INFLUENCE OF METAL CONTENTS ON THE CHARACTERISTICS OF BIODIESEL AND PETROL BLENDS AS TRANSPORTATION FUEL

by

Ines Simbi

Thesis submitted in fulfilment of the requirements for the Degree

of

Master of Engineering: Chemical Engineering

In the Faculty of Engineering & the Built Environment
at Cape Peninsula University of Technology

Cape Town
November, 2021

INFLUENCE OF METAL CONTENTS ON THE CHARACTERISTICS OF BIODIESEL AND PETROL BLENDS AS TRANSPORTATION FUEL

by

Ines Simbi

Supervised by

Dr. Otolorin Adelaja Osibote

Co-supervised by

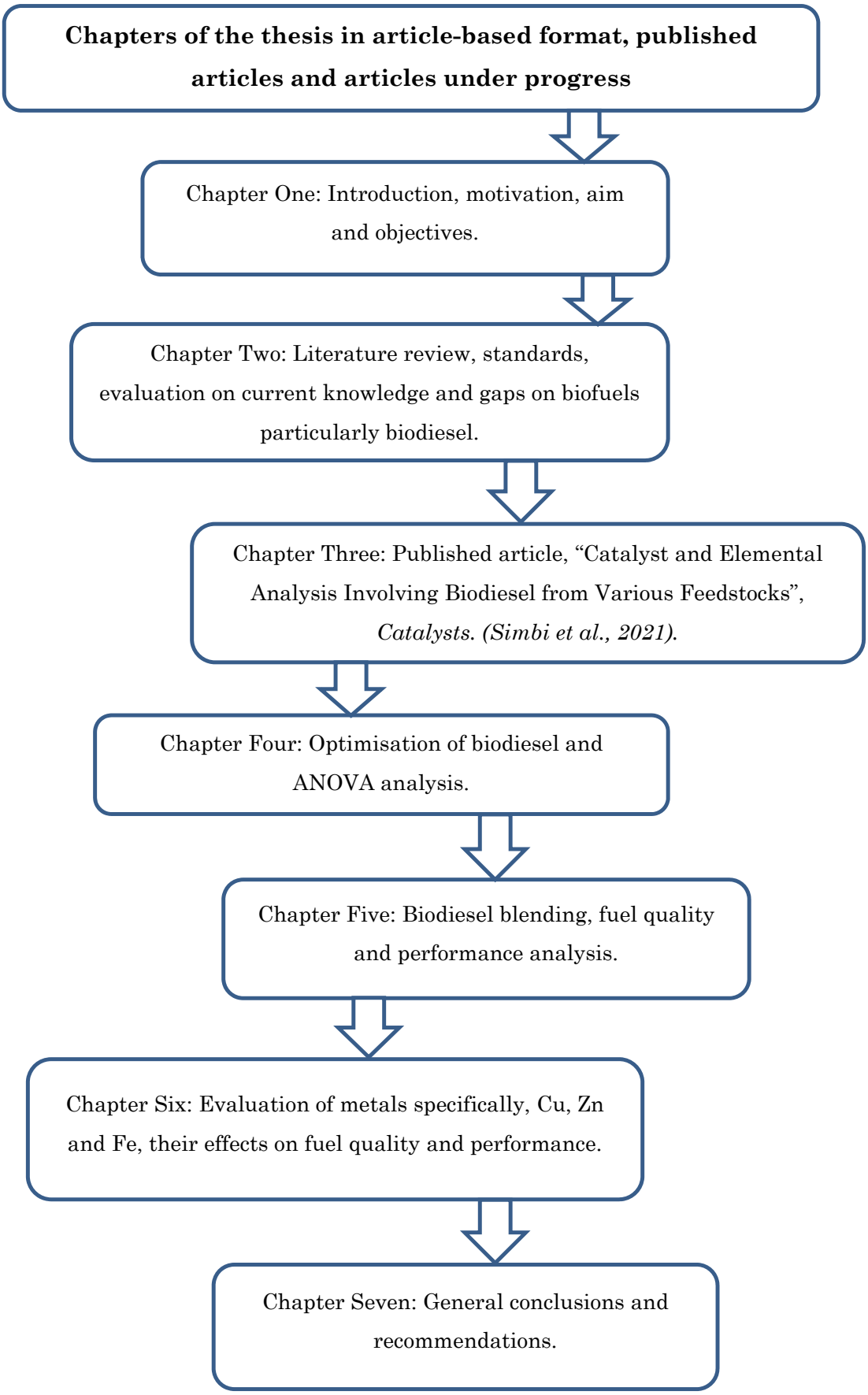
Prof. Oluwaseun Oyekola

Declaration

I, **Ines Simbi**, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signature……. **Date…01-11-2021……**

Chronology of the thesis



Executive Summary

The development of renewable energy seems to be the key player in addressing global climate crisis, caused by the global warming and climate change. To produce less emissions, new engine systems have been developed i.e., petrol compression ignition engines, which promise to produce less emissions, while generating high efficiency, and facilitating economic, social, and environmental sustainability. With the novelty of blending biodiesel with petrol, the challenges caused by biodiesel, and petrol individually, are lessened. Nevertheless, biodiesel's proneness to corrosion and degradation overtime, due to its chemical nature and storage conditions require continuous evaluation.

