

**COLLEGE OF AGRICULTURE, ENGINEERING AND SCIENCE**



**STUDYING THE FEASIBILITY OF HYDROPROCESSING  
USED COOKING OIL INTO HYDROGENATION DERIVED  
RENEWABLE DIESEL FROM LOCAL FEEDSTOCK AND  
CATALYST**

By

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Durban, South Africa

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As the candidate's supervisors, we have approved this thesis for submission.

Signed:



## DECLARATION 1 – PLAGIARISM

I, **Josiah Pelemo** declare that:

1. The research reported in this thesis, except where otherwise indicated, is my original research.
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- Catalytic hydrogenation of UCO into HDRD using BBTPPFS heterogeneous catalyst for compression ignition (CI) engine.
- Formulation of the optimal mixing ratio between silica oxide and BBTPPFS catalyst with potential to mild crack UCO into HDRD.
- To know the effect of hybridization of feedstock on the production of HDRD.
- Hybridization of feedstocks provides a straightforward, easy, cost-effective, and innovative way of adjusting and enhancing the physicochemical properties, thermal, and spectroscopic behavior of feedstock with a view to enhancing their suitability for HDRD productions.
- The research will unveil the elemental composition of thermal, spectroscopic behavior of coal fly ash as a potential catalyst candidate for the conversion of UCO into green diesel.

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## DECLARATION 2 – PUBLICATIONS

This section presents the articles that form part and/or include the research presented in this thesis. The following papers have been published, accepted or are under review:

### ISI/SCOPUS/DoHET Accredited Journals

1. **Josiah Pelemo**, Freddie L. Inambao, & Emmanuel Idoko Onuh. (2020). Potential of used cooking oil as a feedstock for hydro-processing into hydrogenation derived renewable diesel: A review. *International Journal of Engineering Research and Technology* (IJERT). ISSN 0974-3154 Vol. 13, No. 3 (2020), pp. 500-519 International Research Publication House®.  
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2. **Josiah Pelemo**, Omojola Awogbemi, Freddie Inambao, & Emmanuel I. Onuh. (2021). Hybridization of waste cooking oil: An innovative technique for improved feedstock. *International Journal of Mechanical and Production Engineering Research and Development* (IJMPERD) Journal with ISSN (Print): 2249-6890; ISSN (Online): 2249-8001. Vol. 11, No. 3, Jun 2021, pp. 441-454. Transstellar Journal Publications.  
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(Published)
3. **Josiah Pelemo**, Omojola Awogbemi, Freddie Inambao, & Emmanuel I. Onuh. (2020). In-situ hybridization of waste palm oil: A physicochemical, thermal, and spectroscopic analysis. *Jordan Journal of Mechanical and Industrial Engineering* (JJMIE). ISSN 1995-6665. Vol. 14, No. 4, December 2020, pp. 393-400.  
<http://www.jjmie.hu.edu.jo/vol14-4/05-160-20.pdf>  
(Published)
4. **Josiah Pelemo**, Omojola Awogbemi, Freddie Inambao, & Emmanuel I. Onuh. (2021). Development and characterization of coal fly ash reinforced with silica oxide for catalytic green diesel production. *International Journal of Mechanical and Production Engineering Research and Development* (IJMPERD) ISSN (Print): 2249-6890; ISSN (Online): 2249-8001. Vol. 11, No. 3, Jun 2021, pp. 405-420. Transstellar Journal Publications.  
<http://www.tjprc.org/publishpapers/2-67-1622884012-IJMPERDJUN202134..pdf>  
(Published)
5. **Josiah Pelemo**, Freddie Inambao, Emmanuel I. Onuh Omojola Awogbemi, (2021). A study to evaluate optimal catalyst properties sourced from Biowaste for hydro processing of used cooking

oil into green diesel. *International Journal of Mechanical and Production Engineering Research and Development* (IJMPERD) ISSN (Print): 2249-6890; ISSN (Online): 2249-8001; Vol. 11, Issue 5, Oct 2021, 33–50. **Transstellar Journal Publications**

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(Published)

6. Emmanuel I. Onuh, **Josiah Pelemo**, Danladi Bisu Yusuf. (2021). Engine performance, emission and physico-chemical valuation of waste plastic fuel: A case for fly ash catalyst pyrolysis. *International Journal of Advances in Engineering and Management* (IJAEM) [volume.php?issueid=27&title=Volume%203%20,%20Issue%202,%20February%202021](http://www.ijaem.net/abstract.php?issueid=27&title=Volume%203%20,%20Issue%202,%20February%202021)

(Published)

7. **Josiah Pelemo**, Freddie Inambao, & Emmanuel I. Onuh. (2021). Hydro-processing of hybridized used cooking oil into hydrogenation derived renewable diesel using local heterogeneous catalysts. *International Journal of Mechanical and Production Engineering Research and Development* (IJMPERD) ISSN (Print): 2249-6890; ISSN (Online): 2249-8001. **Transstellar Journal Publications.**

(Accepted)

## **DEDICATION**

This work is dedicated to the Almighty God, my helper and my ever dependence. To my family for their prayers, love, and for their consistent prayers and encouragement.

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My academic journey to study at the prestigious University of KwaZulu-Natal, Durban, and the successful completion of this thesis is actually the plan of God. I have given it all my physical, mental, emotional, and psychological strength to pursue this higher degree. I am surrounded by family, friends and colleagues, and those who have made remarkable contributions in my career development, who have been most supportive. I am indebted to them and offer my warm appreciation.

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## ABSTRACT

Identifying and developing heterogeneous catalysts capable of mild-cracking used cooking oil (UCO) into hydrogenation-derived renewable diesel (HDRD) or green diesel production has posed a considerable challenge to commercialization of this fuel type in the energy sector. HDRD has received wide acceptance as alternative renewable energy that guarantees a pollutant-free environment, sustainability, renewability, and possesses a high degree of compatibility with compression ignition (CI) engine with little or no retrofitting needed. This research focuses on the feasibility of locally sourced UCO and catalysts for hydrogenation into green diesel. The objectives of this research are to produce a biofuel for CI engine using biowaste catalyst and UCO as a feedstock. Various studies have highlighted the benefit of UCO as a feedstock for biofuel production. UCO was collected from takeaway outlets. The samples were prepared by the in-situ hybridization method, heated on an electric heater fitted with a magnetic stirrer kept at 110 °C and agitating speed of 50 rpm. The novel approach of in-situ hybridization of waste cooking oil was investigated. The outcome of the investigation showed that hybridization of the samples caused an increase in iodine value from 80.4 cg/g to 100.2 cg/g, affected kinematic viscosity, saponification value, and density, but did not affect cetane number, higher heating value, and acid value. The results are evidence that hybridization is a viable technique for improving the quality of existing feedstock and creating high-quality feedstock for the production of HDRD. Bio-based thermal power plant fly ash (BBTPPFS) was sourced locally from an ESKOM power plant in South Africa, pulverized, and developed into a fine powder, while SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO were procured from a commercial supplier. The samples were reinforced in various proportions and subjected to thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM), and X-ray diffraction (XRD) characterization processes. The results revealed that SiO<sub>2</sub> reinforced with BBTPPFS showed adequate properties that render it viable as a potential low-cost green catalyst for hydrogenation and capable of mild cracking to achieve a green diesel range C<sub>15</sub>-C<sub>18</sub>. The properties of locally sourced catalyst and feedstock were evaluated; experimental results revealed that the BET surface area, pore-volume, and micropore volume of fly ash reinforced with SiO<sub>2</sub> showed high catalytic viability because of its capability to withstand temperatures up to 950 °C. Also, the addition of SiO<sub>2</sub> to BBTPPFS showed a significant percentage increment in quartz, calcite, and mullite. This property is further evidence of its viability as a potential local catalyst for hydrogenation. HDRD were produced from hydro-processed used cooking oil using a locally sourced fly ash catalyst. The properties of HDRD were measured according to the ASTM standards and compared with green diesel. In terms of fuel quality, engine performance, and emission outcome, HDRD showed high yield and exhibited excellent fuel properties. The results from the engine test

and combustion performance in a diesel engine are compatible with results from a CI engine, and meet acceptable performance and emission standards.



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## ACRONYMS/ABBREVIATIONS

Al <sub>2</sub> O <sub>3</sub>	Aluminium oxide
AV	Acid value
ASTM	American Society for Testing and Materials
BBTPPFS	Bio-based thermal power plants fly ash
BET	Brunauer-Emmett-Teller
CaO	Calcium oxide
CI	Compression ignition
CN	Cetane number
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CFA	Coal fly ash
DTG	Differential thermogravimetry
EPA	Environmental Protection Agency
FA	Fatty acid
FAME	Fatty acid methyl ester
FBD	Fossil based diesel
FFA	Free fatty acid
FP	Flash point
FTIR	Fourier transform infrared
GCMS	Gas chromatography-mass spectrometry
ICE	Internal combustion engine
KV	Kinematic viscosity
HDRD	Hydrogenation derived renewable diesel
NO <sub>x</sub>	Oxides of nitrogen
PBD	Petroleum-based diesel
SEM	Scanning electron microscopy
SI	Spark ignition
SO <sub>2</sub>	Sulphur dioxide
SiO <sub>2</sub>	Silica oxide
SV	Saponification value
TEM	Thermal electron microscopy
TGA	Thermogravimetric analysis
HC	Hydrocarbon
UCO	Used cooking oil

ULSD	Ultra-low sulfur diesel
WCO	Waste cooking oil
WPF	Waste plastic fuel
WPO	Waste palm oil
XRD	X-ray diffractometer



## CHAPTER 1: INTRODUCTION

### 1.1 Introduction

The global aggregate energy consumption across the globe was  $6 \times 10^{20}$  J in 2020. About 24 %, 35 %, and 29 % of primary energy is derived from natural gas, coal, and crude oil respectively, while 5 % and 7 % is derived from renewable sources and nuclear energy respectively [1]. This implies that fossil-based fuel has the highest share (88 %) of global energy consumption. A projected increase in the world's energy demand by more than 55 % by 2030 (compared to 2020 consumption) is reported by the International Energy Agency (IEA), and an adequate plan to meet this growing demand in a sustainable manner is imperative [2]. Massive combustion of conventional petrol-based fuel causes environmental pollution and has shifted research efforts toward exploring alternative fuel technologies. In particular, green diesel, which displays similar but superior properties to biodiesel and petroleum diesel, is technically and economically feasible, and sustainable at a lower cost (when environmental costs are factored into the cost computation), and can be used as a drop-in fuel [3]. The increased application of diesel engines in transportation, electricity generation, ships, locomotives, etc., also supports the development of alternative fuels to improve their performance and mitigate the harmful effect of their emissions.

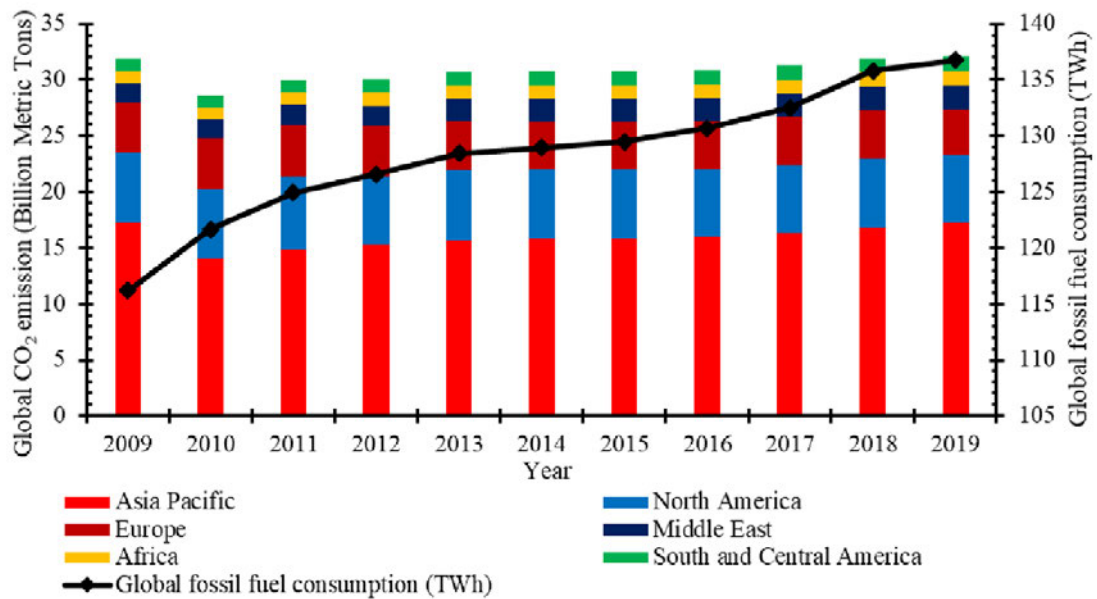


Figure 1.1: Global fuel consumption in selected continents

The growing concern about greenhouse gases (GHGs) and the resulting global warming exacerbated by the release of carbon dioxide (CO<sub>2</sub>) from burning fossil-based fuels may limit their use in the future. In addition, a shortage of oil and gas, and perhaps of coal, may be experienced. Figure 1.1 shows energy consumption and the corresponding emissions in some selected countries. The increasing demand for energy for various applications driven by population growth, socio-economic development, and sustained industrialization across the globe has led to increased consumption of fossil-based fuels. Transportation accounts for a large portion of that consumption. The transportation sector generates the largest share of greenhouse gas emissions, primarily from the burning of fossil fuels. Over 90 % of the energy used for transportation is petroleum-based [4]. Conventional fossil resources are not sustainable due to their non-renewability, depletion rate, and environment protection regulation [5]. The global oil consumption is projected to attain 239 quads in the year 2030, 60 % of which will be used for transportation while 40 % will be used for other applications [6]. The rapid growth in the transportation and industrial sector and the consequent increase in demand for conventional oil have also promoted the depletion of global reserves. Global oil consumption has witnessed a steady increase over the past two decades.

As of 2019, worldwide oil consumption has reached approximately 98.27 million barrels per day [7]. This has a damaging effect on the environment as a result of CO<sub>2</sub> emissions. With the increase of GHG in the biosphere, environmental problems such as global warming and climate change are emerging. There is a need to explore biofuel's potential to mitigate the above problems and be utilized as an alternative, clean, sustainable, and renewable sources of energy compatible with compression ignition (CI) engines without modification [8, 9]. Hydrogenation-derived renewable diesel (HDRD) has evolved as the only technically feasible alternative fuel for transportation due to its excellent low-temperature properties, and cetane number (CN). Hence, green diesel can be utilized as a drop-in fuel in CI diesel engines. HDRD is a reliable renewable energy that has the potential to solve environmental and economic problems as well as improve the standard of living in South Africa. Table 1.1 shows a comparison of other alternative renewable transportation fuels and HDRD. From the table it is evident that HDRD has suitable properties of net-zero carbon emission, excellent oxidation stability, and high cetane number compared to other biofuels. Catalysts and feedstock for hydrogenation can be locally sourced. Hence, commercialization of HDRD production is possible across the globe, and in South Africa, considering the abundant and sustainable UCO and biowaste resources. In addition, the introduction of hydrogen pressure into a reactor during hydrogenation serves the purpose of complete removal of oxygen. The biodiesel production process requires a lot of water which renders it more stressful on natural resources and has the potential for water wastage. The constituent of water in the biodiesel product has a significant effect on the storage and

transportation of the product. HDRD possesses a superior advantage over other alternative and renewable transportation fuels.

**Table 1.1: Comparative properties of green diesel fuel with selected alternative biofuel**

	<b>HDRD</b>	<b>FAME</b>	<b>PBD</b>	<b>ETHANOL</b>
<b>Properties</b>	Zero-oxygen content. Excellent oxidation stability. Net-zero carbon. High cetane number.	Oxygen content up to 11 percent. Very poor oxidation stability. Coking and trumpet formation. Carbon deposits. Oil ring sticking. Thickening and gelling of the lubricating oils. Low cetane number.	No oxygen is present in the fuel. poor oxidation stability. Low cetane number.	Oxygen is present in the fuel. Poor storage stability.
<b>Production process</b>	Hydro-processing,  Pyrolysis	Tran-esterification. Water wastage. The reaction of a fat or oil with an alcohol in the presence of catalyst to forms esters and glycerol.	Fractional distillation of crude oil.	Biorefinery
<b>Feedstock / catalyst</b>	Used cooking oil. Heterogeneous catalyst / biowaste catalyst. Hydrogen pressure	Vegetable oil / animal fat. Methanol as catalyst.	Crude oil.	Corn kernel / wheat kernel. Vegetable oil
<b>Availability/ cost of feedstock</b>	Abundant. Very cheap.	Available and expensive.	Very expensive.	Compete with food security.
<b>Emission</b>	Net-zero carbon	Net-zero carbon	Carbon emission	Net-carbon

HDRD can be produced from any type of bio-based renewable feedstock. The triglycerides and fatty acids in vegetable oil feedstock point to their potential for sustainable biofuel production [10]. Due to the high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility of vegetable oils, these do not burn completely, hence form deposits in the fuel injectors of diesel engines. For this reason, vegetable oils do not support direct application in CI engines [11]. Agricultural industries have been a significant source of edible oils for the production of biofuel [12]. Continual harvest of vegetable oils for biofuel production is practically unsustainable due to the food versus fuel dispute it has triggered [13].

Moreover, large spaces for farming activities are essential for cultivation, planting, and harvesting, and the threat of greenhouse gas emissions is a challenge. A feasible option to overcome these

challenges is to adopt UCO as a feedstock and a catalyst for HDRD production. According to the United Nations, the current world population of 7.9 billion is expected to reach 8.5 billion by 2030, 9.7 billion in 2050, and 11.2 billion in 2100 [14]. Africa's population is projected to reach 1.71 billion by 2030, with 53.5 % of the people living in cities [15, 16]. The demographic trend of South Africa's population will increase from 60 million in 2021 to 65 million in 2030 [17]. This trend is a clear indication of the massive generation of UCO. Apart from the availability and sustainability of UCO, it serves as a waste management method. It is also a potential feedstock for hydro-processing into HDRD.

## 1.2 Statement of problem

The need to improve CI engine performance and reduce tailpipe emissions requires strategies to replace finite fossil-derived ultra-low sulphur diesel (ULSD) with a green alternative that can provide a low cost and sustainable fuel source. The imperative of this quest is amplified by the ubiquity of the CI engine as the main platform for the global transportation of goods and prime mover of infrastructural solutions.

Internal combustion engines (ICEs) in the form of passenger vehicles, off-road machines, earth moving equipment, agricultural machinery, etc., are the main application in power generation, construction, and farming sectors. About 92 million automobiles were produced globally in 2019 compared to about 62 million cars produced in 2009 [18]. Pollutants (compounds of carbon, nitrogen, sulfur, halogenated, etc., and other organic compounds such as hydrocarbons, polycyclic aromatic hydrocarbons, carboxy, etc.) are generated as effluents of fuel combustion in ICEs. These pollutants have harmful effects on public health, air quality, increase the atmospheric temperature, and are precursors for climate change as a result of the emission of GHGs [19]. Carbon dioxide (CO<sub>2</sub>) comprises 74 % of GHG emissions, with about 89 % of CO<sub>2</sub> emissions emanating from fossil fuel consumption in lighting and heating, transportation, and industrialization. Methane, nitrous oxide, and fluorinated gases make up 17.3 %, 6.2 %, and 2.1 % of total GHG emissions from agriculture, waste treatment, gas flaring, and industrial processes, respectively [20]. Currently, biodiesel produced by transesterification of vegetable oils and methanol is widely used as a renewable fuel [21]. However, biodiesel usually suffers from disadvantageous fuel properties such as poor cold flow properties. Another disadvantage is the high oxidative instability of biodiesel which makes it difficult to store, pump and transport over significant distances without challenges, thus rendering it incompatible with current fuel distribution infrastructure. Furthermore, biodiesel has limited compatibility with CI engines, low chemical stability, and low caloric value due to the involved

oxygen atoms and the unsaturated C–C bonds, as compared with current fossil fuels [22]. The only feasible option is to explore local resources to produce HDRD, which offer net-zero carbon emissions that meet world standards.

Catalyst selection is a critical step because this has a significant effect on hydrocarbon quality and yield. The waste generated from Eskom's coal-fired power plants in South Africa is known as bio-based thermal power plant fly ash (BBTPPFS). This waste is a local catalyst available in tons, is sustainable, and can be harnessed as a resource for HDRD production. About 120 million tons of coal is consumed per annum, with almost 90 % of coal fly ash (CFA) being produced in the generation process, posing an environmental management problem. Policymakers in South Africa can address these challenges by harnessing this waste as a local catalyst for biofuel production to meet the increasing consumption of energy demands, reduce GHGs, and increase efficiency. The adaptation of this catalyst will make the value chain completely green. Apart from the availability and sustainability of the CFA, it is locally sourced, which solves the disposal problem. The application of hybridized UCO and a locally sourced catalyst capable of mild cracking to obtain green diesel is a novel area in the energy sector that South Africa needs to explore. This biomass waste and UCO will enhance the commercialization of green diesel production and address the unemployment problem. D Singh et al. used BBTPF as a heterogeneous catalyst for hydroprocessing of UCO. The results showed a higher yield of biofuel products with a lower acidity index over commercial catalysts [23]. The Neste Oil Co. developed a technology to produce over 800 000 tons of high-quality green diesel from vegetable oils per annum [24]. The product showed a high cetane number within 84 and 99, a low cloud point value of 30 °C, and storage stability for extended periods. These properties strengthen the performance of transportation engines [25].

### 1.3 Research motivation

The production of HDRD or green diesel fuel for CI engines using UCO and heterogeneous catalyst derived from waste is highly desirable from the point of view of sustainability. Scholars have highlighted some shortcomings of the use of biodiesel. Apart from the problems associated with the oxides of nitrogen (NO<sub>x</sub>) emissions [26, 27], reduction in engine power [28, 29], cold flow at temperatures between 30- and 50-degrees, oxidation stability, cost of production [30, 31], and water contamination are also significant problems for biodiesel users. This has shown clearly that numerous challenges inhibit the utilization of biodiesel as a fuel for CI engines and transportation fuel. These challenges have prompted the search for alternative energy sources to meet the growing population's

need for energy and mitigate the GHG emission in South Africa cities. Figure 1.2 shows the hydro-processing technique flow chart to obtain green diesel.

The cost of production hampers the commercialization of HDRD. In this research work, local feedstock and catalysts were used to produce HDRD. UCO was collected from canteens, restaurants, and takeaway outlets and processed to remove all the foreign particles. The oils were mixed in proportions to obtain a novel feedstock.

A locally sourced BBTPPFS heterogeneous catalyst from Eskom was collected and pulverized; this biowaste was used for hydro-processing applications. The addition of three support catalysts was experimentally studied to select the one that was able to mild crack UCO to obtain green diesel fuel.

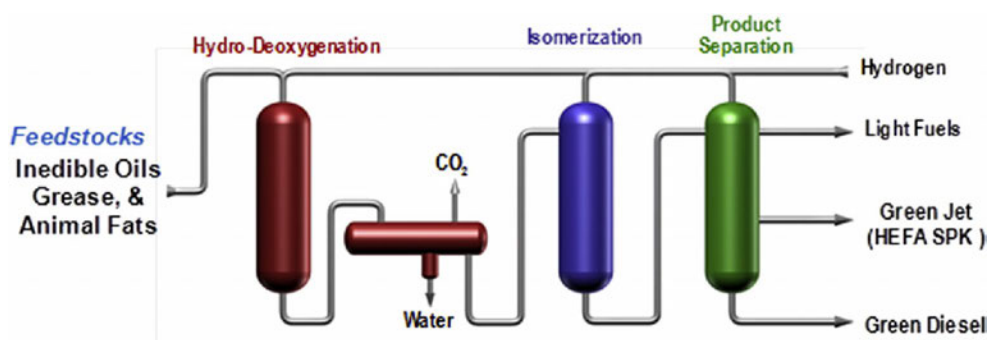


Figure 1.2: Simplified process flow diagram of Eco refining. HEFA, hydro processed ester, and fatty acid [32]

Table 1.2: Properties of HDRD properties compare with other biofuels

Properties	HDRD	FAME	PBD
Bio content	100	100	0
Oxidation stability	Excellent	Poor	Baseline
Oxygen contents	0	11	0
Sulfur content, ppm	< 1	< 1	< 10
Specific gravity	0.780	0.880	0.840
CFPP additive sensitivity	Excellent	Baseline	Baseline
Cloud points °C	Up to -20	-5 to +15	-5
Heating value / Kg	44	38	43
Energy/weight	44/0.78	38/0.88	43/0.84
Cetane number	70-90	50-65	51
NOx	-10%	+10%	Baseline
Distillation °C	200-350	340-355	200-350

Table 1.2 shows the HDRD properties in comparison with petroleum based-diesel and fatty acid methyl ester (FAME) biodiesel. From the table it is evident that HDRD possesses a higher heating value and excellent cloud point compared with FAME. A high cetane number up to 90 and low NO<sub>x</sub> emission make HDRD an outstanding biofuel. In addition, the low density of HDRD and zero percent weight of oxygen makes it an excellent blending component. HDRD has superior properties over FAME that makes it function perfectly well in the CI engine. Unlike conventional oxygenated biodiesel (FAME), whose addition to mineral diesel fuel must not exceed 7 % to aid the performance of CI engine, HDRD can be blended with mineral diesel up to the limit allowed by the commercial specification on density.

Compared with FAME, the benefit derived from HDRD is that HDRD has the same characteristic as fossil diesel in terms of storage stability, operational and loading facilities, without any problems related to distillation, cooling, precipitation, and filter plugging. Another advantage of HDRD is that this fuel has more energy per kilogram than any other fuel type which means that a vehicle loaded with HDRD fuel can cover a longer distance with the same quantity of HDRD as any other fuel. The motivation for this study is that local feedstock and catalysts are viable, cheap, available, and sustainable in the South African context. In addition, the challenge of environmental pollution, transportation fuel scarcity, storage, and poor engine performance can be substantially addressed.

## 1.4 Research questions

In order to ascertain the viability of green diesel application in the energy mix for the local economy, the relevant research questions are listed as follows:

- In the investigation of potential feedstock for renewable biofuels, what are the research gaps identified in the use of UCO waste material for catalyst and adaptable technology that could be deployed for green diesel application?
- To what extent can hybridization of UCO promote its application in conversion to HDRD?
- How can local and cheap catalyst sources be identified, and what are the key parameters that will yield the best outcome for HDRD production in South Africa?
- How can the properties of fly ash obtained from waste bio-sources be consolidated to produce a catalyst with mild cracking hydro-processing capability for use in HDRD technology?
- What are the technical and economic cases in the local economy for the use of UCO as a feedstock for HDRD application in the medium to long term within the transport segment energy mix?

## 1.5 Aim and objectives of the study

The aim of this research was to investigate the feasibility of hydro-processing UCO into HDRD using local feedstock and catalysts.

The objectives of the study were to:

- Investigate the viability of hybridization of UCO to improve the quality as well as to obtain optimal engine performance of the HDRD produced via local feedstock and catalyst substitutes.
- Evaluate the effect of hybridization on the density, kinematic viscosity, saponification value, iodine value, acid value, cetane index, and higher heating value of the feedstock and determine their effect on the hydro-processing process.
- Identify the right type of catalyst/support structure obtained from waste bio source with the capacity to convert UCO into HDRD.
- Reinforcement, development and characterization of CFA with SiO<sub>2</sub> to determine the optimum catalyst and to improve its catalytic performance in HDRD production.
- Study the properties of a green catalyst for mild cracking a locally sourced feedstock into the hydrocarbon range.



- Evaluate the properties and engine performance of HDRD obtained from hydro-processed UCO using fly ash as a catalyst.

## 1.6 Research significance

The search for renewable energy sources to replace petroleum-based oil is on the increase across the globe. In most countries, particularly in South Africa, production of renewable fuel is a challenge despite the serious problem associated with fossil fuel utilization. Biodiesel applications have limitations in relation to the CI engine and the environment. Alternative sources of biofuel that possess superior properties to fossil fuel is the only reliable solution to transportation and environmental pollution challenges. In South Africa, Eskom's coal-fired power stations consume  $\pm$  120-million tons of coal and produce 25-million tons of fly ash per annum. There is a huge amount of waste being generated from Eskom plants. The utilization of fly ash is currently not well marketed in South Africa; and there is a need for all relevant stakeholders to work together to educate the public on the opportunities presented by fly ash. UCO as a feedstock is readily available, does not conflict with food security, does not contend with land, is affordable, and is a means for environmental sanitation.

This research study arose from the need to target a concise investigation into the feasibilities of hydro-processing locally sourced UCO and pulverized CFA collected from Eskom as a catalyst to obtain green diesel that possesses properties that comply with global standards. The application of these local resources to process and obtain HDRD will assist in the commercialization of green diesel production in South Africa.

## 1.7 Expected research outcome

- Catalytic hydrogenation of UCO into HDRD using BBTPPFS heterogeneous catalyst for compression ignition (CI) engine.
- Formulation of the optimal mixing ratio between silica oxide and BBTPPFS catalyst with potential to mild crack UCO into HDRD.
- To know the effect of hybridization of feedstock on the production of HDRD.
- Hybridization of feedstocks provides a straightforward, easy, cost-effective, and innovative way of adjusting and enhancing the physicochemical properties, thermal, and spectroscopic behavior of feedstock with a view to enhancing their suitability for HDRD productions.
- The research will unveil the elemental composition of thermal, spectroscopic behavior of coal fly ash as a potential catalyst candidate for the conversion of UCO into green diesel.

## **1.8 Research scope and delineation**

The scope of this research is restricted to the feasibility of hydro-processing of UCO into HDRD from local feedstock and catalysts. The techniques and tools used were limited by availability, cost, and time constraints.

## **1.9 Main contributions to the field of study**

Fossil fuel and biodiesel have several challenges that limit their application in CI engines and stationary engines related to their emission characteristics. This research explores conversion of UCO and a pulverized BBTPFS heterogeneous catalyst using hydro-processing technologies to produce HDRD that possess properties that are superior to conventional petrol-based oil. A novel feedstock was developed by in-situ hybridization and characterized, using a catalyst derived from waste generated from an Eskom power plant. The properties of the green diesel product were tested and confirmed to meet the EN 15940, EN590 and ASTM D975 standards, engine performance, and emission requirements. It was established that the feedstock is abundant, local catalyst generated from Eskom power plant are available and sustainable. The green value chain of resources will support commercialization of HDRD production.

## **1.10 Thesis chapter layout**

The thesis chapters are arranged in sequential manner in response to the research questions posed in this study. The thesis is a compilation of research outcomes of publications as stipulated by the University of KwaZulu-Natal for the awarding of this Ph.D degree. There is a total of seven publications which occupy seven chapters.

Chapter 1 introduced the background to the study, identified the challenges, highlighted the research motivation, the research questions, and pointed out the aims and objectives of the study. The significance of the study was also stated.

Chapter 2 reviews various vegetable oils as a potential feedstock for hydrogenation, catalyst selection, different hydro-processing techniques for HDRD production, emission characteristics such as CO, CO<sub>2</sub>, NO<sub>x</sub>, UHC, PM, and smoke intensity of a CI engine fueled with green diesel are compared with a CI engine fueled with fossil fuel. International standard specifications of HDRD by

ASTM and EN 14214, ASTM D6751, Worldwide Fuel Charter, and various countries were discussed.

Chapter 3 presents physiochemical, thermal, and spectroscopic analysis of the in-situ hybridization of waste palm oil.

Chapter 4 provides details of an innovation to develop a novel feedstock for hydro-processing of UCO to obtain HDRD.

Chapter 5 presents details of the development and characterization of CFA reinforced with silica oxide for catalytic green diesel production. Pulverized CFA was collected from Eskom, silica ( $\text{SiO}_2$ ) was procured from a commercial supplier, and addition of  $\text{SiO}_2$  to CFA heterogeneous catalyst was developed and characterized by SEM, TEM, XRD, TGA, and FTIR. The outcome of the investigation showed that CFA reinforced with  $\text{SiO}_2$  has the potential to convert UCO to a HDRD.

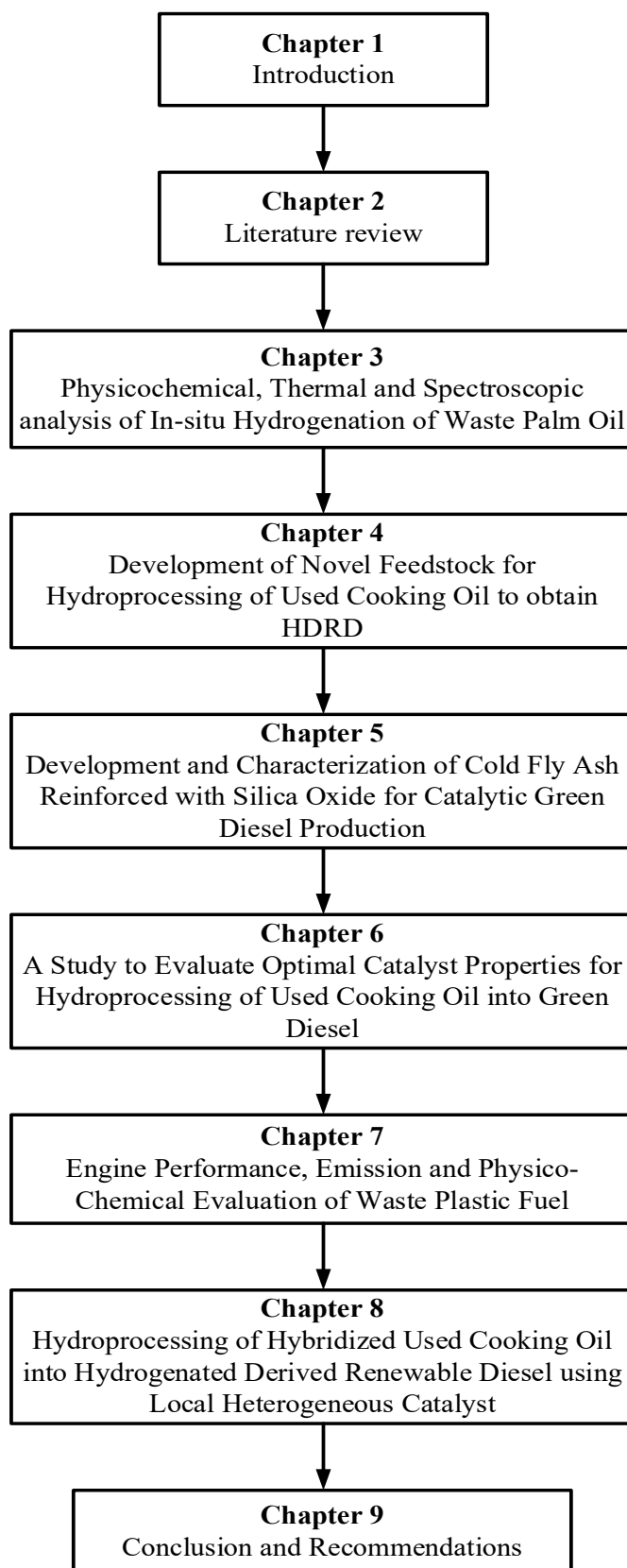
Chapter 6 presents a study to evaluate optimal catalyst properties for hydro-processing of UCO into green diesel. It describes the properties that are required to mild-crack a UCO to obtain green diesel range of  $\text{C}_{15}$ - $\text{C}_{18}$ .

Chapter 7 presents engine performance, emission and physico-chemical evaluation of waste plastic fuel: A case for fly ash catalyst pyrolysis

Chapter 8 presents hydro-processing of hybridized Used cooking oil into Hydrogenation Derived Renewable Diesel using local heterogeneous catalysts.

Chapter 9 presents the conclusions of the study, and recommendation for future work.

## PhD Thesis Flowchart



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## **CHAPTER 2: POTENTIAL OF USED COOKING OIL AS FEEDSTOCK FOR HYDROPROCESSING INTO HYDROGENATION DERIVED RENEWABLE DIESEL: A REVIEW**

This chapter critically reviews the potential of various feedstocks, catalyst selection, application of hydrogen and different production techniques to obtain a HDRD that is compatible with a CI engine without engine modification.

what was lacking in previous work and how to fill the gap

- Reinforcement of 40g silical oxide to 60g BBTPPFS capable of mild-cracking UCO to produce hydrocarbon in green diesel range has not been explored.
- Hydrogenation of UCO to obtain green diesel of high quality without modification is still lacking.

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## Potential of Used Cooking Oil as Feedstock for Hydroprocessing into Hydrogenation Derived Renewable Diesel: A Review

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### Abstract

Feedstock is one of the key resources for the production of hydrogenation derived renewable diesel (HDRD). Used cooking oil is a waste oil generated from vegetable oil after frying and can be easily sourced from domestic, restaurant outlet and food processing industries within the Durban metropolis. The right selection of feedstock contributes to the high yield and quality of HDRD. Current works on several vegetable oil sources for potential feedstock applications are reviewed. Good quality and optimal yields of HDRD can be obtained by proper selection of potential feedstock, the right catalyst, and optimal process parameters for desirable reaction pathway etc. The literature on vegetable oil as potential feedstock is discussed. Literature regarding the selection of catalysts for hydrogenation is reviewed. Biomass-based thermal power plants fly ash (BBTPFS) and calcium oxide sourced from eggshell are identified as viable catalysts for the HDRD process.

**Keywords:** Feedstock, green diesel, catalyst, hydro-processing, compression ignition engine, used cooking oil.

### 1. INTRODUCTION

Energy demand is on the increase due to the improved quality of human life, population growth, and increased industrial development. Depletion of oil resources has led to a search for an alternative fuel that is sustainable and environmentally friendly. Fossil fuel and oil product pollution is on the increase. As governments address the global warming problem with strategies to bring it under control, the lawmakers have targeted pollution generated by transport. Despite the consistent efforts of governments and stakeholders to proffer lasting solutions to the energy crisis, global warming, and the rapid depletion of fossil fuel, the threat is still on the increase and is a major concern globally. The limited supply of biofuel both locally and internationally has affected economic growth. Researchers have been saddled with the task of searching for sustainable alternative fuels for the transportation sector in order to create a healthy environment for humans, plants and animals. Renewable energy is emerging as the only viable solution to the problem of environmental and fuel crises. The compression ignition (CI) engine accounts for a significant percentage of energy-related greenhouse gas emissions worldwide, as shown

in Fig. 1. Pollution in the sector is increasing faster than any other due to steady growth in the use of personal cars and the increase in industries in the developing world. Several researchers have reported the harmful effect of petroleum-based fuel emission and its role in damaging the environment. These challenges have compelled governments to gear their efforts towards investigating suitable alternatives fuel for petroleum products.

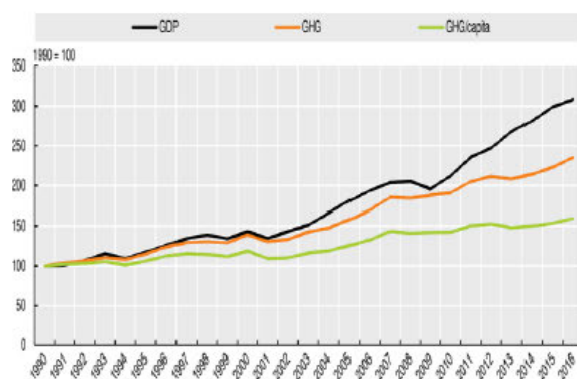


Fig. 1. The steady rise in greenhouse gas emissions due to global industrialization [1]

Prominent among the alternatives to fossil fuel available currently are biodiesel and green diesel. Biodiesel is a fatty acid methyl ester (FAME), which cannot be used directly for CI engines because of its high viscosity compared to conventional diesel. Biodiesel as an alternative transportation fuel comprises oxygenates and unsaturated C-C bonds which pose some major challenges such as low oxidation stability, low freezing point, low calorific value, sulphur, oxygen, water and particles all of which pose significant challenges to CI engines. Generally, many researchers have reported that biodiesel limitations include degradation under storage, blockage of fuel filters, injectors, and hoses, higher nitrogen corrosive nature, extreme engine wear, poor (low) temperature operation (poor pour point and cloud point), composition of O<sub>2</sub> and H<sub>2</sub>O and high kinematic viscosity [2, 3]. Due to these shortcomings, biodiesel is blended with petrol-based diesel with proportions depending on the application. Hence, the need



for a sustainable transport fuel at competitively cheap cost without the need for retrofitting of the CI engine. The properties of green diesel offered by hydrogenation derived renewable diesel (HDRD) make it a superior candidate in terms of high heating value, high energy density, high cetane value (80-90), and lower NO<sub>x</sub> emissions. This green diesel can be used directly without any modification in the CI engine or the fuel. However, access to cheap feedstock, a viable source of hydrogen and a catalyst with optimal performance remains a challenge.

What are the optimal pathways to the production of green diesel produced via hydroprocessing technology with the requisite fuel properties for CI application? Several production technologies have been developed to produce green diesel in recent times e.g. hydrodeoxygenation (HDO), deoxygenation (DO), and pyrolysis using fatty acid and triglycerides as feedstock. HDO is a process of removal of oxygen with the introduction of hydrogen gas under high pressure. DO involves the removal of oxygen from fatty acids or triglycerides under a hydrogen-free process. Pyrolysis involves the application of heat to convert biomass into gases, solid char and condensable pyrolytic vapor with higher value fuels (bio-oil). The production chain and logistics of distribution of biodiesel coupled with feedstock supply is capital intensive which raises the cost of biodiesel. The transportation sector accounts for the largest share of 63 % and 1.1 % of the total growth in world consumption of petroleum and other liquid fuels from 2010 to 2040 [4]. The South African Draft Strategy adopted a 5-year pilot program to achieve a 2 % penetration level of biofuels or 400 million liters in the national liquid fuel supply [5] but this has not been achieved hence the need for a policy that will harness the technology, regular sources of feedstock and incentives to enhance the production of hydrogenation derived renewable diesel (HDRD). Concerted efforts have been made through the Biofuels Regulatory Framework (Act No. 34 of 2008) to commence the commercial production of renewable fuels, but not much has been achieved in that sector due to technical and economic factors [6]. In order to establish a sustainable production plan for HDRD products, a system that allows highly skilled personnel in related technology must be in place and government must be ready to provide incentives to reduce risk.

HDRD can be produced via a desulphurization unit of an existing refinery with basic modification of the catalyst bed [10]. In order to achieve a commercial production capacity, the Government must be willing to provide incentives to reach out to experts through the mechanism of the carbon credit/tax and implement a fuel levy subsidy as stipulated in the biofuel policy [7]. This review sets out to investigate all issues relevant to the optimal production of HDRD from used cooking oil (UCO) with the stated aim of identifying research gaps that, if explored, could be pivotal to the efficient domestication of this technology in sub-Saharan Africa.

## II. BACKGROUND AND HIGHLIGHTS OF HDRD

HDRD has evolved as a technically feasible next-generation transportation fuel. This renewable energy form emerged because of the need for sustainable renewable fuel that is

compatible with a CI engine without modification. Hence, the search for a fuel that is environmentally friendly and economically competitive, which is not the case for conventional biodiesel and fossil-derived diesel. Greenhouse gas (GHG) emissions from the energy sector and power production are increasing significantly and are the major causes of climate change. The second-largest source of GHG is motorized transportation [8]. According to the United States Environmental Protection Agency, carbon dioxide (CO<sub>2</sub>) emissions (which are the major GHG associated with vehicle transportation) rose by 29 % between 1990 and 2007 (EPA, April 25, 2009). Approximately 20 % of the total CO<sub>2</sub> currently released into the atmosphere is as a result of human activities such as transport-related emissions and they are expected to rise in the future. According to Specht [20], transportation utilizes petroleum-based products with gasoline making up more than 50 % of the emissions with diesel and jet fuel contributing to the remainder.

