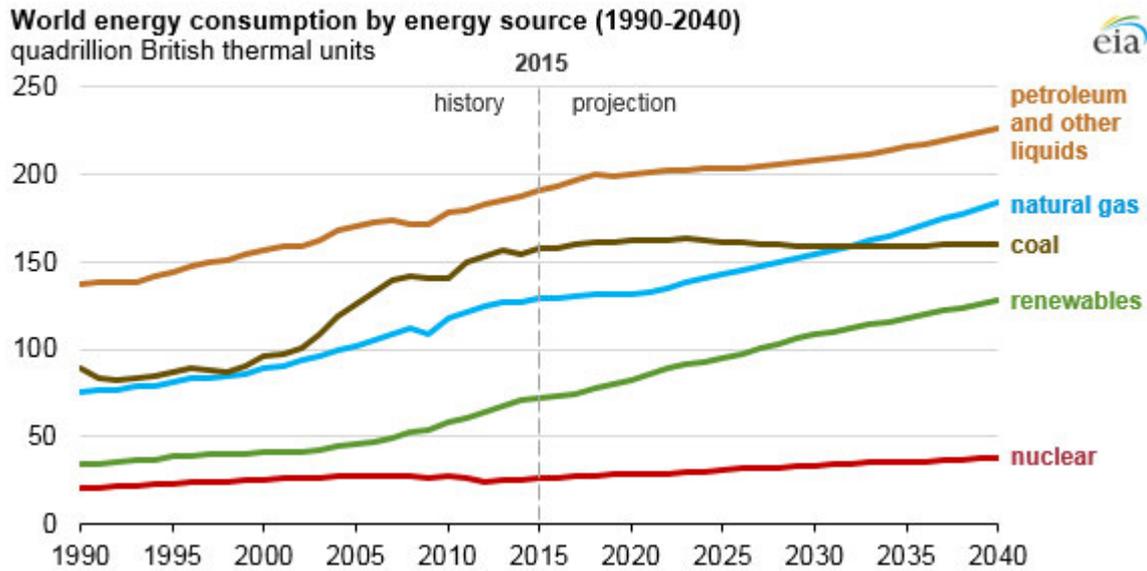


Figure 1-2: Global energy consumption (Prices 2019)

This scenario has prompted research for renewable and clean alternative energy resources. Most renewables enjoy ecological advantages in comparison to fossil derived fuels such as lower net ozone depleting emissions and less environmental contamination (Olkiewicz, Plechkova et al. 2016). In line with this, the IEA Renewable Energy Medium Term Market Report 2016 indicated that the sustainable energy share of world energy utilization is expected to increase by 39 % by 2021 (Olkiewicz, Plechkova et al. 2016). From a transport point of view, one of the major substitutes to conventional fuels that has been researched is biodiesel, which has been identified as having similar fuel properties as those of fossil diesel (FD) fuels (Karmakar and Halder 2019). The American Society for Testing and Materials (ASTM) characterized biodiesel as "mono-alkyl esters of long chain unsaturated fats that is gotten from animal fats or vegetable oils" (Karmakar and Halder 2019).

Biodiesel has great ecological, qualitative, and economic benefits. The manufacture of biodiesel from environmentally friendly power fuel sources is a major inspiration for business. The biodiesel industry contributes to a homegrown economy through promoting local localized small enterprises.

Emeji (2015) reported that in 2000 biodiesel was the first alternative fuel to meet the EPA-required Tier I and Tier II wellbeing impact testing under the Clean Air Act. These tests demonstrated biodiesel's reduced emissions of all the regulated emanations and showed that biodiesel does not present any danger to human wellbeing. Biodiesel contains no sulfur or aromatics and the utilization of biodiesel in a standard diesel motor results in a decrease of un-consumed hydrocarbons, carbon monoxide and particulate matter (that is, a decrease in ozone harming substances). In addition, biodiesel has a positive energy balance. For each unit of energy expected to create a gallon of biodiesel, basically 4.5 units of energy are gained. It has an innate lubricity, low toxicity, is highly biodegradable and its combustion results in reduction most of harmful exhaust emissions. This renewable fuel is derived from a variety of feedstocks. Qualitatively, biodiesel has been normalized and enrolled as a fuel and as a substance that can be added to FD. The two most significant fuel standards are ASTM D6751 (ASTM 2008a) in the United States and EN 14214 (European Committee for Standardization, CEN) in the European Union (Arguelles, Laurena et al. 2018). A study carried out by Anderson and Peters (2016) concluded that GHG

emissions are reduced and air quality improved if biofuels are used to power vehicles. Research in Australia proposed biofuels as a solution for escalating energy demand experienced by that country (Guo, Kang et al. 2014). Biodiesel was also noted as a front runner to replace fossil diesel in a study carried out by Sadeghinezhad, Kazi et al. (2013) who they found that biodiesel showed reduced emissions than fossil fuels. Biodiesel has a high oxygen content, which FD does not, and this is the predominant factor influencing its lower emissions (Enweremadu, Rutto et al. 2011).

To evaluate the technical capability of biodiesel as a viable energy resource for CI engines, it is important to compare its performance behavior to that of FD. Numerous investigations have uncovered some similarities and contrasts between FD and biodiesel. Som, Longman et al. (2010) examined the thermodynamics behind the utilization of biodiesel in CI engines compared to FD. The investigation showed that biodiesel possesses similar performance features in CI engines, and in some cases are superior especially at high compression ratio (Som, Longman et al. 2010). Figure 1-3 portrays the presentation of fossil diesel, B10 blend, and neat biodiesel fuel (B100).

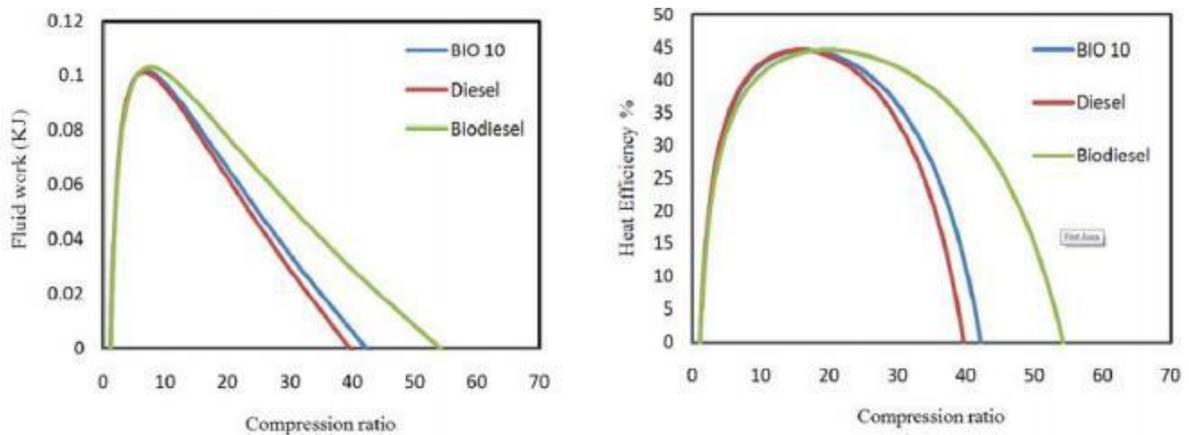


Figure 1-3: Performance features of biodiesel and its blends compared to fossil diesel (Som, Longman et al. 2010)

However, utilization of biodiesel results in a slight reduction brake thermal efficiency and higher brake specific fuel consumption, as depicted in Figure 1-4.

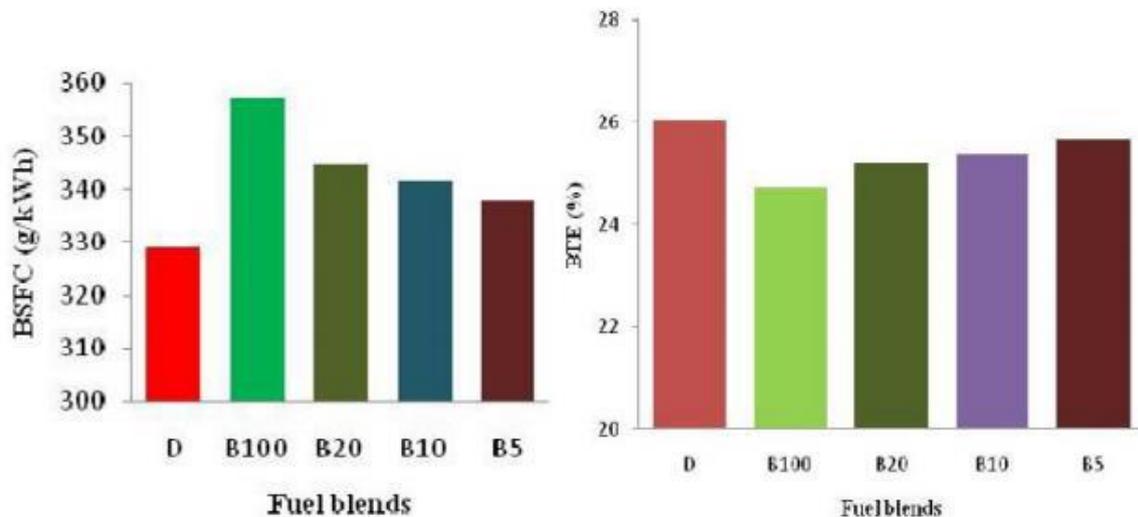


Figure 1-4 BTE and BSFC biodiesel against that of Fossil Diesel fuels (Som, Longman et al. 2010)

Furthermore, the results of exploration by Som, Longman et al. (2010) show that the low fume pressure means that cavitation is lower in biodiesel than FD resulting in a higher viscosity which causes a decrease in fuel flow and lower fuel atomization capability.

1.2. Nanotechnology

Most toxic combustion emissions arise because of incomplete combustion which arises from insufficient oxygen supply into the combustion chamber (Perera 2018). During that period of oxygen shortage, the burning fuel is suffocated and doused, the combustion chamber valves open, and the substances are released as exhaust emissions. One can portray this incomplete combustion as a form COVID-19 and apply a vaccination technique. The root cause of these emissions is the absence of oxygen during burning. If we could make extra oxygen available during burning, we would be able to resolve this issue. As explained in literature, nanotechnology may hold the way to supplying a much-needed vaccine capable of vaccinating the 2 billion combustions engines presently running on non-renewable energy sources, against tainting the world with NO_x, CO₂, and other harmful gaseous substances arising from combustion engines.

In the past recent 20 years, researchers in the nanotechnology field have investigated the fascinating properties of nanoparticles, including their large surface area, unique thermal effects, and high strain resistance (Yetter, Risha et al. 2009). As indicated by Yetter, Risha et al. (2009), adding metallic nanoparticles inside the burning chamber prompts rapid heat transfer which results in combustion ignition delay. These features can be harnessed to improve biodiesel combustion behavior. In addition, nano particles possess unique catalytic characteristics which can be utilized to improve combustion and improve the performance features of biodiesel (Saraee, Jafarmadar et al. 2015). Nanoparticles fundamentally modify fuel properties, diminishing the unburned carbons. A few metallic nano added substances, including cerium oxide (Dale, Cox et al. 2017) and aluminum oxide, have been investigated as added fuel catalysts (Saraee, Jafarmadar et al. 2015). Cerium oxide possesses high catalytic attributes arising from its high surface area to volume ratio. This enables it to decompose soot and unburnt

hydrocarbons and carbon monoxide and reduce their presence in exhaust tail pipes. This unique nano metal also has the capacity to reduce combustion cylinder pressures thereby suppressing NO_x emissions. Aluminum oxide nano metals have a high energy density that fortifies the creation of energy in engines, decreasing the fuel utilization, which, thus, diminishes CO and NO_x emissions. Aluminum oxide forms suspended micro explosions which promote accelerated fuel air mixtures and cleaner combustion profiles (Gumus, Ozcan et al. 2016). Heavy diesel truck engines manufactured after January 1, 2010, must meet the most recent EPA outflows guidelines, among the toughest on the planet, diminishing particulate matter (PM) and nitrogen oxides (NO_x) to approach zero levels. Nanoparticles can lessen NO_x outflows up to 30 % while at the same time decreasing HC and CO emanations by 50 % to 90 %, and PM discharges by 30 % to 50 %. Nanosystems can likewise be coupled to biodiesel technology to accomplish even significantly more noteworthy outflow decreases for PM. In the shipping industry, some nanoparticles have been producing efficiency gains of 3 % to 4 %. Also, off-road machinery, including shipping, construction, and farming, should meet EPA's Tier 4 outflows principles requiring comparable decreases in NO_x, PM and different poisons. Nanoparticles are an innovation that can help rough terrain hardware satisfy these discharges guidelines.

1.3. Waste Cooking Oil Biodiesel

Non-edible feedstocks are gaining consideration since they do not interfere with food supply chains. Amongst such feedstocks, waste cooking oil (WCO) is considered as the most promising option, due to its low acquisition cost (Math, Prem et al. 2010). Additionally, WCO usage is regarded as a solution to the challenges associated with its disposal. Chung, Tan et al.(2019) applied life cycle assessment (LCA) to evaluate the energy utilization and emissions outflows of two commonly utilized feedstock oils (soybean oil and WCO) for the creation of biodiesel in China. Their outcomes showed that the creation of biodiesel utilizing WCO as the feedstock was more viable regarding energy utilization and contamination discharge reduction. WCO possesses the capacity to create new opportunities for growth in the energy sector in the short to medium term since the product is readily available today and can easily be incorporated into liquid fuel channels. The development of WCO biodiesel will not only benefit the South African economy but will be vital in providing a knowledge base capable of powering sub-Saharan African region with a non-polluting renewable energy source. WCO feedstocks are available at a low cost and their usage will facilitate the creation of other supporting industries. Environmental benefits derived from setting up this industry include reduced urban water contamination, reduction in clogging of drainage systems, prevention of soil contamination, and reduction in usage of waste oil for cooking which can cause cancer (Perreira,.2018). Figure 1-5 shows how biodiesel from WCO is produced.

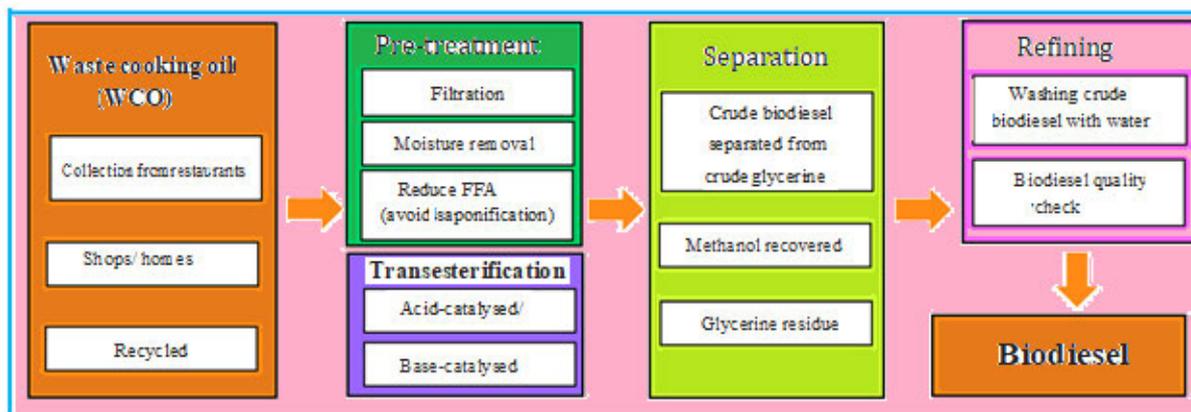


Figure 1-5: Waste cooking oil (WCO) biodiesel production method (Sadaf, Iqbal et al. 2018)

1.4 Research Motivation

Advancement in the biodiesel industry and the utilization of biodiesel in South Africa isn't just in its early stages but has been stagnant for years now. The fundamental motivation of this examination which has delivered a lot of publications is to improve performance and emission features of biodiesel using hybrid nano particles. Nano particles do possess unique features which can improve biodiesel properties resulting in its performance enhancement. Scientists all over have not attempted such a process for improving performance and emission behavior of biodiesel. It is accordingly a new methodology aimed at improving biodiesel performance and emissions attributes.

1.5 Problem Statement

Biodiesel has been identified worldwide as an immediate solution to the substantial reliance on diesel fuel for transportation of goods. Notwithstanding, the prolonged dependence on edible feedstocks for biodiesel has threatened the supply of edible oil to food industry and raised some environmental problems such as serious destruction of vital soil resources, deforestation and usage of much of the available arable land. In addition, over the past ten years the costs of vegetable oil have expanded drastically which will influence the economic suitability of biodiesel industry. Because of these factors, it is vital to find other elective oil feedstock to substitute consumable oil in the creation of biodiesel. Accordingly, the primary target of this examination is to orchestrate biodiesel from a non-edible feedstock that's is waste cooking oil and improve its performance by amalgamating it with using hybrid nano particles.

1.6 Aims and Objectives

This study is a step towards practical advancement of biodiesel by utilizing feedstocks that are non-edible, easily accessible and have superb properties. The overall aim of this research was to formulate a biodiesel blend with hybrid nano fuel additives using WCO derived feedstocks that can set a platform for South Africa to switch to biodiesel (a renewable energy resource) in the transport sector. The objectives of the research were as follows:

1. Pretreatment and production of biodiesel from waste cooking oil (WCO) and its blends using a transesterification technique.
2. Perform engine performance and emission analysis of WCO and its blends and compare the results with those of FD.
3. Amalgamation of WCO-diesel blends with hybrid nano additives and measure the parameters of fuel blends formed by mixing FD and biodiesel with hybrid nano additives.
4. Perform engine tests to evaluate performance and emission characteristics of fuel blends formed by mixing Fossil-diesel with biodiesel with hybrid nano additives.
5. Model and optimize engine performance and emission parameters on a diesel engine fueled with WCO blends.
6. Develop process flow, perform economic assessment, and specify equipment for biodiesel production based on CaO catalyzed ethanolysis technique.

1.7. Research Approach

This research uses the experimental method to evaluate the effects of nanoparticles on WCO derived biodiesel. Experimental evaluation of neat WCO blends are performed initially to analyse the feedstock suitability. Thereafter experimental analysis of WCO doped with hybrid nano particles are performed and results compared with those derived from burning neat biodiesel blends and Fossil diesel fuels. A model is finally developed to evaluate optimal engine parameters and nano particle dosage capable of giving the best engine performance and emissions features.

1.8 Dissertation Outline

The dissertation layout is as follows:

CHAPTER 1: The background, motivation for the research and discussion on the research aims and objectives.

CHAPTER 2: Review of WCO biodiesel as a viable fuel for diesel engines, existing concepts, emerging trends, and prospects. This provides a summarised finding of properties of WCO and its production technologies, treatment methods.

CHAPTER 3: The effects of nano additives on fuel properties, engine performance and emission characteristics of biodiesel fuelled compression ignition engine. This chapter provides recent findings on the impact of metallic nanoparticles on fuel properties, combustion, and engine performance and emission characteristics of compression ignition engines.

CHAPTER 4: Optimization of production process, characterization and engine testing of WCO biodiesel. This chapter analyses the suitability of mixed WCO biodiesel as a viable fuel for diesel engines, and details the experimental investigation that was carried out to assess the feasibility of WCO as a potential feedstock for biodiesel and to verify its performance and emission attributes.

Chapter 5: Investigation of the effects of a hybridized nano-additive on performance and emission behaviour of WCO derived biodiesel and its blends with fossil diesel. This experimental evaluation was carried out to evaluate the effects of hybrid nanoparticles on WCO biodiesel and its blends and compare the results with those of FD.

CHAPTER 6: Modelling and optimization of engine parameters on diesel engine fuelled from waste cooking oil biodiesel blend doped with hybrid nanoparticles. The aim of this investigation was to model and optimize engine parameters on an engine fuelled from WCO doped blend (WCO20) with hybrid nanoparticles consisting of cerium oxide and aluminium oxide.

CHAPTER 7: WCO biodiesel production process flow via calcium oxide catalysed ethanolsis technique.

CHAPTER 8: Conclusion and further studies.

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CHAPTER 2 PART A: A REVIEW ON WASTE COOKING OIL BIODIESEL AS A VIABLE FUEL FOR DIESEL ENGINES: EXISTING CONCEPTS, EMERGING TRENDS AND FUTURE PROSPECTS.

This chapter presents a review on WCO feedstocks, its characteristics, biodiesel production technologies and methods of purification to inform future research endeavours on this subject. The outcome of the work was published in the International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)

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A REVIEW ON WASTE COOKING OIL BIODIESEL AS A VIABLE FUEL FOR DIESEL ENGINES: EXISTING CONCEPTS, EMERGING TRENDS AND FUTURE PROSPECTS

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ABSTRACT

The world is in an irreversible process of switching to alternative fuel sources for diesel engines. This has been necessitated by accelerated depletion of fossil diesel resources coupled with the detrimental impact of exhaust emissions on the environment. Biodiesel is a standout amongst other possible fuel options for diesel engines that have been discussed in the literature. Biodiesel is regarded as a clean source of fuel because its combustion results in a decrease in most harmful emissions when compared with fossil diesel fuels. However, some feedstocks for biodiesel are not feasible due to the exorbitant cost of acquisition and their negative impact on food supply channels. A switch to waste cooking oil (WCO) is viewed as the most encouraging option for biodiesel feedstock despite its disadvantages, like its high free fatty acid (FFA) and water content. In this paper, existing concepts used for WCO biodiesel production process in regard to feedstock pre-treatment, production technologies and purifications methods are analysed, highlighting the merits and demerits of available options. Furthermore, emerging trends and prospects of WCO biodiesel production technologies are presented.

KEYWORDS: Waste Cooking Oil Biodiesel, Pre-Treatment, Production Technologies & Purification

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NOMENCLATURE AND ABBREVIATIONS

AL ₂ O ₃	Aluminum oxide	NO _x	Nitrogen oxide
ASTM	American Society for Testing and Materials	N ₂	Nitrogen gas
BD	Biodiesel	H ₂ SO ₄	Sulphuric acid
CH ₃ ONa	Sodium methoxide	WCO	Waste cooking oil
FD	Fossil diesel		
FFA	Free fatty acid		
KOH	Potassium hydroxide		
NaOH	Sodium hydroxide		

1. INTRODUCTION

With expanding population and modernization, the world is being confronted with a challenge requiring both higher energy generation coupled with reduction in emission of toxic gasses to the atmosphere. Population increase is

stimulating higher energy utilisation bringing about increased generation of greenhouse gas emissions (Franco et al., 2017). Petroleum products are the main energy resources utilized in the automotive industry. However, combustion of petroleum products results in emission of toxic gasses which are the main causes of global warming and air pollution which are posing a risk to the environment and human health (Mofijur et al., 2014). These drawbacks of petroleum products have necessitated the search for renewable fuel resources which are nontoxic and compatible with current automotive engines; biodiesel has emerged as the best option available especially for transportation of heavy goods. This is because biodiesel fuel properties make it suitable for blending with fossil diesel in various proportions (Nisar et al., 2018). Furthermore, pure biodiesel fuel can be utilised in diesel engines with little or no engine modification (R Mohsin et al, 2014). Biodiesel is a renewable, nontoxic, highly biodegradable fuel resource (Roy et al., 2014). Biodiesel is a feasible and inexhaustible fuel resource that is delivered from an assortment of feedstocks, like vegetable oils, animal fats, waste cooking oil, algal oil, among others (Costa et al. 2018). Biodiesel is created through the transesterification of fatty acid containing substances with a short-chain alcohol under the influence of a catalyst (Iso et al., 2001). Several investigations have revealed that the utilization of biodiesel decreases most of the general discharges from a diesel engine. Despite decreases in most emission gases, the usage of biodiesel is reported to cause increased emission of nitrogen oxides (NOx), an issue which is also slowing its adoption (Chen et al., 2018). In general, there are four significant classifications of feed stocks utilized as raw materials for the biodiesel creation based on sustainability, namely, 1st generation (edible feedstocks) such as sugars and grains, 2nd generation (non-edible) feedstocks, 3rd generation (waste-based feedstocks) and 4th generation (genetically engineered crops) of which the issues related to each subgroup are shown in figure 1.

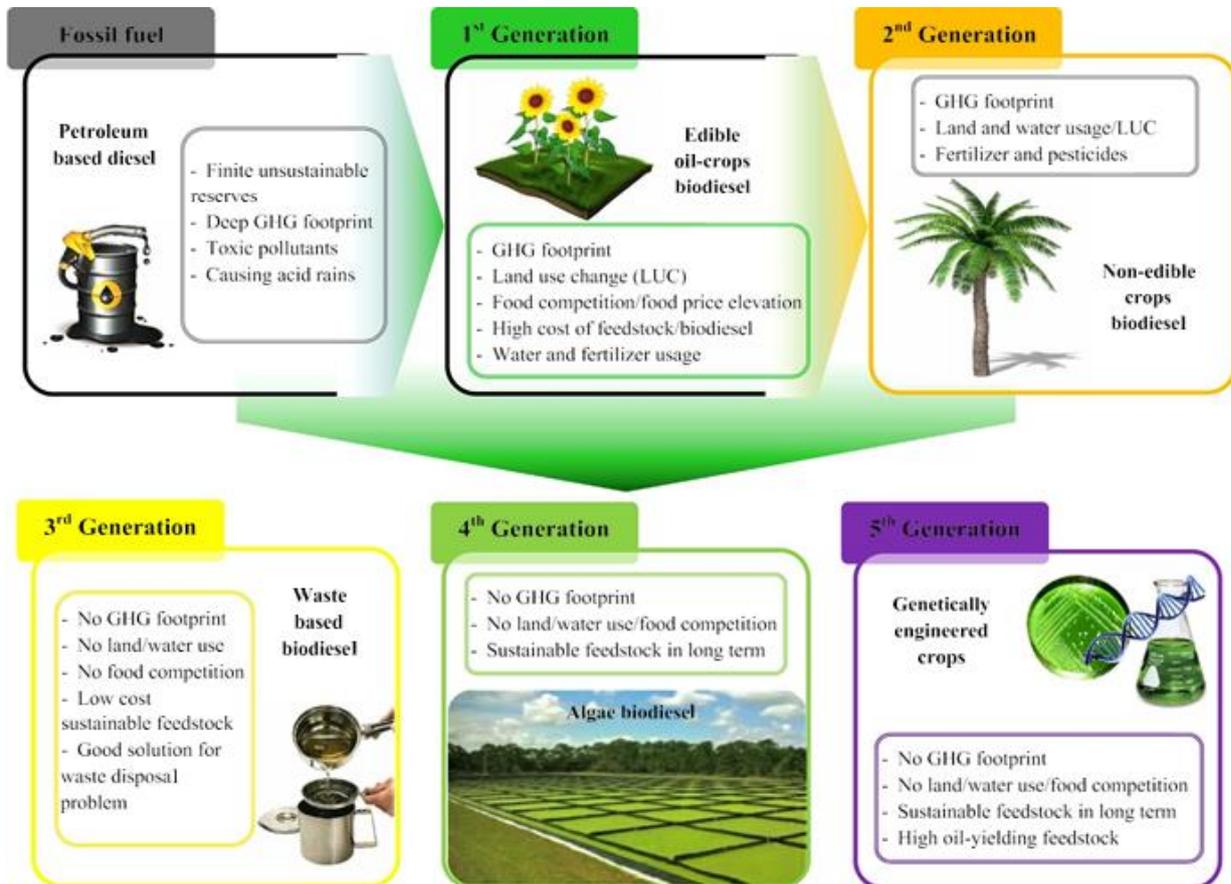


Figure 1: Classification of Biodiesel Feedstocks (Hajjari et al. 2017).

Deployment of biodiesel has been hampered by exorbitant feedstock costs. The cost of biodiesel production has been influenced mostly by cost of feedstock which is almost 74 % of total production cost (de Jong et al. 2017), as illustrated in Figure 2. Currently, edible feedstocks has been most used for the production of biodiesel (more than 95%) (Pinzi et al., 2014). However, the use of food-based edible feedstock for biodiesel production has brought about a food versus fuel debate because of the related increase in food costs and land use changes as more land is allocated to fuel feedstocks. Diverting food resources to fuel production results in a higher return on investment compared to its food resources for consumption (Che et al. 2012). Utilisation of waste cooking oil (WCO) for biodiesel production is not only beneficial to fuel production but will also solve its disposal challenge. Uncontrolled disposal of WCO causes soil and water pollution as well as water system blockages. Furthermore, utilizing waste and nonedible oils in biodiesel creation will also help to resolve the biodiesel contest with food utilization.

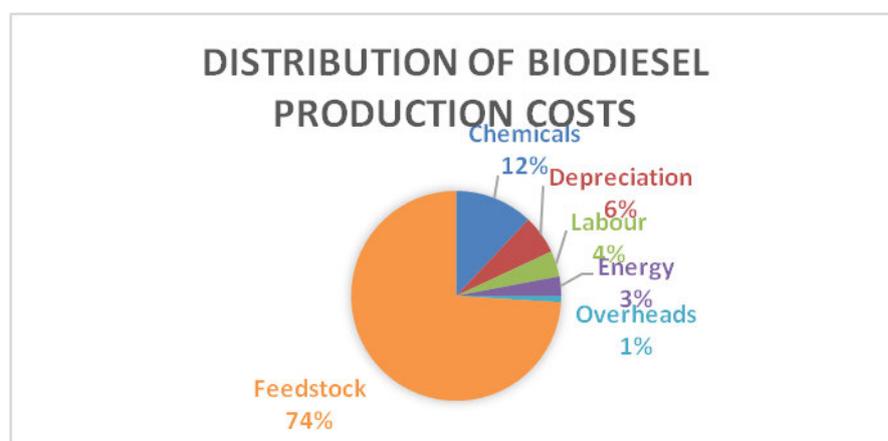


Figure 2: Breakdown of Biodiesel Production Costs (de Jong et al., 2017).

The above analysis reveals that WCO can be a viable source of feedstock for biodiesel production because it has many environmental benefits. Based on that a review is hereby presented to analyse WCO feedstocks, its characteristics, biodiesel production technologies and methods of purification to inform future research endeavours on this subject.

2. WASTE COOKING OIL: A POTENTIAL FEEDSTOCK FOR BIODIESEL FUEL

Huge amounts of WCOs are accessible throughout South Africa. WCO is produced by domestic homes and by industry. Increased human population will result in increased food consumption, leading to higher WCO generation. South Africa alone produces more than 600 000 tons of waste cooking oil each year (Hamze et al., 2015). However, this abundant feedstock resource was ignored when the Department of Energy announced its Sustainable Development strategy (Brent et al., 2009). WCO can be gathered from food producers and deep fryers, for example, potato handling plants and snack food production lines, fast foods, cafés, catering businesses and from domestic households, where it is used for food preparation.

WCO, which is generally wasted, has emerged as the most viable and economic source for biodiesel since it can be acquired at low cost in comparison to all other feedstocks. The cost of feedstock has been identified as the main barrier to accelerated biodiesel deployment hence a switch to WCO will improve the financial viability of its creation. WCO produced in Europe, North America and Asia is around 16.6 million tons in a year, which can mathematically satisfy total oil demand for fuel generation (Azócar et al., 2010). However, there are some disadvantages in utilizing WCO for the creation of biodiesel because it contains contaminants such as free unsaturated fat (FFA) and water. These need to be

eliminated before transesterification due to their unfavourable impact on the engine fuel supply components.

2.1. Characteristics of Waste Cooking Oil and its Feedstock Potential

Given the plenitude and cost of feedstock, WCO has emerged as the number one candidate for biodiesel production. The properties of WCO are marginally not the same as those of virgin oils due to the changes that occur as a result of cooking or frying. Frying is a process that involves the exposure of food in oils or fats to high temperatures ranging from 160 °C to 200 °C. This process is performed in the presence of moisture, antioxidants, and oxygen (Safari et al., 2018). This process results in changes to the chemical and physical properties through hydrolysis, polymerization, and oxidation (Lam, 2010). Most WCO contains water content ranging from 0.5 % to 55% and acid values of around 193 mg-KOH/g-oil. Higher water content causes hydrolysis of the oil while higher FFA content influences formation of soaps, all which reduce oil quality and biodiesel yield. Oxidation processes entail conversion of oil into other compounds in the presence of oxygen. Compounds formed include peroxides, ketones, and aldehydes. The oxidation process is affected by the type of oil, oxygen availability and duration of oil exposure to heat. Hydrolysis defines a process in which the oil is converted into other volatile compounds due to reaction with water, as depicted in Figure 3. A lower measure of free unsaturated fats causes lower oxidation and hydrolysis in the transesterification reaction (Refaat et al., 2008). Addition of a base catalyst results in the FFAs forming soap and water. The soap formation reaction is shown in Figure 4. This implies that before the transesterification process, water and contaminants must be eliminated from the WCO to suppress soap formation. These processes transform fuel properties from those of virgin oil, hence the main WCO fuel properties are shown in Table 1. Many standards are used to qualify biodiesel derived from various feedstocks and these standards are summarised in Table 2.

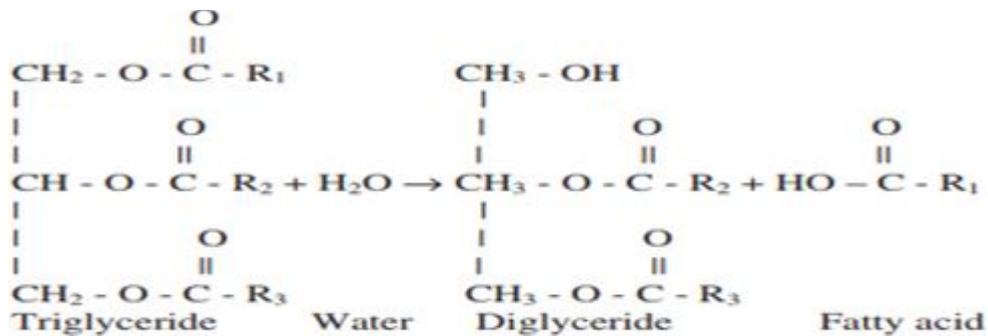


Figure 3: Hydrolysis Process (Farooq et al., 2015).

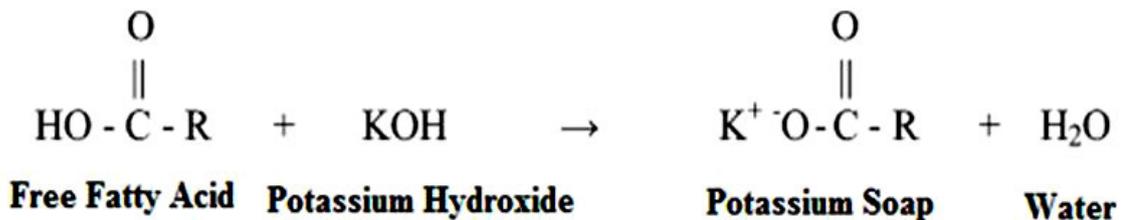


Figure 4: Soap Formation Process.

Table 1: Properties of WCO

Property	Value
Density (g/cm ³)	0.91 – 0.924
Kinematic Viscosity (40°C) (mm ² /s)	36.4 - 42
Saponification	188.2 - 207
Acid value	1.32 – 3.6
Iodine number	83 – 141.5

Table 2: South African and International Biodiesel Standards (Kitani 1999).

Specification or property	Units	Europe (EN 14214)	USA (ASTM 6751-08)	South Africa (SANS 1935)	South African test method
Density @ 15°C	kg/m ³	0.86-0.90	Report	0.86-0.90	ISO 3675
Viscosity @ 40°C	mm ² /s	3.5-5.0	1.9-6.0	3.5-5.0	ISO 3104
Distillation T90	°C	n/a	360	n/a	-
Flashpoint	°C	120 min	130/93 min	120 min	ISO 3679
Sulphur	mg/kg	10.0 max	15 max	10 max	ISO 20846
10% Carbon residue	%mass	0.30 max	n/a	0.3 max	ASTM D1160
100% Carbon residue	%mass	n/a	0.050 max	n/a	-
Sulphated Ash	%mass	0.02 max	0.020 max	0.02 max	ISO 3987
Water and sediment	mg/kg	500 max	500 max	500 max	ISO 12937
Total contamination	mg/kg	24 max	n/a	24 max	EN 12662
Cu strip corrosion	3h@50°C	Class 1 max	No. 3 max	Class 1 max	ISO 2160
Oxidation stability	h@110°C	6 min	3.0 min	6 min	EN 14112
Cetane number	-	51.0 min	47 min	51 min	ISO 5165
Linolenic acid	%mass	12.0 max	n/a	12 max	EN 14103
Acid value	mgKOH/g	0.50 max	0.50 max	0.50 max	EN 14104
Methanol	%mass	0.20 max	0.2 max	0.20 max	EN 14110
Ester content	%mass	96.5 min	n/a	96.5 min	EN 14103
Triglyceride	%mass	0.20 max	n/a	0.2 max	EN 14105
Total glycerol	%mass	0.25 max	0.24 max	0.25 max	EN 14105
Iodine number	gI ₂ /100g	120 max	n/a	140 max	EN 14111
Phosphorus	mg/kg	10.0 max	10 max	10 max	EN 14107
Cloud point	°C	Report on request	Report	Report on request	-

2.2. Pre-Treatment of Waste Cooking Oil Feedstocks

High temperature cooking/frying results in formation of several compounds which lead to a high rate of FFAs which impacts on biodiesel formation (Mittelbach and Remschmidt, 2005). Pre-treatment involves the reduction of FFAs in the oil to under 1mg KOH/g equivalent and reduction of water to acceptable levels depending on standards being followed in fuel preparation. The availability of excessive FFAs make catalysts inactive thereby reducing the biodiesel conversion process. The deacidification process can be undertaken by adding a base catalyst, for example, NaOH, which reacts with FFA resulting in soap formation (Tyson et al., 2004). Pre-treatment of WCO before base catalysed transesterification is done because the catalyst is sensitive to water and FFA content in feedstock (Marchetti et al., 2007). Different sorts of pre-treatment strategies are utilized for WCO purification, for example, steam infusion (Lertsathapornsuk et al., 2005), vacuum filtration and column chromatography (Lee et al., 2002), balance, film vacuum cleaning (Cvengroš & Cvengrošová 2004) and vacuum filtration (Dias et al., 2008). An investigation performed by Shimada Y, et al., (200) using steam and sedimentation of WCO revealed a significant reduction in the hydrolysis process and FFA content. A reduction of water

content from 14 % to 0.4 % was noted as well as a reduction in FFA from 6.3 wt% to 4.3 wt%. Saifuddin N, et al., (2004) suggests that filtration of the oil coupled to microwave drying can remove most of the suspended substances related to the feedstock. Centrifugation has also been noted to be a viable process for pre-treatment of WCO. However, all these above-mentioned processes result in an increase in biodiesel production cost, hence a more suitable and cost-effective method must be selected for each feedstock.

3. PARAMETERS INFLUENTIAL TO TRANSESTERIFICATION REACTION

3.1. Type of Catalyst Used

Transesterification entails production of biodiesel using vegetable oil and an alcohol (methanol or ethanol), under influence of a catalyst. Several versions of catalysts have been used to date and these can be alkali, acidic or enzyme based, although enzyme derived catalysts are limited by the need for rigorous conditions which suppresses their commercial usage. The process to be followed in WCO biodiesel production is primarily based on the amounts of FFAs and water contained by the feedstock oil. Various catalysts that can be utilised for WCO biodiesel production are discussed in subsequent sections and summarised in table 3.

Table 3: Analyses of Transesterification Processes (Gog et al., 2012)

Analysis of Transesterification Processes			
Parameter	Base Catalysis	Acid Catalysis	Enzymatic Catalysis
FFA content	Result in soap formation	FFA converted to methyl esters	FFA is converted to methyl esters
Water content	Promote hydrolysis process which lead to soap formation	Deactivates the acid catalyst	Not affected by water content
Yield	High > 95 %	High > 90 %	High > 90 %
Rate of reaction	High	Lower than base catalysed	Lower acid/base catalysed
Glycerol retrieval	Difficult, poor quality of glycerol	Difficult resulting in poor quality of glycerol	
Catalyst recovery and reuse	Complex, the catalyst reacts with acid to form salts and water, not reusable	Complex, the catalyst ends up in end products. Not reusable	Easy. Can be reused
Cost of catalyst	Low	Low	High

3.1.1. Base Catalysed Transesterification

Base catalysed transesterification processes entail reacting glyceride with an alcohol to form an ester and glycerol in the presence of a base catalyst (Rashid et al., 2008). Base-catalysed transesterification is the most widely recognized method among other transesterification processes since it is the least expensive, simplest, and quickest method which uses the least preparation steps (Varanda et al., 2011). The most widely recognized catalysts utilized in transesterification are potassium hydroxide (KOH) and sodium hydroxide (NaOH). KOH is favoured since its usage suppresses soap formation. Furthermore, the soap formed from the KOH catalysed process is easier to separate from biodiesel fuel. Base transesterification can result in very high biodiesel yields of up to 95 % yield at moderate temperatures, pressure, and reaction time (Leung & Guo, 2006). However, base catalysed processes are affected by high water and FFA contents which are found in WCO feedstock. This process is also impacted by other contaminants such as dirt, solid particles and quality of reactions which makes treating of feedstock before the reaction necessary (Alptekin et al., 2011). Hence, base transesterification is a desirable method when the feedstock contains FFAs under 1 wt. %. This subsequently means that base catalysis is not initially feasible on WCO which contains higher FFA in > 5 % (Xia, 2017). Thusly, direct soluble

catalysed transesterification process utilizing base catalyses is not advised hence pre-treatment techniques including steam refining, extraction by liquor, and corrosive synergist esterification are undertaken to lower the FFA to below 1 % (Günay et al., 2019). However, most of the biodiesel plants at present are utilizing homogeneous soluble base catalyses, i.e., sodium or potassium hydroxides, carbonates or alkoxides since the utilization of these catalyses are financially viable compared to heterogeneous catalyses (Yin et al., 2008). Base catalysed transesterification is influenced by the reaction temperature. As the temperature expands, the rate of reaction increases which increases the biodiesel conversion process. However excessive temperatures promote the saponification process which is more visible the longer the process (Ferrari et al., 2011). The reaction temperature ought to be maintained below alcohol boiling point to deter it from vaporizing, although this will reduce biodiesel production. For optimal biodiesel production, reaction temperatures must be maintained in the range of 40 °C and 60 °C (Li et al., 2013). The process is shown in figure 5.

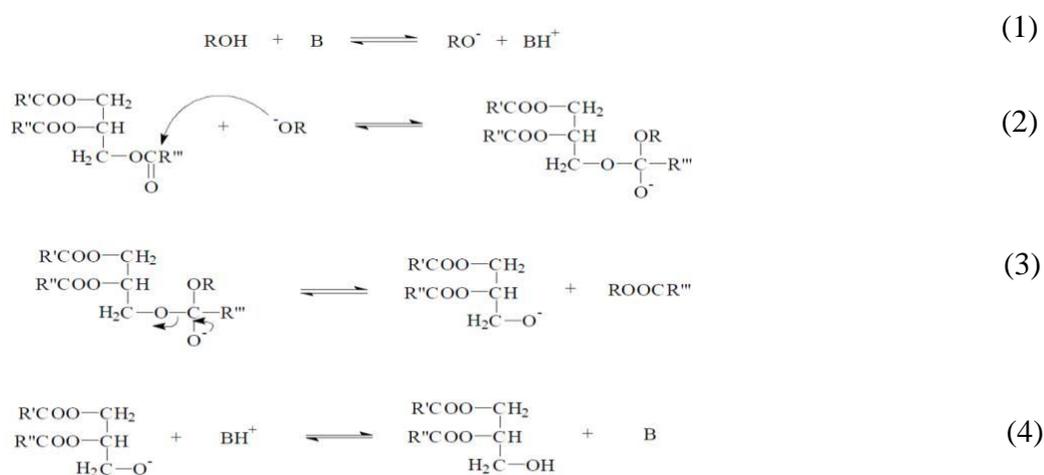


Figure 5: Homogenous base Catalysis Mechanism.

Table 4: Homogenous Catalysed Transesterification.

Ref.	Oil	Used Catalyst	Percentage of catalyst	Alcohol wt.%	Oil to alcohol molar ratio	Reaction conditions	Ester yield (%)
Wang et al. (2006)	WCO	Acid (H ₂ SO ₄)	4	Methanol	01:20	95 LC, 10 h	–
(Karmee & Chadha (2005)	Pongamia pinnata	Base (KOH)	1	Methanol	01:10	60 LC, 1.5 h	–
Rashid et al., (2008)	Rapeseed oil	Base (KOH)	1	Methanol	01:06	65 LC, 2 h, 600 rpm	96
(Rashid et al. (2008)	Sunflower oil	Base (NaOH)	1	Methanol	01:06	60 LC, 2 h, 600 rpm	97.1
Leung & Guo (2006)	Used frying oil (UFO)	Base (NaOH)	1.1	Methanol	1:7.5	70 LC, 30 min	85.3
		Base (KOH)	1.5				86.0
		Base (CH ₃ ONa)	1.3				89.0
Narasimharao et al. (2007)	Soybean oil	Acid (H ₂ SO ₄)	1	Methanol	01:30	65 LC, 50 h	–
				Ethanol		78 LC, 18 h	–

				Butanol		117 LC, 3 h	–
Gof et al. (2004)	Soybean oil	Acid (H ₂ SO ₄)	0.5	Methanol	01:09	100 LC, 3.5 bar, 8 h	–
Meher et al. (2006)	Karanja oil	Base (KOH)	1	Methanol	01:06	65 LC, 2 h, 360 rpm	98

3.1.2. Acid Catalysed Transesterification

In this method, a glyceride is reacted with alcohol under the influence of acid catalysts to form biodiesel and glycerol (Likozar and Levec, 2014). Common acid catalysts utilised for biodiesel production are sulphuric acid and hydrochloric acid. This acid catalyst is not sensitive to feedstock purity such as a base catalyst. In performing this process, the biodiesel is mixed directly with the feedstock. This enables the reaction to progress in a single step unlike a two-step process which has two reactions. A study by Al-Widyan, M, I, et al., (2002) aimed at assessing the effect of HCL and H₂SO₄ yielded low kinematic viscous and high pure biodiesel. H₂SO₄, showed better catalysis compared to HCL. This process is slower and more expensive in comparison to the base catalysed method. Furthermore, this process is performed under intense temperature and pressure as well as higher alcohol to molar ratio making it unfavourable for commercial application (Lam et al., 2010). Acids are also corrosive in nature hence they can react with metals in production equipment to form unwarranted metal oxides. This requires that highly expensive stainless-steel production equipment used for biodiesel production. The mechanism is shown in Figure 6. Heterogenous solid catalysts have been identified as more suitable for WCO and high FFA containing feedstocks since catalyst can be easily recovered from the product mixture, this process produces pure biodiesel and catalyst usage lasts for longer periods compared to homogenous catalysts.