Hydrogenation-derived renewable diesel (HDRD) is a promising alternative fuel due to its excellent low-temperature properties, cetane number (CN), and similarity to biodiesel and fossil diesel. Hence, green diesel can be used as a drop-in fuel in current diesel engines.

Hydroprocessing is a well-known technology in the petroleum refining industry, and can be carried out either by hydrocracking technology or by the less severe hydrotreating technology. When these techniques are applied to oxygenated hydrocarbons, the removal of oxygen can be carried out by decarboxylation, decarbonylation, or HDO [9]. Hydroprocessing of vegetable oil leads to the production of hydrocarbons in the boiling range of diesel, and therefore it is commonly called green diesel or renewable diesel. The basic idea is to transform triglycerides in vegetable oil into high cetane hydrocarbons (mainly n-C<sub>17</sub>H<sub>36</sub> and n-C<sub>18</sub>H<sub>38</sub>) by means of high pressure, high temperature, and a bifunctional catalyst (e.g., sulfide NiMo/γ-Al<sub>2</sub>O<sub>3</sub>). Compared with biodiesel (fatty acids of methyl esters), green diesel, in general, has higher oxidation stability, lower specific gravity and higher CN, and when it is blended with petroleum diesel it has much better cold flow properties. In addition, green diesel is totally compatible with petroleum diesel engines, thus retrofitting is not required.

The new technology for the production of green diesel, namely, HDO of triglycerides and fatty acids, compared to conventional hydrotreating catalysts, suffers from fast catalyst deactivation in the absence of hydrogen combined with high temperatures and high fatty acid content in the feedstock.

The commercialization of green diesel has commenced in recent times. Currently, some industries have embarked on green diesel production in Finland (Nestle oil) with two plants and a total capacity of 170 000 tons/year [10]. The same company (Nestle oil) floated a commercial green diesel production firm in Rotterdam and Singapore in 2010 and 2011 respectively with a plant capacity of 800 000 tons/year [11]. In 2009 Eco fining technology started converting vegetable oil using catalytic hydro processing [12]. The fuel has a high cetane value and can conveniently replace diesel fuel [12]. H-Bio/Petrobras constructed a hydrotreating unit to process



vegetable oil and mineral diesel blends into green diesel that can be used as a diesel fuel enhancer which can reduce the sulphur content [12]. Table 1 shows green diesel production plants and capacity. Production of green diesel has witnessed slow advancement due to a lack of clear knowledge of the production technology of the process in South Africa. On the local scene not much is known regarding this field, so there are

research gaps in the areas of processing conditions, feedstock selection, catalyst composition, catalyst hydrotreating/preconditioning and optimization of the reaction conditions. Furthermore, in order to make green diesel production more competitive with petrol-diesel locally, process economies need to be fully investigated.

Table I. Green diesel production plants and capacity [13]

Industry / Location	Cost of capital investment (USD)	Feedstock used	Capacity (ML/yr)	Date of commencement	Remarks	Ref
Nestle oil / Tuas, Singapore	725 million	Palm oil	906	2011	Operational	[14]
Dynamics Fuels (Syntroleum and Tyson Foods joint venture) Geismar, Louisiana	150 million	Soybean oil and Animal fats	283	2010	Operational	[15]
Nestle Oil / Netherlands, Rotterdam	1 billion	Rapeseed oil Palm oil, Animal fats	906	2010	Operational	[14]
Nestle oil/ Finland, Porvoo	130 million	Rapeseed oil, Animal fat, Palm oil	215	2009	Operational	[16]
Nestle oil/ Finland, Porvoo	130 million	Rapeseed oil, Animal fats, Palm oil	215	2007	Operational	[16]
Valero and joint venture, /Louisiana, Norco	300 million	Soybean oil and animal fats	509	Proposed starting date: 2012	Under construction	[17]
UPM biofuels/ Finland, Lappeenranta	200 million	Tallow oil	117	Proposed starting date: 2014	Construction begins 2012	[18]

Total existing capacity 2,525 ML / yr

Total existing + Future capacity (Firm) 3,035 ML/ yr

Total existing + Future capacity (Possible) 3,151 ML / yr

Green diesel is a potential and promising renewable energy that can solve environmental and economic problems. Furthermore, green diesel can be produced in large volumes at existing centralized petroleum refineries. Green diesel or renewable diesel is a mixture of diesel-like hydrocarbons produced via a catalytic reaction involving hydroprocessing and/or decarboxylation/decarbonylation of triglycerides from various feedstocks [19]. While HDO eliminates oxygen by reacting triglycerides and FFAs with hydrogen to form water and n-paraffins, decarboxylation or decarbonylation eliminates

oxygen to form carbon dioxide or carbon monoxide and n-paraffins [20]. This leads to a diesel product that is indistinguishable from petroleum diesel, while biodiesel is chiefly composed of oxygenated species that can have vastly different properties compared to traditional petroleum diesel [19]. HDRDs are lipid-derived liquid transportation biofuels and do not contain oxygen-based molecules. This characteristic of green diesel results in high heating value and high energy density [21]. The selection of feedstock that will offer optimal yield with low production cost is a critical step [22]. Therefore, there is a need to investigate suitable and available feedstocks, identify local and cheap catalyst sources, and the key parameters that will yield the best outcome for HDRD production in South Africa.

### III. FEEDSTOCK OPTIONS

The triglycerides and fatty acids found in vegetable oil are promising feedstocks for the production of renewable and sustainable biofuel. These feedstocks can produce diesel and gasoline-range hydrocarbons via hydroprocessing [23]. Green diesel is produced by hydroprocessing of triglycerides contained in feedstocks such as vegetable oils (e.g. rapeseed, soybean, cottonseed, palm, corn, sunflower, coconut, peanut, camelina, carinata, and jatropha oils), fats, micro-algal oils and UCOs [24]. These vegetable oils cannot be used directly in the modern CI engine due to their high viscosity but can be used as a green source after some modification of fuel properties [22]. Table 2 shows the current potential feedstock for HDRD production worldwide. Sunflower oil constitutes about 40 % to 50 % of vegetable oil production in Ukraine, Turkey, the

Russian Federation, Argentina, and Europe. The prominent sources of feedstock for biofuel in Europe are sunflower and rapeseed oils [25]. The percentages of production of vegetable oils across the globe are sunflower (10%), rapeseed (55%), cottonseed (10%) and soybean (55%) [26]. Malaysia has developed palm oil as a source of feedstock for renewable energy production [27, 28].

Feedstocks sourced from edible oils for the production of biofuel has become practically impossible due to the high cost of food and threats to food security. The requirement for large land spaces for cultivation, planting and harvesting, the threat of deforestation and the high cost of farming are major challenges facing edible oil. UCO as a feedstock for HDRD application has been adopted in recent times.

**Table II.** Current Potentials Feedstocks for green diesel production worldwide [29]

S/N	FEEDSTOCKS	WORLDWIDE
1	Animal fat and waste oil	Mexico
2	Rapeseed	Germany
3	Rapeseed, Animal fat, Yellow grease /tallow, Soybeans/mustard	Canada
4	Waste plastic oil/waste tyre oil/sunflower, Peanut/Jatropha /kangara	Indian
5	waste oil/ Soybeans, Peanut	USA
6	Rapeseed, sunflower, Waste plastic	Italy
7	sunflower/ Rapeseed	France
8	Cottonseed	Greece
9	Rapeseed	Sweden
10	Animal fat/ Frying oil	Ireland
11	Palm oil	Malaysia
12	Waste cooking oil/ Rapeseed	UK
13	Waste cooking oil/Tallow	New Zealand
14	Waste cooking oil	Japan
15	Rapeseed /Waste cooking oil /Jatropha	China
16	Frying oil/Animal fat	Ireland
17	Soybeans	Argentina
18	Jatropha /Palm oil/Coconut	Thailand
19	Palm oil	Singapore
20	Soybeans, Cottonseed, Palm oil, Castol oil	Brazil
21	Jatropha, Coconut	Phillipine
22	Palm oil, Coconut,Jatropha	Indonesia



The cheapest source of feedstock for the production of HDRD is UCO [30]. Rocha Filho et al. reported that more than 200 000 tons of used cooking oil is generated in South Africa per/annum [31, 32]. Given the yield rate of 80%, 205 million litres of HDRD could be produced annually from this waste. This would supply 1 % of the 2 % set aside for the renewable fuel in the biofuel policy of the government of South Africa. The current price of UCO is R3 /l and diesel is R14 /l, therefore a value-added industry generating R2.04 billion can be created producing premium diesel (HDRD) along with the creation of thousands of jobs. Other potential secondary sources of feedstock are cellulosic waste from pulp and paper industries plus a diverse range of agricultural waste with a far greater capacity than UCO [7].

UCO is an oil generated from vegetable oils after frying and is abundant and readily available in food processing industries, restaurants, households, and fast food outlets. UCO is the second most abundant waste residue which is generated in enormous quantities every day. The global demand for edible vegetable oil is on the increase. Research indicates that annual consumption of edible oils in China is approaching 22 million tons; the country produces more than 4.5 million tons of used oil and grease per year [33]. Vegetable oil used for frying undergoes various physical and chemical changes, with some undesirable compounds like free fatty acids and polymerized triglycerides being formed during frying which causes a rise in molecular mass and condenses the volatility of the oil. UCO is a renewable resource and does not contain any aromatics, metal or sulphur contaminants. Reuse of UCO can exacerbate environmental problems and health challenges including hypertension, diabetes, and vascular inflammation [34]. Vegetable oil can be used for frying a variety of food items including chicken, beef, yam/potatoes. Currently, one of the barriers to renewable fuel commercialization is the high cost of feedstock compared to petroleum-based diesel. It has been established from literature that approximately 70 % to 85 % of the production costs of green diesel arise from the cost of raw materials. Therefore, application of UCO as a feedstock for processing of HDRD will reduce the production cost as it is available at a significantly lower price. The HDRD production process involves conversion of fatty acids in triglycerides into normal and/or iso-paraffin which can be obtained by HDO, decarbonylation, decarboxylation, isomerization and hydrocracking or a combination of two or more thereof.

UCO possesses high acid value due to the high content of free fatty acids [32]. In recent years, several petroleum companies have directed their resources into the production of renewable green fuels from hydroprocessing of vegetable oil feedstock, setting in motion a tremendous commercialisation process.

The Neste Oil Co. has developed a technology to produce high-quality hydrocarbon from vegetable oils and animal fats. The NExBTL technology process produces green diesel by hydrotreating vegetable oils or waste animal fats. Neste Oil has opened a plant in Singapore using NExBTL technology with a plan to produce over 800 000 tons renewable diesel per annum from feedstocks [35]. The characterisation of the product by engine and automotive manufacturers using NExBTL has shown a high cetane value of between 84 and 99, low cloud point value (as low as 30 °C below zero), and the

ability to withstand storage for extended periods. These properties enhance the performance of both car and truck engines [36].

The UOP/Eni Ecofining process is primarily based on hydrotreating of triglycerides and free fatty acids which gives DO via HDO and decarboxylation as outcomes [37, 38]. The next step after hydrotreating is an isomerization process step which is performed to obtain isoparaffin rich diesel fuel with good cold flow properties and the same chemical properties as Petro diesel. The renewable diesel product by the Ecofining process has been reported by life cycle assessment (2009) to be economically and environmentally competitive with biodiesel production [39]. UOP Honeywell Co with its 90 years of refining technology experience is offering an alternative process to produce green fuels from various bio-feedstocks. The UOP/ENI Ecofining process [40] has been designed to convert non-edible oils to renewable diesel, which is applicable in any percentage in the existing fuel tanks, trucks, pipelines and automobile engines without modification.

Tyson Foods Inc. has commenced operations at a renewable diesel production plant in Geismar, LA, USA, for the production of green diesel through hydrotreating of non-edible grade animal fats including chicken fat, beef tallow and pork lard. Tyson and Syntroleum Corporation have created a joint venture which has developed a technology to produce synthetic fuels targeting the green diesel, jet, and military fuel markets. Syntroleum reported that the renewable diesel produced at the plant is 75 % less in volume than that of petroleum diesel. The plant was designed to produce up to 75 million gallons of renewable diesel fuel per year [41].

Haldor Topsoe developed a new hydrotreating technology for production of green diesel and jet fuel from raw tallow. The feedstock used was a non-edible material, hence, the problems of global food shortage are not affected. Preem Gothenburg Sweden Refinery has adopted the technology which has been completed by Topsoe [42].

ConocoPhillips opened a commercial production plant for hydrogenation of vegetable oils to obtain renewable diesel fuel components that meet European Union standards at the company's Whitegate Refinery in Cork, Ireland. The HDRD is produced using existing equipment at the refinery and is being blended and transported with Petrodiesel. The refinery is producing 365 000 barrels per annum of green diesel fuel for sale into the Irish market. The report of the tests conducted by ConoPhillip indicated that HDRD burns cleaner than petrol diesel, is sulfur free and emits less NO<sub>x</sub> [42].

Valero Energy Corporation has developed a plant at St Charles Refinery in Norco LA which converts UCO and animal fat into renewable diesel via hydrogenation and isomerization processes [43]. The fat and oil feedstocks are supplied by Darling International which is Valero's partner in the venture.

Toyota Motor Corporation (TMC), Hino Motors, the Tokyo Metropolitan Government and Nippon Oil Corporation (NOC) started a joint project aimed at commercializing bio hydrofined diesel (BHD), a second-generation renewable diesel fuel produced by hydrogenating a vegetable oil feedstock. Nippon Oil and Toyota have worked jointly on the development of



BHD technology since 2005. The use of refinery-based hydrogenation processes to produce a synthetic, second-generation renewable diesel is driven by several issues, including some technical considerations regarding the properties and effects of first-generation fatty acid methyl ester biodiesel (storage, oxidation, possible effect on fuel handling systems). In its studies, Nippon Oil explored reaction temperatures ranging from 240 °C to 360 °C, with reaction pressures of 6 MPa and 10 MPa, and used a common hydrodesulfurization catalyst. The resulting fuel is claimed to be aromatics- and sulfur-free, with a CN of 101 [42].

Table 3 shows the annual volume of used cooking oil collection in some countries; about 200 000 tons of UCO not collected is disposed of in South Africa which contributes to soil and water contamination, sewage blockages, and damage to aquatic life [23].

**Table III.** The annual collection of Used Cooking Oil (UCO) (Million tons)

Country	UCO Collection (Million tons)
South Africa	0.6
UK	0.2
China	5.0
Canada	0.14
Malaysia	0.5

The consumption rate of vegetable oil has witnessed a tremendous increase globally [13]. Most of these vegetable oils are used for frying and cooking by restaurants, fast-food outlets, and households. The annual collection of used cooking oils as shown in Table 3 is an estimate of the UCO collected in some countries. About 125 000 and 140 000 tons of UCO is generated per annum in Canada [44, 45]. In South African 0.6 million tons of UCO is collected annually from bakeries, takeaway outlets, and restaurants. [46, 47]. The UK and the European Union countries produced 0.7 tons to 1.0 tons and 0.2 tons of UCO per annum, respectively [48]. Apart from the cost-benefit of using UCO as a feedstock, it is also available and sustainable. Research shows that UCO contributed 17 % and 9 % of the feedstock for the production of 11.92 million tons and 26.62 million tons of renewable energy globally in 2015 [49].

The chemical composition of UCO has been investigated; revealing the following predominant chemical properties of the fatty acids in UCO: palmitic acid 38.35 %, oleic acid 43.67 %, linoleic acid 11.39 % [50]. The fatty acids and properties of UCO make them viable as potential feedstock for hydrogenation. Table 4 shows the properties of UCO samples of sunflowers oil, palm oil and sunfoil.

**Table IV.** Properties of HDRD over another Biofuel [49]

Properties	Used Cooking Oils Samples		
	Sunflowers	Palm oil	Sunfoil
Density (Kg/m <sup>3</sup> )	920.4	913.4	923.2
pH value	5.34	6.19	6.61
Viscosity (mm <sup>2</sup> /s)	31.381	38.407	35.236
Acid value	2.29	1.13	1.44
Congeaing temp. °C	-5.15	14.7	-3.4
Molecular wt. (g/mol)	51.94	586.05	395.28
Iodine value (cg/g)	111.1	54.2	54.2

Feedstock plays an important role in determining production costs; using UCO as a feedstock can change the prices or break the profitability of an HDRD operation. Vegetable oil feedstocks cost makes up approximately 80 % of the total production expenses and hydrogen and utilities make up approximately 15 % [32] of biofuel. UCO is very cheap, requires little effort to source, and offers a good yield when used. Green diesel is oxygen-free, hence oxidation stability is high, it is non-corrosive and has a high heating value similar to petroleum-based diesel. Green diesel has superior stability in cold weather compared to biodiesel, it does not increase NO<sub>x</sub> emissions, and it has a higher CN which aids ignition in CI engines. Furthermore, green diesel produced by the hydro-processing of triglycerides has propane as a by-product which is a gaseous fuel of good market value. This property makes green diesel production more attractive in economic terms when compared to the production of biodiesel [51]. Preparation of UCO is a critical stage in achieving a standard biofuel product, hence there is a gap regarding investigation of preparation protocols for UCO as a feedstock for production of green diesel.

#### IV. HYDROGENATION DERIVED RENEWABLE DIESEL (HDRD) AS AN ALTERNATIVE FUEL FOR COMPRESSION IGNITION ENGINE

There is a pressing need to develop a new technology that is capable of converting vegetable oils into high-quality diesel fuel or diesel blend that is fully compatible with the CI engine. The new technology needs to be capable of utilizing widely available vegetable oil feedstock to produce renewable energy with a high cetane, low gravity, aromatics- and sulphur-free biofuel. The production process under consideration involves the conversion of fatty acids in triglycerides into alkanes which can be obtained by hydrogenation, decarboxylation, decarbonylation, isomerization, and hydrocracking.

Hydrotreating technology is a prominent technique in a refinery to remove S, N, and metals from petroleum-derived feedstock including heavy gas-oil or vacuum gas-oil [52]. Furthermore, catalytic hydrotreating is an effective technology with various applications in the petrochemical industry that has recently adopted and expanded into bio-oil upgrading. The hydrotreating process is beneficial because the required



infrastructure is widely available in refinery units. By means of hydrotreating processes, a deoxygenated product is obtained with high oxidation stability and low sulphur content which is fully compatible with a CI engine. Hydrotreating also offers more benefits compared to the transesterification process of FAME due to its lower cost, compatibility with CI engine, NO<sub>x</sub> emission reduction, and feedstock flexibility.

DO technology involves managing the oxygenated compounds in the feedstock which have an effect on chemical stability and energy content of the biofuel. Renewable energy has a higher degree of stability and excellent combustion properties which can be obtained by the DO process through a reaction that includes decarbonylation, dehydration, and decarboxylation. The decarbonylation process aims at removing carbonyl groups from the hydrocarbon to reduce its heating value and improve its oxidation stability. In the dehydration process oxygen is removed in the form of water. Decarboxylation is a process that involves removal of oxygen from carboxylates, in order to make it more suitable for producing diesel with reduced acidity.

HDO is a process for the production of HDRD through the removal of oxygenated compounds from feedstock. The process requires a feedstock which contains oxygenated compounds and double bonds which can be converted into biofuel through the saturation of the double bonds and the removal of oxygen. In the HDO process high temperatures and pressures are required in the presence of hydrogen [53, 54]. High water content in biofuel is a challenge, therefore DO has an advantage in terms of economic and quality product yield.

The processes of hydrotreatment consists of two main stages. The first stage involves conversion of triglycerides to oxygen-free hydrocarbons (normal paraffin). The product in the first stage contains poor cold flow and low CN which is not suitable as transportation fuel. The hydro processing stage furthers the process to obtain normal paraffin by isomerization/dewaxing to obtain optimum iso-paraffin fuel with good cold flow properties. The hydrotreatment of liquid feedstocks occur when high temperatures and pressures are induced over a catalytic material using hydrogen.

Hydroprocessing of triglycerides to hydrocarbon products depends on some process reactions [55]. The process is achieved by the reactions during the conversion of triglycerides over a selected catalyst in a high-pressure atmosphere of H<sub>2</sub>. Insufficient H<sub>2</sub> results in coke formation on the catalyst surface and catalyst deactivation. As a result, the green diesel yield will decrease and the profile of the green diesel species changes [56]. Hydroprocessing techniques are clearly a better choice of production route, but the best approach on how to adopt it in process design is not yet defined. The two choices available to be considered are: standalone unit reactor and co-processing in an existing hydroprocessing unit reactor. Co-processing is clearly an attractive option for refinery applications, since an existing refinery facility can be harnessed for HDRD application. Vegetable oil feedstocks contain trace metals and impurities such as phosphorus, potassium, calcium, and sodium which requires a separate reactor to hydrotreat the vegetable oils for proper removal of all the contaminants. Another challenge is that the volume of catalyst in the existing reactor will not be sufficient for treating the catalyst and the thermal

reaction that exists requires a device that can turn it off which is not available in the reactor. The DO products (H<sub>2</sub>O, CO, CO<sub>2</sub>) require a revamping of the recycle gas system for removal or use of a substantial purge stream. Therefore, a large size standalone reactor unit dedicated to UCO is considered to be more cost-effective and has the potential for producing high yield of hydrocarbons.

The production of green diesel depends on the choice of processing pathways. HDRD is produced via a hydroprocessing pathway with propane, carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) as by-products. Fig. 2 and Fig. 3 show the production pathways for both HDRDs.

In the process shown in Fig. 2, the feedstock is mixed with hydrogen with a reaction temperature and pressure of 330 ° to 360 °C, and oxygen is removed at the DO unit in the form of water and is then sent to the isomerization reactor where the vegetable oil is converted from n-paraffins to iso-paraffins with cracking to naphtha and gas. Cloud point can be varied with lower cloud point producing higher naphtha yield where the CN is less than 70.

The product is separated from the recycle gas in the product separator unit where the green diesel and by-product are collected.

Green diesel development has numerous and some basic benefits over FAME production processes in a refinery setup. The hydrogen required for the process is available in the refinery and does not require any special handling. The products can also be easily blended with conventional refinery products.

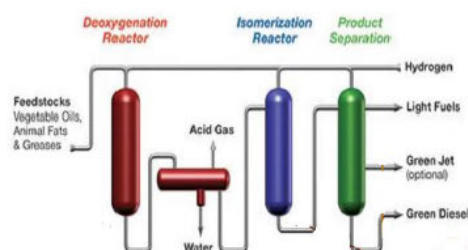
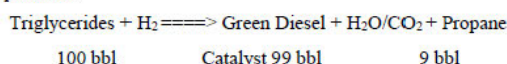


Fig. 2. Production process of green diesel [57]

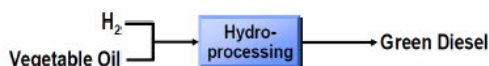


Fig. 3. Vegetable oil processing routes

Free Fatty Acid (FFA) content is not a problem for HDRD production because FFAs can easily be converted to paraffin [10]. Table 5 shows some properties of HDRD over petrol-based diesel and biodiesel.

Table V. Properties of HDRD over another Biofuel [58]

S/N	Properties	Petrol based diesel	Biodiesel (FAME)	Green diesel
1	Carbon, Wt%	86.8	76.2	84.9
2	Hydrogen, Wt%	13.2	12.6	15.1
3	Oxygen%	0.0	11.2	0.0
4	Specific gravity	0.85	0.88	0.78
5	Cetane Number	40-45	45-55	70-90
6	T <sub>90</sub> , °C	300-330	330-360	290-300
7	Viscosity, mm <sup>2</sup> /sec. @ 40°C	2-3	4-5	3-4
	Energy content(LHV)			
8	Mass basis, MJ/KG	43	39	44
9	Mass basis BTU/LB	1850	16600	18900
10	Volume basis BTU/gal	130	121	122

HD can be produced from virtually any type of bio-based wable feedstock; the advantage of the HDRD production ess is that it makes use of existing refining technology and be blended into the conventional diesel pool in very high

concentrations, up to 100%, with little or no adverse eff Table 6 shows some studies on the reactor type, feedst catalyst, and process parameters.

Table VI Examples of Reactors and Process Parameter for HDRD Production

S.No	Reactor	Feedstock	Catalyst	Temp.(k)	Time(h)	Press. (MPa)	Remark	Ref.
1	Trickled-bed	Crude palm oil	NiMo/Al <sub>2</sub> O <sub>3</sub>	533-613	LHSV=1h <sup>-1</sup>	40-90	Catalyst showed slight deactivation	[59]
2	Fixed bed	Vegetable and jatropha oil	1%pt/H-ZSM-5	543-573	LHSV=1-2h <sup>-1</sup>	65,86% H <sub>2</sub> in N <sub>2</sub>	67% C <sub>15</sub> -C <sub>18</sub> Re/Al <sub>2</sub> O <sub>3</sub>	[60]
3	Fixed bed	Rapeseed oil	Co-Mo/Mesoporous Al <sub>2</sub> O <sub>3</sub>	523-623	WHSV=1.5h <sup>-1</sup>	7-70	High temperature and low pressure give rise to the increase in HDC	[61]
4	Bench-scale trickle-bed	Refine and acidic vegetable oil	NiMo/γ-Al <sub>2</sub> O <sub>3</sub> , Co-Mo/γ-Al <sub>2</sub> O <sub>3</sub>	583.15-623.15	WHSV=1.4h <sup>-1</sup>	33	52 ± 3% hydrocarbon conversion	[62]
5	Fixed bed	Rapeseed oil	Mo/Al <sub>2</sub> O <sub>3</sub> , NiMo/Al <sub>2</sub> O <sub>3</sub> , sulfided Ni/Al <sub>2</sub> O <sub>3</sub>	583	WHSV=2h <sup>-1</sup>	35	NiMo/Al <sub>2</sub> O <sub>3</sub> produced HDC, HDO hydrocarbon, Ni/Al <sub>2</sub> O <sub>3</sub> produced DC, Mo/Al <sub>2</sub> O <sub>3</sub> produce absolutely HDO product	[63]
6	Fixed-bed flow reaction system	vegetable oil	Ni-Mo/SiO <sub>2</sub> or Al <sub>2</sub> O <sub>3</sub>	623	LHSV=7.6 h <sup>-1</sup>	H <sub>2</sub> /Oil=800m L/Ml <sub>l</sub>	n-C <sub>10</sub> H <sub>18</sub> , n-C <sub>11</sub> H <sub>16</sub> , n-C <sub>12</sub> H <sub>14</sub> , and n-C <sub>13</sub> H <sub>12</sub> hydrocarbons	[64]
7	Laboratory flow	Rapeseed oil	NiMo/Al <sub>2</sub> O <sub>3</sub>	583.15	WHSV=1h <sup>-1</sup>	70 and 150	Hydrocarbon yield	[65]
8	High-pressure batch	Soybean oil	Ni-Mo/γ-Al <sub>2</sub> O <sub>3</sub> , pd/γ-Al <sub>2</sub> O <sub>3</sub> , Ni-/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> , Ru/γ-Al <sub>2</sub> O <sub>3</sub>	673	Catalyst/oil weight ratio of 6.04	92	NiMo and CoMo good for the pathway	[66]
9	Fixed bed	Sunflower oil	Sulfided commercial hydrocracking catalyst	633-693	WHSV=1.5h <sup>-1</sup>	180	Low heating properties	[67]
10	Batch reactor	Rapeseed oil	Pt/zeolite(HY-H-ZSM-5)/sulphide Ni-Mo/Al <sub>2</sub> O <sub>3</sub>	573-673	LHSV=3 h <sup>-1</sup>	50-110	Highest amount of hydrocarbon obtained.	[68]
11	Fixed bed	Rapeseed oil	Co-Mo/MCM-41	573-593	WHSV=1-4h <sup>-1</sup>	20-110	Lower conversion than CoMo/Al <sub>2</sub> O <sub>3</sub>	[69]
12	Quartz tubular reactor	Oleic acid and canola oil	Mo, W, V, nitrides/ Al <sub>2</sub> O <sub>3</sub>	653-683	LHSV=0.45h <sup>-1</sup>	715	Oxygen removal exceeded 90%	[70]
13	Small scale pilot plant unit of CPER/CERTH	Waste cooking oil	Commercial hydrocracking catalyst	603-671	LHSV: 0.5, 1.0, and 1.5 h <sup>-1</sup>	827 and 965	Nitrogen and sulphur removal above 99% oxygen removal, less than 90% oxygen was removed.	[71]

LHSV: Liquid Hour Space Velocity.

WHSV: Weight Hour Space Velocity.



## V. CATALYST SELECTION

The choice of catalyst determines the yield and quality of the biofuel product; therefore, catalyst selection is a critical step for the production of green diesel. The purpose of any catalyst is to ensure the conversion of triglycerides to a high yield of hydrocarbon products [72]. Micro-physical properties and ionic composition of a catalyst have a great influence on the production of HDRD. The structural information of a catalyst can be studied using a transmission electron microscope (TEM) from single nanometric range to 500 nm range. The nano size, structural dimensions and active components of a catalyst provided effective surfaces for their catalytic effectiveness during hydrogenation processes. The total surface area of a catalyst can be obtained by Brunauer-Emmett-Teller (BET) using a nitrogen adsorption/desorption analyser. Morphological and structural studies of catalysts can be conducted by scanning electron microscope with energy dispersive X-ray detector (SEM-EDS), while thermal stability of the catalysts can be examined by a thermo-gravimetric analyser. Hydro-processing catalysts that are commonly used in literature are Ni, Co, and Mo as active metals which are usually supported by alumina or silica alumina [51]. Also, Co-Mo and Ni-Mo catalyst with alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) have been widely used for hydrogenation, HDO, and hydrocarboxylation which is also a good desulphurisation (HDS) catalyst [73]. The activities of catalysts are to break the bonds and these are most likely to influence the route and the degree of C-C and C-O bond cleavage [74, 75]. A variety of catalysts can be used for this process including NiMo/-Al<sub>2</sub>O<sub>3</sub> or CoMo/-Al<sub>2</sub>O<sub>3</sub> [75], CoMo/C [76], CoMo/Si [74], depending upon the hydroprocessing route and reaction required.

Many researchers have investigated the right catalyst for the production of biodiesel and HDRD and discovered that the choice of catalyst selectivity for hydrocarbon conversion of triglycerides depends on the catalyst's activities and the nature of the catalyst. The hydrocarbon product expected during hydrodeoxygenation will inform the choice of catalyst selection and will also depend on the reaction conditions i.e. temperature, pressure, liquid space hour velocity (LSHV) and H<sub>2</sub> to oil (volume/volume) ratio [77]. Water vapor removal from HDRD during HDO requires selection of a catalyst that will stimulate the activity stability, which ultimately reduces the degree of the oxygenation [78]. Marker et al. [79] investigated the type of catalysts that can accommodate water and generate hydrogen [79]. Brady et al. [79] processed rapeseed oil, sewage sludge fish oil, corn oil, and canola oil soybean oils, etc. [79]. Herskowitz et al. [79] conducted studies for (C<sub>14</sub>-C<sub>18</sub>) n-paraffin with a low aromatic composition produced from animal fats and vegetable oil [79]. Myllyoja et al. [80, 81] produced biofuel with isomerization in diesel range (C<sub>15</sub>-C<sub>18</sub>) using different techniques. The elimination of liquid during HDO reaction is important because its presence in the reaction mixture can cause catalyst deactivation especially when batch reactors are used.

Studies from the literature have shown that sulphided Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are the active catalysts for hydrodesulphurization (HDS) that are mostly used for sulphur removal in HDO [82]. Several catalysts can be used during hydroprocessing to obtain green diesel products from vegetable

oil or animal fats, depending upon the choice of production pathways. Hydrocracking and hydrogenation are another important route to consider to obtain optimal hydrocarbon in green diesel range by hydro-processing technology. A combined sulfided Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst offers the best yield for diesel range of C<sub>15</sub>-C<sub>18</sub> product from a mixture of waste soya oil and gas-oil due to minimal cracking, while a sulphided Ni-W/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst gives considerable jet range product due to catalytic cracking [7]. Zhang et al. reported that several routes have been practiced to produce biofuels from vegetable oil and animal fats [83]. HDO and hydroisomerization-hydrocracking routes are employed to produce long-chain paraffin and to improve the cold flow properties respectively in a reactor. Sinha et al. [84] carried out research on bio-jet fuel production using jatropha oil as feedstock by a single-step route using hierarchical ZSM-5-supported with NiMo or NiW catalysts. The selection of route and the type of catalyst used will determine the cost and feasibility of obtaining optimal yield of green diesel. There is a research gap regarding the preparation of the type of feedstock, and the type of catalyst and the type of reactor that are most suitable in order to obtain quality green diesel. How to identify the right type of catalyst/support structure with the capacity of converting UCO into HDRD is a critical step.

Kim et al. [18] concluded that the DO of triglycerides via hydrotreatment should occur in a separate reactor through hydrocracking. Having studied various parameters in the catalytic hydro-processing of palm oil to optimize the production of bio-jet fuel, the authors affirm that the CO generated during DO can result in corrosion, which can lead to deactivation of the catalyst during DO of triglyceride via hydrotreatment process. Harnos et al. [85] tested Pd/activated C, Pd/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, and Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts with a temperature at 613.15 K and pressure at 21 bars and found that the major product distribution was C<sub>17</sub>, C<sub>18</sub>, and small alkanes.

Gusmao et al. [53] obtained maximum conversion by the HDO route using vegetable oil, Ni/SiO<sub>2</sub> and Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts 623 K to 673 K temperature at 10 bars to 200 bars pressure for 2 h in a batch reactor [53].

Veriansayah et al. [86] used soybean oil for HDO in the presence of many sulphided catalysts such as Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Process parameters of 92 bars and 673 K and an oil/weight ratio of 6.044 was used in the batch reactor. The following results were obtained from higher to lower catalysts: NiMo > Pd > Castor > Ni > Pt > Ru, at the catalyst/oil weight ratio of 0.044 and Ni > NiMo > Pd > CoMo at the catalyst/oil weight ratio of 0.088 [86].

Aslam et al. [87] reported newly introduced catalysts for hydroprocessing of Jatropha curcas oil and FFA Mesua ferrea L. and Jatropha curcas oil, known as Musa balbisiana Colla underground stem (MBCUS), a nanomaterial, and a biomass-based thermal power plant fly ash (BBTPFS). The production pathway showed that the desired hydrocarbons in C<sub>18</sub>-C<sub>19</sub> occurred through hydrocracking, decarboxylation, hydrolysis, and thermocatalytic cracking. When they compared the conversion rates they discovered that catalyst acidity and



heteroatom removal also showed BBTPFS to be a better choice than MBCUS. Knoshaug et al. [88] investigated the production of green diesel using biomass from the green alga *Scenedesmus acutus* to produce succinic acid; the lipids produced in this reaction as a by-product, with 83% yield, were deoxygenized through HDO and hydroisomerization to produce green diesel. Toth et al. [89] produced hydrocarbon fuel in the diesel range by the HDO of mixture of gas oil and sunflower oil. He found out that products with less aromatic and fewer sulphur contents were produced at 80 bars and 634.15 K pressure and temperature respectively with LHSV of 1.0 h<sup>-1</sup> and hydrogen/feedstock ratio = 600 Nm<sup>3</sup>/m<sup>3</sup> on varied vegetable oil contents (0 wt% to 15 wt%). The 15 wt% vegetable oil gave the highest CN. Similarly, the isomerization properties of the products were enhanced at low temperatures [89]. Huber et al. [90-92] investigated HDO by co-processing of sunflower oil and heavy vacuum oil (HVO) mixtures. Nickel molybdenum / alumina was used, with pressure at 50 bars and temperature at 573 K to 723 K in a tubular reactor. They observed that the selectivity for HDO products increased under certain reaction conditions. Another co-processing experiment was carried out by Bezergianni et al. [93]. They conducted HDO by using heavy atmospheric gas oil (HAGO) and WCO. The active catalysts like Co-Mo/Al<sub>2</sub>O<sub>3</sub> and Ni-Mo/Al<sub>2</sub>O<sub>3</sub> were used at 56 bars pressure and temperatures of 603 K, 623 K, and 643 K in a fixed bed continuous flow reactor. It was found that Ni-Mo catalysts for HDO are the best under suitable reaction conditions [94]. The research works on HDO were carried out using model compounds to develop certain approaches to understand the kinetics of the single-step reactions in a reactor [95]. The model compounds such as decanoic acid [96], oleic acid [87, 97, 98], palmitic acid [79], stearic acid [99], and linoleic acid [100] were all tested for HDO. The detailed mechanism study of model compounds helps researchers to understand their action kinetics. Snare et al. [101] used oleic acid, linoleic acid (unsaturated fatty acid) and the monounsaturated fatty acid ester, methyl oleate as the model compounds of vegetable oil for HDO using Pd/C 5 wt% catalyst, 15 bars and 27 bars and 573 K to 633 K for 6 h in a semi-batch reactor. They observed a high selectivity and high yield towards the hydrocarbon conversion. The catalyst properties for upgrading vegetable oils to obtain quality and optimal yield using the hydroprocessing technique must possess the following factors: zero coke formation, high resistance to chemical attack, sustainability in commercial processes, resistance to water, high DO activity [102]. In order to make the resources of the production chain completely green, biomass-based thermal power plants fly ash (BBTPPFS) and calcium oxide (CaO) need to be aggressively explored.

## VI. PRODUCTION TECHNIQUES AND PARAMETERS

The technology for producing fossil-based fuel has been in operation in refineries for many years. The same catalysts, reactor types and the distillation facilities used for the production of petroleum-based fuel can be used for the hydroprocessing of biologically derived feedstocks to obtain high-quality hydrocarbon which means that large savings are possible since the same refinery facilities are used. The same production technology used in conventional refinery for

desulfurization and fractional distillation can be adapted for hydroprocessing of vegetable oils and animal fats to produce green diesel or HDRD. Vegetable oils can be co-processed with the diesel oil feed or by building a stand-alone hydrotreatment unit for producing HDRD. However, co-processing involves shutting down the reactor when necessary changes are required between catalyst bed, operating condition and mode of operation. Since the process gives off heat, and large amounts of hydrogen are required in hydroprocessing of vegetable oils feed, a co-feed of above 15 % may pose serious challenges. Hydroprocessing of renewable feedstocks using stand-alone units can be optimized and controlled to achieve higher yields of HDRD production. Stand-alone units can be constructed as an attachment to existing refineries and the existing hydrogen in the refinery can be streamlined as recycled gas. Neat HDRD or blending of HDRD with conventional diesel is possible on-site before distribution, hence the blend percentage can be determined based on market conditions with no significant changes in operating conditions. The main drawback of a stand-alone production facility is the initial high capital costs for the building of infrastructure.

The choice of feedstock can greatly influence the production of green diesel, a second-generation biofuel known as "renewable diesel", also known as hydrogenation derived renewable diesel (HDRD). The feedstocks used for the production of HDRD are plant-derived edible oils such as, rapeseed, soybeans, and palm [103-106], and non-edible oils such as Jatropha and algal oils and UCO products which are now considered the most popular feedstock [105, 107]. Many researchers have confirmed UCO as being the most viable, cost-effective and available feedstock in recent years. Researchers are still investigating the most suitable technology for the production of green diesel that is cost-effective and CI engine compatible. Production of green diesel from biomass can be accomplished through four technologies: (i) Hydro-processing, which aims to convert the triglycerides of the feedstock oils and fats into saturated hydrocarbon products through catalytic processing with hydrogen; (ii) Catalytic upgrading of sugars, starches, and alcohols, which involves liquid phase technologies such as aqueous phase reforming (APR); and (iii) Thermal conversion (pyrolysis) and upgrading of bio-oil which is then refined into green diesel; and (iv) Biomass to liquid (BTL) thermochemical processes, which involve the high-temperature gasification of the biomass for the production of syngas which is rich in H<sub>2</sub> and CO. The green diesel produced by the Fischer-Tropsch method is referred to as FT green diesel [108, 109]. Hydroprocessing is mainly comprised of two steps viz hydrocracking and hydrotreating [110].

Kumar et al. produced green diesel by hydroprocessing and reported that about 85% (by vol.) biofuel was produced while 10 % were gases which escaped in the form of non-condensable gases and 4 % to 5 % collected at the base of the flask in the form of water [111]. Green diesel is a mixture of straight-chain and branched saturated hydrocarbons which contain carbon atoms of C<sub>15</sub> to C<sub>18</sub>. This composition is the same as conventional petroleum diesel which makes green diesel compatible with CI engines without engine modifications [112, 113]. In this context, green diesel is reliable and is emerging as the most promising biofuel because



it has better fuel properties compared to biodiesel and petroleum diesel. Green diesel has been found to possess a high CN, oxidation stability, cold flow properties, and cloud point compared to biodiesel and petroleum diesel [114]. The energy density of green diesel is greater compared to petroleum diesel and biodiesel. Fahmi et al. reported that the CN of green diesel is between 80 to 99 which is much higher than conventional diesel standards [115]. The density and the net heating value of green diesel are in the range of 0.77 g/ml to 0.83 g/ml and 42

MJ/kg to 44 MJ/kg respectively, which also meets the biodiesel and petrodiesel standards [116]. The regulatory bodies have come up with a standard to control the quality of HDRD. Table 7 shows the properties of biofuels according to the standards American Society for Testing and Materials, ASTM D975, EN 15940:2016, EN 590:2013 in Europe, Canadian General Standards Board (CGSB) in Canada, and Neste Renewable Diesel.

**Table VII.** Typical properties of pure Neste Renewable Diesel and how it relates to EN 15940, EN 590 and ASTM D975 Standards

Properties	unit	ASTM D975	EN 15940:2016 Class A	EN 590:2013	Neste HDRD	HDRD CGSB
		Standard		Standard		
Density at +15°C	Kg/m <sup>3</sup>	-	765 - 800	820 - 845	770 - 790	-
Ash	% (m/m)	0.01	≤ 0.010	≤ 0.010	< 0.001	0.01
Carbon residue on 10% distillation	% (m/m)	0.35	≤ 0.30	≤ 0.30	< 0.10	0.15
Cetane Number		40	≥ 70	≥ 51.0	> 70	40
Appearance at +25°C		-	-	-	Clear	-
Water	Mg/kg	-	≤ 200	≤ 200	< 200	-
Flash point	°C	52	> 55	> 55	> 61	40
FAME-content	%(V/V)	-	≤ 7.0	≤ 7.0	0	-
Water and sediment	%(V/V)	0.05	-	-	≤ 0.02	0.05
Polyaromatics	% (m/m)	-	-	≤ 8.0	< 0.1	-
Copper corrosion	-	-	Class 1	Class 1	Class 1	-
Lubricity HFRR at 60°C	µm	-	≤ 460	≤ 460	≤ 460 650	-
Conductivity	Ps/m	-	-	-	≥ 50	-
Final boiling point	°C	-	-	-	< 330	-
Distillation 95%(V/V) 90%(V/V)	°C °C	-	≤ 360	≤ 360	< 320 282-338	-
Total contamination	Mg/Kg	-	≤ 24	≤ 24	< 10	-
Oxidation stability	M/g <sup>3</sup>	-	≤ 25, ≥ 20**	≤ 25, ≥ 20**	< 25	-
Sulphur	Mg/Kg	15	≤ 5.0	≤ 10.0	< 5.0	1.5
Final boiling point	°C	-	-	-	< 330	-
Viscosity at +40°C	mm <sup>2</sup> /s	1.9-4.1	2.000-4.500	2.000-4.500 ≥ 1.200	2.000---4.000	1.7-4.1
Antistatic additive		-			added	-
Cloud point and CFPP ****	°C	-	As in EN590	Down to -34	As needed -5---34	-
Total aromatic	%(m/m)	-	≤ 1.1	< 1.0	< 1.0	-
Cetane index	-	40	-	-	-	-
Acid number	MgKOH/g					0.10

Source: Eco Resources consultants for Natural Resources Canada.



#### *Process Parameter*

The optimum operating parameter is an important consideration in the hydroprocessing of green diesel. The parameters to be evaluated are reaction temperature, pressure, and low hourly space velocity (LHSV). The LHSV is a key parameter to control catalyst effectiveness and life expectancy,  $H_2$ /oil ratio, catalyst, catalyst amount, type of feed, feed rate, reactor type and type of solvent. Critical reviews of reactors for hydroprocessing catalysts have been conducted by many researchers [117], reporting the following: batch reactor or fixed-bed microreactors can successfully screen new catalysts either in particle or in powdered form which makes it possible to compare a catalyst in line with their rate of inert reaction. The reaction conditions in the reactor during hydroprocessing activities has a significant influence on the yield and the quality of hydrocarbon products. Heteroatoms are atoms like sulfur, nitrogen, and oxygen which are present in the bio-based and fossil-based feedstock. Bio-based feedstock comprises oxygen with no sulfur and nitrogen. The presence of oxygen is a threat to the green diesel product because it increases acidic and corrosion attack and reduces oxidation stability [118]. UCO has been used by many researchers and is considered as the best feedstock. The effect of the process parameters affects the composition of the green diesel products [119].

### VII. HYDROGEN

The applications of hydrogen in the production cycle of green diesel is the focus of this section. Hydrogen plays a significant role in hydroprocessing technology. Hydrogen carries the energy and can be produced from fossil fuels, nuclear, solar, wind, biomass, hydro, geothermal and urban waste resources [7]. Electrical power is another source which can produce hydrogen on the scale required to sustain the energy sector. The availability of various resources to produce hydrogen makes hydrogen a promising energy resource. Hydrogen is one of the most abundant elements in the world. Hydrogen has tendencies to combine with other chemical elements to form substances like hydrocarbon, or alcohol, or water. Municipal solid waste product is the cheapest, available and sustainable resource for production of hydrogen using the electrolysis method. These resources can be harnessed to produce hydrogen at a cheap price. The production of hydrogen per year is estimated to be 55 million tons with 6 % increase in consumption per annum. However, currently, almost 50 % of the demand for hydrogen is generated from steam reforming of natural gas, 30 % from naphtha from refineries, 18 % from coal gasification, 3.9 % from electrolysis, and 0.1 % from other sources [120]. Technological processes to produce hydrogen include

electrolysis, thermal energy, and photolysis. Hydrogen is produced by the steam reforming (SR) of natural gas which leads to massive emissions of pollutants [121, 122]. The effect of these emissions in the environment renders production of hydrogen unsustainable. High efficiency can be obtained by electrolytic and plasma processes but the high consumption of energy is a challenge [123]. Coal gasification is another potential source of hydrogen production because of the abundant deposits globally and a cheap price [123]. However, the production of hydrogen from this source is not sustainable because the energy required for confiscation of  $CO_2$  will increase the consumption rate of coal. Hydrogen production from renewable energy resources like geothermal, solar derived, nuclear, and wind energy are sustainable, but the challenge is that the unit cost of electricity will increase the cost of production.

Sourcing hydrogen from solid waste for HDRD application in South Africa offers many benefits like waste management and income generation (waste to wealth). South Africa generated 10.8 million tons of waste per annum, which amounted to 295 890 tons per day, in 2011 [124]. However, 70 % of this waste is biodegradable from which 394 520 tons/annum of hydrogen yield can be obtained. Biomass is available but it cannot meet the required supply of hydrogen because the growing of crops as a source of fuel will attract significant resistance.

Hydrogen can be produced via the water pyrolysis method. Temperatures of approximately 2000 °C are required for direct thermal water splitting that produces a mixture of hydrogen and oxygen [125]. A few thermal chemical cycles have been identified; chemical cycles can be used to lower temperatures to produce hydrogen and oxygen in separate steps, for example sulphuric acid ( $H_2SO_4$ ) at 850 °C and hydrogen iodide (HI) at 450 °C [126]. The design of a fission reactor must consider the mechanical properties of the materials that can offer adequate heat to enhance stability under operating conditions of HI and  $H_2SO_4$ . But the operating cost of nuclear and waste handling makes this source unsustainable. Production of hydrogen can be achieved by photo-biological [127] and photo electro-chemical processes [128, 129]. This is a technology that uses direct irradiation and water resources for the production of hydrogen and it has the tendency to increase the efficiency of the solar-to-hydrogen pathway [130]. This technology allows the use of seawater as feedstock, and open land space is used to collect sunlight energy, thus it is sustainable and cost-effective. These technologies are under investigation for future applications.

These sources for the production of hydrogen will enhance the HDRD production value chain so that it is completely green.



**Table VIII.** Advantages and disadvantages of different hydrogen(H<sub>2</sub>) production technology [131]

Technology	Disadvantages	Advantages	Efficiency (%)
Biomass pyrolysis	Feedstock contamination, seasonal availability lead to varrying content	Abundant and cheap feedstock, neutral CO <sub>2</sub>	35-50
Steam reform (SR)	Use fossil fuels, CO <sub>2</sub> emmission	Existing facilities reduces cost, developed technology	74-85
Electrolysis	Overall efficiency is low, capital cost is high	Use of existing technology, good technology, available and abundant technology, O <sub>2</sub> is the only by-product, pollution free with renewable sources	40-60
Thermolysis	Corrosive problems, toxic element, high cost	Abundant feedstocks, clean and sustainable.	20-45
Biomass-gasification	Feedstock contamination, tar formation, seasonal availability.	Abundant and cheap feedstocks, neutral CO <sub>2</sub>	-
Photo-electrolysis	Conversion rate is low, sunlight requires, poor effective photocatalyst materials	Available feedstocks, pollution free, O <sub>2</sub> is the only by product.	0.06
Partial oxidation (POX)	Depend sole on petroleum product, CO <sub>2</sub> emission	Make use of existing technology, proven technology	60-75

#### A. Effect of Reaction Temperature

The effect of temperature during hydrotreating of feedstock has a great impact both on the biofuel yield and the quality of the expected fuel. Simacek et al. [132] obtained the conversion of rapeseed oil between the temperatures of 310 °C and 360 °C. Kubicka [133] and [134] obtained a fully converted biofuel yield within the range of 80 wt% to 90 wt%. Kikhtyanin et al. [40] achieved full conversion of sunflower oil with optimal temperature range of 320 °C to 350°C in the presence of Pd/SAPO catalyst, while Hancsok et al. [52] used Pt/HZSM-22/Al<sub>2</sub>O<sub>3</sub> catalyst at 350 °C to convert sunflower oil to biofuel. Bezergianni et al. studied catalyst effectiveness over the temperature range prescribed by catalyst manufacturers, i.e. within the temperature range of 330 °C to 390 °C, under constant LHSV (1hr-1) and a range pressure of 1200 psig to 2000 psig. The results showed that the hydrotreating catalysts exhibited the highest conversion (~83 %) as well as the highest diesel selectivity.

Bezergianni et al. [87] investigated the hydrotreatment of UCO in terms of the rate of conversion, heteroatom removal, product yield, temperature variation, saturation of double bond, and selectivity. The scholars deduced that the higher the temperature the higher the product yield. Temperature plays a vital role in the elimination of oxygen content in order to increase the heating value of the biofuel; an increase in temperature and pressure reduces the concentration of oxygen significantly, but during hydroprocessing, high temperatures cause low oil yield and high hydrogen consumption. There is a need to further investigate optimization of operating conditions in order to find out the relationship between temperature, hydrogen consumption, and oil yield. A temperatures range of 300 °C to 400 °C and a hydrogen pressure range between 6 MPa to 20 MPa is commonly used for hydrotreating processes [135].

Biofuel production via hydroprocessing of UCO was studied by Bezergianni et al. They discovered that temperature is the most significant operating parameter which enhances catalyst performance and the life span of catalysts. Their study utilised temperatures of 330 °C, 350 °C, 370 °C 385 and 398 °C [136].

#### B. Effect of Hydrogen Pressure

The effect of hydrogen on the production of biofuel is the focus of this section. Hydrogen has a great impact during hydroprocessing of biofuel. In the reaction mechanism, hydrogen pressure strongly affects hydrotreatment, isomerization, hydrogenation and cracking processes. Hydrogen pressure was varied between 8.27 MPa and 9.65 MPa to investigate the effect during the hydrotreating of UCO [137]. It was reported that higher hydrogen pressure of 9.65 MPa gave a higher diesel-like yield of 71.36 %, oxygen removal efficiency of 94.25 %, 4.03 % and 5.16 %, and gasoline-like fuel yield was obtained at 8.29 MPa and 9.65 MPa pressure respectively. This implies that higher hydrogen pressure gives lower yield while higher hydrogen pressure gives higher yield in diesel-like fuel, consequently, an increase in the cost of hydrogen. Sotelo-Boyas et al. reported that a hydrogen pressure of 8 MPa to 10 MPa is sufficient for liquid yield. Their study investigated hydrogen pressure and the catalyst and their effect on product yield [63].

Sunflower and gas oil blends over NiMo/ Al<sub>2</sub>O<sub>3</sub> catalyst with 0 wt%, 15 wt% or 30 wt% zeolite beta was co-hydro processed [138]. The authors found that the increase in hydrogen pressure from 30 bar to 60 bar for all the catalysts offered a good conversion. It was observed that the NiMo-30BEA catalyst was more active, and at 30 bar hydrogen pressure, 93 % yield was obtained [138].



High hydrogen pressure inhibits liquid to a gaseous product, high hydrogen pressure does not support isomerization, and as higher hydrogen pressure consumption increases energy costs.

#### C. Effect of liquid hourly space velocity

Liquid hourly space velocity (LHSV) is the ratio of the mass feed rate of liquid (g/h) over the catalyst mass (g) and is expressed  $\text{h}^{-1}$  [139]. Mathematically, space velocity can be expressed as:

$$SV = v_0 / V \dots\dots\dots \text{Equation (1)}$$

Where  $v_0$  represents the volumetric flow rate of the reactants entering the reactor and  $V$  is the volume of the reactor itself.

This expression is the reciprocal of the definition for the reactor space-time,  $\tau$  (i.e.  $SV = 1/\tau$ ). However, space-time is measured at the conditions of the reactor entrance while the space velocity is often measured at a set of standard conditions, so the reported space velocity may be different from the reciprocal of the measured space-time.

Bezergianni et al. varied LHSV of 0.5  $\text{h}^{-1}$ , 1.0  $\text{h}^{-1}$ , 1.5  $\text{h}^{-1}$  on the liquid product formed from hydrotreating of UCO over NiMo catalyst. The authors obtained a maximum conversion of 83.08 % with an LHSV of 1.0  $\text{h}^{-1}$ . The increase in LHSV to 1.5  $\text{h}^{-1}$  caused an increase in diesel yield to 97.46 %; a higher amount of diesel-like fuel was formed while sulfur and nitrogen present were removed with an increase in LHSV [137]. Bezergianni et al. obtained the same results during the hydrotreating of used cooking oil [140]. Hydro-processing of jatropha oil and the effect of LHSV on product yield was studied; it was reported that product yield decreased up to 6  $\text{h}^{-1}$  at 300 °C, and increased slightly at 8  $\text{h}^{-1}$  due to change in the reaction pathways [141]. Hourly space velocity supports the removal of nitrogen and sulfur removal but reduces oxygen removal.

High hourly space velocity results in the formation of wax. An increase in hourly space velocity increases the choice of diesel selectivity.

## VIII. CONCLUSION

The search for alternative sustainable renewable energy has influenced researchers to develop solutions to the environmental crises and global demand for fuel. Green diesel has received significant attention in the modern economy because HDRD offers higher stability, higher heating value, and emission of harmless pollutants. The use of non-edible oil such as UCO is more viable as it reduces the production cost and has the potential to settle the concerns related to the edible oil market. This critical review has identified UCO as a potential feedstock for hydroprocessing of HDRD. The main conclusions are:

- Used cooking oil has the potential to be a sustainable feedstock for HDRD; the production cost of green diesel will reduce when UCO is protected and harnessed as a source of feedstock.

- The right technology for HDRD production will promote the commercialization of green diesel.
- Catalyst selection has a great effect on hydrocarbon yield. BBTPPFS sourced from Eskom, characterized and prepared will offer optimal hydrocarbon yield. This choice of catalyst will make the value chain completely green. The effect of process parameters that influence the production of diesel range hydrocarbon has been studied via effect of temperature,  $\text{H}_2/\text{oil}$  ratio, hydrogen pressure, and liquid hourly space velocity.
- As for the reaction temperature, a balance must be maintained in the selection of fuel range hydrocarbons and conversion rates of UCO, regarding hydrogen pressure. High hydrogen pressure does not support isomerization, high hourly space velocity results in the formation of wax, and an increase in hourly space velocity increase the choice of selectivity. UCO has a low pH value which offers the best potential for hydrogenation.
- HDRD possesses superior fuel qualities such as CN, low pour point, and excellent oxidation stability which offers a great benefit for the CI engine and the environment.
- Used cooking oil sourced from domestic, restaurant and food industry can be harnessed for commercial production of HDRD.

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### CHAPTER 3: HYBRIDIZATION OF WASTE COOKING OIL: AN INNOVATIVE TECHNIQUE FOR IMPROVED FEEDSTOCK

This chapter investigates the effect of hybridization of waste cooking oil to obtain a novel feedstock for HDRD production.

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## HYBRIDIZATION OF WASTE COOKING OIL: AN INNOVATIVE TECHNIQUE FOR IMPROVED FEEDSTOCK

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### ABSTRACT

*The quest to improve the quality and conversion efficiency of waste cooking oil (WCO) as biodiesel feedstock has resulted in increased research in recent years. Hybridization of feedstocks has been proposed as an easy way to achieve these objectives. In the current research, three samples of WCO were collected at three different restaurants just before disposal. The samples were blended in varying proportions and subjected to characterization. The outcomes of the analyses revealed that hybridization affects the density, kinematic viscosity, saponification value, and iodine value of the feedstock but has no influence on the acid value, cetane index, and higher heating value. The iodine value of the parent feedstocks varied between 54.4 cg/g and 67.9 cg/g while that of the hybridized samples ranged between 80.4 cg/g and 100.2 cg/g. The parent and the hybridized samples witnessed single-stage thermal decomposition at approximately 330 °C while the derivative thermogravimetric degradation occurred between 350 °C and 475 °C. More targeted investigations are needed to explore the impact of hybridization on conversion efficiency, properties, storage, transportation, and performance of biodiesel.*

**KEYWORDS:** Biodiesel; feedstock; hybridization; waste cooking oil.

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### INTRODUCTION

The increased demand for biofuel (particularly biodiesel) to replace fossil-based diesel (FBD) fuel either in a blended or unblended form, has made the existing production capacity inadequate and insufficient to meet global demands. Worldwide oil demand has been predicted to rise to 105.4 MMbpd in 2030 compared with the 96.9 MMbpd in 2018 [1]. The projected increment in energy demand has made the continuous search for sustainable alternative energy a priority if the global energy demand is to be met. Due to the depletion of oil reserves, the decline of oil exploration, and the increased cost of FBD fuel, the need to switch to low-carbon fuels has become a priority. Researchers have invested significant effort, time, and financial resources into the synthesis of biodiesel from various sources due to the advantages derivable from its production and utilization [2, 3]. Biodiesel, otherwise referred to as fatty acid methyl ester (FAME), is an eco-friendly liquid fuel consisted of long-chain fatty acids (C<sub>12</sub>-C<sub>22</sub>) and is considered a good replacement for FBD fuel. Transesterification (alcoholysis) is acknowledged as one of the best routes for conversion of biomasses to FAME. Biodiesel is more environmentally benign, is biodegradable, can be produced from waste, and emits less carbon monoxide during usage. Compression ignition (CI) engines fueled with FAME show less noise, less vibration, and require less maintenance when compared with those powered with FBD fuel. With superior cetane number and flash point, absence of sulphur, less toxicity, and safer handling and transportation infrastructure, FAME is a more preferable fuel than FBD [4-6].

However, there have been factors militating against the sustainable application of biodiesel in the energy mix. Technical, social, economic, and environmental considerations have continued to impact on the sustainable,

affordable, and cost-effective production and utilization of biodiesel. Economically, high production costs have been recognized as a potent impediment to its commercialization [7]. The cost of feedstock accounts for between 60 % and 75 % [8-10] and 70 % and 95 % [11-15] of the entire production cost. One of the ways to make biodiesel more affordable and economically viable and competitive is the choice of feedstock. The use of uneatable oil, used vegetable oil, and recovered animal fats have contributed to a significant reduction in the production expenses of FAME. The utilization of used vegetable oil and recovered animal fat as raw materials for FAME synthesis does not interfere with the food chain and serve as a viable channel for waste disposal. Although the use of non-edible neat oil lowers the production costs, it does not have as much of an impact on the overall cost as does the use of waste cooking oil, and yellow and brown greases. For example, biodiesels generated from waste cooking oil (WCO) have been found to be nearly four times lower in cost than the biodiesel synthesised from neat palm oil [16-19]. Lee et al. [14] reported a 55 % reduction in the total production cost of biodiesel when waste canola oil was used as feedstock compared with when neat canola oil was used. At 1.65 US \$/L, WCO is a cost effective feedstock for FAME production when compared with the price of virgin vegetable oil at 4.2 US \$/L [18, 20], and fresh soybean oil at about 6.23 US \$/L [21]. Owing to considerations such as urbanization, population explosion, cost, and change of standard of living and lifestyles, the domestic consumption of sunflower oil and palm oil has grown in the last five years, as shown in Fig. 1 [22]. This trend is predicted to continue for the foreseeable future. During frying, vegetable oil is heated to a temperature above 200 °C, and sometimes mixed with water and salt which exposes the oil to thermal decomposition and contamination. Household consumption of vegetable oil that has been repeatedly applied for frying can have deleterious health consequences on humans and animals [23, 24].

Bearing in mind the unique impact of feedstock on the production, conversion efficiency, properties, and performance of biodiesel, researchers have proposed hybridization or blending of feedstock. Hybridization is the blending of two or more different feedstocks in various percentages to produce an entirely new feedstock. The need for hybridization of feedstock is reinforced by the desire to create novel feedstocks from the existing feedstock. The hybridized feedstock will possess the aggregate of the features and fingerprints of the individual parent feedstock. The hybridized feedstock will always possess the distinct physicochemical properties, behaviour, and compositions of the parent stocks. Hybridization of feedstock can be performed either in-situ or ex-situ. When two feedstocks are mixed together, it is called bi-hybridization while poly-hybridization refers to the mixing of more than two feedstocks. The main intent of hybridization is the creation of a new feedstock with improved physical and chemical properties, and better conversion efficiency [25, 26]. In poly in-situ blending of feedstock, which is the procedure used in this study, three used vegetable oils with different histories were mixed to generate a product with distinct properties from the parent feedstock. Hybridization of feedstock allows WCO collected from different sources to be mixed together directly for possible conversion to biodiesel. Using WCO in this way will enhance the commercial utility and availability of WCO, and will mitigate the problem associated with non-availability of WCO commercial quantities.

In separate research, Uloka-Uboka and Inambao [25, 26] examined in-situ and ex-situ hybridization by blending oils and methyl esters produced from the transesterification of *Moringa oleifera* and *Jatropha curcas* in varying proportions. The hybridized oil possessed dissimilar properties from the parent feedstock and initiated a new vista in the selection of feedstock for biofuel production. The present effort is a continuation of our previous research where the properties and fatty acid compositions of neat and WCOs were determined [23]. The pertinent query, therefore, is whether the benefits derivable from hybridization of feedstock in inventing new sets of feedstocks has been adequately interrogated. In the current effort, the authors carried out the examination of the physical and chemical properties, and thermal and spectroscopic analyses of



three different WCOs that had been hybridized to create seven additional samples. The motivating factor behind this work was to create a different set of feedstocks from the existing two waste palm oil (WPO) and one waste sunflower oil samples. The new samples were expected to possess improved properties and biological configurations. The present effort is limited to poly in-situ hybridization of three WCO samples in different proportions and the subjection of the hybridized feedstocks to property determination, and thermal and spectroscopic characterization.

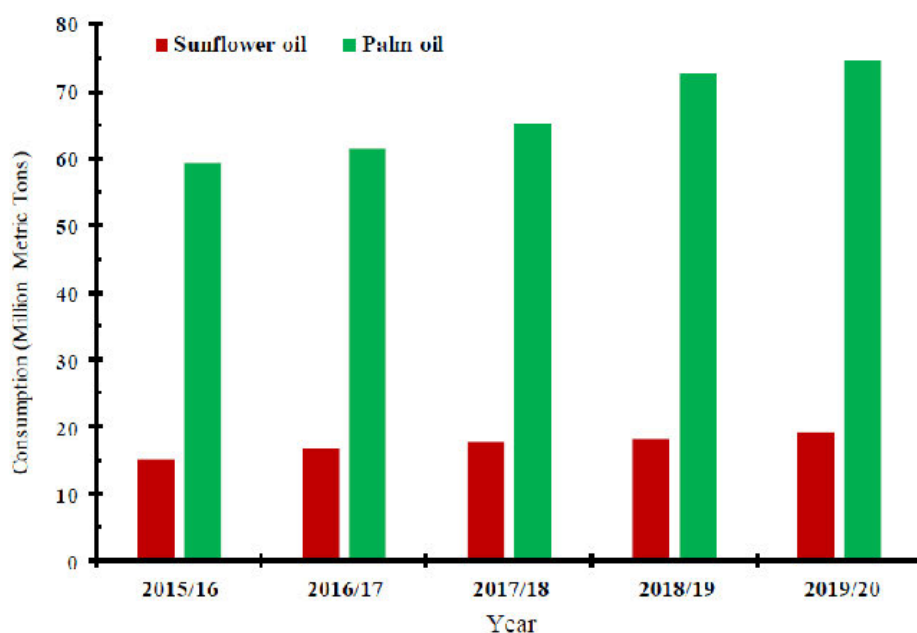


Figure 1: Consumption of palm oil and sunflower oil (Million Metric Tons). Adapted from [22]

## MATERIALS AND METHODS

### Material Collection and Preparation

The parent WCO samples were collected from three take-away outlets in Durban, South Africa, just before disposal. The details of the three parent samples and their sources are displayed in Table I. The samples were heated on an electric heater fitted with a magnetic stirrer kept at 110 °C and agitating speed of 50 rpm. This allowed the water trapped in the oil to escape by evaporation.

Table 1: Details of the Parent Samples

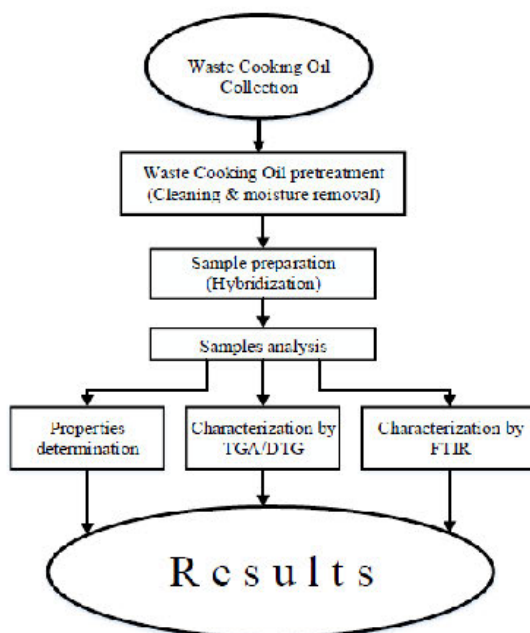
Source of Oil	Usage (Days)	Food Items Fried	Designation
Sunflower oil	14	Chips	WSF <sub>C</sub>
Palm oil	14	Chips and fish	WPO <sub>FC</sub>
Palm oil	14	Sausages and chips	WPO <sub>SC</sub>

The samples were later filtered to eliminate food residue and other unwanted objects. The WCO samples were prepared by the in-situ hybridization of the WSF<sub>C</sub>, WPO<sub>FC</sub>, and WPO<sub>SC</sub> as shown in Table II. The oils were allowed to cool to about 60 °C and mixed thoroughly in specified proportions to ensure an homogeneous mixture of the oils. In the current

effort, the authors adopted a simple mixing ratio. The flowchart for the methodology is shown in Figure 2. The samples were poured into airtight glass bottles and warehoused in the refrigerator at 5 °C for analysis and testing.

**Table 2: Details of the Samples Composition**

Samples Notation	Hybridization Protocol Ratio		
	WSF <sub>C</sub>	WPO <sub>TC</sub>	WPO <sub>SC</sub>
A	0	0	1
B	0	1	0
C	1	0	0
D	1	1	0
E	1	0	1
F	0	1	1
G	1	1	1
H	1	1	0.5
I	1	0.5	1
J	0.5	1	1



**Figure 2: Flowchart of the Methodology**

### Property Determination

The density, kinematic viscosity (KV), acid value, iodine value (IV), and saponification value (SV) of the WCO samples were determined using suitable established methods and procedures as presented in Table III. Details of the procedures are highlighted in our previous works [23]. The cetane index and the higher heating value (HHV) of the samples were estimated via equations (1) and (2).



Table 3: Methods for Determining Physicochemical Properties of Samples

Property	Unit	Method
Density at 20 °C	Kg/m <sup>3</sup>	ASTM D1298
KV at 40 °C	mm <sup>2</sup> /s	ASTM D445
Acid value	mgKOH/g	AOCS Ca 5a-40
IV	cg/g	AOCS Cd 1b-97
SV	mg KOH/g	AOCS Cd 3-25
Cetane index	N/A	By estimation
HHV	MJ/kg	By estimation

$$\text{Cetane index} = 46.3 + \frac{5458}{SV} - \frac{0.225}{IV} \quad [27] \quad (1)$$

$$HHV = 49.43 - 0.041(SV) - 0.015(IV) \quad [28] \quad (2)$$

#### Thermal and Spectroscopic Characterization

The thermal characterization consisted of thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). The TGA and DTG analyses of the samples were made using DTG (DTG-60AH, Shimadzu) and TGA (TA-60WS, Shimadzu) thermal analyzer. About 10 mg of the sample was weighed into an aluminium cup with the machine maintained at a temperature between 30 °C and 500 °C, a heating rate of 20 °C/min, and under a nitrogen atmosphere flowing at 50 cm<sup>3</sup>/min. The TGA and DTG data were obtained simultaneously and evaluated by means of the TA-60 ch 1 DTG-60AH workstation.

The spectroscopic analysis were conducted by Fourier transform infrared spectroscopy (FTIR) and evaluated with the aid of a Perkin-Elmer Spectrum 100 spectrometer from 300 cm<sup>-1</sup> to 4 000 cm<sup>-1</sup> on a spectrometer (model system 1000 FTIR, Perkin Elmer Co., USA) with a resolution of 2.0 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

The outcome of properties determination, TGA, DTG, and FTIR characterization are presented under the following headings.

#### Effects of hybridization on physicochemical properties

The outcome of the laboratory determination of density, KV, acid value, IV, and SV and calculated values for the cetane index and the HHV are depicted in Table IV. The density and KV of the hybridized samples decreased marginally when compared with the parent WCO samples A, B, and C. This might be attributed to the fact that blending is not accompanied by any form of chemical reaction. The minor reduction in the values of density and KV is probably due to the physical mixing of the samples [25, 26]. In-situ hybridization elicited a slight change in the acid value of samples, although the changes do not affect the choice of method of conversion to biodiesel. The acid values of the samples are still less than 2 mgKOH/g, thereby making a single step transesterification process feasible. The iodine value of the parent sample is less than the iodine value of the hybridized samples. This can be attributed to the impact of the blending of the samples. The SV, cetane index and the HHV of the samples are not significantly affected by the blending of feedstock since no chemical reaction takes place during mixing. In all, the physico-chemical fingerprints of the hybridized samples are not the same as that of the parent samples, thereby creating an entirely new feedstock.

Table 4: Physico-Chemical Properties of the Samples

Samples	Density @ 20 °C (Kg/m <sup>3</sup> )	KV @ 40 °C (mm <sup>2</sup> /s)	Acid value (mgKOH/g)	IV (cg/g)	SV(mg KOH/g)	Cetane index	HHV( MJ/kg)
A	9188.3	35	1.38	54.4	197.6	73.92	40.51
B	9171.2	34.2	0.97	64.4	194.9	74.30	40.47
C	9198.3	31.8	1.09	67.9	196.8	74.03	40.34
D	9160	29.2	1.01	100.2	199.2	73.70	39.76
E	9168.4	30	1.22	87.9	193	74.58	40.20
F	9150.2	30.7	1.18	89.7	197.9	73.88	39.97
G	9167.3	30	1.16	86.4	198.2	73.84	40.01
H	9169.1	30.2	1.09	92	193	74.58	40.14
I	9168.8	30.8	1.16	86	198	73.86	40.02
J	9160.8	30.8	1.16	80.4	192.2	74.69	40.34

**Effects of hybridization on TGA and DTG**

The weight loss percentage against the temperature plot for the samples is shown in Fig. 3 comparing the thermal behavior of the parent samples A, B, and C with the hybridized samples D, E, F, G, H, I, and J. As shown, all the samples experienced one stage thermal degradation commencing from about 330 °C though the adopted temperature range was 30 °C to 500 °C [29]. The samples showed varying weight loss percentages compared to sample I, which demonstrated a significantly different decomposition profile, proceeding into the negative region of the plot. Samples A, B, C, D, E, F, G, H, and J commenced at between 8.91 % and 13.86 % and ended at approximately 0 %, while sample I occurred between 3.15 % and -6.58 %. The recorded decomposition temperature was attributed to the existence of some intricate chemical compounds and unsaturated fatty acids in the oil samples [30-32].

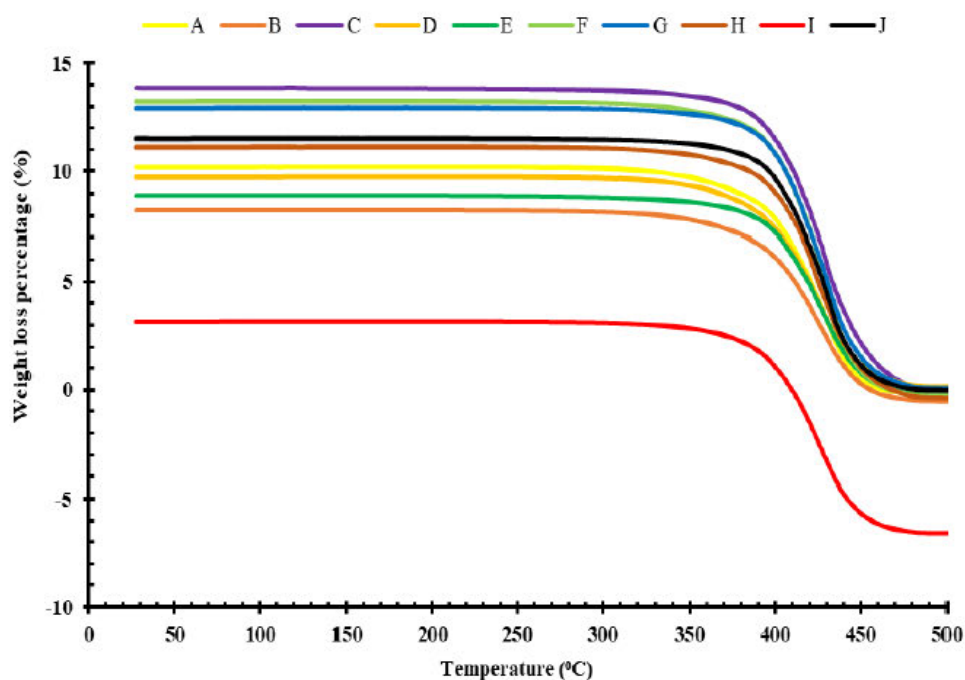


Figure 3: TGA Curves for the Samples

The DTG curves of the WCO samples are shown in Figure 4. The samples showed one peak and the derivative weight percentage of between  $-0.05\%/m$  and  $-0.11\%/m$  occurred between degradation temperature of  $350\text{ }^{\circ}\text{C}$  and  $475\text{ }^{\circ}\text{C}$ . The shape of each curve of the samples indicate that hybridization slightly affected the derivative weight percentage of the samples, an indication that hybridization will give rise to novel feedstocks distinct from the parent feedstocks with the ability to improve the ease of feedstock conversion [33-35].

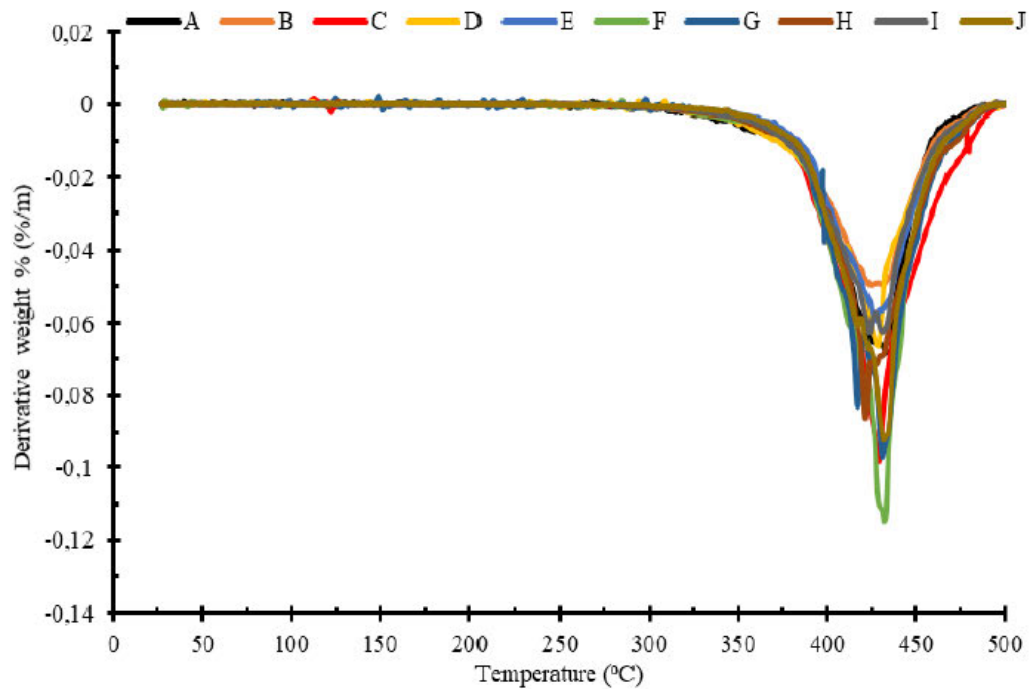


Figure 4: DTG curves for the Samples

#### Effects of hybridization on FTIR

Figure 5 shows the FTIR spectra of both the parent and hybridized samples. They are four unique sections with characteristic peaks in the FTIR spectrum viz.  $4\,000\text{ cm}^{-1}$  to  $2\,500\text{ cm}^{-1}$ ,  $2\,500\text{ cm}^{-1}$  to  $2\,000\text{ cm}^{-1}$ ,  $2\,000\text{ cm}^{-1}$  to  $1\,500\text{ cm}^{-1}$ , and  $1\,500\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . These regions are identifiable in the curves. A strong band appeared at  $1\,744\text{ cm}^{-1}$  for each FTIR spectrum of the samples. Nonetheless, the FTIR spectrum in the second region denoted by  $2\,500\text{ cm}^{-1}$  to  $2\,000\text{ cm}^{-1}$  is nonexistent in the curves. This agrees with the findings of comparable investigation as reported by Michael [36] and Kamaranzaman et al. [37].



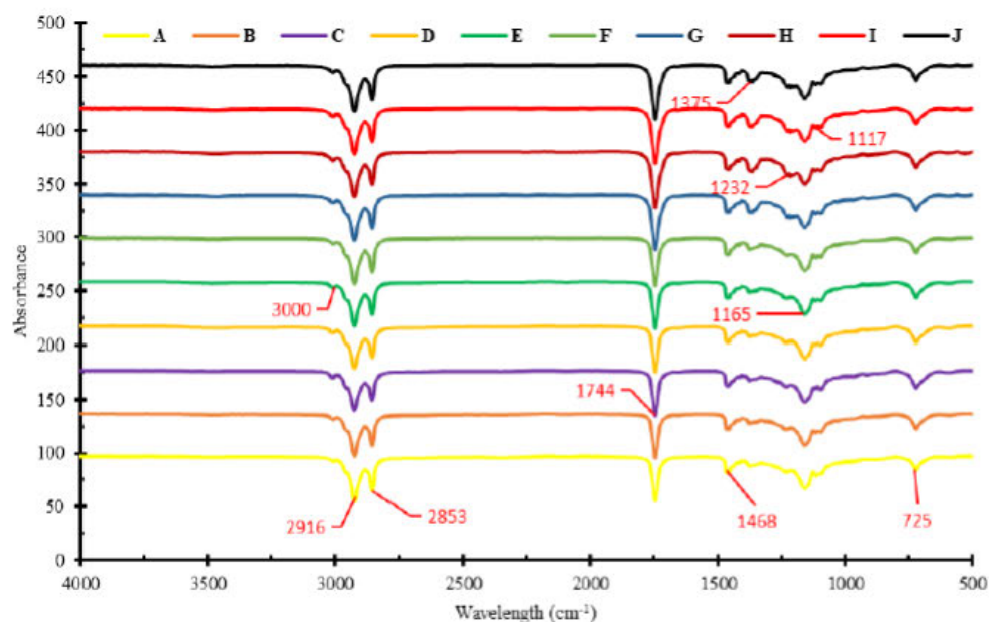


Figure 5: FTIR Spectra of the Samples

The ten samples have dominant and distinguishable peaks at  $725\text{ cm}^{-1}$ ,  $1165\text{ cm}^{-1}$ ,  $1744\text{ cm}^{-1}$ ,  $2853\text{ cm}^{-1}$ , and  $2916\text{ cm}^{-1}$  signifying the presence of related chemical groups in the configurations and comparable fingerprints [38–40]. It was noticed that the peaks at  $1117\text{ cm}^{-1}$ ,  $1232\text{ cm}^{-1}$ , and  $1375\text{ cm}^{-1}$  are more pronounced in the hybridized samples than the parent samples A, B, and C. The esteric ( $\text{-COC}$ ) vibration almost appeared between  $1165\text{ cm}^{-1}$  and  $1017\text{ cm}^{-1}$  which shows the existence of medium intensity bands. The band  $1165\text{ cm}^{-1}$  illustrates the occurrence of methyl ester and carbonyl groups in close proximity. The vibration band observed at  $725\text{ cm}^{-1}$  is accountable for the presence of both  $\nu(\text{C-H})$  and  $\nu(\text{-(CH}_2\text{)}_n$  compounds [41]. The major vibrations and their respective functional groups are as shown in Table V.

## CONCLUSIONS

In the current work, new sets of feedstock have been produced from the existing feedstock by means of the hybridization technique. The parent and the hybridized feedstocks have been subjected to physicochemical property determination, thermal and spectroscopic characterizations, and the outcomes have been presented. In the current research, three parent samples of WCO were blended in different proportions to get seven additional samples and a total of ten samples were analyzed for property, TGA, DTG, and FTIR, and their results compared. It has been revealed that through hybridization the properties, thermal and spectroscopic properties of feedstock can be altered. The outcome of these investigations is that hybridization of feedstock has generated a completely new set of feedstock distinct from the parent feedstock with enhanced properties and characteristics regarding biodiesel production. A hybridized feedstock is envisaged to fuse the fingerprints and individualities of the parent feedstocks. In this research, three samples of WCO were blended in different proportions and a total of ten samples were analyzed for properties determination, TGA, DTG, and FTIR, and their results compared. From the results of these investigations, it is possible to deduce the following:

- Whereas properties of the WCO feedstocks such as acid value, cetane index, and HHV were unaffected by hybridization, the density, KV, and SV of the feedstocks decreased after poly-hybridization. The IV of hybridized samples were higher than that of the parent samples A, B, and C.
- Both the TGA and DTG of the samples were influenced by the hybridization of the feedstocks. The rate of thermal degradation was found to increase after hybridization despite the fact that all the samples experienced single-stage thermal decomposition. The thermal decomposition of all the samples took place within the identical temperature range. Sample I, however, showed a significantly different thermal decomposition profile and proceeded into the negative region of the plot.
- The FTIR spectra of the parent WCO samples A, B, and C appeared slightly different from that of the poly-hybridized samples. Though the ten samples presented similar peaks particularly at  $725\text{ cm}^{-1}$ ,  $1\ 165\text{ cm}^{-1}$ ,  $1\ 744\text{ cm}^{-1}$ ,  $2\ 853\text{ cm}^{-1}$ , and  $2\ 916\text{ cm}^{-1}$ , the peaks at  $1\ 117\text{ cm}^{-1}$ ,  $1\ 232\text{ cm}^{-1}$ , and  $1\ 375\text{ cm}^{-1}$  are more pronounced in the hybridized samples than the parent samples A, B, and C.
- Hybridization of feedstocks provides a straightforward, easy, cost-effective, and innovative way of adjusting and enhancing the physicochemical properties, thermal, and spectroscopic behavior of feedstock with a view to enhancing their suitability for biodiesel synthesis.
- Going forward, there is a need for more investigations into in-situ hybridization of more feedstocks from dissimilar feedstocks like neat vegetable oil, used vegetable oil from various sources, and recovered animal fats. The impact of mixing protocols, mixing ratios, and oil source of in-situ poly-hybridization on the properties and characterization of feedstock are recommended for further investigations. The effects of in-situ, ex-situ, bi-, and poly-hybridization protocols on the conversion efficiency, biodiesel fingerprints, and utilization of FAME in compression ignition engine also warrant further investigation.

Table 5: Characteristics of FTIR Spectra Peaks of the Samples

Wave Number ( $\text{cm}^{-1}$ ) <sup>a</sup>	Types of Vibration	Functional Group	Ref.
2 916 (m)	Asymmetric stretching	$\nu(\text{C-H})$ of alkanes	
2 853 (s)	stretching	$\nu(\text{C-H})$ of methylene	
1 744 (s)	Stretching	$\nu(\text{C=O})$ of ester carbonyl group	
1 378 (w)	Bending in plane	$\nu(-\text{C-H}(\text{CH}_3))$	
1 363 (w)	Bending	$\nu(\text{CH}_2)$	
1 165 (s)	Stretching, Bending	$\nu(-\text{C-O})$ , $\nu(-\text{CH}_2-)$	
725 (w)	Bending of alkanes and overlapping of rocking vibration of methylene	$\nu(\text{=C-H})$ and $\nu(-(\text{CH}_2)_n)$	

<sup>a</sup>m = medium; s = strong; w = weak

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## CHAPTER 4: IN-SITU HYBRIDIZATION OF WASTE PALM OIL: A PHYSICOCHEMICAL, THERMAL, AND SPECTROSCOPIC ANALYSIS

This chapter examine the physiochemical properties of UCO and thermal behaviour of the new feedstock developed. This feedstock was subjected to density, kinematic viscosity, acid value, iodine value, and saponification value testing to analyse their potentials for hydro-processing into HDRD.