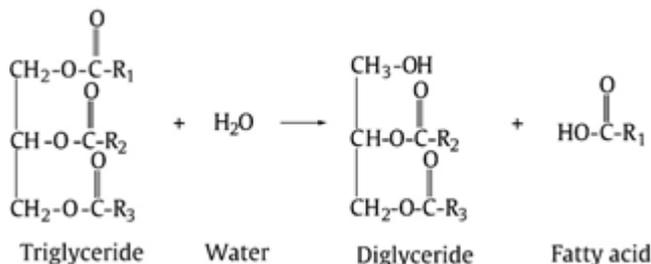


Figure 6: Mechanism of Homogenous acid Catalysis.

3.1.3. Other Heterogenous Catalysts

Fly ash, an inorganic by-product derived from the coal burning cycle comprises mainly SiO₂ and Al₂O₃ components as impurities which are ecological toxins. Considering its significant conservation and ecological ramifications, the removal or use of fly ash will address these thereof. Thus, the advancement of naturally safe applications for the usage of coal fly ash is vital. Fly ash is currently mainly utilized as a building material and in other structural design work (concrete) however, much of it is still disposed of in lakes or landfills. Items produced using fly debris utilize refined fly ash which has been cleaned of impurities (López-Delgado et al., 2020). Fly ash can be utilized to make zeolite. Fly ash is an agglomerate of microspheres, which are primarily made from Si and Al with minor measures of Fe, Na, K, Ca, P, Ti, and S. The significant mineral compound is formless aluminosilicate (glass) however other glasslike minerals are additionally present, for example, mullite, quartz, hematite, magnetite, lime, anhydrites, and feldspar (López-Delgado et al., 2020). This substance's mineralogical and textural properties make fly ash suitable as a source material for zeolite amalgamation. The transformation of fly ash into zeolite circumvents the disposal challenges and transforms waste material into a valuable

one. A few investigations have effectively developed zeolites from fly ash under various reaction conditions. Development of various zeolite mineralogies and cations are dependent on the properties of the used fly ash. These conditions include temperature, pressure, and time (Sánchez Hernández, 2018)

Many metal oxides have been studied for their transesterification interaction with oils; zirconium oxide and zinc oxide have shown great reactant catalytic effectiveness and great dependability when used to catalyse esterification and transesterification at the same time. Nonetheless, they have not been by and large utilized in the modern creation processes, predominantly on account of the high cost and challenges arising. Calcium oxide has a high essential strength and less ecological effects because of its low immiscibility in methanol. When contrasted with KOH or NaOH, calcium oxide was shown to be effective with the added benefit of simple catalyst recuperation and better environmental performance.

3.1.4. Two-Step Transesterification

Both acid and base catalysed processes have their pros and cons regarding WCO biodiesel production. Consequently, both can be utilised in WCO biodiesel production in a two stage transesterification process. In the first stage, the acid catalysed method is utilised to lower the FFA below 1 wt% after which the base catalysed method is performed for the second stage of the biodiesel formation process. Esterification is performed to lower the acid value of the feedstock oil. Typically, the esterification process is carried out using an acid catalyst such as hydrochloric, sulphuric, or sulfonic acid (Ali et al., 2013; Raqeeb & Bhargavi, 2015). The acid value of oil is usually evaluated by titration of a combination of oil with ethanol and diethyl ether (1:1) against KOH utilizing phenolphthalein as indicator. Its value is determined by the equation $\text{Acid worth} = 56.1 \cdot \text{CV}/m$; while V is the volume of KOH (mL); C is the concentration of KOH (M) and m is the mass of used in the test (g) (Sunthitikawinsakul and Sangatith, 2012). This titration technique is governed by international standard ASTM D-664 (Farooq, 2015). Based on acid value evaluated, the type of catalysts is chosen. For an FFA under 1%, the feedstock can be transesterified with a homogenous base catalyst with no pre-treatment step (Patil et al., 2018). Lessening water by preheating in an oven can limit the FFA (Patil et al., 2018). The primary parameters influencing the esterification process are the alcohol to methanol proportion, catalyst and its concentration utilized, and the reaction temperature (Javidialesaadi & Raeissi, 2013). A study by Leung et al. (2010) utilising the two-step process on the waste canola oil biodiesel production process revealed superior results compared to conventional acid and base processes. The researchers initially evaluated the optimal conditions that were suitable for the feedstock.

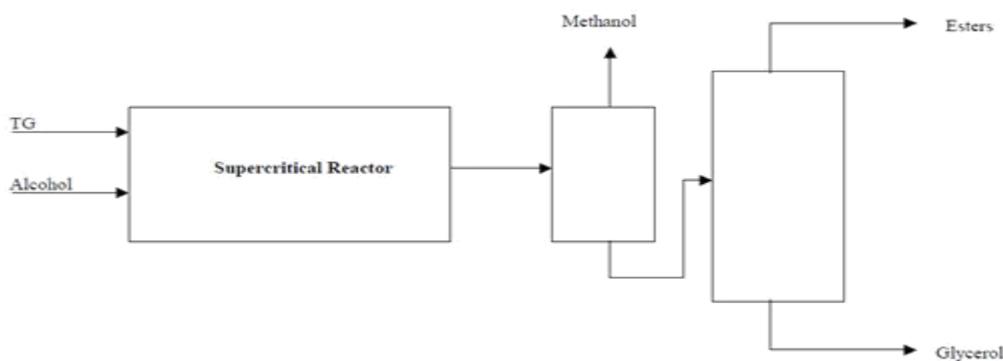
3.1.5. Non-Catalysed Transesterification

Supercritical methanol has been created to provide another method of delivering biodiesel. Under this supercritical condition, the transesterification process is rapid producing high yields of WCO biodiesel. Increasing temperatures have been noted to result in increased conversion efficiency of biodiesel (Demirbas, 2005). Besides, this technique has made cleansing of biodiesel a lot simpler as no catalysts are utilized in biodiesel production. In this process, soap formation is avoided as there is no water content available to enhance its formation (Barnwal & Sharma, 2005). Be that as it may, the downsides of this supercritical transesterification method are a result of high pressures and temperatures which require advanced equipment. This is hampering its adoption as well because this will increase the capital cost of plant development. Other strategies that have been adopted to lower these critical working conditions include the addition of cosolvents such as CO₂, calcium oxide and subcritical liquor (Vyas et al., 2010). Much exploration work has been completed for biodiesel creation from different feedstocks under various conditions utilizing supercritical liquor. Some conditions for non-catalysed processes are shown in Table 5.

Table 5: Reports on Non-Catalysed Processes.

Ref.	Vegetable Oil	Molar Ratio	Alcohol	Temperature and Pressure	Reaction Time	Reactor Type	Conversion (%)
Dincer (2008)	Rapeseed oil	42:01:00	Methanol	350 °C, 45 MPa	240 s	5 ml Inconel-625 reactor	95
Madras et al. (2004)	Sunflower oil	40:01:00	Methanol	350 °C, 200 bar	40 min	8 mL SS reactor	96
Rathore and Madras (2007)	Jatropha oil	40:01:00	Methanol	350 °C, 200 bar	40 min	11 mL reactor of SS 316	>90
	Soyabean oil	40:01:00	Methanol	310 °C, 35 MPa	25 min	75 ml tube reactor	–
Bunyakiat et al. (2006) Bunyakiat et al. (2006)	Coconut, palm oils	42:01:00	Methanol	350 °C, 19.0 MPa	400 s	Tubular flow reactor	95–96
Demirbas (2009)	Hazelnut kernel oil	41:01:00	Methanol	350 °C, NA	300 s	100 ml stainless steel reactor	95

A study by Hawash et al. (2009) uncovered that a 100 % yield of biodiesel can be produced in 240 seconds by utilizing supercritical methanol at a temperature of 320 °C and under a pressure of 8.4 MPa. In addition, safety issues are a major issue of concern due to high pressure and temperature conditions required for this method. The process progression is depicted in figure 7.

**Figure 7: Supercritical Transesterification Process.**

3.1.6. Enzyme Catalysis

The quest for ecosystem-harmless approaches for biodiesel creation has intensified investigation into the utilization of enzymes as process catalysts. The drawbacks of conventional acid and base such as feedstock pre-treatment, catalyst expulsion, high energy usage and generation of wastewater which require post treatment, are reduced in enzyme catalysed processes. Enzyme catalysts perform as biocatalysts using lipases derived from microorganisms, animals, and plants. These

lipases are categorised as extracellular lipases and intracellular lipases. Intracellular lipases are normally utilized in the entire cell structure, thereby eliminating chemical purification and selection process hurdles. To improve its stability and reus-capacity, lipases can be immobilized on a few materials. Biocatalysts are described as having high selectivity and as an effective method, resulting in a high biodiesel yield without side reaction occurrence. Furthermore, in this method glycerol recovery is simpler and of higher grade when contrasted with those from base catalysed processes. In addition to that, enzyme catalysed processes are compatible with a wide scope of fatty oil sources, and are applicable with FFA lying within the range of 0.5 % to 90 %. A study performed with *Rhizopusoryzae lipase* demonstrated that free unsaturated fats (FFA) contained in WCO oils and fats can be efficiently converted to biodiesel at lower temperatures ranging from 30 °C to 40 °C (Sattari et al., 2015). This gives enzyme catalysis an edge over base catalysts which produce lower yields at higher temperatures when the feedstock oil is of high FFA content. While ethanol and methanol are ordinarily used as alcohol in most transesterification process, these are shown to have significant inhibitory consequences for biocatalysts. An examination by López-Fernández et al. (2021) found that chemical deactivation expanded with expanding carbon chain of the liquor. Notwithstanding, this inhibitory impact can be resolved by utilizing a stepwise addition of the liquor.. An examination by Shimada et al. (2002) showed that the ideal methanol:oil proportion in dissolvable free biocatalytic framework was 1.5. The utilization of natural solvents, for example, n-hexane, n-heptane, petroleum ether and cyclohexane is another factor that influences the efficiency of bio. Despite the allure of biocatalysis, its business applications are hampered by specific drawbacks. These are: 1) high creation cost of the lipase catalyst, 2) higher response times when contrasted with base-catalysed response systems; and 3) recovery and re-utilization of biocatalysts restricted with a long working time. Reaction times of up to 90 h are possible utilizing different reactor types. Also, there is an interaction between the operational conditions and the reactant properties of the catalysts.

3.2. Alcohol to Oil Molar Ratio

The molar ratio of alcohol to oil is influential to transesrification process progression. This is because the molar ratio influences the reverse reaction process. Different alcohols like methanol, ethanol, tert-butanol, butanol, and isopropanol can be applied for transesterification of oils (Shuit et al., 2012). Lower alcohols are preferred since they are acquired at a low cost compared to higher alcohol options. Methanol is invaluable over other lower alcohols, fundamentally because of its chemical and physical qualities. Methanol reacts with feedstock oil at a faster rate speeding up the rate of reaction. This alcohol dissolves quickly in most alkali catalysts such as KOH and NaOH. However, the alcohol must contain optimal water content since an excessive amount will react and cause saponification of the oil. From the stoichiometric equation, it can be noted that a ratio of 3:1 is the most appropriate alcohol to oil ratio for the process. Higher ratios have been adopted since they favour higher yield formation in shorter reaction duration. This has necessitated utilisation of higher molar to oil ratio of 6:1 and higher (Wu et al., 2016). The biodiesel production process produces glycerol as a by-product which can be separated from the fuel with ease as it isolated from slurry by settling or hand centrifugation since it is basically insoluble in biodiesel (Chuah et al., 2016). Be that as it may, when utilizing high liquor to-oil molar proportions, glycerol dissolvability in biodiesel increases and free glycerol may remain suspended. This can be caused by alcohols becoming a reaction agent promoting dissolving of glycerol in biodiesel fuel. This will result in higher process costs as separation of glycerol becomes more difficult. This calls for proper selection of optimal alcohol to oil molar ratio for a favourable economic biodiesel production process. Wu et al. (2016) performed a study on soyabean biodiesel production using NaOH catalysed transesterification process (from 4.5:1 to 9:1) which revealed that the optimal molar to oil ratio was 7:1. The optimal molar ratio yielded 98 % within an hour of reaction. This also justified that utilisation of higher molar ratio above

6:1 was possible and could bring better outcomes. A study by Sanli et al. (2019) evaluated the optimal molar ratio from 3:1 to 20:1 and several alkali-based catalysts gave similar outcomes. The researchers concluded that the appropriate molar ratio of 8:1 with sodium methoxides of 1.40 wt.% for 120 minutes yielded the best results. Under those conditions, a conversion efficiency of 99 % was unveiled.

3.3. Biodiesel Production Modes

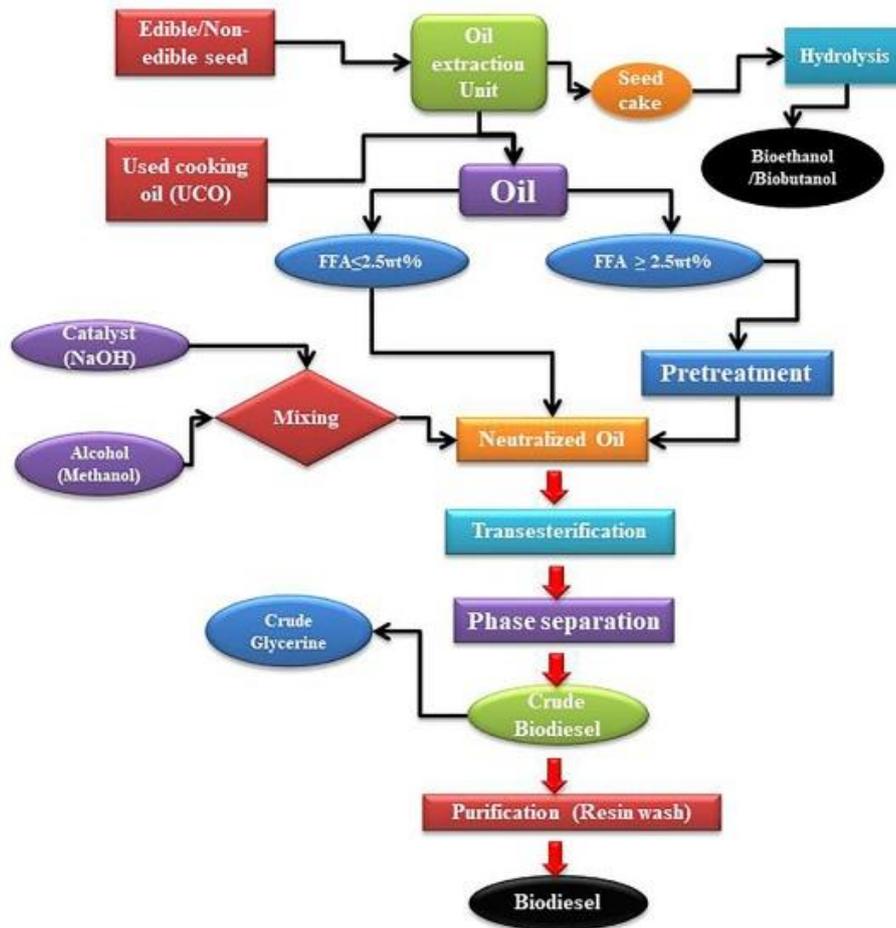


Figure 8: Waste Biodiesel Production Process.

Batch, semi batch, or continuous modes are the most utilised production modes for biodiesel production. The most normally utilized strategy for industrial biodiesel is the batch process. In a batch process, there is no inflow and outflow of materials during the process, and a limited number of reactants is orchestrated into the reactor a given time. When the process is complete, the whole slurry is shipped off to a purification process. Semi-batch process mode is a variation of batch process mode having higher selectivity and better control on reaction temperature. In semi batch process mode, as the reaction continues, one reagent or item is added at intervals whilst the reactants will be eliminated also at scheduled intervals from the reactor. Like the batch mode process, the production rate in the semi-batch process is restricted, and the biodiesel creation cost is moderately high. In the continuous process mode reagents are added continually and the products are continuously removed from the reactor. The batch process is the predominantly utilised process mode for biodiesel creation plants worldwide since it is suitable for small to medium scale biodiesel plants.

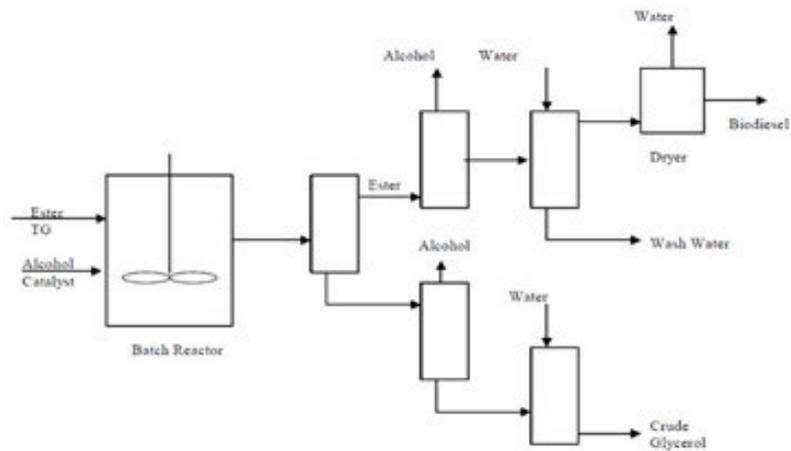


Figure 9: Batch Process Flow Diagram. Batch Process Mode.

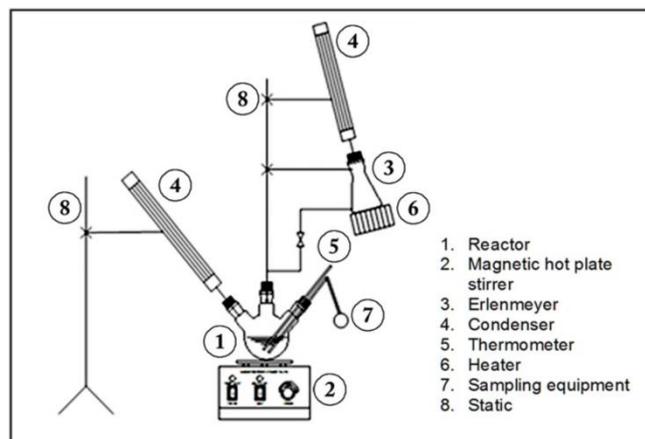


Figure 10: Batch Reactor (Patil et al., 2018).

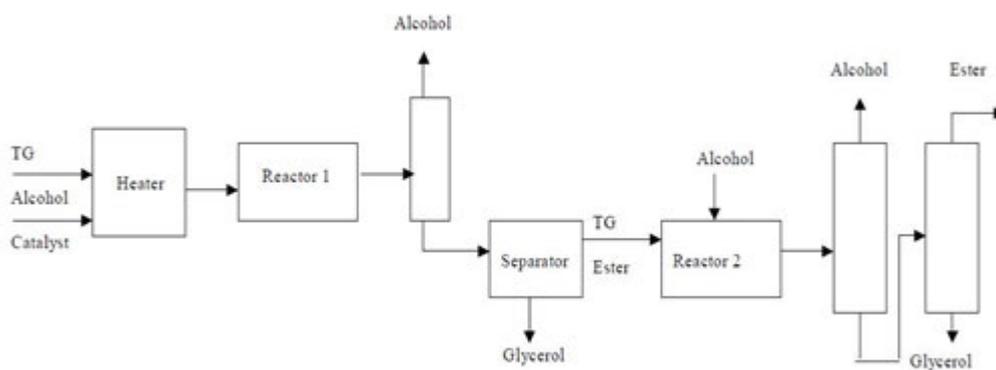


Figure 11: Continuous Process Flow Diagram.

3.4. Ultrasound Assisted Transesterification Method

The ultrasonic method has been perceived as being a useful technique to improve the mass exchange rate between immiscible fluids and a heterogeneous reaction media (Aghbashlo et al., 2019). Consequently, it has been utilized to increase the reaction rates for various chemical reactions. Ultrasound is that sound whose frequency cannot be detected by human ear. The ordinary sound frequency that can be identified by humans lies somewhere in the range of 16 kHz and 18 kHz, however the frequency of ultrasound for the most part lies between 20 kHz and 100 MHz. This high frequency sound wave has the capability to cause expansions and compressions of the molecules within the medium it penetrates. This enhances the creation of fine bubbles due to this phenomenon (Pukale et al., 2015). These bubbles contain energy capable of influencing chemical and mechanical changes. In line with that, the bubbles penetrate the phase boundaries and resulting in formation of an emulsified liquid phase. This method has been demonstrated to be an effective blending tool which gives adequate activation energy which can be utilised to increase biodiesel production (Singh et al., 2007). Furthermore, this technique will result in lowering the molar ratio and a significant reduction in energy utilisation (Vyas et al., 2010). A few studies have utilised ultrasound aided transesterification of WCO and yielded favourable outcomes (Delavari et al., 2015; Jian-Xun et al., 2007; Gharat & Rathod, 2013).

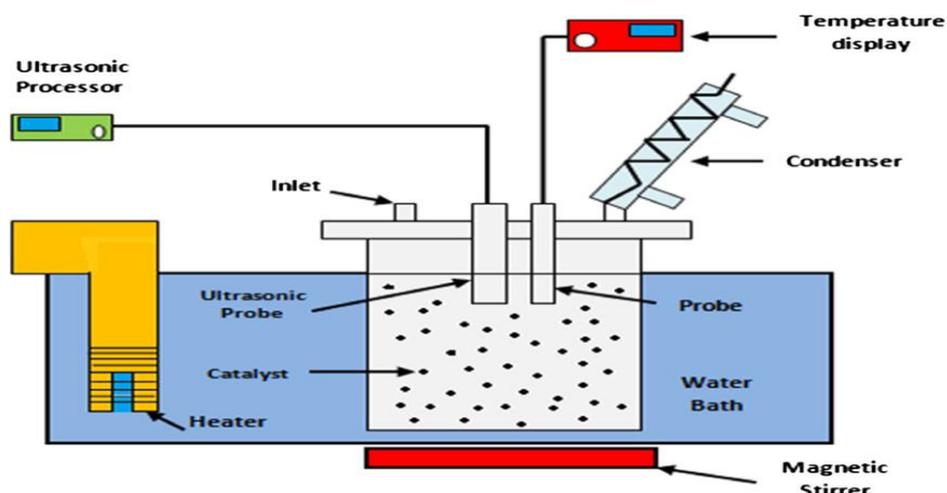


Figure 12: Schematic of Ultrasound Assisted Transesterification Process (Buchori et al., 2016).

3.5. Biodiesel Purification Process

Biodiesel should be purified before usage to reduce the possibilities of its contaminants blocking fuel supply line components such as injectors, pumps, and filters. Residue from WCO, for the most solid contaminants, can be eliminated by centrifugation as well as filtration before the biodiesel creation process. These contaminants need to be removed in order to maintain biodiesel quality. Generally, there are two methods used to purify and filter biodiesel fuel. The more customary wet washing technique is generally used to eliminate excess contaminants and reagents used for biodiesel production. In this method, a fine mist of water is showered over the fuel. The fuel's contaminations are removed as the water settles to the lower part of the tank. Nonetheless, the incorporation of extra water into the process offers numerous drawbacks, including increased production cost and prolonged duration. This has brought about utilization of the dry purification method. In the dry wash method, the duration of biodiesel production is reduced significantly, as is the cost of production as the water required is minimal in comparison to the wet wash method. In addition, the dry wash method requires less space and the product production is of higher quality. The resin used for purification can also be reused.

The principal benefits of utilizing the dry washing method are the significant reduction in effluent formation (making the process harmless to the environment), and the considerable decrease in the time taken to perform the purification process. The wet washing method is time consuming as it entails performing two washing process followed by centrifugation, all of which can be substituted by the one stage dry wash method. Faccini et al. (2011) examined the expulsion of glycerol from biodiesel from WCOs containing a high FFA content by utilizing silica and accomplished high biodiesel yields. Another promising dry washing resin is Amberlite BD10 DRY[®] which has since been adopted for WCO biodiesel purification. Purolite PD 206[®] is also very useful for purifying biodiesel containing higher water content, soaps, and glycerol, resulting in higher biodiesel yields and quality. A study performed by Berrios and Skelton (2008) affirmed that usage of Purolite PD 20 results in better yields and high-quality biodiesel when compared to wet purification methods.

3.6. Prospects of Waste Cooking Oil Biodiesel Production

Energy is a fundamental factor in promoting economic development and is key in alleviating poverty. Biodiesel, a renewable biofuel, has been portrayed in this survey as a fuel with the potential to supplant fossil diesel in the future. Biodiesel and its blends have gone through several corroborative tests and revealed better emission attributes hence they will play an important role as a fuel of the future. The availability of plenty of feedstock coupled with the introduction of advanced biodiesel processing technologies has cemented biodiesel as a viable alternative fuel to fossil diesel fuel. The utilization of WCO furthermore has aided in resolving the food versus fuel debate. The worldwide WCO market is expected to extend at a faster rate in the upcoming future. The increase of the worldwide market can partly be caused by the expanding interest in biodiesel by both developed and developing countries. Most developing economies are switching to biofuels due to increases in air contamination, therefore is speeding up the development of the worldwide WCO market.

Table 6: Average Costs of Feedstock for Biodiesel Production.

Oil	Price (Us dollar /ton)
WCO	225
Rape seed	825
Soyabean	770
Palm Oil	705

It can be noted from Table 6, that WCO feedstock oil can be acquired at a lower cost compared to virgin vegetable oil. WCO cost is two to three times lower than vegetable oil, and this results in lower feedstock costs. The cost of biodiesel from WCO is reported in the range of \$0.36/l to \$0.42/l (Sanjib, Kumar, Karmee et al., 2015). The utilization of WCO is high in animal feed production but this has been discouraged especially in Europe because of the side-effects which have been identified with its usage (T, D.Tsoutsosa et al ., 2016). Despite its numerous benefits as a sustainable renewable fuel, biodiesel presents various technical challenges that must be rectified before it will be more attractive as an alternative to fossil diesel. These issues include improving its cold flow properties, and oxidation stability related issues. Storage related issues are becoming a barrier to biodiesel deployment, but these can be circumvented by the use of fuel additives. This requires proper tank treatment before filling them with biodiesel to eliminate moisture and other substances which can promote oxidation of fuel. In addition to that, regular checks ought to be performed for indications of degradation. The utilization of fuel additives and other fuel property enhancements can remain a vital strategy in the foreseeable future to enhance biodiesel competitiveness unless upgraded compositional alterations are invented. Likewise, additives utilized for blends of a given feed stock might be incompatible with the types of feed stock available in different regions which underlines the requirement for further research on fuel additives that are suitable for localized feed stocks.

The essential market for biodiesel in the future is probably going to be a blended mixture with fossil diesel. Thus, it is important to study how biodiesel prepared from different feed stocks impacts significant fuel properties of the resultant fossil diesel/biodiesel blends. Biodiesel in the coming years may face competition from non-ester sustainable diesel fuels like those delivered from hydro-processing of vegetable oils or animal fats. Nonetheless, the numerous ecological advantages and utilizations of biodiesel will continue to ensure that a considerable market exists for this option compared to traditional fossil diesel fuel. However, to yield substantial benefits large scale bio-processing plants for future biodiesel creation must be set up now.

4. CONCLUSIONS

Considering the reviews and analysis introduced in this paper, it is of paramount importance to note that biodiesel production requires continuous process development that will enable it to reinforce its possibilities of becoming a viable alternative fuel for diesel engines. The above analyses provide a concise summary of the various catalysts and pathways that can be utilized for WCO biodiesel production. WCO is a viable feedstock for biodiesel production considering its accessibility and the minimal cost of acquisition. However, this feedstock oil has contaminants which impact negatively on biodiesel production. These compounds are a result of the frying process through which the oil passes. These undesirable substances are polymers, FFA compounds and high-water content. To eliminate these substances, pre-treatment of the WCO has to be performed. If the FFA and water substance are <1 wt % and <0.5 wt %, respectively, base catalysed process will be the ideal method of biodiesel production. Higher FFA substances in oil (>1 wt %) require acid catalysed transesterification in order to suppress soap formation. However, considering the necessity of high catalyst concentration and high molar proportion, the acid catalysed process is not encouraged for WCO biodiesel production. This then calls for a two-step method, although it may require more steps which, if not properly managed, can increase the production cost. Supercritical catalysed transesterification is emerging as the most promising alternative to all conventional catalysed processes, however, the requirements such as high temperature (300 °C), high pressures (40 MPa), and high molar proportion of oil to liquor (1:42) makes the utilization of this process unfavourable for commercial production. In this exploration study, the principal objective is the quest for proficient cycles of delivering WCO biodiesel that will reinforce its possibility as the cutting-edge green fuel through the different methods. The initially optimized twostep process conditions will be examined and thereafter methanolysis of calcium oxide coupled to pre-treatment will be utilized for process design and evaluation of batch process ultrasound and constant stream circle measure advancements by the utilization of homogeneous base impetuses. In addition, this investigation will utilize nano particles to circumvent the fuel property shortfalls which could have been identified in WCO feedstocks. In addition, further investigation will be undertaken to develop a viable catalyst that can be utilized for both virgin and used oils. The trial examinations performed on WCO to fulfil the research objectives will be documented in subsequent papers.

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CHAPTER 2 PART B: EFFECTS OF NANO ADDITIVES ON FUEL PROPERTIES, ENGINE PERFORMANCE AND EMISSION CHARACTERISTICS OF BIODIESEL FUELLED CI ENGINE.

This chapter provides a review on published work on effects of nano additives on biodiesel fuelled engines. The outcome of the work was published in the International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)

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EFFECTS OF NANO ADDITIVES ON FUEL PROPERTIES, ENGINE PERFORMANCE AND EMISSION CHARACTERISTICS OF BIODIESEL FUELED CI ENGINE

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ABSTRACT

Biodiesel is emerging as a magnificent alternative source of fuel for compression ignition engines. This renewable source of energy can reduce excessive reliance on fossil-derived fuels and decrease the emission of ozone-depleting gases because of its closed carbon cycle. However, biodiesels have combustion drawbacks such as low power output, high fuel consumption and high NO_x emissions. These shortcomings are a result of high density, high kinematic viscosity, low calorific value, high cloud and pour point and high oxygen content compared with fossil diesel fuel. The addition of nano additives is a cheap and easy fuel reformulation method that can improve biodiesel fuel properties. The benefits of fuel additives are better fuel economy, reduced emissions, and improved combustion characteristics. The test results from the numerous authors have not been analyzed to reach a consensus regarding the impact of nano particles on the properties, performance, and emission behavior of biodiesel fuels. Hence, this work is aimed to summarize the recent findings on the impact of metallic nanoparticles on fuel properties, combustion, and engine performance and emission characteristics of compression ignition engines.

KEYWORDS: *Biodiesel, Nano particles, Fuel properties, Combustion, Engine performance & Emissions*

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Nomenclature

Al ₂ O ₃	Aluminum oxide	CV	Calorific value
ASTM	American Society for Testing and Materials	FAAE	Fatty Acid Alkyl Esters
BD	Biodiesel	FD	Fossil diesel
BSFC	Brake specific fuel consumption	HOME	Honge methyl ester
BTE	Brake thermal efficiency	NaOH	Sodium hydroxide
CeO ₂	Cerium oxide	MWCNTs-HOME	Multi-walled nano tubes
CN	Cetane number	NO _x	Nitrogen oxide
CI	Compression ignition	N ₂	Nitrogen gas
CNT	Carbon nanotubes	PM	Particulate matter
CO	Carbon monoxide	UBHC	Unburnt hydrocarbon
CO ₂	Carbon dioxide		

1. INTRODUCTION

Diesel engines have been broadly utilized in the transportation of heavy goods, power generation and in the agricultural sector because of their high dependability, toughness, low fuel consumption and high compression

ratio. There are three fundamental challenges that have emerged regarding its usage in modern-day economies. The first challenge relates to its nonrenewable nature and the second to its occurrence in only specific parts of the world which impacts a country's gross domestic product as it has to be acquired using foreign currency. The third challenge concerns human and environmental contamination. It is difficult to eliminate the outflow of nitrogen oxide (NO_x) and particulate matter (PM) at the same time in diesel engines, because of the generation criteria (Molina & Molina 2004). Therefore, based on these factors, researchers are searching for alternative fuels for compression ignition (CI) engines, and biofuels have been identified as the front runners to replace FD fuels. Biodiesel (BD) offers many untapped opportunities to develop a more balanced energy mix that will address issues to do with energy security, sustainable development, and waste-to-resources economies— all of which lead to a cleaner global economy. BD is gathering attention as an alternative fuel for diesel engines because these energy resources are renewable, nontoxic, highly biodegradable and will lead to a carbon-neutral atmosphere (Tan et al., 2010). BD mixes well with FD at all proportions and their usage requires little or no engine modification. BD is possibly the most plentiful resource that remains unexploited, and it is capable of drawing in large renewable investments for the African continent. Despite its above-mentioned favorable factors, BD has met international resistance due to engine compatibility issues related to engine fouling, injector closing, high NO_x and sometimes high CO₂ emissions, poor low-temperature compatibility, and storage oxidation stability issues. Inferior quality BD is regularly created from unrefined feedstocks in uncontrolled home-fermenting plants, containing adverse foreign substances which cause injector fouling and increased fuel consumption. There has been an improvement though in its adoption since the introduction of international standards such as ASTM 6751 and EN14213 which have set the standards for BD fuels.

While BD utilization has appeared to decrease directed and unregulated emissions, various investigations have shown that its utilization brings about slight increases in NO_x emissions compared to FD (Hess et al., 2007). NO_x emission influences the formation of acid rain, smog, and ground-level ozone. The utilization of BD has increased but the concomitant rise in NO_x discharges could turn into a critical obstruction to its commercialization. In addition to that, ignition quality is affected by the size of fuel particles, lacking atomization execution, and obstruction of the fuel passageways in the chamber because of the higher kinematic viscosity of the fuel. The chemical makeup of the BD fuel results in higher viscosity which promotes injector coking, ring sticking and gumming in the combustion chamber. To curb such engine performance and emission setbacks, fuel additives have been gathering attention as the smartest option available. According to Neeft et al. (1996), almost 20 biofuel drawbacks can be circumvented by adding nano additives to BD and its blends. Fuel additive substances are normal substances with unique characteristics which can be tapped to improve the fuel properties of the base fuel. Fuel additive substances are incorporated at a level from a small ppm to two or three thousand ppm. It is essential that fuel additive substances that are added to address a specific drawback do not disable other properties and impair fuel quality (Neeft et al., 1996).

The fuel modification technique of the addition of nano-added substances is generally acknowledged by many scientists. The nano-added substances are utilized to accomplish explicit fuel properties and to improve the fuel-burning features and achieve a reduction in emissions from the CI engine with no engine adjustment.

An intensive review of the accessible literature points towards inconsistencies and contradictory conclusions regarding performance and emissions characteristics of nano fuel blended BD and its blends with fossil diesel fuels. This provides an impetus for further reviews aimed at finding common consensus regarding the effects of nano additives on

properties, performance and emissions of BD fueled CI engines. A critical literature review is hereby carried out aimed at creating a platform for further experimental investigations to close the gap on the effects of nano particles on the performance and emission of nano particles in BD.

2. BIODIESEL FEEDSTOCKS AND ITS ADVANTAGES

BD can be harnessed from edible or non-edible feedstocks. Edible feedstocks such as soybean oil, rapeseed oil, sunflower palm and beef tallow are facing immense competition from food. Palm oil is receiving more attention due to its high yield and high oil content. The first-generation feedstock is readily available and the conversions to BD processes are simple but the competition with food crops has given rise to debate on their usage. Researchers argue that increased production of first-generation feedstocks will lead to food price increases. The setbacks of first-generation resulted in biofuel producers seeking alternative sources which could be grown in marginal lands and these are defined as second-generation feedstocks. The second-generation feedstocks are non-edible oils also termed 'advanced biofuels'. These feedstocks include *Jatropha curcus*, Karanja oil, *Calophylluminophyllum*, Neem oil, Mahua, rubber seed, etc. Second-generation biofuels are receiving attention as they do not compete for land with food crops but their drawback is low yield when produced from marginal lands (Sakthivel et al., 2018). BD derived from algae is also attracting attention. Sakthivel et al. (2018) claim that most micro algae oil content exceeds 80 % weight by dry mass. Micro algae are regarded as the wonder of BD as it is proclaimed to meet global renewable fuel demand for the transportation industry. Commercialization of micro algae is suffering a setback because of high production costs of algae BD as it will require very large-scale reactors. The advantages of BD of using BD are: (1) BD can be blended with conventional diesel at any proportion and used in unmodified CI engines with ease. (2) BD has better lubricity compared to conventional diesel due to its slightly higher viscosity compared to conventional diesel fuel (3) BD is biodegradable and nontoxic when used in its pure form. (4) CN for BD is higher compared to conventional diesel. (5) BD is less combustible with a higher flashpoint of around 150°C compared to diesel of 77°C which makes it easy to store and handle and transport. (6) BD is oxygenated, and this enhances continuous combustion (Tate et al., 2006).

2.1 Biodiesel properties Influential to Performance and Emission Characteristics

Fuels used in diesel engines must conform to international standards. The most common BD standards are ASTM D6751 and EN14214. The properties which impact significantly on the combustion, performance and emission characteristics are kinematic viscosity, density, cetane number (CN), cloud and pour point and oxidation stability (Ashraful et al., 2014).

Kinematic viscosity gives a measure of fluid resistance to deformation at a given rate. It is also defined as a ratio of viscous forces to inertia forces. Demirbas (2005) defines kinematic viscosity as resistance to flow. For instance, kinematic viscosity entails the oil thickness and is evaluated by measuring the time the oil passes a given orifice of given dimensions. High viscosity causes greater resistance to the flow of diesel in the combustion chamber and this is reported to result in increased air-fuel mixture formation. Viscosity is reduced considerably during the transesterification process. The viscosity of vegetable oil ranges from 27.2 mm²/s to 55.6 mm²/s whereas viscosity for vegetable methyl ester is around 3.59 mm²/s to 4.63 mm²/s. Kinematic viscosity is the significant motivation behind why animal fats and vegetable oils are trans-esterified into BD. Very high kinematic viscosities of vegetable oils and animal fats have led to engine operational issues when utilized in their raw state. Notwithstanding this, BD kinematic viscosity is more than that of FD but slightly less than that of raw vegetable oil and or animal fats. The burning nature of fuel relies enormously on the mixing rate of

fuel to air inside the combustion chamber. Kinematic viscosity assumes a significant role in this blending process of fuel and air. Low kinematic viscosity fuel rapidly dissociates and blends in with the air inside the engine cylinder, which decreases the generation of the fuel-rich zone which gives fragmented burning, because of lack of oxygen for complete combustion. High kinematic viscosity fuel likewise prompts slow atomization, affects the fluidity of fuel, promotes bigger particle size, smaller slow atomization, and carbon deposits. This will subsequently influence soot formation and other deposits caused by poor spray patterns. The lower the kinematic viscosity of fuel the easier it is to be pumped and sprayed within the combustion chamber (Arpa et al., 2010). Common standard tests used for evaluating kinematic viscosity are ASTM D445 (1.9 mm²/s to 6 mm²/s and EN ISO 3104 (3.5 mm²/s to 5 mm²/s). Kinematic viscosity varies with the feedstock used; some have high kinematic viscosities such as neem oil of about 25.6 mm²/s whilst others such as *Jatropha* have low kinematic viscosity of about 3.7 mm²/s (Prasad & Agrawal 2012). Viscosity is vital for BD as it impacts performance. Given that the critical explanation behind generally regulated and unregulated diesel emissions is a result of inadequate burning, all things considered, low kinematic viscosity fuel is preferable to higher kinematic viscosity fuel. The kinematic viscosity of fuel is to a great extent influenced by temperature, so issues related to high kinematic viscosity are generally perceptible at low-temperature regions and during cold starting conditions.

The density of BD is affected by the molecular weight of the fuel (Alptekin & Canakci 2008). Density is defined as the weight of a unit of volume. The density of oil impacts the performance of the injector nozzle (Verduzco, 2013). Regardless of feedstock used, BDs are denser than conventional diesel. ASTM D1298 and EN ISO 3675/12185 standards are used to evaluate the density of a given BD as an alternative fuel for a diesel engine. Most BDs are in the range of 869 kg/m to 877 kg/m. High densities result in poor spray atomization of the fuel and the amount of fuel injected into the combustion chamber (Alptekin & Canakci 2008). The higher the density of fuel the greater the droplet diameter and the less the atomization of fuel. This will eventually impact overall engine performance. Less dense fuel increases efficiency atomization and promotes faster fuel-air mixture formation and better combustion characteristics. High density causes an increase in particulate matter (PM) and NO_x emissions (Yusop, Mamat, et al. 2014).

Cetane number (CN) is a dimensionless parameter that implies the knock tendency of fuel. The higher the CN the easier it is to be ignited when injected into the combustion chamber. The CN of BD is higher than that of DF. The higher CN results in the combustion of BDs becoming smoother and quieter compared to that of FD. Straight and longer saturated carbon chain BDs have high CN compared to short and unsaturated carbon chain BDs. A high CN number determines short ignition delay and better combustion of fuel. Long ignition delay causes diesel fuel knock and results in increased PM emissions. CN of BD is a factor of short, saturated carbon chains. Excessively high CN causes overheating of injectors giving rise to fuel deposit accumulation. CN is resolved as per ASTM D613 and is one of the essential markers of diesel fuel quality. Generally, the higher the CN, the shorter the ignition delay and this subsequently prolongs the combustion duration of fuel and the other way around. CN of fuel is evaluated against that of Hexadecane which has a very short ignition delay allocated a value of 100. The CN influences the diesel-burning cycle by lessening the start delay, which prompts a decrease in premixed ignition and diminishes the abrupt spike of in-chamber temperature that might be the reason for expanding the thermal nitric oxide (NO). As warm NO is viewed as one of the most significant pathways for in-chamber NO development, an expansion in CN will constantly decrease NO generation. Chiong et al. (2018) proposed that NO emissions can be diminished by 2.5 ppm vol% per unit increment of CN, in the range of 51-67. Despite the CN of BDs derived from most feedstocks being more prominent than that of FD, it has been generally stated in the literature that utilization of BD in diesel motors builds NO_x outflows. Because of NO_x outflows, different properties of BD which

improve in-chamber NO_x development are probably going to supersede the smothering impact of CN.

Calorific value (CV) gives the proportion of heat energy a fuel releases during combustion, and this fuel property is evaluated according to ASTM D240, however, this parameter is not documented in either ASTM D6741 or EN 14214. The CV of BD and its blends are lower than those of neat FD fuels. For instance, the CV of B20 obtained from soya bean oil is 43.8 MJ/kg contrasted with 46.7MJ/kg for FD fuel names (DeOliveira et al., 2006). Increasing the BD in the blend results in a corresponding reduction in CV. Moser (2011) suggests that the CV makeup of fuel is impacted by oxygen and carbon to hydrogen proportion. Generally, as the oxygen substance of fatty acid alkyl esters (FAAE) is increased, for instance, its CV will subsequently increase. For example, methyl stearate (C18:0 ME) have higher energy content (40.07 MJ/kg) than methyl laurate (C12:0 ME) which shows a value of (37.97 MJ/kg) (Mosser 2014). Along these lines, the CV of FAAE is directly linked to chain length (Moser 2011), since longer-chain FAAE contains more carbons yet a comparable number of oxygen particles. Another huge factor is the carbon to hydrogen ratio. Lower carbon to hydrogen-containing FAAEs show higher energy content when compared to those with higher carbon to hydrogen ratios.

2.2 Biodiesel fuel properties Analysis

Properties of BD are dependent on hydrocarbon chain length, hydroxyl group type degree of saturation, and chemical structure. A study by researchers concluded that the performance and emission of a BD-powered engine were impacted by the physical properties of the fuel (Tesfa et al., 2013). BSFC was reported to be higher by 15 % compared to conventional DF. Puhan et al. (2010) carried out an investigation on a 4.4 kW engine using linseed derived BD which contained greater portions of unsaturated acids (linoleic) and concluded that the fuel was not suitable for diesel engines. This emphasizes the fact that the chemical makeup of the fuel has a great influence on the performance of the derived fuel. Early combustion and short ignition delays were reported by Shahabuddin et al. (2013) and these were reported to be a result of higher CN and the chemical structure of the fuel. A study on performance and emission of a CI engine fueled byBD- diesel blends unveiled that both injection and ignition delay was lowered with an increase in BD addition (Devarajan, Nagappan et al. 2019). Better engine performance and lower emissions were reported at the expense of NO_x increment. The variations in both performance and emission characteristics were blamed on increased density and viscosity of the fuels with an increase in BD addition. An investigation by Shojaefard et al. (2013) revealed better performance when lower percentages of BD-diesel blends are utilized, specifically pointing to waste cooking oil derived BD as an alternative source of fuel for CI engines. Improved engine performance and reduced emissions are influenced by the spray atomization of the fuel. BD contains larger particle droplets when compared with diesel fuels. High viscosity disrupts the formation of spray formation. BDs possess better lubrication properties compared to FD. Its lubricity properties are said to last between 2 to 4 years after which they will be lost. This is caused by the oxidation of unsaturated molecules and water absorption.