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# In-situ Hybridization of Waste Palm Oil: A Physicochemical, Thermal, and Spectroscopic analysis

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## Abstract

Hybridization is one of the techniques for unearthing novel feedstock and diversifying the existing waste cooking oil feedstock stream. In the present research, in-situ hybridization was carried out on waste palm oil (WPO) samples obtained from different sources. The aim of this current study is to investigate the effect of hybridization on the physicochemical properties, thermal degradation, and spectroscopic on both the WPO and hybridized samples. Two WPO samples were mixed in different ratio and subjected to property determination and characterization. Hybridization was found to increase the iodine value, and reduce the density, kinematic viscosity, and saponification values but does not affect the acid value, cetane index and higher heating values of the samples. All the samples witnessed one stage of thermal decomposition; samples A, B, C, D, and E experienced 13 %, 11 %, 10 %, 8 %, and 3 % weight loss respectively between 320 °C and 470 °C. The peak of derivative weight percentage of  $-0.06 \text{ \%m}^{-1}$  was observed at 433 °C,  $-0.05 \text{ \%m}^{-1}$  at 430 °C,  $-0.11 \text{ \%m}^{-1}$  at 432 °C,  $-0.09 \text{ \%m}^{-1}$  at 422 °C, and  $0.06 \text{ \%m}^{-1}$  at 430 °C for samples A, B, C, D, and E respectively. The infrared spectrum curves revealed that the peculiar peaks at  $1226 \text{ cm}^{-1}$ ,  $1363 \text{ cm}^{-1}$ , and  $1378 \text{ cm}^{-1}$  found in the parent samples A and B disappeared in the spectrum curves of hybridized samples C, D, and E. The outcome of this investigation shows that hybridization is a viable technique for improving the quality of existing feedstock as well as creating novel high-quality feedstock for biodiesel generation

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**Keywords:** Characterization, feedstock, in-situ hybridization, waste palm oil;

## 1. Introduction

Renewability, biodegradability, environmental sustainability, and affordability are some of the factors that have popularized the application of biodiesel as a sustainable replacement for fossil-based diesel (FBD) fuel to run compression ignition (CI) engines. The International Energy Agency has projected that the global oil demand will escalate to 105.4 MMbpd in 2030 from the 96.9 MMbpd recorded in 2018 [1]. This increased energy demand has made the use of alternative energy a priority in order to meet the soaring global energy demand. Similarly, the damaging effect of the exploitation and utilization of FBD fuel, depletion of oil reserves, deteriorating oil production capacities, and the increasing price of FBD fuel in the global market has brought about the necessity to move to low-carbon emitting fuels a global priority. The depletion of fossil fuel reserves has made the search for alternative and sustainable fuel inevitable. Such alternative fuel must be affordable, environmentally benign, and carbon neutral [2-4].

Consequently, researchers have continued to commit considerable time and resources to the production and utilization of biodiesel [5, 6]. Biodiesel is biodegradable, more environmentally friendly, more lubricating, and it emits less carbon monoxide, soot, and unburnt hydrocarbon emissions, and generates less engine noise and vibration as

well when compared with FBD as CI engine fuel. Biodiesel has also been found to exhibit a higher cetane number and flash point, low sulphur content, and is non carcinogenic, less toxic, and safer to handle when compared with FBD fuel [7-11].

The high cost of feedstock, the conflict between some food-based feedstock and the food chain, and scarcity of feedstock have continued to negatively impact the commercialization of biodiesel. Economically, the price of feedstock has been found to account for between 60 % to 80 % of the overall production expenditure of biodiesel [10, 12-14]. The use of inedible oil, waste cooking oil (WCO), and recovered animal fats have been discovered to considerably lower the production cost of biodiesel. The use of these feedstocks does not conflict with the food chain and serve as a sustainable waste disposal mechanism. For example, biodiesel generated from WCO was much cheaper than that generated from neat palm oil [15-17]. Lee et al [18] reported a production cost of 0.7 US\$/L of biodiesel when using waste canola oil compared to 1 US\$/L for fresh canola oil. At 1.65 US \$/L, WCO [19] is the cheapest feedstock when compared with neat vegetable oil at 4.2 US \$/L [16], and neat soybean oil at 6.234 US \$/L [20].

Waste palm oil (WPO) is commonly used as biodiesel feedstock due mainly to its availability and reasonably low cost when compared with other forms of inedible vegetable oil [21, 22]. WPO is obtained when palm oil is used domestically for frying. Palm oil is obtained from palm

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fruit, which is predominantly grown in tropical Africa, South America, and Southeast Asia. About 90 % of palm oil is believed to be consumed domestically as food, while the remaining 10 % is used for industrial, cosmetics, lubricants, fuels, and as a bio-asphalt binder, among other uses [23, 24]. The domestic consumption of palm oil as food has continued to increase over the last five years (Figure 1). This is because of urbanization, increased population, and change of lifestyles. Exposure of palm oil to temperatures above 200 °C in the presence of moisture and salt during frying predisposes the oil to physico-chemical and thermal decomposition. Domestic consumption of palm oil that has been used for frying is harmful to health, causing cancer, diabetes, and other diseases [25, 26].

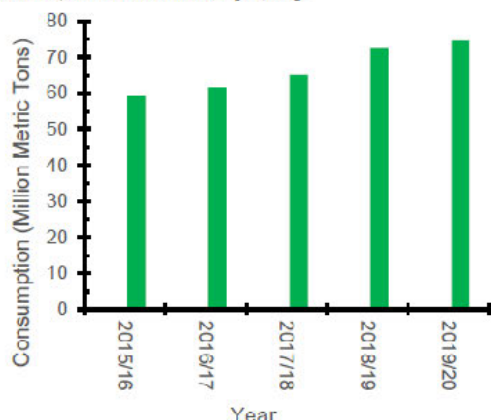


Figure 1 Consumption of palm oil (Million Metric Tons) from 2015/16 to 2019/20

Hybridization is the mixing of two or more distinct feedstocks in varying fractions to create a novel feedstock. The hybridized feedstock has always different properties compared with the parent stocks. Feedstocks can be hybridized in-situ, ex-situ, bi or poly, with the main target being the generation new feedstocks with enhanced physicochemical properties, improved conversion efficiency, and thermal properties [27, 28]. In in-situ blending, which is the method for this research, two different WPO are blended to generate another feedstock with a distinct fingerprint from the parent feedstock.

Not many studies on hybridization of used vegetable oil as feedstock are published in literature. In separate researches, Eloka-Eboka and Inambao [27, 28] carried out in-situ and ex-situ mixing of oils and biodiesels from *Moringa oleifera* and *Jatropha curcas* in varying proportions. The new products possess distinct properties from their parent feedstock and methyl esters with the potential to open a new vista in the biofuel industry. The relevant question to ask, therefore, is whether the possibility of hybridization of feedstock in creating new and improved feedstocks has been well interrogated. The objective of this research is to investigate the effects of hybridization of two samples of WPO on the properties, thermal degradation and spectroscopic transformation of the outcome of the hybridization.

Specifically, in-situ hybridization was carried out between two WPO samples that have been utilized to fry different food. The samples were mixed in different proportions and the resulting mixtures were tested and

analyzed. The motivation was to create different sets of feedstocks, which are expected to have different properties and thermal behavior from the parent WPO samples. The scope of the current research was limited to in-situ hybridization of two WPO samples in varying proportions which were then subjected to density, kinematic viscosity, acid value, iodine value, and saponification value testing as well as characterization by thermogravimetric analysis (TGA), derivative thermogravimetric analysis (DTG) and Fourier Transform Infrared Spectroscopy (FTIR).

## 2. Materials and methods

### 2.1. Material collection and samples preparation

Two WPO samples were collected from two restaurants in Durban, KwaZulu-Natal Province, South Africa at the point of disposal. One of the WPO samples had been used to fry fish and chips (WPO<sub>FC</sub>) for 14 days while the second WPO sample was used to fry sausages and chips (WPO<sub>SC</sub>) for 14 days. The samples were pretreated by subjecting them to heating on an electric stove / magnetic stirrer maintained at 110 °C and stirring speed of 50 rpm to remove the moisture trapped in the oil. The samples were later subjected to vacuum filtration to eliminate food particles, debris, and other foreign bodies in the oil [25]. Figure 2 shows the picture of the parent samples.

The oils were heated to 60 °C and poured into a clean beaker and weighed on an electric weigh balance and poured into a bigger beaker where the oils were mixed in a specified ratio. In the present investigation, simple mixing ratios were adopted in order to prevent undue influence of the one parent sample over the other. The oils in the mixing beaker were stirred with the aid of a magnetic stirrer maintained at a speed of 50 rpm for 20 min to allow for a homogeneous mixture of the oils.

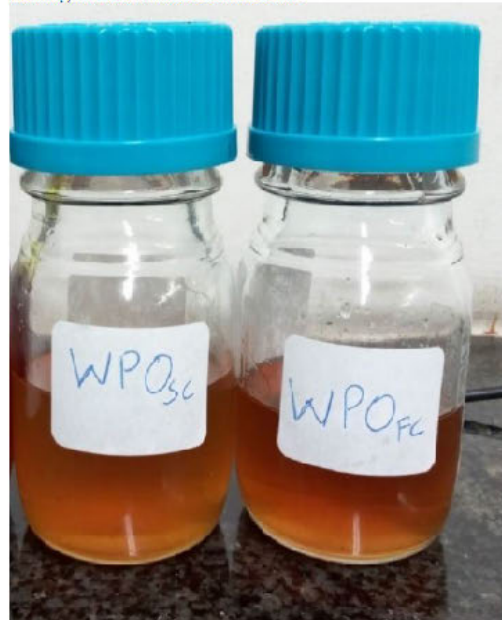


Figure 2: Picture of the parent samples

The hybridized samples are labeled accordingly and stored in airtight glass bottles for property determination.



and characterization procedures. The details of the in-situ hybridization are shown in Table 1 while Figure 3 illustrates the flowchart of the methodology. The hybridization protocols are chosen to have different scenarios of mixing the two parent samples WPO<sub>FC</sub> and WPO<sub>SC</sub>.

Table 1. Details of the samples and hybridization protocol

Sample notation	Hybridization protocol ratio	
	WPO <sub>FC</sub>	WPO <sub>SC</sub>
A	0	1
B	1	0
C	1	1
D	2	1
E	1	2

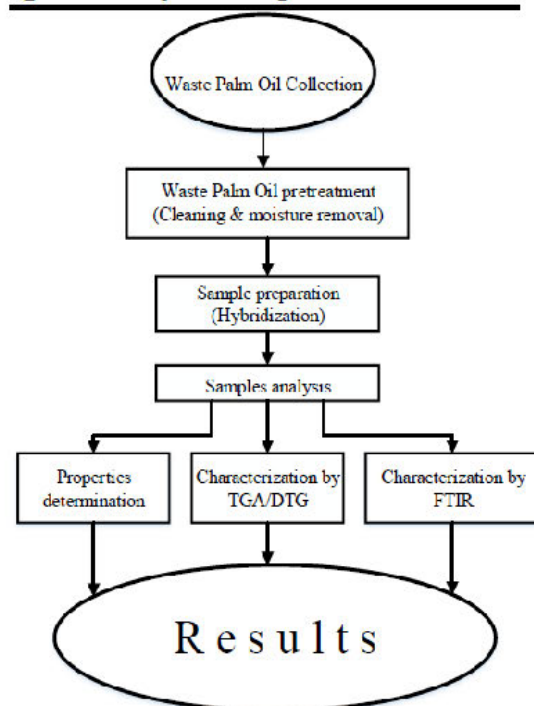


Figure 3. Flowchart of the methodology

## 2.2. Property determination of samples

The density, kinematic viscosity, acid value, iodine value, and saponification value of the samples were determined by using the appropriate method as shown in Table 2, and the procedures were highlighted in our previous works [18].

Table 2. Methods for properties determination

Property	Unit	Method
Density at 20 °C	Kg/m <sup>3</sup>	ASTM D1298
Kinematic viscosity at 40 °C	mm <sup>2</sup> /s	ASTM D445
Acid value	mgKOH/g	AOCS Ca 5a-40
Iodine value (IV)	cg/g	AOCS Cd 1h-97
Saponification value (SV)	mg KOH/g	AOCS Cd 3-25
Cetane index (CI)	N/A	By calculation
Higher heating value (HHV)	MJ/kg	By calculation

The CI and the HHV were calculated using the mathematical relations shown in equations 1 and 2.

$$CI = 46.3 + \frac{5458}{SV} - \frac{0.225}{IV} \quad [29]$$

(1)

$$HHV = 49.43 - 0.041(SV) - 0.015(IV) \quad [30]$$

(2)

## 2.3. Spectroscopic characterization of samples

In order to obtain a recognizable absorption spectrum, the dilution and homogenization of the samples were measured and recorded from 300 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> on a spectrometer (model system 1000 FTIR, Perkin Elmer Co., USA) with a resolution of 2.0 cm<sup>-1</sup>.

## 2.4. Thermal characterization of samples

The TGA/DTG analyses were performed using a DTG 60AH simultaneous DTA-TG apparatus coupled with a TA-60WS thermal analyzer (Shimadzu). The sample weight was about 10 mg, a temperature range of 30 °C to 500 °C, a heating rate of 20 °C/min and a nitrogen flow rate of 50 cm<sup>3</sup>/min. The data were analyzed by using the TA-60 ch 1 DTG-60AH workstation

## 3. Results and Discussions

### 3.1. Effects on physicochemical properties

The density, kinematic viscosity, acid value, IV, SV, CI, and HHV of the samples are presented in Table 3. The density of the individual parent samples and the hybridized samples are within the same range, though the hybridized samples C, D and E presented slightly lower density than the samples A and B. The kinematic viscosity of the hybridized samples C, D, and E are marginally lower than those of samples A and B. The slight reduction recorded in the values of density and kinematic viscosity can be attributed to the effects of the physical mixing of the parent samples. This conforms with the outcomes of similar work reported in the literature [27, 28]. Rahman and Santhoshkumar [31] reported that the density of liquid does not only affected by mixing or blending but also by the temperature. They attributed the variation to the effect of the intermolecular interactions between mixing liquids. The acid value of the samples is not affected by hybridization while the saponification value of the hybridized samples C, D, and E were lower than that of the parent samples A and B. Hybridization lowers the iodine value of the samples when compared with the parent samples. CI and HHV are not affected by hybridization since mixing did not affect the heating capacity of the samples. Since hybridization of the samples took place at room temperature and no chemical reaction was witnessed, the variations in the physicochemical properties of the hybridized samples can only be traced to the effect of the mixing compared with the parent samples.

### 3.2. Effects on TGA

The outcomes of the TGA examination of the five samples are presented in Figure 3. The TGA plot compares the percentage weight loss of the two-parent WPO samples

with the three hybridized samples concerning the change in temperature. A temperature range of 30 °C to 500 °C was adopted for the five samples. The samples experienced single-stage thermal degradation which starts at around 330 °C for all the samples. With the test temperature differential, sample A, B, C, D, and E witnessed 13 %, 11 %, 10 %, 8 %, and 3 % weight loss, respectively. The thermal degradation commenced at between 320 °C to 330 °C for all the samples. The thermal degradation stopped at 450 °C for samples A, B, C, and D while that of sample E ended at 470 °C. Only the degradation curve for sample E dovetailed into the negative region of the curve. The commencement of the degradation temperature agrees with the outcome of our earlier work [26]. The high degradation temperature was due to the presence of several complex chemical compounds in the samples [32]. Waste cooking oil is susceptible to thermal decomposition at high temperatures as a result of the existence of unsaturated fatty acids which require low thermal energy to break [33-35].

### 3.3. Effects on DTG

The samples exhibited a similar trend of percentage derivative weight during the thermal degradation process. As shown in Figure 4, the thermal decomposition occurred between 350 °C and 500 °C with each curve presenting a single noticeable peak. The peak in the curves were observed as  $-0.06 \text{ \%m}^{-1}$  at 433 °C for sample A,  $-0.05 \text{ \%m}^{-1}$  at 430 °C for sample B,  $-0.11 \text{ \%m}^{-1}$  at 432 °C for sample C,  $-0.09 \text{ \%m}^{-1}$  at 422 °C for sample D, and  $-0.06 \text{ \%m}^{-1}$  at 430 °C for sample E. During the degradation process, sample C showed the greatest percentage derivative weight, followed by sample D and sample E in that order. This indicates that hybridization slightly influenced the derivative weight percentage and showed that hybridization can produce new sets of feedstocks different from the parent feedstock with the capability of positively influencing biodiesel conversion efficiency [36-38].

Table 3. Properties of the oil samples

samples	Density @ 20°C (Kg/m <sup>3</sup> )	Kinematic viscosity @ 40 °C (mm <sup>2</sup> /s)	Acid value (mgKOH/g)	Iodine value (cg/g)	Saponification value (mg KOH/g)	Cetane index	Higher heating value (MJ/kg)
A	9188.3	35	1.38	54.4	197.6	73.92	40.51
B	9171.2	34.2	0.97	74.4	199.9	74.30	40.32
C	9150.4	31.7	1.18	89.7	195.9	73.88	39.97
D	9161	30	1.09	92	193	74.58	40.14
E	9169.3	30.8	1.16	86	192	74.72	40.27

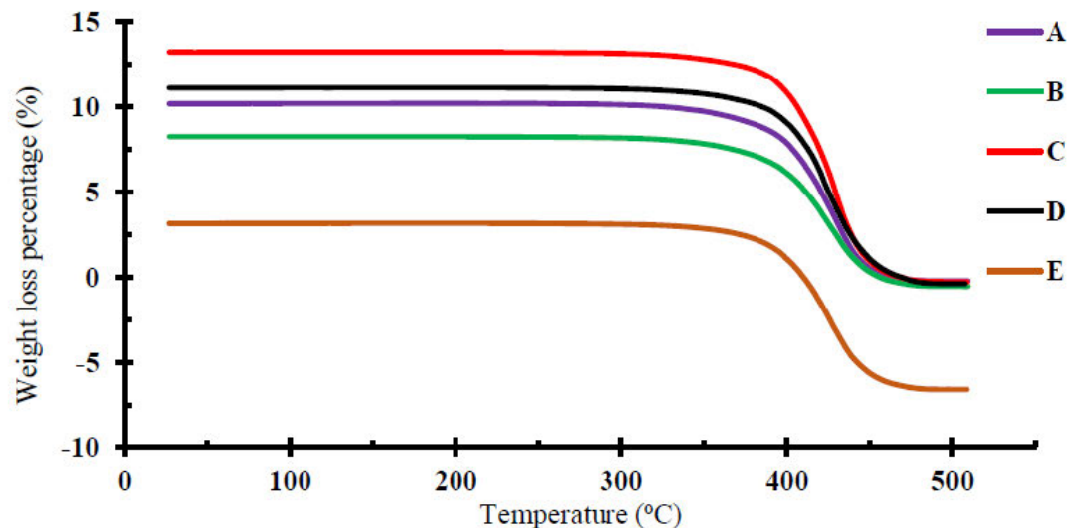


Figure 3. TGA curves for the samples



### 3.4. Effects on FTIR

The FTIR spectra depicting the functional groups of the five samples are shown in Figure 5. Four regions are identifiable with characteristics peaks in the IR spectrum. The four peculiar regions are distinguishable with characteristic peaks in the FTIR spectrum namely  $4000\text{ cm}^{-1}$  to  $2500\text{ cm}^{-1}$ ,  $2500\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$ ,  $2000\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$ , and  $1500\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  are present in the curves. These peaks could be assigned to (C-H) symmetrical, asymmetrical stretching of the saturated carbon carbon bond, C=O group of triglycerides, and stretching vibrations of the (C-O) esters group. However, the FTIR spectrum in the second region represented by  $2500\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$  is absent in the curves. This is in agreement with the outcome

of similar research as reported in the literature [39, 40]. The five samples have common significant and recognizable peaks at  $723\text{ cm}^{-1}$ ,  $1165\text{ cm}^{-1}$ ,  $1747\text{ cm}^{-1}$ ,  $2855\text{ cm}^{-1}$ , and  $2924\text{ cm}^{-1}$  indicating the existence of similar chemical groups in the compositions and similar fingerprints [41-43]. However, the parent samples A and B have peculiar peaks at  $1226\text{ cm}^{-1}$ ,  $1363\text{ cm}^{-1}$ , and  $1378\text{ cm}^{-1}$  that were found to either disappear or be minimized in the hybridized samples C, D, and E spectrum. The band  $1165\text{ cm}^{-1}$  shows the manifestation of methyl esters close to carbonyl groups. The vibration band noticed at  $723\text{ cm}^{-1}$  accounts for  $\nu(\text{C-H})$  and  $\nu(\text{-(CH}_2\text{)}_n\text{)}$  functionals. The type of frequencies, functional group, and absorption intensity of the wave numbers noticed in the spectrum are presented in Table 4.

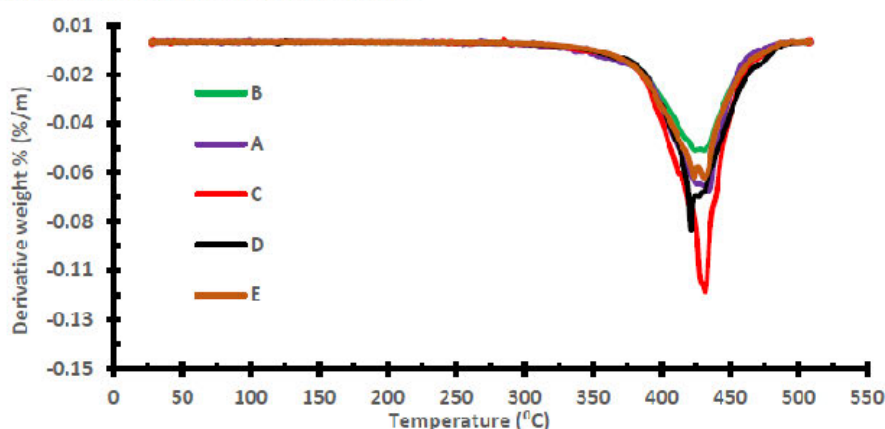


Figure 4. DTG curves for the samples

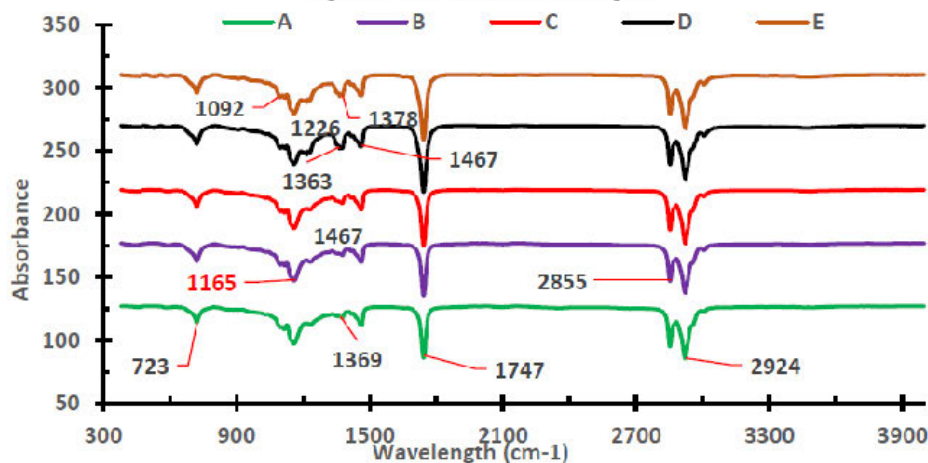


Figure 5. FTIR spectra of the samples

Table 4. Description of the peaks of the spectrum of the samples

Wave number ( $\text{cm}^{-1}$ )	Types of vibration	Functional group	Absorption intensity	Ref
2924	Asymmetrical stretching	C-H of alkanes	Middling	[44]
2855	Asymmetrical stretching	C-H of methylene	Strong	[44]
1747	Stretching	C=O ester band	Strong	[45]
1378	Bending in plane	-C-H(CH <sub>3</sub> )	Weak	[46]
1363	Bending	CH <sub>2</sub>	Weak	[47]
1165	Stretching, Bending	-C-O, -CH <sub>2</sub> -	Strong	[46]
723	Bending	-C-H and -(CH <sub>2</sub> ) <sub>n</sub>	Weak	[48]

#### 4. Results in Comparison with previous findings

Availability, ease of conversion to biodiesel, and the desire to find an affordable feedstock for biofuel production have triggered interest of researchers in WCO. Among the properties investigated are density, viscosity, saponification value, acid value, fatty acid composition, and iodine value. Table 5 showed outcomes of some of the investigations as published by various authors. When compared with the outcome of this research as shown in Table 3, it can be shown that the properties of WCO are largely dependent on factors such as source of the oil, degree of usage, frying temperature, food used to fry, and hybridization [27, 49].

The Muppaneni et al.[53], Almazrouei et al.[54], Ullah et al.[52], and Çaylı and Küsefoğlu [55] reported that WCO witnessed one stage thermal degradation. The TGA thermographs showed that thermal decomposition commenced at between 350 °C and 400 °C and were completely decomposed at temperature between 450 °C and 500 °C. This agrees with the outcome of this research. The shapes of the TGA curves were similar to the one shown in Figure 3. The authors attributed the slow thermal degradation of WCO to the high viscosity and molecular tension produced by bulky triglyceride molecule in the oil samples.

The outcome of the DTG characterization as reported by researchers showed that WCO witnessed derivative weight lost at between 350 °C and 500 °C with the peak weight loss of 38.76 % at 414 °C [55]. The thermal and spectroscopic properties of WCO are affected by source of the neat oil, degree of usage, frequency of usage, food items the oil was used to fry.

The outcome of the FTIR characterization by Ullah et al. showed peak vibrations at 2920.30 cm<sup>-1</sup>, 2851.9 cm<sup>-1</sup>, and 1743.1 cm<sup>-1</sup> which are assigned to (C-H) symmetrical, asymmetrical stretching of the saturated carbon-carbon bond, and (C=O) group of triglycerides respectively. A small band at 1656.69 cm<sup>-1</sup> resulting from cis C=C bond. The Bands at 1463.79 cm<sup>-1</sup> resulting from the bending vibrations of CH<sub>2</sub> and CH<sub>3</sub> aliphatic groups were also noticed. Other bands noticed at 1157.19 cm<sup>-1</sup> and 1116.87 cm<sup>-1</sup> could be attributed to the stretching vibrations of the (C-O) esters group. These and other similar peaks exhibited by the samples at 2924 cm<sup>-1</sup>, 2855 cm<sup>-1</sup>, 1747 cm<sup>-1</sup>, 1467 cm<sup>-1</sup>, 1363 cm<sup>-1</sup>, 1167 cm<sup>-1</sup>, and 723 cm<sup>-1</sup> as shown in Figure 5 and described in Table 5. However, to the best of authors knowledge, the effects of hybridization of WCO on TGA, DTG, and FTIR have not been reported.

#### 5. Conclusion

The outcome of the effects of the hybridization of feedstock on the physicochemical properties, thermal characterization, and infrared spectroscopy has been

presented. Hybridization is one of the novel ways of improving the quality of feedstocks. Hybridization of feedstock creates an entirely new feedstock from the existing feedstock with better properties and behavior regarding biodiesel generation. A hybridized feedstock is expected to combine the properties and peculiarities of the parent feedstocks by mixing the parent feedstocks in each ratio. In this research, two samples of WPO were mixed in different ratios and a total of five samples were analyzed by property determination and characterization by TGA/DTG and FTIR. The results of the parent samples were compared with that of the hybridized samples. From the outcome of this research, it is possible to conclude as follows:

1. Apart from the effects of oil source, degree of usage, the food the oil was used to fry, contamination, the frying frequency, the frying temperature, etc on the properties, thermal and spectroscopic properties of WCO, hybridization has a major influence on the physicochemical properties and the characterization behaviour of WCO.
2. Hybridization has no significant effect on the acid value, cetane index, and HHV of the feedstock. However, the density, kinematic viscosity, and saponification value was found to reduce with hybridization while the iodine value of the hybridized feedstock was found to be higher than the iodine value of the individual parent feedstock.
3. TGA and DTG of feedstock are affected by the hybridization of feedstock. The rate of thermal decomposition increases with the mixing of feedstocks, though all the samples witnessed single-stage thermal degradation. The TGA and DTG of both the parent and the hybridized samples occurred within the same temperature range.
4. The FTIR of the parent WPO samples were slightly different from the FTIR of the hybridized samples. Though the five samples A, B, C, D, and E presented similar peaks, the parent samples A and B showed peculiar peaks at 1226 cm<sup>-1</sup>, 1363 cm<sup>-1</sup>, and 1378 cm<sup>-1</sup> which were not noticeable in the spectrum of the hybridized samples.
5. Hybridization of feedstock provides an easy, cheap, and novel way of improving the properties, thermal decomposition, and infrared spectroscopy of feedstocks thereby improving their conversion efficiency to biodiesel.

Going forward, more investigations are needed in in-situ hybridization particularly in mixing more than two different feedstocks at different mixing ratio of feedstocks, more property determination, and characterization techniques. The effects of hybridization of feedstocks on the conversion efficiency, biodiesel fingerprints, combustion, performance and emission characteristics of biodiesel needs to be quantitatively ascertained.

Table 5. Some properties of WCO mined from literature.

Properties	Unit	[49]	[49]	[50]	[51]	[52]
Density	Kg/m <sup>3</sup>	904.3	913.4	870	910 – 924	901.3
Kinematic viscosity@ 40 °C	mm <sup>2</sup> /s	44.25	38.41	5.03	36.4 – 42	44.956
Saponification value	mgKOH/g	NA	NA	NA	188.2 – 207	177.97
Acid value	mgKOH/g	0.66	1.13	0.29	1.32 – 3.6	4.03
Iodine number	cg/g	81.7	54.2	NA	83 – 141.5	NA



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## CHAPTER 5: DEVELOPMENT AND CHARACTERIZATION OF COAL FLY ASH REINFORCED WITH SILICA OXIDE FOR CATALYTIC GREEN DIESEL PRODUCTION

This chapter focuses on the development and characterization of coal fly ash reinforced with silica oxide for catalytic green diesel production. In the article, coal fly ash collected from Eskom was pulverized, and reinforced to produce a silica oxide catalyst. This was characterized by TGA, DSC, TEM, FTIR. The analysis was done to investigate the suitability of the waste received from Eskom combined with silica oxide as a potential catalyst for HDRD production.

Importance of TGA;

- TGA help to analyse the reaction of a feedstock and biowaste catalyst at elevated temperature.
- The outcome of TGA result depend on the selectivity of the catalyst for hydrogenation.
- Analysis of the sample can be done at different temperature.

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## DEVELOPMENT AND CHARACTERIZATION OF COAL FLY ASH REINFORCED WITH SILICA OXIDE FOR CATALYTIC GREEN DIESEL PRODUCTION

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### ABSTRACT

*The prohibitive cost of commercial catalysts has inhibited the production and utilization of biofuel as a reliable alternative to fossil-based fuel. Researchers have suggested the conversion and development of wastes as a panacea for this challenge. Towards this end, this study investigated the effects of silica oxide ( $\text{SiO}_2$ ) as support for coal fly ash (CFA) as a heterogeneous catalyst for green diesel production was investigated. CFA, sourced from a power plant, was pulverized and developed into a fine powder while  $\text{SiO}_2$  was obtained from a commercial supplier. Three samples, namely CFA, commercial  $\text{SiO}_2$ , and CFA reinforced with  $\text{SiO}_2$ , were subjected to thermal, spectroscopic, Brunauer-Emmett-Teller (BET), and X-ray diffraction characterization processes. The results showed that CFA reinforced with  $\text{SiO}_2$  showed the most potential for catalytic applications as it attained thermal equilibrium at 700 °C and withstood temperatures as high as 950 °C without thermal degradation. The BET surface area, pore-volume, and micropore volume of CFA increased due to the addition of  $\text{SiO}_2$  to the CFA. Also, the spectroscopic analysis showed that the CFA sample reinforced with  $\text{SiO}_2$  showed distinctive peaks at 430  $\text{cm}^{-1}$ , 705  $\text{cm}^{-1}$  and 831  $\text{cm}^{-1}$  which revealed the presence of Al-O-Si and Si-O-Si bending vibrations, and (Si, Al)-O-(Si, Al) symmetric stretching. The percentage of quartz, mullite, and calcite in CFA increased from 33%, 11.78%, and 1% to 87%, 39% and 5% respectively in the  $\text{SiO}_2$  reinforced sample. Judging by the outcome of the characterization, reinforcing CFA with  $\text{SiO}_2$  has the capacity to improve its catalytic performance in green diesel production.*

**KEYWORDS:** Coal Fly Ash, Characterization, Heterogeneous Catalyst, Green Diesel, Silica Oxide

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### 1. INTRODUCTION

Research into alternative sources of energy to power the socio-economic activities of the modern world has gained traction over the past decades. The rapidly increasing demand for energy for various applications is attributed to increased socioeconomic activities and sustained industrialization across the world. The problem is exacerbated by other factors such as urbanization, modernization, and population growth which have led to increased consumption of fossil-based fuel [1]. Internal combustion engines (ICEs) in the form of passenger vehicles, off-road engines, earth moving equipment, agricultural machinery, etc. have continued to find inevitable applications in power generation, construction, and agricultural sectors. About 92 million automobiles were produced globally in 2019 as compared with about 62 million automobiles produced in 2009 [2]. Pollutants (compounds of carbon, nitrogen, sulfur, halogenated, etc., and other organic compounds such as hydrocarbons, polycyclic aromatic hydrocarbons, carboxy, etc.) are generated as effluents of fuel combustion in ICEs. These pollutants have harmful effects on public health, air quality, increase the atmospheric temperature, and are precursors for climate change as a result of the emission of greenhouse gases (GHGs) [3]. Carbon dioxide ( $\text{CO}_2$ ) comprises 74 % of GHG emissions with about 89 % of  $\text{CO}_2$  emissions emanating from fossil fuel consumption in lighting and heating, transportation, and industrialization. Methane, nitrous oxide, and fluorinated gases make up 17.3%, 6.2%, and 2.1% of total GHG emission from



agriculture, waste treatment and gas flaring and industrial processes, respectively[4].

The sectoral contribution of global GHG emissions shows that energy use in industry, buildings, and the transport sector contributed 24.2%, 17.5%, and 16.2% respectively as shown in Figure 1[4]. CO<sub>2</sub> is a product of the combustion of fuels in ICEs mainly from the transport sector. The Asia Pacific region is the largest emitter of CO<sub>2</sub> with over 17 billion metric tons of CO<sub>2</sub> in 2019 with North America, Europe, and Africa recording 5.98 billion metric tons of CO<sub>2</sub>, 4.1 billion metric tons of CO<sub>2</sub>, and 1.3 billion metric tons of CO<sub>2</sub>, respectively. The global consumption of fossil fuel increased from about 116 Terawatt-hour (TWh) in 2009 to above 129 TWh and 136 TWh in 2015 and 2019 respectively. Fig.2 shows the global CO<sub>2</sub> emission, by region, and the corresponding global fossil fuel consumption from 2009 to 2019. China contributed 28.8 % of the worldwide CO<sub>2</sub> emissions in 2019 and 11886.8 Mt CO<sub>2</sub>e representing 25.76% of total GHG emission.

Increased CO<sub>2</sub> emissions from ICEs contribute to an imbalance of the global carbon cycle with associated detrimental environmental, physical, and health impacts such as altering crop growth, prompting severe weather conditions, and increased sea levels[5]. The quest for cleaner, safer, and environmentally benign energy is also driven by the damaging effects of the exploration and utilization of fossil-based fuels. The use of renewable energy technologies like solar, wind, hydropower, biofuels, etc. is a strategy aimed at mitigating the effect of emission of GHGs and preserving the atmosphere for the coming generations.

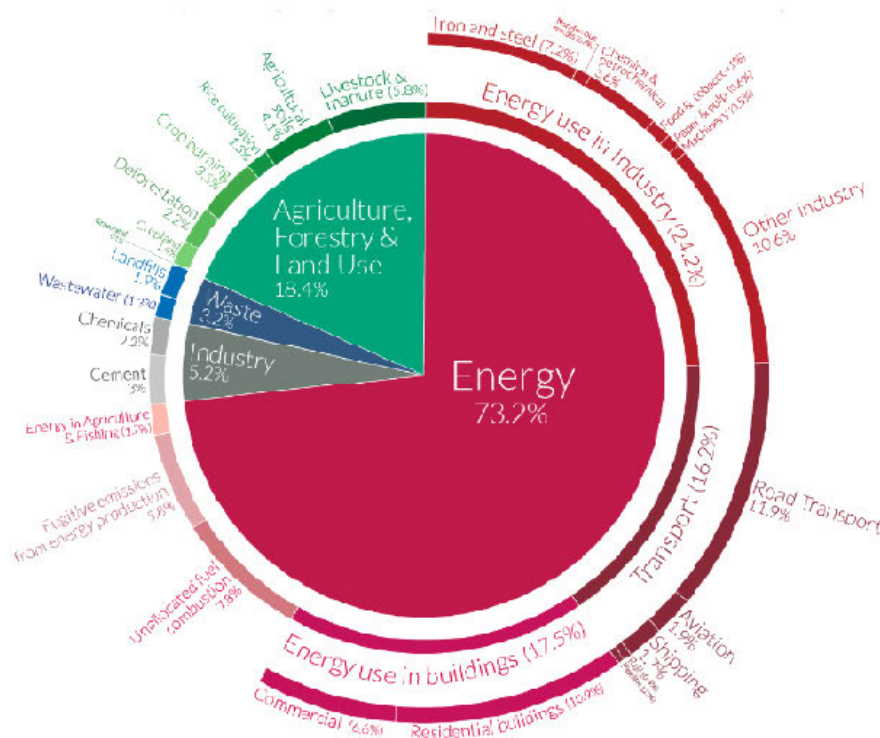
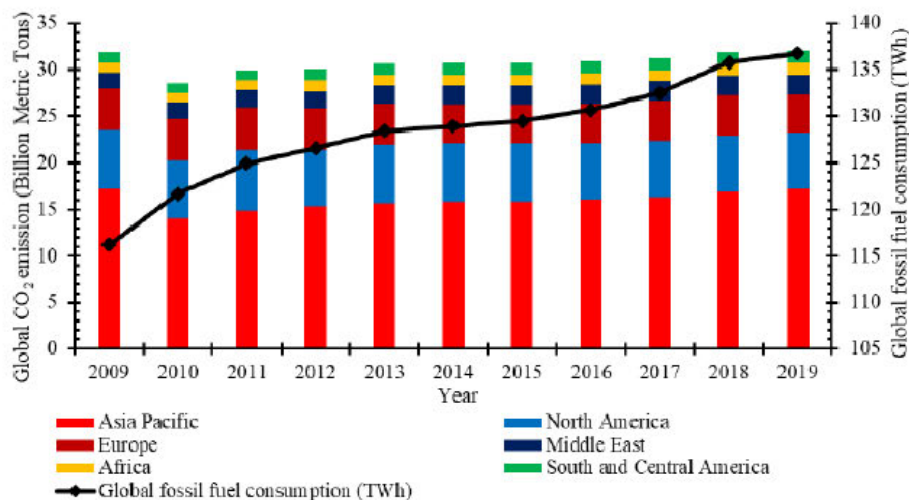


Figure 1: Global GHG Emissions by Sector in 2016[4].



**Figure 2: Global Fossil Fuel Consumption (TWh) and the Global CO<sub>2</sub> Emission, by Region (Billion Metric Tons) from 2009 to 2019.** Adapted from [5, 6]. Developed by the Authors.

The adaptation of biofuels (biogas, biomethane, hydrogen, biodiesel, green diesel, bioethanol, biosyngas, etc) to power IC engines has been identified as a panacea for unsatisfactory performance and injurious emissions emanating from IC engines fueled by fossil-based fuels. Green diesel, also known as renewable diesel, hydrotreated vegetable oil, hydrogenated derived renewable diesel of hydro processed esters, and fatty acids, is a second-generation liquid biofuel. While biodiesel is produced through transesterification, catalytic hydro processing or hydrogenation is the most popular route for producing green diesel from renewable biomass. Green diesel must be produced to meet the ASTM D975 and EN 590 specifications [7]. To ensure cost-effective and sustainable production of green diesel, efforts are being made to produce green diesel from wastes including used vegetable oils. Feedstock (harvesting, pre-processing, and transportation) accounts for between 70 % and 95 % of the total production costs of green diesel and biodiesel [8, 9]. Various wastes, including wood ash, coal fly ash, eggshell, and other agricultural wastes, have been adopted as possible catalysts for hydrogenation [10, 11]. The utilization of biomass-based wastes for catalytic hydrogenation offers many advantages [12, 13]: (1) proper disposal of waste, (2) utilization of waste thereby reducing the cost of waste disposal, (3) generation of additional revenue to companies by selling their waste to green diesel producers, and (4) reduction in the total cost of green diesel production.

### 1.1 Coal Fly Ash

Coal fly ash (CFA) is waste material and by-product generated when coal is burned for energy production in thermal power plants. CFA is a complex waste and consists of abundant anthropogenic compounds. Improper disposal of CFA pollutes water and soil, disrupts the ecological balance, and poses environmental risks. The global ash market is projected to become USD 6.86 billion by the year 2026 up from USD 4.13 billion in 2018 [14]. CFA has found applications in soil stabilization, gas absorbents, wastewater treatment, production of concrete, glass, and ceramics, and solid catalysts and catalyst reinforcements [14–16]. Physically, CFA is lightweight ash, spherically shaped solid particles with sizes varying from 0.5  $\mu\text{m}$  to 300  $\mu\text{m}$ . The constituents of CFA include silica dioxide, aluminum oxide, iron (III) oxide, calcium oxide (CaO), as well as some rare earth and trace elements [17]. Fig. 3 is a pictorial representation of the properties and applications of fly ash. Unutilized fly ash is inappropriately disposed into ash ponds, lagoons, or landfills causing huge



environmental hazards and costs. Eskom, a 100% South Africa-owned enterprise, consumes an average of 120 million tons of coal per year and generates 25 million tons of ash per year to produce 36 479 MW of electricity from its coal-fired stations. The majority of the over 17 000 tons of ash per day produced by Eskom are dumped at various disposal sites with grave environmental impacts. In recent times, a small fraction of the generated ash is being sold to be used for brick making, dam building, and as a cement extender [18].

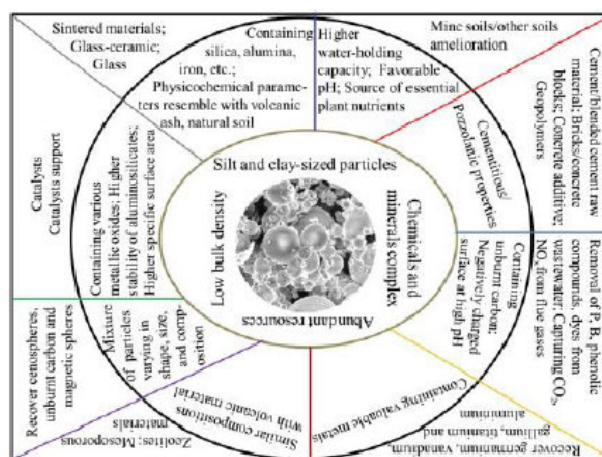


Figure 3: Properties and Applications of Fly Ash [15].

## 2. LITERATURE REVIEW

The utilization of waste as a solid catalyst for green diesel production has been investigated by various researchers with varying outcomes thereby necessitating further study. Various researchers, including Basumatary et al. [10], Hamza et al. [12], Abdullah et al. [13], Yao et al. [15], Blissett and Rowson [16], and Munoz et al. [19] have reported the application of biomass-based waste for the production of liquid biofuel. Stanković et al. [17], Yusup et al. [20], and Galadima and Muraza [21] have chronicled the various techniques, technologies, applications, advantages, and limitations of CFA as a catalyst for biofuel production. In most cases, CFA is modified and treated through calcination, impregnation, alkali fusion, coprecipitation, sulfonation, and hydrothermal process, ostensibly to improve its catalytic properties [17, 22, 23]. However, these modification and treatment processes constitute additional costs associated with the catalyst which increased the total production cost of the biofuel. Also, some of the modification techniques require the use of sophisticated equipment and highly skilled personnel, are time consuming, and operators are susceptible to accident. This has necessitated more research into the use of unmodified CFA as a catalyst.

Also, outcomes of recent literature searches by the authors revealed that though CFA has been used previously as a catalyst, especially for the synthesis of biodiesel, it has needed to be converted to other forms. Sikarwar et al. [24] applied a wet impregnation method to synthesize mesoporous silica from CFA while Manique et al. [25] and Shabani et al. [26] synthesized sodalite through a hydrothermal process to produce biodiesel. In other research, CFA was supported by CaO/zeolite-based catalyst obtained from waste chicken eggshell for biodiesel production [27]. The novelty of the current work is in the use of unmodified and unsupported CFA for hydrogenation of waste cooking oil to green diesel.

### 2.1 Motivation, Aim, and Scope

Despite the reported applications of waste as a possible solid biogenic catalyst for hydrogenation, the relevant questions to



ask which form the motivation for this work are: what are the effects of various forms of support that can improve the catalytic properties of CFA? What are the effects of  $\text{SiO}_2$  as potential support for coal ash? This study aims to develop and characterize CFA supported by  $\text{SiO}_2$  as a potential heterogeneous catalyst for green diesel production. The objective of this current investigation is to determine the effect of  $\text{SiO}_2$  as support for CFA's potential for catalytic hydrogenation, using characterization techniques. The motivation for the current study is to expand the frontiers of available information on the improvement of the application of CFA generated by Eskom and supported by  $\text{SiO}_2$  as a possible catalyst based on the outcome of characterization processes. This investigation is limited to the effects of the addition of  $\text{SiO}_2$  as support for CFA using characterization techniques. The CFA is used as received from Eskom without any modification or treatment except grinding and sieving.

### 3. MATERIALS AND METHODS

#### 3.1 Materials Collection and Sample Preparation

The CFA used for this research was supplied by Eskom from their Lethabo power generation plant, South Africa. The as-received CFA was ground into fine particles using a laboratory mechanical grinder and made to pass through a sieve  $< 50 \mu\text{m}$  mesh to ensure a uniform particle size. The sieved CFA was transferred into a clean, dry, and airtight glass vial, and designated as sample A.  $\text{SiO}_2$  (analytical grade) was procured from Lichro Chemical and Laboratory Supplies, South Africa. The as-received  $\text{SiO}_2$  was pulverized into fine particles using a laboratory mechanical grinder and sieved using a  $< 50 \mu\text{m}$  mesh. The fine  $\text{SiO}_2$  powder was transferred into a clean, dry, and airtight glass vial, and labeled as sample B. Part of samples A and B were thoroughly mixed in ratio 20:80 (sample A: sample B), and stored in a clean, dry, and airtight glass vial, and marked as sample C. The containers of the samples were kept in a cool environment to avoid contamination and oxidation.

#### 3.2 Sample Preparation

The samples were prepared according to the flowchart illustrated in Figure. 4 while Figure. 5 shows the picture of the three samples A, B, and C before they were transferred into an airtight glass vial.

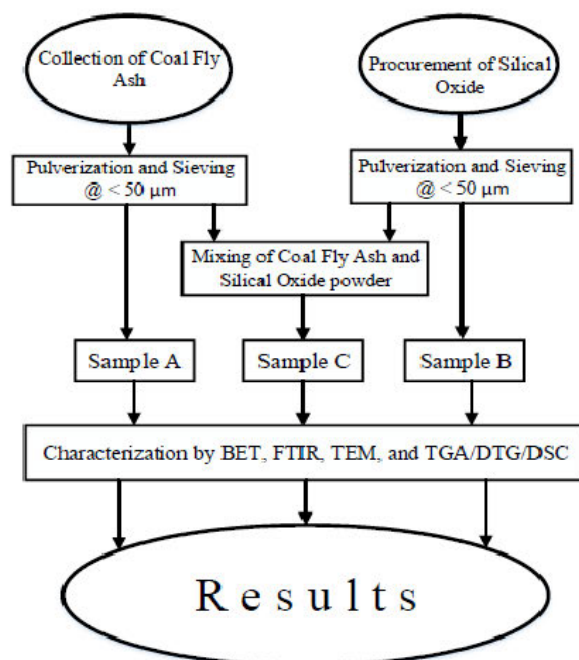


Figure 4: Flowchart of Sample Preparation.



Figure 5: Picture of Samples.

### 3.3 Methods of Characterization

The three samples (A, B, and C) were characterized by various techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal electron microscope (TEM), differential scanning calorimetry (DSC), and Brunauer-Emmett-Teller (BET).

#### 3.3.1 XRD Analysis

Measurements are performed using a multipurpose X-ray diffractometer D8-Advance from Bruker AXS (Germany) operated in a continuous  $\theta$ - $\theta$  scan in locked coupled mode with Cu-K $\alpha$  radiation. The sample was mounted in the centre of the sample holder on a glass slide and levelled up to the correct height. The measurements were run within a range in  $2\theta$  defined by the user with a typical step size of  $0.034^\circ$  in  $2\theta$ . A



position-sensitive detector, Lyn-Eye, was used to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter.

Data were background subtracted so that the phase analysis was carried out for a diffraction pattern with zero background after the selection of a set of possible elements from the periodic table. Phases were identified from the match of the calculated peaks with the measured ones until all phases had been identified within the limits of the resolution of the results. The outcome of the XRD analysis revealed the elemental composition of the samples and their suitability for catalytic hydrogenation.

### 3.3.2 Thermal Analysis

The thermal analysis of the three samples was analyzed by a DTG (DTG-60AH, Shimadzu) and TGA (TA-60WS, Shimadzu) thermal analyzer. About 10 mg of dry powder of each sample was weighed into an aluminum pan and scanned between the temperature range of 29°C to 1000 °C, the heating rate 10 °C/min, then held for 5 min at 1000 °C and under nitrogen atmosphere at a flow rate of 10 ml/min for simultaneous TGA, DTG, and DSC analysis. The data were analyzed using a TA-60 ch 1 DTG-60AH workstation. The outcome of the TGA provided insight into the thermal behavior of CFA and its appropriateness as a suitable catalyst for hydrogenation.

### 3.3.3 Spectroscopic Analysis

To obtain a recognizable absorption spectrum, further dilution and homogenization of the three dry powder samples with KBr (spectroscopic grade) was carried out with additional grinding and mixing in an agate mortar. Discs (12.7 mm ID and  $\approx 1$  mm thick) were prepared in a manual hydraulic press (model 15.011, Perkin Elmer Co., USA) at about 10 tonnes for a pressing time of 30 s to 60 s. The spectrum was measured and recorded from 300  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  on a spectrometer (model system 1000 FTIR, Perkin Elmer Co., USA) with a resolution of 2.0  $\text{cm}^{-1}$ . The suitability of CFA as a catalyst for the hydrogenation of waste cooking oil to green diesel was based on the location and the quality of the peaks from the sample spectra.

### 3.3.4 BET Characterization

The nitrogen sorption analysis of the samples was performed with a Micromeritics ASAP 2460 instrument. About 0.25 g of each sample was degassed at 100 °C under nitrogen gas overnight. Thereafter, they were allowed to cool under a vacuum to make their surfaces and pores available for probing. The surface area of the sample ( $\text{m}^2/\text{g}$ ) was computed by the Brunauer-Emmett-Teller (BET) method, while the pore size distributions like the total pore volume ( $\text{cm}^3/\text{g}$  at STP) and average pore radius ( $\text{\AA}$ ) were calculated using the Barrett-Joyner-Halenda (BJH) method. BET analysis revealed the surface area, pore-volume, and pore area which showed the catalytic activity of the CFA as a potential green catalyst for the synthesis of green diesel from waste cooking oil.

### 3.3.5 TEM Analysis

The samples were prepared on a Quorum Q150A ES sputtering machine before transferring to the Zeiss Ultra Plus in field emission gun scanning electron microscope (FEG-SEM) for morphology analysis of the powder sample. A JEOL JEM-2100 operating at an accelerating voltage of 20 kV was used for the high-resolution transmission electron microscopy (TEM) analysis. Necessary structural information of the CFA was revealed through TEM analysis which helped in the determination of CFA as a suitable green catalyst for the conversion of waste cooking oil to green diesel.



## 4. RESULTS AND DISCUSSIONS

### 4.1 BET Analysis

The data on the BET surface area, external surface area, average pore radius, pore-volume, micropore volume, and micropore area are shown in Table 1. The surface area, external surface area, and pore volume of unmodified CFA (sample A) were substantially increased by the addition of SiO<sub>2</sub> (sample B) from 0.5928 m<sup>2</sup>/g, 0.8611 m<sup>2</sup>/g, and 0.00532 cm<sup>3</sup>/g to 35.1102 m<sup>2</sup>/g, 32.5753 m<sup>2</sup>/g, and 0.1281 cm<sup>3</sup>/g respectively. The total pore volume of 0.1281 cm<sup>3</sup>/g fell within the 0.08 cm<sup>3</sup>/g to 0.3 cm<sup>3</sup>/g recorded when CFA was synthesized, modified with copper oxide, and converted to zeolites by hydrothermal activation, atmospheric crystallization, and double-stage fusion-hydrothermal for catalytic applications [28]. These increases were accompanied by a decrease in the average pore radius of sample A from 179.68 Å to 72.98 Å in sample C. This showed that the addition of SiO<sub>2</sub> caused a reduction in average pore radius in the mesoporous range as a result of impurities. However, there was an increase in the micropore volume of sample A from -0.000121 cm<sup>3</sup>/g to 0.000582 cm<sup>3</sup>/g in sample C. The surface area and average pore radius of sample C were higher than the 17.542 m<sup>2</sup>/g and 32.59 Å reported when raw CFA was impregnated by calcium metal and calcined at a temperature of 500 °C for 4 hours as reported by Arif et al. [29] and BET surface area of 9.028 m<sup>2</sup>/g and pore volume of 0.01055 cm<sup>3</sup>/g reported for biomass fly ash by Vargas et al. [30].

The increase in pore volume lends credence to the view that new mesopores can be formed not only by the activation process but also by the addition of supports [29, 31]. The BET surface area is an important physical property that determines the catalytic activity of a solid particle because a higher surface area is a precursor for better catalytic activity and more interactions with the reactants [25]. In this case, a high BET surface area of 35.1102 m<sup>2</sup>/g will aid a combination of SiO<sub>2</sub> and CFA's catalytic activity for the adsorption and desorption of molecules such as triglycerides, glycerin, and green diesel [30, 32]. The outcomes of the BET analysis of the samples are a testimony to their suitability as a low-cost and green catalyst for the conversion of waste cooking oil into green diesel by hydrogenation [33, 34].

Table 1: Textural Properties of the Samples.

Properties	Unit	Sample A	Sample B	Sample C
BET surface area	m <sup>2</sup> /g	0.5928	317.2404	35.1102
External surface area	m <sup>2</sup> /g	0.8611	279.1870	32.5753
Average pore radius	Å	179.68	70.72	72.98
Pore volume	cm <sup>3</sup> /g	0.005326	1.1218	0.1281
Micropore volume	cm <sup>3</sup> /g	-0.000121	0.014827	0.000852
Micropore area	m <sup>2</sup> /g	*NR	38.0533	2.5349
*NR=Not responding				

### 4.2 XRD Analysis

The XRD spectrometry plot for the samples is depicted in Fig.6 while Table 2 shows the description of the major constituents of the samples. The semi-quantitative mass composition shows that the percentage of quartz increased from 33.22 % in sample A to 87.67 % in sample C while the mullite increased from 11.78 % in sample A to 39.2 % in sample C. This is due to the addition of SiO<sub>2</sub> to sample A. The pattern shows that raw CFA is composed mainly of quartz (SiO<sub>2</sub>) and

mullite ( $\text{Al}_{4.4}\text{Si}_{1.209.6}$ ) minerals. The quartz's diffraction pattern is shown predominantly at around  $2\theta = 21^\circ$ ,  $26^\circ$ ,  $50^\circ$ , and  $68^\circ$  while the mullite diffraction peak is shown at  $2\theta = 16.5^\circ$ ,  $24^\circ$ ,  $41^\circ$ , and  $61^\circ$ . Though the XRD diffraction of sample B did not display any peak, it can be seen that the addition of sample B to sample A significantly altered the composition of sample C. The absence of peaks in sample B is due to the amorphous nature of the sample [35, 36]. As shown in Figure 7, sample C was composed mainly of quartz ( $\text{SiO}_2$ ), mullite ( $\text{Al}_{4.4}\text{Si}_{1.209.6}$ ), and a small percentage of calcite ( $\text{CaCO}_3$ ) minerals. The quartz peaks were detected at  $2\theta = 20.8^\circ$ ,  $26.5^\circ$ ,  $36.4^\circ$ ,  $50^\circ$ ,  $60^\circ$ , and  $68^\circ$ , and the mullite peaks were detected at around  $2\theta = 16.5^\circ$ ,  $26.2^\circ$ ,  $31^\circ$ ,  $33^\circ$ ,  $35.3^\circ$ ,  $40.8^\circ$ , and  $60.7^\circ$ . The only noticeable calcite peak was noticed at around  $2\theta = 29.3^\circ$ . Similar results were also reported by Sharma et al. [37], Ho et al. [38], Bhandari et al. [39], and Maneerung et al. [40]. These results show a high possibility of using sample C as a potential catalyst for the conversion of waste cooking oil to green diesel [25, 29, 30].

As shown in Table 2,  $\text{SiO}_2$  is the major constituent of the samples. Available information from the literature shows that the presence of  $\text{SiO}_2$  either as a base or support catalyst accelerates the hydrogenation process [41-43]. Though CFA has been largely used for the transesterification of waste cooking oil to biodiesel, the application of silica supported by CFA as the heterogeneous catalyst for the conversion of waste cooking oil to green diesel will be a productive and worthwhile venture.

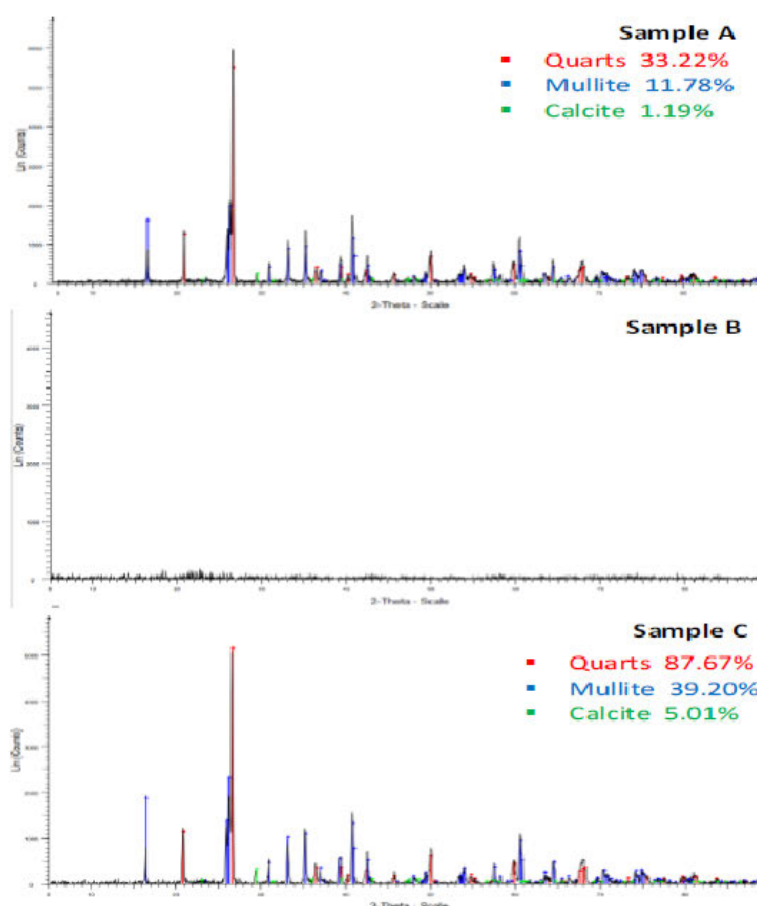


Figure 6: XRD Spectrometry for (a) Eskom CFA, (b)  $\text{SiO}_2$ , and (c) Eskom CFA +  $\text{SiO}_2$  Samples.



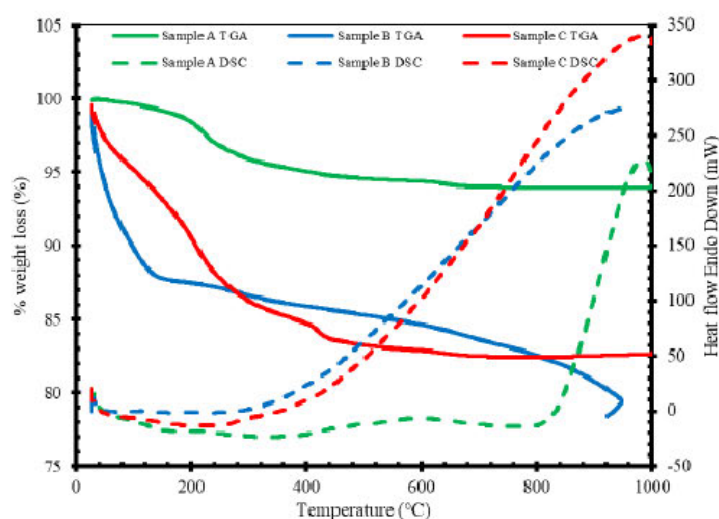
Table 2: Composition of the Major Constituents of the Samples

Compound Name	Chemical Formula	Lattice	Molecular Weight	Volume	Sample Composition (%)		
					A	B	C
Quartz	SiO <sub>2</sub>	Hexagonal	60.08	113.59	33.22	N/A	87.67
Mullite	Al <sub>4</sub> Si	Hexagonal	132.02	49.71	11.78	N/A	39.2
Calcite	CaCO <sub>3</sub>	Rhombohedral	100.09	367.78	1.19	N/A	5.01

### 4.3 Thermal Analyses

The outcome of the thermal analyses of the samples is reported under TGA and DSC. The TGA of the samples is shown in Figure 7 which has been plotted with the temperature range of 30 °C to 1000 °C to ascertain the percentage weight loss concerning temperature using nitrogen as the heating medium. Sample A lost about 2 % of its weight between 30 °C and 220 °C with no further thermal degradation. On the other hand, sample B witnessed 13 % weight loss between 30 °C and 140 °C, and the weight loss became slower until 950 °C. From 30 °C to 250 °C, sample C witnessed about 15 % weight loss and another 5 % weight loss between 250 °C and 650 °C. Sample C effectively achieved thermal equilibrium with no further weight loss at 700 °C. This shows the high thermal stability of sample C, a property believed to be inherited from the CFA (sample A). This conforms to the pattern reported by Kumar et al. [44]. As shown in Table 2, the composition of calcite (CaCO<sub>3</sub>) which is an unstable compound in the sample, is low, indicating that weight loss during the thermal degradation is minimal. This indicates that the CFA is thermally stable and can be relied upon to be stable in the high temperatures needed during hydrogenation [45].

The DSC curve of the samples is shown in Fig. 7 revealing the distinction in the heat content of the samples concerning temperature. This provided information on phase transition parameters like crystallization point, melting point, the heat of reaction, and thermal stability of samples [46]. From the curves, sample A witnessed rapid heat input between 820 °C and 930 °C. However, the addition of SiO<sub>2</sub> to CFA caused sample C to behave differently and show a more uniform differential heat addition, higher than sample B.

Figure 7: TGA and DSC Curves for (a) Eskom CFA, (b) SiO<sub>2</sub>, and (c) Eskom CFA + SiO<sub>2</sub> Samples.



#### 4.4 Spectroscopic Analysis

The FTIR spectra of the samples are shown in Fig. 8. The results show that the samples have major absorption bands at the same wavelength. This is due to the effect of the addition of the  $\text{SiO}_2$  to sample A to form sample C. For the CFA, it can be seen that the absorption at a wavelength of  $3754\text{ cm}^{-1}$  is characteristic of rhombohedral OH stretching. The major absorption band at  $1054\text{ cm}^{-1}$  noticed in sample B is similar to that observed by Maneerung et al. [40] and Sharma et al. [37] which they ascribed to the presence of  $\text{SiO}_2$  which is not prominent in sample C. The existence of the absorption sharp band at  $3745\text{ cm}^{-1}$  which is ascribed to the -OH band, was detected in the CFA catalyst; this band agrees with the presence of  $\text{CaCO}_3$  in sample A but is unnoticeable in sample C, as determined by XRD (Table 2), which is a proof of the effect of the addition of  $\text{SiO}_2$  support. This matches with the result described by Boey et al. [47]. The presence of a major absorption band at wavelength  $1054\text{ cm}^{-1}$  is attributed to the asymmetric O-Si-O while the wavelength at  $451\text{ cm}^{-1}$  in sample B has moved to  $429\text{ cm}^{-1}$  in sample C. The peak shown by sample C at  $\sim 430\text{ cm}^{-1}$  characterizes the Al-O-Si and Si-O-Si bending vibrations. The distinctive peaks at  $705\text{ cm}^{-1}$  and  $831\text{ cm}^{-1}$  are due to the (Si, Al)-O-(Si, Al) symmetric stretching [48]. Also, the wide peak at  $1011\text{ cm}^{-1}$  can be ascribed to the (Si, Al)-O-(Si, Al) asymmetric transmission stretch. The absorption recorded by sample C falls within that reported by Arif et al. [29] who compared raw CFA with modified CFA. Going by the outcomes of the FTIR analysis, CFA supported by  $\text{SiO}_2$  is a good catalyst for hydrogenation. The peaks at around wavelength  $1010\text{ cm}^{-1}$  and  $1420\text{ cm}^{-1}$  are characteristic of the peculiar bands for tested hydrogenation catalysts [49, 50].

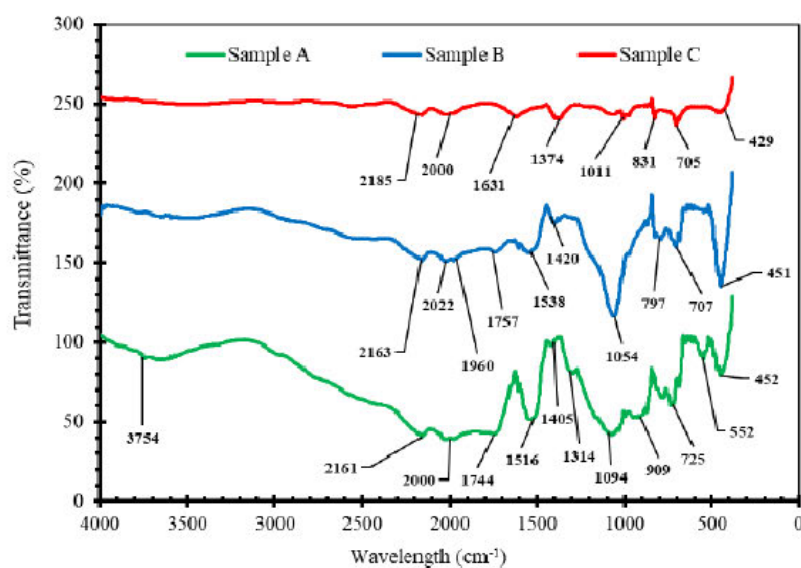


Figure 8: FTIR Spectra for (a) Eskom CFA, (b)  $\text{SiO}_2$ , and (c) Eskom CFA +  $\text{SiO}_2$  Samples.

#### 4.5 TEM Analysis

The TEM micrographs showing the structural information of the samples are shown in Figure.9. The mesostructure is detectable in the TEM pictures of the samples confirming that active metals are homogeneously filled and dispersed within the mesoporous structure [51]. The nano size, structural dimension, and active components of the CFA and its support provided effective surfaces capable of enhancing the samples' catalytic efficacy during the hydrogenation of triglyceride, irrespective of the FFAs present in the oil. Sample C has more pores, a regular surface structure, and hexagonal-shaped particles which reflects the presence of a high percentage of  $\text{SiO}_2$  when compared with samples A and

B. The TEM micrographs confirm the results of the XRD analysis that sample C has the capacity to effectively catalyze triglycerides to green diesel. This agrees with the outcomes of a similar sample as reported by Kumar et al. [44].

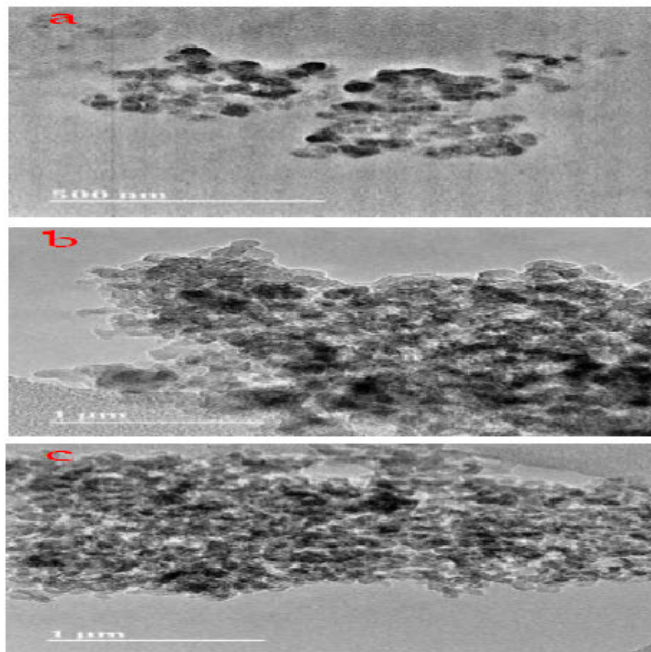


Figure 9: TEM Images for (a) Eskom CFA, (b) SiO<sub>2</sub>, and (c) Eskom CFA + SiO<sub>2</sub> Samples.

## 5. CONCLUSIONS

CFA is a waste generated from power plants. There is increased interest in the application of CFA as a green, eco-friendly, readily available, and low-cost heterogeneous catalyst as a replacement for expensive commercial catalysts. In this research, the effect of SiO<sub>2</sub> as support for CFA obtained from South African's Eskom plant was studied. The Eskom CFA (sample A), SiO<sub>2</sub> (sample B), and CFA reinforced with 20% SiO<sub>2</sub> (sample C), were characterized by thermal, spectroscopic, XRD, BET, and TEM analyses. The outcome of the characterization processes are as follows:

- The result of the XRD analysis revealed that the percentage of quartz, mullite, and calcite in sample A increased from 33%, 11.78%, and 1% to 87%, 39%, and 5% respectively in sample C, due to the SiO<sub>2</sub> reinforcement.
- The BET surface area, external surface area, pore-volume, and micropore volume of CFA increased with the addition of SiO<sub>2</sub> while the average pore radius decreased with the addition of SiO<sub>2</sub>. These are attributed to the effect of the reinforcement by the SiO<sub>2</sub> which has been discovered to have a high surface area.
- The TEM result revealed that the CFA sample reinforced with SiO<sub>2</sub> possessed more pores, a regular surface structure, and a hexagonal-shaped particle compared to CFA without reinforcement.
- The sharp absorption band at 3745 cm<sup>-1</sup> noticed in sample A during spectroscopic characterization was erased in sample C. The distinctive peaks at 430 cm<sup>-1</sup>, 705 cm<sup>-1</sup>, and 831 cm<sup>-1</sup> symbolize the presence of Al-O-Si and Si-O-Si bending vibrations, and (Si, Al)-O-(Si, Al) symmetric stretching. This makes sample C appear to be a better heterogeneous catalyst candidate than sample A for hydrogenation purposes.



- The thermal characterization processes (TGA and DSC) revealed that sample C is more thermally stable and can withstand the high temperature needed for green diesel production without degradation. This can be attributed to the high temperature involved in the generation of CFA.

It is therefore safe to conclude that the addition of  $\text{SiO}_2$  to CFA has improved its thermal, spectroscopic, composition, and surface area of the powder. This has increased its potential as a viable catalyst for green diesel production.

Going forward, more investigations are required to find the optimal mixing ratio between CFA and  $\text{SiO}_2$  for green diesel production. Also, the effects of other reinforcements like alumina, CaO, etc. on CFA need to be investigated. The use of CFA as a catalyst will drastically reduce the cost of catalysts in biofuel production, providing a means of converting waste to use chemicals and a pathway for sustainable utilization of CFA as a contribution towards achieving energy security.

**Conflict of Interest:** No conflict of interest.

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## CHAPTER 6: A STUDY TO EVALUATE OPTIMAL CATALYST PROPERTIES SOURCED FROM BIOWASTE FOR HYDROPROCESSING OF USED COOKING OIL INTO GREEN DIESEL

This article reported on the evaluation of optimal catalyst properties sourced from waste for hydro-processing of UCO into green diesel. The addition of calcinated BBTPPFS with calcium oxide, alumina, and silica oxide catalysts in varying proportions was characterized by using BET, TGA, DSC, SEM, FT-IR, TEM to study the optimal properties of the sample to investigate which one possesses the potential to mild crack UCO into the green diesel range. Commercialization of HDRD is possible with the discovery of locally sourced feedstock and catalyst for hydrogenation.

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## A STUDY TO EVALUATE OPTIMAL CATALYST PROPERTIES SOURCED FROM BIOWASTE FOR HYDRO PROCESSING OF USED COOKING OIL INTO GREEN DIESEL.

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### ABSTRACT

*The need for alternative fuels to replace fossil-based fuels has been given more attention by various stakeholders. Commercial catalysts are a major component required for hydro processing of vegetable oil into hydrocarbon. However, the high cost of commercial catalysts hinders the commercialization of green diesel. This research work investigates the viability of biowaste fly ash collected from Eskom with supports like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO. These three support catalysts and BBTPPFS were pulverized, calcinated, and subjected to Brunauer-Emmett-Teller, thermal, spectroscopic, scanning electron microscope. A significant increase in the value of catalytic properties was noticed when 60 g BBTPPFS (sample D) was reinforced by adding 40 g of SiO<sub>2</sub> (Sample A) to obtain sample A1. The value of the micropore volume of -0.0001 cm<sup>3</sup> increased to 0.0014 cm<sup>3</sup>, and the surface area(external) increased from 0.8611 to 41.2571 m<sup>2</sup>/g, total surface area 0.5928 to 45.2771 m<sup>2</sup>/g and pore volume of 0.0053 increased to 0.1564 cm<sup>3</sup>/g. This combination showed properties that reveal it to be a potential green catalyst for hydrogenation and capable of mild cracking to achieve a green diesel range of C15-C18.*

**KEYWORDS:** HDRD, BBTPPFS, Heterogeneous Catalyst, Used Cooking Oil & Hydrogenation

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### 1.0 INTRODUCTION

The sustained increase in demand for renewable energy across the globe has challenged researchers to develop and implement technologies for processing vegetable oils (edible and inedible) and animal fats into green diesel. The increase in energy demand can be traced to increased socioeconomic activities, industrialization, urbanization, modernization, and population growth [1]. The resulting increase in greenhouse gases (GHGs), and the depletion of fossil-based oil, has triggered the opinion for the search for alternative fuels that offer a pollution free environment and are sustainable. In recent years, the stakeholders have paid much attention to an effort to reduce the atmospheric temperature with policies to curb the effect, the members of legislative body otherwise known as the lawmakers have targeted pollution generated by automobile as major contributor to the GHGs which is one area to pay attention to. Despite the effort of the governments to offer a permanent solution to the threat posed by non-renewable energy and, depletion of oil reserves, the challenge is still on the increase and has attracted the attention of stakeholders globally.

Hydrogenation-derived renewable diesel (HDRD), otherwise known as green diesel has emerged as the only feasible and sustainable automobile fuel. Hence, the pressing need for a transportation fuel that is suitable for a compression ignition engine without modifications. Therefore, more research is required by the scholars to

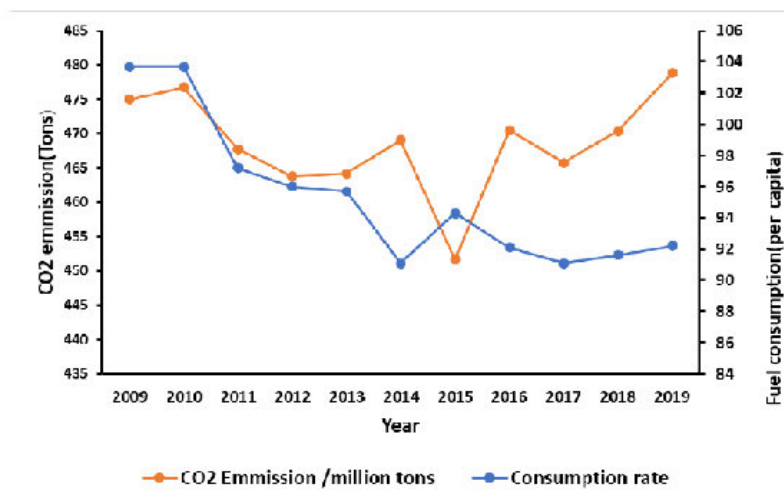
investigate the resource availability to produce H2RD that can will offer zero carbon to the environment. The tailpipe emissions generated by trucks and stationary engines are the major contributor to GHGs. Transportation sector is the second largest source to global warming [2]. About 92 million automobiles were produced globally in 2019 compared with about 56 million automobiles produced in 2001 [3]. Environmental Protection Agency (EPA), United States reported, carbon IV oxide (CO<sub>2</sub>) gases increased by 9 %, Methane emission decreased by 6% between 1990 and 2014. About 20 % of carbon dioxide discharged to the environment can be traced to daily activities such as transport-related emissions, which will continue to rise in the future [4].

Thermal power plants stations are set up to convert heat energy to electrical energy to meet the energy demands of society [5]. The waste generated from a power plant is usually referred to as coal ash, this is the end product of the burning of coals; the highest percentage is fly ash, while the coarse materials that settle at the base of the heating chamber are known as base or bottom ash. The fly ash product generated from burning any form of agricultural waste is known as Bio-Based Thermal Power Plant fly ash [6]. Elemental composition of bio-based ash is determined by the source of biomass and combustion technology. Therefore, BBTPFSs are different from coal ash in terms of their chemistry and mineralogy [7].

Several researchers have investigated and reported the adaptation of catalysts sourced from waste such as eggshell, mud shell, and soda-lime as being active catalysts for decarboxylation [8]. The motivation of the current research work is the addition of CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> to BBTPFS to obtain a mixture that possesses optimal catalytic properties that can adequately mild crack used cooking oil (UCO) into the green diesel range. This study focuses on the evaluation of the optimal catalyst properties for hydrogenation. This research is set to determine the effect of calcinated support catalysts with freshly prepared BBTPFS heterogeneous catalysts, in order to characterize and evaluate the optimal properties for hydrogenation purposes. The scope of this study was to admixure a catalyst and its support, calcinate, and characterize the effect on the hydroprocessing of UCO.

Compression ignition (CI) engines in metro vehicles, stationary engines, agricultural machinery, etc. are the mainstay in power generation, transportation, and agriculture sectors. Carbon dioxide (CO<sub>2</sub>) comprises 74 % of GHG emissions, with about 89 % of CO<sub>2</sub> emissions emanating from fossil fuel consumption in lighting, heating, transportation, and industrialization. Methane, nitrous oxide, and fluorinated gases make up 17.3 %, 6.2 %, and 2.1 % of total GHG emissions from agriculture, waste treatment, and industrial processes, respectively [9]. Figure 1 shows the consumption rate and CO<sub>2</sub> emission in South Africa from 2009 to 2019. From this figure, it is evident that the consumption rate drops between 2015 to 2018 and rose in 2019, but there is a steady increment in the emission per million tons.





**Figure 1: Fuel Consumption (per capita) and CO2 Emission (tons) in South Africa from 2009 to 2019 [10].**

Catalytic hydro processing of vegetable oils for converting low-grade oils into HDRD has continued to attract more attention in recent years [11]. Utilization of biowaste catalysts for renewable diesel production has become more significant especially when it is generated or derived from waste materials [12]. The selection of a suitable catalyst offers good product with better properties; hence, selecting an appropriate catalyst for hydroprocessing purposes becomes a challenge. Hence, the need to critically study and evaluate the right catalyst that contains the properties suitable for the production of HDRD. The primary objective of catalyst activities in hydro-processing of a feedstock is to ensure adequate triglyceride conversion to a high quality and high yield of biofuel products by lowering the activation energy [13].

In South Africa, about 109 tons of coal is used per year by Eskom power stations, and about 25 million tons of ash is generated. However, 1.2 tons of coal fly ash are supplied to Lafarge for chemical additives in the cement industry. The bottom ash is a fine spherical particle, which has high pozzolanic activity (or reactivity), with unusually high consistency. Apart from the benefit of high quality and concrete economy fly ash also serve as a material for brick making and dam building. The construction of Katse Dam project received a supply of 250 000 tons of coal ash from Lethabo Power Station (LPS). In India, 90 metric tons of fly ash is generated per year and only 3% is used, while Germany used 80% of the coal fly ash product [14]. In most of the BBTPFS thermal power plant producing industries, the method of disposal adopted is either landfill without any restriction [8]. Waste generated and accumulated in an open space causes significant pollution in the environment that can impose health challenges in the geographical area. Indiscriminate disposal of waste products has a significant negative effect on underground water, then the land space occupied inhibits the use of large surface areas for other purposes. Solid waste produced by thermal power plants can be harnessed and used as a green catalyst that will significantly reduce the total cost of production of biofuel. As stated, BBTPFS is also usable by cement production companies [15, 16]. The volume of BBTPFS generation is increasing globally, which also increase the cost of waste management. In South Africa, this waste can be harness as potentials green catalyst resources [17]. The sulfur content in BBTPFS is lower, because is generated from biomass that has low sulfur content. In addition, this will further reduce GHGs effect caused by combustion of petroleum oil [18].

The properties and ionic composition of a catalyst greatly affect the hydro-processing of green diesel. Samples morphological of a catalyst was characterized using a transmission electron microscope (TEM) and a scanning electron microscope (SEM-EDS) from a single nanometric range to 500 nanometres. The structural dimension, molecular size, and the components of a catalyst provide enhance their activity during hydro processing. Brunauer-Emmett-Teller analysis provides information on surface area using a nitrogen adsorption/desorption analyser, while thermo-gravimetric analyser (TGA) examined the thermal stability of the catalysts.

Catalyst samples that have been applied in the production of biofuel as reported in the literature are nickel, columbium, and molybdenum. The active metals are mostly reinforced with aluminium oxide/silica dioxide [19]. Also, Columbium molybdenum, nickel catalysts and alumina ( $\gamma\text{-Al}_2\text{O}_3$ ) are frequently used for hydro carboxylation, hydrodeoxygenation, and hydrogenation which are also good desulphurization catalysts [20]. Catalyst is to break the bonds and activate the route of C-C and C-O bond cleavage [21, 22]. However, any of the catalysts can be used for the activities, eg Ni-Mo/( $\gamma\text{-Al}_2\text{O}_3$ ) [22], Co-Mo [23], and CoMo/Si ( $\gamma\text{-Al}_2\text{O}_3$ ) [21]. The choice of hydro-processing route, reaction mechanism, and process parameter required will influence the selection of catalyst. [24]. Removal of oxygen from HDRD products during hydrogenation requires an appropriate selection of a catalyst to control the process of oxygen removal [25].

Varieties of commercial catalysts can be used for hydrogenation using vegetable oil or animal fats as a feedstock to obtain hydrocarbon products. The best route that offers optimal yield and high-quality biofuel product is hydro processing technology. Hydrodeoxygenation (HDO) and hydro isomerization routes are engaged to produce long-chain paraffins. The choice of route and catalyst suggests the yield and quality of HDRD. The objectives of this research work were to carry out a study to evaluate optimal catalyst properties for hydroprocessing of UCO with the aim of obtaining high quality green diesel. However, this poses the research question of which catalyst is suitable for conversion of UCO to HDRD, and how to identify the choice of catalyst/support structure that is capable of converting UCO into HDRD.

Musa balbisiana Colla underground stem (MBCUS), a nanomaterial, and a BBTPFS was used as a catalyst for hydro processing of *Jatropha curcas* oil and FFA *Mesua ferrea* L. and *Jatropha curcas* oil [26]. The conversion rate showed BBTPPFS as the best catalyst that has the capacity to upgrade vegetable oil to an optimal yield than MBCUS. The catalyst potentials for upgrading vegetable oils to biofuel depend on the following properties among others: coking deactivation, resistance to water, and high deoxygenation activity [27]. These properties are found in BBTPPFS.

In this study, the catalysts underwent the following characterization: TGA, FTIR, SEM-EDS, TEM, x-ray diffraction (XRD), and BET. The outcome obtained from characterization suggested the type of catalyst with the best potential for catalytic hydroprocessing of UCO into green diesel. Catalytic parameters were investigated in order to identify the most suitable parameters to obtain an optimal yield

### 1.1 Bio Based Thermal Fly Ash

Biomass is derived from plant material, the source of energy includes agricultural waste materials, wood waste, municipal solid waste, and methane captured from dumpsite. These waste materials can be harnessed and developed as catalysts which can be used effectively for the conversion of UCO to biofuel. This biowaste catalyst was found to be highly efficient for the hydro-processing of UCO to obtain 93.85 vol% and 66.29 vol.% of bio-crude and organic liquid fraction, respectively [28].



BBTPPFS has found applications in brick production, gas absorbents, glass and ceramics, and solid catalysts and catalyst reinforcements [29, 30]. The global ash market is projected to become USD 6.86 billion by the year 2026, up from USD 4.13 billion in 2018 [29]. Physically, BBTPPFS is lightweight ash, spherically shaped solid particles with sizes varying from 0.5  $\mu\text{m}$  to 300  $\mu\text{m}$ . The composition of a typical BBTPPFS is shown in Table 1 [31]. Waste ash is thrown in open ground or lagoons, causing mass environmental hazards and health risks. Eskom, a 100 % South Africa-owned enterprise, consumes an average of 120 million tons of coal per year generating 25 million tons of ash per year to produce 36 479 MW of electricity from its coal-fired stations [32] [33].