2.3. Effects of Nanoparticles on Fuel Properties

This section presents only work published on the impact of nanoparticles on fuel properties of BD fuels. The analysis is based on density, kinematic viscosity, calorific values, cetane number and flashpoint since these are fundamental properties that influence the performance and emission behavior of BD fuels. According to the authors' analysis of the available literature, metal-based added substances reduce kinematic viscosity, pour point, and flash point of BD fuel. 57% of the studies found that the addition of nanoparticles results in a decrease in kinematic viscosity, while 38% reported that the addition of nanoparticles resulted in an increase in kinematic viscosity. Karthikeyan et al. (2014) studied the impact of zinc oxide and cerium oxide on B20-Pomoline stearin wax BD and concluded that the introduction of nanoparticles resulted in

caloric value and flash point reduction. Shaafi and Velraj (2015) performed an evaluation of adding alumina nanoparticles, ethanol, and isopropanol blend as an additive to a diesel-soybean BD blend. Analysis of results showed that kinematic viscosity was decreased along with calorific value while CN was increased with the addition of nano particles. Vedagiri et al. (2019) experimentally investigated the influence of CeO₂ and ZnO on grape seed BD and tested the fuel properties according to ASTM standards. The results showed that ZnO doped fuel had a higher CV than that of CeO₂. Gürü et al. (2010) investigated the impact of an Mg-based additive to chicken fat methyl ester on fuel properties. The authors conducted their tests by varying Mg from 0 mg/L to 16 mg/L and found that the additive addition resulted in a reduction in kinematic viscosity from 5.184 cSt to 4.184 cSt, and flash point from 129°C to 122°C. Another study by Gürü et al. (2009) was performed to evaluate the impact of Mg and Ni on animal fat BD fuel properties. According to the results, varying the additive from 0 mg/L to 12 mg/L showed a reduction in pour point of by 3.5°C to 5°C, a reduction in kinematic viscosity from 5.40 to 4.95 and flash point from 138°C to 132°C. This is credited to the catalytic effect of nano particles which react with base fuels to form smaller hydrocarbon structures that promote favourable fuel properties. The Mg additive revealed better fuel properties in comparison to the Ni additives due to the impacts on the fuel colligative properties of the added substance. A study by Sharma et al. (2016) on the influence of cerium oxide (CeO₂) and carbon nanotubes (CNT) on fuel properties showed that the addition of CeO₂ reduced both kinematic viscosity and density while CNT increased both fuel properties. It was reported by Arockiasamy and Anand (2015) that there was a surprising slight increment in kinematic viscosity from 4.10 cSt for neat BD to 4.25 cSt and 4.30 cSt by addition independently of 30 ppm of aluminum oxide (Al₂O₃) and 30 ppm of CeO₂ respectively. A slight reduction in calorific values and increments in density were also recorded by these authors. Attia and Kulchitskiy (2014) performed various experiments aimed at evaluating the properties, performance and characteristics of the B20-Jojoba BD blend mixed with the addition of Al₂O₃. From the experiments, it was noted that kinematic viscosity decreased while density and CN increased with Al₂O₃ addition. A study by Çaynak et al. (2009) on the influence of Mg (12 mg/L) additive on pomace oil BD fuel properties reported a reduction in kinematic viscosity of 20 % and lowering of flash point by margins ranging from 7 °C to 8 °C. The addition of Mg and Ni to crude tall oil BD that was produced from a craft or sulphate pulping process showed improved fuel properties. The evaluation was performed by varying the additive between 8mg/L to 12 mg/L. Analysis of results showed that the addition of the additives resulted in a reduction in flashpoint and kinematic viscosity. The minimum kinematic viscosity and flashpoint of 4.3 and 79 were recorded by adding 12 mg/L of Ni additive to base fuels. There were no significant changes in kinematic viscosity although slight gains were recorded on CN with nano particle addition compared to neat grape seed BD (Vedagiri et al., 2019). A study by Aalam and Saravanan (2017) on the impact of Al₂O₃ on *Jatropha* BD showed a decrease in flash point, kinematic viscosity and density whilst calorific value was slightly improved. A study by Attia et al. (2014) on the influence of Al₂O₃ nano particles on fuel properties of BD revealed significant improvements. Ranjan et al. (2018) studied the effect of adding magnesium oxide (MgO) nanoparticles on performance properties and emissions of waste cooking oil derived BD. Different fuel mixtures were utilized in the experiments, namely, 0 %, 80 %, and 90 % blending proportions of BD to FD mixed with 20 ppm, 30 ppm and 50 ppm of MgO. The addition of 30 ppm MgO showed significant improvement in cloud point, pour point and cold filter plugging point. Selvan et al. (2014) performed an analysis of the impact of CeO₂ nanoparticles as added substance to BD on the chemical physical properties of the fuel. The researchers applied varying CeO₂ dosages of 20 ppm, 40 ppm, 60 ppm, and 80 ppm to evaluate the optimal level for favorable fuel properties. The outcome their evaluation demonstrated that the kinematic viscosity and flash point of the BD increased by adding the CeO₂ nanoparticles. Chen et al. (2018) performed an evaluation of the impact of various nano particles on the

fuel properties of neat FD fuel. The researchers performed experimental investigations using Al₂O₃, CNT, and silicon oxide (SiO₂) nanoparticles with dosing levels of 25 ppm, 50 ppm, and 100 ppm. The analysis of the results showed that addition of Al₂O₃ nanoparticles caused an increment in kinematic viscosity and calorific value of the neat base fuel. The authors noted that CNT addition had no influence on density but decreased viscosity which they attributed to changes in lubricity due to the addition of the nano particles. CNT doped FD is reported to have showed higher calorific values compared to neat FD fuels, because of the lubricity of carbon particles. According to the report, SiO₂ mixes showed a lower fuel density and lower kinematic viscosity but had no impact on calorific values of the fuel. Chandrasekaran et al. (2016) conducted a study on the effects of copper oxide nano additives on BD derived from mahua feedstock. The test results showed significant improvement in fuel properties and better performance characteristics. Mixing BD and diesel in proportions of 20%, 40%, 60%, 80%, 100% coupled with the addition of 50 ppm of copper oxide additives showed a marginal decrease in kinematic viscosity and density. Reduction in flash and fire point were also reported. An increase in CV of fuel by 0.6 MJ/kg was noted. Özgür et al. (2015) studied the role of mixed nano additives MgO and silicon dioxide on stability and performance. Reduction in emissions, improved fuel stability, increased brake thermal efficiency was found compared to diesel fuels. A significant reduction in density from 896 kg/m³ to 895 kg/m³ was reported by MgO addition. Portions of 25 ppm and 50 ppm were used in this study. No changes in properties were reported when 25 ppm of MgO was added, but when 50 ppm was added changes were noted. Addition of 25 ppm of SiO₂ showed a reduction in density but no changes were noticed on addition of 50 ppm. Viscosity decreased with an increase in additive addition for both MgO and SiO₂ additions. Prabakaran and Udhoji (2016) conducted experiments on performance and emissions characteristics of direct injection engine fueled from BD-diesel blends with ethanol mixed with zinc oxide nano additives. Density, calorific values, and flashpoint increased while kinematic viscosity and CN decreased with addition of 250 ppm of nano additive. A summary of articles on the impact of nano particles on fuel properties is shown in Table 1.

Table 1: Summary of reports on effects of Nano Additives on Fuel Properties

	Total number of References	Increase		Similar		Decrease	
		Number	%	Number	%	Number	%
Kinematic viscosity	21	8	38	1	5	11	52
Density	18	10	56	0	3.2	8	44
Calorific value	19	6	32	0	5.8	13	68
Cetane Number	13	11	85	0	5.3	2	15
Flash Point	15	7	7	0	3.0	8	53

3. EFFECTS OF NANOPARTICLES COMBUSTION CHARACTERISTICS

The different combustion characteristics such as ignition delay, heat release rate, and spray peak pressures of different fuels doped with nanoparticles are reviewed in a detailed manner in the subsequent paragraphs.

3.1. Effects of Nanoparticles on Ignition Delay

Ignition delay (ID) is defined as the timeframe between the beginning of fuel injection to the beginning of fuel that is burning inside the combustion chamber. A test study performed by Kannan et al. (2011) with FeCl₃ nanoparticles blended

in a waste cooking palm oil BD to examine the burning characteristics of diesel engines, found that the impact of nano-added substances is to shorten the ignition delay. This is because of better atomization of fuel and enhanced air-fuel mixing process. A comparative clarification for the decrease in ID was introduced by Basha and Anand (2014) when working with CNT nanoparticles. Shaafi and Velraj (2015) performed a study on the impact of alumina nanoparticles in diesel soya bean BD fuel in a diesel engine and found that at the no-load condition the ID of BD fuel mix was higher than that of FD. The authors argue that this is caused by the higher kinematic viscosity and density of BD fuels which impacted negatively on the fuel atomization process. Higher kinematic viscosity promotes large fuel particle generation which might slow the ignition process by slowing the burning process. Nonetheless, the addition of nanoparticles will impact the fuel properties reducing its kinematic viscosity, bringing it closer to that of FD. This, together with increased CN, has enabled nanoparticle doped fuels to produce a shorter ID compared to neat FD fuels. From past investigations done by various authors, the addition of nanoparticles to BD and its blends with FD significantly affects the ignition and burning characteristics of the engine. Risha et al. (2007) performed an analysis of the influence of nano aluminum and water emulsion on the burning features without the utilization of any gelling agents under varying pressures, dosages, and particle sizes. Analysis of the results revealed that the addition of nanoparticles resulted in a reduction in ID and ignition temperature. Tyagi et al. (2008) carried out a study to examine and improve the ID of diesel fuel by exploring the impact of adding aluminum and Al_2O_3 nanoparticles to diesel. The authors performed droplet ignition tests on a hot plate utilizing various nanoparticle sizes ranging from 15 nm to 50 nm and volumetric proportions of 0%, 0.1 %, and 0.5%. For each fuel combination, several fuel drops were dropped on the hot plate from a fixed stature and under identical conditions, and the likelihood of the start of ignition that fuel was recorded dependent on the quantity of drops that ignited. These tests were repeated at a temperature ranging from 688°C to 768°C. Analysis of results showed that the ID of fuels that contained nanoparticles was higher than those of neat Fuels. The authors argued that the addition of nanoparticles to the fuel caused transformation to its heat transfer features which resulted in fuel droplets igniting at a much lower temperature compared to pure diesel fuel. Sajith et al. (2010) explored the impact of CeO_2 added substances (molecule size 32 nm and portion level 25 ppm) in diesel and diesel-BD-ethanol mixes on the performance behavior of a diesel engine. They found that the addition of CeO_2 added substances in the mix was improved by ultrasonicator. It was also concluded that the introduction of nanoparticles into diesel-BD-ethanol mixes reduced fuel utilization, expanded peak pressure, and shortened ID. This phenomenon was credited to the addition of CeO_2 which had a catalytic effect resulting in shorter ID. A study by Nassir and Haroun (2018) on combustion characteristics showed that the ID was shortened with higher dosages of nanoparticles. Also, the impact of Al_2O_3 nanoparticles on viscosity revealed significant changes when compared with the TiO_2 showed. However, TiO_2 nanoparticles showed the most significant decrease in the ID, which the authors credited to its lower viscosity compared to Al_2O_3 .

3.2. Effects of nanoparticles on the heat release rate

The heat release rate of neat BD and its blends are usually lower when contrasted with neat FD. This is because of the greater molecular weight and laminar burning features of BD fuels compared to the lightweight and turbulent profile of FD fuels (Fatah et al., 2012). The introduction of nano additives results in higher heat release rates when compared with neat BD fuels. This might be credited to the improved impact of higher surface area to volume proportion, higher thermal conductivity and the upgraded ignition features of the transformed fuels (the BD fuels and or its blends with FD) which promote shorter ignition delay hence higher heat release. Shorter ignition delay produces a prolonged combustion process hence more heat release rates when compared with those of unaltered fuels. A study undertaken by Gad et al. (2021) using

alumina nanoparticles found a significant increase in the heat release rate of 62J/CA for alumina blended ethanol BD fuel when contrasted with 51.60J/CA recorded for the B20 blend. The researchers stated that the generation of higher temperatures, higher pressures and improved combustion process were the reason behind this phenomenon. Comparative patterns of results were cited by analysts with almost 4.6% higher heat release rates being revealed, demonstrating that addition of different nanoparticles to diesel BD fuel blends have been found to give higher heat release rates than that of neat diesel and BD fuel.

3.3. Effects of Nanoparticles on Pressure Release

The pressure release curve depicts the rate at which pressure is being generated inside the combustion chamber. Under typical conditions, the peak pressure rise rate will be positioned immediately after the top dead center (Heywood, 2018; Stone, 1999). This indicates that the greater portion of the heat that has already been released by the fuel during the premixed phase of combustion. This peak pressure rise is trailed by a drastic fall in pressure release and then a steady variation (Heywood, 2018). This parameter is a vital pointer of the engine combustion process that indicates how well the process is proceeding. Generally, the pressure release rate of neat BD and their blends is lower than that of neat FD fuels (Radwan et al., 2007). This is attributed to the lamina combustion profile of neat BD fuels which result in lower heat release rates and hence lower pressure release rates. The addition of nano additives to BD prompts the increment of fuel droplet evaporation rate, and better fuel-air blending, which transforms the burning velocity from lamina to turbulent profiles. This will subsequently result in the generation of higher pressures when compared with neat BD fuels. This phenomenon can be credited to the catalytic effects of nanoparticles which promote lower hydrocarbon carbon particles, leading to rapid heat generation hence higher-pressure release (Radwan et al., 2007). Selvan et al. (2014) performed engine tests to examine the performance and emission attributes of a VR engine utilizing CeO₂ nanoparticles and CNT as fuel-borne nanoparticles added substances in diesterol (diesel-BD-ethanol) blends. Castor oil was added to the blends to avoid phase separation as diesel and ethanol are immiscible in nature. Varying levels of CeO₂ nanoparticles and CNT of 25 ppm, 50 ppm, 100 ppm were added to the fuels. The authors reported increased pressure release rates which they credited to CNT addition which resulted in rapid fuel burning rates which promoted reduced ignition delay, hence, higher pressure release rates when contrasted to neat diesterol mixes. The CeO₂ nanoparticles also act as oxygen buffers donating oxygen atoms for accelerated oxidation of fuel to carbon dioxide and water. All this helps in generating high pressure release rate profiles for the engine. Sathiamurthi et al. (2019) explored the performance, emission, and combustion attributes of a single chamber with two modified fuel mixes: BN20 (BD from neem oil) and CeO₂ nanoparticles added to the BN20. An ultrasonicator was utilized to blend the CeO₂ nano-added substances with the BN20 to suppress phase separation. The authors concluded that addition of CeO₂ showed higher cylinder pressures when compared with BN fuel. Banapurmath et al. (2014) explored the performance and emission attributes of diesel engines powered from BD doped with graphene, silver, and multi-walled carbon nanotubes and showed that the peak pressure was expanded. This occurred because of the addition of the nanoparticles, which prompted shorter ignition delay and prolonged combustion process.

4. EFFECTS OF NANOPARTICLES ON ENGINE PERFORMANCE PARAMETERS

The performance parameters such as power output, specific fuel consumption, and brake thermal efficiency of different base fuels mixed with nanoparticles have been reviewed and are summarized in subsequent paragraphs.

4.1. Effects of Nanoparticles on Engine Power and or Torque

Engine power decreases with an increase in BD proportion in blends due to a reduction in the heating value of the fuels (Aydin & Bayindir, 2010; Ozsezen et al., 2009). Some have attributed the reduction in power to the combined impact of high kinematic viscosity, density, and lower heat values (Hansen et al., 2006). According to Karabektas (2009), engine power and or torque drops with increasing BD proportion in the fuel blend due to its lower heat value, higher kinematic viscosity, and lubricity. A few authors have reported conflicting results by indicating that engine power increases with increases in BD proportion in the blend and they have attributed this to the higher CN of BD fuel (Karabektas, 2009). Generally, key properties of BD fuel that impact brake power are heat value, kinematic viscosity and density (Xue et al., 2011). The higher the heat value the greater the energy that the fuel can liberate and the higher the brake power and vice versa. Higher kinematic viscosity impacts the fuel atomization process and will promote the generation of higher fuel droplets which ignite slowly resulting in low brake power (Utlu and Koçak, 2008). Higher lubricity of BD brings about decreased frictional force subsequently resulting in higher brake power (Xue et al., 2011). Several researchers have reported on the impact of various added substances on brake power and or torque. Fangsuwannarak and Triratanasirichai (2013) investigated the impact of TiO₂ nano additives on neat diesel and palm BD (B5) fuels. According to their results, the addition of the nano additive to neat diesel and palm BD resulted in an increment in brake power (BP) of 7.78% and 1.36% respectively. Torque was also increased by 1.01% and 1.53% respectively. A study by Gumus et al. (2016) on the influence of Al₂O₃ and CuO on neat FD also revealed BP improvements. The scientists performed their investigation by doping the neat FD with 50 ppm of Al₂O₃ and CuO separately and evaluated the torque and BP. An increase in BP of 3.30% was recorded for Al₂O₃ and CuO and torque increments of 1% were also reported by the scientists. A study by Kumar et al. (2017) on the impact of CeO₂ revealed higher BP with nanoparticles doped BD fuels in comparison to neat BD fuels. According to the research, increasing the loading from 2.1 kg to 15.9 kg showed an increasing trend in BP. The authors argued that the increase in BP with nanoparticles doped fuels was caused by a better combustion process due to the catalytic effect of CeO₂ nano particles. Keskin et al. (2008) examined the influences of metal additives on tall oil BD. Performing tests on a 4-stroke single cylinder engine at full load fueled by B60 fuel revealed no significant changes to the BP. Mofijur et al. (2012) explored the impact of antioxidants on BD blends. The authors reported that B35 fuel with 1% NPAA added substances gave 6.12% higher BP than neat B35 and 2.7% lower than DF because of the lower viscosity of the additive. A study by Ranjan et al. (2018) on the impact of nanoparticles on performance and emission behavior showed significant BP improvements of a BD-powered engine. The BP for PBD were 11.69%, 9.26%, 11.35%, 11.08%, 8.92%, and 9.12% higher than B100, B20, B10, B100W30A, B20W30A and B10W30A respectively. The authors attributed the high BP of PBD to its high CV and low kinematic viscosity. High density was also noted by some authors as being the reason behind a reduction in BP of some BD fuels. Kumar et al. (2017), and Khalife et al. (2017) studied the influence of hybrid multiwall carbon nanotubes (MWCNT) and CeO₂, nanoparticles on B5 and B20 blended fuels. The investigation was performed at a constant speed of 1500 rpm and full loading conditions. The combined nano particles were added in dosages of 30 ppm up to 90 ppm. Analysis of the results showed that addition of combined nano particles resulted in an increase BP of 0.58%, 1.79% and 3.52% when compared with neat B5 fuel. Furthermore, addition of 30ppm, 60ppm, 90 ppm to B20 revealed an increment of 2.28%, 5.72% and 7.8% when evaluated against neat B20 blended fuel. Mirzajanzadeh et al. (2015) reported a significant improvement in performance parameters of a diesel motor energized with diesel-BD blends with the addition of mixed nanoparticles containing CeO₂ on amide-functionalized multiwall carbon nanotubes (MWCNT-CeO₂ nano particle). The authors recorded an improvement in engine performance with the fuel mix

containing 20% BD and 90 ppm of the mixed nanoparticles. Engine torque and power improved by 4.91% and 7.89%, respectively. Some studies reported that for that there were surprising decreases in BP with the addition of fuel additives. Khalife et al. (2017) recorded lower BP with B5 mixed with water emulsion when compared with neat B5 fuel. The addition of 90 ppm of CeO₂ to B5 mixed with water emulsion however showed higher BP. The authors also performed another investigation in which they added an additional 90 ppm to B5 water emulsion fuel mixed with 90nm CeO₂ and recorded a drop in BP. The authors pointed out that the reduction might have been caused by the cooling impact of water emulsion which was able to surpass the catalysis effect of nano particle resulting in a drop in BP. Keskin et al. (2011) led an investigation on single cylinder direct injection (DI) diesel engines fueled from chicken fat BD doped with 12 μmol/L Mg added substance and its impact on engine performance and emission features. From analysis of the results, it was noted that engine torque was not impacted by addition of the nano particles to neat BD fuels.

4.2. Effects of Nanoparticles on brake specific Fuel Consumption

Brake specific fuel consumption (BSFC) is a proportion of the use of fuel provided to the engine for creating brake power. BSFC is defined as the mass flow rate of fuel per unit brake power created. Attia et al. (2014) performed an investigation on the influence of Al₂O₃ on the performance behavior of B20-JojobaBD and its blends with FD and found that a maximum reduction in BSFC of 6 % was accomplished with nanoparticle addition when it was evaluated against neat FD fuel. Sajith et al. (2010) examined the impact of adding CeO₂ and showed that it diminishes BSFC on the grounds that the presence of CeO₂ oxidizes carbon on combustion cylinder walls prompting smooth and efficient combustion of fuel. Zhang et al. (2013) utilized nanoceria in diesel and managed to decrease fuel utilization by 12%. Basha and Anand (2013) found that the BSFC was improved with the addition of nanoparticles to mixed BD emulsion fuel because of the unique higher surface area to volume ratio, higher thermal conductivity, and catalytic features, all of which enhance rapid fuel combustion. BD emulsion with 100 ppm alumina nanoparticles mixed fuel showed a lower BSFC of 0.31 kg/kW at full load. This resulted in significant reduction in BSFC. Singh and Bharj (2015) produced emulsion fuels containing 83% diesel, 15% water and 2% surfactant and CNT dosages fluctuating from 50 ppm, 100 ppm and 150 ppm. The fuel emulsions were utilized in a single-chamber diesel engine coupled to a current dynamometer to evaluate the performance and emissions characteristics of the engine. The results showed a diminished pattern of BSFC with increasing levels of CNT. A BSFC of 0.27 kg/kW h was recorded for fuel containing 150 ppm CNT additives contrasted with 0.31 kg/kW h for neat FD. This was because the water present in fuel quickly dissipates resulting in a finer splash. Furthermore, reactant movement of CNT advances the evaporation rate of fuel resulting in lower BSFC values. Manibharathi et al. (2014) utilized Pongamia BD as a base fuel with rhodium oxide (Rh₂O₃) nanoparticles tested on a single-cylinder, 4-stroke, air-cooled CI engine to evaluate performance and emissions parameters. Performing engine tests with 100 nm doped fuels revealed a decrease of BSFC of about 3% with the addition of Rh₂O₃ compared to neat base fuel. Keskin et al. (2011) recorded a significant decrease in the BSFC with 16 μmol/l Mn added substances because of the catalytic features which promote better fuel combustion characteristics hence reduce fuel consumption. Zhu et al. (2012) reported that BSFC diminished with increased dosing proportion of nanoparticles under varying loading conditions. Some researchers, though, recorded BSFC reduction as not being directly linked to dosing proportion (Ganesh & Gowrishankar 2011). Ganesh and Gowrishankar (2011) utilized magnalium and cobalt oxide nanofluid added substances to evaluate their impact on *Jatropha* BD (JBD) in a single chamber, AC, DI engine. Higher BSFC were recorded and this phenomenon was because of lower calorific JBD. However, the addition of magnalium and cobalt oxide improved BSFC significantly when contrasted to JBD without the added substance. The improvement in BSFC for magnalium added substance compared to JBD without the

added substance was about 1%. Some research studies have shown an opposite trend (Gurusala & Selvan 2015; Çaynak et al. 2009; Sharma et al., 2016; Gürü et al., 2010), reporting increased BSFC with nano particle addition. Ranjan et al. (2018) studied the effect of adding MgO nano particles on the property, performance and emission of waste cooking oil derived BD. Different fuel mixtures were utilized with 0%, 80%, and 90% blending proportions of BD to FD mixed with 20 ppm, 30 ppm and 50 ppm of MgO. The BSFC of B100W30A, B20W30A and B10W30A fuels were 28.2%, 9.48%, and 2.45% higher than the B100, B20 and B10 fuels respectively.

4.3. Effects of Nanoparticles on Brake Thermal Efficiency

Arockiasamy and Anand (2015) analyzed the combustion and emission characteristics of *Jatropha* BD with the addition of alumina and CeO₂ nanoparticles. Nanoparticles were added to the BD using an ultrasonicator. Both blends were stable without any phase separation up to 48 hrs. BTE increased up to 5% for both samples. Tewari et al. (2013) investigated the impact of diesel multiwalled carbon nanotubes (MWCNTs) in BD blends and discovered that the BTE of the MWCNTs-honge methyl ester blended fuels was seen to be higher when contrasted with neat BD fuels. The authors attributed this to the better ignition qualities of MWCNTs. A similar pattern was reported by Khan et al. (2020) who researched the influence of two fuel additives (n-butanol and synthesized asymmetric graphene oxide nanoparticles) on performance enhancement and emission reduction of *Nigella sativa* BD (NSME25). The researchers noted that the nano-sized particles have a high surface area and receptive surfaces that add to higher thermal conductivity and this might be the reason behind this phenomenon. El-Seesy et al. (2017) studied the impact of MWCNT with jojoba BD (JB20D) on BTE. The test was performed by varying the load and speed. The MWCNT were added at various levels of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L and analysis of results showed that BTE increased by a maximum of 16% when contrasted with neat BD. According to this research, 40 mg/L was revealed as the optimal level of additive because it showed the best performance and emissions results.

Sathiamurthi et al. (2019) performed an evaluation of engine performance and emissions behavior by adding 50 nm Al₂O₃ nano particles to neat diesel fuel. Venkatesan and Kadiresh (2016) even though they utilized a more modest size of nanoparticles (40 nm) and a different. The research was conducted on a single cylinder 4 stroke engine under varying loading conditions. The authors recorded higher BTE with nanoparticle doped fuels compared with neat diesel fuels. These outcomes indicate that molecule size has a significant effect on start and ignition. Moreover, the addition of nanoparticles was found to improve the burning qualities of the fuel. From the outcomes, a significant increment in BTE and a considerable decrease in the NO_x and unburnt hydrocarbon (UBHC) substances of all loads were seen when contrasted with unadulterated diesel fuel. This could be because of the improved burning qualities of nanoparticles and improved air blending proportion. Vedagiri et al. (2020) researched the influence of different chamber geometry calculations on the performance and emissions features by adding ZnO nanoparticles to grapeseed oil methyl ester (GOME) BD as a fuel added substance. With the addition of ZnO nanoparticles, the BTE was discovered to increase by a margin of 4 % compared to that of neat GOME. Tamilvanan et al. (2019) explored the impact of adding 30 ppm Cu to *Calophylluminophyllum* seed oil (CISO) BD in a single-cylinder diesel engine maintained at constant speed but varying loading conditions. From the analysis of results, it was concluded that higher BTE vales were recorded from the BD doped Cu nanoparticles when contrasted with undoped CISO BD. Nevertheless, the BTE unveiled was lower than for FD fuels. The decrease in BTE in BD can be attributed to the lower CV of burning The researchers suggested that addition of Cu nanoparticles in BD fuel mixes improved its performance and emissions features, hence, nanoparticles are a viable solution

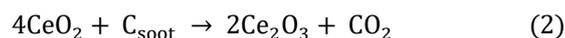
to BD fuel property enhancement and this will help accelerate its adoption as an alternative fuel for CI engines. Nanthagopal et al. (2017) performed some engine tests utilizing TiO₂ and ZnO nanoparticles at dosing levels of 50 ppm and 100 ppm added to BD with the aid of an ultrasonicator. Performance evaluation showed that BTE was higher with BD doped with TiO₂ and ZnO nanoparticles when contrasted with neat BD fuel. An increment in BTE of 17 % was recorded with 100 ppm of TiO₂ nanoparticles when contrasted with that of neat BD. Comparable results were reported by Vigneswaran et al. (2021) who investigated the impact of TiO₂ on the performance of Mimusopselengi methyl ester (MEME) BD. This phenomenon has been attributed to the fact that TiO₂ has the capability to donate oxygen atoms which are used to increase oxidation of fuel resulting in better combustion and ultimately resulting in higher BTE values. Selvaganapthy et al. (2013) explored the impact of different nanoparticles with diesel on a diesel engine and found that BTE for the nano molecule fuel mix was higher when contrasted with that of neat FD fuel. Prajwal et al (2013) investigated a diesel motor fuelled with MWCNTs mixed BD blends, discovered that the BTE of the MWCNTs-HOME blended fuels was better contrasted with neat BD fuels. They attributed this to the better ignition qualities of MWCNTs. They reported BSFC increased with increment in the addition of MWCNTs. A similar pattern was reported Banapurmath et al. (2014), who noted that the nano-sized particles have a high surface area and receptive surfaces that add to higher thermal conductivity which could explain the above pattern.

5. EFFECTS OF NANOPARTICLES ON EMISSION CHARACTERISTICS.

BD mainly emits particulate matter nitrogen oxide, carbon monoxide (CO) and unburnt hydrocarbons emissions. A brief review has been made about these pollutants emitted from BD doped with nanoparticles is presented.

5.1. Effects of nanoparticles on PM

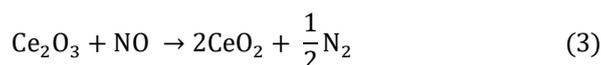
Bagri and Chaube (2013) conducted experimental work on the effects of SCD5 additive on performance and emission behaviour of a single cylinder two-stroke direct engine. The additive was added at varying proportions to the neat FD fuel. The outcome of this investigation revealed that the addition of additive resulted in a reduction of 35% respectively with nanoparticle addition compared to neat FD fuel. Karthikeyan et al. (2014) studied the effects of the addition of zinc oxide nanoparticles in palm oil BD and the results indicated 7% decrease with the addition of nanoparticles compared to neat Bd fuel. Jayanthi and Rao (2016) experimentally investigated the effects of copper oxide Nano additives on linseed BD using proportions of 50ppm 100ppm and 150 ppm with the assistance of an ultrasonic mixer. The results from this analysis showed no changes to soot with the addition of nanoparticles. According to Shaafi and Velraj (2015), CeO₂ transforms soot to carbon dioxide using Equation 2.



5.2. Effects of nanoparticles on NO_x emissions

The main factor that impacts NO_x discharges in ICEs is the in-cylinder temperatures. Moreover, the level of oxygen content in fuel likewise impacts the development of NO_x outflows. Specifically, a high post-burning temperature promotes increments NO_x discharge rapidly. Several research works have been done on the effects of nano additives on NO_x emissions. Prabu (2018) carried out an experimental investigation on a single cylinder 4-stroke DI engine fueled with *Jatropha* derived BD mixed with Al₂O₃ and CeO₂ nano particles. The research claims a reduction in NO_x emissions by 30% compared to B100. The author claims that the reduction in NO_x emissions was caused by the reduction in engine delay which accelerated the early combustion, and lowered heat release. Hybridized nano additive produced the most

improvement in engine performance and reduced emissions compared to B100. This pattern might be credited to the oxygen content of BD (since it contains 13% O₂) which expands the concentration of oxygen accessible for oxidation of fuel and hence the development in the response temperature prompting an expansion in w NO_x gas emissions (Zel-dovich principle). These have also been echoed Radwan et al. (2007) and Shehata and Razek (2011). The addition of nanoparticles to BD prompts a reduction in NO_x emanations compared to the neat BD fuels. This phenomenon is credited to the higher surface to volume ratio and thermal conductivity of nanoparticles which speeds up the burning process (heterogeneous ignition) with reduced hydrocarbon thermal reduction. This might be the underlying reason behind NO_x reduction with nanoparticle addition. The authors also reported that NO_x emissions were decreased by a maximum of 30% with the addition of 80 ppm nanoparticle in comparison to that of neat BD fuels. This was necessitated by the reaction of NO with Ce₂O₃ (+3) to form CeO₂ (+4) and nitrogen N₂ as shown in Equation 3.



Basha and Anand (2011) performed the analysis of the impacts of nano additive mixed water diesel emulsion fuel on the emission behavior of neat FD fuels. The scientists performed this analysis in three stages. Initially, emission characteristics of neat diesel were evaluated. Secondly, water emulsion diesel emission parameters were measured and finally, emission parameters resulting from the combined impact of aluminum nanoparticles and water emulsion were evaluated. Analysis of results showed that the quantity of NO_x emissions at full load was 891 ppm for D2S15W100A (83% diesel+2% surfactant+15% water+100 ppm of alumina), though it was 1009 ppm and 1340 ppm for D2S15W (83% diesel+2% surfactant+15% water) and neat FD respectively. Sadhik Basha and Anand (2012) further assessed the impact of nanoparticle added substances in the water diesel emulsion fuel on the emission attributes of a diesel engine at various loading conditions at a constant speed. The results of NO_x and smoke outflows were significantly diminished for the nanoparticles mixed water–diesel emulsion fuels, contrasted with those of perfect diesel activity at all loads. The extent of NO_x emissions recorded was 978ppm, 1012 ppm, 1046 ppm and 1340 ppm for D2S5W50Al (93% diesel+2% surfactant+5% water+50 ppm of alumina), D2S5W25Al (93% diesel+2% surfactant+5% water+25 ppm of alumina), D2S5W (93% diesel+2% surfactant+5% water) and neat FD respectively at full load. Venu and Madhavan (2017) performed an evaluation of Zr nanoparticles on the *Jatropha* BD on performance and emission features of a CI engine. From the results, the analysis it was noted that the addition of Zr resulted in slight increases in NO_x emissions.

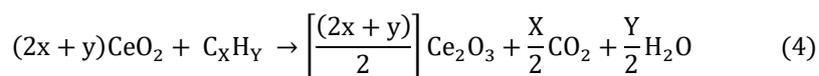
5.3. Effects of Nanoparticles on CO Emissions

The emissions of CO depend on the fuel's properties. The main variable influencing CO emissions generation is the absence of oxygen and a low burning temperature because these lead to incomplete fuel combustion. CO is a result of lost energy during the combustion process. Prabakaran and Udhoji (2016) conducted a study on a single cylinder 4 stroke DI engine at a constant speed of 1500 rpm. Eighteen diesel-BD-ethanol fuel mixtures were prepared and tested for solubility. Thereafter, one was chosen for performance testing with and without the addition of zinc oxide (ZnO) nanoparticles. Palm oil methyl ester (POME) derived BD was used in this experiment. The authors claim a massive reduction between CO emissions ranging between 62% and 92% with POME-ethanol and POME-ethanol plus nano additives respectively. A study by Kannan et al. (2011) on a four-stroke engine powered from used cooking oil BD mixed with ferric chloride (FeCl₃) resulted in CO emissions reduction and better engine performance. The investigation was carried out in a two-step process in which the fuel was initially prepared then mixed with the nano additive in dosages of 5 micro mol/l of fuel. This

research reported a significant reduction in CO emissions. Ganesh and Gowrishankar (2011) also experimented with a 4-stroke engine at a constant speed and powered from *Jatropha* BD fuel mixed with magnalium (Mg-Al) and cobalt oxide (CO₃O₄) nano additives. Their experimental results showed that the addition of cobalt oxide showed CO reduction both at part and full load compared to neat B100 fuel. The authors attributed the reduction to the addition of cobalt oxide which acted as an oxygen buffer enhancing complete combustion and emissions reduction. Furthermore, Chandrasekaran et al.(2016) investigated the effect of the addition of copper oxide nano additives on mahua BD-diesel blends. Initial experiments were carried out using neat BD blends of B20, B40, B60 and B80 and B100 to ascertain their performance and emissions characteristics. The authors reported that B20 yielded the best results. The resulting B20 was mixed with copper oxide nanoparticles and tests were performed and compared with base fuel. Significant CO emissions reduction was reported by the authors. Improved surface area to volume ratio, increased fuel-air mixing rates were echoed as the reasons behind the considerable performance and emissions characteristics from this investigation. Santhanamuthu et al. (2014) studied the iron oxide D'Silva et al. (2015) carried an investigation to determine the properties, performance and emission of diesel with titanium oxide nano additives. Reported results there was a 25% reduction in CO with nanoparticle addition when compared with neat diesel fuel.

5.4. Effects of Nanoparticles on UBHC Emissions

Sajith et al. (2010) carried out a trial examination on performance and emission qualities of single-chamber constant speed diesel engine fuelled with CeO₂ nanoparticles (10 nm to 20 nm) doped *Jatropha* BD with dosing level of CeO₂ fluctuating from 40 ppm to 80 ppm. The authors argued that the addition of nano additives suppresses the deposition of carbon on an engine's cylinder walls which promotes improved fuel consumption. CeO₂ nano particle possesses the capability to change its valency from CeO₂ (+4) to Ce₂O₃ (+3), through a low energy requirement reaction process. This allows the nanoparticle to donate an oxygen atom which is used to oxidize unburnt hydrocarbons to carbon and water as shown in Equation 4.



Janakiraman et al. (2020) carried out a comparative study on impacts on performance and emission characteristics of CeO₂, zirconium oxide (ZrO₂) and titanium oxide (TiO₂) with B20 blend (20% *Garcinia gummi-gutta* BD+80% diesel) in Kirloskar make, TAF-1 single-cylinder engine as nanoparticle added substances. The nano additives were prepared in dosages of 25 ppm and mixed with BD blend with the aid of an ultrasonicator. Results analysis showed that the HC of TiO₂, CeO₂, and ZrO₂ mixed with B20 (20% *Garcinia gummi-gutta* BD + 80% diesel) were lower than the neat B20 by 6.39%, 3.99%, and 5.64%, individually, Hosseini et al. (2018) investigated the performance and emission of BD-diesel blends with graphene oxide nano additives. A study by Prabu (2018) showed UBHC reduction by a margin of 44%. The research claims a reduction in NO_x emissions by 30% compared to B100. Prabu (2018) claimed that the reduction in NO_x emissions was caused by a reduction in engine delay which accelerated the early combustion, and lowered heat release. Hybridized nano additive produced the most improvement in engine performance and reduced emissions compared to B100.

6. CONCLUSIONS AND FURTHER STUDIES

This review underlines the importance of adding nano metallic particles to BD and or BD blends to improve fuel properties, performance and reduce emissions. Physio-chemical properties such as calorific value, cetane number,

viscosity, density, flashpoint and cold flow properties are improved with the addition of nano additives. Some researchers reported an increase in viscosity which will create a problem as it affects spray atomization of the fuel. Reduction in brake-specific fuel consumption is noted and this is caused by improved calorific values due to nano additive addition and complete combustion since nano additives act as catalysts increasing reaction efficiency. BTE is increased in most cases with the addition of nanoparticles. Significant reduction in CO, UBHC, NO_x, smoke opacity and soot are reported by many authors. Aluminum metal, zinc oxide, Al₂O₃ and CeO₂ seem to yield better results with BDs from various feedstocks. The available literature also reveals that some analysts detailed that NO_x gas discharge was higher with the addition of nanoparticles to neat BD fuels. The inconsistency happened because of the various kinds of BD, sorts of nanoparticles and their size, and likewise their volume of blending. Molecule size is one of the significant key factors that influence ignition quality. Further examination is accordingly expected to address this disparity by utilizing localized BD feedstocks oils and various kinds of nanoparticles and their size by shifting the dosing level of nanoparticles. The review also highlights the lack of studies pertaining to hybridized nanoparticles for use as fuel additives; more studies will improve results. Key to improved properties, performance and emission characteristics are a selection of appropriate nano metallic additive for given BD feedstock and optimal dosage of nanoparticles. The authors conclude that the addition of fuel additives offers a good option for engine performance and emissions reduction in engines powered from BD and or BD-diesel blends.

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CHAPTER 3: OPTIMIZATION OF PRODUCTION PROCESS, CHARACTERIZATION AND ENGINE TESTING OF WASTE COOKING OIL BIODIESEL

This chapter provides a report on an experimental work performed to optimize production parameters and evaluate the fuel properties of Waste Cooking Oil Biodiesel. The produced biodiesel was tested in a two-cylinder engine to evaluate its performance and emissions features. The outcome of the work was published in the International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)

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OPTIMIZATION OF PRODUCTION PROCESS, CHARACTERIZATION AND ENGINE TESTING OF WASTE COOKING OIL BIODIESEL

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ABSTRACT

This paper analyzes the suitability of mixed waste cooking oil (WCO) biodiesel as a viable fuel for diesel engines. WCO feedstock was purchased from a Enfields Chemicals a waste cooking oil buying firm based in Durban, boiled and cleaned to remove food particles and water. The oil was then evaluated for free fatty acid (FFA) composition and acid value and other physiochemical properties. The WCO acid value was found to be higher than the stipulated value for a single-step process hence a two-step production method of esterification and transesterification was instituted. Esterification was performed using sulphuric acid and methanol at a molar ratio of 9:1, 1 wt% H₂SO₄, 60 °C for 90 minutes until it became 0.688 mg of KOH down from an initial value 8.67 mg of KOH. Thereafter homogenous alkali transesterification was performed with a methanol molar ratio of 6:1, 1 wt% NaOH and temperature 60 °C for 60 minutes. Four factors selected for optimization were: molar ratio, catalysts concentration, reaction time and reaction temperature. The process parameters were optimized using a combination of Taguchi method using the MINI TAB-16 programming tool and ANOVA test. A total of 27 experiments were performed by varying the process parameters and manipulation of the S/N ratio. The best conditions found were molar ratio of 7:1, temperature of 65°C, catalyst concentration of 1.5wt% and reaction time of 80 minutes. In terms of influence on yield the ranking was: reaction temperature, catalysts concentration, molar ratio and reaction time. The optimal parameters resulted in an increase in yield from 93% to 96 %. The biodiesel was property evaluated and compared with fossil diesel (FD) using ASTM D6751 standards. Four fuel samples namely, FD fuel, WCO100, WCO20 and WCO40 were formulated and tested in a single cylinder Kirloskar engine for performance and emissions behavior. The results showed a maximum reduction of BTE of 17.8 % with WCO100 and a BSFC increase of 23.7 % compared with FD fuel. Emission parameters revealed a reduction in CO of 62.5 %, UBHC of 27.2 % and smoke opacity of 34.45 %. However, an increase in CO₂ of 28.43 % and NO_x of 27.2 % were determined when compared with FD fuel. The researchers concluded that WCO biodiesel can be utilized as an alternative fuel for diesel engines as its properties conform to ASTM D6751 and EN14214 and its combustion and emission behavior showed similar trends to those of FD fuel.

KEYWORDS: Waste Cooking Oil Biodiesel, Taguchi Method, process parameters, engine performance, exhaust emissions.

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NOMENCLATURE AND ABBREVIATIONS

ANOVA	Analysis of Variance	CV	Calorific value
ASTM	American Society for Testing and Materials	DOE	Design of Experiments
BD	Biodiesel	EGT	Exhaust Gas Temperature
BD20	Biodiesel blend of 80 % Fossil diesel and 20 % biodiesel	EN	European Committee for Standardization
BD30	Biodiesel blend of 70 % Fossil diesel and 30 % biodiesel	GHG	Green House Gas
BD50	Biodiesel blend of 50 % Fossil diesel and 50 % biodiesel	GC-MS	Gas Chromatography Mass Spectrometry
BD80	Biodiesel blend of 20 % Fossil diesel and 80 % biodiesel	S/N	Signal to Noise Ratio
BP	Brake Power	SNR	Signal to Noise Ratio
BSFC	Brake Specific Fuel Consumption	KW	Kilowatt
BTE	Brake Thermal Efficiency	NaOH	Sodium Hydroxide
FD	Fossil Diesel	NO _x	Nitrogen oxide
FFA	Free fatty acid	WCO20	Waste Cooking Oil Biodiesel blend of 80 % Fossil diesel and 20 % biodiesel
CN	Cetane Number	WCO40	Waste Cooking Oil Biodiesel blend of 60 % Fossil diesel and 40 % biodiesel
CO	Carbon Monoxide	WCO100	100% Waste Cooking Oil Biodiesel fuel
CO ₂	Carbon Dioxide	WHO	World Health Organization
		UBHC	Unburnt hydrocarbon

INTRODUCTION

There is a global transition to alternative fuels for CI engines due to the evident depletion of fossil derived energy resources coupled with harmful environmental effects arising from production and usage of these fossil-based fuels (Naylor & Higgins, 2018). Fossil diesel (FD) fuel has enjoyed huge market share powering heavy trucks, locomotives, agricultural equipment and sea transport. FD fuel engines have been the preferred choice because they are reliable, provide good fuel economy and high efficiency (Pirouzfard et al., 2008). However, diesel engines produce hazardous emissions such as nitrogen oxides (NO_x), unburnt hydrocarbons (UBHC), carbon monoxide (CO), carbon dioxide (CO₂), soot and sulphur and these have detrimental environmental and human health effects. Research has shown that amongst the available alternative energy sources to mitigate greenhouse gas emissions, bioenergy is the only solution of which biofuels are the leading candidates for the transport sector (Pirouzfard et al. 2009; Pirouzfard et al. 2012). Biofuels development will lead to a

carbon neutral environment, and will aid in development of a waste to resources circular economy and increased energy security (Ahmad et al., 2011). Biodiesel is gaining attention as a viable replacement for FD due its non-toxic, biodegradable, renewable nature, and its generation of lower emissions. This renewable fuel can be derived from a variety of feed stocks which can be vegetable oil, edible or non-edible, animal fats or algae and waste cooking oil (WCO) (Atabani et al., 2012; Kafuku&Mbarawa, 2010; Rashid et al., 2008). Commercialization of biodiesel (BD) production will depend on its financial viability and technical advancement of the process. This is mainly dependent on feedstock selection as this constitutes 70 % of the total production cost (Firestone, 1989). Despite all that, there was a 700 % increase in BD production in the period 2005 to 2015 and this is expected to be 35% higher than that by 2025 (Neeft et al. 1996). Usage of edible vegetable oils for BD production has also faced some negative publicity due to the food vs fuel controversy. This has necessitated the switch to non-edible feedstocks. Nonedible feedstocks such as Karanja, Jatropha, neem, cotton seed and micro algae can be farmed on marginal lands and do not compete with food chain supplies for resources. This has also led to the introduction of WCO as a viable feedstock for BD production (Alarcón et al., 2017; López et al., 2015). According to Rodríguez et al. (2017), 15 million tons of WCO are being generated per year globally creating disposal challenges for many municipalities (Kalam et al., 2011). A study undertaken by the WHO revealed that every 1 liter of WCO oil disposed of is bound to contaminate 1000 liters of water (Martinez et al. 2013). In line with that a lot of WCO is illicitly being unloaded into waterways and landfills causing environmental contamination and higher energy consumption in water works (Martinez et al. 2013). Utilization of WCO to deliver BD will offer economic benefits since it will reap substantial benefits from reduction in water contamination, employment creation, improving energy security and boost in localized business growth. Usage of WCO as a BD feedstock is therefore a novel solution aimed at tackling disposal challenges by moving towards a circular economy creating employment and reduction in GHG emissions and so make the world more habitable (Yan et al., 2014). WCO contains high free fatty acid content (FFA) due to its exposure to high temperatures of cooking (Chhetri et al., 2008). High FFA will lower the WCO to BD conversion rate and yield. It also has high water content which can cause hydrolysis issues (Carlini et al., 2014). To circumvent all these challenges the oil is first preheated and acid esterified to remove water and lower the FFA content before transesterification is initialized.

Biodiesel is extracted from various feedstock oils using the transesterification process. Transesterification is a reaction through which a triglyceride which is present in vegetable oil and animal fats reacts with an alcohol usually methanol or ethanol in the presence of a catalyst (acid, alkali or enzyme) to form an ester and glycerol. Tyson and McCormick (2006) suggest that utilizing methanol results in less viscous methyl ester compared to ethanol. Knothe and Steidley (2005) report that methyl esters are destined to yield better engine performance in comparison to ethyl esters. Some researchers have argued that higher and more branched alcohols result in better engine performance (Huber et al., 2006). Reports of increased injector gumming and clogging has been reported with higher, more branched and expensive alcohols (Narasimharao et al., 2007). This process can be base, or acid catalyzed. The base catalyzed process is quick and consumes less alcohol. Transesterification is influenced mainly by molar ratio, type of catalyst and its concentration, reaction time and reaction temperature. The main objective of transesterification is to reduce the viscosity of the oil which has detrimental effects on engine durability. BD feedstocks differ from one country to another hence localized feedstock characterization and development is vital. It is advisable to produce the feedstock locally to make the BD supply chain cost effective. A study by Paper and Bilgin (2015) aimed at producing the lowest kinematic viscosity BD found that an optimum alcohol/oil molar ratio ranging from 6:1 to 15:1, catalyst concentration ranging from 0.5 % to 1.75 %, reaction temperature ranging from 60 °C to 90°C were determined to be the optimal conditions. Other researchers have suggested the optimal

approximate proportions of reactants and products of transesterification process to be 100 kg of oil plus 10 kgs of methanol or ethanol equals 100 kgs of BD plus 10 kgs of glycerol (Datta & Mandal, 2016). The fatty acid content is the key factor in determining the number of steps to be carried out for transesterification. The first step is acid catalyzed and is aimed at reducing the fatty acid level to within the required level to undertake the alkali process. Cooking results in conversion of vegetable oil make-up and its properties. High exposure to high temperatures leads to oxidation and hydrolysis of the oil (Datta & Mandal, 2016) This increases the viscosity of the oil as a result of polymeric and dimeric acid formation hence the high FFA from cooking must undergo pretreatment to lower it to below 1 wt%. This helps to inhibit the saponification process. After transesterification the BD is washed, and the byproduct glycerol separated accordingly. Parameters of transesterification have been arrived at using the trial-and-error method but few studies have tried to optimize these to suite their feedstock makeup. In order to be sure about the optimal conditions required for the WCO available in this study, the Taguchi method was utilized since it has the capability to lower costs. The parameters for transesterification are interrelated since molar ratio is also dependent on catalyst concentration and type. The concentration is also influenced by difference in molar ratio as well as feedstock make up of catalyst to be used. Optimal conditions are vital for maximum yield which will subsequently result in lowering the cost of BD production. A study by Sahoo and Das (229) extracted BD from non-edible feedstocks such as Jatropha, Polanga and Karanja. In this evaluation method influence of process was verified. It was concluded that the influential process for transesterification of BD were type of catalyst, molecular ratio of alcohol, reaction time and temperature.

Masjuki (2014) attempted to optimize the process of high FFA WCOBD production. The researcher developed a model for optimizing pretreatment with ferric chloride. The researcher managed to optimize process parameters by utilizing surface response methodology modelling. From the model result analysis, it was concluded that the optimal conditions for high FFA content were molar ratio of 7:1, reaction time of 3 hours and temperatures of 60 °C. Performing BD under the optimal conditions resulted in a yield of 81 %.

Rodriquez et al. (2017) extracted BD from Polanga oil. Initial evaluation of FFA content unveiled that the oil had a high FFA composition of 59.30 mg of KOH. The researchers had to perform degumming esterification, and then transesterification to better the BD quality. The FFA was reduced to 0.34 mg of KOH before initializing transesterification. Molar ratio of 10:1 methanol to oil ratio, 1 wt% of NaOH temperature of 50 °C for 2 hours were the process parameters utilized in the process. The BD produced conformed to ASTM D6571 and EN14214 standards. The BD produced was blended with FD at 10 % Bd to 0 90 BD. Performance result analysis revealed a 2.3 % brake thermal efficiency increment and 3.06 % reduction in brake specific fuel consumption. This was key in suggesting that the Polanga oil was aviable alternative fuel forCi engines.

Chumuang and Punsuvon(2017) produced BD from an alkali catalyzed transesterification of WCOBD process with the aid of tetrahedron as a cosolvent. Preforming a 5 level 4 factor coupled to surface response technology the researchers were able to evaluate the optimal parameters for BD production. The researchers managed to develop a prediction scheme for BD yield from given feedstock oil make up. According to this report amolar ratio of 11.6:1, 100.14 min, 2.85 wt% of catalyst and 8.65 % v/v of tetrahedron were optimal values for maximum yield. A yield of 99.43 % was determined under these optimal process parameters.

Chakraborty et al. (2009) performed an extraction of Termilia derived BD. Fatty acid composition, kinematic viscosity and energy content of 28.7 linoleic, 32.9 palmitic and 31.4 oleic acid and 25.5 cst.3740 MJ/kg according to

EN14214 Standard. Despite most of properties conforming to set standards, flash point was noted to be 90 °C which was less than required minimum value of 120 °C.

Xuan and Leung (2011) extracted BD using transesterification from camelia seed oil. Analysis of process parameters revealed that reaction time, catalyst concentration, Molar ratio of alcohol to oil and reaction temperature were influential in BD production quality. The optimal process parameters which yielded the highest yield were methanol ratio of 8:1, 70 min reaction time, 1 wt% catalyst concentration and temperature of 51°C. The BD produced conformed to ASTM D67571 AND EN14214 international norms.

The above literature survey has indicated that process conditions vary, therefore ideal parameters that suite each type of feed stock accessible locally becomes a priority. Hence this work is aimed to assess the suitability of WCO as a viable of feedstock for BD creation. The production parameters were optimized utilizing the Taguchi technique. This was done in MINITAB-16 programming that could perform experimental design and analysis of several factors. The BD created was characterized and properties evaluated in contrast to neat diesel and thereafter tested in an engine. Motor preliminaries were done to check the presentation and discharge conduct of WCO from confined feedstock. Fuel mixes of WCO20, WCO40 and WCO100 were tested and results contrasted with those of Fossil diesel. Performance parameters such as brake thermal efficiency, brake specific fuel consumption and exhaust gas temperature were measured and or evaluated. Exhaust emission parameters evaluated were NO_x, CO, CO₂, UBHC, and smoke opacity compared to FD.

2. RESEARCH METHODS AND MATERIALS

2.1. Characterization of Waste Cooking Oil

WCO was purchased from Enfield, a company that deals with collection of industrial and domestic used oils. The oil was heated to 100 °C to get rid of food components as well as all unwanted residues. Thereafter the WCO was prepared and evaluated for fatty acid composition by using gas chromatography coupled to a mass spectrometer (GC/MS), Shimadzu model QP 2010 GC-MS, capillary column Durabond, stationary phase DB-5HT (280 (W) X 280 (H) X175 (D)). The fatty acid composition was evaluated based on ASTM standards. The results are tabulated in Table 1. The fatty acid composition evaluation was necessary to gain an understanding of the makeup of the feedstock and so help to explain the characteristics of the BD

Prior to the transesterification process the WCO was also subjected to physicochemical property valuation in relation to ASTM D6751 standards. The properties evaluated were density, kinematic viscosity, acid value, saponification, and water content, The results are shown in Table 1. The properties were assessed in three trials which were then averaged to gain mean value and results.

Table 1: Fatty Acid Composition of the oil and Physicochemical Properties of Waste Cooking Oil

Property	C- Chain	Measured WC Oil property	Waste cooking oil as reported by [32]
Myristic	C14:0	0.11	0.41
Palmitic	C16:0	5.06	8.22
Palmitoleic	C16:1	0.44	0.89
Stearic	C18:0	8.22	5.61
Oleic	C18:1	54.22	48.83
Linoleic	C18:2	19.88	10.94
Linolenic	C18:3	5.72	2.68
Arachidic	C20:0	0.61	0.56
Eicosenoic	C20:1	1.31	0.97
Lignoceric	C24:0	0.08	
Others		4.36	20.89
Density (kg/m ³)		922	
Acid Value (mg of KOH)		8.67	
kinematic Viscosity (cst)		34.67	
Iodine Value g I ₂ /100g		88	
Saponification value mg of KOH		212.1	

FFA Evaluation and Pretreatment Waste Cooking Oil

High FFA of above 2 % require a two-step production process. Titration method was utilized to evaluate the acid value of the oil so as guide the researcher to perform single or two step transesterification process. The material used in titration method were 0.1% of KOH solution, phenolphthalein, and isopropyl alcohol sulphuric acid (H₂SO₄), the process was performed according to ASTM D974 standard. all the chemicals were obtained from Sigma Aldrich (South Africa). Phenolphthalein is hereby utilized to locate the reaction end point. A small beaker is used to make clear water by mixing it with isopropyl alcohol then small drops of are added until the mixture reaches endpoint by staying at constant pink color for about 12 seconds.

The oil was evaluated Acid Number of the oil was calculated using the following **Eq.1** below.

$$\text{Acid Value} = \frac{56.1 \times 0.1 \text{ N} \times 15.46 \text{ mL}}{10 \text{ g}} \text{ Eq} \quad (1)$$

Where: 56.1 was the molecular weight of KOH used in the titration (g/mol), 15.46 was volume of KOH consumed during titration (ml). 0.1 N standard solution represents the concentration of KOH used in the titration, and 10g was the mass of oil sample used in the analysis.

The acid number was 8.67 mg of KOH which corresponds to 4.33 % FFA (Chhetri 2008). The acid was evaluated by the following formula, $\frac{\text{Acid Value}}{2}$ and was found to be higher than 1 % FFA so warranted alkali transesterification hence pretreatment was performed to reduce FFA %. WCO was placed in a flask which was put on hot plate maintained at 60 °C. Methanol molar ratio (9:1) and H₂SO₄ at 1 wt% were separately mixed in a beaker and stirred for 4 minutes. The methanol acid mixture was then added to the flask (1 liter) containing WCO. The flask contents were then left for 75 minutes before transesterification was begun.

Transesterification

The product of the esterification process was FFA evaluated using titration to confirm the content percentage and was found to be 0.688 mg of KOH. This was in the within the range required to initialize transesterification. The process

was performed at molar ratio 6:1, 1 wt% at 65 °C for 65 minutes and yield was calculated using Eq. 2 below. And the process is depicted in Figure 1 below.

$$\text{Yield \%} = \frac{\text{Mass}_{\text{ester}}}{\text{Mass}_{\text{oil}}} \% \text{ Eq (2)}$$

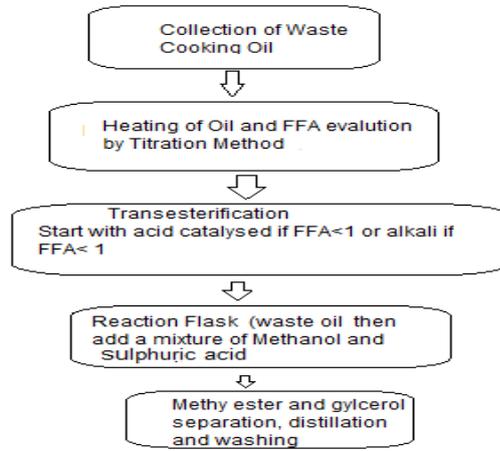


Figure 1: Biodiesel Production Process

Figures 2 and Figure 3 show the stages that the WCO underwent before biodiesel was formed.

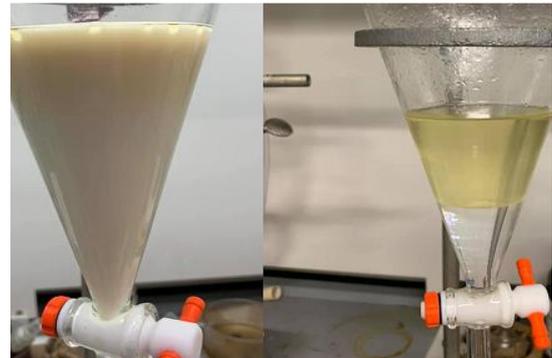


Figure 2: Biodiesel Production Process Initial Stages **Figure 3: Biodiesel Production Process: Final Stages**

2.4. Waste Cooking Biodiesel Process Parameter Optimisation

Most system processes rely upon some controllable variables and in line with that, the BD production process depends on alcohol to oil (molar ratio), type and concentration of catalyst, reaction temperature and reaction time. To understand the impact of these control factors on production of BD several trials must be performed. The number of these can be reduced by utilising the Taguchi design of experimental methods since it is capable of generating reliable data sets for analysis. Design of Experiments (DOE) offer efficient examination of the control factors that impact the reactions. Taguchi analysis was developed by a Japanese quality administrator Dr Genichi Taguchi. This tool is utilised for optimising manufacturing processes. Each exploratory condition is called a "Run" and the reaction estimation a perception. The whole arrangement of runs is the "Design". To limit time and cost, we can utilize plans that prohibit a portion of the factor level mixes. Factorial plans in which at least one level mixes are rejected are called partial factorial plans. These are valuable in factor screening since they diminish the quantity of trials to a reasonable size. The base number of examinations required is given by the Eq.3

$$N = [(L-1) * P] + 1 \quad \text{Eq} \quad (3)$$

Where N= least number of tests, L =number of levels, P = number of variables

Basic strategies in DOE are done by trial and error but the Taguchi method is a statistical design approach used to lower experimental attempts thereby reducing the cost and duration of the evaluation process. The chart Figure 4 shows the design flow chart for the Taguchi method. In this method a variable denoted signal to noise ratio (S/N) is used to denote the influence of noise contribution on performance. The higher the S/N ratio the better the quality of yield value(Gadhave&Ragit, 2020).

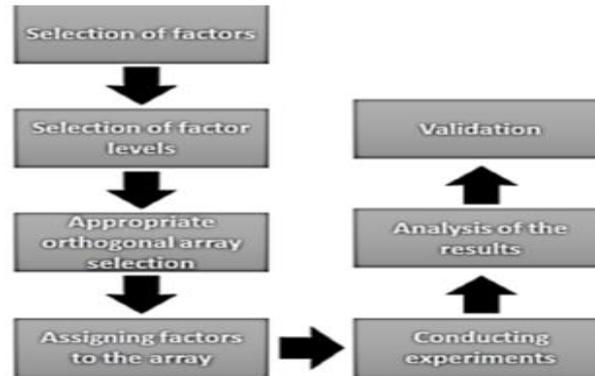


Figure 4: Taguchi Process Parameter Optimisation Method

S/N measures the variety of reaction comparative with ostensible or target esteem. S/R is the estimation used to portray what amount of wanted sound is available in a sound chronicle, rather than undesirable sound (noise). Two kinds of S/Nutilized in the current work were: ‘smaller the better’, and ‘bigger the better’. At the point when the reaction is to be boosted, ‘smaller the better’ S/R was suitable and was registered utilizing Eq.4, while ‘bigger the better’ SNR was well-suited for the limiting reaction, applying Eq. 5. ‘Bigger the better’ was selected and used for optimisation process parameters in this research.

The Signal to Noise ratios (S/N) (Gadhave&Ragit, 2020):

For system responses Smaller the better:

$$S/N = -10 \text{ Log}_{10} [\text{mean of sum of squares of measured data}] \quad \text{Eq} (4)$$

This type of S/N ratio is chosen for undesirable system outputs like emissions, fuel consumption, etc. whose ideal value is zero.

For system responses bigger the better:

$$S/N = -10 \text{ Log}_{10} [\text{mean of sum squares of reciprocal of measured data}] \quad \text{Eq} (5)$$

2.5. Selection of Process Parameters

Factors that were selected for this optimisation process were methanol oil ratio (molar ratio), KOH catalyst concentration, reaction time and reaction temperature as these have influence on yield of BD produced. In the Taguchi method a performance test was undertaken by varying all the factors simultaneously and this minimised the number of tests to be performed. The variation in the selected factors are shown in orthogonal array L9 shown in Table 2.

Table 2: Orthogonal Array L9 for the Assigned Factors and Their Levels

Run no.	Molar Ratio	Concentration (wt%)	Reaction Time (min)	Reaction temperature (oC)	Average Yield (%)	S/N ratio
1	6:1	0.5	60	65	88.93	38.98
2	6:1	1.0	70	75	91.21	39.2
3	6:1	1.5	80	85	88.64	38.65
4	7:1	1.0	70	85	85.62	39.43
5	7:1	1.5	80	65	93.63	39.29
6	7:1	0.5	60	75	92.12	38.81
7	8:1	1.5	80	75	87.22	38.95
8	8:1	0.5	60	85	88.59	39.38
9	8:1	1.0	70	65	93.14	39.07

Engine Test Arrangement

The experimental set up included a single cylinder water cooled direct Kirloskar engine operated at constant speed of 1500 rpm. The engine was coupled to an eddy current dynamometer that was utilized for engine loading purposes. Engine details are shown In Table 3 below. The set comprised all essential instruments for injection pressure and angle evaluation. All these were linked to a PC for analysis. Instrumentation was also provided for measuring air flow, temperature and fuel flow rate. The whole system set is illustrated in Figure 6. Injection pressure and angle crank instruments were linked to data acquisition for analysis. The load cell was used to load, monitor and control the progress of the tests. Volumetric fuel utilization and gas fumes emanation, for example, CO, HC, and NO_x were estimated. From the underlying estimation, brake thermal efficiency (BTE), brake explicit fuel consumption (BSFC), brake power (BP) for various mixes and distinctive injection pressure were determined and recorded. An AVL 444 di-gas analyzer was utilized for gas measurements for NO_x, UBHC, CO₂ and CO and an AVL 437 C smoke meter was used for smoke opacity measurement. The engine was initially fueled by FD fuel during warm up for about 15 minutes. The results of the analyzed gas emission measured against load setting are discussed under the Results and Discussion section.

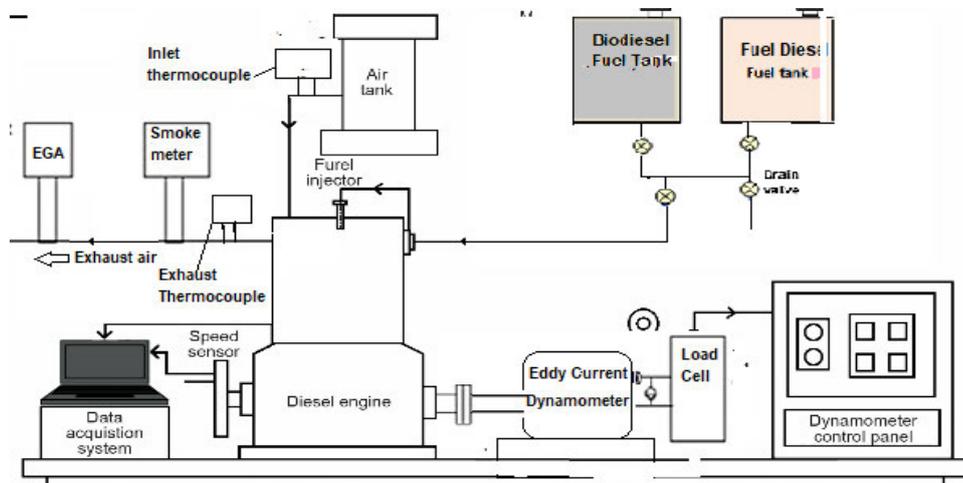


Figure 6: Engine Test Configuration

Table 3: Engine Specifications used in the Experiment

Parameter	Position value
Engine Model	Kirtoskar
Type	Two cylinder, horizontal 4 -stroke, DI
Cooling Medium	Water cooled
Revolutions per Minute	1300 rpm (constant)
Rated Brake Power	4.4 kW (7Hp)
Cylinder Bore	87.5 mm
Piston Stroke	110 mm
Compression Ratio	17.5 (variable)
Injection Timing	23° BTDC
Injection pressure	220 bars
Loading system	Eddy Current Dynamometer

Table 4: Uncertainties Estimations of Measured and Calculated Parameters

Quantity		Range	Accuracy	Uncertainty
AVL gas analyzer	NO _x	0–5000 ppm	±10 ppm	±0.2
	HC	0–20000 ppm	±1 ppm	±0.3
	CO	0–10 vol %	±0.01%	±0.22
	CO ₂	0–20 vol %	±0.03%	±0.21
AVL smoke meter		0%–100%	±0.2%	±0.22
Thermocouple		0 – 1000 °C	±1 °C	±0.15
Dynamometer		0–250 V, 0–25 A	±1 V, ±0.5 A	±.05,±0.1
In-cylinder pressure		0–220 bars	±0.2 bar	±0.1
Crank Angle encoder			±1	±0.25
Exhasut gas temprature			±2 °C	±0.1
Brake Power				±0.75
Brake specific fuel consumption				±0.80

The error of the experimental procedure was evaluated as follows and the overall uncertainty was 1.26 %. The uncertainties of measured and calculated parameters are shown in Table 4.

$$\text{Overall uncertainty} = \sqrt{\text{uncertainty of } (N)^2 + (BTE)^2 + (BSFC)^2 + (CO_2)^2 + (CO)^2 + (NOX)^2 + (UBHC)^2 + (EGT)^2 + (\text{smoke})^2}$$

RESULTS AND DISCUSSION

Table 5 shows the average yield and S/N values determined by the experiments that were performed for nine sets of arrangements as detailed in the orthogonal array in Table 2 above. Average yield assessed by the evaluation was 89.91 with the maximum yield being from run number 5 which was based on molar ratio of 7:1, 1.5 wt%, 80 minutes and 65°C. The mean S/N value was 39.07 with the highest S/N yield being shown by run number 8. The S/N distribution for set of experiments is shown in Figure 7 below.

Table 5: Average Yield and S/N Ratios Resulting from the Experiments

Run no.	Sample 1	Sample 2	Sample 3	Av Yield	S/N ratio
1	88.78	88.90	88.93	88.93	38.98
2	91.28	90.88	9.21	91.21	39.2
3	88.87	88.58	88.64	88.64	38.95
4	84.21	84.52	85.62	85.62	39.65
5	95.10	93.00	93.63	93.63	39.43
6	92.16	92.04	92.19	92.12	38.29
7	87.10	87.24	87.22	87.22	38.81
8	88.36	88.56	88.59	88.59	39.95
9	93.12	93.28	93.14	93.14	39.38
Average				89.91	39.07

Table 5 portrays the S/N proportions and the association between the yield and the S/N in relation to WCOBDas seen in the various example results. The variation of S/N values for the four factors are summarized in Table 6. The impact of every preliminary factor was settled from the greatest qualification in the characteristics between the mean S/N extents at every level. To play out an examination of the relative essentials of each limit, an examination of contrast (ANOVA) was conducted based on the results obtained to improve utilization of the Taguchi strategy and make it more productive. This provided in formation on the general effects of limits and their correspondences concerning the different results. Considering the ANOVA results, the fundamental factor in the formation of biodiesel were reaction temperature e, followed by catalysts concentration, molar ratio and reaction time. The variations for the four variables are summarized in Table 6. The commitments of each trial factor were resolved from the maximum distinction in the qualities between the mean S/N proportions at each progression. To play out an investigation of the family member significance of every boundary, an investigation of difference (ANOVA) was utilized for the outcomes acquired to utilize the Taguchi technique more efficiently. This provided data on the overall impacts of boundaries and their communications concerning the various outcomes. Considering the ANOVA results, the main factor in the creation of biodiesel was reaction temperature followed by catalyst concentration which showed the highest contribution.

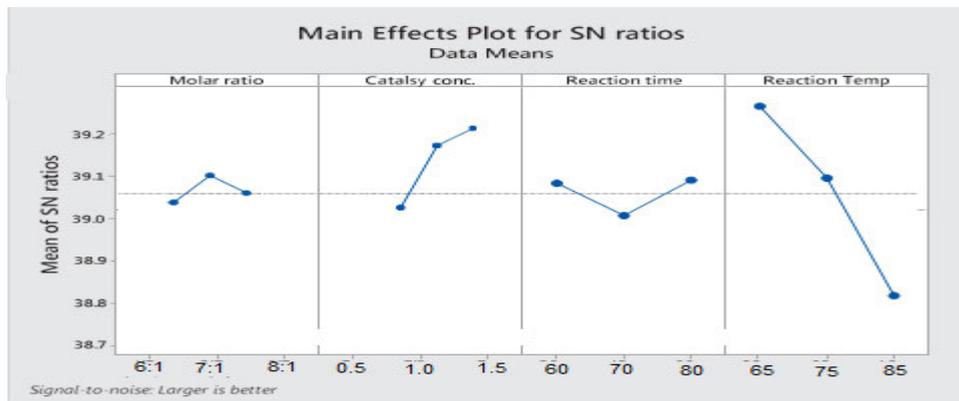


Figure 7: Mean S/N Ratio, Variation and Distribution

Table 6: Mean S/N Ratios and their Distribution

Factors	Level			Variations		
	1	2	3	L2-1	L3-1	L3-1
A. Molar ratio (methanol/oil)	39.04	39.12	39.07	0.08	0.03	-0.05
B. Catalyst concentration (wt%)	39.03	39.17	39.22	0.14	0.393	0.05
C. Reaction time (min)	39.08	38.88	39.14	-0.2	0.001	0.26
D. Reaction temperature (°C)	39.25	39.09	38.81	-0.16	0.44	-0.28

Table 7: Optimum Conditions for Settling the Control Parameters and their Contributions

Factors	Level	Level description	Contribution
A. Molar ratio (methanol/oil)	2	7:01	0.054
B. Catalyst concentration wt%	3	1.5	0.393
C. Reaction time (min)	3	80 min	0.001
D. Reaction temperature (°C)	1	65 °C	0.44

It can be noted that based on the S/N ratio from Table 6, the optimal parameters were molar ratio of 7:1, catalyst concentration of 1.5 %, reaction time of 80 minutes, and reaction temperature of 65°C. These are shown in Table 6 along with their contribution to yield value. It is vital to be able to evaluate optimal conditions that best suit the feed stock make up. Molar ratio is an important variable which impacts the yield of BD produced. Very low yield promotes backward reaction in which the BD produced will react with the glycerol to form an alcohol plus oil. This will result in low yields and high production costs. Increasing the molar ratio increases the BD yield to an optimal value thereafter it begins to decrease. Catalyst concentration shares the same variation as molar ratio, i.e., increasing concentrations increase yield up to peak value thereafter decrease in yield occurs. This is because a higher concentration of catalyst will enhance creation of several active sites for reaction to occur. However, recovery of the BD becomes more difficult when excessive concentrations of catalysts are used. Furthermore, from a financial point of view, higher concentrations of catalyst are not feasible since the cost of catalysts is high. Therefore, the proportion of oil to alcohol ratio is key in deciding the catalyst concentration required (Jagadale&Jugulkar, 2012; Kansedo, 2009). Reaction temperature is also key as higher temperatures speed up the rate of fuel conversion. Optimal temperatures must be determined since excessive temperatures will render the reactants inactive. Reaction time has influence on the production of BD as well in that if the process continues beyond the optimal peak period backward reaction is likely to initialize as well. Increasing reaction time will increase yield but this is up to peak value. Most researchers have proposed that maximum BD yields are determined at durations < 1hour 0 minutes. Prolonged duration will reverse the reaction resulting in lower yields and acceleration of the saponification process (Mathiyazhagan& Ganapathi, 2011).

Table 8: ANOVA of Yield Values

Symbol	Source	df (Degree of Freedom)	Adj. SS (adjusted sum of squares)	Adj. MS (adjusted mean squares)	F-value	P-value
A	Regression	4	67.848	16.962	5.82	0.148
	molar ratio	1	4.4326	4.4326	0.81	0.435
B	Catalyst concentration	1	36.2542	36.2542	13.14	0.068
C	Reaction time	1	0.0850	0.0850	0.25	0.883
D	Reaction temp.	1	32.4522	32.4522	13.66	0.041
	Error	4	9.3264	2.3316		
	Total	8	82.5504			

Table 8 shows the ANOVA of yield values based on impact of the parameters which were selected for study. As shown in the Table 7, if the p-estimation of a variable is more prominent than 0.05, it shows that the impact of that variable is practically negligible. Moreover, high F-values are demonstrative of high effect. Catalyst concentration and reaction temperature showed the lowest P-values of 0.041 and 0.068 respectively. Reaction time and molar ratio revealed the highest p-value of 0.883 and 0.435 respectively meaning their impact on the reaction were low in the evaluation process. The most prominent factors therefore were reaction temperature, catalyst concentration, molar ratio and then lastly reaction time. Reaction temperature also showed the highest F-value of 13.66 and catalyst concentration of 13.14 signifying their highest impact on the determined results. Contribution from catalyst concentration, reaction temperature, molar ratio, and reaction time were 44 %, 39.3 %, 5.4 % and 0.1 % respectively as shown in Table 7. Application of optimal conditions improved yield percentage from a maximum of 93.63 % to 96.8 %

Fuel Properties

Characterization of fuel samples was performed and is tabulated in Table 8. The fuels were tested according to ASTM D6751 methods in the laboratory at the University of KwaZulu-Natal. The tested parameters were kinematic viscosity, density, calorific value, flash point and cetane number. The kinematic viscosity of WCO100 was 4.12 centistokes which was about 70% higher than that of FD. The kinematic viscosity of FDFuel increased with the addition of WCOBD to the blend. Flash point was noted to increase with the addition of WCOBD to the blend for all FDFuels.

Table 9: Waste Cooking Oil Biodiesel Properties and Instruments Used for Measurement

Fuel blend	Kinematics viscosity, $\mu\text{m}^2/\text{s}$	Heating value, HV (KJ/kg)	Flash point, FP ($^{\circ}\text{C}$)	Density, (kg/m^3)	Cetane number
Fossil Diesel	2.42	44,250	65	0.836	49.00
WCO20	3.48	40,800	93	0.851	52.64
WCO40	3.64	37,920	98	0.854	54.12
WCO100	4.12	34,800	130	0.900	56.80
Measurement and apparatus standard test method	Redwood viscometer ASTM D445	Bomb calorimeter ASTM D240	Penkys martens ASTM D93	Hydrometer ASTM D1298	Ignition quality te ster ASTM D613

Performance Characteristics

Brake Thermal Efficiency

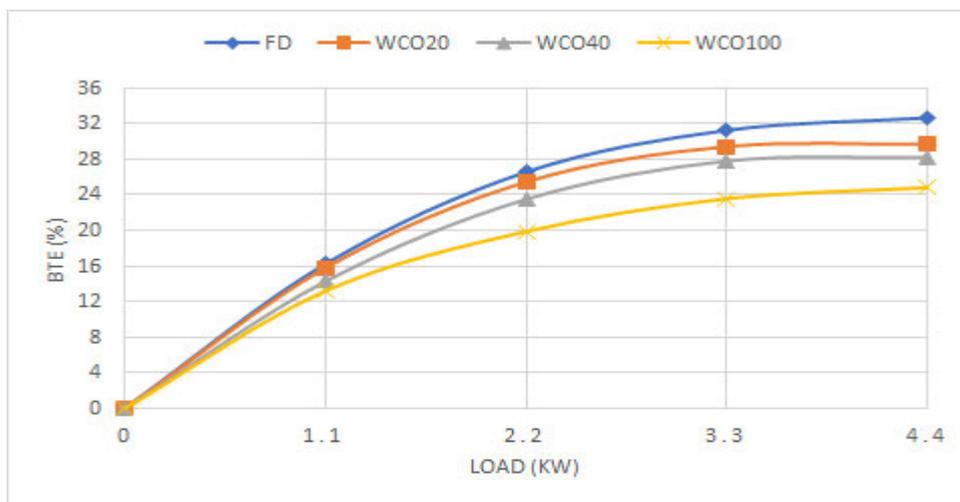


Figure 10: BTE vs Load

Brake thermal efficiency(BTE) showed increased variation with loading for all fuels. According to (Yadav et al., 2016) BTE is the ratio of actual engine work in relation to the energy supplied by fuel. It is calculated by dividing the engine brake power by energy derived from the fuel. This parameter is used to measure engine ability to convert stored chemical energy to mechanical energy. As shown in Figure 10, maximum BTE for FD, WCO20, WCO40 and WCO100 were 32.64 %, 29.68 %, 28.2 % and 25.8 % respectively. Mean BTE for FD, WCO20, WCO40 and WCO100 were 21.34 %, 20.07 %, 18.76 % and 17.17 % respectively. These results showed a maximum reduction in BTE of 26.51 % with WCO100 compared to FD at full load. Results also revealed that the BTE decreased with increased in WCOBD content in the blends. The reduction in BTE with WCO and its blends can be attributed to lower calorific value (CV), high kinematic viscosity and density of WCO and its blends compared to FD. CV denotes the energy content of the fuel hence the lower CV of WCO and its blends which showed lower energy capability compared to FD. This is a similar trend to those found by other researchers (Ashok et al. 2017; Khalife et al., 2017; Raju et al., 2018). The reduction is mostly attributed to an increase in BD content in the blends. A study performed by Carraretto et al. (2004) showed a reduction in brake thermal efficiency and brake power with BD20, BD30, BD50 and BD80. Murillo et al. (2007) found the same trend in decreasing brake power with increasing BD content in the blend. Utlu and Koçak(2008) concluded from their study results that WFMOE showed a reduction of 4.5 % in BTE which they attributed to higher kinematic viscosity and CV of the blends. Most researchers reports that a reduction in BTE can be traced to heat value which decreases with increase in BD content in the blend and kinematic viscosity which increases with blending. Kinematic viscosity will impact kinematic viscosity which will promote poor atomization of fuel and this subsequently results in larger particle generation and poor combustion profile. All this will point towards a lower energy BTE with WCO and its blends compared to FD. However, this result is opposite to what was reported by Song and Zhang (2008) who found higher power with an increase in BD content in the blends. Song and Zhang (2008) argued that this was caused by the fact that fuels are delivered on a volumetric basis in the engine. Since the BD has higher density it is able to supply more fuel hence more power output and this is able to compensate for the lower CV of BD blends. The other explanation is based on higher O₂ content which the authors say helps to adjust injection timing and shorted ignition delay improving the combustion profile of the BD and its blends. This still needs to be substantiated as it is an unbelievable result with BD.

Brake Specific Fuel Consumption (BSFC)

Variation of BSFC with loading is shown in Figure 11. It is evident that BSFC was decreased with loading. WCO100 had higher trends compared to FD and this decreased with an increase in blending. The results are similar to those found by many researchers (Murillo et al. 2007; Song & Zhang 2008; Utlu & Koçak, 2008). The CV of BD is lower than that of FD hence to compensate for lower heat values BD must consume more for same 1 kWh. Surprisingly, the CV of WCO100 was 29 % lower than that of FD. These results are closer to what was found by Armas et al. (2010), that BD was 12.9 % lower and BSFC also showed an increment of 12 compared to FD. Haşimoğlu et al. (2008) found similar trends of BSFC vs FD in which CV of BD was 13.8 % lower and showed 13 % higher BSFC in comparison to FD. Lin et al. (2009) found similar results with VOME showing BSFC in the range 9 % to 15 % with blends lower than FD in the range 12 % to 16%. The underlining factors influencing higher fuel consumption with BD and its blends is lower heat values of which the engine must consume more to compensate for the lower CV. Others have suggested that higher density will compensate for lower CV and reduce the consumption significantly. Luján et al. (2009) argued that a difference in CV of 19 % resulted in almost 13 % increase in BSFC due to higher density compensating for lower CV.

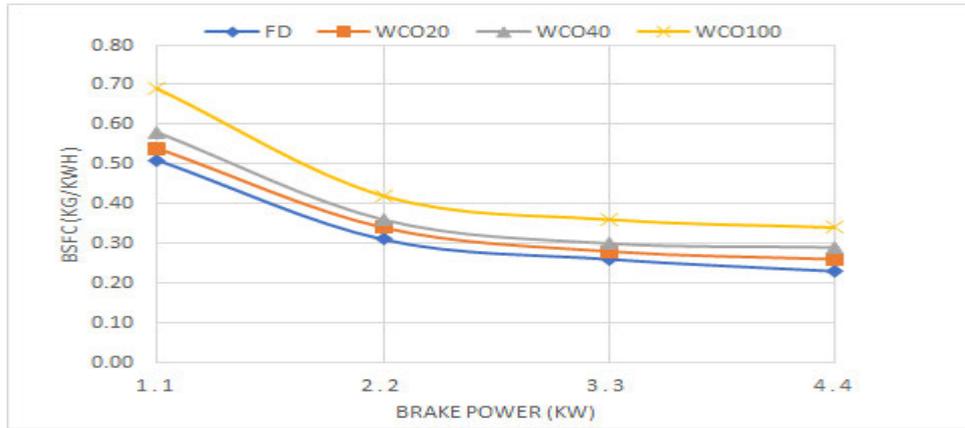


Figure 11: BSFC vs Load

Exhaust gas Temperature

Figure 12 depicts the variation of EGT with load. It can be noted that EGT increased with load for the fuels that were utilized in this investigation. The highest EGT for FD, WCO20, WCO40 and WCO100 were 640, 680, 720, and 740°C respectively. The analysis of these trends revealed that FD showed lower trends in comparison to WCO blends. WCO100 showed the highest trend. According to Usta et al. (2005) the highest trends for WCO blends are influenced by longer ignition delays and decreased burning rate compared to FD. This prolongs the combustion process resulting in higher EGT being reached. Muralidharan and Vasudeven (2011) argue that the rise is caused by the high CN numbers of WCO blends compared to FD. High CN and kinematic viscosity are said to cause poor atomization which results in unburnt fuel particles available in the premix phase. This will cause higher temperatures. Analysis of WCO20 and WCO40 and WCO100 showed that the increase in WCO BD in the blends also showed an increase in EGT.

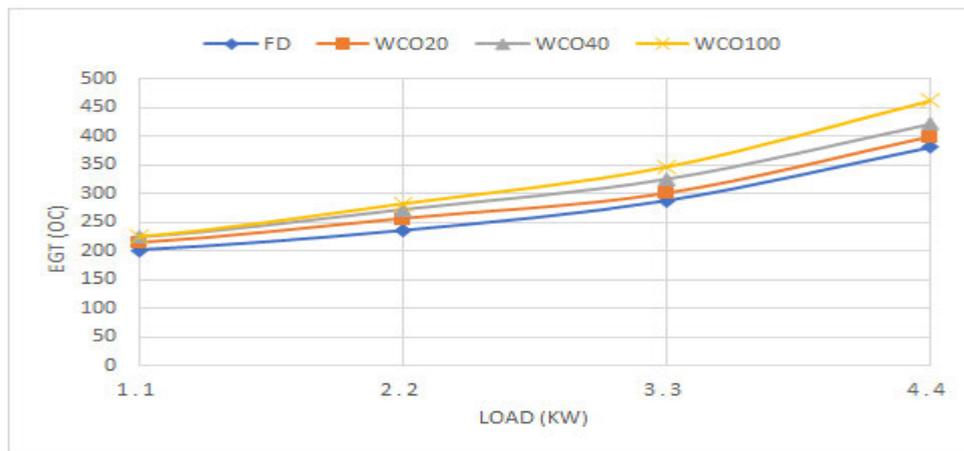


Figure 12: EGT vs Load

Emission Parameters

Nitrogen oxides (NO_x)

The variations of NO_x emission against load are shown in Figure 12. The highest NO_x was obtained with WCO100 at full load. NO_x is generated at high temperatures. WCO and its blends showed higher NO_x with load in comparison to FD. BD usually produce higher flame temperatures compared to FD and this will influence formation of higher NO_x emissions compared to FD. NO_x is generated at higher temperatures with high O₂ concentration and this the case with most BDFuels

(Hansen et al., 2006; Ozsezen et al., 2009). These results agreed with those of Ozsezen et al. (2009) in which NO_x emissions were increased by 22.3 % compared to FD fuel. Dorado et al. (2003) also found an increase of 20 % in emissions with BD derived from waste olive oil. These results disagreed with those of Utlu and Koçak (2008) and Qi et al. (2009) who found a 5 % decrease in NO_x with BD. A study by Godiganur et al. (2010) which evaluated a variety of BD feedstocks also found an increase in NO_x emissions. According to Al-Widyanet al. (2002), increase in NO_x can be attributed to high CN of BD and its blends compared to FD. This was echoed by many other researchers (Lapuerta et al., 2008; Özgünay et al., 2007; Puhan et al., 2005). CN promotes shorter ignition delay hence prolonged combustion duration and high temperature generation which will subsequently lead to high NO_x generation. Another factor is high O_2 content of BD fuels. A study by Labeckas and Slavinskas (2006) revealed that maximum NO_x generation was directly related to max O_2 content of rape methyl ester. The increase in NO_x with load can be traced to development of higher cylinder temperatures which is linearly related to NO_x production. As the load is increased the engine consumes more fuel and the air fuel ratio will be increased, leading eventually to high combustion temperatures. The high temperatures are the ones which will influence NO_x generation (Zhu et al., 2010; Luján et al., 2009).

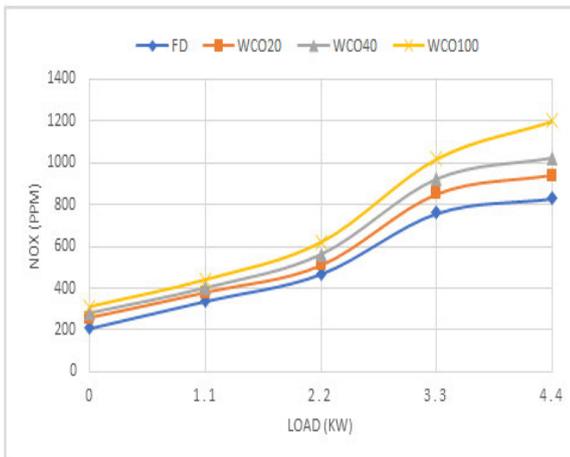
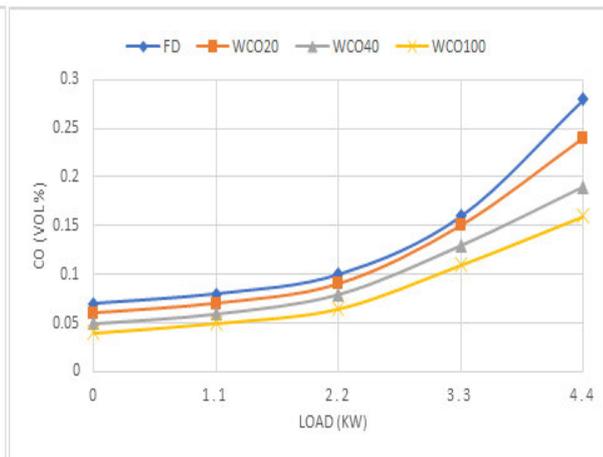
Figure 12: NO_x vs Load

Figure 13: CO vs Load

Carbon Monoxide (CO)

CO variation with load is shown in Figure 13. CO increases with load and WCO and its blends depicted lower trends in comparison to FD. WCO and its blends contain higher O_2 content compared to FD which promotes complete oxidation. An increase in WCO proportion in the blend showed a reduction in CO emissions. The highest reduction of 62.5 % was found with WCO100 at 100 % loading. CO is generated in fuel rich zones where there is O_2 defiance. WCO and its blends have extra O_2 available to suppress formation of CO compared to FD fuels. Higher CN also causes shorter ignition which will ultimately prolong combustion and promote conversion of CO to CO_2 (Ha et al., 2019). A study by Krahl et al. (2003) showed a reduction in CO of 50 % with rape seed derived BD compared to that of FD. A study by Raheman and Phadatare (2004) with Karanja derived BD and its blends (B20, B40, B60, B80) revealed a reduction in CO of 94 %. Ozsezen et al. (2009) performed an evaluation of WMPOME and found that CO was reduced by 86.89 %. Puhan et al.' (2005) results showed a reduction of 30 % in CO when compared with FD. However, research by Fontaraset al. (2009) showed an increase in CO of 54% with B50 compared to FD. The same researchers also found a decrease in 95 % with B100 compared to FD although the researchers did not offer reasons for these findings. The reduction in CO has been attributed to higher O_2 content which promotes complete combustion. CO is generated in oxygen deficient portions of the

combustion chamber. This is reduced with BD since it has high O₂ content compared to FD. High CN has also been pointed as an influencing factor in CO reduction. A study by Wu et al. (2009) revealed that a decrease in CO correlates with an increase in CN.

Unburnt hydrocarbon (UBHC)

Variation of UBHC with loading is shown in Figure 14. There is an increase in UBHC with load. The results were similar to the results by Wu et al. (2009) who performed experiments with different types biodiesel oil feed stocks with an analysis of results showing a 45 % to 67 % reduction in UBHC emissions. An experimental investigation by Puhan et al. (2005a) found similar results of 63 % reduction in UBHC compared with FD. Another significant reduction in HC was revealed by Alam et al. (2006) who found a 60 % reduction in HC compared to FD fuels. UBHC are generated at fuel rich zones of the combustion engines. BD contains higher O₂ content compared to FD and this will be utilized for complete combustion purposes reducing generation of UBHC emissions (Choi & Oh, 2006). High CN also causes reduction in ignition delay which causes longer combustion and HC reduction. These results disagree with those reported by Fontaras et al. (2009) and Banapurmatha et al. (2008) who reported an increment of UBHC with BD. Fontaras et al. (2009) reported a 54 % increase in UBHC at 1500 rpm with BD compared to FD which they attributed to poor engine combustion efficiency resulting from poor spray pattern from high kinematic viscosity of BD and its blends. The decreasing trend is also linear with increasing content of DB in the blend. This was similar to what was found by Godiganure et al. (2010) who reported an inverse relationship of HC reduction to the BD portion increase in the blend. However, a study by Luján et al. (2009) revealed a small decrease with B100 of 16.4 % compared to B50 of 17.7 %. The authors attributed this to development of local air ratios which influenced high UBHC emissions generation.

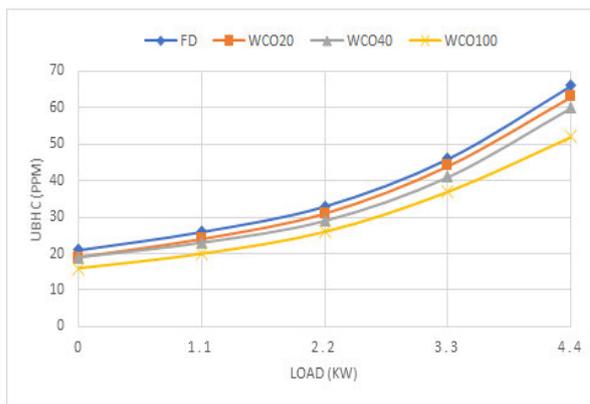


Figure 14: UBHC vs Load

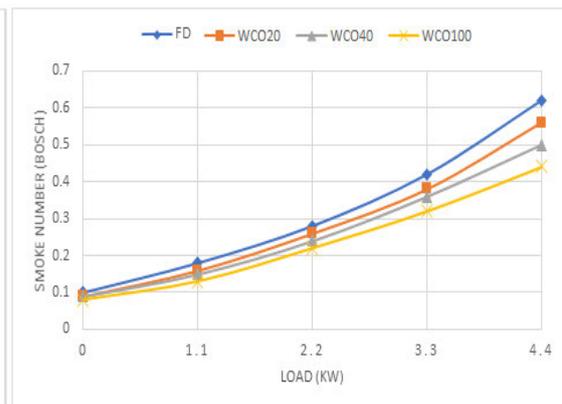


Figure 15: Smoke opacity vs load

Smoke Opacity

According to Venkatesan et al. (2017), smoke opacity is a measure of the solid hydrocarbon soot particles present in exhaust gases of IC engines. This parameter is used to track generation of smoke within the combustion process. The increasing trend of smoke opacity with loading is shown in Figure 15. FD exhibited higher trends with load compared to WCO100 and its blends. WCO100 and its blends contain a higher content of O₂ which is used for complete combustion, suppressing the generation of high amounts of smoke. According to Devan and Mahalakshmi (2009), lower kinematic viscosity which decreases the combustion process results in high smoke emission. WCO100 and its blends have a high CN which will promote a shorter ignition delay. Short ignition will subsequently prolong combustion duration resulting in a better combustion process and therefore smoke reduction.