**Table 1: The Chemical Composition of BBTPPFS [34]**

Element	CaO	SiO <sub>2</sub>	MgO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Cl	Na <sub>2</sub> O
Composition (Wt%)	30.74	27.87	6.67	13.96	2.36	2.83	4.83	1.35	3.36	1.14

The following chemicals with insignificant percentage weight can also be found in bio-based thermal power plant ash, e.g., SrO, TiO<sub>2</sub>, MnO, ZrO<sub>2</sub>, BaO, ZnO, Br, Cr<sub>2</sub>O<sub>3</sub>, CuO, NiO, and As<sub>2</sub>O<sub>3</sub>. It is evident from Table 1 that the highest weight percentage is CaO and SiO<sub>2</sub>, with weight percentage 30.74 and 27.87, respectively. Both elements are the most active compounds for hydroprocessing catalysts [34].

## 2.0 MATERIAL AND METHODS

### 2.1 Materials Collection and Sample Preparation

The BBTPPFS was sourced from Eskom from their Lethabo power generation plant, South Africa. Al<sub>2</sub>O<sub>3</sub>, CaO, and SiO<sub>2</sub> (analytical grade) were procured from Lichro Chemical and Laboratory Supplies, South Africa. The as-received catalyst was grinded into nano size using a mechanical grinder then sieved with a < 50  $\mu\text{m}$  mesh. The fine particle was dished into clean, dry, and airtight glass vials and labeled as indicated in Table 2. The BBTPPFS collected from ESKOM was ground into fine particles using an IKA MF 10 basic laboratory mechanical grinder and made to pass through sieve < 50  $\mu\text{m}$  mesh to ensure uniform particle size. The sieved BBTPPFS was measured, weighed, and transferred into a clean, dry, and airtight glass vial, and labeled as indicated in Table 2. The containers of the samples were kept in a cool environment to avoid contamination and oxidation. Figure 3 shows a flowchart of the preparation method of samples.

**Table 2: Details of Sample Preparation**

Sample Notation	Catalyst Samples			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	BBTPPFS
A	1	-	-	-
A1	1	-	-	1
B	-	1	-	-
B1	-	1	-	1
C	-	-	1	-
C1	-	-	1	1
D	-	-	-	1



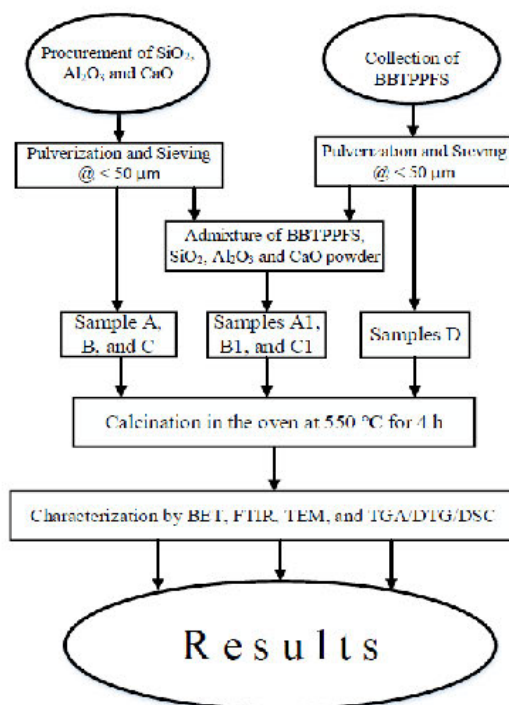


Figure 2: Flowchart of the Preparation Method of Samples.

## 2.2 Catalyst

The samples were characterized using various techniques which includes SEM-EDX, XRD, FTIR, TGA, TEM, differential scanning calorimetry (DSC), and BET.

### 2.2.1 Thermal Analysis

The samples of seven calcinated dry powder fly ash, otherwise referred to as BBTPPFS, were subjected to thermal analysis using TGA (TA-60WS, Shimadzu) thermal analyzers. The aim was to observe the reaction of the samples at different temperature, which would aid the selectivity of the catalyst for hydrogenation. 10 mg of each sample was measured into an aluminium pan and scanned between 29 °C to 1000 °C, raising the heating rate 10 °C per minute, then held for 5 min at 1000 °C under nitrogen atmosphere at a flow rate of 10 ml/min in TGA and DSC analyser. The data were analysed using a TA-60 ch 1 DTG-60AH workstation.

### 2.2.2 Spectroscopic Analysis

This analysis is expected to offer a reliable absorption spectrum, the dilution and homogenization of the seven samples with spectroscopic grade. The experiment uses Perkin Elmer Co., USA, model 15.011, discs with 12.7 mm ID and  $\approx 1$  mm thick which was made of manual hydraulic press at about 10 tons for a time between 30 s to 60 s. The spectrum was measured from  $300\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  and recorded on a spectrometer of model system 1000 FTIR with a resolution of  $2.0\text{ cm}^{-1}$ . The applicability of BBTPPFS as a viable catalyst for conversion of UCO into HDRD depended on the location and peaks from the sample spectra.

### **2.2.3 BET Characterization**

Analysis of nitrogen sorption was carried out by a Micromeritics ASAP 2460 devices. 0.25 g of the seven samples were degassed at 100 °C under nitrogen gas for a night. Thereafter, the samples were kept in a vacuum to cool gradually to make their surfaces and pores available for close investigation. The surface area of the sample (m<sup>2</sup>/g) was computed by the BET method, while the pore size distributions, like the total pore volume (cm<sup>3</sup>/g at STP) and average pore radius (Å), were calculated using the Barrett-Joyner-Halenda (BJH) method. BET analyses revealed the pore volume, surface area, and pore area, which determined the capability of the sample as a potential green catalyst to mild crack UCO into green diesel.

### **2.2.4 TEM Analysis**

A Quorum Q150A ES sputtering machine was used as a platform to prepare the seven samples. The fly ash was analysed for morphology with the aid of Zeiss Ultra Plus in field emission gun scanning electron microscope (FEGSEM). However, A JEOL JEM-2100 operating at a speed of 20 kV was used for the high-resolution TEM analysis. The morphological, structural information unveiled through TEM analysis helped to determine catalysts that would support the hydrogenation of UCO.

### **2.2.5 XRD Analysis**

The fly ash powder was secured at the middle of sample holder and well positioned diffractometer D8-Advance manufactured by Bruker AXS(Germany). The measurement was observed in a continuous  $\theta$ - $\theta$  scan in locked coupled mode, tube: Cu-K $\alpha$  radiation ( $\lambda K\alpha_1=1.5406\text{\AA}$ ); detector: LynxEye (Position sensitive detector). The measurements ran within 2 $\theta$  Range available from 0.5° to 130° in an Increment of  $\Delta 2\theta$ : (0.034°) at 0.5 sec/step. The phase analyses were done when the data were subtracted in line with diffraction pattern with zero background after choosing the identified elements from the periodic table. Phases were identified by comparing the calculated peaks with the measured ones until all phases had been identified within the limits of the resolution of the results. The results of the XRD analysis showed the elemental composition of the samples and their catalytic hydro-processing potentials.

### **2.2.6 SEM Analysis**

The SEM analysis was conducted on a Phenom ProX Desktop SEM. Desktop SEM with EDS has the capability of massive, easier, and flexible elemental and SEM analyses.

The samples were charged via an optional low vacuum sample holder with up to 25 mm diameter (optional 32 mm). SEM experiment was conducted at 15 kV in ambient temperature. The SEM outcome revealed sample images and the EDXS was used to determine the elemental composition which provided a structural idea of the biomass viability of the catalyst for hydrogenation of UCO.

## **3.0 RESULTS AND DISCUSSIONS**

### **3.1 Thermal Analysis**

The results of TGA of BBTPPFS collected from Eskom mixed with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO is shown in figure 3. The samples exhibited decomposition processes when subjected to heat in a controlled environment. It was observed that samples A1 and B1 followed the same pattern in response to thermal degradation. The weight loss occurred at 100 °C and 200 °C, respectively, and remained stable till to 1000 °C, which describes the thermal stability of the samples. This confirms that SiO<sub>2</sub> mixed with BBTPPFS catalyst had the ability to withstand the hydrogenation process to obtain a green



diesel product. Reports from literature indicate that calcination enhances decomposition of a catalyst [34, 35]. Therefore, the percentage weight loss (% weight loss) and the corresponding temperature obtained from Figure 3 shows that sample A, A1, B, B1, D maintained a thermal equilibrium considering the trend of decomposition. Sample A1 with 0.8 % weight loss at 99 °C with no additional loss in weight percentage reveals a potential catalyst for hydrogenation. This agrees with the calcination temperature of 550 °C adapted for this research. The thermal decomposition observed shows the sustainability of the catalyst in the face of the high temperature, up to 1000 °C. This could be traced to the high percentage of SiO<sub>2</sub> in the elemental composition of BBTPPFS as shown in Table 1. However, sample B has zero decomposition but could only be used as a supportive catalyst. Sample A's sharp decomposition may have been due to the moisture content and impurities contained in the sample but at 90 °C the sample slightly maintained a steady decomposition pattern up to 1000 °C and corresponding weight loss of 91 wt%. The reaction of sample D to the heat flow showed the ability of the sample to withstand heat which is a credit to its application for catalytic hydrogenation. The significant decomposition of calcium oxide occurred around 400 °C and 700 °C due to loss of water during the process and CO<sub>2</sub> from carbonated CaO. In contrast, C1 was a mixture of CaO and BBTPPFS; the decomposition pattern in Figure 3 was a result of high percentage of calcium oxide present in the fly ash. The addition of silica oxide (SiO<sub>2</sub>) support catalyst to heterogeneous (BBTPPFS) catalyst could improve the catalytic activity for hydroprocessing of green diesel. This result conforms with the findings as reported by Alipour et al. [36].

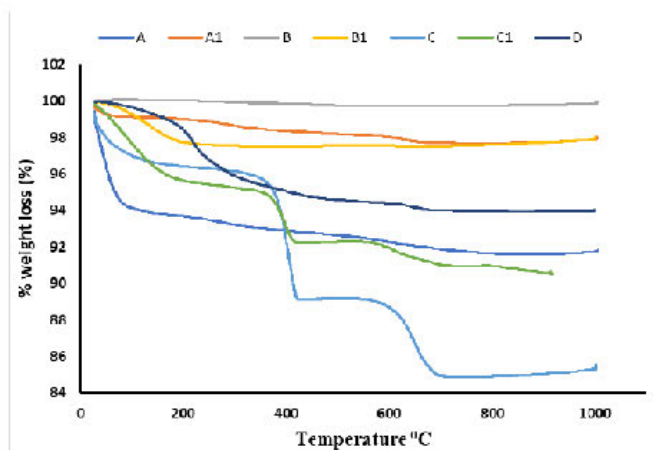
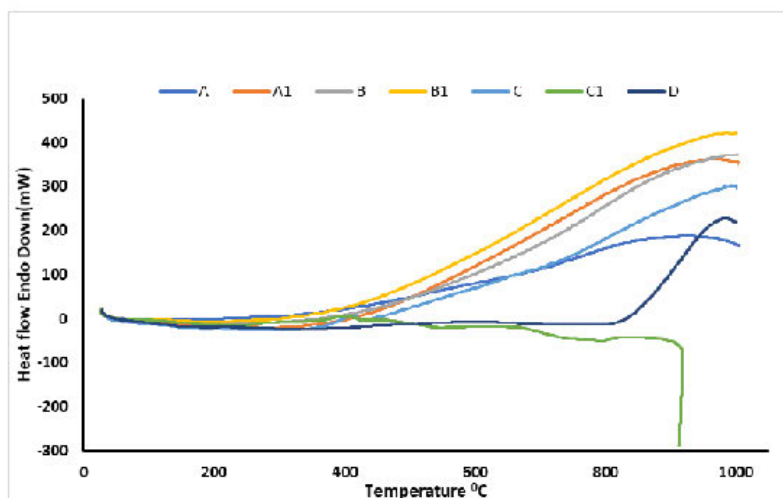


Figure 3: TGA Curve for the Samples.

### 3. 2 Differential Scanning Calorimetry(DSC)

The DSC curve reveals the endothermic reaction that occurred as a result of heat flow to the sample. Figure 4 shows the phase transformation in terms of thermal stability, the melting point of the heat reaction, and the crystallization point of the sample [37]. The heat flow follows the same pattern for samples A, A1, B, B1, C, D, while sample C1 behaved differently. From the curve, it is evident that the C1 sample could not absorb heat above 912 °C because of the moisture content and the presence of CO<sub>2</sub>. This implies that the samples possessed the ability to sustain heat at different phases during hydrogenation.

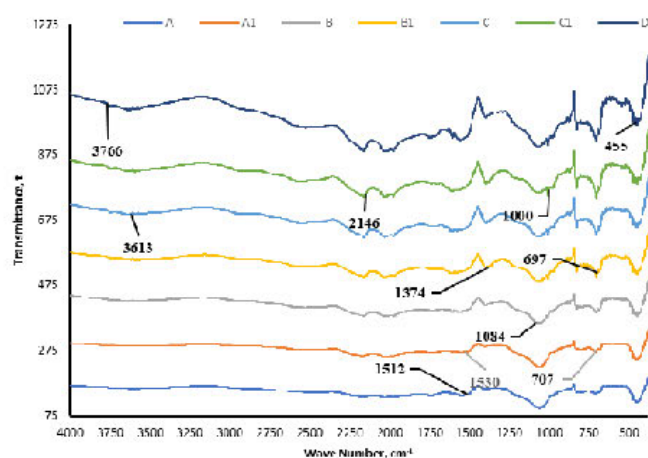




**Figure 4: DSC Curve for the Samples.**

### 3.3 Spectroscopic Analysis (FTIR)

Figure 5 is an FTIR spectra analysis that shows the wavelengths of samples with significant absorption bands. This effect can be traced to the addition of support catalyst samples to the BBTPPFS heterogeneous catalyst. This is in agreement with the findings of Maneerung et al. [38] and Sharma et al. [39]. Samples D, C1, and C values in the wavelengths with sharp absorption bands at  $3766\text{ cm}^{-1}$  and  $3613\text{ cm}^{-1}$  are noticed on the BBTPPFS, CaO, and BBTPPFS mixed with CaO catalyst, which is the -OH rhombohedral band. This band agrees with the presence of  $\text{CaCO}_3$  in samples D, C1, and C, but was not noticed in other samples, which is a confirmation of the result described by Boey et al. [40]. Samples A and A1 show a major absorption band at the wavelength of  $1084\text{ cm}^{-1}$  and  $707\text{ cm}^{-1}$ . This is attributed to the asymmetric O-Si-O while the wavelength at  $701\text{ cm}^{-1}$  in sample A has moved to  $707\text{ cm}^{-1}$  in sample A1. The peaks at  $707\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$  are due to the (Si, Al)-O-(Si, Al) symmetric stretching [28]. Also, the wide peak at  $2159\text{ cm}^{-1}$  was because of the (Si, Al)-O- (Si, Al) asymmetric transmission stretch. The absorption recorded by sample A1 falls within that reported by Arif et al. [41], who compared raw CFA with modified CFA. The outcomes of the FTIR analysis confirm the admixture of BBTPPFS and silica oxide as a potential catalyst for hydrogenation.

Figure 5: FTIR Spectra of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and BBTPPFS.

### 3.4 Brunauer-Emmett-Teller (BET) Analysis

Table 3: Textural Properties of the Samples

Properties	Unit	Samples						
		A	A1	B	B1	C	C1	D
Micropore Volume	cm <sup>3</sup> /g	0.0010	0.0014	-0.0002	-0.0003	0.0007	-0.0002	-0.0001
Micropore Area	m <sup>2</sup> /g	2.8080	4.0200	*NR	*NR	1.5244	*NR	*NR
External Surface Area	m <sup>2</sup> /g	30.6498	41.2571	0.4884	1.0087	2.9926	3.6274	0.8611
Total Surface Area	m <sup>2</sup> /g	33.4578	45.2771	0.0321	0.4581	4.5171	3.3098	0.5928
Pore Size	Å	141.3157	139.8311	*NR	245.0010	292.4526	204.1373	359.3611
Pore Volume	cm <sup>3</sup> /g	0.1182	0.1564	0.0002	0.0029	0.03303	0.0169	0.0053

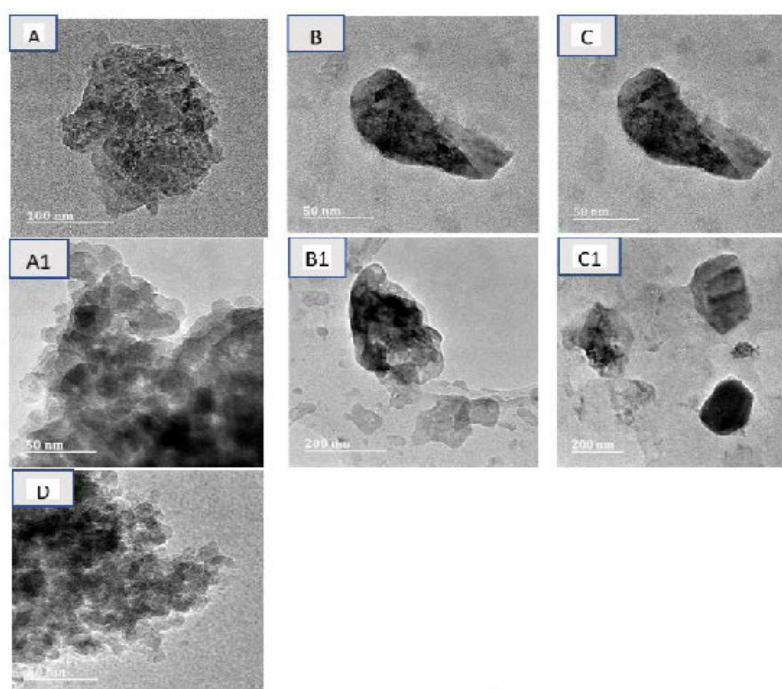
\*NR- Not responding.

The catalytic properties of BBTPPFS and support catalyst were investigated by BET. Table 3 shows the data analysis on the micropore volume, micropore area, external surface area, pore size, and pore volume. A significant increase was noticed when 60 g BBTPPFS (sample D) was modified by adding 40 g of SiO<sub>2</sub> (Sample A) to obtain sample A1. The values of micropore volume of -0.0001 cm<sup>3</sup> increased to 0.0014 cm<sup>3</sup>, and external surface area increased from 0.8611 to 41.2571 m<sup>2</sup>/g, total surface area from 0.5928 to 45.2771 m<sup>2</sup>/g, and pore volume of 0.0053 cm<sup>3</sup>/g increased to 0.1564 cm<sup>3</sup>/g. These values describe the ability of the green catalyst for H<sub>2</sub>O<sub>2</sub> optimal production. The parametric properties found in sample A1 support catalytic activities within the temperature range (300 °C to 400 °C) of mild cracking of the UCO for the purpose of hydrogenation to obtain green diesel in liquid hydrocarbon (C<sub>11</sub>-C<sub>18</sub>). This agrees with Deepak et al.'s findings [28]. The pore volume of 0.564 cm<sup>3</sup>/g in sample A1 falls within the range 0.08 cm<sup>3</sup>/g to 0.3 cm<sup>3</sup>/g reported when fly ash was synthesized, mixed with copper oxide, and converted to zeolites by hydrothermal activation, atmospheric crystallization, and double-stage fusion-hydrothermal for catalytic applications [42]. The value pore volume obtained in sample A1 is clear evidence that novel mesopores can be achieved by the admixture of two heterogeneous catalyst supports [41, 43]. The properties of a catalyst determine the choice of its selection; surface area as a physical property supports its catalytic activity. The higher the surface area the better the catalytic activity in terms of mild cracking and for more interactions with the reactants [25]. However, a high surface area of 45.2771 m<sup>2</sup>/g will speed up its catalytic activity for the adsorption and desorption of molecules such as triglycerides, glycerine, and green diesel [44, 45]. The outcome of the

BET analyses of samples reveals BBTPPFS mixed with SiO<sub>2</sub> as a potential green catalyst for the conversion of UCO into HDRD by hydrogenation [46, 47].

### 3. STEM Analysis

Heterogenous catalyst fly ash powder was examined using high-resolution transmission electron microscopy (HRTEM). Figure 6 shows the TEM micrographs with sample structural information. The calcined samples' mesostructure as detected in the TEM image is evidence of homogeneous active metals dispersed on the mesoporous structure [48]. The pore size and total surface area of BBTPPFS and its support enhance the catalytic activities capable of mild cracking the UCO during hydrogenation. Sample A1 has the highest pores and surface structure, and hexagonal-shaped particles compared to samples A, B, B1, C, C1, and sample D. This may due to the high weight percentage (wt.%) of calcinated SiO<sub>2</sub>. The TEM results is in line with XRD analysis. The calcinated sample (SiO<sub>2</sub> + BBTPPFS) A1 poses the properties that makes it viable for the conversion of UCO into HDRD using hydro processing technique as reported by Pandit and Fulekar [49] And Navajas et al. [50].



**Figure 6: TEM Micrograph for Sample (A, A1, B, B1, C, C1, and D).**

### 3.6 XRD Analysis

Table 4 describes the composition of major components of sample A, A1, B, B1, C, C1 and sample D. The percentage weight of calcinated sample D, BBTPPFS was 33.22 % quartz, 11.78 % mullite, 1.19 % calcite which increases to 100 % quartz, 41.67 % mullite, 2.08 % calcite respectively when sample A, SiO<sub>2</sub> was added. The significant increase is due to the predominant nature of silica oxide in BBTPPFS. Various studies available in the literature have proved that the existence of SiO<sub>2</sub>, either as base or support catalyst increase the rate of hydrogenation of waste cooking oil [51, 52]. This characteristic points to sample A1, BBTPPFS + SiO<sub>2</sub> with 100 % quartz as being a better green heterogeneous



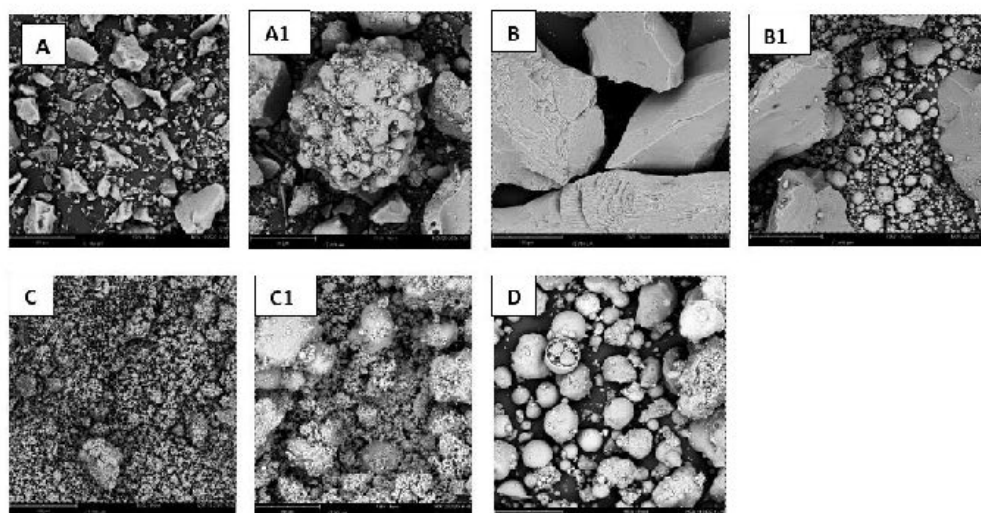
catalyst for hydro-processing of UCO to green diesel.

**Table 4: Composition of Major Components of the Samples**

Compound Name	Chemical Formula	Lattice	Sample Concentration %						
			A	A1	B	B1	C	C1	D
Quartz	SiO <sub>2</sub>	Hexagonal	-	100	-	20.83	-	12.15	33.22
Mullite	Al <sub>4</sub> Si	Hexagonal	-	41.67	-	4.17	-	4.17	11.78
Calcite	CaCO <sub>3</sub>	Rhombohedral	-	2.08	-	0.65	-	0.65	1.19
Corundum synthetic	Al <sub>2</sub> O <sub>3</sub>		-	-	100	8.33	76.15	42.13	-
Amonium Aluminium oxide.	(NH <sub>4</sub> ) <sub>2</sub> -Al-O		-	-	7.81	7.81	10.20	7.81	-

### 3.7 SEM Analysis

Scanning electron microscope (SEM) analysis was performed with the target to investigate surface morphology of a calcinated BBTPPFS heterogenous catalyst collected from Eskom with support catalysts added. The morphologies of the samples were very similar. Figure 7 shows a large and irregular particle of the samples. The image of BBTPPFS (sample D) indicates a spherical shape with a smooth surface. The image of sample A (SiO<sub>2</sub>) reinforced with sample D (BBTPPFS) reveals large surface and pores in sample A1, which was confirmed by XRD analysis. The weight percentage of gain and increase in silica oxide from 18.94 % to 25.65 % has a great impact in mild cracking of UCO to green diesel range. The white spots that appear on the catalyzed samples are elements from various categories. Silica oxide mixed with BBTPPFS has the tendency to withstand high temperatures up to 1000 °C, pointing to sample A1 being a reliable and superior green catalyst for hydrogenation.



**Figure 7: SEM Micrographs for Samples A, A1, B, B1, C, C1, and Sample D.**

### 4.0 CONCLUSIONS

Eskom generates a lot of fly ash from their power plants and discharges same in an environment which creates additional pollution in South Africa. This BBTPPFS waste can be harnessed as a green and biowaste catalyst to reduce the total cost of production of green diesel.

These research investigated the properties and effect of calcinated BBTPPFS, and three support catalysts were procured and used as received.

- BBTPPFS is available in tons in South Africa. Fly ash, which is a waste, can be harnessed to replace expensive commercial catalysts.
- The properties that favor catalytic hydrogenation were revealed by the results, which show that the surface area, external surface area, pore-volume, and micropore volume of calcinated BBTPPFS increased with the addition of SiO<sub>2</sub>. The effect of the reinforcement by the SiO<sub>2</sub> proves the novelty of the viable and potential catalyst for conversion of UCO to green diesel.
- The thermal decomposition observed shows that sample A1 (SiO<sub>2</sub> +BBTPPFS) catalyst could be sustained at a temperature up to 1000 °C. This temperature stability supports the hydroprocessing of UCO into HDRD.
- The percentage concentration of sample A1 increased from 33.22 % quartz to 100 % quartz, 11.78 % mullite to 41.67 % mullite, and 1.19 % calcite to 2.08 % calcite respectively. This increment was a result of the addition of SiO<sub>2</sub>.

The application of a calcinated 40 g silica oxide admixture with 60 g BBTPPFS increased the potential of a catalyst to mild crack UCO to green diesel.

#### **Conflict of Interest**

There is no potential conflict of interest in this research work.

#### **ACKNOWLEDGEMENT**

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## **CHAPTER 7: ENGINE PERFORMANCE, EMISSION AND PHYSICO-CHEMICAL EVALUATION OF WASTE PLASTIC FUEL: A CASE FOR FLY ASH CATALYST PYROLYSIS**

This chapter evaluated the engine performance, emissions, and physico-chemical properties of a waste plastic fuel (WPF) using catalytic pyrolysis and tested it in a compression ignition (CI) engine test rig. Results obtained revealed the viability of the fly ash with a competitive oil yield, engine test showed good performance as well as pollution emission well within acceptable limits.

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# Engine Performance, Emission and Physico-Chemical Evaluation of Waste Plastic Fuel: A Case for Fly Ash Catalyst Pyrolysis

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**ABSTRACT:** Municipal plastic waste (MPW) as a component of municipal solid waste (MSW) poses significant challenge to stakeholders because of the ubiquity of use, non-biodegradability and the considerable danger it poses to public health. This work accessed the qualitative as well as the quantitative profile of MPW in the target municipality, composed a waste dump fly ash catalyst for catalytic pyrolysis, produced the waste plastic fuel (WPF) and had it tested in a compression ignition (CI) engine test rig. Result obtained revealed the viability of the fly ash with a competitive oil yield, engine test showed good performance as well as pollution emission well within acceptable limits.

**KEYWORDS:** Municipal plastic waste (MPW), Fly Ash Catalyst, Pyrolysis, Waste Plastic Fuel (WPF), Test rig, Performance, Emission.

## I. INTRODUCTION

The municipal solid waste (MSW) is currently one of the chronic environmental, health and economic problems prevalent in most developing countries [1]. About 1.3 billion tons per year of MSW is generated in developing world and, in Africa, only 57% of this waste is biodegradable where a dismal 4% is recycled [2]. This challenge is set to increase because of rapid increase in population, urbanization, and raised living standards [3, 4]. In the last few decades, millions of people have shifted from rural to urban areas in many parts of the world [5]. Currently half of the world's population lies within urban areas [6]. Moreover, according to a United Nation (UN) report, the 5.9 billion current urban population will increase to 6.3 billion by 2050, with a 90% increase only in urban areas of Africa and Asia (UN, 2014). A key component of this challenge is municipal plastic waste (MPW). Indeed, the ubiquity of plastic is considered one of the gauge of uncontrolled urban

growth and the consumer culture it promotes. Plastic products are used widely because of their durability, low cost, versatility and their compatibility with urban lifestyle. Increasing plastic waste generation bears a direct correlation with MSW and the challenge the posed are exacerbated by: population growth, particularly in urban centers, economic growth, absence of effective waste management practice, weak municipal waste governance and, to a large extent, under-funded waste management architecture [2].

Stakeholders have recognized the need to arrest this development because of the associate risk non-biodegradable plastic pose to public health on the longer term. Plastics are mostly non-biodegradable and remain in the environment for hundreds of years [7]. Plastic waste valorization has been identified as one of the sustainable ways by which the environment can be rid of plastic waste [2]. Conventional recycling methods such as sorting and grinding can recycle only 15-20% of total plastic waste [8]. As a result, energy recovery technologies such as thermal and catalytic pyrolysis, gasification and plasma arc gasification are receiving more attention as alternative methods of plastic waste recycling [6, 9]. Plastic waste is a mixture of: low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene-terephthalate (PET). PE and PS plastics are the main components of most municipal plastic waste [10].

Pyrolysis process converts plastic waste into liquid oil, solid residue (char) and gases at high temperatures (300-900°C) via thermal decomposition mostly in an inert environment. However, there are certain limitations in the conventional thermal pyrolysis, where the whole process is temperature-dependent [11, 12]. The quality of the liquid yield is difficult to control, the



energy requirement is comparatively high and, the liquid oil produced from thermal pyrolysis may contain impurities like residues, chlorine, and sulphur [13]. Moreover, the thermal pyrolysis of PE type plastics such as HDPE and LDPE along with PP are difficult to conduct due to their crossed chain hydrocarbon structures [14]. Therefore, catalytic pyrolysis is being advocated to overcome the problems of thermal pyrolysis [15]. A range of catalysts have been utilized, including Red Mud [15], spent FCC [16], ZSM-5 [15], HZSM-5 [17], Y-Zeolite [16], Fe<sub>2</sub>O<sub>3</sub> [18], Al<sub>2</sub>O<sub>3</sub>, Ca(OH)<sub>2</sub> [19] and natural zeolite [20], in catalytic pyrolysis to improve the quality of liquid oil [20]. At the domestic level, available catalyst performance needs to be evaluated and matched with the right process parameter to determine optimal conditions that will facilitate the adoption of the process as a feasible method of dealing with the MPW challenge.

The catalyst increases the lighter fractions in the liquid oil produced, such as gasoline [22], and decreases the overall process energy-inputs [15]. Moreover, the use of the ZSM-5 catalyst decreases impurities like sulphur, nitrogen, and phosphorous in the produced liquid oil [23]. It is also reported that the use of catalysts with a high BET surface area allows more contact between reactants and the catalyst surface, resulting in an increased rate of cracking reaction to produce more gases [20].

MPW is clearly a challenge in almost all municipality in Nigeria but, it could also be an opportunity to create a new business that generate economic value, create employment and effectively deal with the risk posed by indiscriminate disposal of plastic waste. There exists sufficient incentive to explore this technology within the local context, namely, vast mineral resources that could serve as catalyst in the pyrolysis process and the abundance of the feedstock. But, the grand challenge is twofold: identification and characterization of locally available catalyst that could yield optimal outcome and, the conceptualization of a catalytic pyrolysis process that can be domesticated. To overcome these challenge, factors affecting the catalytic pyrolysis process, such as temperature, retention time, feedstock composition, and the use of catalysts, need to be evaluated. The effect of different catalysts on the quantity and quality of pyrolysis products need to be examined in detail against characteristics of catalyst. Furthermore, catalyst reforming and the regeneration and exploration of new cheaper catalysts also need to be focused upon in order to make the catalytic pyrolysis process more economical and sustainable within the domestic environment. Available data on the waste management challenge in Africa indicates

that on the average, only 57% of MSW are biodegradable. In addition, only about 55% of generated waste are collected and greater than 90% of the collected waste are disposed in mostly unregulated landfills. It further state that of the total waste collected, only about 4% is recycled [2]. These figures reflect a dismal failure in waste governance and the evidence are there for all to see in every municipality on the continent. These challenge subsist on a continent that is set to undergo a major transformation in the foreseeable in: population explosion, faster level of urbanization and, a changing consumer purchasing habits. The convergence of these factors will invariably leads to exponential growth in waste generation [2]. This narrative can be changed if the right approach in waste governance are deployed. This will start by seeing waste as a resource, collecting relevant data and instituting the right mechanism. Historically in Nigeria, there exist a dearth of data on waste generation, characterization and management. On a more specific note, data available indicates that about 80% of plastic waste generated in Nigeria is mismanaged. Available data on the waste management challenge in Africa indicates that on the average, only 57% of MSW are biodegradable. In addition, only about 55% of generated waste are collected and greater than 90% of the collected waste are disposed in mostly unregulated landfills. It further state that of the total waste collected, only about 4% is recycled [2]. These figures reflect a dismal failure in waste governance and the evidence are there for all to see in every municipality on the continent.

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For most municipality in Nigeria and, particularly for Bauchi municipality, the prevailing problem of plastic waste management includes: a lack of actionable data on MPW characterization and composition, a lack of advocacy and domestication of waste valorization scheme that feeds into the local economy, scant identification



and study of technically feasible catalyst available locally for plastic pyrolysis, and the study on a suitable reactor design that meets local condition while giving optimal yield. The aim here is to qualitatively and quantitatively characterize MPW with the stated aim of determining the optimal parameter for its catalytic pyrolysis into usable Internal Combustion Engine (ICE) fuel. The overall aim of this study is to determine, using research based approach, a technically feasible and commercially viable pathway to the production of Internal Combustion Engine (ICE) fuel from the catalytic pyrolysis of Municipal Plastic Waste (MPW) obtained from the target municipal area (Bauchi municipality). The objectives include following: To quantitatively and qualitatively characterize Municipal Solid Waste (MSW) obtained in the target area with the stated aim of determining the averaged MPW composition; To identify, prepare and determine key properties of locally available pyrolytic catalyst that could be used in the catalytic pyrolysis of MPW collected from the target municipality; To determine, using lab. Size reactor, the optimal mix of catalyst and reactors operating parameters that will yield desirable oil output from the characterized MPW; To produce waste plastic oil (WPS) from the plastic sourced from the MSW obtained from the pilot area; To characterize and test the quality of fuel produced with the aim of establishing if it meets the internationally acceptable benchmark for ICE grade fuel or, if there are quality gaps, to suggest remediation strategies.

## II. BACKGROUND

Pyrolysis is a recycling process in which organic compound are converted into liquid oil, char and gas at high temperature via thermal decomposition [24]. The process can be conducted at different temperature, however, for plastic waste, the optimal temperature range is about 500 – 550°C [24]. Furthermore, the heating rate and retention time are an important parameter in pyrolysis processes. Several studies have been conducted using heating rate that ranges between 4 °C/min – 25 °C/min [25-27]. With regards to retention time, Lopez et al [15] carried out pyrolysis of plastic waste at retention time of 0 – 15, 15 – 30 and 120min. other studies showed retention time of 40 – 70min [27], 120min [25] and 45min [28]. Most studies showed that increase in temperature results in reduction of retention time. It has also been proven that a further reduction in retention time and process temperature can be achieved via the introduction of catalyst, hence the need for catalyst pyrolysis.

Thermal pyrolysis (or non-catalytic pyrolysis) is an endothermic process that requires significant heat budget. Extensive study on this has been conducted on the past, these include: PE [29-32]. Thermal pyrolysis of PE (HDPE and LDPE) and PP requires light temperature for degradation, as compared to PS plastic [23]. Furthermore, in the absence of catalyst, PE is converted into wax instead of liquid oil [16]. Where liquid oil is produced by thermal degradation it contains heavy oil compound with large carbon chains as a major compound [15]. A further disadvantage is that the liquid is of low quality due to its low octane number and the presence of high solid residues. It also contains impurities such as sulphur, nitrogen and phosphorus [16].

Catalytic pyrolysis, on the other hand, is the thermal decomposition process that is carried out in the presence of a suitable catalyst. The catalytic process shows high potential for the conversion of plastic waste into liquid oil, it has better product quality, lower temperature and retention time when compares to thermal pyrolysis. These factors make catalytic pyrolysis a more energy efficient and optimal process [33].

As a result, FCC [14], spent FCC [16], HZSM-5 [34] ZSM-5 [23] Cu Al<sub>2</sub>O<sub>3</sub> [35], Co Mo/Z [36] Zeolite –  $\beta$  [37], Red mud [15] Al(OH)<sub>3</sub> Ca(OH)<sub>2</sub> [19] and Fe<sub>2</sub>O<sub>3</sub> [18] have been used to enhance the oil yield and mechanism of catalytic pyrolysis. In addition, hydrocarbon (IIC) produced from different plastic waste such as HDPE, LDPE [38], PP [39] and PS [40] contain low carbon chain compound in the gasoline range of IICs when compares with a similar thermal pyrolysis yield [38, 41, 42]. However, the downside to catalytic pyrolysis is that, it produces more gaseous product and reduce the liquid yield, albeit marginally, when compares to thermal pyrolysis [43]. Factors Affecting Pyrolysis are: Temperature [44], retention time [45], feedstock composition, use of catalyst [22], moisture content [24], heating rate and particle size are some of the factors that determine the outcome of catalytic pyrolysis [44].

Temperature is one of the factor that plays important role in the product quality and quantity of catalyst pyrolysis [15]. Temperature affects the cracking reactions that determines the amount of gasses and liquid produced. However, it has little effect on the amount of char produced (Yoshioka et al 2004, Ji et al 2006) at low temperature reactivity is reduced and long chain hydrocarbons are produced but, an increase in temperature results in the production of short chain compounds due to the cracking of C-C bonds. But a further higher temperature results in a diminishing returns as



aromatic compounds are produced due to the triggering of secondary reaction [15, 17].

Retention time has been reported widely to bear no significant effect upon the yield of pyrolysis process. Lopez et al. [15] stated that the same yield of oil is observed at 30 min and 120 min retention time. In a similar study, the aromatic compounds present in liquid oil were found to be the same at different retention times using the same temperature [45]. However, feedstock composition were found to affect the yield of pyrolysis process. According to Miskolczi et al [23], the PE and PP require higher temperatures for their degradation as compared to PS plastic, due to different and complex hydrocarbon structures.

Catalyst plays an important role in catalytic pyrolysis. They serve to improve the quality of the products as well as reducing the process temperature and retention time for overall process optimization.  $\text{Fe}_2\text{O}_3$ ,  $\text{Ca}(\text{OH})_2$ , FCC, natural zeolite and synthetic zeolite are the different types of catalyst that hence been investigated by scientist [19]. The use of catalyst increases the rate of cracking reactions that leads to an increase in the production of gases consequently resulting in the reduction of liquid yield [20]. On a positive note however, the quality of the liquid oil produced is improved. The viability of any given catalyst are determine by characteristics such as Brunauer Emmett and teller (BET) surface area, pore size, pore volume, and acidity. These are the factors that determine the activity of a catalyst. Studies has revealed that thermal cracking occurs at the external surface of the catalyst (in catalytic pyrolysis) the internal porous structure of the catalyst then acts as channels for selective breakdown of larger compound into smaller ones [16]. Hence, small pore size supports the production of gases, whilst wax production occurs due to external cracking on the external site of the catalyst [46]. Catalyst can be applied directly as solid mix with the feedstock or on organic vapour produced in separate chamber. Either way, the cracking will be improved via a reduction of reaction temperature and retention time [15, 24]. However, catalyst recovery is different for direct contact this is because the pores are blocked due to the sticky nature of the plastic feedstock [20]. Only few studies have investigated catalyst regeneration [47]. In addition, direct contact contaminates the catalyst through the deposition of impurities such as chlorine, sulphur and nitrogen on the surface of the catalyst [42]. Vapour phase contact has been investigated using Y-zeolite for PE [48], ZSM -5 for PS [49] and ZSM -5 for industrial packaging waste [15].

Another important point to note in the use of catalyst for plastic waste pyrolysis as it affects the oil yield is the level of acidity. Silica alumina catalyst are amorphous catalyst having Lewis acid site as an electron acceptors and Bronsted acid site with an ionizable hydrogen atom. The acidity level of these catalyst is determined by the mole ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . The higher the acidity, the lower the oil yield [18]. Hence a good of catalyst-temperature will be to use low acidity silica alumina catalyst and high process temperature. Other important characteristic of the catalyst are their porosity and thermal stability. A microporous catalyst with a high internal crystalline structure increases the catalyst process, produce more gases, and decrease the liquid yield [15]. While a catalyst with macro pore volume will not affect the liquid yield quantity. It is desirable to have high thermal stability for a catalyst [1].

### III METHODS

#### 3.1 Qualitative and quantitative sampling of waste in Bauchi municipality

The collection of data techniques adopted in carrying out the study includes research design, study area, population of the study sample size, sampling techniques and mode of data analysis. Characterization of municipal waste is necessary to collect actual data that will aid in determining the waste per capita generated within the municipality, determine the waste composition, and ultimately, the plastic composition of the total waste. The study sampling area is Gwallameji. Gwallameji is a suburb of Bauchi located in Bauchi state, Nigeria. The sampling of Gwallameji will be extrapolated to determine total waste per capita of the entire metropolis as the suburb represent the demography of the entire city.

##### 3.1.1 Location

Bauchi, metropolis, capital of Bauchi State and its foremost traditional emirate, is in the North Eastern geopolitical zone of Nigeria. It is located between Latitudes  $10^{\circ}16' 30'' - 10^{\circ}21' 0''$  North of the Equator and Longitudes  $9^{\circ}48' 0''$  and  $9^{\circ} 52'30''$  East of the Greenwich Meridian. It is on the northern edge of the Jos plateau, at an elevation of 616m. The topography of Bauchi metropolis is relatively flat in the Centre. The town lies over 609.6 meters above sea level; it occupies a total land area of 3, 604 hectares [50]. The Bauchi Urban area according to the Bauchi State Urban Development Board has a radius of about 32km and comprises of only one local government area i.e. Bauchi. Bauchi town lies on the railroad from Maiduguri to Kafanchan (where it joins the line to Port Harcourt)

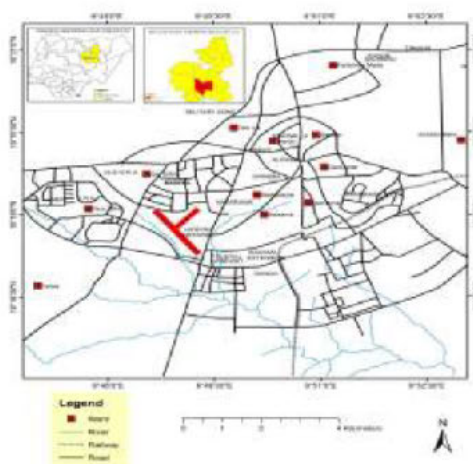


and has road connections to Jos, Kano, Maiduguri and Gombe [50].