Carbon dioxide (CO₂)

Variations of CO₂ with load are shown in Figure 16. It is self-evident from the data shown in Figure 16 that CO₂ increased with loading for all fuels. A maximum increment of 21.2 % was found for WCO100 when evaluated against diesel fuel. CO₂ emission increased with increase in WCOBD content in the blend. According to Zareh et al. (2017), expanding CO₂ gas outflows at higher loads results in an increase in fuel being injected into the combustion chamber. Various reports have associated expanding CO₂ outflows at raised motor burdens to a more complete burning (Fontaras et al. 2009). Despite FD having superior C/H ratios, it showed lower CO₂ emissions. The underlying explanation behind increased CO₂ emissions when compared with FD is that this can be attributed to increased fuel consumption resulting in higher CO₂ generation as BD blends try to compensate for their lower calorific values (Ozsezen et al., 2009). Other researchers have contended that the CN values promote prolonged combustion process resulting in CO being oxidized to CO₂ (Puhan et al., 2005b). Varying opinions have been suggested, with others pointing to the trend of increased combustion chamber temperatures (Fontaras et al. 2009) and high density from BD and blends (Wu et al., 2009). The more satisfactory explanation related to the increase in fuel available in the chamber as the causative factor for CO₂ which is similar to the trend in BSFC.

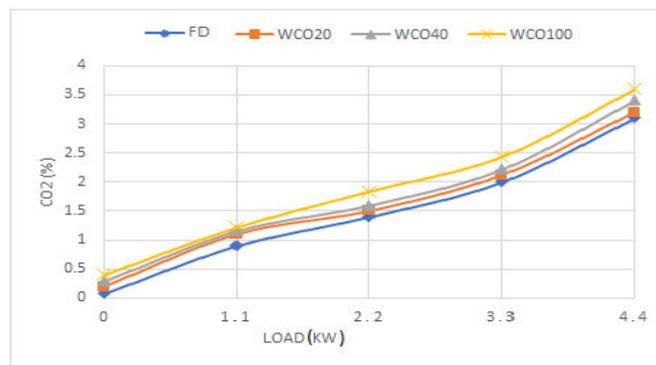


Figure 16: CO₂ vs Load

4. CONCLUSION

This study was aimed at evaluating the viability of using WCO as an alternative fuel for a diesel engine. WCO was produced using a two-step esterification process. The parameters were optimized using the Taguchi method and found to be molar ratio 7:1, temperature 65 °C, 80 minutes reaction time and catalyst concentration 1.5 wt%. The optimization process pointed to reaction temperature and catalyst concentration as being the most influential parameters in BD production scoring 44% and 39.3 % contribution to yield percentages respectively. Molar ratio of 7:1 and reaction time of 80 minutes scored 5.4 % and 0.1 % contribution to yield values respectively, signifying that reaction time has negligible effect on yield percentage determination. The BD produced conformed to ASTM D6751 standards.

When the five fuels FD, WCO20, WCO40 and WCO100 were tested in a diesel engine it was found that:

- BTE decreased with increased loading showing maximum reduction of 17.8 % at 100 % loading.
- Decreasing BTE increased with biodiesel content in the blend.
- BSFC increased with loading when compared with FD fuel revealing an increase of 27.3 % and the increase correlated with the increase in WCOBD in the blend.

- CO emissions decreased with load showing a reduction of 62.5 % when evaluated against those of FD.
- UBHC decreased with loading and reduction of 27.2 % was shown by analysis of the results.
- Smoke opacity decreased with blending and showed a reduction percentage of 34.45 % when compared with that of FD.
- NO_x increased with blending, the increment being 27.3 %.
- CO₂ increased with load and blending and an increment of 28.43 % was shown by experimental evaluation.

Properties of WCO conformed to international standards of ASTM and its performance and characteristics were similar to FD therefore it can be a viable fuel for a diesel engine. Lower blends WCO20 and WCO40 showed similar performance trends and can be utilized as alternative fuels in unmodified diesel engines.

Further Research:

- In most cases the BD produced from the two-step trans esterification process does not conform to international standards hence addition of additives becomes a necessity for property improvement and subsequently improved performance and emission reduction.
- Performance enhancement of WCO is hereby advised as this will circumvent the performance shortfall and help in reducing exhaust emissions.
- A study involving the combined impact of other engine conditions such as compression ratio, injection pressure, and injection timing is suggested in order to gain in-depth understating of addition of WCO to diesel.

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CHAPTER 4: PERFORMANCE AND EMISSION ANALYSIS OF A HYBRIDIZED NANO ADDITIVE IN WASTE COOKING OIL BIODIESEL AND ITS BLENDS IN A DIESEL ENGINE

This chapter provides a report on an experimental work performed to evaluate the effects of hybridized nano particle on fuel properties, engine performance and emissions of Waste cooking oil and its blends. The outcome of the work was published in the International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)

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PERFORMANCE AND EMISSION ANALYSIS OF A HYBRIDIZED NANO ADDITIVE IN WASTE COOKING OIL BIODIESEL AND ITS BLENDS IN A DIESEL ENGINE

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ABSTRACT

This work investigated the effects of a hybridized nano additive on performance and emission behavior of waste cooking oil (WCO) derived biodiesel and its blends with fossil diesel (FD). Three different oil portions of WCO from soya bean (WCO01), cotton seed (WCO02), and sunflower seed (WCO03) were purchased from Enfields Chemicals, a waste cooking oil buying firm based in Durban, South Africa. The samples were evaluated for fatty acid composition and characterization of physicochemical properties to select WCO3 which showed with most superior properties which was then transformed into biodiesel by transesterification. The biodiesel produced from transesterification was mixed with 100 ppm of a hybridized nano additive consisting of 50 ppm of aluminum oxide (AL₂O₃) and 50 ppm of cerium oxide (CeO₂) to produce nano fuel blends. The base fuel and nano additives were mixed with the aid of an ultrasonicator to produce a well-blended mixture as well as to avoid clustering problems. The resulting fuel samples were utilized immediately to avoid occurrence of sedimentation. Thereafter the fuel was tested for properties then tested in a two-cylinder Kirloskar engine operated at constant speed of 1 500 rpm. From the experimental analysis, addition of hybridized nano additives improved BTE by a maximum value of 6.22 % compared to FD fuel when evaluated against load. A maximum decrease in BSFC of 10.20 % was noted with hybrid nano fuel WCO20A50C50 compared to FD fuel. A significant reduction in NO_x of 25.62 % was found compared to FD. CO, unburnt hydrocarbons (UBHC) and smoke opacity were reduced by 36.8 %, 27.8 % and 17.68 % respectively compared to FD. WCO20A50C50 produced the most superior characteristics of all the fuels tested in this research. The research concluded that addition of a hybridized nano additive of CeO₂ and AlO₂ is a novel catalyst capable of improving engine performance and reducing emissions significantly. This will subsequently increase adoption of biofuels and help save planet earth.

KEYWORDS: Waste Cooking Oil Biodiesel, Properties, Performance, Emissions & Blend

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Nomenclature		WCPBD Waste Cooking palm biodiesel B20W30A 80 % diesel 20 % waste cooking oil biodiesel plus 30 ppm MgO additive	
BSFC	Brake specific fuel consumption	Mg	Magnesium
BTE	Brake thermal efficiency	TiO ₂	Titanium dioxide
BSEC	Brake specific energy consumption	Co ₃ O ₄	Cobalt oxide
PM	Particulate matter	Ni	Nickel
CI	Compression ignition	Fe ₂ O ₃	Iron oxide
CN	Cetane number	CNT	Carbon nano tube
CP	Cloud Point	AN	Aluminum nanofluid
PP	Pour Point	CuO	Copper oxide
CV	Calorific Value	MnO	Manganese oxide
CO ₂	Carbon dioxide	CoCl ₂	Cobalt chloride
NO _x	Oxide of nitrogen	Al ₂ O ₃	Aluminum oxide
HC	Hydrocarbon	CuSO ₄	Copper sulphate
CO	Carbon monoxide	Al-Mg	Magnallium
WC	Water cooled	CeO	Cerium oxide
UBHC	Unburnt hydrocarbons	CuCl ₂	Copper chloride
ASTM	American Society for Testing and Materials	TiO	Titanium oxide
AC	Air cooled	FeCl ₃	Ferric chloride
DI	Direct injection	n-Al	Nano aluminum
JBD	Jatropha biodiesel	AO	Aluminum oxide
DB0PSWE20	80%Diesel 20% Pomoplion stearin wax biodiesel	Al	Aluminum
PM	Particulate Matter	Ti	Titanium
DB0SBD15E4S1AL]	methyl 80%Diesel 20% soya bean	POME	Palm oil methyl
B100W30A 100 %	Waste Cooking oil 30 Ppm	ester	
Mgo		ppm	Parts per million

1. INTRODUCTION

The world energy situation is influencing energy researchers to look for alternative energy supplies which are sustainable and less polluting compared to fossil fuels. It is a well-known fact that the current energy supply mix dominated by fossil fuels is limited (Shafiee & Topal, 2007). Fossil fuels have dominated worldwide energy supplies because they have supported the growth of business and personal lifestyles leading to world dependence on fossils for energy (Shafiee & Topal, 2007). Fossil derived fuels have dominated the global energy mix because (1) this energy is accessed at a low cost of production (2) the sector is well established (3) fossil fuel industries supports other industries directly or indirectly by itself or its byproducts (Ruben et al., 2007). Global energy utilization is currently around 12 billion tons of oil equivalent up from 738 million tons of oil equivalent in 1980 (United States Energy Information Administration, 2015). This increasing consumption pattern is expected to continue because of expansion in the worldwide population, and expansion in industrialization and wasteful usage of energy, which is producing unnecessary energy waste streams. As per the United States Energy Information Administration (2015) report, 80% of this energy supply is derived from fossil-based fuels and the rest from renewables and atomic energy. This rate of fossil fuel consumption has resulted in dwindling fossil fuel resources, especially petroleum-based products. Oil sources are discovered in specific parts of the world which restricts its accessibility to different parts of the world such as here in South Africa. This impacts national energy security because the control or access to this resource is controlled by certain countries. Furthermore, the volatility of oil prices has an impact on national progress as it directly affects a country's GDP as consumption of energy is linked directly to its growth. Fossil diesel (FD) has been preferred for powering long distance heavy road transportation of goods, trains, horticultural machinery and ships. Diesel fuel is favored in the transportation sector as a fuel source due to its high dependability, better fuel economy and high efficiency compared to its spark ignition counterparts. Research has been conducted on electric cars and solar powered vehicles but such an energy source is not compatible for heavy transportation of goods. There appears to be no clear-cut alternative for diesel engines especially for heavy duty transportation of goods. The only option is to perform research on the current diesel engine and make it more efficient and reduce emissions. A study by Neeft et al. (1996) proposed three measures to improve diesel engine performance and emission behavior: (1) fuel alteration, (2) engine modification and (3) exhaust after treatment methods. Fuel alteration is becoming the favored option considering the huge number of vehicles already on the roads and that it is the cheapest and easiest method to implement. Biodiesel is in a leading position to replace FD fuel in compression ignition engines.

Biodiesel is a sustainable, biodegradable energy resource derived from vegetable oil and animal fats (Shafiee and Topal, 2007). Biodiesel and its blends with FD results in combustion with significant reduction in exhaust gas emissions such as carbon monoxide (CO), unburnt hydrocarbons (UBHC) and smoke opacity. However, an increase in NO_x emissions has been found by several researchers (Ambozik & Chdopek, 2001; Chandrasekaran et al., 2016; Colgan, 2014; Colgan et al., 2011; Kannan et al., 2011; Knothe & Steidley, 2010; Kumar et al., 2015; Muralidharan et al., 2011; Prabu, 2018; Sajith, Sobhan, & Peterson, 2010). Biodiesel contains 10 % to 11 % more oxygen more than FD and has a high cetane number which improves the burning cycle. Notwithstanding biodiesel gaining attention as a suitable alternative fuel, its acceptance has been hindered by a few engine combustion setbacks such its high viscosity, high density, low calorific value, poor low temperature performance, and poor storage stability. These operational difficulties can be circumvented by introducing fuel additives. Advancement in nanotechnology has opened a niche within the fuel additive sector in which nano metals have been reported to mix easily with the base fuels unlike the previous powdered counterparts. Nano metals possess favorable properties which can be harnessed to enhance fuel properties, improve engine performance, and reduce

exhaust gas emissions. Nano metals have high conductivity, high surface area to volume ratio, and can act as catalysts thereby increasing the rate of reaction (Shafiee & Topal, 2007). Nano particle fuel additives are not a well-researched area despite reports pointing out that nano additives in biodiesel can shorten ignition delay, decrease burn rates, and increase oxidation intensity of the base fuel. These factors are essential for complete combustion and emission reduction. Addition of nano particles improves the calorific value of biodiesels and brings biodiesel closer to the properties of FD fuels.

Biodiesel adoption has been slow due to high feedstock costs which has necessitated research on cheap alternative feedstock sources such as waste cooking oil (WCO) (López et al., 2015). Worldwide the generation of WCO is around 15 million tons annually which creates disposal challenges which are hurting the climate and the environment (Colcan, 2014; Cogan et al., 2011). Disposal can cause water contamination and high energy utilization in wastewater treatment plants. Biodiesel production and utilization has been demonstrated as a suitable answer for the liquid fuel sector. Biodiesel can be derived from edible or non-edible feedstocks. Use of edible feedstocks has caused negative consequences because of its competition with food supplies (López et al., 2015) which has resulted in a search for alternative feedstocks of which WCO is preferred because of its easy accessibility and the cheap cost of procurement. There are many restaurants and cafés in the Durban area, South Africa. These businesses produce WCO in huge volumes causing disposal challenges with reports of sewage blockages, and soil and water contamination. WCO biodiesel production will decrease this challenge. Thus, WCO as a feedstock for biodiesel is an innovative solution aimed not only at solving disposal challenges but also in helping to create local employment. Human consumption of WCO is reported to cause cancer as a result of toxic contaminants which are formed during oxidation of the oil (Colgan, 2014). Usage of waste cooking oil for fuel production discourage recycling for cooking which is being carried out by various companies.

Colgan et al. (2011) analyzed the effects of POME diesel blend with nickel oxide nano particles and biodiesel. A single cylinder VCR diesel powered by B10, B20 and B30 POME diesel with and without nickel oxide nano added was used in this analysis. Doses of 20 ppm and 40 ppm were blended with base fuels during the test examination. The outcomes indicated an increase of 6.2 % in BTE with addition of nickel oxide nano particles to the POME diesel blend compared with neat base fuels. The authors also reported a BSFC and BSEC reduction of 5.11 % and 5 % respectively in comparison to neat biodiesel blends. B20 with nano additives showed the best engine improvement compared to base fuels thus underlining the need for additives and optimal dosages of nano particles. The authors claim that better atomization of fuel which promoted complete combustion was the reason behind the performance improvement with the addition of nano particles.

Prabu (2018) carried out experiments on a single cylinder 4 stroke DI engine fueled with Jatropha derived biodiesel blended in with Al_2O_3 and CeO_2 nano particles. The engine speed was kept at a steady speed of 1 500 rpm. Three fuel portions: biodiesel-diesel (B20), biodiesel-diesel-nanoparticles (B20A30C30) and biodiesel-nanoparticles (B100A30C30) were utilized for examination. Analysis of experimental results revealed an increase in BTE of 12 % with addition of hybridized nano additives of aluminum oxide and cerium dioxide. CO emissions were significantly decreased by 60 % when compared with FD fuel. Hydrocarbon emissions decreased by a margin of 44 %. The author found a reduction in NO_x emissions of 30 % compared to B100. Prabu (2018) claimed that the reduction in NO_x emissions was caused by reduction in engine delay which accelerated early combustion and lowered heat release. Hybridized nano additive fuel produced the most improvement in engine performance and reduced emissions compared to B100.

Kannan et al. (2011) performed an experimental investigation on the effects of ferric chloride ($FeCl_3$) on waste

palm oil derived biodiesel. The authors performed experiments on an engine operating at a constant 1 500 rpm, and constant pressure of 250 bars and injection timing of 25.5 degrees. The author reported improvements in performance and emissions reduction. From the analysis of results, it was concluded that CO, total hydrocarbons and smoke opacity were reduced by 52.6 %, 26.6 % and 6.9 % respectively with nano particle addition compared to neat biodiesel blends. However NO and CO₂ were noted to have increased by 4.1 % with addition of nano additives compared to neat biodiesel blends. The researchers claim that the increase in NO_x was influenced by the high oxygen content in biodiesel blends which promoted high cylinder temperatures which resulted in formation of these highly hazardous gases.

Chandrasekaran et al. (2016) conducted a research study on the effects of copper oxide nano additives on biodiesel derived from mahua feedstock. The test results showed significant improvement in fuel properties and better performance characteristics. Mixing biodiesel and diesel in proportions of 20 %, 40 %, 60 %, 80 %, and 100 %, coupled with the addition of 50 ppm of copper oxide additives, showed a marginal decrease in kinematic viscosity and density. Reduction in flash and fire point were also reported. An increase in calorific value of fuel by 0.6 MJ/kg was noted.

Muralidharan et al. (2011) experimentally investigated the influence of WCO proportion in FD blends. Using 20 %, 40 %, 60 % and 80 % proportions of blending ratios the authors found that exhaust gas temperatures for biodiesel blends were higher than that for FD fuels. The authors attributed this increase to lower calorific value and the existence of oxygen components in higher percentages.

Kumar et al. (2015) performed an experimental investigation into the effects of magnesium additives on performance and emission characteristics of chicken fat derived biodiesel and diesel blends in CI engines, using 16 µmol/l of magnesium additive. From the experimental analysis it was reported that kinematic viscosity decreased from 5.184 centistokes to 4.812 centistokes with addition of fuel additives compared to neat biodiesel blends. A reduction in flash point from 129 °C to 122 °C was also noted by the authors. This research pointed out that the catalytic effect of metal additive resulted in enhancement of fuel properties.

Knothe and Steidley (2005) evaluated the effects of an aluminum oxide nano additive on B20 Jojoba oil derived biodiesel. From the experimental evaluation it was noted that addition of this fuel additive resulted in a significant reduction in kinematic viscosity although an increase in density was also noted by the researchers. This research also reported an increased cetane number with the nano additive addition to the blend. This research points out that a metal oxide nano additive has the capacity to improve fuel properties which will ultimately result in performance improvement and gas emission reduction.

Sajith, Sobhan and Peterson (2010) performed an experimental investigation on the influence of CeO₂ in Jatropha derived biodiesel in diesel engines. Mixing the base fuel with dosages of 20 nm in intervals up to 80 nm revealed significant engine performance improvements and emissions reduction. According to the authors, CeO₂ can act as an O₂ buffer which promotes improved combustion processes. CeO₂ introduction promotes accelerated oxidation of CO, HC, and soot into CO₂ and water vapor.

Several research studies have been carried out on effects of fuel additives and property enhancement, performance and emission behavior of biodiesel and its blends with fuel diesel in a CI engine. Most of the researchers reported significant reduction in CO, unburnt hydrocarbons (UBHC) and smoke opacity but an increase in NO_x and CO₂. Introduction of metal-based fuel additives have been found to enhance better thermophysical properties of biodiesel blends.

Addition of fuel additives result in better thermal conductivity and high surface area to volume ratio. Metal-based nano additives act as reaction catalysts which ultimately improve fuel combustion behavior and result in emission reduction. From the literature it is evident that few studies have been performed with hybrid nano particles in order to capitalize on the different properties derived from each type of nano particle.

A nano particle additive is used in a diesel engine once it can satisfy the following requirements, according to Ambrozik and Chdopek (2001):

- It should be capable of reducing engine exhaust emissions and increasing oxidation intensity in the engine and particulate filters.
- It must be able to retain typical engine operational properties.
- The nano particle must be able to retain its chemical stability within the fuel mixture under all conditions.
- It must be able to retain working effectiveness of particulate filters.

The role of nano scale fuel additives in biodiesel fuels is not a well-researched area although many researchers have reported shorter ignition delay, decreased burn time, and high fuel oxidation rate, all which promote improved engine performance and emission reduction (Gurjar & Tyagi, 2020).

The objective of this research was to evaluate performance and emissions behavior of mixed nano particles i.e., hybrid nano additives, on WCO derived biodiesel in a CI engine. In doing so the research produced WCO biodiesel mixed with purchased nano additives to form a hybrid nano fuel blend. Biodiesel production is influenced by sources of feedstocks as well as process conditions hence it is vital that localized production is enhanced in order to understand the free fatty acids (FFA) makeup of local feedstocks and to evaluate optimum conditions for biodiesel in South Africa. The produced nano fuel was tested for physiochemical properties then tested in a diesel engine.

2. MATERIALS AND METHODS

2.1 Waste Cooking oil Biodiesel Production

Three distinct portions of WCO derived from soya bean oil, cotton seed oil and sunflower oil, named as WCSWO1, WCO2 and WCO3 respectively, were bought from a local firm that deals with collection and purchasing of waste oils. Samples of WCO feedstocks were taken from the three portions and physicochemical property evaluation was performed. The sample with WCO3 was chosen for biodiesel production after which acid value determination was initialized before transesterification. The samples were at first heated to 105 °C to eliminate food components and undesirable deposits. Gas chromatography coupled to mass spectrometer model (GC/MS), Shimadzu, model QP 2010 GC-MS, capillary column Durabond, stationary phase DB-5HT (280 (W) X 280 (H) X175 (D) was utilized for fatty acid composition analysis of samples of 3.5 ml at 200 °C with helium as carrier gas and a flow rate of 3 ml/min. Table 1 depicts temperature settings of the gas chromatography equipment utilized in the fatty acid composition analysis.

The results are tabulated in Table 2. The fatty acid composition evaluation was necessary to gain an understanding of the makeup of the feedstock which would assist in explaining the characteristics of the biodiesel produced. Evaluation of oil samples physiochemical properties revealed that WCO3 was suitable for biodiesel production (Table 3).

Table 1: Gas Chromatography Temperature Settings

	Oven T (°C)	Duration
Initial temperature	120	1 min
Heating slope 1	40 up to 200	1 min
Heating slope 2	15 up to 350	5 min
Heating slope 3	7 up to 450	3 min

Table 2: FFA Composition

SAMPLE	Palmitic (C16:0)	Palmitoleic (C16:1)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)	Arachidic (C20:0)	Behenic Others (C22:0)
WCO1	6.2	0.78	2.2	12.48	52.8	5.82	0.66	21.69
WCO2	8.44	0.88	2	56.84	17.48	3.48	0.58	10.3
WCO3	9.8	0.38	3.4	52.62	19.88	10.6	0.9	0.6

Table 3: Properties of Waste Cooking Oil Samples

Sample	Kinematic Viscosity Cst	Density kg/	Flash Point
WCO1	34.88	920	221
WCO2	34.42	912	213
WCO3	32.68	878	213

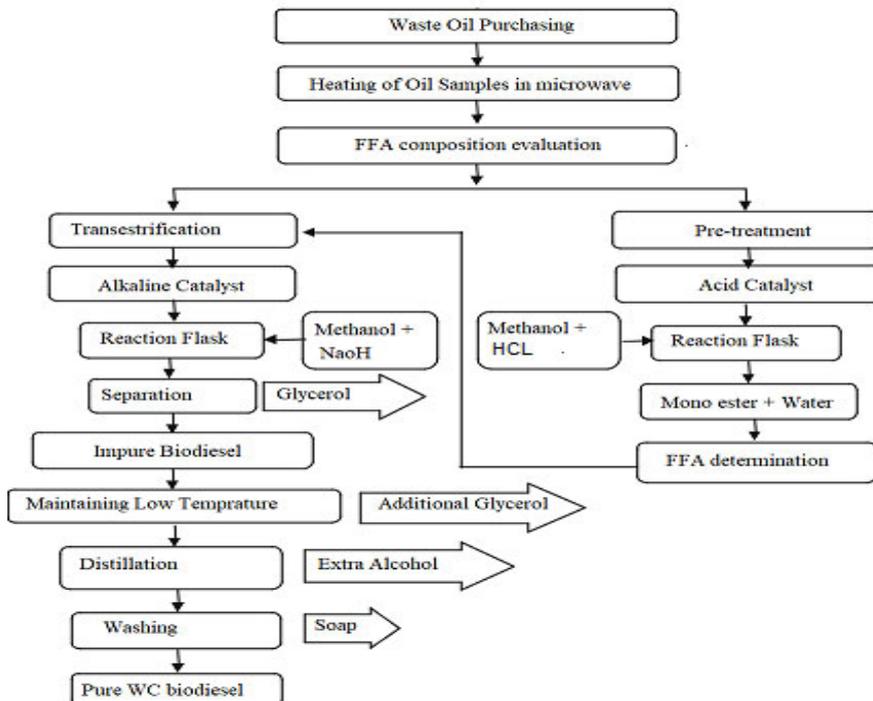


Figure 3: Waste Cooking Oil Biodiesel Production

Adapted from (Kumar et al., 2015)

Summary of steps in WCO biodiesel production (Figure 3):

- The raw waste cooking oil was evaluated for acid value in order to determine whether to perform a one-step or two-step process. The acid number of the oil was evaluated with the titration method using 0.1 N KOH, phenolphthalein, and isopropyl alcohol according to the ASTM D974 standard (Banani et al., 2015).
- Acid Value = $\frac{56.1 \times 0.1 \text{ N} \times 20.07 \text{ mL}}{10 \text{ g}}$ (1)
- Whereby: 56.1 is the molecular weight of KOH used in the titration (g/mol). 20.07 is the volume of KOH consumed during titration (ml). 0.1 N standard solution represents the concentration of KOH used in the titration. 10 g was the mass of oil sample used in the analysis.
- FFA: The acid was evaluated by the following formula, $\frac{\text{Acid Value}}{2}$ and it was found to be higher than 1 wt% FFA which warranted alkali transesterification hence pretreatment was performed to reduce the FFA wt%. The acid number was 11.26 mg of KOH which corresponds to 5.63 wt% FFA [17] (Banani et al., 2015).
- Pretreatment was done with HCL until it became 0.786 mg of KOH equivalent to 0.393 wt% FFA which is below 1 wt% FFA, therefore the next step was alkali transesterification as shown in Figure 3.
- The WCO biodiesel was made by reacting 100 mL of oil, with methanol using a molar ratio of 6:1 and 0.5 g of sodium hydroxide (NaOH) and the reaction was maintained at 60 °C by means of a water bath giving a yield of 95 %.
- The WCO biodiesel was separated from glycerol after an interval of 12-hour.
- FFA and glycerol were removed from the flask and bubble washing was utilized to get rid of the remaining FFA and glycerol.
- Methyl esters were collected from the flask and heated to 120 °C to remove the water content make pure biodiesel as shown in Figure 3 above.

WCO biodiesel was produced from the two-step transesterification process in order to maximize the yield of fuel. According to Atadashi et al. (2012a) and Atadashi et al. (2012b), alkali transesterification has been found to be suitable when FFA composition of oil is below 1 wt% although some researches have emphasized that 3 wt% FFA is the minimum acceptable value for the homogenous alkali catalyzed transesterification process (Atadashi et al., 2012a). In this research 1 wt% was taken as the benchmark for the alkali catalyzed process initiation.

2.2. Nano Blended Fuels Preparation

The nano particles Al_2O_3 and CeO_2 were bought from Sigma-Aldrich (Johannesburg, South Africa). The nano particles nCeO_2 (nano powder 50 nm, CAS No 1312-38-01), nAl_2O_3 (50 nm, 20 wt% in water, CAS No 1344-28-10) were characterized using a ZEISS scanning electron microscope (SEM) (Germany) at 20.0 kV and specs and appeared as shown in Figure 1 and Figure 2. The nano particles were weighed in 50 ppm dosages by utilizing an electronic balance and then mixed with biodiesel fuel blends by use of an ultrasonicator set at a frequency of 100 W and 50 kHz for 30 minutes. The formed nano fuel was utilized immediately to counter the occurrence of sedimentation which would otherwise impact

negatively on the outcome. Five fuels were prepared for tests and these were FD, WCO (WCO100), WCO nano additive biodiesel comprising 50 ppm Al₂O₃ and 50 ppm CeO₂ (WCO100A50C50), WCO biodiesel fossil fuel blend consisting 20 % biodiesel and 80% fuel diesel (WCO20), and WCO biodiesel blend comprising 20 % WCO biodiesel and 80 % FD plus 50 ppm Al₂O₃and 50 ppm CeO₂(WC20A50C50).

Table 4: Description of Nano Particles used

Description	Specification	
	1	2
Manufacturer	Sigma -Aldrich Johannesburg	Sigma -Aldrich Johannesburg
Nano Particle	Cerium Oxide (CeO ₂)	Aluminum Oxide (Al ₂ O ₃)
CAS No	1312-38-01	1344-28-10
Average Size	30 - 50 nm	30- 60 nm
Surface Area	32 m ² /g	120 m ² /g
Appearance	White to Yellow	White

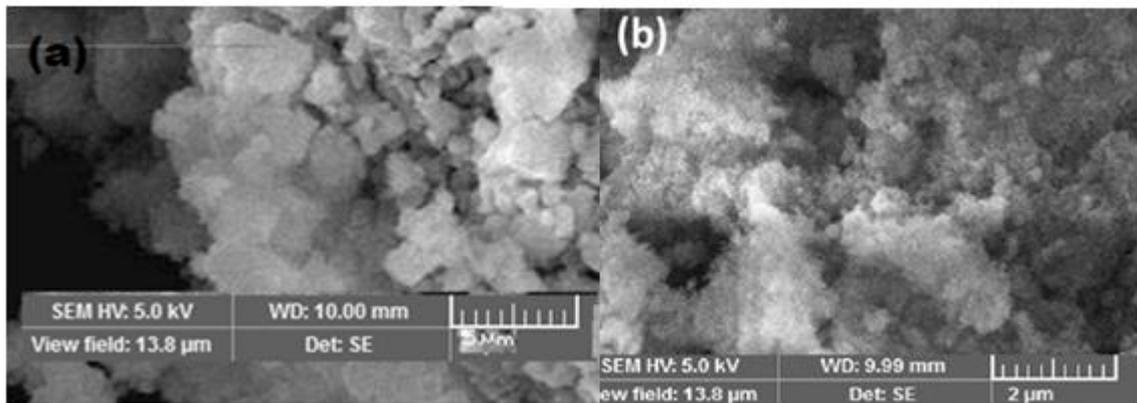


Figure 1: Aluminum Oxide as received from Manufacturer

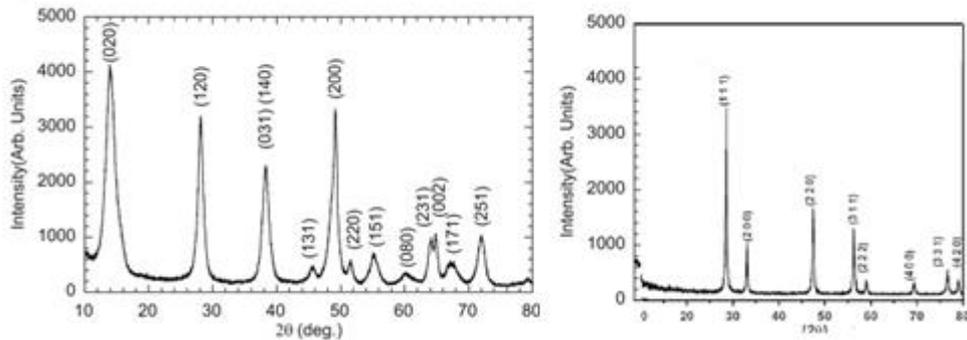


Figure 2: Aluminum Oxide and Cerium Oxide as received from Manufacturer

3. EXEPRIMENTAL CONFIGURATION

3.1. Engine Test and Procedure

The experimental analysis was executed at University of KwaZulu-Natal Mechanical Engineering research center. The engine test was performed on a two-cylinder Kirloskar engine 4-stroke water-cooled that was run at a steady speed of 1 500 rpm. The engine was coupled to an eddy current dynamometer, the setup is shown in Figure 4. Computerized data

acquisition was utilized for data retrieval and storage. A load cell on the dynamometer was used to evaluate the load ratings. Inlet and exhaust gas temperatures were measured using two thermocouple modules. Fuel measurement were done using two burettes which were attached to each fuel tank as shown in Figure 5. Engine loading in 10 % increments was conducted at a constant speed of 1 500 rpm. An AVL 444DI gas analyzer was used for gas estimations of NO_x, UBHC, CO₂ and CO while an AVL 437 C smoke meter was utilized for smoke opacity measurement. The experimental analysis of fuel properties, engine performance, and emission behavior is discussed in the results section. The engine was at first fueled by FD fuel during warm up for 10 minutes to reach steady state conditions after which performance and emission characteristics were evaluated. At that point FD, WCO100, WCO100A50C50, WCO20, WCO20A50C50 were evaluated over the course of three tests at each stage then averaging of the results.



Figure 4: Engine and Data Acquisition Set up

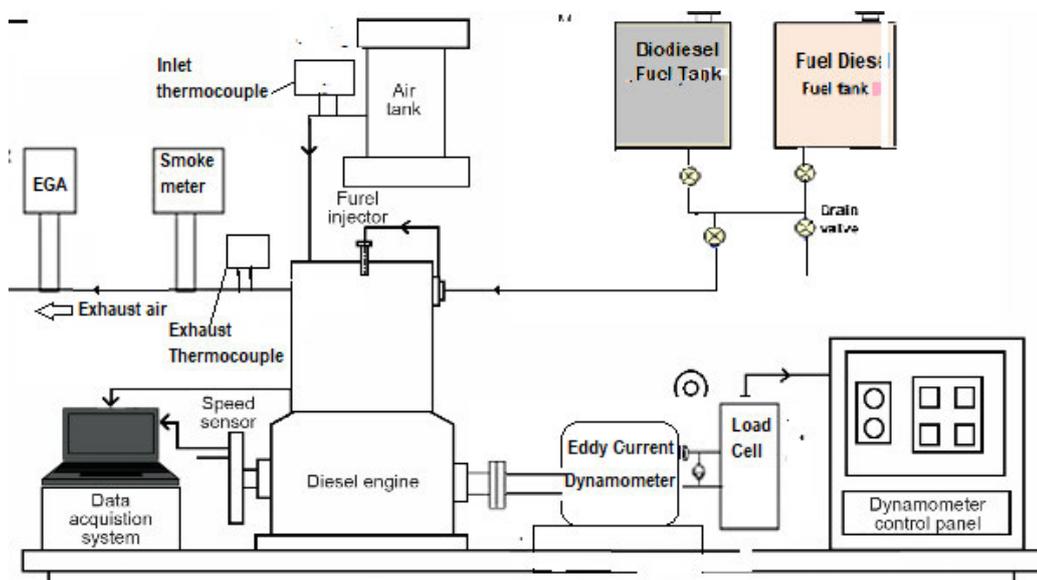


Figure 5: Engine Test Configuration

Table 4: Engine Specifications used in the Experiment

Parameter	Position value
Engine Model	Kirloskar
Type	Two cylinder, horizontal 4 - stroke, DI
Cooling Medium	Water cooled
Revolutions per Minute	1300 rpm (constant)
Rated Brake Power	5.2 kW (7Hp)
Cylinder Bore	87.5 mm
Piston Stroke	110 mm
Compression Ratio	17.5 (variable)

Injection Timing 23° BTDC

Injection pressure 220 bars

Loading System Eddy Current Dynamometer

Table 5: Properties of the Fuels used in the Research

Property	ASTM standards	Fossil Diesel	WCO100	WCO100A50C50	WCO20	WCO20A50C50
Density (kg/m ³) @ 20	D1298	833	880	870	862	844
Viscosity (cSt) @ 40	D445	2.28	3.53	3.10	2.84	2.52
Cetane Number	D613	56	58	54	55	52
Calorific Value KJ/KG		43.1	40.1	41.8	41.4	42.9
Flash Point °C	D92	82	156	162	161	164
Cloud Point °C	D97		-2	-3	-2	-4
Pour Point °C	D97		-3	-3	-3	-3

Table 6: Uncertainties Estimations of Measured and Calculated Parameters

Quantity		Range	Accuracy	Uncertainty
AVL gas analyzer	NO _x	0–5000 ppm	±10 ppm	±0.2
	HC	0–20000 ppm	±1 ppm	±0.3
	CO	0–10 vol %	±0.01%	±0.22
	CO ₂	0–20 vol %	±0.03%	±0.21
AVL smoke meter		0%–100%	±0.2%	±0.22
Thermocouple		0 – 1000 °C	±1 °C	±0.15
Dynamometer		0–250 V, 0–25 A	±1 V, ±0.5 A	±.05,±0.1
In-cylinder pressure		0–220 bars	±0.2 bar	±0.1
Crank Angle encoder			±1	±0.25
Exhaust gas temperature			±2 °C	±0.1
Brake Power				±0.75
Brake specific fuel consumption				±0.80

The error of the experimental procedure was evaluated as follows and the overall uncertainty was 1.26 %. The uncertainties of measured and calculated parameters are shown in Table 6 above.

$$\text{Overall uncertainty} = \sqrt{\text{uncertainty of } (N)^2 + (BTE)^2 + (BSFC)^2 + (CO_2)^2 + (CO)^2 + (NOX)^2 + (UBHC)^2 + (EGT)^2 + (\text{smoke})^2}$$

4. RESULTS AND DISCUSSIONS

4.1. Fuel properties

The results of fuels were tested according to the ASTM D6751 method in the laboratory at University of KwaZulu-Natal Mechanical Engineering research center and tabulated in Table 5. The tested parameters were kinematic viscosity, density, calorific value, flash point and cetane number. Kinematic viscosity of FD, WCO100, WCO100A50C50, WCO20 and WCO20A50C50 were 2.28 mm²/s (cSt), 3.38 mm²/s (cSt), 2.83 mm²/s (cSt), 2.72 mm²/s (cSt) and 2.42 mm²/s (cSt) respectively. Kinematic viscosity of WCO100 was about 48.6 % higher than that of FD while that of WCO was 24.65 % higher than that of FD. Addition of nano additives reduced the base fuel kinematic viscosity significantly with WC100A50C50 improving viscosity of WCO100 by almost 14 % and WC20A50C50 decreasing it by 12 %. Kinematic viscosity of base fuels decreased with addition of the hybrid nano additive. Kinematic viscosity is vital for enhancing atomization of fuel in the combustion chamber (Knothe & Steidley, 2005). The kinematic viscosity of all fuels was within the acceptable limits of between 3.5 cSt and 5 cSt as required by the ASTM D445 standard. Calorific value is also a vital fuel property as it denotes the amount of energy which can be liberated by a given fuel and the greater the CV the higher the energy produced by the fuel. The CV of WCO100 and WCO20 increased with addition of the hybrid nano additive. The increases in CV with the addition of the hybrid nano additive were in tandem with the values found by Prabu (2018) and Mirzajanzadeh et al. (2015). The CV values of the tested fuels for FD, WCO100, WCO100A50C50, WCO20, WCO20A50C50 were 43.10 kJ/kg, 40.10 kJ/kg, 41.8 kJ/kg, 41.4 kJ/kg and 42.9 kJ/kg respectively. This shows that addition of nano additives improved the CV values of the base fuels significantly. Cetane number is used to measure fuel tendency to self-ignite, a key property in cold starting conditions; this was higher for WCO100 and its blends compared to FD. Cetane number for WCO100, WCO100A50C50 WCO20, WCO20A50C50 and FD were 58, 56, 55, 52 and 56 respectively. All cetane numbers for WCO100 and its blends were higher than the ASTM D6751 stipulated minimum value of 47. Flash point was noted to increase with additive addition for all base fuels. Thus, a decrease in cetane number and an increase in flash number were noted from the analysis of tests results with addition of hybrid nano particles to base fuels. The results were in tandem with what was revealed by Kannan, Karvembu and Anand (2011).

4.2. Effects on Performance Characteristics

4.2.1. Brake Thermal Efficiency (BTE)

According to Yadav et al. (2016) brake thermal proficiency (BTE) is defined as the proportion of actual engine work output to the energy provided by fuel. It is a measure of the engine' ability to convert fuel energy into mechanical energy. This parameter is a critical pointer of engine performance estimation particularly when engine performance is evaluated against load. From the experimental results the BTE of all fuels increased marginally with load. Mean BTEs for WCO20A50C20 FD, WCO20, WCO100A50C50 and WCO100 were 28.01 %, 26.43 %, 25.56 %, 22.70 % and 21.21 % respectively. A maximum increase of 11.10 % with WCO20A50C50 compared to FD at full load was noted. The

improvement in BTE can be attributed to reduced ignition delay and complete combustion with nano additive addition compared to neat biodiesel blends (Ozsezen & Canakci, 2011). Furthermore, addition of nano additives promoted higher cylinder temperatures, increased oxidation rates, and a better evaporation of the fuels which ultimately resulted in improved BTE. WCO100 exhibited the lowest BTE in all tests. This can be attributed to its high kinematic viscosity and density. WCO100 kinematic viscosity was 48.6 % higher than FD fuel and this can be the causative effect on the reduction in BTE of 24.6 % compared to that of Fossil diesel fuel. Kinematic viscosity has an impact on the spray characteristics of a fuel. Higher kinematic viscosity results in poor spray pattern and large particle generation which will eventually lead to poor combustion profiles and lower BTE. The kinematic viscosity of WCO20 was also higher than that of FD by a small margin of 18.8 % which explains why the average BTE of WC20 was closer to FD falling short by a small margin of 3.4 %. Thus, addition of hybrid nano additive the fuel blends improved kinematic viscosity. WCO10A50C50 and WCO20A50C50 exhibited better kinematic viscosity compared to their neat WCO100 and WCO20 counterparts. Nano additives act as catalysts which improved the fuel blends. Nano additives promote rapid evaporation in the combustion chamber and shorter ignition delays which improves the engine combustion process.

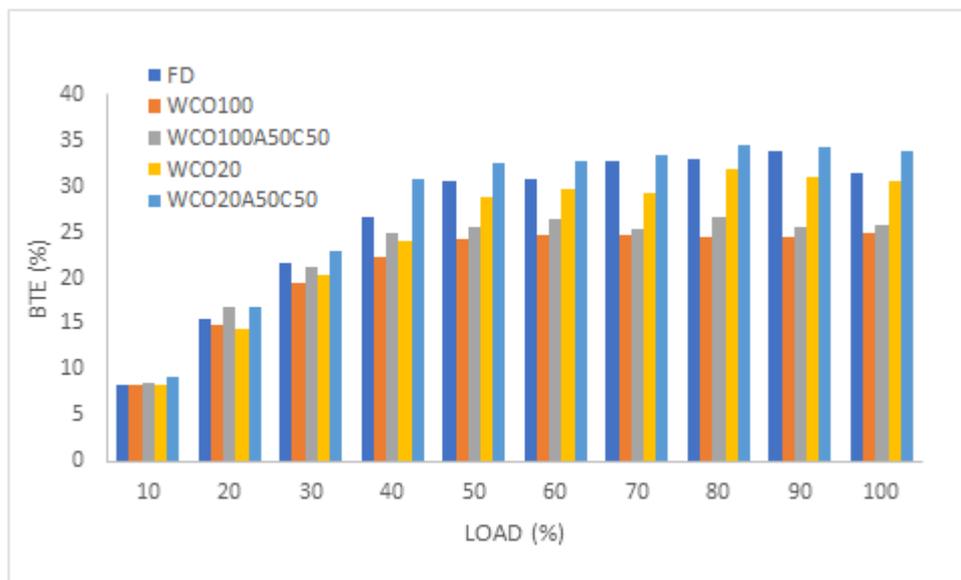


Figure 6: BTE vs Load

4.1.2. Brake specific Fuel Consumption (BSFC)

The analysis of experimental outcomes shows a decreasing trend of BSFC with load as shown in Figure 7. BSFC gives a measure of the amount of fuel that is burned through to create 1 KW per hour. These decreasing patterns when evaluated against load are influenced by the increasing trend in BP with load. Mean BSFC from the analysis for FD, WCO100, WCO100A50C50, WCO20, WCO20A50C50 were 313 g/kWh, 348.8 g/kWh, 292.1 g/kWh, 320.5 g/kWh and 280 g/kWh respectively. WCO100 showed higher BSFC in comparison to FD and this is attributed to its calorific value which is 7 % lower than that of FD. Lower CV will promote retarded evaporation rate and poor combustion profiles resulting in more fuel being burnt to produce 1 kW per hour. This pattern follows a comparative pattern to BTE variation with load. WCO20 likewise demonstrated higher BSFC in comparison to that of FD, although this increase was marginal. Introduction of nano additive substances comprising Al_2O_3 and CeO_2 improved the CV of fuel mixes and brought them closer to that of FD. This resulted in the base fuel exhibiting improved BSFC in comparison to that of FD. Nano additive substance have higher

surface area to volume proportion, higher thermal conductivity, and initiate increased evaporation rate and shorter ignition in comparison to that of FD.

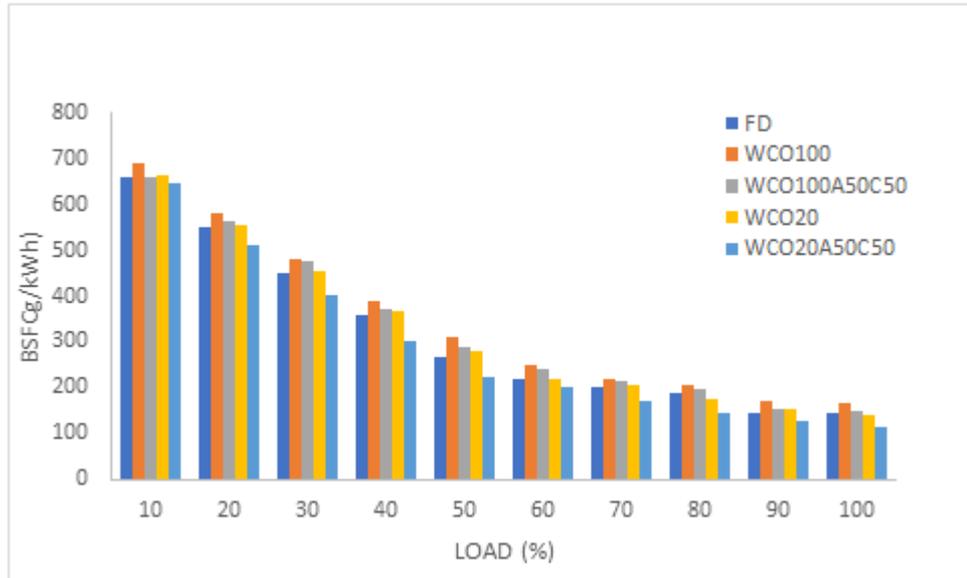


Figure 7: BSFC vs Load

4.2. Effects of on Emission Characteristics

Exhaust emissions are created at various temperatures and oxygen availability during the combustion process; this makes it impossible to simultaneously target their disposal (Tock et al., 2013). Carbon monoxide is created at low temperature cycles while NO_x are generated during high temperature durations of the combustion cycles. Both UBHC and CO are a result of inadequate oxygen thus these can be wiped out by increasing oxidation measures. An outline of exhaust substances is provided below along with certain clarifications regarding the outcomes derived from exploratory assessment. Both Al₂O₃ and CeO₂ have the capacity to shift their valence thus empowering the freedom of oxygen which can at that point be used to improve the oxidation process. This will lessen most of the harmful gases created inside the combustion chamber. CeO₂ has the ability to shift its valence from Ce⁴⁺ to Ce³⁺ and this low redox reaction makes CeO₂ a unique nano particle as shown in Eq. (2) below (Ozsezen & Canakci, 2011). Al₂O₃ additionally breaks down into Al₂O and O of which Al₂O is very unsteady separates into 2Al and 1/2O₂ empowering it to free another O₂ which is likewise accessible for oxidation of CO into gases into CO₂ as shown Eq. (3) and Eq. (4).



This reaction permits CeO₂ to free an oxygen particle which is accessible to advance burning inside the chamber. Essentially Al₂O₃ separates to Al₂O and 2O of which Al₂O is insecure at high temperatures and separates to shape 2Al 1/2 and O₂ as in Eq. (3 and 4) permitting it to free O₂ for oxidation measures during the burning cycle:



4.2.1 Nitrogen Oxides (NO_x)

NO_x refers to a combustion mixture of nitrogen oxide (NO) and nitrogen dioxide (NO₂). NO_x are hazardous gases which contribute immensely to ozone depletion and human respiration problems. NO_x also constitute other gases such as N₂O and N₂O₄ but these are in negligible quantities. NO_x is comprised mostly of NO gases (almost 90 %) and the rest is NO₂ and small traces of N₂O and N₂O₄. Hence, the NO_x of neat biodiesel blends is higher than FD. Hybrid nano particles availability within the base fuel promote chemical conversion of NO_x to N₂. Variation of NO_x with load is shown in Figure 9. NO_x emissions for biodiesel blends WCO100 and WCO20 are higher compared to those of FD with load. This is attributed to higher O₂ content in biodiesel which promotes higher temperatures (Ozsezen & Canakci, 2011). High temperatures form a favorable environment for atmospheric nitrogen to react with oxygen to form NO and NO₂ gases. Addition of a hybrid nano additive resulted in significant reduction in NO_x for neat biodiesel blends using Eq. (5) and Eq. (6).



Al₂O₃ likewise reacts with NO to produce nitrogen gas at high chamber temperature duration of burning cycle (Scattergood, 2006). Sajith, Sobhan and Peterson (2010) credit formation of NO and NO₂ from high temperature conditions which initiate reaction of oxygen and nitrogen. The authors report that this may be the reason for biodiesel and blends producing NO_x emissions. In contrast to that, the authors contend that incomplete combustion brings about increased deposition of carbon on the walls of the combustion chamber which consequently creates an insulation layer. This insulation layer is noted to promote higher temperature generation inside the combustion chamber which subsequently brings about higher NO_x development. This phenomenon assists with clarifying the explanation for significant decrease in NO_x with the addition of a nano additive substance. The Al₂O₃ and CeO₂ hybrid nano additive has oxygen atoms which are used for oxidation. This makes complete combustion which inhibits creation of an insulation layer on the walls of the combustion chamber absence of this insulation layer promotes high heat transfer and low temperature combustion chamber profiles. This will subsequently suppress NO_x generation thereby reducing their emission into the atmosphere.

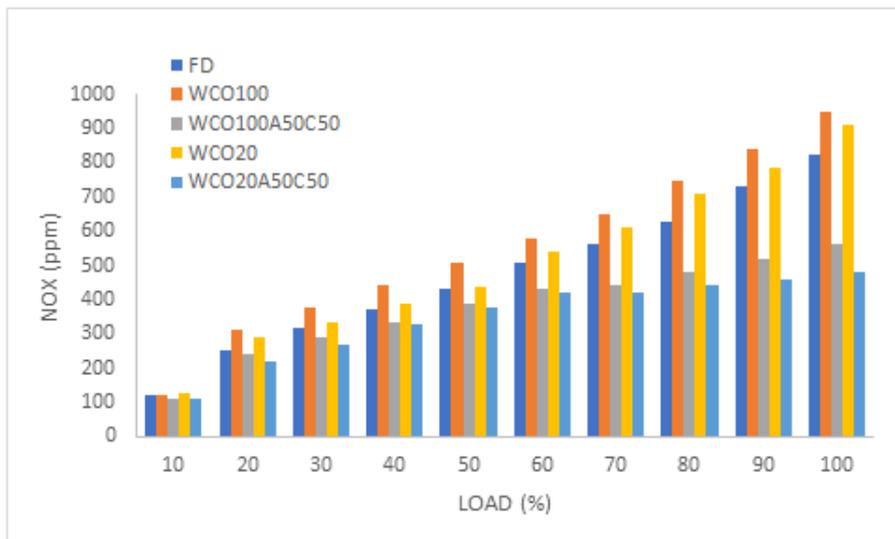


Figure 8: NO_x vs Load

4.2.2. Carbon Monoxide (CO)

WCO100 and its blends displayed lower CO discharges when compared with FD fuel. This is attributed to the availability of a higher oxygen content in biodiesel compared to FD. The availability of oxygen influences higher transformation of CO to CO₂. The introduction of a hybrid nano additive has the capacity to act as a reaction catalyst which increases the gap found between CO₂ values of FD and the biodiesel and its blends. Mean CO values for WCO20A50C20 FD, WCO20, WCO100A50C50 and WCO100 were 0.042 %, 0.059 %, 0.061 %, 0.068 % by volume when measured against load. A gradual decrease in CO emissions with load was noted for loading below 40 % after which it began to show a rise with increase in load. The greatest reduction in CO of 36.8 % was noted with WCO20A50C50 when compared with FD results. Addition of Al₂O₃ promotes rapid oxidation of CO to CO₂ (Santhanamuthu et al. 2016). Al₂O₃ disintegrates into Al₂O and O at higher temperatures. The formed Al₂O is reported to be unstable and further disintegrates into 2Al and ½O₂ as shown above in Eq. (3) and Eq. (4). The resulting O₂ will be available for converting CO to CO₂ as per Eq. (7).



CeO₂ tends to shift its valence from CeO₂ (+4) to Ce (+3) enabling it to provide an oxygen atom for reduction processes. According to Ozsezen and Canakci (2011), carbon monoxide is produced as result of incomplete combustion. Making more oxygen available within the combustion chamber is essential to suppress CO formation processes. The oxygen donated will be able to accelerate rapid oxidation of CO to CO₂ as shown in Eq. (8)



This clarifies why addition of the nano additive to biodiesel reduced the CO emissions significantly.

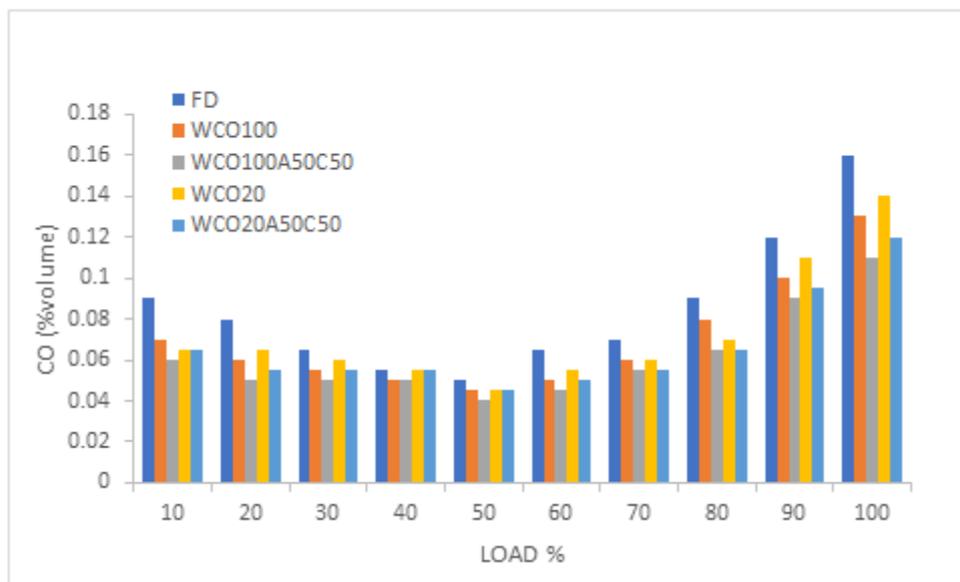


Figure 9: CO vs Load

4.2.3. Unburnt Hydrocarbons (UBHC)

The variation of UBHC depicted by the various fuels used in the experiment against load is shown in Figure 10. Biodiesel fuels and their blends showed lower UBHC compared to those of FD. UBHC are produced in oxygen deficient regions of the combustion chamber hence their generation is suppressed by the higher oxygen content available in biodiesel fuels.

Addition of a hybrid nano particles which can act as an oxygen buffer lowered the UBHC even further. At higher loads WCO100A50C50 showed the lowest UBHC values compared to all other fuels. Eq. (9) shows how the addition of Ce_2O_3 enables the reduction of UBHC by oxidizing them into CO_2 plus water vapor (Chandrasekaran, Arthanarisamy, & Nachiappan, 2016).

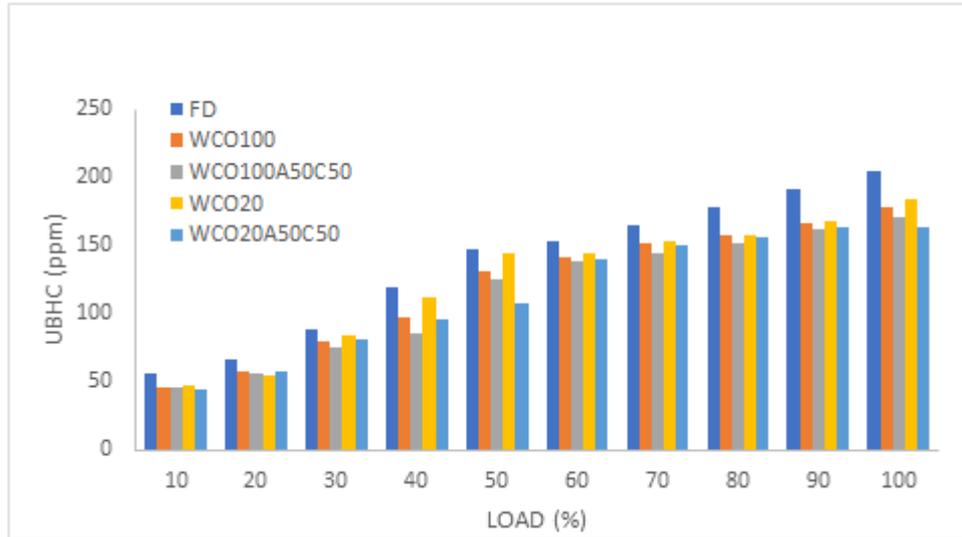


Figure 10: UBHC vs Load

4.2.4. Smoke Opacity

As indicated by Venkatesan et al. (2017) smoke opacity quantifies the solid hydrocarbon soot particles occurring in the exhaust gases of internal combustion engines. This measure is utilized to underline the rate of smoke generation during the combustion process. In this study smoke opacity showed an increment with increase in loading for all the fuels as shown in Figure 11. This came about because of an increment of fuel utilization with increasing load. FD showed higher smoke opacity at all loading conditions. This can be attributed to its low kinematic viscosity compared to the other fuels which tends to shorten combustion duration which result in more smoke generation (Devan & Mahalakshmi, 2009). WCO100 and its blends contain a higher oxygen content which improves total burning rates which results in less smoke creation in comparison to that FD. From experimental analysis it can be deduced that WCO100 revealed lower smoke opacity compared WCO20 at higher loading conditions. Smoke is generated in oxygen deficient or fuel rich zones within the combustion cylinder. The reduction in smoke opacity with WCO100 signified that biodiesel fuels show better oxidation characteristics than FD fuels do. Addition of the hybrid nano particles resulted in a significant reduction in smoke opacity compared to neat WCO biodiesel. High cetane number and high surface area to volume ratio of the nano additives result in rapid evaporation, shorter ignition delay, and improved combustion processes which causes lower smoke generation hence lower smoke opacity compared to biodiesel FD and their neat blends. The soot is converted to carbon dioxide as shown in Eq. 10 below.



Ignition delay is the duration between start of injection and start of combustion. Shorter ignition influences an

improved air-fuel mixing process hence better combustion characteristics and lower smoke generation. Addition of nano additives improved the cetane number of base fuel and lowered kinematic viscosity, factors which are essential for better combustion efficiency. The lower the kinematic viscosity the smaller the viscous drag on fuel particles during injection and this result in generation of smaller droplet size and better spray profile prompting the lower smoke creation. These discoveries are comparable to those unveiled by Bari (2014) in which a decrease of 65 % in smoke opacity was found with nano added substance addition in comparison to that of FD.

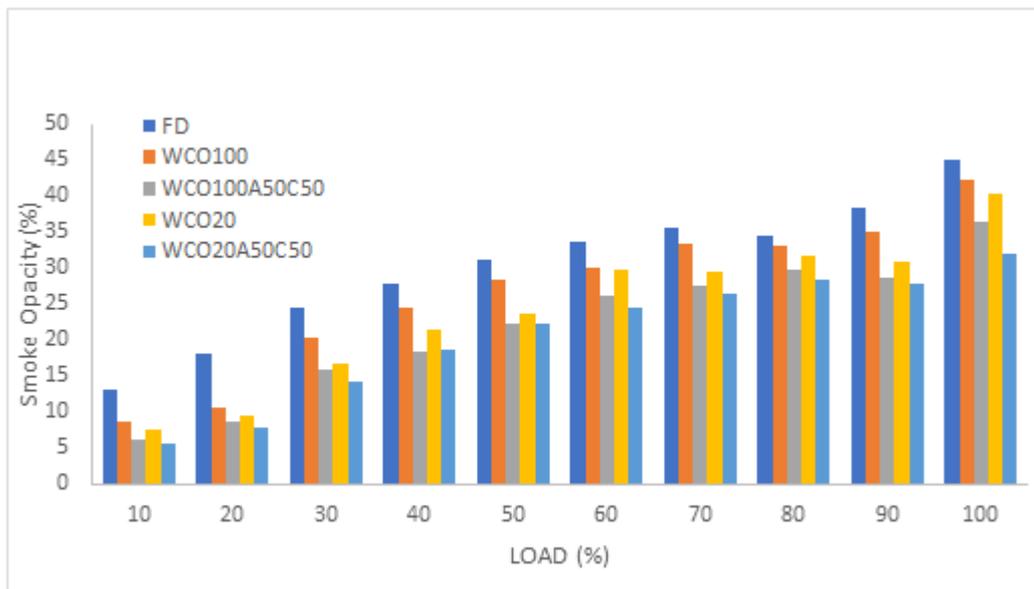


Figure 11: Variation of Smoke Opacity with Load

4.2.5. Exhaust Gas Temperature (EGT)

Exhaust gas temperature (EGT) gives a measure of amount of waste heat present in exhaust gas emissions. The variation of EGT with load are shown in Figure 12. It is evident that EGT increases with load for all fuels. EGT increases can be attributed to an increase in fuel consumption as the engine heats up to load. Increase in flame temperature with load subsequently results in a rise in EGT as load increases. WCO100 revealed the highest EGT with load at full load.

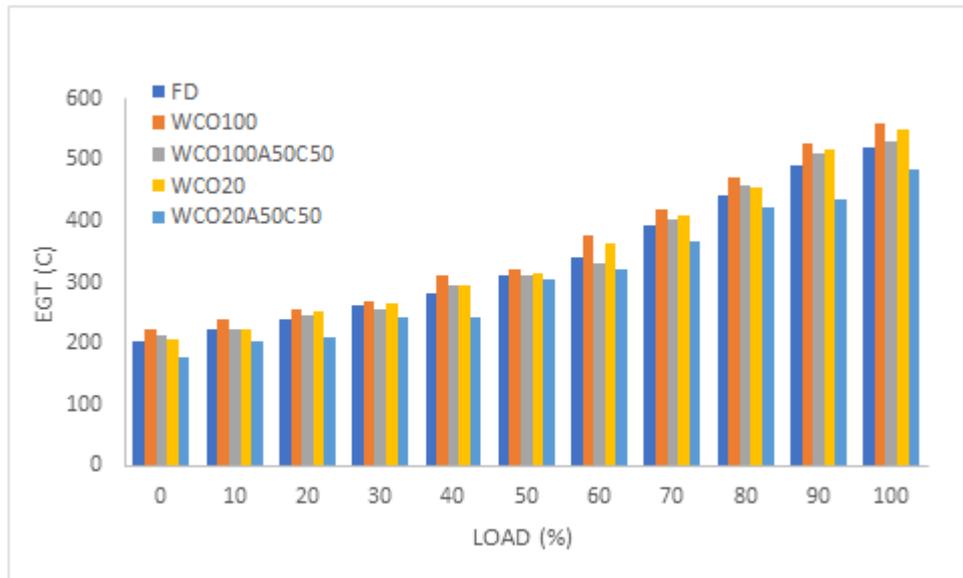


Figure 12: Variation of Exhaust Gas Temperature (EGT) with Load

4.2.6. CO₂

Variation of CO₂ emissions are shown in Fig. 13 below. It is clearly evident that CO₂ emissions were lower for FD in comparison to neat biodiesel and its blends WCO100 and WCO20 respectively. This can be credited to unrivaled C/H proportion for FD contrasted with biodiesel and its mixes. Other prominent clarifications on the variables are efficient fuel utilization profile for BD and its blends which advance higher CO₂ generation because of consuming more fuel to create a similar work out as that of FD (Basha & Anand, 2011). Babu and Anand (2017) report that the higher CO₂ is brought about by high oxygen content bringing about expanded conversion of carbon into CO₂. Babu and Anand (2017) attributes the higher CO₂ discharges from higher CN quantities of WCO100 and its blends prompting more reduced ignition delay, and increased conversion of CO to CO₂.

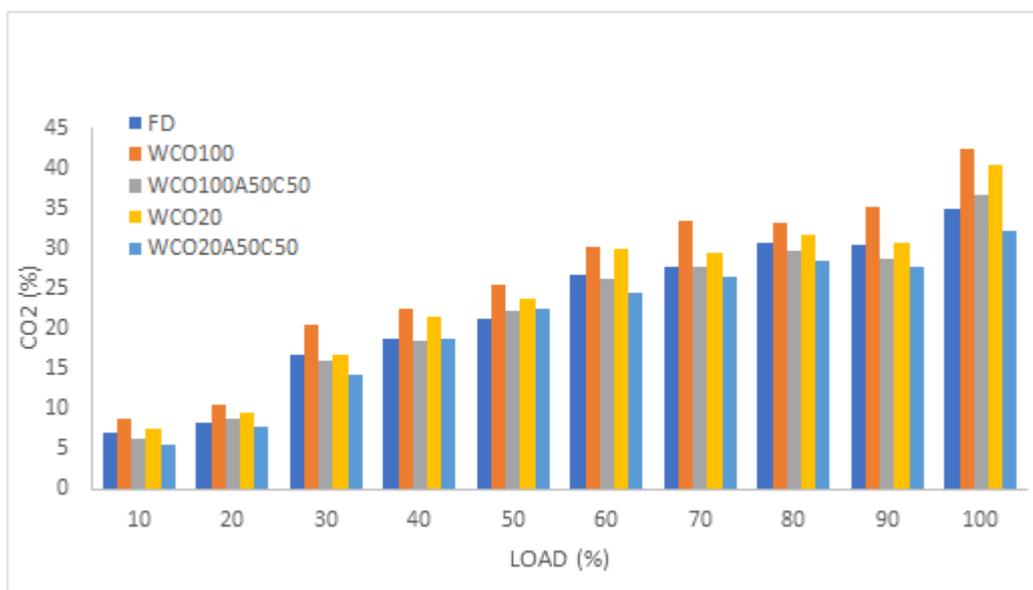


Figure 13: Variation of CO₂ with Load

5. CONCLUSIONS

This work underlines the significance of adding nano metallic particles to WCO biodiesel and its blends to improve fuel properties, engine performance, and reduce exhaust gas emissions. The experimental analysis arose because of the lack of agreement between previous research results regarding the addition of nano particles to biodiesel and blends and the influence on performance and emissions behavior. Therefore, hybrid nano particles were developed and added to base fuels which increased the calorific value of biodiesel and its blends bringing them closer to the calorific value of FD. This research study found that the addition of nano particles decreased kinematic viscosity of the biodiesel fuels and its blends. A reduction in kinematic viscosity enables biodiesel and its blends to improve their fuel atomization capability enabling better combustion profiles, better engine performance, and emissions reduction.

As per the performance test results it is possible to infer that addition of hybrid nano particles prompted BTE improvement by a limit of 6.22 % and decreased BSFC by a limit of 10.2 %. From the investigation of emission results it was noticed that NO_x was diminished by 25.62 %, CO by 36.8 %, UBHC by 27.8 % and CO₂ by 31.23 % with addition of a hybrid nano additive to biodiesel compared to FD NO_x emissions. Decrease in smoke opacity by 17.68 % was likewise noted with the addition of nano additives to biodiesel and its blends. The results of WCO20A50C50 are highlighted since this blend revealed superior fuel properties, engine performance, and exhaust gas emissions features.

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CHAPTER 5: MODELING AND OPTIMIZATION OF ENGINE PARAMETERS ON DIESEL ENGINE FUELED FROM WASTE COOKING OIL BIODIESEL BLEND DOPED WITH HYBRID NANO PARTICLES

This chapter provides a report on an experimental work performed to model and optimize engine parameters on a diesel engine fueled from hybridized nano particles. The outcome of the work was published in the International Journal of Innovative Science, Engineering and Technology, ISSN 2348 - 7968

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Modeling and Optimization of Engine Parameters On Diesel Engine Fueled From Waste Cooking Oil Biodiesel Blend Doped With Hybrid Nano Particles

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Abstract

The aim of this investigation was to model and optimize engine parameters on an engine fueled from waste cooking oil (WCO) doped blend (WCO20) with hybrid nano particles consisting of cerium oxide and aluminum oxide. Experimental investigation was performed on a variable compression engine at varying load conditions. To understand the combined impact of several engine conditions on performance and emissions, several engine trials ought to be performed. However, engine tests are tedious and expensive the more variables there are being evaluated. Modeling and use of advanced statistical tools can reduce the number of engine trials and make engine research more cost effective. Hence, in this examination, design of experiments (DOE) using the response surface method (RSM) was performed to model and optimize WCO20 performance and emissions parameters. This was done by utilizing a variable compression engine and selecting three variables (hybrid nano particle blends [fuel blend]), compression ratio (CR) and load as input parameters while the analyzed responses were brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), nitrogen oxides (NO_x), unburnt hydrocarbons (UBHC), carbon monoxide (CO) and smoke. Optimization of engine response parameters was done utilizing Derringers desirability approach. From the analysis of results it was revealed that a desirable CR of 14.71, load of 74.98 % and hybrid blend of 60 ppm yielded the best engine responses with BTE of 33.63 %, BSFC of 0.292 kg/kWh, NO_x of 700 ppm, UBHC of 25 ppm, CO of 0.361 % and smoke opacity of 33.9 %. Once the optimal variables were determined, confirmation tests were performed to compare the experimental values against those found by the optimization process. The R² value, which provides an indication of the quality of the model against experimental data, showed that these were in high agreement. The outcomes acquired from this examination showed that RSM is a viable technique for improvement of parameters of biodiesel blends doped with nano particles in diesel engines.

Keywords: Waste cooking oil biodiesel, properties, performance, emissions, modelling and optimization, response surface method, nano particles, compression ratio.

NOMENCLATURE AND ABBREVIATIONS

AL ₂ O ₃	Aluminum oxide	NOx	Nitrogen oxide
ANOVA	Analysis of variance	N ₂	Nitrogen gas
ASTM	American Society for Testing and Materials	UBHC	Unburnt hydrocarbon
BD	Biodiesel	WCO20	Waste cooking oil biodiesel blend of 80 % fossil diesel and 20 % biodiesel
BSFC	Brake specific fuel consumption	WCO20H20	Waste cooking oil biodiesel blend of 80 % fossil diesel and 20 % biodiesel containing 10 ppm cerium oxide and 10 ppm aluminum oxide
BTE	Brake thermal efficiency	WCO20H40	Waste cooking oil biodiesel blend of 80 % fossil diesel and 20 % biodiesel containing 20 ppm cerium oxide and 20 ppm aluminum oxide
CeO ₂	Cerium oxide	WCO20H60	Waste cooking oil biodiesel blend of 80 % fossil diesel and 20 % biodiesel containing 30 ppm cerium oxide and 30 ppm aluminum oxide
CN	Cetane number	WHO	World Health Organization
CO	Carbon monoxide		
CO ₂	Carbon dioxide		
CV	Calorific value		
DOE	Design of experiments		
FD	Fossil diesel		
FFA	Free fatty acid		
kW	Kilowatt		
KOH	Potassium hydroxide		
NaOH	Sodium hydroxide		

1. INTRODUCTION

The current continuous expansion in the global population has promoted interest in transportation fuel because the fossil diesel (FD) fuel global demand is anticipated to reach around 50 million oil-equivalent barrels each day by 2040 (Brown 2014). The downside of increased FD utilization in the transportation area is that such fuel is a significant cause of greenhouse gas emissions. These emissions have greatly impacted on human health globally. The WHO states that there are about 4.2 million deaths yearly because of air contamination mostly coming from combustion engines exhaust gases (Zhang et al., 2020). To make diesel engines sustainable, three options are available for emission reduction and performance improvement: engine modification, fuel adjustments and/or exhaust after-treatment measures. Fuel modification is gaining most attention because it is easily achievable considering that it is possible to implement on the engines already on the road (Shaafi et al., 2015). Biodiesel (BD) fuel has emerged as the frontrunner to replace FD in combustion ignition engines. BD is a nontoxic, sustainable biodegradable methyl ester derived from vegetable oil and animal fats (Saraee et al., 2015). Combustion of BD and its blends with FD result in significant reduction in exhaust gas emissions. BD burning results in a decrease in discharge of carbon dioxide (CO₂) and hydrocarbon emissions, but drawbacks are high viscosity, low energy content, low volatility, poor cold flow properties and high NO_x emissions, as shown in Table 1.

Table 1. Drawbacks of using neat biodiesel / diesel blends as fuels (Tomar & Kumar, 2020)

Drawback	Drawback cause
1. Poor cold flow properties	Higher cloud, pour point of diesel/biodiesel
2. Appalling lubrication characteristics	Non-combustible fuel diluting the engine oil
2. Low engine output	Lower heating value, incomplete combustion of fuel
3. High specific fuel consumption	Higher density and viscosity
4. Higher ignition lag	Lower calorific value, low cetane number
5. Poor atomization characteristics	Bigger sauter mean diameter, high surface tension, high viscosity
6. Higher NO _x emissions	Improper combustion, higher oxygen
7. Deterioration of engine parts	High viscosity, incomplete combustion of fuel

Increased engine deterioration is also a major drawback for BD due to its high viscosity. High viscosity also results in poor spray atomization leading to incomplete combustion. Viscosity influences formation of fuel droplets as higher viscous forces disturb the rate of fragmentation which results in formation of large fuel droplets. Most of above-mentioned operational drawbacks can be corrected by blending the BD or BD-FD mixes with fuel additives, a process called fuel adulteration or fuel reformulation. Fuel reformulation is cheap and simple to execute (Ying et al., 2006). Over the last 20 years, researchers in the nanotechnology field have investigated the intriguing properties of nano particles, including their high surface area to volume ratio, exceptional thermal conductivity features, high melting point, and good stability properties which can all be utilized to improve properties of fuels (Yetter et al., 2009). According to (Yetter et al., 2009), adding metallic nanoparticles inside the burning chamber expands the heat transfer rate which shortens the ignition delay. This enables performance enhancement and emissions reduction.

Metal oxide nano additives are reported to increase surface area to volume ratio by donating their oxygen atoms to the fuel mixture (Shaafi & Velraj, 2015). Decrease in ignition delay and better burning features are some of the unique properties of nano materials which have been utilized by ignition design specialists (Mehta et al., 2014). The most well-known utilized metal-based nano added substances are boron, iron, aluminum and ferric chloride as well as metal oxide-based nano added substances, for example, cerium oxide, titanium oxide, zinc oxide, and manganese oxide. Metal oxide nano additives are preferred due to their better composition which promotes improved fuel combustion (Saraee et al., 2015). Several metallic nano added substances, including cerium and aluminum, have been researched (Saraee et al., 2015). For viable fuel and nano added substance blends, ultrasonic machines and surfactants are used for better outcomes. The added substance must fulfill certain necessities in order to meet all requirements for fuel debasement: 1) reduction in exhaust gas emissions 2) Must not decrease in particulate filter operational effectiveness 3) hold the chemical stability of the base fuel 4) be able to retain engine operational conditions (Chłopek et al., 2005). Introduction of fuel additives assist in rectifying the drawbacks mentioned above as well as ensuring that the BD conforms to international standards.

Various investigations have found that waste cooking oil (WCO) BD is a viable alternative source of fuel for compression ignition (CI) engines (Enweremadu & Rutto, 2010; Ghobadian et al., 2009; Lin et al., 2011). However, increment of the WCO BD proportion in diesel-biodiesel blends produces higher exhaust gas temperatures and NO_x emissions in a CI engine. Increased BSFC has also been reported with WCO methyl esters when contrasted with FD because of the lower heating value of biodiesel and its blends. Likewise, BTE reduction with

higher WCO increase in blends have been noted. Di et al., (2009) performed an experimental investigation on the impact of WCO on engine performance and emission features. Engine tests were performed with WCO20 and WCO30 fuels and it was reported that BSFC increased with BD proportion in the blend. The research also reported that BTE decreased with increase in BD and this was accredited to the lower energy value of BD fuel and its blends with FD. Another experimental study by Muralidharan and Vasudevan (2011) performed using WCO BD blends of 20 %, 40 %, 60 % and 80% by volume in a single cylinder engine revealed that lower blends of WCO with FD could be used an alternative fuel for diesel engines.

The performance and emission behaviour of an engine is affected by many variables such as compression ratio, load, blend, injection pressure and injection timing and speed (Heywood 2018). Among the different variables that influence performance and emission behaviour compression ratio (CR), load and level of dosage of additive are essential (Pandian et al., 2011). Several studies have been performed on the impact of nano additives on performance and emission behaviour of BD fuels (Zhang et al., 2020). Therefore, an efficient multivariate examination could give thorough, reasonable, and clear information on the combustion behaviour of the engine in comparison with the methodology of varying one parameter at a time. One such technique for analysing the impact of several parameters on engine performance and emission behaviour is design of experiments (DOE). DOE strategies are utilized for displaying and examining several parameters by utilizing exploratory outcomes. In this technique a strategic array of variables is varied at each stage thus unveiling the impact of such variable at each step. Among the DOE strategies available, response surface method (RSM) has proven to yield reliable and efficient optimal engine parameters capable of ensuring maximum engine performance coupled with exhaust emission reduction (Awad et al., 2017). Other DOE methods such grey relational analysis (Pathak et al., 2018), non-linear regression (Tosun et al., 2016), and the Taguchi method (Ganapathy et al., 2009) may require a combination of at least two of them in order to perform meaningful engine data analysis. RSM is a numerical modelling tool that reduces the overall number of experiments by combining the impact of several factors (Singh et al., 2018). This multivariate measurement technique at the same time advances the impacts of different components and the connection between the factors to accomplish the best framework for execution.

Various analysts have found that the RSM method to be an effective tool for modelling and predicting engine parameters. Bharadwaz et al.(2016) performed a study to optimize engine performance and emission parameters by combining the effects of compression ratio, load and palm oil biodiesel-methanol using RSM and found that optimal engine performance and emission values were recorded as 9.03 kg load, 5 % methanol blending at a CR of 18. Sivaramakrishnan and Ravikumar (2014) carried out an investigation into the influence of CR on the performance and emission behavior of biodiesel blends with FD. Performing experiments by varying BD percentage in 10 % increments from 20 % BD to 50 % BD and CR between 17.5 to 18.1, the authors produced effective optimization of the parameters. A desirability factor of 0.97 was revealed at CR of 17.9, with B10 at 3.18 kW brake power. At these optimized parameters responses of 33.65 % of BTE, 0.2718 kg/kWh of 0.109 % CO, 158 ppm of UBHC and 938 of ppm of NO_x were unveiled. It was concluded from this analysis that the RSM is an appropriate, economical, and effective method of modelling and optimizing engine data sets. Analysts have noticed a significant

expansion in BTE because of addition of nano particles to base fuels. Nano particles have high thermal conductivity values which expands thermal conductivity of the combination (base liquid + nanoparticle), subsequently expanding the heat transfer rate which thus decreases ignition delay consequently increasing rate of pressure rise and peak of pressure. Another RSM study was conducted by Kumar and Dinesha (2018) to evaluate optimal engine conditions capable of maximizing engine performance and reducing emissions showed that a CR of 16, load of 86.3 %, blending ratio of 15 and injection timing were the best engine variables to maximize BTE and reduce NO_x emissions. A study by Nayyar et al. (2017) to evaluate the combined impact of load, compression ratio, and blending, showed that with a 20 % n-butanol-diesel mix (B20) at a higher-pressure proportion of 19.5 BTE was improved by 5.54 % and smoke and nitrogen oxides diminished by 59.56 % and 15.96 %, respectively at 100 % load.

From the above literature it can be deduced that RSM is a fundamental modelling tool that can be utilized to perform modeling and optimization of engine data. It was also shown that nano particle addition to biodiesel blends result in significant improvement in engine performance and reduction in exhaust emission characteristics. No literature is available on the optimal levels of nanoparticle addition to base fuels. Excessive levels of nano particle addition may lead to abnormal combustion profiles. Consequently, more exploratory examination is required to evaluate optimal values of nanoparticles levels in BD blends to bring about an improvement in performance and a decrease in emissions and assess the interaction of these effects with effects of CR and load. This work therefore is aimed at modelling and optimization of the combined impact of load, compression ratio and hybrid nano additive on the performance and emission behavior of a blend (WCO20). The engine performance parameters under consideration were brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) while emission parameters under observation were nitrogen oxides (NO_x), unburnt hydrocarbons (UBHC), carbon monoxide (CO) and smoke.

2. MATERIALS AND METHODS

2.1 Waste Cooking Biodiesel Production

Mixed waste cooking oil (WCO) was initially heated then assessed for free fatty acid content (FFA) using the titration method follow by a one step or two step transesterification process. The titration was performed with 0.1 N KOH, phenolphthalein, and isopropyl liquor as per the ASTM D974 standard. Initially acid value was calculated as shown in Equation 1.

$$\text{Acid Value} = \frac{56.1 \times 0.1 \times N \times 20.07 \text{ mL}}{10 \text{ g}} \quad (1)$$

The whole biodiesel production process is shown in Figure 1.

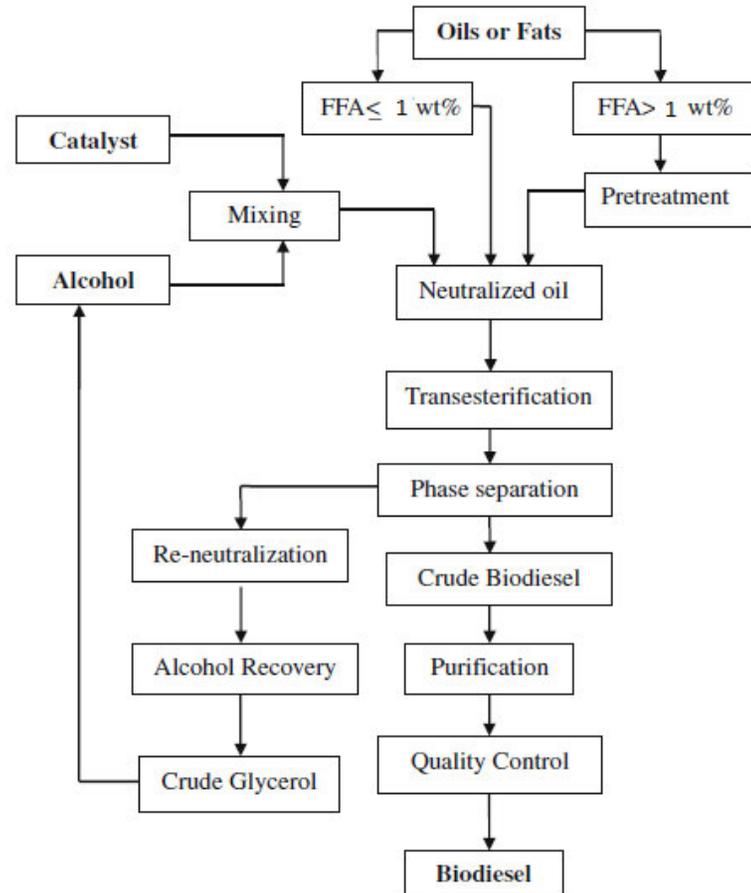


Figure 1. Waste cooking oil biodiesel production

Acid value was found to be 10.86 which is equivalent to 5.43 FFA content. This value was higher than 1 which warranted a two-step process. Pretreatment was undertaken using HCL until acid value became 0.994 which gave an FFA of 0.497. Thereafter the transesterification was performed by utilizing a cone shaped flask with a reflux condenser and thermometer with magnetic stirrer. WCO was added to the flask and heated to 60 °C and thereafter a mixture of methanol and sodium hydroxide (NaOH) 1 % wt was added. The temperature of reaction was maintained at 60 °C by means of a water bath. A molar ratio of 6:1 methanol to oil was utilized and the reaction flask was left to progress for 24 hours. The BD which was produced was separated from glycerol then washed multiple times using warm water. The remaining methanol and catalysts were recovered to be reused in the following experiments. Waste cooking BD methyl was dried at 105 °C. The BD produced was blended with diesel oil at 20 % by volume. The whole biodiesel production process is shown in Figure 1. The fuel properties were characterized as shown in Table 4.

2.2. Nano blended fuels preparation

The nano particles Al_2O_3 and CeO_2 were purchased from Sigma-Aldrich (Johannesburg, South Africa). The nano particles $nCeO_2$ (nano powder 50 nm, CAS No 1312-38-01), nAl_2O_3 (50 nm, 20 wt% in water, CAS No 1344-28-10) were characterized utilizing a ZEISS scanning electron microscope (SEM) (Germany) at 20.0 kV and the specs are depicted in Figure 2. The nano particles were prepared in 20 ppm measurements by using an electronic balance and afterwards blended in with the BD fuel blend by utilization of an ultrasonicator operated at 100 W and 50 kHz for 30 minutes. The produced fuel was used immediately to counter the issues related to sedimentation which would impact on the result. Three fuels were prepared, namely, (1) WCO20H20, WCO BD blend comprising 20 % BD and 80% FD plus the addition of 10 ppm Al_2O_3 and 10 ppm CeO_2 , (2) WCO20H40, WCO BD blend comprising 20 % BD and 80 % FD plus 20 ppm Al_2O_3 and 20 ppm CeO_2 and (3) WCO20H60, WCO BD blend comprising 20 % BD and 80 % FD plus 30 ppm Al_2O_3 and 30 ppm CeO_2 , as per Table 2.

Table 2. Description of nano particles used

Description	Specification	
	1	2
Manufacturer	Sigma-Aldrich Johannesburg	Sigma-Aldrich Johannesburg
Nano particle	Cerium oxide (CeO_2)	Aluminum oxide (Al_2O_3)
CAS No	1312-38-01	1344-28-10
Average size	20 to 50 nm	20- 60 nm
Surface area	32 m ² /g	120 m ² /g
Appearance	White to yellow	White

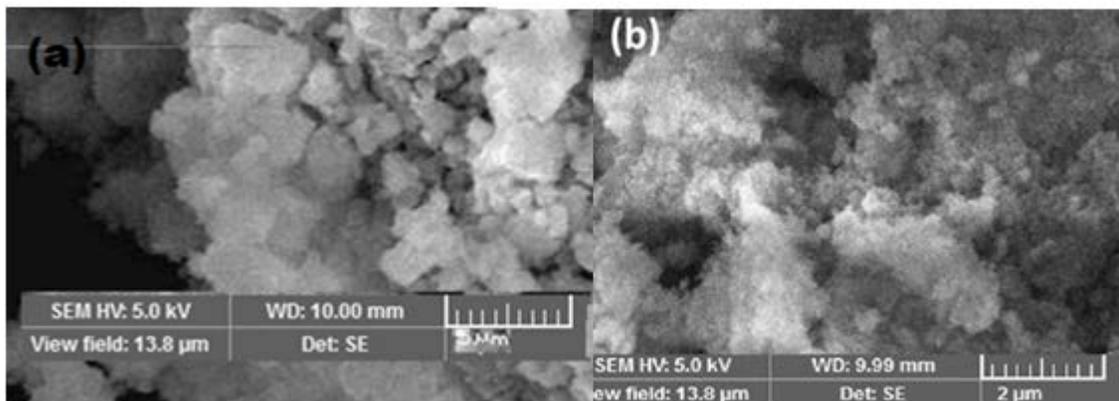


Figure 2: Aluminum oxide as received from manufacturer(a)aluminum oxide (b) cerium oxide

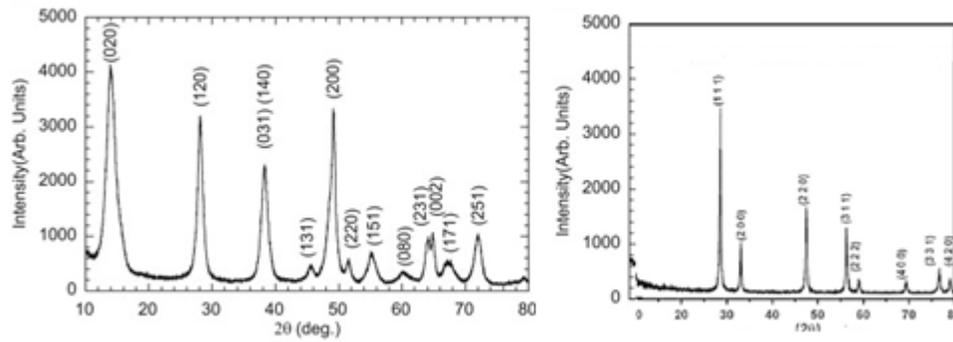


Figure 3. Aluminium oxide and cerium oxide as received from manufacturer (a)aluminum oxide (b) cerium oxide

3. EXEPRIMENTAL CONFIGURATION

3.1. Engine test and procedure

The experimental set comprised a two-cylinder direct injection variable compression ratio engine. The engine details are detailed in Table 3 and the setup is shown in Figure 4 and Figure 5. Details of the gas analyzer and smoke meter specifications used to analyses the exhaust emissions are shown Table 5. Three distinct fuels were formulated from the WCO20 blend by adding varying amounts of hybrid nano particles ranging from 20 ppm to 60 ppm. For this examination three distinctive test fuels were prepared by adding hybrid nano particles to the WCO20. The fuels formed were as follows: (1) WCO20H20 (80 % FD +WCO BD +10 ppm CeO₂ and 10 ppm AlO₂) (2) WCO20H40 (80 % FD +20 WCO BD +20 ppm CeO₂ and 20 ppm AlO₂ ppm, and (3) WCO20H60 (80 % FD +20 WCO BD +30 ppm CeO₂ and 30 ppm AlO₂). When performing the experiment WCO20H20 was represented by fuel blend 20, WCO20H40 by fuel blend 40 and WCO20H60 by fuel blend 60. The properties of the formulated fuel blends are shown in Table 4. Zero calibration was ensured after every emission by testing using fresh air. To guarantee consistency and validity of the results the tests were performed under steady state conditions. The experiments were designed based on RSM tool Design-Expert 13 using a design matrix as shown in Table 7.