### 3.1.2 Climate

According to the Koppen Climate Classification system, Bauchi has a tropical savannah climate. Two main seasons are experienced in the study area; cold dry season and hot wet season. It enjoys a rainfall total of up to 1091.4mm annually; its hottest month is usually April (with 40.56°C) while the coldest months are December and January with typically 6.11°C and 7.22°C respectively. The minimum and maximum annual temperatures in the metropolis are 18.33°C and 32.39°C respectively (Nigeria: People, Population and Settlement, 2003).

Figure 3.1 Map of Bauchi State Metropolis



### 3.1.3 Population and Economic Activity

Projected from the 2006 census, using the states inter census growth rate of 3.39%, the population of Bauchi metropolis (i.e. 493,730) as at 2014 was 644,641. The sex ratio generally across the state was 105 males to 100 females. The population of Bauchi town comprises many ethnic groups, the main ones being Gerawa, Sayawa, Jarawa, Bolawa, Fulani and Hausa (United Nations High Commission on Refugee Statistical Yearbook, 2006).

### 3.2 Amount of Solid Waste Generated

We estimated the amount of municipal solid waste generated using the formula below.

$$n = \frac{N}{1 + N \times 0.07^2} \dots \dots (1)$$

(Slovin's Formula)

Where N is Total population in the study area n, is sample size requires, and given the finite population of Gwallameji estimated at 30000, sample size was put at approximately 203 given the average of 13 persons per household. Hence a plastic bin 15 in number were obtained for the study.

### 3.2.1 Sampling Stage

To determine the number of waste bin responded to in each location, Bowels (1962) proportional allocation technique was use, it is given as;

$$Nh = \frac{ni}{N} \dots \dots \dots (2)$$

Where N is total house hold population, n is total sample size, h is total household population ward (13), ni, sample size for each ward, thus, the total (13) house hold were sample in the study location with each location getting proportional amount.

### 3.2 Catalyst preparation protocol

The Fly ash (FA) catalyst sample used for this research was obtained from the municipal waste dump. The as-received FA was pulverized into fine particles using a mechanical grinder, and sieved via sieve < 50 µm mesh in line with established protocol. The sieved FA was transferred into a clean, dry, and airtight glass vial, and designated as sample A. SiO<sub>2</sub> (analytical grade) was procured from Lichro Chemical and Laboratory Supplies, South Africa. The as-received SiO<sub>2</sub> was pulverized into fine particles using a mechanical grinder and sieved using a < 50 µm mesh. The fine SiO<sub>2</sub> powder was transferred into a clean, dry, and airtight glass vial, and labelled as sample B. Part of samples A and B were thoroughly mixed in ratio 30:70 (sample A: sample B), stored in a clean, dry, and airtight glass vial, and marked as sample C. The containers of the samples were kept in a cool environment to avoid contamination and oxidation.

### 3.2.1 Sample preparation

The samples were prepared according to the flowchart illustrated in Figure 4. The three samples (A, B, and C) were characterized by various techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal electron microscope (TEM), differential scanning calorimetry (DSC) and Brunauer-Emmett-Teller (BET).



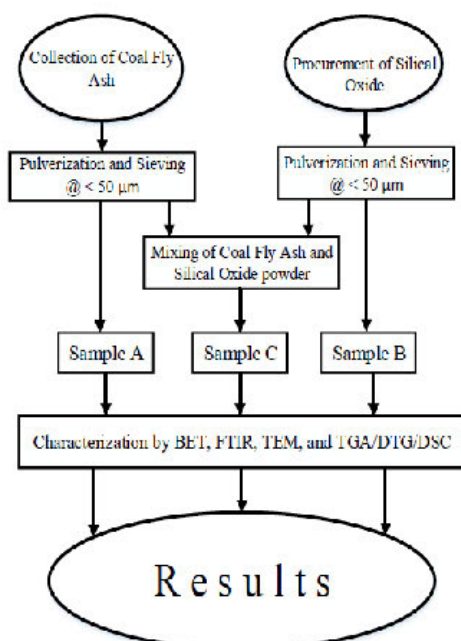


Figure 3.2: Flowchart of samples preparation

### 3.2.2 Methods of characterization

The three samples (A, B, and C) were characterized by various techniques including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), thermal electron microscope (TEM), differential scanning calorimetry (DSC) and Brunauer-Emmett-Teller (BET).

### 3.2.3 XRD analysis

Measurements are performed using a multipurpose X-ray diffractometer D8-Advance from Bruker AXS (Germany) operated in a continuous  $\theta$ - $2\theta$  scan in locked coupled mode with Cu-K $\alpha$  radiation. The sample is mounted in the centre of the sample holder on a glass slide and levelled up to the correct height. The measurements run within a range in  $2\theta$  defined by the user with a typical step size of  $0.034^\circ$  in  $2\theta$ . A position-sensitive detector, Lyn-Eye, is used to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter.

Data are background subtracted so that the phase analysis is carried out for diffraction pattern with zero background after the selection of a set of possible elements from the periodic table. Phases are identified from the match of the calculated peaks with the measured ones until all phases have been identified within the limits of the resolution of the results.

### 3.2.4 Thermal analysis

The thermal analysis of the three samples was analyzed by a DTG (DTG-60AH, Shimadzu) and TGA (TA-60WS, Shimadzu) thermal analyzer. About 10 mg of dry powder of each sample was weighed into an aluminum pan and scanned between the temperature range of  $29^\circ\text{C}$  to  $1000^\circ\text{C}$ , the heating rate  $10^\circ\text{C}/\text{min}$ , then held for 5 min at  $1000^\circ\text{C}$  and under nitrogen atmosphere at a flow rate of 10 ml/min in a simultaneous TGA, DTG, and DSC analyses. The data were analyzed using a TA-60 ch 1 DTG-60AH workstation.

### 3.2.5 Spectroscopic analysis

To obtain a recognizable absorption spectrum, the dilution and homogenization of the three dry powder samples with KBr (spectroscopic grade), were carried out with additional grinding and mixing in an agate mortar. Discs (12.7 mm ID and  $\approx 1$  mm thick) were prepared in a manual hydraulic press (model 15.011, Perkin Elmer Co., USA) at about 10 tonnes for a pressing time of 30 s to 60 s. The spectrum was measured and recorded from  $300\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  on a spectrometer (model system 1000 FTIR, Perkin Elmer Co., USA) with a resolution of  $2.0\text{ cm}^{-1}$ .

### 3.2.6 BET Characterization

The Nitrogen sorption analyses of the samples were performed with a Micromeritics ASAP 2460 instrument. About 0.25 g of each sample was degassed at  $100^\circ\text{C}$  under nitrogen gas overnight. Thereafter, they were allowed to cool under a vacuum to make their surfaces and pores available for probing. The surface area of the sample ( $\text{m}^2/\text{g}$ ) was computed by the Brunauer-Emmett-Teller (BET) method, while the pore size distributions like the total pore volume ( $\text{cm}^3/\text{g}$  at STP) and average pore radius ( $\text{\AA}$ ) were calculated using the Barrett-Joyner-Halenda (BJH) method.

### 3.2.7 TEM analysis

The samples were prepared on a Quorum Q150A ES sputtering machine before transferring to the Zeiss Ultra Plus in field emission gun scanning electron microscope (FEGSEM) for morphology analysis of the powder sample. A JEOL JEM-2100 operating at an accelerating voltage of 20 kV was used for the high-resolution transmission electron microscopy (TEM) analysis.

### 3.4 Waste Plastic Oil Pyrolysis

In the fixed bed reactor, the catalyst is usually in palletized form and packed in a static bed. It is easy to design but the irregular particle size and shape of the plastic feedstock create challenges



during feeding process. Beside, access to catalyst reaction site are restricted. Some research has been conducted with fixed bed reactors but, with subdued interest [43, 52]. In some instances, the fixed bed reactor is used as secondary pyrolysis reactor with the primary feed coming in as liquid and gases [53-55]. However, two-step process is not cost effective, fluidized bed reactor, on the hand, solve the fixed bed challenge. Here the catalyst sits on the distributor plates where the fluidizing gas passes through it and the particles are carries in fluid state. As a result, the catalyst is well mixed with the reactant. Many researchers preferred to use fluidizing bed reactor in catalytic cracking of plastic over fixed bed reactor [56, 57]. Jung et al [58] used fluidizing bed reactor in their research because it provides almost a constant temperature with high mass and heat transfer, giving shorter residence time in the reactor and consequently more uniform range of products. The temperature ranges for plastic pyrolysis in fluidize bed is normally 290 °C – 830 °C for both thermal and catalyst process. Ino et al [59] used fluidize bed for the plastic pyrolysis in the presence of silica – alumina catalyst. A liquid yield of 87 wt% for PP feedstock and 85 wt% for HDPE feedstock were obtained at 500 °C. Fluidized bed reactor is generally considered to be the best reactor to perform catalytic pyrolysis of plastic waste. This is because the catalyst can be reuse many times. In addition, its operation is more flexible than batch reactor since feedstock can be continually fed into the reactor in a continuous process format fluidize bed reactor are best suited for large scale operation for the same reasons. In his study, the fixed bed reactor was used with the catalysis being deployed in free slurries within the bed. Below is the picture of the reactor vessel used. It consists of the main vessel, the thermocouple meter and probes, the inert nitrogen feed tube and the product exit tube with three distillation flask for product distillation and analysis.

Plate 1: Pyrolysis reactor used



### 3.5 ICE test bed and WPO analysis

The test engine was a single cylinder, four stroke and air cooled TD111 Techquipment direct injection diesel engine. The test rig set up is shown in figure 3.3 and technical details are

given in Table 3.1 A hydraulic dynamometer TD 115 also from Techquipment with water flow pressure head of 6-12m was used to measure the torque which is displayed on the instrument display panel TD114. TD114 also displays the engine speed, exhaust temperature, air flow and houses the The test engine was a single cylinder, four stroke and air cooled TD111 Techquipment direct injection diesel engine. The test rig set up is shown in figure 3.3 and technical details are

given in Table 3.3. A hydraulic dynamometer TD 115 also from Techquipment with water flow pressure head of 6-12m was used to measure the torque which is displayed on the instrument display panel TD114. TD114 also displays the engine speed, exhaust temperature, air flow and houses the fuel flow pipette which measures the fuel flow rate. Measurement input signals are received from the test bed via tachometer connector, thermocouple terminal, torque transducers and manometer tapping from the air bag. The engine speed is measured electronically by a pulse counting system. An optical head mounted on the dynamometer chassis contain an infrared transmitter and receiver. A rotating disc with radial slot is situated between the optical sources and the sensor. As the engine and slotted disc rotates the beam is interrupted. The pulse train is electronically processed to provide read-out of engine speed. Engine torque is measured by the TD115 Hydraulic Dynamometer and transmitted to a torque meter located on the TD114 instrument unit. A linear

calibration of the torque meter is checked intermittently to confirm accuracy of the data set via an eight step process on the equipment manual (Techquipment, 2003). The exhaust gas temperature is measured with a chrome/Alumina thermocouple located in a 1/8" BSP union brazed into the exhaust port of the engine. Color coded leads from the thermocouple are connected to terminal underneath the TD114 instrument unit. The test engine is a 3.5kw rated, direct injection (DI), single cylinder diesel engine. Selected test speed was 1800, 2000, 2500, 3000 and 3600rpm. Each test cycle at selected torque consist of running the engine for 1 minute at idle speed and 9 minute at selected load in accordance with test cycle G3 of ISO 8178 – 4 (Commission 1999). The engine rated power was taken as 100% load. The test cycle was repeated for 20%, 40%, 60% and 80% load. This test cycle procedure was followed for diesel, and waste plastic oil. The SV-5Q exhaust gas analyzer was in accordance with ND112 (Non – Dispersive infra Red) method utilize via micro computer analysis to measure the thickness of HC, CO and CO<sub>2</sub> in the exhaust gas and to inspect the density of NOX and O<sub>2</sub> via electrochemical sensor. The excess air coefficient,  $\lambda$  was also computed automatically by the analyzer and double checked manually to confirm accuracy. The analyzer is equipped with a microprocessor, an induction tachometer, temperature sensor, and an inner micro printer. The sampling probe is normally installed in the exhaust line where gas could be drawn through a

Table 3.2: Test rig Data

filter into the analyzer

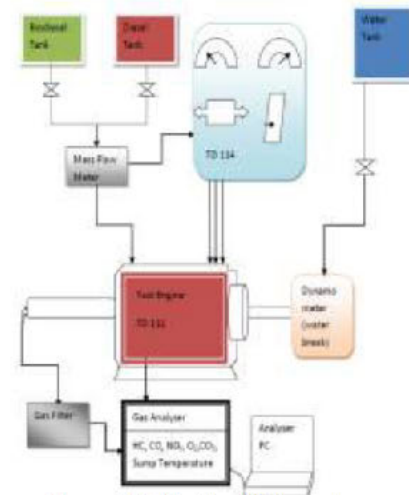


Figure 3.3: Test bed Schematics

#### IV RESULTS AND DISCUSSION

The results from the waste sample, catalyst analysis and preparation, pyrolysis process. Waste plastic oil test and engine test are presented and discussed below.

##### 4.1 Waste Sample Collection

Waste accumulated in the waste bin was collected from selected site into a waste bin was weighed and sample and before taken for any laboratory test/ processes. Details are given below:

Device	Description	Detail
Engine	Model	TQ:TD 111
	Maximum power(Kw)	3.5
	Type	Naturally aspirated, four strokes.
	Rated speed(rpm)	3900
	Number of cylinder	1
	Compression ratio	17.5:1
	Combustion	Direct injection
Hydraulic dynamometer	Model	TQ:TD115
	Type	Hydraulic
	Water pressure	6-12m head of water (60KPa)
	Range	0-14Nm
	Water flow rate	4lt/min
Exhaust gas analyzer	Model	SV-5Q
HC	Range	1-10000 $10^{-6}$ (ppm) Vol.



	Resolution	1 ppm	
CO	Range	1-1000	10 <sup>-2</sup> (%) Vol.
	Resolution	0.01%	
CO <sub>2</sub>	Range	0-20	10 <sup>-2</sup> (%) Vol.
	Resolution	0.01% Vol.	
O <sub>2</sub>	Range	0-25	10 <sup>-3</sup> (%) Vol.
	Resolution	0.01% Vol.	
NO <sub>x</sub>	Range	0-50000	10 <sup>-8</sup> (ppm) Vol.
	Resolution	1 ppm	

**Table 4.1 Household Population, Sample Size and Percentage**

Location	Household population	Sample weight (kg)	Percentage (%)
----------	----------------------	--------------------	----------------

Business non-groceries 1	5	20	75%
Business non-groceries 2	10	12	7.52%
Business non-groceries 3	5	19.9	9%
Business groceries 1	2	70.5	23.25%
Business groceries 2	3	42.2	14.9%
Business groceries 3	6	8.09	0.51%
Lower class family 1	5	23.9	7.59%
Lower class family 2	4	13.36	4.13%
Lower class family 3	3	20.4	7.01%
Student lodge 1	3	12.5	3.79%
Student lodge 2	2	13	4.1%
Student lodge3	5	12.58	3.93%
Upper class family	3	13.5	4.12%
Upper class family	10	44	0.11%
Upper class family	4	10.4	3.75%
TOTAL	70	292.77kg	100%

**Table 4.2 Household population, Sample Size and Percentage**

Category	Population	Weight	Percentage
Student lodge	9 persons	38.86kg	12.2%
Lower class family	13 persons	56.88kg	18.53%
Upper class family	13 persons	31.99kg	8.36%
Business groceries	20 persons	102.5kg	22.65%
Business non-groceries	15 persons	156.7kg	38.26
TOTAL	70 persons	386.93kg	100%

**Table 4.3 Total Plastic Generation**

Weeks	Plastic waste in (kg)	Change in percentage
First week	11.12kg	76%
Second week	3.88kg	3%
Third week	6.96kg	5%

Fourth week	8.7kg	16%
TOTAL	30.66kg	100%

#### 4.1.2 Total Population in Bauchi

According to 2004 census is given as 493,730

using this formula  $p = p_0 e^{rt}$  to get our recent population in bauchi state

where

$$p_0 = 493,730$$

$$t = 2020 - 2004 = 16 \text{ years}$$

$$r = 3.6\% = 0.036$$

$$p = 493,730 \times e^{0.036 \times 16}$$

$$p = 493,730 \times e^{0.576}$$

$$p = 835171.8726$$

$$\text{total waste plastic generated in bauchi} = \text{total plastic per capita} \times \text{total population}$$

$$\text{total waste of plastic generated} = 30.66\text{kg} \times 835171.8726$$

$$\text{total waste of plastic generated} = 25606.3696 \text{ ton/month}$$

The annual waste plastic generation in Bauchi is therefore 307,276.32 tons/annum. While there are no local data to compare this result with, existing annual national data point to a consensus. A study published in 2019 which worked with a project population of 173 million Nigerian estimated a plastic waste generation of 19,865,593 tons [60]. This put the average generation for the 36 sub-national entity at 551,822.02 tons/annum. The scale of this waste underscore the enormity of the challenge and highlight the imperative of plastic waste valorization.

#### 4.2 Catalyst Analysis

##### 4.2.1 BET analysis

The data on the BET surface area, external surface area, average pore radius, pore volume, micro-pore volume, and micro-pore area are shown in Table 4.2.1. The surface area, external surface area, and pore volume of unmodified FA (sample A) have been substantially increased by the addition of  $\text{SiO}_2$  (sample B) from 0.5928  $\text{m}^2/\text{g}$ , 0.8611  $\text{m}^2/\text{g}$ , and 0.00532  $\text{cm}^3/\text{g}$  to 35.1102  $\text{m}^2/\text{g}$ , 32.5753  $\text{m}^2/\text{g}$ , and 0.1281  $\text{cm}^3/\text{g}$  respectively. The total pore volume of 0.1281  $\text{cm}^3/\text{g}$  falls within the 0.08  $\text{cm}^3/\text{g}$  to 0.3  $\text{cm}^3/\text{g}$  recorded when FA was synthesized, modified with copper oxide, and converted to zeolites by hydrothermal activation,

atmospheric crystallization, and double-stage fusion-hydrothermal for catalytic applications. Though these increases have been accompanied by a decrease in the average pore radius of sample A from 179.68 Å to 72.98 Å in sample C. This shows that the addition of  $\text{SiO}_2$  causes a reduction in average pore radius in the mesoporous range as a result of impurities. However, there was an increase in the micro-pore volume of sample A from -0.000121  $\text{cm}^3/\text{g}$  to 0.000582  $\text{cm}^3/\text{g}$  in sample C. The surface area and average pore radius of sample C are higher than the 17,542  $\text{m}^2/\text{g}$  and 32.59 Å reported when raw FA was impregnated by Calcium meral and calcined at a temperature of 500 °C for 4 hours as reported by Arif et al. [61] and BET surface area of 9.028  $\text{m}^2/\text{g}$  and pore volume of 0.01055  $\text{cm}^3/\text{g}$  reported for biomass fly ash by Vargas et al. [62]. The increase in pore volume lends credence to the view that new mesopores can be formed not only by the activation process but also by the addition of supports [61, 63]. The BET surface area is an important physical property that determines the catalytic activity of a solid particle. In this case, a high BET surface area of 35.1102  $\text{m}^2/\text{g}$  will aid its catalytic activity for the adsorption and desorption of molecules such as triglycerides, glycerin, and green diesel [62, 64].

Table 4.4 Textural properties of the samples

Properties	Unit	Sample A	Sample B	Sample C
BET surface area	$\text{m}^2/\text{g}$	0.5928	317.2404	35.1102
External surface area	$\text{m}^2/\text{g}$	0.8611	279.1870	32.5753



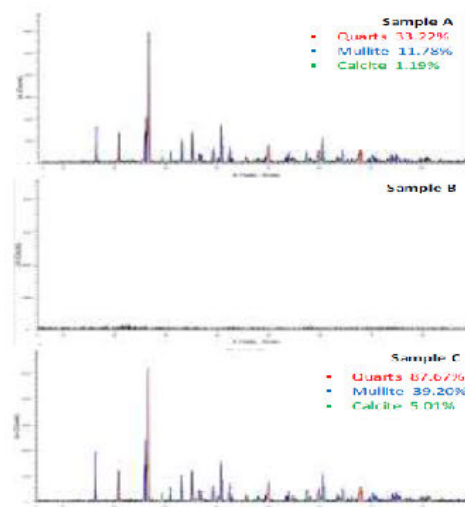
area				
Average	Å	179.68	70.72	72.98
pore radius				
Pore volume	cm <sup>3</sup> /g	0.005326	1.1218	0.1281
Micropore volume	cm <sup>3</sup> /g	-	0.014827	0.000852
Micropore area	m <sup>2</sup> /g	*NR	38.0533	2.5349

\*NR=Not responding

#### 4.2.2 XRD analysis

The XRD spectrometry plot for the samples is depicted in Figure 6 while Table 4.2.2 shows the description of the major constituents of the samples. The semi-quantitative mass composition shows that the percentage of quartz increased from 33.22 % in sample A to 87.67 % in sample C while the mullite increased from 11.78 % in sample A to 39.20 % in sample C. This is due to the addition of SiO<sub>2</sub> to sample A. The pattern shows that raw CFA is composed mainly of quartz (SiO<sub>2</sub>) and mullite (Al<sub>4.4</sub>Si<sub>1.209.6</sub>) minerals. The quartz diffraction pattern is shown predominantly at around 2θ = 21°, 26°, 50°, and 68° while mullite diffraction peak at 2θ = 16.5°, 24°, 41°, and 61°. Though the XRD diffraction of sample B did not display any pick, it can be seen that the addition of sample B to sample A significantly altered the composition of sample C. As shown in figure 7, sample C was composed mainly of quartz (SiO<sub>2</sub>), mullite (Al<sub>4.4</sub>Si<sub>1.209.6</sub>), and a small percentage of calcite (CaCO<sub>3</sub>) minerals. The quartz peaks were detected at 2θ = 20.8°, 26.5°, 36.4°, 50°, 60°, and 68° and mullite peaks were detected at around 2θ = 16.5°, 26.2°, 31°, 33°, 35.3°, 40.8°, and 60.7°. The only noticeable calcite peak was noticed at around 2θ = 29.3°. Similar results were also reported by Sharma et al.[65], Ho et al. [66], Bhandari et al.[67], and Maneerung et al. [68]. These results show a high possibility of using sample C as a potential catalyst for the conversion of waste plastic oil to diesel [61, 62, 69].

Plate 2a, b and c: Catalyst Micro-Electronic Analysis



#### 4.2.3 Thermal analyses

The outcome of the thermal analyses comprised of the samples is reported under TGA and DSC. The TGA of the samples is shown in Figure 7 which has been plotted with the temperature range of 30 °C to 1000 °C to ascertain the percentage weight loss concerning temperature using nitrogen as the heating medium. Sample A losses of about 2 % of its weight between 30 °C and 220 °C with no further thermal degradation. On the other hand, sample B witnessed 13 % weight loss between 30 °C and 140 °C and the weight loss becomes slower until 950 °C. From 30 °C to 250 °C, sample C witnessed about 15 % weight loss and another 5 % weight loss between 250 °C and 650 °C. Sample C effectively achieved thermal equilibrium with no further weight loss at 700 °C. This shows the high thermal stability of samples C, a property believed it inherited from CFA (sample A). This conforms with the pattern reported by Kumar et al. [34].

The DSC curve of the samples is shown in Figure 9 which reveals the distinction in the heat content of the samples concerning temperature.



This provided information on phase transition parameters like crystallization point, melting point, the heat of reaction, and thermal stability of samples [71]. From the curves, sample A witnessed rapid heat input between 820 °C and 930 °C. However, the addition of SiO<sub>2</sub> to CFA motivated sample C to behave differently and show a more uniform differential heat addition higher than sample B.

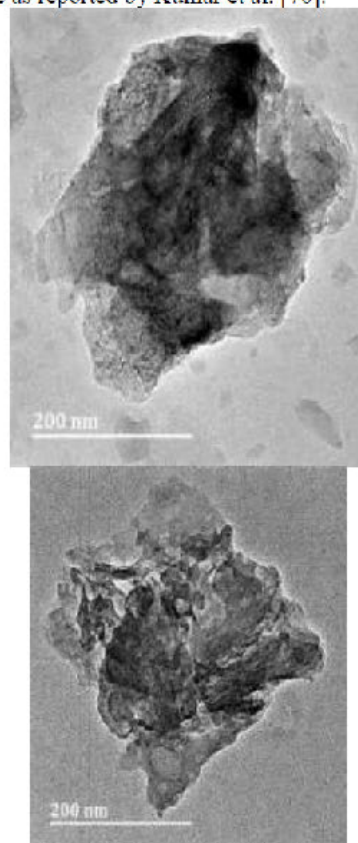
#### 4.2.4 Spectroscopic analysis

The FTIR spectra of the samples are shown in Figure 8. It shows that the samples have major absorption bands at the same wavelength. This is due to the effect of the addition of the SiO<sub>2</sub> to sample A to form sample C. For the CFA, it can be seen that the absorption at a wavelength of 3754 cm<sup>-1</sup> is characteristic of stretching OH rhombohedral. The major absorption band at 1054 cm<sup>-1</sup> noticed in sample B is similar to those observed by Maneerung et al.[68] and Sharma et al.[65] which they ascribed to the presence of SiO<sub>2</sub> which is not prominent in samples C. The existence of the absorption sharp band at 3745 cm<sup>-1</sup> which is ascribed to -OH band, was detected in the CFA catalyst, this band agrees with the presence of CaCO<sub>3</sub> in sample A but unnoticeable in sample C, as determined by XRD (Table 2) is a proof of the effect of the addition of SiO<sub>2</sub> support. This matches with the result described by Boey et al. [72]. The presence of a major absorption band at wavelength 1054 cm<sup>-1</sup> is attributed to the asymmetric O-Si-O while the wavelength at 451 cm<sup>-1</sup> in sample B has moved to 429 cm<sup>-1</sup> in sample C. The peak shown by sample C at ~430 cm<sup>-1</sup> characterizes the Al-O-Si and Si-O-Si bending vibrations. The distinctive peaks at 705 cm<sup>-1</sup> and 831 cm<sup>-1</sup> are due to the (Si, Al)-O- (Si, Al) symmetric stretching [73]. Also, the wide peak at 1011 cm<sup>-1</sup> can be ascribed to the (Si, Al)-O- (Si, Al) asymmetric transmission stretch. The absorption recorded by sample C falls within that reported by Arif et al. [61] who compared raw CFA with modified CFA.

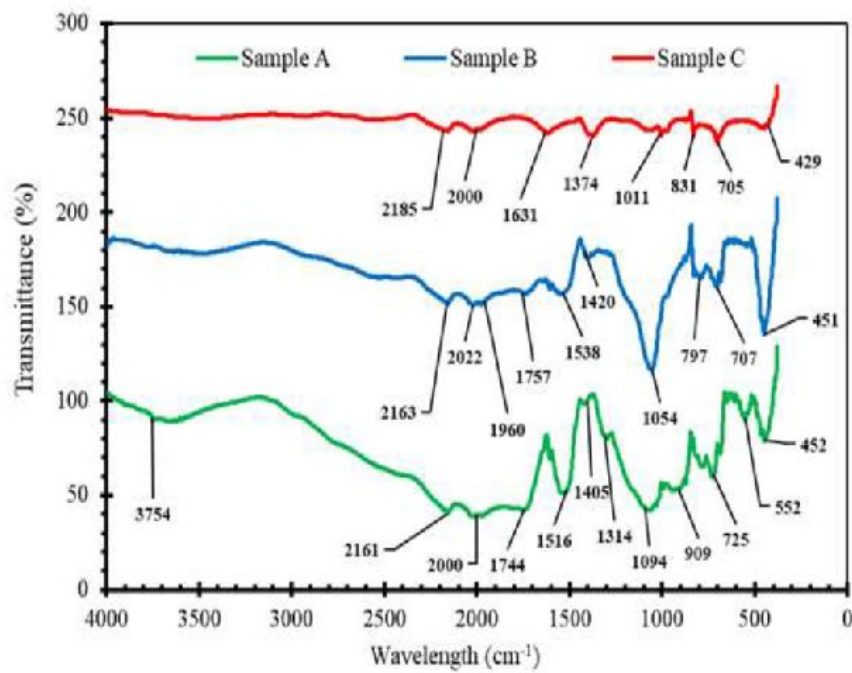
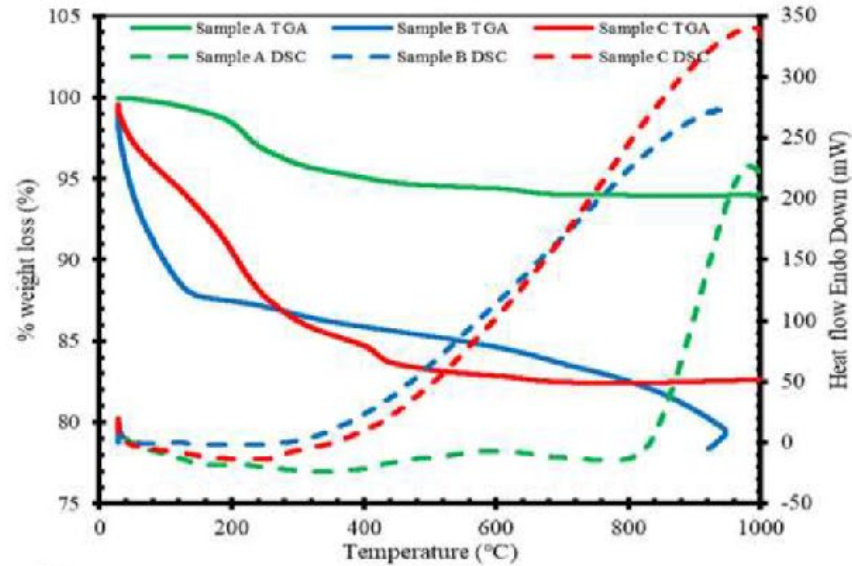
#### 4.2.5 TEM analysis

The TEM micrographs showing the structural information of the samples are shown in Figure 9. The mesostructure is detectable in the

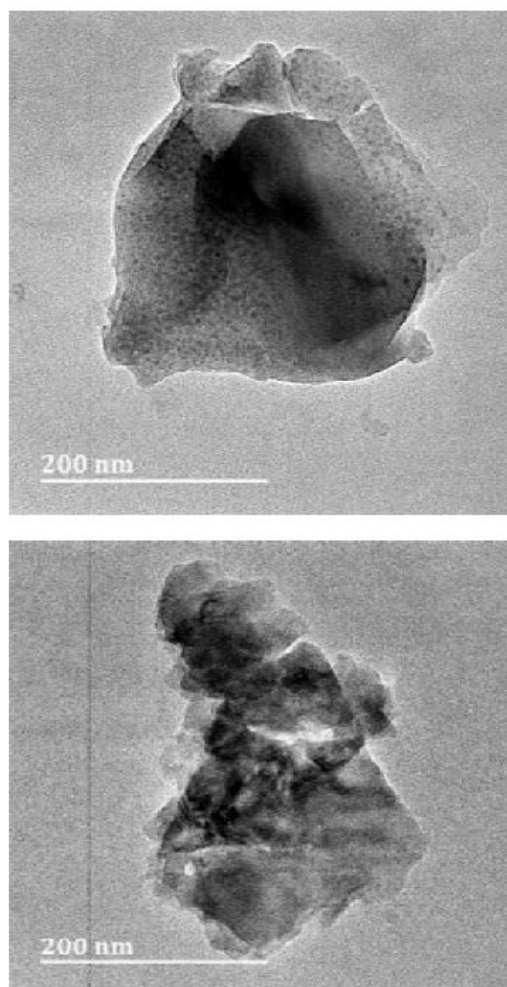
TEM pictures of the samples confirming that active metals are homogeneously filled and dispersed on the mesoporous structure [74]. The nano size, structural dimension, and active components of the FA and its support provided effective surfaces capable of enhancing its catalytic efficacy during the hydrogenation of triglyceride, irrespective of the FFAs present in the oil. Sample C has more pores, a regular surface structure, and hexagonal-shaped particles which reflects the presence of a high percentage of SiO<sub>2</sub> when compared with samples A and B. The TEM micrographs confirm the result of the XRD analysis that sample C has the capacity to effectively crack plastic waste to WPO. This agrees with the outcomes of a similar sample as reported by Kumar et al. [70].



Compound name	Chemical formula	Lattice	Molecular weight	Volume	Sample Composition (%)		
					A	B	C
Quartz	SiO <sub>2</sub>	Hexagonal	60.08	113.59	33.22	N/A	87.67
Mullite	Al <sub>2</sub> Si	Hexagonal	132.02	49.71	11.78	N/A	39.2
Calcite	CaCO <sub>3</sub>	Rhombohedral	100.09	367.78	1.19	N/A	5.01







**Plate 3:** Sample A, B, C, C1 in descending order

#### 4.3 Waste Plastic Oil Pyrolysis

From table 4.6 shown below, the pyrolysis yield from the different catalyst can be seen to favour a more synthetic mix of the fly ash and silicate although, it appears to produce more chars which rapidly damage the catalyst pore opening and makes regeneration difficult, its gas yield is minimal compared to the other catalyst. Its wax production is also negligible. From the data, cracking tend to be more severe in the  $\text{SiO}_2$  catalyst. This is understandable as its BET data and SEM profile indicates a disposition to behave in

such manner. What is difficult to explain is a combination of high wax production occurring simultaneously with severe cracking. Often, these are diametrically opposed to each other as suggested in several literatures [74]. The high point of the pyrolysis data is the encouraging result obtained from the Fly Ash catalyst result. At 61.5% oil yield, it competes quite well with the commercially available alternative and since it is obtained from the same waste dump, it enhances the valorization scheme of the municipal waste value chain at no additional cost.



Table 4.6: Pyrolysis Results

Catalyst	Yield (%)			
	Liquid Oil	Char	Gases	Wax
Fly Ash (A)	61.5	13.2	22.5	2.8
SiO <sub>2</sub> (B)	55.2	10.4	31.4	3.0
Fly Ash + SiO <sub>2</sub> (C)	63.4	14.2	22.0	0.4

#### 4.4 Engine Performance and Emissions

The oil obtained from the pyrolysis were analyzed and result obtained are shown in table 4.4 below. The oil was then blended with Diesel in the ratio of 20% WPF-80% diesel, 30% WPF-70%

diesel and 100% diesel for the purpose of performing engine test and emission analysis on an engine test rig whose configuration has been given earlier.

S/N	Properties	WPF	Diesel	ASTM D6751	Methods
1	Kinematic Viscosity at 40°C	2.149	3.05	6(max)	EN ISO 3104
2	Density (Kg/m <sup>3</sup> )	796	843	875-900	EN ISO 3675 EN ISO 12185
3	Calorific Value(kJ/kg)	41.800	43.000		
4	Refractive Index	1.32	1.44	1.245-1.675	Abbe refractometer (prolabo)
5	Flash point (°C)	72	91	90.00-130	D93
6	Ash Content (%)	<1.01%wt	<0.045wt		
7	Colour	Pale	Light green		
8	Sulphur Content %	<0.002	<0.035		D5453
9	Pour Point (°C)	-4	3-9	-15-10	Van Garpen et al (2004)
10	Cetane Number	51	55		EN ISO 5165

The engine test results are hereby presented in Figure 4.1 to 4.4. They include the engine efficiency, brake specific fuel consumption (BSFC), brake specific carbon monoxide (BSCO) emission and brake specific nitrogen oxides (BSNOx) emission, all plotted against the engine speed. The plots are a comparative evaluation of the waste plastic fuel (WPF) versus the conventional diesel. The first two plots give an indication of engine performance whilst the last two, an indication of the emission when WPF is used compared to the diesel.

In figure 4.1 generally the engine efficiency at low speed for both WPF and diesel were low at low engine speed but the pattern trend higher as the speed increases. This is a common trend for compression ignition (CI) engines [ref]. This is because combustion efficiency at low speed is low due to engine inertia and low temperature. At low speed WPF efficiency was better than diesel

by about 6.7% because of a lower viscosity of the WPF which allows for good fuel flow and vapour dynamics but as the speed increases, diesel efficiency began the increase due to higher calorific value and better combustion efficiency. This trend is supported by similar work in literature [75]. The brake specific fuel combustion (BSFC) data is shown in figure 4.2. At initially low engine speed, the values for both WPF and diesel were high, they both trended lower at medium level mid-engine speed because of improve combustion efficiency and began to increase with increasing power demands, giving a bath-tube shape curve. This is common for CI engine [76]. The BSFC data generally showed a mix outcome for WPF and diesel, indicating a statistically equal performance throughout the entire load spectrum. This is a slightly different outcome from observation in literatures of similar works. This trend, it is

believed, arise as a result of non-homogeneity of fuel mix for the WPF.

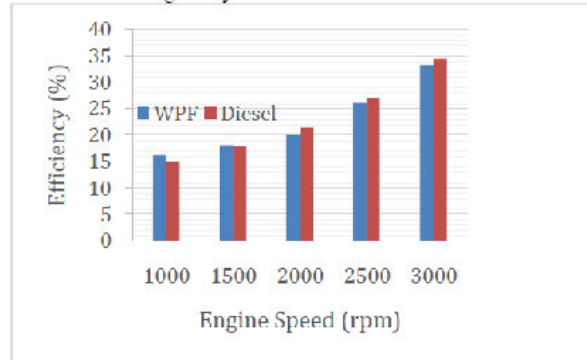


Figure 4.1: Engine Efficiency

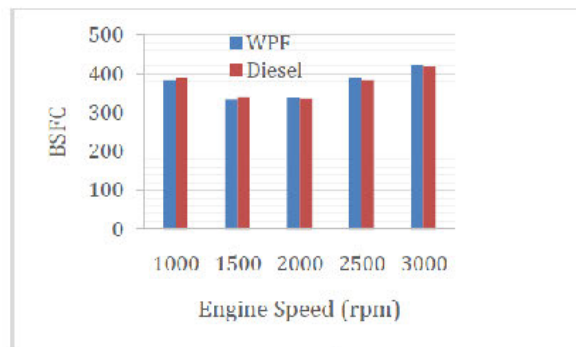


Figure 4.2: Engine BSFC

Figure 4.3 and 4.4 shows the BSCO and BSNO<sub>x</sub> emission for the two types of fuel. The former decreases with increasing engine speed whilst the later increases with increasing speed. The obvious reason for both trends being the engine temperature. Increasing engine temperature improves combustion efficiency thus lowering CO production whilst the same phenomenon increases

NO<sub>x</sub> emission due to Zeldovich mechanism for NO<sub>x</sub> emission. A wide array of literature agrees with this result [77].

The important highlight is that WPF compared to diesel, is quite competitive in performance and emission and, if all technical as well as economic factors are considered, WPF is a viable alternative to conventional diesel.

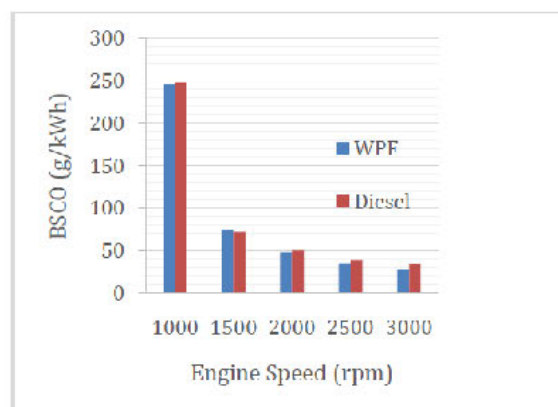


Figure 4.3: Engine BSCO



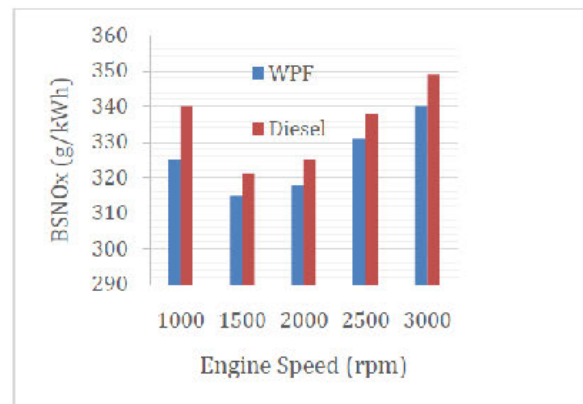


Figure 4.4: Engine BSNOx

## CONCLUSION

The result has established the challenge associated with municipal plastic waste (MPW) disposal in Bauchi metropolis, determine the viability of waste fly ash as a potential catalyst for MPW pyrolysis, proven the physico-chemical suitability of WPF for use in CI engine and determined the emission from WPF falls within current level of diesel emissions.

## ACKNOWLEDGMENT

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## **CHAPTER 8: HYDRO-PROCESSING OF HYBRIDIZED USED COOKING OIL INTO HYDROGENATION DERIVED RENEWABLE DIESEL USING LOCAL HETEROGENEOUS CATALYSTS**

This article is the seventh contribution to the thesis. The chapter describes the hydro-processing of hybridized UCO into hydrogenation derived renewable diesel using local heterogeneous catalysts.

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# **Hydro-processing of Hybridized Used Cooking Oil into Hydrogenation Derived Renewable Diesel using Local Heterogeneous Catalysts**

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## **Abstract**

The search for alternate energy to proffer permanent solutions to energy crises, fossil fuel depletion, and global warming is a pressing task. In this study, hybridized used cooking oil (UCO) was explored for hydro-processing using locally sourced biowaste catalyst. Coal fly ash (CFA) heterogeneous catalyst was reinforced with silica oxide ( $\text{SiO}_2$ ) in a ratio of 60 wt% to 40 wt%. A Parr reactor was used for hydroprocessing and conversion of UCO into hydrogenation-derived renewable diesel (HDRD). The value of the micropore volume of  $-0.0001 \text{ cm}^3$  increased to  $0.0014 \text{ cm}^3$ , and the external surface area increased from  $0.8611 \text{ m}^2/\text{g}$  to  $41.2571 \text{ m}^2/\text{g}$ , total surface area  $0.5928 \text{ m}^2/\text{g}$  to  $45.2771 \text{ m}^2/\text{g}$  and pore volume of  $0.0053 \text{ cm}^3/\text{g}$  increased to  $0.1564 \text{ cm}^3/\text{g}$ . These properties showed the potential that this biowaste catalyst has for hydrogenation. The fractionated bio-crude product known as HDRD exhibits excellent fuel properties compared to conventional biodiesel. The total yield of bio-crude product was 67.15 %. The product's high yield and the excellent quality confirmed the potential of CFA reinforced with  $\text{SiO}_2$  as a suitable catalyst. Hydrogenation of UCO into HDRD using an optimal catalyst is a promising technology that will enhance commercialization, and the product is carbon-free, environmentally friendly, and economically viable.

Key word: CFA, hybridized UCO, hydro-processing, HDRD, fuel properties.