Figure 4. Engine and data acquisition set up

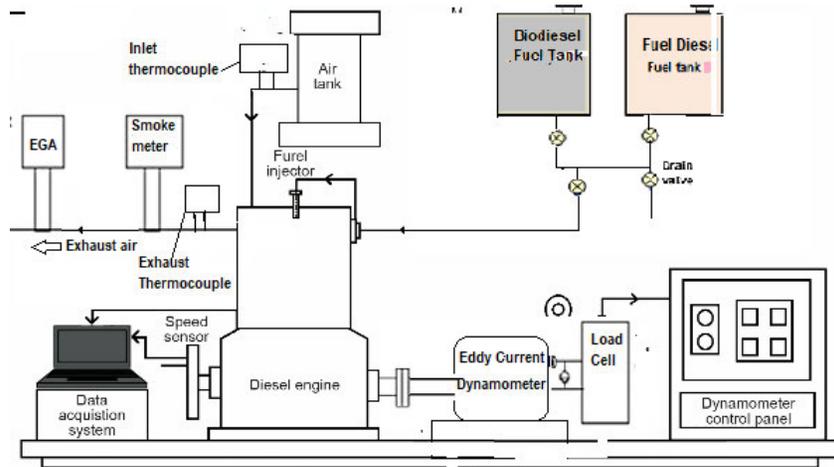


Figure 5. Engine test configuration

Table 3: Engine specifications used in the experiment

Engine specifications used in the experiment

Parameter	Position value
Engine Model	Kirloskar
Type	Two cylinder, horizontal 4 -stroke, DI
Cooling Medium	Water cooled
Revolutions per Minute	1300 rpm (constant)
Rated Brake Power	5.2 kW (7Hp)
Cylinder Bore	87.5 mm
Piston Stroke	110 mm
Compression Ratio	17.5 (variable)
Injection Timing	23° BTDC
Injection pressure	220 bars
Loading System	Eddy Current Dynamometer

Table 4. Properties of the fuels used in the research

Fuel	Cetane Number	Lower heating value (KJ/KG)	Density (kg/m ³) @ at 15 °C	Viscosity (cSt) at 40 °C	Pour point (C°)	Flash point (C°)
WCO20H20	56.2	39.64	837.00	4.68	-22	166
WCO20H40	57.2	39.76	864.00	4.22	-21	159
WCO20H60	58.0	40.10	852.13	3.88	-18	157

Table 5. AVL gas analyzer and smoke meter specifications

SL. No	Instrument	Measurement	Range	Resolution	Accuracy
1	Five gas Analyzer	CO	0–10%	0.00%	±0.22%
		UBHC	0–20,000 ppm	1 ppm	±0.3 ppm
		NOx	0–5000 ppm	10 ppm	±0.2 ppm
2	Smoke meter	HSU	0–99.9	0.10%	±0.1%
		K	0-0.02	0.02 m-1	±0.1 m-1

Table 6. Uncertainties estimations of measured and calculated parameters

SL. No	Measured	SL. No	Calculated
	Parameters		Parameters
	% uncertainty		% uncertainty
1	Engine speed (rpm)	1	Power
2	Temperatures (°C)	2	Brake thermal efficiency
3	Carbon monoxide (%)	3	Brake specific fuel consumption
4	Hydro carbons (ppm)		
5	Nitrogen oxides (ppm)		
6	Crank angle (°)		
7	Load (kg)		

The error of the experimental procedure was evaluated as follows and the overall uncertainty was 4.10%. The uncertainties of measured and calculated parameters are shown in Table 6 above and computation is shown in Equation 2.

$$\text{Overall uncertainty} = \sqrt{\text{uncertainty of } (N)^2 + (BTE)^2 + (BSFC)^2 + (CO_2)^2 + (CO)^2 + (NOX)^2 + (UBHC)^2 + (EGT)^2 + (\text{smoke})^2} \quad \text{Eq (2)}$$

3.2 Design of Experiments

RSM is an assortment of statistical tools used to analyze, model and optimize parameters influenced by several factors. Furthermore, RSM can evaluate the relationships between these factors and compute their combined impact on the outcome. In this investigation Design-Expert Version 13 was utilized to develop the models and optimize the parameters in the following manner: 1. Transform the data profile or otherwise maintain at an option at "None". 2. Select the suitable model to be utilized. The fit summary shows the sequential F-tests, lack-of-fit tests and other variables that could be utilized to help in selecting the best fitting model. 3. Compute ANOVA tables and perform post ANOVA analysis to check data anomalies. 4. Perform diagnostic evaluation on the data to inspect if the model was valid. 5. Generate the contour and 3D plots once the model has been validated. The model is validated by inspecting whether it is lack-of-fit significant or lack-of-fit insignificant. Also, a good model shows higher R² values and this ought to be near 1. The design process flow diagram is shown in Figure 6.

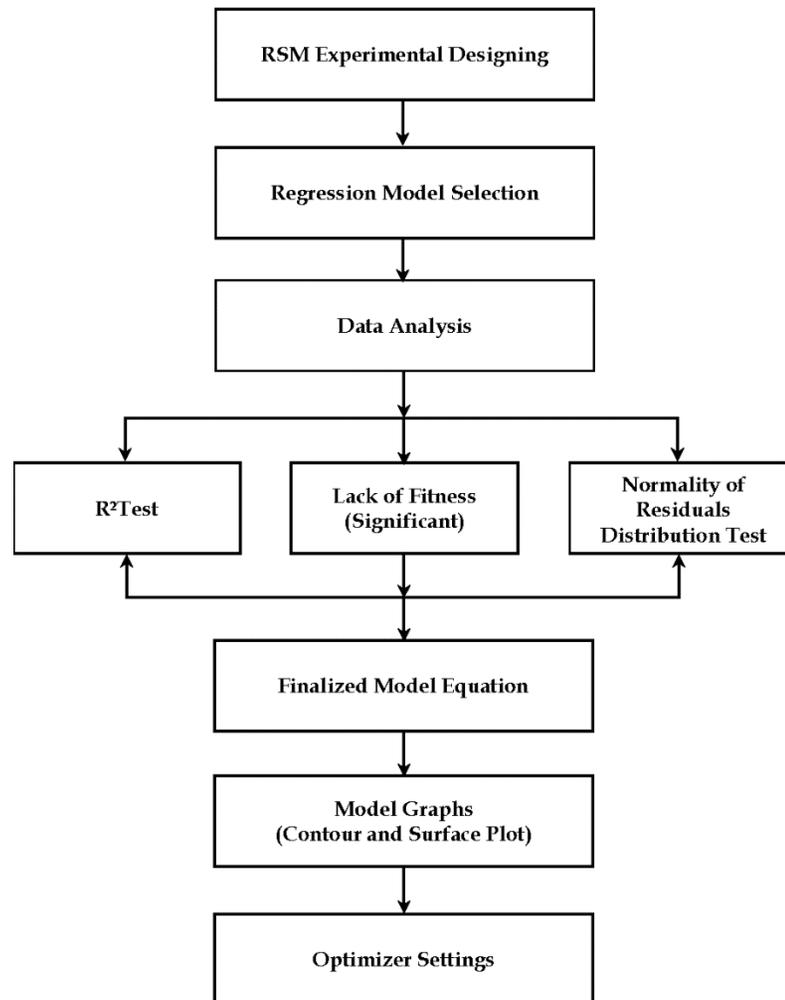


Figure6. Flow chart of the design of the experiment using Design-Expert 13

In the current investigation, there are three influential parameters which were investigated, namely, compression ratio, fuel blend and load and the outcomes desired were BTE, BSFC, NO_x, UBHC, CO and smoke. Design-Expert 13 was utilized to design the experiments; the factor levels and outcomes results are shown in Table 7 and Table 8. This done by utilizing second degree polynomial models. The created models were checked for significance utilizing fundamental statistical tests and analysis of variance (ANOVA). These models introduce a relationship amongst the given factors and measure parameters which can be utilized to predict the outcomes once statistical evaluation is done. Design-Expert 13 was then used to perform the modelling and optimization process. To enhance data validity and improve results reliability, three sets of experiments were performed and the results averaged and compared with model optimized results. An error was computed to verify the variation between model and experimental results.

Table 7. Factors and levels

Factor	Name	Units	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
Compression								
A	Ratio		14	18	14	18	16,00	1,59
B	Fuel Blend	ppm	20	60	20	60	41,00	16,51
C	Load	%	20	100	20	100	52,00	28,58

Table 8. Design matrix

		Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3	Response 4	Response 5	Response 6
Std	Run	A:Compression Ratio	B:Fuel Blend	C:Load	BTE	BSFC	NOx	UBHC	CO	Smoke
				%	%	g/kWh	ppm	ppm	%	%
5	1	14	40	60	26,42	0,35	905	34	0,56	38,50
13	2	16	20	60	28,02	0,34	865	44	0,44	32,87
12	3	18	60	80	32,66	0,33	698	26	0,38	37,38
7	4	16	60	40	26,5	0,43	710	42	0,53	38,48
19	5	18	20	100	27,71	0,33	880	37	0,50	29,10
9	6	14	20	20	12,93	0,86	864	82	0,76	64,57
11	7	16	60	60	32,61	0,33	755	31	0,44	30,78
14	8	14	40	40	22,32	0,41	902	52	0,66	47,32
16	9	18	60	60	29,8	0,35	881	18	0,41	25,30
20	10	14	60	100	29,34	0,4	677	38	0,30	43,26
17	11	16	20	40	24,43	0,37	850	37	0,46	42,79
8	12	16	40	40	23,45	0,4	806	40	0,48	28,40
10	13	14	60	60	31,8	0,35	688	28	0,48	37,78
4	14	16	20	100	25,75	0,36	817	38	0,45	31,51
2	15	16	60	20	16,44	0,67	640	70	0,63	46,50
15	16	18	40	20	12,98	0,76	890	82	0,38	57,34
6	17	16	40	20	14,67	0,68	756	70	0,54	39,59
18	18	18	40	20	12,57	0,68	860	72	0,62	36,78
1	19	18	20	80	30,76	0,3	1020	36	0,54	32,28
3	20	18	20	20	15,24	0,58	798	52	0,46	41,14

4. RESULTS AND DISCUSSION

4.1. Model Analysis

Equations in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. A coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Analysis of variance (ANOVA) utilizes p-values to reject or accept influence of input parameters. Those factors that have p-values ≥ 0.05 are rejected or are referred to as insignificant. The model coded regression equations are shown in Equations 3 to 7. A is the CR, B is the fuel blend (WC020) with hybrid nano particles and C is the load (in %).

$$BTE = +29,31+1.09XA+1.94XB+6,39XC-1,59XAB+1,40XAC+1,38XBC -1,50XA^2+1,47XB^2-8,30XC^2 \quad (3)$$

$$BSFC = +0,257-0,0221XA+0.0159XB-0.1554XC + 0,0504XAB + 0.0314XAC + 0.0035XBC + 0.0625XA^2 + 0.0254XB^2 + 0.2240XC^2 \quad (4)$$

$$NO_x = +834,54 + 42,34XA - 54,03XB +36,56XC + 137,16XAB + 43,21XAC + 37,50XBC + 113,07A^2-23,98XB^2-44,53XC^2 \quad (5)$$

$$UBHC = 28,08-1,24XA + 3,58XB - 12,76XC + 10,93XAB + 4,71XAC + 0,3782BC + 6,64A^2-1,57B^2+28,18C^2 \quad (6)$$

$$Smoke = + 21,81- 5,85XA + 0,8205B - 6,25XC + 13,66XAB + 7,34AC+6,75BC + 11,12A^2 + 11,71B^2 + 11,76C^2 \quad (7)$$

4.2 Model Evaluation

The variation between the actual and predicted plot is called a residual (Montgomery 2017). Figure 7 shows the actual and predicted plot for BTE, BSFC, NO_x, UBHC, CO and smoke. These plots are used for checking measured data for normality. These plots are vital in evaluating distribution of residuals. It can be deduced from Figure 7 that the responses BTE, BSFC, NO_x, UBHC, CO and smoke followed normal distribution. The overall impression from actual and predicted information is that the error is minimal and there no huge deviation between them. Additionally, Figure 7 affirms that the model equations were reliable. Based on the summary of ANOVA shown in Table 9, it can be deduced that that the plots of impact of the linear factor's CR, nano particles (fuel blend) and load were found to be exceptionally significant on the engine parameters. All R-squared terms were additionally found to be significant which implies there was a curved relationship input parameter. The model also showed that there was an interactive relationship between fuel blend and CR, CR and load, and load and fuel blend resulting in a significant impact on engine parameters. In this case A, C, AB, AC, BC, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The predicted R² of 0.992, 0.8794,0.9987, 0.9941,0.9917 and 0.9725 for BTE, BSFC, NO_x, UBHC, CO and smoke respectively are in reasonable agreement with the adjusted R² of 0.9926, 0.6872,0.9967, 0.9987,0.9783 and 0.937 respectively i.e., the differences were less than 0.2. The R² (also defined as goodness of fit value) depicts variability of responses after considering the significant factors and the adjusted R² represents the quantity of predictors in the model. Both the qualities demonstrate that the model fits the data very well.

Table 9. Model evaluation

Model	BTE	BSFC	NOx	UBHC	CO	Smoke
Mean	23,82	0,464	813.1	45,45	0,526	39,08
SD	0,3762	0,0596	3,49	1,51	0,0122	1,6
R-squared	0.9985	0,9365	0.9993	0,9969	0,9956	0,9855
Model degree	Quadratic	Quadratic	Quadratic	Quadratic	Quadratic	Quadratic
Adj. R2	0,9926	0,6872	0,9967	0.9987	0,9783	0,937
Pred. R2	0,9972	0,8794	0,9987	0.9941	0,9917	0,9725

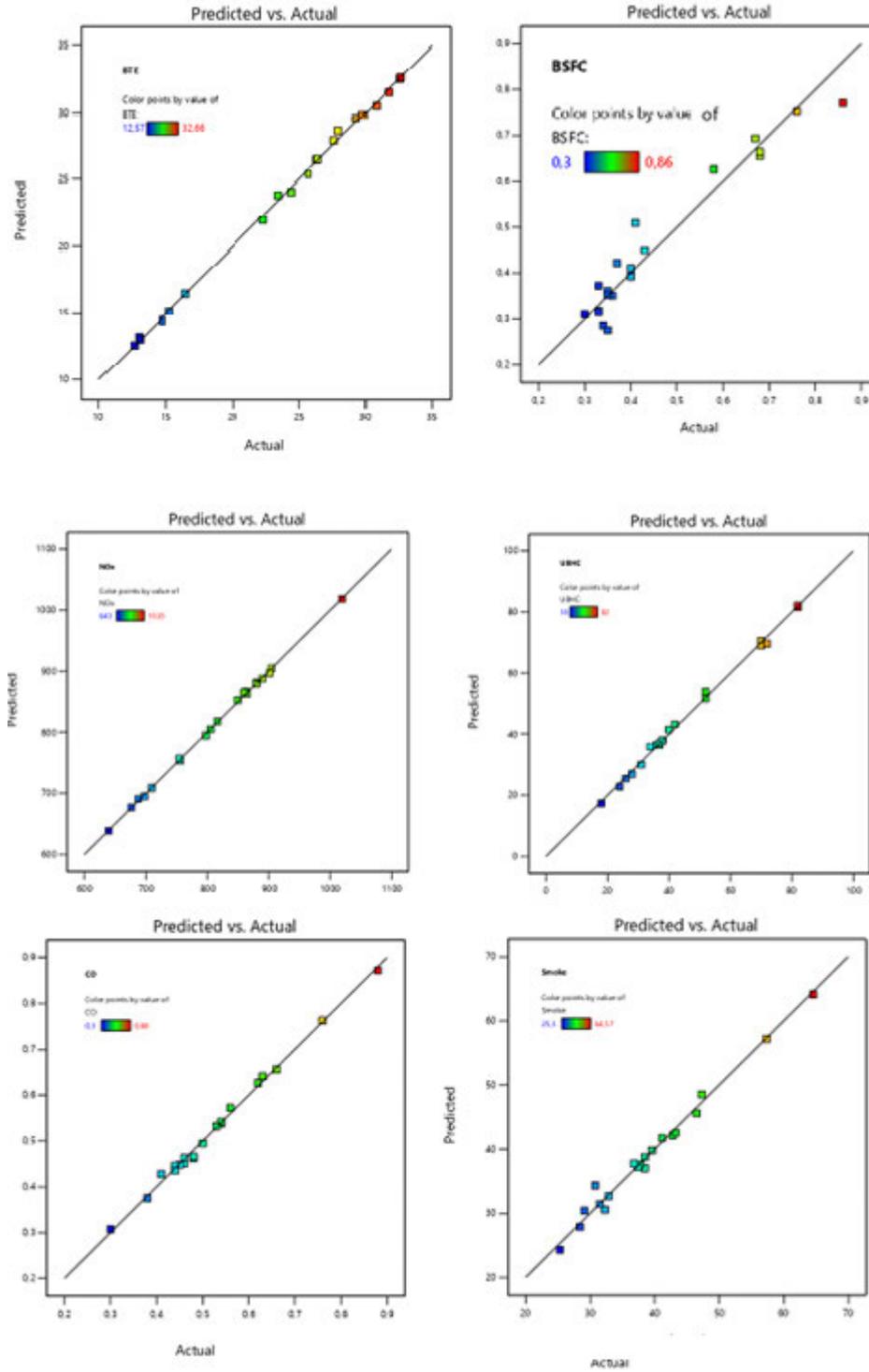


Figure 7. Actual and predicted plot for (a) BTE, (b) BSFC, (c) NO_x, (d) UBHC, CO and (e) smoke emissions

4.3 Optimization of Engine Parameters

Optimization criteria utilized in this investigation are depicted in Table 10. All the responses were equally desirable and allocated significance values of 3. In the Derringers desirability approach the most desirable parameter is allocated a value of 5 and least desirable a value of 1. The most elevated significance of 5 was given to NO_x and smoke whilst both BTE and BSFC were allocated significance of 4. Desirability will generate multiple solutions and the one with the highest desirability is then selected as the optimal solution. A desirability of 0.898 was found to be the highest and this was selected as the best solution. At this optimal solution the CR value of 14.71, load 74.98 % and nano particle blending of 60 ppm were recorded as the optimal input parameters that gave the best engine performance and emissions features. Table 11 shows the 17 solutions which were generated, and the selected solution.

Table 10. Optimization criteria

Source	Lower limits	Upper limits	Weight		Importance	Goal
			Upper	Lower		
Compression ratio	14	18	1	1	3	In range
Fuel blend	20	60	1	1	3	In range
Load	20	100	1	1	3	In range
BTE	12,57	32,66	1	1	4	Maximize
BSFC	0,3	0,86	1	1	4	Minimize
NOx	640	1020	1	1	5	Minimize
UBHC	18	82	1	1	3	Minimize
CO	0,3	0,88	1	1	3	Minimize
Smoke	25,3	64,57	1	1	5	Minimize

Table 11. Solution of optimized engine parameters

Number	CR	Fuel Blend	Load	BTE	BSFC	NOx	UBHC	CO	Smoke	Desirability	
1	14,71	60	74,98	33,63	0,292	700	25	0,361	33,985	0,898	Selected
2	14,70	60	75,14	33,62	0,292	700	25	0,361	34,025	0,898	
3	14,71	60	74,67	33,62	0,292	700	25	0,362	33,947	0,898	
4	14,69	60	74,81	33,61	0,292	699	25	0,362	33,996	0,898	
5	14,70	60	75,62	33,63	0,292	700	25	0,359	34,078	0,898	
6	14,74	60	74,87	33,66	0,291	701	25	0,361	33,917	0,898	
7	14,73	60	74,19	33,63	0,291	700	25	0,364	33,858	0,898	
8	14,66	60	75,06	33,58	0,293	699	25	0,362	34,087	0,898	
9	16,92	20	72,15	30,52	0,242	846	18	0,396	24,224	0,836	
10	16,89	20	71,68	30,48	0,242	845	18	0,396	24,363	0,836	
11	16,88	20	71,32	30,46	0,242	845	18	0,396	24,433	0,836	
12	16,87	20	72,28	30,47	0,242	845	18	0,396	24,397	0,836	

13	16,85	20	70,59	30,41	0,243	845	18	0,396	24,638	0,836
14	16,90	20	75,16	30,49	0,243	844	19	0,398	24,193	0,835
15	16,94	20	65,81	30,23	0,249	846	18	0,394	24,83	0,834
16	16,89	20	76,18	30,46	0,243	844	19	0,398	24,195	0,834
17	16,71	20	74,07	30,31	0,243	844	19	0,399	24,986	0,833

4.4 Validation Tests

To assess the regression model, confirmation tests were performed with the desired input parameters of CR of 14.71 load of 74.98 % and fuel blend consisting of 60 ppm of hybrid nano particle. Three tests were conducted, and averaged values were then compared with the model’s desired outcomes. The experimental data reaffirmed that the model results were significant as the error values depicting the variance between measured and modeled data was minimal as shown in Table 12.

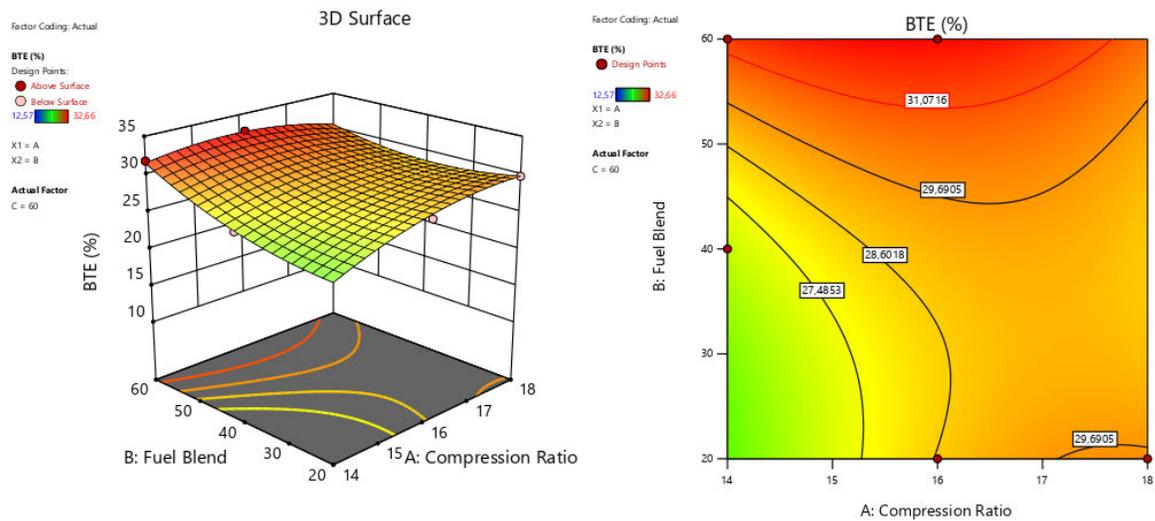
Table 12. Validation of test results

Optimized parameters			Value	BTE (%)	Bsfc (kg/kWh)	NOx (ppm)	UBHC (ppm)	CO (%)	Smoke (%)
CR 14.71	Load (%) 75	Blend 60	Predicted	33,63	0,292	700	25	0,361	34
			Actual	32,96	0,287	671	24	0,35	32
			Error	-0,67	-0,005	-29	-1	0,011	-2

5. INTERACTION EFFECTS ON ENGINE PARAMETERS

5.1. Interaction Effects on BTE

Figure 8 depicts interaction effects of CR and the fuel blend on BTE. From the plot it is seen that BTE increased with increased fuel blend. These results show that increasing the hybrid nano particles resulted in an increased BTE for WCO20 fuel. The plot also shows that BTE increased with increased CR. Higher levels of nano particles increased the calorific value (CV) of the fuel blend. This subsequently resulted in more energy being released by the fuel during combustion process. The elevation in BTE with CR can be credited to the rise in cylinder chamber pressure and temperature factors which promote higher fuel injection and better combustion profiles. All this will result in increased BTE of the engine. This is also because of expansion in CR which initiates better air-fuel blending and quicker fuel evaporation and promotes complete combustion. The highest BTE of 33.96 % and was recorded with 60 ppm dosages of nano particles at a load of 80 % as shown in Table 11. The least BTE occurred at fuel blend 40 ppm at CR of 14 and 20 % load.



5.2. Interaction Effects on BSFC

BSFC is a significant indicator of engine performance. Figure 9 depicts the interaction plots of the impact of CR and fuel blend on BSFC. From the plot it can be deduced that BSFC decreased with increase in both CR and fuel blend. Reduction of BSFC with increased fuel blend might be credited to the increased CV values due to nano particle addition resulting in improved combustion hence lower fuel utilization. The highest BSFC of 0.78 kg/kWh was recorded at 18 CR, 60 ppm fuel blend and 20 % load whereas the lowest BSFC was recorded at 18 CR, 20 ppm fuel blend and 80 % load, as shown in Table 11. The decrease of BSFC with CR is attributed to the increase in temperatures and pressure which will improve the burning efficiency and diminish the fuel utilization. This is because of expansion in CR which prompts a decrease in dilution of charge by the remaining gases, which brings about better BTE and lower BSFC. Furthermore, the low volatility and higher cetane number (CN) bring about improved burning at high pressure proportions. The presence of increased oxygen from the nanoparticles in the BD blends improved the fuel properties leading to higher burning efficiency, which prompted lower

2019; Nayak & Pattanaik, 2014).

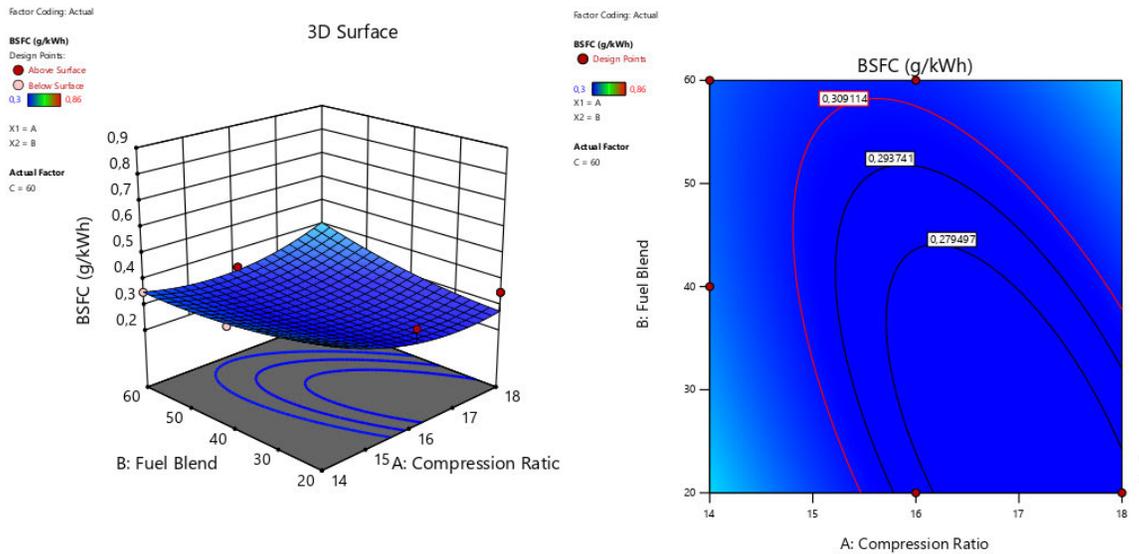


Figure 9. The interactive effects of CR and fuel blend on BSFC

5.3. Interaction Effects on NO_x

NO_x discharges are influenced by high temperatures and higher oxygen concentration. Figure 10 shows the interaction effect of CR and fuel blend on NO_x emissions at constant load. It is noted from the plot that NO_x discharges diminish with an increase in nano particle addition. From Table 11, it is seen that the highest NO_x emission of 1 020 ppm was recorded at a CR of 18, 20 ppm of nano particles and 80 % load whilst the lowest value of 620 ppm was recorded at a CR of 16, 60 ppm of nano particle and 20 % load. The development of NO_x inside the combustion chamber requires high temperatures and pressures which are accessible at high loads and CR and this might be the reason behind the increase of NO_x with CR. It also depends upon the compression ratio, equivalence ratio, geometry of the combustion chamber, advanced fuel injection, and pressure and temperature of the inlet air. At higher CR there is shorter ignition delay but higher peak pressures and this will result in higher cylinder temperatures which are a favorable environment for NO_x generation. A decrease of NO_x with the fuel blend can be attributed to the addition of hybrid nano particles which promotes transformation of NO_x to N₂. Addition of hybrid nano particles enhance the reaction of NO to N₂ as shown in Equations (8) and (9).



According to Scattergood (2006), Al₂O₃ at higher cylinder temperatures reacts with NO to form nitrogen gas (N₂). Sajithet al. (2010) have also attributed the conversion of both NO and NO₂ to nitrogen gas on high cylinder temperatures and oxygen availability. Some authors have pointed out that deposition of carbon on cylinder walls

prompts higher cylinder temperatures which promotes higher NO_x generation. The deposition of carbon on cylinder walls might be caused by incomplete combustion. Introduced hybrid nano particles consisting of Al₂O₃ and CeO₂ have the capability to act as oxygen buffers providing higher oxygen atoms which are used in the oxidation of carbon-to-carbon dioxide. This suppresses carbon accumulation on combustion cylinder walls reducing high temperature generation and lowering NO_x production. This will therefore stifle NO_x generation thereby lessening their outflow into the air.

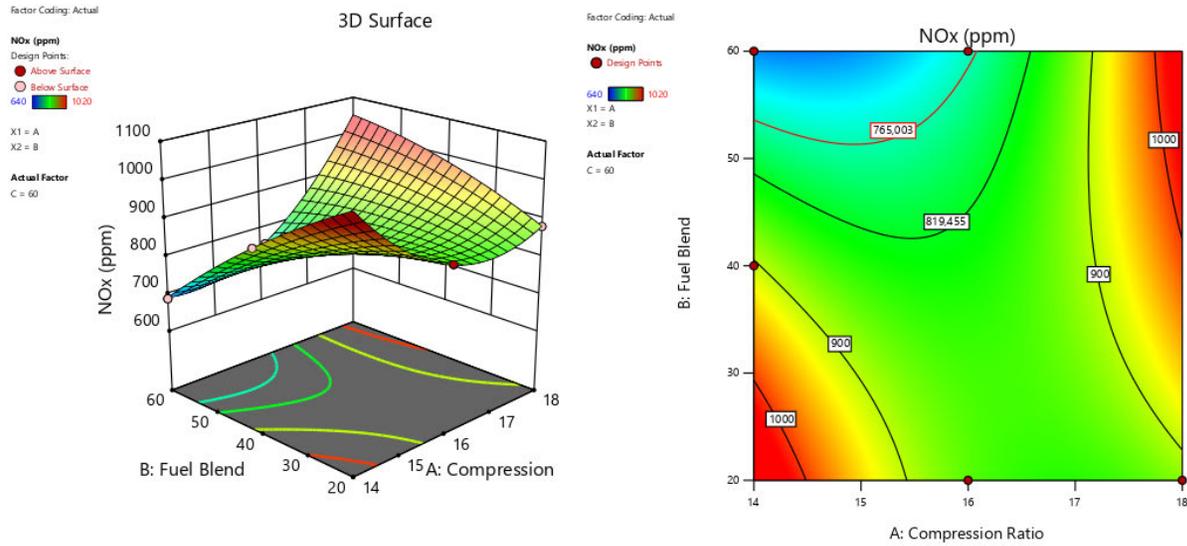
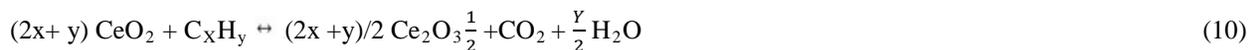


Figure 10. The interactive effects of CR and fuel blend on NO_x emissions

5.4. Interaction Effects on UBHC

Figure 11 depicts the impact of the hybrid fuel blend and CR on UBHC discharges. From the plot it is noticed that there is a decrease in HC outflows with increase in both nano particle addition and CR. The outcomes in Table 11 show the highest UBHC of 82 was revealed at CR 18, 40 ppm of fuel blend and 20 % load whilst the lowest UBHC of 18 recorded was CR 18, 60 ppm of fuel blend and load of 60 %. This can be attributed to higher air temperature improvement in cylinder pressure and temperature and decrease in charge dilution which prompts better fuel combustion and decrease in hydrocarbon discharges. CeO₂ can act as an oxygen buffer enhancing the combustion of hydrocarbons emissions. Equation 10 shows how the addition of Ce₂O₃ enables the reduction of UBHC by oxidizing them into CO₂ plus water vapor (Chandrasekaran et al. 2016).



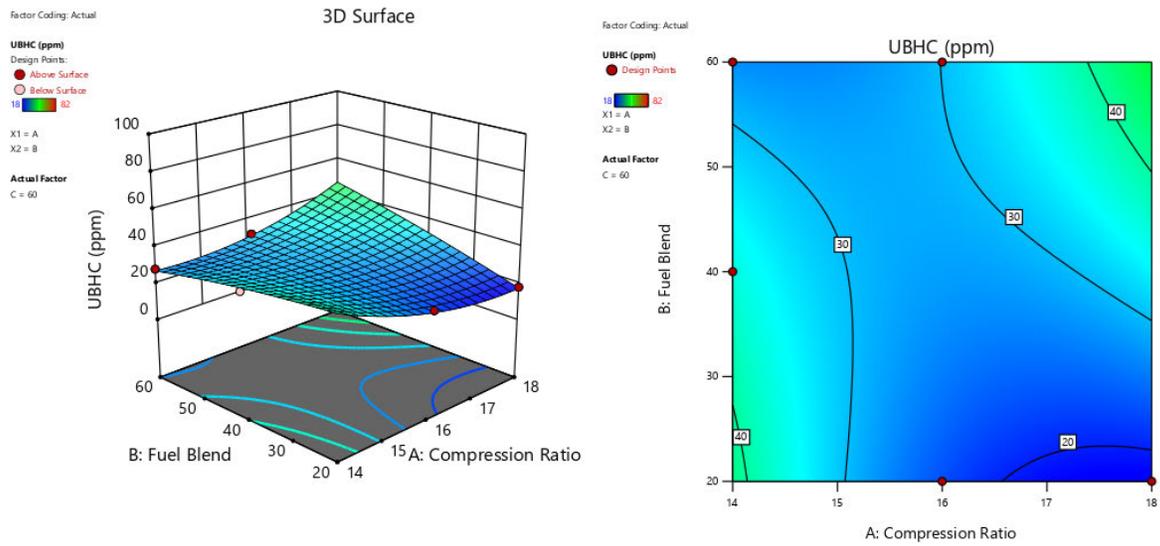


Figure 11. The interactive effects of CR and Fuel blend on UBHC emissions

5.5. Interaction Effects on CO emissions

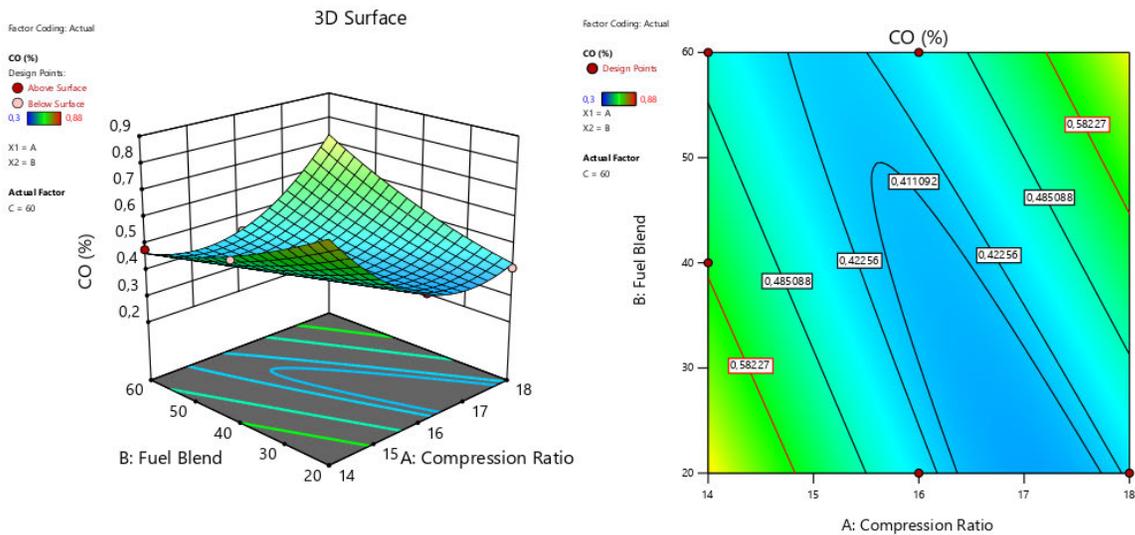
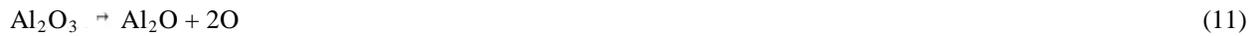


Figure 12. The interactive effects of CR and Fuel blend on CO emissions

The interaction impact of fuel blend on CO fumes at a constant load is shown in Figure 12. As can be seen in the figure, increasing the hybrid nano particle levels in WCO20 leads to a decrease in CO emissions. It can also be deduced that CO emissions decreased with increase in compression ratio. Higher fuel blends represent a higher hybrid nano particle dosage in the WCO20 fuel. Higher levels of nano particles will contribute a higher number of oxygen atoms available for complete oxidation of CO emissions of fuel into CO₂. This is because of complete combustion and reduced dilution of charge of residual gases which promotes rapid reaction of carbon with oxygen to

form CO₂. Furthermore, this decrease of CO emissions is because of expansion in pressure proportion which expands the air temperature inside the chamber resulting in a decrease in ignition delay which causes better and complete consumption of the fuel and brings down the CO outflows.

Inclusion of Al₂O₃ advances quick oxidation of CO to CO₂ (Santhanamuthu et al., 2014). Al₂O₃ transforms into Al₂O and O at higher temperatures. The resulted Al₂O is very unstable and will furtherer disintegrate to 2Al and ½O₂ as demonstrated in Equations (11) and (12). The subsequent O₂ will be accessible for oxidizing CO over to CO₂ according to Equations (15).



CeO₂ tends to shift its valence from CeO₂ (+4) to Ce (+3) enabling it to provide an oxygen atom for reduction processes. According to Ozsezen & Canakci (2011), CO is produced as result of incomplete combustion. Making more oxygen available within the combustion chamber is essential to suppress CO formation processes. The oxygen donated will be able to accelerate rapid oxidation of CO to CO₂ as shown in Equation (14)



This clarifies why addition of the nano additive to biodiesel reduced the CO emissions significantly.

5.6. Interaction Effects on Smoke

Figure 13 shows the interaction effects of CR and fuel blend on smoke emissions. Smoke generations is influenced by local fuel air ratio. It is seen from the figure that smoke outflows decreased with the increment of fuel blend up to some extent then began to rise. It is noted from the outcomes in Table 11 that the highest smoke emissions of 64.57 were generated at a CR of 14, 20 ppm and 20 % load and the lowest smoke of 25.30 was recorded at a CR of 16, 60 ppm of fuel blend and 60 % load. Smoke emissions are also noted to decrease with increasing CR values. This can be attributed to better fuel-air mixing at higher pressures which enhanced fuel combustion and lowered smoke generation. The decrease in smoke emissions with increasing nano particles can be traced to high CN and high surface area to volume proportion of the nano added substances which bring about heat dissipation, shorten ignition delay, and improve burning profiles which causes lower smoke generation. The soot is converted to CO₂ as shown in Equation 15.



Ignition delay is the time between beginning of fuel injection and beginning of fuel combustion. Reduction in ignition delay will enhance longer combustion duration and this will enable smoke reduction. Ignition delay is influenced by CN. The addition of hybrid nano particles improved CN hence lowered ignition delay as well as kinematic viscosity. All these factors are influential in improving combustion efficiency and lowering smoke generation.

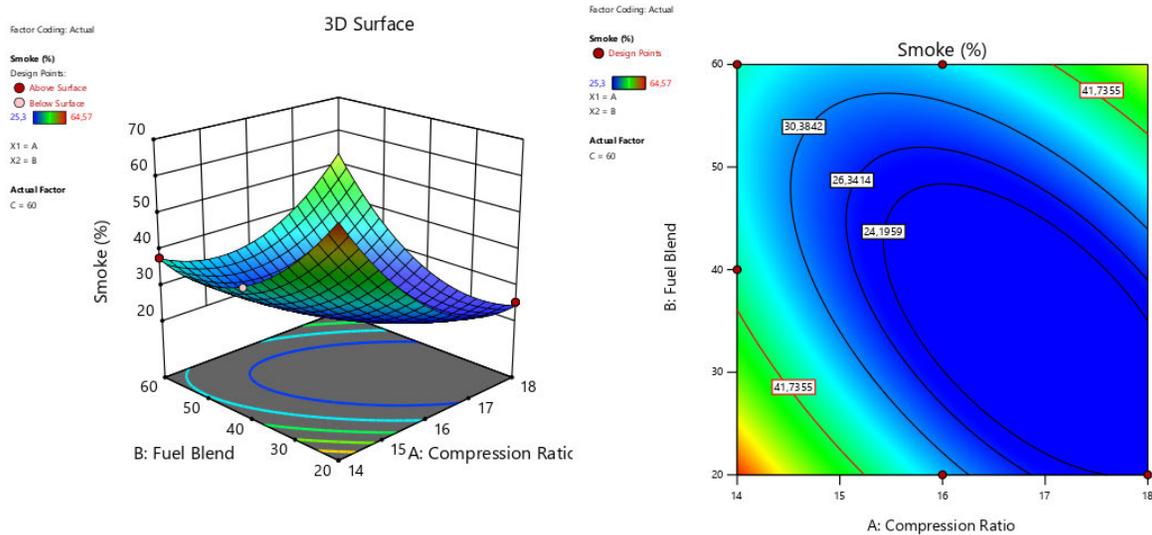


Figure 13. The interactive effects of CR and fuel blend on smoke emissions

5. CONCLUSIONS

1. The Response Surface Method (RSM) design tool (Design-Expert 13) aided in the design of the experimental analysis, being able to model engine responses as influenced by several factors. This programming tool was profoundly useful to plan the investigation and perform statistical analysis. The RSM method diminished the time required for the investigation by limiting the number of engine trials of tests to be performed and generated statistically sound models for the responses under investigation.
2. Derringers Desirability approach of RSM has shown itself to be the most straightforward and proficient optimization method in the current investigation with a solution of highest desirability of 0.898 (Table 11).
3. Optimization process revealed that the desirable compression ratio of 14.71, load of 74.98 % and hybrid blend of 60 ppm yielded the best engine responses.
4. Engine responses at optimal level were BTE of 33.63 %, BSFC of 0.292 kg/kWh, NO_x of 700 ppm, UBHC of 25 ppm, CO of 0.361 % and smoke opacity of 33.9%. Interaction charts showed that increasing the hybrid nano particle showed increased BTE and significant reduction in BSFC. Also, significant reduction in NO_x, UBHC, CO and smoke was noted with increment in nano particle addition to the biodiesel blend (WCO20).

- Mixing nano particles in biodiesel blends results in some improved fuel features which include the high oxygen content, the low pour point and the low viscosity and higher calorific value which help to offset biodiesel drawbacks and improve its features such that they are even better than those of fossil diesel fuels.

The contribution of this exploration is to introduce a more precise decision support technique that allows informed engine performance and emission behavior parameters evaluation and comparison. This approach provides a new method for estimating and optimizing engine data derived from hybrid nano particles doped waste cooking oil biodiesel blend. The two generally extraordinary advantages of the investigation are as follows: (1) original data sets derived from varying engine load, compression ratio and nano particle dosages are unveiled and (2) the subtleties of the strategy are additionally discussed. Even though the new methodology (RSM) is complicated, it gives higher adaptability and precision with less convoluted experimentation, as the input parameters and numerical models can predict the outcomes accurately. Thus, the quantity of experimentation can be decreased, and this brings about lower costs and less time required for the research process. This method can be used in any type of engine model. It can also be applied to various engine variables.

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CHAPTER 6: BIODIESEL PRODUCTION PROCESS FLOW DESIGN VIA CALCIUM OXIDE CATALYSED ETHANOLYSIS TECHNIQUE.

This chapter provides a detailed report on waste cooking oil biodiesel production process flow design. The aim of this chapter was to design a plant model which incorporates modern advanced biodiesel creation technologies, perform economic assessment of the process, and develop equipment specifications. The outcome of the work has been published in the International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)

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BIODIESEL PRODUCTION PROCESS FLOW DESIGN VIA CALCIUM OXIDE CATALYSED ETHANOLYSIS TECHNIQUE

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ABSTRACT

This paper presents a report on the design of a process flow method and a case study of a mini-waste cooking oil biodiesel (WCOBD) plant. This report comprises a detailed process development, technical and economic assessment incorporating material and energy computations, equipment cost estimations, and specifications. The designed plant is expected to produce 16.88 tons per annum. The cost of biodiesel was evaluated based on researched cost variables and plant data. The designed plant seems economically viable, and a biodiesel production cost of ZAR10.10 per kg was evaluated by the investigation giving a total production cost of ZAR10,100.00 (US\$673.33) per ton. Mass balances were utilized to design a 50 L pressurized reactor tank which is suitable for small to medium sized biodiesel producers.

KEYWORDS: Waste Cooking Oil Biodiesel; Waste Cooking Oil; Cetane Number; Free Fatty Acid & FATTY Acid Alkyl Esters

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NOMENCLATURE

ASTM	American Society for	CV	Calorific value
Testing and Materials		FAAE	Fatty acid alkyl esters
CaO Calcium Oxide		FD	Fossil diesel
(Ca (NO ₃) ₂ .4H ₂ O)	calcium nitrate tetrahydrate	NaOH	Sodium hydroxide
EtOH	Ethanol	NO _x	Nitrogen oxide
FFA	Free fatty acid	US \$	United States Dollars
H ₃ PO ₄ .	Phosphoric acid	WCO	Waste Cooking Oil
CN	Cetane number	WCOBD	Waste Cooking Oil
CI	Compression ignition	Biodiesel	
CO	Carbon monoxide	ZAR	South African Rand
CO ₂	Carbon dioxide	EAC	Equipment acquisition cost

1. INTRODUCTION

Massive reliance on fuel has impacted negatively on climate and the environment (Perera 2018). This scenario has

been caused by the emission of toxic gases generated when fossil fuels are burnt inside internal combustion engines which are the transport sector's major sources of energy. These have been the main drivers of global warming and climate change. This scenario has encouraged a search for renewable fuels which are non-toxic, and biodiesel has been identified as a viable replacement for fossil diesel fuel. Biodiesel is a long chain methyl ester derived from transesterification of vegetable oils or animal fats. These energy resources possess similar fuel properties to those of fossil diesel fuel. Despite gaining global attention, biodiesel is yet to gain significant market share due to the high cost of feedstock acquisition, which is why waste cooking oil (WCO) is a promising option.

Homogeneous catalyzed reactions are frequently used to transform free fatty acids (FFA) via methanol to biodiesel. However, this process has proven to be rigorous, costly, and harmful to the environment (Abdullah, Hanapi et al. 2017). The recuperation of the catalyst from the reaction byproducts is complex and challenging. Moreover, a tremendous measure of glycerol is created, and filtering the products yields a lot of wastewater, raising the cost of the purification process. Furthermore, biodiesel produced with this technique has proven to be insignificant when evaluated economically against fossil diesel. This is chiefly on the grounds that the catalyst is sensitive to high FFA containing feedstocks and can only handle feedstocks with FFA under 0.5% wt %. These high-quality feedstocks are acquired at high cost rendering an expensive fuel product. Several studies have researched the potential of other options which can possibly be more financially viable. These must incorporate utilization of less expensive feedstock and easily attainable catalysts as technological options. This specific technique must utilize less expensive catalysts with somewhat higher reactant capability, and requires simple catalytic recuperation, which enables repeated utilization of the catalysts. Heterogeneous catalysts have the capability of avoiding the drawbacks shown by homogenous base catalysis techniques. Heterogeneous catalysts have stood out as most appropriate among promising catalysts because of their high capacity to catalyze transesterification reactions and because of their reusability behavior. Besides being insensitive to feedstock FFA content, these catalysts are derived from locally accessible resources such as clay, eggshells, and so forth.

Amongst the heterogenous catalysts studied, calcium oxide (CaO) has risen to be the most fascinating option available. CaO has risen to be the most broadly researched heterogeneous catalysts among the metal oxides, capable of delivering around 96 % biodiesel yield (Ljupković, Mičić et al. 2014). This catalyst is nano crystal in nature which gives it a high surface area to volume ratio. In addition, CaO is easy to manufacture and can be developed from locally available resources such as eggshells, limestone and seashells, making it cheaper to produce compared to NaOH and KOH. Ljupković, Mičić et al. (2014) investigated the properties of CaO catalysts in the creation of biodiesel and found that these catalysts possess unique features capable of significantly improving the process. These unique properties include a shorter reaction duration (up to 120 minutes), standard working temperature (64 °C) and pressures, a generally low molar proportion (6:1), and catalysts concentration (1 wt.%). This investigation found that all the above variables enable the development of high-quality biodiesel reaching purity as high as 96 % (Ljupković, Mičić et al. 2014). A study by Avhad, Sánchez et al. (2016) revealed that ideal conditions for CaO catalyzed ethanolysis were 120 minutes reaction time, reaction temperature of 75 °C, molar ratio of 9:1 and catalyst concentration of 7 wt %.

The significant challenges related to the manufacture of biodiesel as a fuel are its high cost of creation, having generally less energy content when evaluated against fossil diesel, and delivering higher nitrogen oxide discharges when it is burnt (Avhad, Sánchez et al. 2016), with the main challenge being cost (Marchett et al., 2008). There are three ways to achieve unit cost decreases: improving the yield, diminishing capital expenses, and decreasing the crude material costs

with feedstock cost being the most significant cost (Mulugetta 2009). All these potential ways require investigation with different technologies encompassing various catalysts and feedstocks. In addition, localized engineering design of biodiesel plants is non-existent as most researchers are focusing on the chemistry side of the technologies. No studies on process design and evaluation using a batch reactor and ethanolysis catalyzed by CaO have been performed to date. Therefore, this research is aimed at designing a process flow for WCO biodiesel production from a CaO catalyzed ethanolysis process with an economic assessment of the selected system. The information acquired from this research will be used to set up a biodiesel plant in South Africa and the technology will be applicable to most of the sub-Saharan region.

2. PROCESS DESIGN AND CASE STUDY

2.1. METHODS AND MATERIALS

2.1.1. Materials

Waste cooking oil was purchased from Enfield at ZAR3.25/kg and its properties were evaluated as shown in Table 1. glycerol (GL), phosphoric acid CAS number 7662-29-3, molar ratio 97.994 g/mol and 85 % purity were purchased from Corebit (Pty) Ltd at ZAR3/kg and ZAR 5.45/ kg respectively. Magnesium silicate (MgSiO₃) CAS (1343-88-0) at ZAR 728/kg was purchased from Sigma Aldrich. Chemicals for nano CaO production were purchased from Sigma Aldrich, namely, calcium nitrate tetrahydrate (Ca (NO₃)₂·4H₂O) 13477-34-4 and ethylene glycol (C₂H₆O₂) CAS number: 107-21-1, sodium hydroxide (NaOH) CAS number: 1310-73-2 at ZAR 400, ZAR12.00 and ZAR6.00 respectively. The safety precautions described for each chemical reagents from the suppliers were followed during the experimental process.

Table 1: Waste Cooking Oil Properties

Oil Property	Values	ASTM Limits*	Units
Flash point	168	>130	°C
Density (40 °C)	890		Kg/m ³
Kinematic viscosity	3.9	1.9–6.0	mm ² /s
Water and sediments	0.04	<0.05	%
Acid number	2.56	0.50 max	mg KOH/g
Free glycerol	0.013	0.020	wt.%
Total glycerol	0.018	0.024	wt.%

2.1.2. CaO nano- Catalysts Synthesis

0.74 kg of CaO catalyst was developed using the thermal decomposition technique as per Tang, Claveau et al. (2008). 3.20 kg of calcium nitrate tetrahydrate (Ca (NO₃)₂·4H₂O) was dissolved in a 6.43 ml of ethylene glycol solution. Thereafter 0.57 kg of NaOH was added. The mixture was thoroughly stirred for 12 min and thereafter kept in static conditions to enhance uniform gel formation. The mixture was then purified with distilled water and vacuum dried before the nano particles were calcinated. The calcination was performed at 700 °C for 2 h using a dry helium gas stream of 150 mL/min, then, at that point cooled to 150 °C under the same gas stream medium.

2.2. System Design

This investigation developed a mass balance model focusing on pretreatment, ethanolysis, neutralization, quenching, centrifugal phase separation, waterless purification and vacuum filtration, and vacuum distillation processes for biodiesel production (Figure 1). These mass balances were utilized afterwards to design a biodiesel plant reactor and other equipment reacquired for biodiesel production. Starting with 37 kgs of WCO, a series of pretreatments and ethanolysis

were performed. Glycerol was added to enhance the breakdown of triglycerides to diglycerides. This process lowered the acid values of the feedstock. Utilization of glycerol lowers the cost of pretreatment since the glycerol can be recovered from the biodiesel production process. The mass balances evaluate masses entering and leaving a process thereby enabling the development of correct sizing and specifications of required equipment. Detailed explanations regarding the developed processes are described in sections 2.2.1 to 2.2.7.

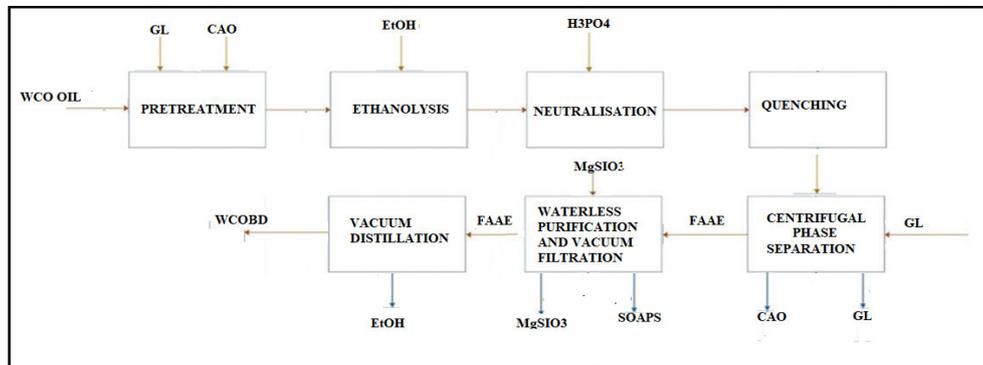


Figure 1: Developed Process Flow Diagram.

2.2.1. Procedure for Pretreatment

Pretreatment of FFAs was performed to lessen the contaminants and acid value of the feedstock oil and glycerolysis. Glycerolysis refers to the transesterification reaction of glycerol with triglycerides (fats/oils) to form mixtures of monoglycerides and diglycerides. This is preferred due to its lower cost. The pretreated WCO oil feed stock was premixed with CaO to enable improved ethanolysis reaction. These two compounds are immiscible hence a magnetic stirrer was utilized at 1 250 rpm for 5 min. Crude glycerol was then added during pretreatment to lower the acid value and facilitate a quicker reaction, and this reaction was performed in a batch reactor at an elevated temperature of 200 °C. Acid number was evaluated every 15 min until it dropped below 1 wt % at which point glycerol addition ceased. The process was deemed to be completed when the FFA dropped below 1 wt %.

2.2.2. Ethanolysis Reaction Procedure

This strategy was performed with a molar ratio of 9:1 by weight of WCO under the influence of a CaO catalyst. Ethanolysis was performed by adding ethanol to the pretreated premixture at 120 °C for 2 h. The conditions under which ethanolysis was performed are shown in Table 2. This process was stopped and mass evaluated by measuring the duration of the process (2 h).

Table 2: Conditions for Ethanolysis

Reaction temperature [°C]	120
Reaction time [min]	120
EtOH-to-oil molar ratio	09:01
Mixing speed [rpm]	1250

2.2.4. Quenching Strategy

When ethanolysis was finished, the products were dipped in cold water of around 5 °C and this was done to suppress any possibility of reversible reaction which would subsequently lower biodiesel yields. The products of ethanolysis were

immersed in a simple reactor for 6 min and stirred at about 1 000 rpm.

2.2.3. Neutralization Strategy

The mixture was mixed with H_3PO_4 . This process was performed at room temperatures of 20 °C and 1 atm. The duration of this process was 2 min to 5 min and was repeated until a pH of 7 was reached. The mixture was then dried at 105 °C in an oven for 8 h. This process required around 700 W. The process was deemed to be complete when pH reached 7.

2.2.5. Centrifugal phase Separation Process

This stage was performed to recuperate fatty acid alkyl esters (FAAE) from the products of ethanolysis. The reactants were centrifuged at 3 500 rpm for 12 min. This resulted in the formation of upper and lower layers.

2.2.6. Waterless and Vacuum Filtration Strategy

This process was aimed at purifying the Fatty acid methyl ester using waterless method. Waterless method is preferable to water purification due to its ability to eliminate loss of biodiesel and reduce soap formation. Ten percent Magnesium silicate ($MgSiO_3$) wt % (of oil was added to the fatty acid alkyl esters (FAAE) and mixture was thereafter stirred at 1250 rpm for 6 minutes. The products of this process were then vacuum filtered.

2.2.7. Vacuum Distillation Process

This is the stage for recuperating a portion of the unreacted EtOH and purifying of WCOBD. The FAEE derived from the waterless purification was heated to 100 °C (slightly above boiling point of EtOH). Then, at that point a vacuum pump was utilized to extricate the EtOH fumes at 1 MPa. These conditions will eventually result in conversion of EtOH gas into liquid.

2.3. RESULTS

2.3.1. Mass balance Evaluations

CaO catalyzed ethanolysis was developed following a progression of pretreatments and ethanolysis processes until 34.04 portions of WCOBD was produced. Starting with 37 kg of crude WCO oil and following the designed processes it was found that each batch required 3.90 portions of glycerol for pretreatment and 0.74 (2 % wt of oil) portions of CaO and 3.70 (1:10) portions of EtOH for ethanolysis process. Immediately after ethanolysis the products were quenched in water baths at 5 °C for 8 min. After the quenching process, neutralization was brought about by adding 0.52 portions of H_3PO_4 until pH of 7 was reached. Separation of biodiesel and glycerol is difficult because of stable emulsion formations. To improve the separation of products, an additional 9.25 (25 % wt of oil) portions of glycerol were added to the mixture. Centrifugal phase separation was performed which resulted in recovery of 41.44 portions of FAEE, 21.09 portions of glycerol and 0.51 portions of CaO catalysts. This process was followed by waterless purification and vacuum filtration in which 34.12 portions of FAEE (biodiesel) and 3.65 portions of magnesium silicate ($MgSiO_3$) were blended in with the top layer (FAEE) and afterwards the combination was vacuum separated. This sub-process delivered 1.83 parts of soaps and 3.75 portions of $MgSiO_3$ and 5.49 portions of other substances consisting of unreacted reagents represented by 'others' on the process flow diagram. The top layer comprised 34.12 parts FAEE which was further vacuum refined to deliver 34.04 parts of biodiesel (WCOBD) and 0.08 parts of EtOH.

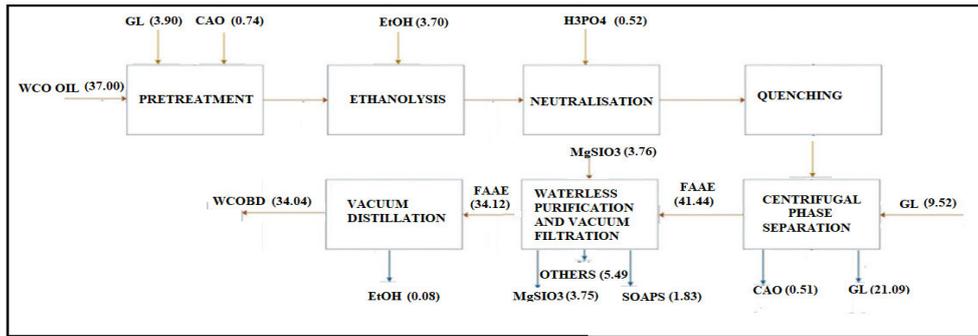


Figure 2: Material Balance Evaluated through Series of Pretreatments and Ethanolysis Processes.

Table 3: Summary of Mass Balances from Developed from Series of Experiments

Mass Balance of Wcobd Plant			
IN	WCO oil	37.00	
	Ethanol	3.70	
	CaO	0.74	
	H3PO4	0.52	
	Glycerol	13.15	
OUT	WFAAE	34.04	
	Glycerol	21.09	
	CaO	0.51	
	Soaps	1.83	
	Others	5.49	

2.3.2. Evaluation of Annual Production

Considering weekends and 13 holidays on the South African calendar, 248 working days are available per year. In a day two batches are possible giving a total of 68.08 kg of daily production. Multiplying the daily production and available working days gives an annual production of 16 880 kg (16.88 tons).

2.4. Economic Assessment of WCO Production

A technical evaluation of CaO catalyzed ethanolysis showed that this technique is very suitable for delivering biodiesel of high yields and quality. A high yield of 92 % (34.04/37) was unveiled by this technique. This result is similar to yields found from a comparative study (Avhad et al. 2016). Another evaluation performed by Velickovic (2016) yielded a higher volume (about 98 %) of biodiesel created under comparable reaction conditions. Nonetheless, very few studies have researched the financial assessment of delivering biodiesel from WCO oil utilizing CaO as a catalyst. In this investigation, the current best costs of materials, utilities, and costs of labor utilized was used to evaluate capital venture costs and working capital using the process model that was developed. The total equipment acquisition cost (EAC) was evaluated from the researched cost units and plant equipment shown in Table 4. Total EAC was found to be R34,480.00 and its calculation is shown in Table 5. The value of the EAC was then utilized to evaluate most of the costs related to construction of a biodiesel plant based on the percentage allocation as per Karmee et al. (2015). Total investment capital costs for the biodiesel plant was determined by utilizing costing information acquired from suppliers in the biofuels business. These expenses were then scaled to evaluate average costs needed for standard a biofuel plant. Other local factors, for example, land value, utility expenses and work rates are aligned to the SA economy. Engineering procurement and construction (EPC) contracts from ethanol innovation suppliers were also utilized to provide a value estimation that

was utilized to consider the plausibility of the process. While this estimation can fluctuate by around 30 %, it is adequate to ascertain biofuel creation costs as they are substantially less sensitive to changes in capital expense than to changes in other factors, for example, feedstock costs. The summarized calculations are shown in Table 6. A total plant direct cost of **R83 919.27** was derived from direct costs such as equipment installation, piping, instrumentation of the plant, building and so forth. Having incorporated all the costs related to plant construction, a total capital investment of **R166 276.64** was assessed.

Market Variables	Minimum Value	Standard Value	Maximum Value
Biodiesel selling price (ZAR kg/1)	11.2	11.7	12.3
Feedstock oil cost (ZAR kg/1)	3.25	5.1	6.2
Cost of ethanol acquisition (ZAR kg/1)	1.6	4.8	5.3
Cost of CaO acquisition (ZAR kg/1)	1.2	1.7	3
Equipment care (% of PC)	30	75	300
Local tax (% of DFC)	230	430	650
Cost of Labour (basic rate in ZAR h/1)			
Operator	25	40	50
Reactor operator	35	45	65
Charge hand	40	50	80
Total basic rate (ZAR h/1)	100	135	195

Table 5: Equipment Acquisition cost Value Evaluation

Equipment Name	Units	Unit Cost (ZAR)
WCO tank (0.1 m3)	1	8,378.00
Splitter, mixer (1Kw)	1	4,698.00
Reactor (0.05 m3)	1	12,45170
Separator (decanter)	1	6,480.44
Extraction column, distillation	1	6,471.86
EAC		38,480.00

Table 6: Capital costs for the Construction of a Biodiesel Production Plant with 16.880-ton Annual Production Capacity

Cost Categories	% Allocation*	
Direct plant cost (DC)		
Equipment acquisition cost (EAC)		38 480,00
Equipment installation	20 × EAC	7 696,00
Refinery piping	20 × EAC	7 696,00
Instrumentation	10 × EAC	7 728,87
Insulation	3 × EAC	1 154,40
Electrical	10 × EAC	3 848,00
Utilities building	10 × EAC	3 848,00
Yard improvement	10 × EAC	3 848,00
Auxillary facilities	10 × EAC	3 848,00
Purchasing cost of unlisted equipment (UEPC)	10× EAC	3 848,00
Installation cost of unlisted equipment	50 × EAC C	1 924,00
Total plant direct cost (TDC)		83 919,27
Indirect plant cost (IC)		
Engineering	25 × TDC	20979,818
Construction	25 × TDC	20979,818
Other indirect costs		2625
Total plant indirect cost (PIC)		44584,635
Contractors' fee	5 × (TDC + PIC)	6425,1953

Contingency	$10 \times (\text{TDC} + \text{PIC})$	12850,391
Sum of contactor's fee and contingency (CFC)		3435
Total direct fixed capital cost (TDC + PIC + CFC)		131 938,91
Working capital (WC) (25 x DFC)		32 984.73
Startup and training (S &T)		1350
Total capital investment cost (TDC +PIC+ CFC + WC + SVC)		166,273.64
*Percentage allocation is based on Karmee et al. (2015)		

For the chosen creation process, the base selling cost of biodiesel for the business to be beneficial is ZAR10.10 /kg (673.33 US\$ /ton) at the current exchange rate of ZAR15/US\$. This cost concurs with the biodiesel selling value estimate in the Food and Agricultural Organization – Organization for Economic Co-activity and Development (FAO-OECD) Agricultural Outlook 2016–2025. Raw materials for ethanolysis constitute 56 % to the production cost which is far lower than Gebremariam and Marchetti (2019) who estimated 80 % contribution for the cost of raw materials. The calculation method followed to evaluate this cost is shown in Table 6. These results reveal that WCO is the cheapest feedstock for commercial biodiesel production since this is only 14.84 % higher than that of fossil diesel fuel.

Table 7: Biodiesel Production Cost Based on 16 883 kg Production per Annum

Cost Category	Calculation	Amount (ZAR) %	%
1. Raw materials	From material balance	94,780,30	55,57
2. Utilities cost	From material balance	17,140,00	10,05
Variable Costs (VC)	(1) + (2)	111,920,30	0,00
3. Maintenance	$5\% \times \text{EAC}$	1,924,00	1,13
4. Operating labor	Manning estimates	564,00	0,33
5. Laboratory cost	$30\% \times (4)$	169,20	0,10
6. Depreciation	$10\% \times \text{TDC}$	8,931.93	5,71
7. Insurance	$2\% \times \text{DFC}$	2,638,77	1,55
8. Cooperate tax	$28\% \times \text{DFC}$	36,942,90	21,66
9. Factory expense	$5\% \times \text{DFC}$	6,596,95	3,87
10. Miscellaneous	Fixed	70,00	0,04
Fixed costs (FC)	(3) + (4) ++ (9)	57,819.75	
Annual operating cost	(VC) + (FC)	169,740.05	
Unit production cost	169,740.05 ZAR/16 880 Kg WFAEE	= 10.10 ZAR kg⁻¹	
	= 9.10 ZAR/ L (1liter = 0.90 kg)		

2.5. WCOBD Plant Equipment Design and Specifications

According to Van Gerpen, Shanks et al. (2004), the easiest method of biodiesel production is to utilize a batch reactor. In this type of reactor, two charging points located at the highest point on the tank are used to introduce the reactants into the reactor tank. Nothing is retrieved or added to the reactor until the reaction is completely finished. The authors' investigation explained that this reactor tank reactor comprises a tank with an agitator and essential heating system and cooling method. The tank is a jacket vessel for minimizing heat losses. Biodiesel yield will in general increase with reaction temperature, however, excessive temperature increases beyond the alcohol boiling point (ethanol 75 °C) diminish the yield because of ethanol vaporization. Therefore, a pressurized batch reactor was selected to cater for higher temperatures.

A 50 L reactor was selected based on the sizeable feedstock supply and to lower initial construction costs and its experimental evaluation is shown in Table 7. Masses and densities of the reactants were measured, and these were utilized

to size the tank. The proportions determined from mass balances were retained and the glycerol portion was lowered to reach the 50 L capacity. Lowering glycerol from 25 % to 12.1 wt % of oil will prolong pretreatment but lower the cost of production.

Table 8: Reactor Tank Sizing from Experimental Evaluation

Compounds	Mass of (M)[kg]	Volume of (V)[m ³]	Density (ρ)[kg/m ³]	Experimental data [wt%]	Overall density (ρ) [kg/m ³]
WCO oil	37,00	4,16E-02	890	83.00	
EtOH	3,70	4,68E-03	790	21.12	
CaO	0,74	2,22E-04	3340	0.44	
GL	4,48	3,48E-03	1288	7.00	
Total	45,36	5,00E-02		100,00	907,55

The formula used to evaluate the tank masses are shown in Equations 1 to 6

- Mass of WCO oil

Mass of WCO (M_{wcoil}) was assessed utilizing Equation 1

$$M_{wcoil} = v_{oil} \rho \quad (1)$$

- To assess the mass of ethanol (EtOH), test technique and molar proportion of 9 were used including its Table 8.

$$\text{Mass of ethanol (EtOH)} = 0.1 (M_{wcoil})(1:10) \quad (2)$$

- Mass of catalyst (CaO)

Test assessment was used to assess the measure of catalyst (calcium oxide, CaO) giving

$$\text{Mass of CaO} = 2 \text{ wt\% of } (M_{oil}) \quad (3)$$

- Evaluation of measure of added glycerol (GL)

Weight of WCO oil along with test investigation uncovered that

$$\text{Mass of added GL (MGL)} = 12 \text{ wt\% of } (M_{wcoil}) \quad (4)$$

- Total mass of reactants in the tank (MT)

$$MT = (v_{oil} \rho) + (0.1 M_{wcoil}) + (2 \text{ wt\% of } M_{wco}) + (25 \text{ wt\% of } M_{wcoil}) \quad (5)$$

- Overall density of reactants = $(MT)/0.05 \text{ m}^3$ (6)

2.4.1. Reactor Tank Design

According to Perry et al. (1997), the ratio of diameter to height of an unbaffled reactor should lie within the range of 0.75 and 1.5. In this design a proportion of 1: 1 is selected for use.

Reactor volume: $V = 0.05 \text{ m}^3$ (From Table 8)

$$V_T = \frac{\pi D_T^2}{4} H_T$$

But $H_T = D_T$

$$V_T = \frac{\pi D_T^3}{4} \quad (7)$$

Tank Diameter

$$D_T = 3 \sqrt{\frac{4 \times 0.05}{\pi}} \quad (8)$$

$$D_T = 0.4 \text{ m}$$

Considering that the V_T is 60 % of total reactor height, (H_R) is computed as follows:

$$H_R = \frac{0.40}{0.6} = 0.663 \text{ m}$$

2.4.2. Impeller Design

According to Verschuren et al. (2001), the diameter of impeller (D_{IM}) ranges from $(0.3 - 0.6) D_T$ and in this design a factor of 0.4 was chosen and therefore:

$$D_{IM} = 0.4 \times 0.4 = 0.16 \text{ m} \quad (9)$$

Impeller spacing equals $\frac{D_R}{2.6918}$, giving:

$$\text{Impeller spacing} = \frac{0.4}{2.6918} = 0.148 \text{ m} \quad (10)$$

Number of impellers equals $\frac{D_R}{\text{Impeller Spacing}} = \frac{0.4}{0.16} = 2.5$ which translates to three impellers.

Shaft impeller was designed based on torsional stresses

$$D_{IS} = 0.208 D_{IM} = 0.033 \text{ m} \quad (11)$$

Impeller blade width and height were evaluated using the following equation

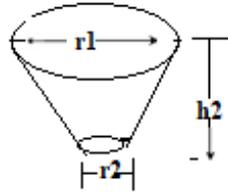
$$\text{Blade width} = \frac{D_{IM} - D_{IMS}}{4} \quad (12)$$

$$\frac{0.16 - 0.033}{4} = 0.032 \text{ m}$$

$$\text{Blade Height} = \frac{D_{IM} - D_{IMS}}{2} \quad (13)$$

$$= \frac{0.16 - 0.033}{2} = 0.064 \text{ m}$$

Clearance height from the tank bottom H_C is given by the volume of funnel shaped area (V_c) of the round and hollow vessel (where r_1 and r_2 are the radii of the reactor and outlet tap, separately) was given by the Equation 9.



$$V_C = \frac{\pi h_2}{3} (r_1^2 + r_1 r_2 + r_2^2) = 0.17 D_T \pi (0.25 D_T + 0.125 D_T + 0.00625) = 0.0078 \text{ m} \tag{14}$$

Hence, clearance will be approximately 0.1 m by applying volume of conical section as the clearance.

$$H_C = 0.1 \text{ m}$$

2.4.3. Mixing Power Evaluation

Reynolds number describes the level of laminarity or turbulence inside the reactor (which is under 10 for laminar or more than 10⁴ for turbulent stream systems),

$$N_{RE} = (D_{IM})^2 * \frac{N\rho}{\mu} \tag{15}$$

Whereby D_{IM} is impeller diameter 0.16m, N is impeller rotational speed 20.83 rev/s (1250 rpm) rev/s, ρ is density of reactants 907.6 kg/m³ (Table 8), μ is fluid viscosity of the oil 0.21 Pa s. Computing Reynolds number gives N_{RE} of 2304 (Liley et al. 1999).

$$P_{DELIVERED} = N_p * \rho N^3 D^5 \tag{16}$$

where N_p is the power number, which relies upon the Reynolds number calculated in Equation 15 and was acquired from nomographs as defined by Green and Southard (2019). Other variables are those defined in Equation (15). The relationship evaluated in Equation (16) is given by plots of power number versus Reynolds number for various sorts of impellers (Tilton, 1999). The power number relating to a Reynolds number of 2304 corresponding to an impeller with two blades fall within 1 and 5, giving a power range of 746 W and 3112 W. 0.746 kW was selected.

Power density of mixing = P_{delivered}/Volume of tank (V_T)

$$P_{DENSITY} = \frac{0.746}{0.05} = 15 \text{ kw/m}^3 \tag{17}$$

Utilizing the discoveries by McCabe, Smith et al. (1993) for power density must be above of 2.0 kW/m³, the computation for Equation (17) showed that effective blending is possible under these conditions.

Table 9: Summary of Designed Equipment Specifications

Parameter	Designed Value	
Tank capacity (L) or [m ³]	50	
Total tank height [m]	0.663	
Tank diameter [m] for reaction	0.4	
Tank height [mm] liquid/ solid fill	388	
Liquid/ solid fill for reaction [%]	60	
Impeller diameter[mm]	160	
Impeller blade width [mm]	32	

Impeller blade length [mm]	50	
No. of impellers	3	
Impeller location height [mm]	100	
Diameter of impeller shaft [mm]	33	

5.3 CONCLUSIONS

This research work was aimed at designing a novel process flow based on CaO catalyzed ethanolysis process. From process design assessment, the evaluation affirmed that the establishment of a mini pilot plant by small to medium fuel producers in South Africa is achievable. However, the reaction process displayed high energy consumption owing to CaO thermal decomposition and pretreatment at raised temperatures to enhance the ethanolysis process. Nevertheless, it has been affirmed that biodiesel creation by means of CaO catalyzed ethanolysis is a novel way to enhance biodiesel from WCO. The developed technique, though challenging in terms of the many sub-processes, produced biodiesel of high quality, with a lower environmental impact as waterless purification was utilized. In terms of economic assessment this production process seems viable as the production cost per ton lies within the FAO anticipated production cost per ton. From mass balances a 50 L reactor was successfully designed together with some of its key auxiliaries.

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CHAPTER 7: CONCLUDING REMARKS, RECOMMENDATIONS AND FURTHER RESEARCH

This chapter provides detailed concluding remarks, contributions, and recommendations by the study

CHAPTER 7: CONCLUSION AND FURTHER STUDIES

7.1. Concluding Remarks

The concerns arising from massive exploitation of fossil derived energy resources assets requires a shift to alternative and renewable energy sources. Biodiesel has been identified as perhaps the most versatile option in contrast to FD, with comparable properties and various ecological advantages. This study was performed to promote biodiesel development in South Africa to evaluate the effects of nano particle properties of WCO and compare them with those of FD and international standards. This was done to discover how CI engines can fulfill future emission guidelines when WCO doped with hybrid nanoparticles is utilized as an elective fuel rather than FD. When contrasted with investigations described in the literature, this investigation is novel in that a hybrid nanoparticle was utilized. This enabled the researcher to eliminate most of the harmful emissions such as NO_x, PM, CO₂, UBHC and CO.

Of the multitude of methods that can be used to enhance biodiesel performance and simultaneously reduce NO_x emissions studied to date, nano particles seem to be most suitable. These incorporate higher surface area to volume ratio, higher oxygen content, higher catalytic properties and so on as reported in the literature review earlier in this thesis. Considering the results arising from the experimental investigations, it is evident that biodiesel doped with hybrid nanoparticles can become an alternative source of fuel for CI engines and assist engine manufacturers to meet stringent emissions standards with ease. Nonetheless, very little work has been done on this yet, especially towards NO_x gas emissions and performance enhancement. An engine testing facility was set up to enable retrieval of critical data sets that was used for analysis. WCO biodiesel was manufactured from localized feedstock, characterized, and utilized in performance and emissions evaluations. As per investigation of the impact of nanoparticles on engine parameters, it was concluded that the addition of nano additives can be utilized as an added substance in biodiesel because of their expanded surface area to volume proportion and their higher catalytic capability. Nano additives have been shown to improve the overall combustion process of biodiesel. Other concluding remarks are detailed as follows:

- Addition of a hybrid nano particles improved the calorific value of biodiesel and its blends and brought them closer to those of FD in all experiments performed. The CV values of the tested fuels for FD, WCO100, WCO100A50C50, WCO20, WCO20A50C50 were 43.10 kJ/kg, 40.10 kJ/kg, 41.8 kJ/kg, 41.4 kJ/kg and 42.9 kJ/kg respectively.
- Addition of hybrid nano particles showed a significant reduction in kinematic viscosity of the WCO biodiesel. Addition of nano additives reduced the base fuel kinematic viscosity significantly with WC100A50C50 improving viscosity of WCO100 by almost 14 % and WC20A50C50 decreasing it by 12 %. Kinematic viscosity of base fuels decreased with addition of the hybrid nano additive. This will prove to be a vital discovery. Biodiesel has higher kinematic viscosity which subsequently causes injector chocking, blockage of fuel lines and poor combustion behavior. Reduction in kinematic viscosity will enable biodiesel to be compatible with most engines using FD.

- As per the performance test results it is possible to infer that addition of hybrid nano particles prompted BTE improvement by a limit of 6.22 % and decreased BSFC by a limit of 10.2 %. From the investigation of emission results it was noticed that NO_x was diminished by 25.62 %, CO by 36.8 %, UBHC by 27.8 % and CO₂ by 31.23 % with addition of a hybrid nano additive to biodiesel compared to FD NO_x emissions. Decrease in smoke opacity by 17.68 % was likewise noted with the addition of nano additives to biodiesel and its blends.
- Optimization process revealed that the desirable compression ratio of 14.71, load of 74.98 % and hybrid blend of 60 ppm yielded the best engine responses. Engine responses at optimal level were BTE of 33.63 %, BSFC of 0.292 kg/kWh, NO_x of 700 ppm, UBHC of 25 ppm, CO of 0.361 % and smoke opacity of 33.9%. From analysis of the experimental results it is noted that the addition of nano particles plays a pivotal role in upgrading biodiesel fuel properties and bringing them closer to those of FD, thereby increasing its technical viability and the possibility of becoming a fuel for the future for CI engines.
- From analysis of the experimental results it is noted that the addition of nano particles plays a pivotal role in upgrading biodiesel fuel properties and bringing them closer to those of FD, thereby increasing its technical viability and the possibility of becoming a fuel for the future for CI engines.
- A detailed biodiesel process flow design was developed and economic assessment incorporating material balance was performed. The designed plant is expected to produce 16.88 tons per annum. The cost of biodiesel was evaluated based on researched cost variables and plant data which resulted in a biodiesel production cost of ZAR10.10 per kg giving a total production cost of ZAR10,100.00 (US\$673.33) per ton.

7.2 Thesis Contributions

This research work has made a critical contribution towards strategies to control NO_x emissions and improve biodiesel's performance attributes by means of utilizing nanoparticles. Results unveiled by this research provide a platform for more investigations of biodiesel doped with nano particles. Results discussed in this thesis are vital and can be useful to elevate nano particle doped fuels examination to accomplish practical framework plan, better execution, and diminished emissions along with providing directions for future exploration. The subsections below provide illustrate how this research filled some of the research gaps

(1) The effect of hybridized nano particles in controlling NO_x and all other exhaust emission gases is reported for the first time in the literature. Results acquired from this investigation were evaluated against neat FD therefore can be a useful tool for decision-making by policy makers and engine manufacturers.

(2) The modelling and optimization process for investigation of the engine parameters on an engine fueled with biodiesel doped with hybrid nanoparticles is done for the first time. This research work provides a vital tool that can be utilized to lessen engine trials that would be required to evaluate the impact of several variables on a diesel engine fueled with biodiesel doped with nanoparticles

(3) Influence of hybrid nanoparticles on engine performance features such as BTE and BSFC is reported in the literature for the first time. Signification gains were recorded with WCO biodiesel doped with hybrid nano particles; the fuel outperformed FD.

(4) The influence of hybrid nanoparticles on performance and emission behavior of a diesel engine fueled by WCO on NO_x has been performed for the first time and results are documented in this thesis report. This is accepted as being the main piece of this research since this examination affirmed that nanoparticles can reduce NO_x and PM discharges in a diesel engine and improve the performance features of biodiesel, bringing them closer to those of neat FD. This research is likely to attract more attention from researchers across the globe.

(5) A thorough survey of existing techniques utilized to produce biodiesel was conducted and documented which informed the production methods that were used in this research. Methods for evaluating properties of WCO properties were documented in detail providing a good platform for further research.

(6) Engine tests to derive performance and emission data were planned, designed, set up, , and documented, thereby providing vital information that was previously missing, for upcoming combustion researchers.

(7) Optimization of process parameters based on localized WCO feedstocks was conducted and method documented.

8) The process flow for WCO biodiesel production was completed together with an economic analysis, further affirming the economic viability of this feedstock for biodiesel production.

7.3. Further Studies

(1) It is suggested that further investigation be conducted on more varieties of nano added substances to discover which of them would be ideal to use with WCO in respect of engine performance enhancement and emission reduction. Definite examinations on the chemistry of these added substances ought to be done to realize which of their properties are vital for emission reduction.

(2) A search for a suitable surfactant that will enable prolonged stability of nano particles inside the base liquid (diesel/biodiesel) as these were identified as a major barrier to their usage.

(3) In order to fully understand combustion characteristics of nano particles doped biodiesel, studies of spray attributes, such as Sauter mean diameter and cone angle are needed, to investigate for better atomization.

(4) Studies on the impact of nanoparticles on exhaust emission equipment are recommended as this might aid in evaluating the existence of spillage of nano particles into the environment which could be harmful.

(5) Experiments should be conducted to trap the conceivable unburnt nanoparticles from the fumes of the diesel engines to protect the worldwide climate.

(6) Computational fluid dynamics on combustion involving nano additives is advised.

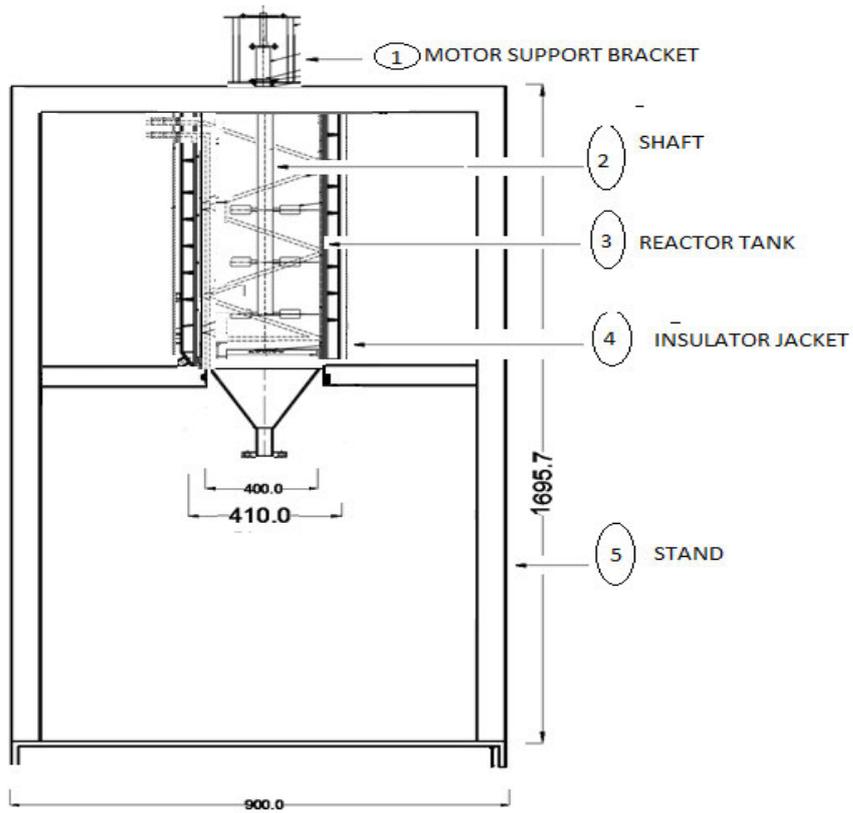
(7) Studies to assess the impact of nanoparticles on unregulated outflow need to be explored.

APPENDICES

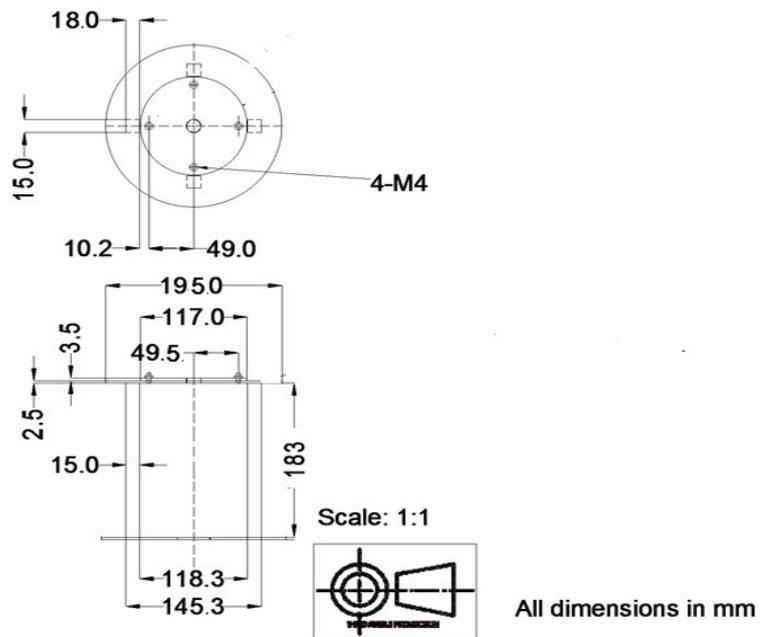
APPENDIX 1: DETAILED MASS BALANCE

Materials and utilities		Batch process
		kg/batch
Final Product	WCOBD	34.04
Raw material	WCO oil	37.00
	Feed of EtOH (Ethanolysis)	3.70
	CaO (Ethanolysis)	0.72
	Feed of GL (separation)	9.25
	H3PO4	0.52
	Feed of MgSiO3	3.76
Byproduct	Reusable GL	21.09
	Recyclable EtOH	0.08
	Reusable CaO	0.51
	Waste soaps	1.83
	MgSiO3	3.75
Utilities	Pre-treatment	
	Heating [MJ/batch]	8,480.00
	Stirring (mechanical)[MJ/batch]	132.00
	Reaction	
	Heating [GJ/batch]	9,270.00
	Stirring (mechanical) [MJ/batch]	154.00
	Centrifugal separation [MJ/batch]	68.00
	WCOBD purification	
	Mechanical stirring [MJ/batch]	26.32
	Vacuum filtration [MJ/batch]	19.10
	Vacuum distillation (heating) [MJ/batch]	25.10

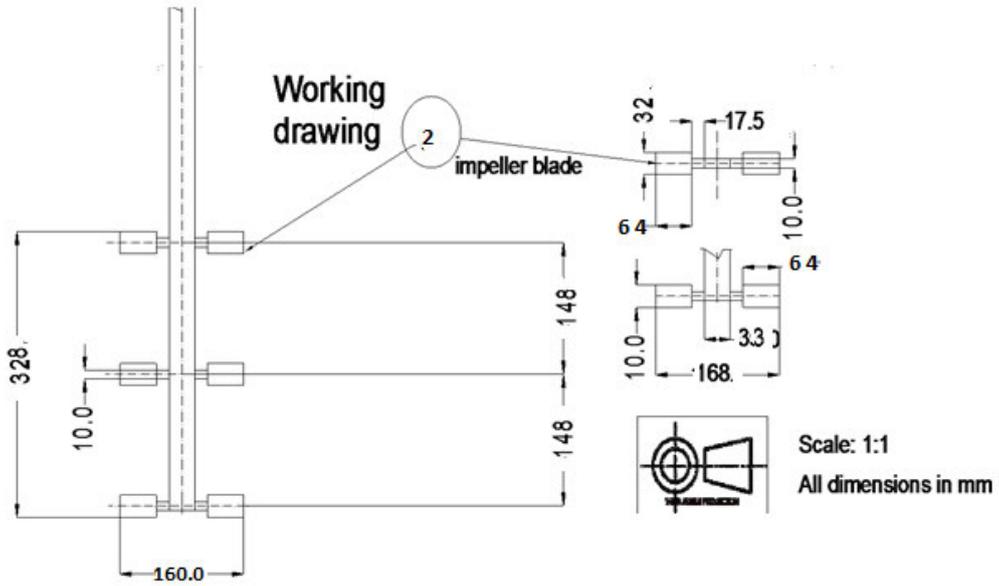
APPENDIX 2: ASSEMBLED PRESURED BATCH REACTOR



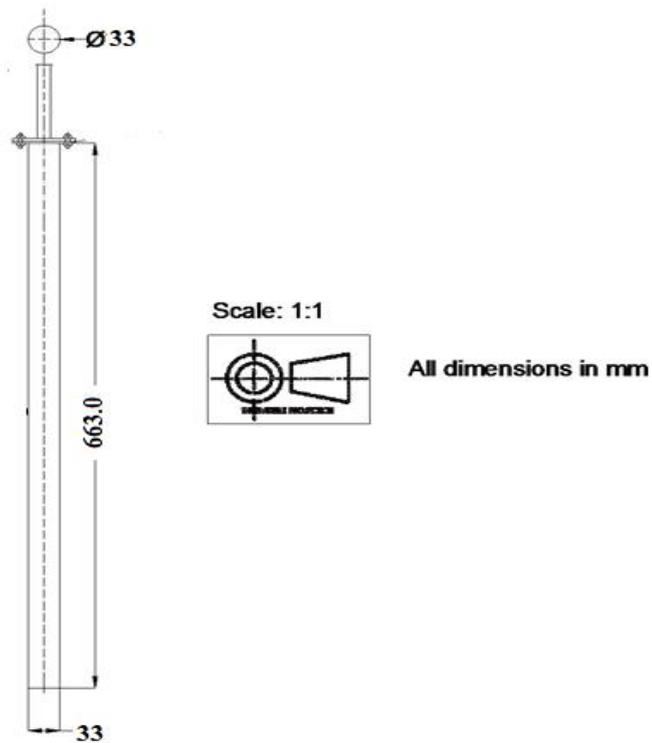
APPENDIX 3: DETAILS OF MOTOR SUPPORT BRACKET



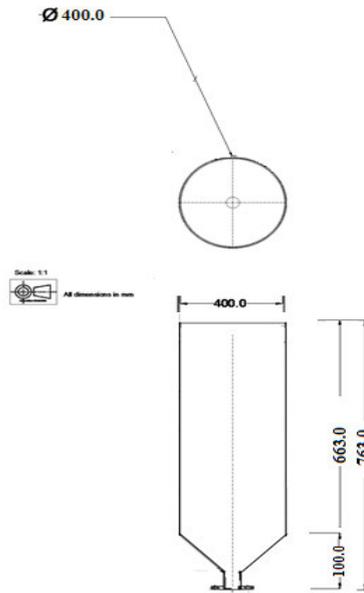
APPENDIX 4: IMPELLER BLADE SCHEMATIC



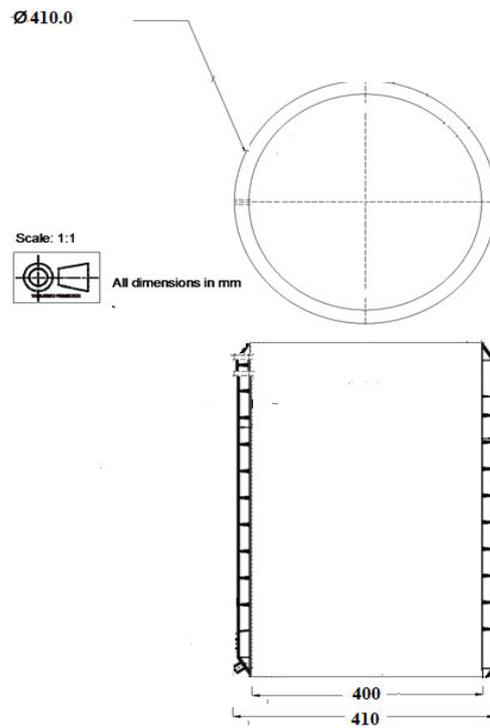
APPENDIX 5: SHAFT DESIGN



APPENDIX 6: REACTOR TANK



APPENDIX 7: INSULATOR JACKET



APPENDIX 8.1

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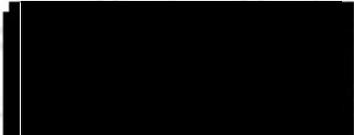
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