## **1.1 Introduction**

Increasing concerns for environmental pollution, global warming, persistent depletion of fossil fuel reservoirs, and greenhouse gas emissions have reinvigorated the search for alternative renewable energy sources. The ever-increasing applications of petrol-based fuel in compression ignition (CI) engines for transportation, domestic, commercial, and industrial purposes, and the increasing population, modernization, and industrialization, have become a challenge in meeting increased energy needs [1]. The CI engine exhaust emissions of fossil fuel account for a significant percentage of harmful environmental pollution and consequently increase global warming [2]. These challenges

have engaged governments and scholars to search for a suitable alternative to mitigate petroleum products' adverse effects on the environment.

Green diesel, otherwise known as hydrogenation-derived renewable diesel (HDRD), is a biofuel that possesses a superior property to biodiesel and fossil diesel. The conversion of vegetable oil to HDRD by hydro-processing technology removes oxygen from feedstock and replaces it with hydrogen to produce a fuel similar to petroleum-based fuels. This can be achieved by placing a feedstock in a reactor in the range of 300 °C to 400 °C and pressure in the range of 5 MPa to 80 MPa with a heterogeneous catalyst in the presence of hydrogen gas for conversion of UCO into green diesel (mainly  $n\text{-C}_{17}\text{H}_{36}$  and  $n\text{-C}_{18}\text{H}_{38}$ ) [1, 3-5]. Biofuel can be processed using a desulphurization unit of an existing refinery with essential modification of the catalyst bed [6]. Organic liquid fraction (OLF) is obtained when the bio-crude is distilled at different temperature ranges, producing a product of paraffin hydrocarbon with high cetane number and high calorific value. The fuels also have sulfur of less than 5 mg/kg, aromatic content of less than 1 %, nitrogen of less than 2 mg/kg, and of olefin less than 0.2 % double bond-containing components [7, 8].

The catalyst used in this study enhances the reaction mechanism rate for the conversion of triglycerides to produce a high yield of hydrocarbon products [9]. This can be achieved by removing heteroatom elements, breaking down the unsaturated molecules, and removing the acidity component. Micro-physical properties and ionic composition of a catalyst affect the activity for the production of HDRD. CFA reinforced with silica oxide ( $\text{SiO}_2$ ) was used as a biowaste catalyst for the hydroprocessing of triglycerides [10].

Singh *et al.* [4] reported that CaO wt% is the highest elemental composition of BBTPPFS catalyst. Therefore, adding more CaO (wt%) in BBTPFS catalysts could increase biofuel yield and its properties.  $\text{SiO}_2$  is close to CaO in the elemental composition of BBTPPFS with a weight percentage of 27.87 %.  $\text{SiO}_2$  can be found in red mud, fly ash and eggshell, etc.  $\text{SiO}_2$ , also known as silica, is a natural compound made of two of the earth's most abundant materials: silicon (Si) and oxygen ( $\text{O}_2$ ).  $\text{SiO}_2$  is often known in the form of quartz. The earth's crust is 59 % silica. Therefore, this novel study investigated the viability of hydro-processing a hybridized used cooking oil (UCO) by mixing  $\text{SiO}_2$  and freshly prepared CFA catalysts appropriately to explore the effect on the yield and characteristics of biofuel and their corresponding organic liquid fractions products. This was analyzed as per American Society of Testing and Materials (ASTM) standards. Locally sourced catalyst and UCO resources can be adopted for the production of HDRD which was the motivation of this study. This work aimed to produce biofuel at the range of  $\text{C}_{15}\text{-C}_{18}$  using hybridized UCO and locally sourced

catalyst generated from biowaste. At the same time, the scope was limited to reinforcing SiO<sub>2</sub> into BBTPPFS to obtain a higher yield of HDRD products. There is an increase in the global consumption rate of vegetable oil in recent times, as shown in Fig. 8.1. This is evidence of the availability and sustainability of UCO worldwide [17].

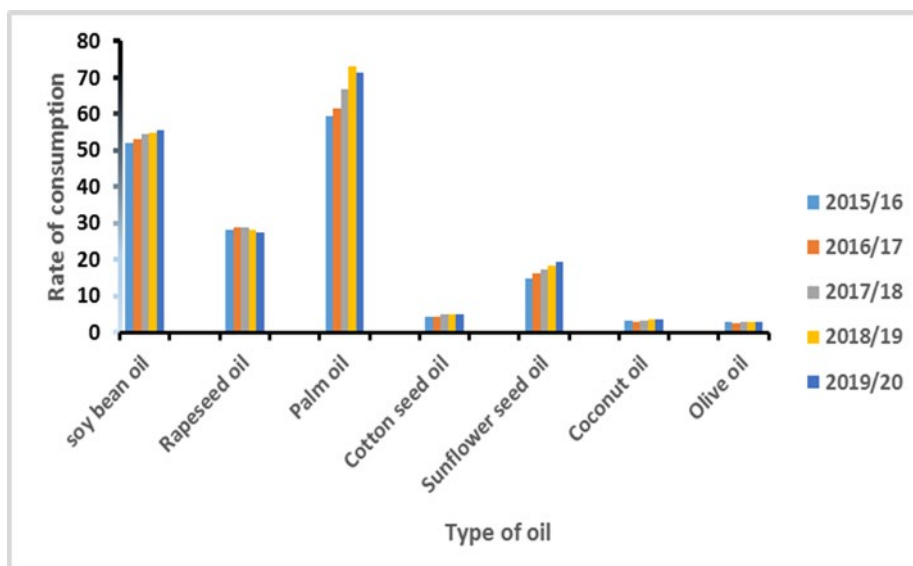


Figure 1: Global consumption by oil type 2015/16 to 2019/2020

## 1.2 Used cooking oils as potential feedstock

The global consumption rate of vegetable oil shows a tremendous increase in population, as shown in Fig.1 and Table 1 [11]. Fig.8.1 is evidence of cost-benefit, availability, and sustainability of used cooking oil across the globe.

Table 1 Annual consumption of vegetable oil per capita

Country	Population/ 2020	Consumption(kt)	Per capita Food
United State	331,002,651	14684	39.2
North America	368,869,647	48824	25.8
Canada	37,742,154	1108	26.5
Europe	447,710,000	27617	23.2
Australia	25,694,393	641	26.6
Japan	126,027,215	2236	17.6
South Africa	59,308,690	1246	22.0
Malaysia	32,365,999	4335	24.8
Turkey	85,384,918	2283	30.0
Russia	146,007,035	3387	23.7
Mexico	130,501,308	2382	19.5



Brazil	214,310,027	6718	21.1
Iran	83,992,949	1739	19.6
Indian	1,380,004,385	18885	14.8
Pakistan	220,892,340	3762	19.8
Saudi Arabian	34,813,871	512	17.6
Indonesia	273,523,651	10814	19.6
Argentina	45,195,774	3384	29.7
Algeria	43,851,044	62015.7	21.8
Korea	51,269,185	1073	21.8
Egypt	102,334,404	1832	22.1

Canada consumes about 1108 metric kilotons of UCO per annum [12, 13]. About 600 000 tons of UCO have been collected annually from bakeries, takeaway outlets, and restaurants in South African [14, 15]. The UCO for this research was sourced from fast-food outlets used for frying chicken, sausage, fish and chips in South Africa.

The available source and sustainable feedstock for the production of HDRD are UCO [16]. The huge generation of UCO across the globe as reflected in Table 1 shows the sustainability of UCO resources when harnessed for production and commercialization of biofuel.

### 1.3 Biowaste catalyst

Scholars have studied several chemical agents to search for a catalyst that has the potential to produce biodiesel and HDRD. They found that the conversion of triglycerides depends on selecting a suitable catalyst with adequate properties to support the production. Choice of catalyst plays a vital role in the production processes and the hydrocarbon product during hydrogenation. The choice also depends on the reaction conditions, i.e., temperature, pressure, liquid space hour velocity (LSHV), and H<sub>2</sub> to oil (volume/volume) ratio [17].

Marker et al. [18] researched various catalysts that can drain out the water and produce hydrogen. Applications of commercial catalysts have been unsuccessful, setting back the commercialization of green diesel. Munoz et al. [19], Abdullah et al. [20], and Yao et al. [21] reported the utilization of a catalyst derived from biomass-based waste for hydrocarbon production, while Stanković et al. [22] and Yusup et al. [23] suggested various methods, technologies, benefits, and shortcomings of bio-based fly ash catalysts for biofuel production. Apart from the abundant and sustainable CFA resources in South Africa, the choice of biowaste catalyst for this research was to make the value chain green in the process of production and commercialization of biofuel. This research aimed to

investigate hydro-processed hybridized UCO being used to produce HDRD using two reinforced heterogeneous catalysts. This research also examined the effect of the addition of SiO<sub>2</sub> to CFA catalysts in varying proportions on the hydro-processing of hybridized UCO and explore the yield of biofuel and its properties. The motivation for this study was the use of biowaste and hybridized UCO to produce green diesel. The product was characterized as per ASTM/EN standards and compared with FAME and petrol-based diesel.

## **1.4 Materials and method**

The UCO samples were collected from three takeaway outlets in Durban, South Africa, just before disposal. The profile and chemical composition of UCO was analyzed, as shown in Table 1. All the chemicals used were of analytical reagent grade. The catalyst (SiO<sub>2</sub>) was procured from Lichro Chemical and Laboratory Supplies, Durban, South Africa, and CFA sourced from Eskom Lethado Power Station and calcinated in a muffle furnace at 550 °C for two hours. The chemical analysis of both the catalysts was conducted by means of the Brunauer-Emmett-Teller (BET) and spectroscopic analysis (FTIR).

### **1.4.1 BET Analysis**

Three samples consisting of 0.25 g were subjected to a Micromeritics ASAP 2460 device for analysis. Water was removed from the samples at a temperature of 100 °C under nitrogen gas for 24 hours. Then, the samples were allowed to cool gradually in a vacuum to make their surfaces and pores area open for close analysis. The surface area of the sample (m<sup>2</sup>/g) was determined by the BET method, while the pore size, total pore volume (cm<sup>3</sup>/g at standard temperature and pressure and average pore radius (Å), were estimated using the Barrett-Joyner-Halenda (BJH) method. BET analyses outcome showed that the pore volume, surface area, and pore area possess the potential green catalyst to mild crack UCO into green diesel.

### **1.4.2 Spectroscopic analysis**

A spectroscope (Perkin Elmer Co., USA, model 15.011) was used for the analysis of the samples to obtain the absorption spectrum, the dilution and homogenization of the samples. Discs with 12.7 mm ID and ≈ 1 mm thickness were subjected to 10 tons manual pressure for less than 60 s.

The measurement of spectra between 300 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> was conducted and recorded on a spectrometer of model system 1000 FTIR with a resolution of 2.0 cm<sup>-1</sup>. The utilization of CFA as a potential's catalyst for conversion of UCO into HDRD depended on the location and peaks from the sample spectra.

### 1.4.3 Production of biofuel

The production of HDRD from UCO was carried out in a Parr reactor using a mechanical stirrer, pressure and temperature sensor heating unit, and reading gauge. For this research work, a biowaste catalyst was used after being pulverized and calcinated in a muffle furnace at 550 °C. The novelty of this work was the in-situ hybridization of the feedstock, which comprised waste sunflower oil for frying chicken (WSF<sub>C</sub>), waste palm oil for frying fish and chips (WPO<sub>FC</sub>), and waste palm oil for frying sausages and chips (WPO<sub>SC</sub>). Hybridization of feedstocks provides a straightforward, easy, cost-effective, and innovative way of adjusting and enhancing the physicochemical properties, thermal and spectroscopic behaviour of feedstock to enhance the suitability for biofuel production. The UCO sourced from the restaurants were blended in different proportions to obtain a new feedstock and analysed for properties determination with the results showing good properties for hydrogenation. The hybridization of UCO was described in the authors' previous work [24]. The hydrocarbon production was performed by introducing 300 ml of oil at 380 °C, with 5 MPa initial hydrogen pressure and 90 min reaction time using the catalysts. The reaction parameters were kept constant for every reaction. The reactor was allowed to cool at room temperature after the completion of the hydro-processing. After this, the total product is collected. The ratio of the mass of bio-crude obtained after separating the catalyst particle to the volume of feedstock introduced to the reactor was estimated.

The conversion of the products can be calculated by applying Equation 1:

$$\text{Conversion (\%)} = \frac{\text{Feed(temp.)} - \text{Product(temp.)}}{\text{Feed(temp.)}} * 100 \quad [25] \quad (1)$$

where Feed(temp) and Product(temp) are the weight percent of the feed and product, respectively, which depend on the boiling point of the temperature.

Applying Equation 2 to determine the diesel selectivity:

$$\text{Diesel selectivity (\%)} = \frac{\text{Product}(\Delta\text{temp.}) - \text{Feed}(\Delta\text{temp.})}{\text{Feed(temp.)} - \text{Product(temp.)}} * 100 \quad [25] \quad (2)$$



**Table 2: Catalyst effect on biofuel yield**

Parameter catalysts	The volume of used cooking oil (%)	Temp (°C)	H <sub>2</sub> pressure (MPa)	Catalyst (g)	Catalyst (wt%)	Time (min)	Water loss (%vol)	Total yield (%vol)
SiO <sub>2</sub>	300	380	5	40	3	90	8.15	67.85
CFA	300	380	5	40	3	90	7.20	67.20
SiO <sub>2</sub> + CFA	300	380	5	40	3	90	6.85	69.15

Table 2 shows the effect of catalysts on the oil yield and the parameter for hydro processing of UCO. From the table it is evident that the highest product of 69.15% volume was obtained from SiO<sub>2</sub>+CFA<sub>E</sub> catalyst, while 67.85% and 67.20 % yield were obtained from SiO<sub>2</sub>, and CFA<sub>E</sub> respectively. The char of 9 % volume and 8 % volume of the feedstock volume charged into the reactor was obtained.

### 1.5 Result and discussion

The hydroprocessing of hybridized UCO using heterogenous catalyst (CFA reinforced SiO<sub>2</sub>) under the reaction conditions provided in Fig. 3 was done. The authors' previous work reported the preparation protocol and the in-situ hybridization of UCO using this novel feedstock [26]. The optimal catalyst, feedstock, and operating parameters were employed in a Parr reactor to produce HDRD. The chemical transformation that occurs during hydro processing in a reactor is hydrocracking, hydrodeoxygenation, isomerization, etc. The bio-crude is separated and fractionated to obtain green diesel while the residual fuel is collected at the base of the fractional distillation column. The water and gas formed during the hydrocracking process is evidence that oxygen is removed from the feedstock in the form of H<sub>2</sub>O, CO<sub>2</sub> and CO.



Table 1 shows the physicochemical properties of UCO. The fatty acid composition makes them viable as a potential feedstock for the production of green diesel. The available source and sustainable feedstock for the production of HDRD are UCO [18]. This feedstock was adopted for this research work.

**Table 3: The physicochemical properties of used cooking oil**

Properties	Experimental Value	Standard Value	Method used	Reference
Acid value (Mg of KOH/gm)	2.48	3.0 <sub>max</sub>	AOCS Cd3d-63	[27]
Density @ 20 °C (Kg/m <sup>3</sup> )	919.7	923	ASTM D4052	[28]
Iodine value (cg/g)	51.5	100 <sub>max</sub>	AOCS Cd 1-25	[27]
pH value	6.52	7.00	AOCS	[28]
Kinematics viscosity @ 40 °C	36.14	43.52	ASTM D446-12	[28]
Saponification value KOH/g	196.2	195 <sub>max</sub>	AOCS Cd3d-63	[27]
Heating value MJ/kg	41.12		IS:1359-1959	
Fatty acid composition of UCO				
Palmitic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	0.36		
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	0.8		
Stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	—		
Caprylic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	—		
Linoleic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.10		
Myristic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	—		
Linoleic acid	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	4.5		
Elemental composition (wt%)				
Carbon		75		
Hydrogen		12,4		
Nitrogen		0.20		
Oxygen		10.90		

### 1.5.1 BET analysis

The BET analysis on surface area, pore volume, pore size, external surface area, average pore radius, micropore volume, and micropore area are presented Table 4. The catalyst such as surface area, pore volume external surface area, and pore volume of CFA were significantly increased when SiO<sub>2</sub> with the values of 0.5928 m<sup>2</sup>/g, 0.8611 m<sup>2</sup>/g, and 0.00532 cm<sup>3</sup>/g is added to CFA with the value 35.1102 m<sup>2</sup>/g, 32.5753 m<sup>2</sup>/g, and 0.1281 cm<sup>3</sup>/g respectively. The addition of SiO<sub>2</sub> caused a reduction in the value of average pore radius in the mesoporous range as a result of impurities. Hence, there was an increase in the micropore volume of SiO<sub>2</sub> from -0.000121 cm<sup>3</sup>/g to 0.000582 cm<sup>3</sup>/g. Vargas et al. [29] reported a value of 9.028 m<sup>2</sup>/g BET surface area and pore volume of 0.01055 cm<sup>3</sup>/g for biomass fly ash.

The incremental changes that occur in pore volume caused the formation of new mesopores, which can also be formed by the addition of a support catalyst [30]. The BET surface area is a principal

physical property that controls the catalytic activity of a solid particle; higher surface area of a catalyst enhances better catalytic activity and more interactions with the reactants [31]. The high BET surface area of 35.1102 m<sup>2</sup>/g will support the addition of SiO<sub>2</sub> and CFA's catalytic activity for the adsorption and desorption of triglycerides, glycerine, and HDRD [32]. The results of the BET analysis of the catalyst samples has shown their acceptability as a low-cost and biowaste catalyst for hydrogenation of UCO into HDRD [33].

The addition of SiO<sub>2</sub> to CFA was used for the hydroprocessing of hybridized UCO because of the excellent thermal, spectroscopic, composition, and surface area of the coal fly ash. In addition, the biowaste catalyst possesses the hydrocracking potential to convert the feedstock to HDRD range of C<sub>15</sub>-C<sub>18</sub>.

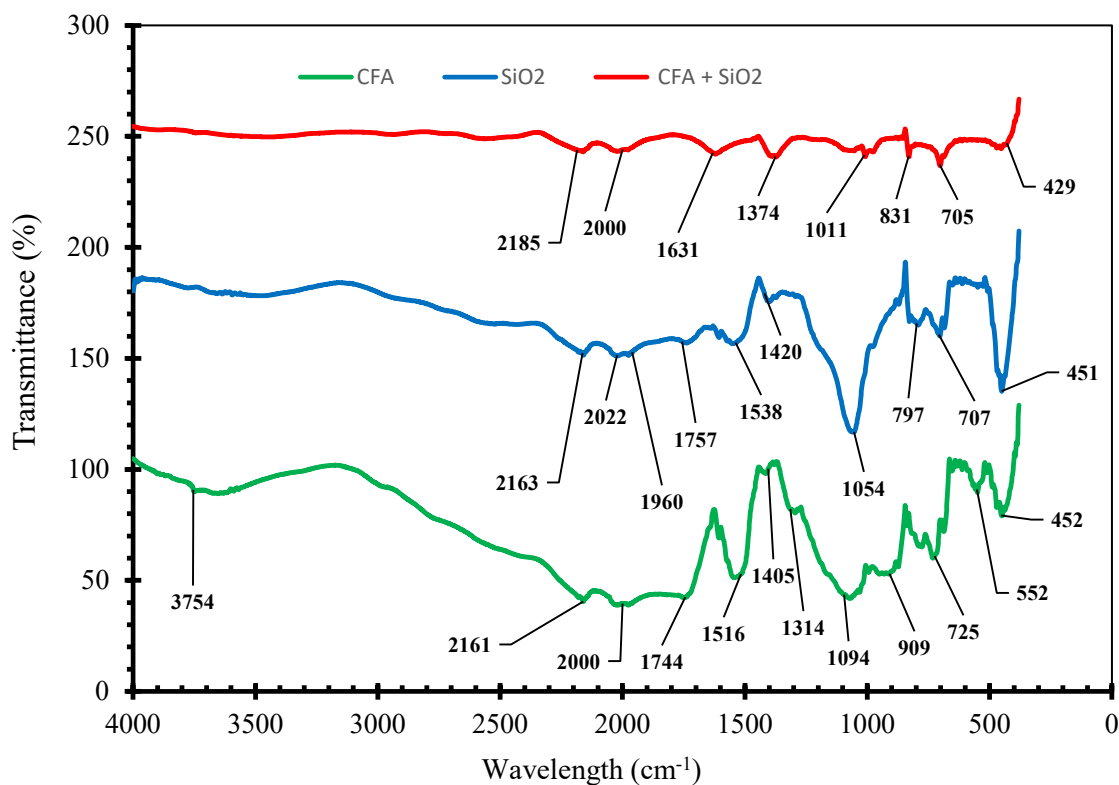
**Table 4: Properties of heterogenous catalyst for hydrogenation**

Properties	Unit	SiO <sub>2</sub>	CFA	SiO <sub>2</sub> +CFA
BET surface area	m <sup>2</sup> /g	0.5928	317.2404	35.1102
External surface area	m <sup>2</sup> /g	0.8611	279.1870	32.5753
Average pore radius	Å	179.68	70.72	72.98
Pore volume	cm <sup>3</sup> /g	0.005326	1.1218	0.1281
Micropore volume	cm <sup>3</sup> /g	-0.000121	0.014827	0.000852
Micropore area	m <sup>2</sup> /g	*NR	38.0533	2.5349

### 1.5.2 FTIR analysis

The FTIR spectra analysis of the biofuel obtained from the SiO<sub>2</sub> + CFA catalyst is shown in Fig. 3. The FTIR result shows that the trend of the wavelength bands was associated with the chemical functions of biofuel such as hydrocarbon and organic fatty acids from the thermo-chemical conversion of hybridized UCO into HDRD. The wavelength peak at 1010 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> have the potentials of the peculiar bands for tested hydrogenation catalysts [34]. FTIR spectroscopy confirms C<sub>11</sub>-C<sub>18</sub> as the significant hydrocarbon, and other compounds like organic acids, aldehydes, and ketones are oxygenated compounds. Apart from this, the density (carbon, oxygen, hydrogen, sulfur, and nitrogen) contained in the biofuel reveals the high value of hydrogen and oxygen, which support UCO conversion into hydrocarbons [4].

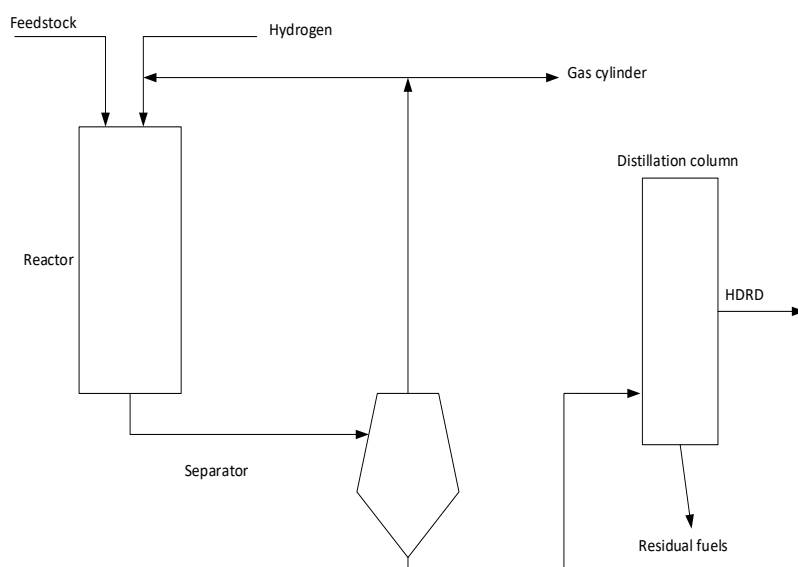




**Figure 2: FTIR Spectra of biofuel**

The optimal catalyst, feedstock, and operating parameters were employed to produce HDRD in a reactor. The chemical transformation that occurs during hydroprocessing in a reactor is hydrocracking, hydrodeoxygenation, isomerization, etc. The bio-crude is separated and fractionated to obtain green diesel while the residual fuel is collected at the base of the fractional distillation column.

HDRD containing the highest percentage yield of 67.15 % volume, and volume the residue is 32.85 % obtained and separated from the remaining hydrocarbon. The optimal yield outcome obtained can be traced to the high percentage of silica oxide in CFA that enhanced the catalytic activities for the production of HDRD.



**Figure 3: Flow chart of conversion of UCO to HDRD**

**Table 5: Properties of biofuel produced by catalyst**

Properties	Unit	SiO <sub>2</sub> +CFA value	SiO <sub>2</sub> value	CFA value
Density	g/mL	0.832	0.848	0.845
Kinematic viscosity	cSt	3.50-7	2.9	2.8
Cetane number	-	>90	85	87
Flash point	°C	85	81	83
Net heating value	MJ/kg	54	45	47
Water	%vol.	0	0	0
Calorific value	MJ/Kg	49.85	46.23	45.73

The HDRD produced had superior properties. The biofuel was free from impurities such as sulfur, oxygen, nitrogen, and water compared with conventional petroleum-based fuel. The net heating value of petrol diesel is 42-43 MJ/kg while HDRD is 54 MJ/Kg. The cetane number of the biofuel was greater than 90, while petroleum diesel is less than 60. In addition, the oxidation stability of HDRD is very high and has a nominal acid value. The flashpoint of HDRD is significantly higher, and the paraffinic compound of HDRD withstands long-term storage as biodiesel. Other contaminants like sulfur, nitrogen and aromatic contents are very low compared to petrol-diesel. The cold flow properties of HDRD are better when compared with petrol-based diesel [4].

## **1.6 Conclusion**

HDRD obtained by hydro-processed hybridized UCO using biowaste as a catalyst is feasible. In this research, the novel feedstock and the mixture of  $\text{SiO}_2$  with CFA used to produce HDRD resulted in a high yield of 69.15 % volume with excellent properties. Apart from the benefit of low cost, eco-friendly, availability, and sustainability of the production resources, it is highly effective for hydrogenation of UCO. The FTIR analysis of the biofuel revealed that the main product found in the optimal yield of HDRD are paraffinic hydrocarbons. Furthermore, HDRD has excellent properties (high cetane number, oxidation stability, kinematic viscosity, zero water, and zero acid value) compared to biodiesel and petroleum-based diesel. The value chain of locally sourced catalyst and UCO, which form the significant resources for the production of HDRD, will enhance the commercialization of HDRD.

## **1.7 Conflict of interest**

No conflict of interest.

## **1.8 Acknowledgment**

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## CHAPTER 9: CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

### 9.1 Conclusion

The rapid growth witnessed in socio-economic activities, industrialization, commercialization, and standard of living has driven the quest for an alternative and sustainable fuel to fossil fuel to power CI engines. In this study, the hydro-processing technologies for the production of HDRD have been developed. Utilization of feedstock and catalyst derived from waste has been explored for hydrogenation into HDRD. In this effort, experimental analysis of the product was performed for properties determination and prediction, engine performance and emission characteristic of a CI engine fueled by green diesel. The conclusions drawn from the thesis are stated below.

- Hybridization of UCO feedstocks offers great potential in terms of physicochemical, thermal, and spectroscopic properties that confirm its suitability for conversion to HDRD.
- In-situ hybridization has no significant effect on the acid value, cetane index, and HHV of the feedstock. However, the density, kinematic viscosity, and saponification value was found to reduce with hybridization, while the iodine value of the hybridized feedstock was found to be higher than the iodine value of the individual parent feedstock.
- CFA is a waste generated from coal fired power plants. There is increased interest in the application of CFA as a green, eco-friendly, readily available, and low-cost heterogeneous catalyst as a replacement for expensive commercial catalysts. Addition of SiO<sub>2</sub> to CFA improved the thermal, spectroscopy, composition, and surface area of the powder. This increased its potential as a viable catalyst for green diesel production.
- The possibilities of conversion of waste to heterogeneous catalyst is established; BBTPPFS and support catalyst has the capability of mild-cracking UCO to obtain good green diesel yield.
- South Africa can overcome the challenges of commercialization of biofuel production if feedstock and catalysts derived from waste are harnessed using hydrogenation technologies to obtain HDRD with superior properties.
- The choice of locally sourced feedstock and heterogeneous catalyst for hydro-processing allows for sustainable, easy to use, and environmentally friendly production of HDRD.
- The composition range of the green diesel is C<sub>15</sub>-C<sub>18</sub>
- The biowaste and feedstock sourced locally will enhanced the commercialization of green diesel

## 9.2 Recommendations for future work

The demand for biofuel with superior properties, combustion efficiency, availability, and environmentally sustainability able to power CI engines is on the increase. The future challenges for the energy sector are to improve the quality of the product and find sustainable feedstocks with a lower carbon footprint. Hydrogenation requires more research to discover new technologies to treat waste and residues to obtain hydrogen, which will make the value chain completely green. While the potential of a local catalyst and UCO has been demonstrated, a critical study of the catalyst activity has to be undertaken.

More investigation is required on lab-scale reactor experiments that adapt waste cooking oil and a local catalyst for optimal production of HDRD. In addition, the challenge of obtaining a cheap and reliable source of hydrogen, going forward, must be tackled before the potential of this option can be realised.

## APPENDICES

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### APPENDIX I: EDITING CERTIFICATES

#### Appendix A: Front page, Introduction and Conclusion

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I confirm that I have edited the selected material from this thesis and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many master's degree dissertations during that period.

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---

### **EDITING CERTIFICATE**

Re: **Josiah Pelemo**

Journal article: **In-situ Hybridization of Waste Palm Oil: A Physicochemical, Thermal, and Spectroscopic Analysis**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years.

Dr Richard Steele

**13 October 2020**

*per email*



## Appendix E: Chapter 5

### **DR RICHARD STEELE**

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### **EDITING CERTIFICATE**

**Re: Josiah Pelemo**

**Journal article: Development and characterization of coal fly ash reinforced with silica oxide for catalytic green diesel production**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many master's degree dissertations during that period.

Dr Richard Steele

**05 April 2021**

*per email*

**DR RICHARD STEELE**

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**EDITING CERTIFICATE**

**Re: Josiah Pelemo**

For editing journal article: **A STUDY TO EVALUATE OPTIMAL CATALYST PROPERTIES SOURCED FROM BIOWASTE FOR HYDROPROCESSING OF USED COOKING OIL INTO GREEN DIESEL**

I confirm that I have edited this article and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many master's degree dissertations during that period.

Dr Richard Steele

**28 June 2021**

*per email*

## Appendix G: Chapter 7

### DR RICHARD STEELE

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### EDITING CERTIFICATE

**Re: Josiah Pelemo**

**For editing journal article: Hydro-Processing of Hybridized Used Cooking Oil into Hydrogenation Derived Renewable Diesel Using Local Heterogeneous Catalysts**

I confirm that I have edited the selected material from this thesis and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many master's degree dissertations during that period.

Dr Richard Steele

**31 August 2021**

*per email*



## Appendix H: Chapter 8

### **DR RICHARD STEELE**

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### **EDITING CERTIFICATE**

Re: **Josiah Pelemo**

For editing journal article: **Hydro-Processing of Hybridized Used Cooking Oil into Hydrogenation Derived Renewable Diesel Using Local Heterogeneous Catalysts**

I confirm that I have edited the selected material from this thesis and the references for clarity, language and layout. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many master's degree dissertations during that period.

Dr Richard Steele  
**31 August 2021**  
*per email*

## **DR RICHARD STEELE**

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### **EDITING CERTIFICATE**

Re: **Josiah Pelemo**

For checking final version of PhD: **STUDYING THE FEASIBILITY OF  
HYDROPROCESSING USED COOKING OIL INTO HYDROGENATION  
DERIVED RENEWABLE DIESEL FROM LOCAL FEEDSTOCK AND  
CATALYST**

I confirm that I have checked the text and the formatting and layout of this thesis and the references. I returned the document to the author with track changes so correct implementation of the changes and clarifications requested in the text and references is the responsibility of the author. I am a freelance editor specialising in proofreading and editing academic documents. My original tertiary degree which I obtained at the University of Cape Town was a B.A. with English as a major and I went on to complete an H.D.E. (P.G.) Sec. with English as my teaching subject. I obtained a distinction for my M.Tech. dissertation in the Department of Homoeopathy at Technikon Natal in 1999 (now the Durban University of Technology). I was a part-time lecturer in the Department of Homoeopathy at the Durban University of Technology for 13 years and supervised many master's degree dissertations during that period.

Dr Richard Steele

**31 August 2021**

*per email*

## **APPENDIX II: ACCEPTANCE LETTERS**



Gmail

International Research Publication House <irpeditor@gmail.com>

## Paper Code: 19379-IJERT

International Research Publication House <irpeditor@gmail.com>  
To: Freddie Inambao <Inambaof@ukzn.ac.za>

Wed, Feb 12, 2020 at 5:53 PM

Dear Dr. Freddie Inambao,

Paper Code: 19379-IJERT

We are very pleased to inform you that your paper "Potential of Used Cooking Oil as Feedstock for Hydroprocessing into Hydrogenation Derived Renewable Diesel: A Review", is accepted by our Editor-in-chief for our journal, International Journal of Engineering Research and Technology (IJERT) ISSN 09743154, scopus indexed.

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Google+: [www.google.com/+irphouse](http://www.google.com/+irphouse)

For any query please **feel free to write back**.

—

Thanking you and looking forward to hear you soon,  
With warm regards,

Mar 02, 2021

To

**Professor Freddie L. Inambao,**  
UNIVERSITY OF KWAZULU NATAL  
PRIVATE BAG X54001  
DURBAN  
4000  
SOUTH AFRICA  
VAT NUMBER \_ 4860209305

**Dear Professor Freddie L. Inambao,**

Greetings.


**Subject:** Acceptance of research paper for publication in our International Journal

It's our pleasure to inform you that, after the peer review of your paper, **Titled: "HYBRIDIZATION OF WASTE COOKING OIL: AN INNOVATIVE TECHNIQUE FOR IMPROVED FEEDSTOCK"** authored by "Josiah Pelemo, Omojola Awogbemi, Freddie Inambao & Emmanuel I. Onuh" submitted to us for an evaluation by you on 24<sup>th</sup> Feb 2021 has been accepted by the Review Board for publishing in **International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)** Journal with **ISSN (Print): 2249 -6890; ISSN (Online): 2249-8001; Impact Factor (JCC):9.6246; NAAS Rating: 3.11; IBI Factor: 3.2; ICV 2015:60.6**

Again, thank you for working with TRANSSTELLAR. We believe that our collaboration will help to accelerate the global knowledge creation and sharing one step further. TRANSSTELLAR looks forward to your final publication package. Please do not hesitate to contact us if you have any further questions.

Thanking you,

Yours sincerely,

For Transstellar Journal Publications  
& Research Consultancy Pvt. Ltd.  
  
Authorized Signatory

Associate Editor

IJPRC Pvt Ltd.

Apr 09, 2021

To

**Professor Freddie Inambao**  
University of Kwazulu Natal  
Private Bag X54001  
Durban  
4000  
South Africa  
Vat Number – 4860209305

**Dear Scholar. Professor Freddie Inambao,**

**Subject:** Acceptance of research paper for publication in our International Journal

Greetings.

It's our pleasure to inform you that, after the peer review of your paper, Titled: "DEVELOPMENT AND CHARACTERIZATION OF COAL FLY ASH REINFORCED WITH SILICA OXIDE FOR CATALYTIC GREEN DIESEL PRODUCTION" authored by " Josiah Pelemo, Omojola Awogbemi , Freddie Inambao & Emmanuel I. Onuh " submitted to us for an evaluation by you on Apr 08, 2021 has been provisionally accepted by the Review Board for publishing in "International Journal of Mechanical and Production Engineering Research and Development (IJMPERD) journal with ISSN (Print): 2249-6890; ISSN (Online): 2249-8001; Impact Factor (JCC): 9.6246; NAAS Rating: 3.11; IBI Factor: 3.2; ICV 2015:60.6.

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Thanking you,

Yours sincerely,

For Transstellar Journal Publications  
& Research Consultancy Pvt. Ltd.

Authorized Signatory

Associate Editor

TJPRC Pvt Ltd.



Jul 01, 2021

To

Professor Freddie Inambao  
University of Kwazulu Natal  
Private Bag X54001  
Durban  
4000  
South Africa  
Vat Number – 4860209305

Dear Scholar, Professor Freddie Inambao,

Subject: Acceptance of research paper for publication in our International Journal


Greetings.

It's our pleasure to inform you that, after the peer review of your paper, Titled: "A STUDY TO EVALUATE OPTIMAL CATALYST PROPERTIES SOURCED FROM BIOWASTE FOR HYDROPROCESSING OF USED COOKING OIL INTO GREEN DIESEL" authored by "Jostah Pelemo, Freddie Inambao, Emmanuel I. Onuh, Omojola Awogbemi " submitted to us for an evaluation by you on Jun 29, 2021 has been provisionally accepted by the Review Board for publishing in "International Journal of Mechanical and Production Engineering Research and Development (IJMPERD) journal with ISSN (Print): 2249-6890; ISSN (Online): 2249-8001; Impact Factor (JCC): 9.6246; NAAS Rating: 3.11; IBI Factor: 3.2; ICV 2015:60.6.

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Thanking you,

Yours sincerely,

For Transstellar Journal Publications  
& Research Consultancy Pvt. Ltd.  
  
Authorized Signatory

Associate Editor

TJPRC Pvt Ltd.

Sep 08, 2021

To

**Professor Freddie Inambao**

University of Kwazulu Natal

Private Bag X54001

Durban

4000

South Africa

Vat Number – 4860209305

**Dear Scholar. Professor Freddie Inambao,**

**Subject:** Acceptance of research paper for publication in our International Journal


Greetings.

It's our pleasure to inform you that, after the peer review of your paper, **Titled: "HYDRO-PROCESSING OF HYBRIDIZED USED COOKING OIL INTO HYDROGENATION DERIVED RENEWABLE DIESEL USING LOCAL HETEROGENEOUS CATALYSTS "** authored by "Josiah Pelemo, Professor Freddie Inambao & Emmanuel I. Onuh" submitted to us for an evaluation by you on Sep 06, 2021 has been provisionally accepted by the Review Board for publishing in "International Journal of Mechanical and Production Engineering Research and Development (IJMPERD) journal with ISSN (Print): 2249-6890; ISSN (Online): 2249-8001; Impact Factor (JCC): 9.6246; NAAS Rating: 3.11; IBI Factor: 3.2; ICV 2015:60.6.

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Thanking you,

Yours sincerely,

For Transstellar Journal Publications  
& Research Consultancy Pvt. Ltd.  
  
Associate Editor

Associate Editor

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### APPENDIX III: PHOTOGRAPHS



**Plate A: Oven for BBTPPFS, SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub> calcination**



**Plate B: Weighing of catalysts**





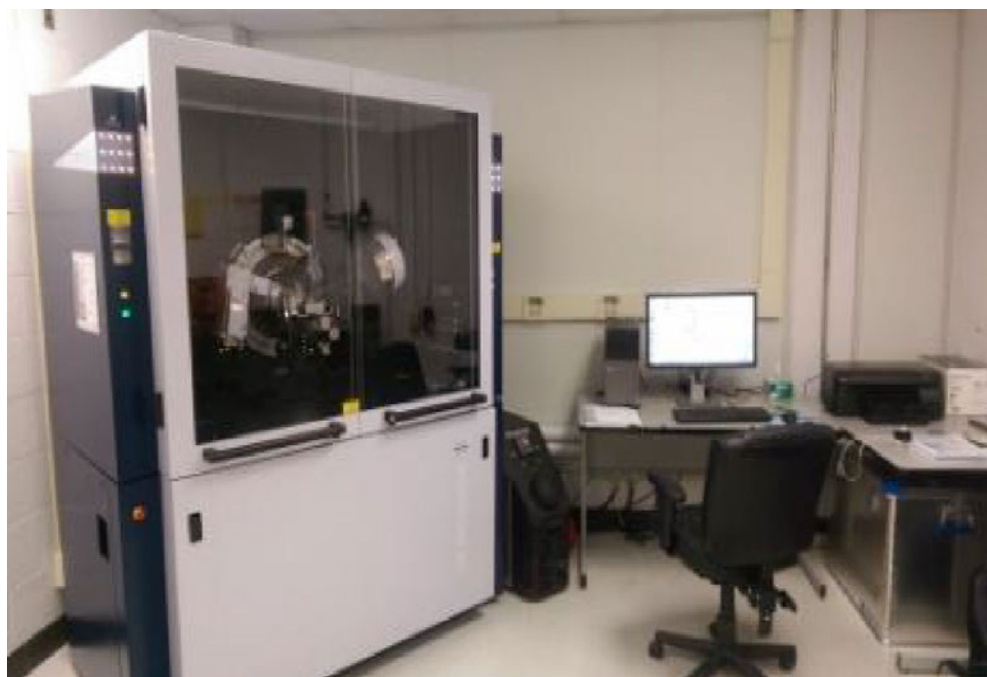
**Plate C: Simultaneous thermal analyser**



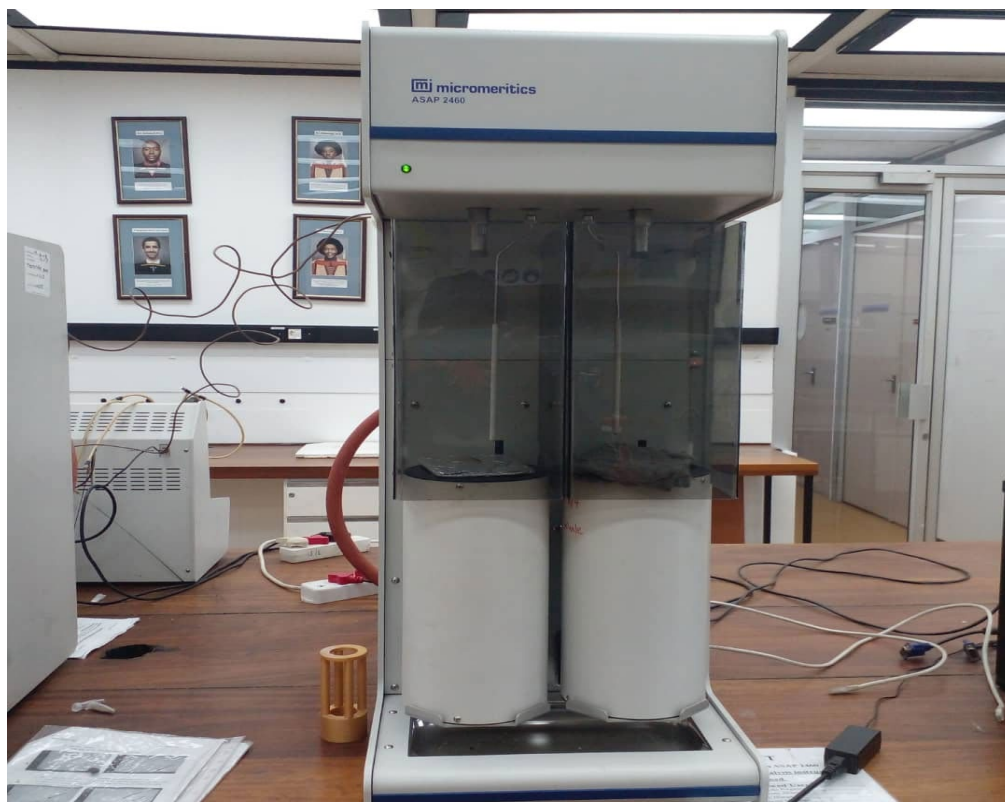
**Plate D: FT-IR spectrometer**



**Plate E: FEG-SEM**



**Plate F: X-Ray diffractometer**



**Plate G: Micromeritics ASAP 2460 for Brunauer-Emmett-Teller (BET) analysis**