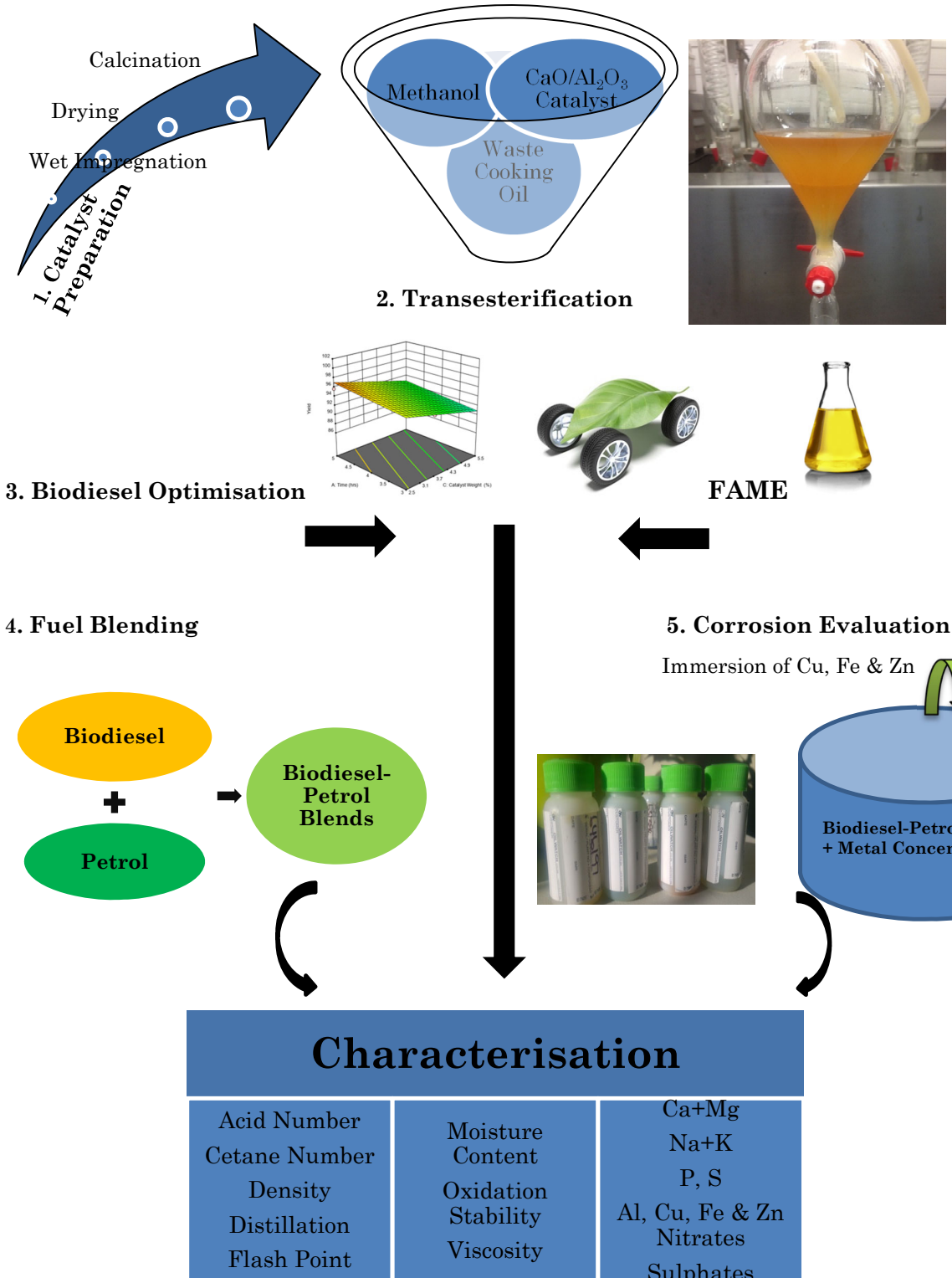
In the initial part of this study, the bi-functional catalyst (75%CaO/25%Al_2O_3) was synthesised via adjusted wet impregnation method. Results showed that, the catalyst presented enhanced activity, good porosity, and type H1 desorption hysteresis loop, with the high surface area and the pore diameter of 13.006 m^2/g, 24.0371 nm. The catalyst characterisations were conducted through BET, XRD, FTIR and SEM. The obtained bi-functional catalyst favoured the transesterification reaction of high free fatty acids feedstocks, with high yields of above 98% of methyl esters in biodiesel produced from waste sunflower oil. With the use of GC, fatty acids compositions of waste sunflower and waste palm oils were determined. The results also showed that the chemical composition of these different feedstocks i.e., degree of saturation, chain length, produced biodiesels with varying fuel properties. While sunflower biodiesel indicated better viscosity, palm biodiesel had excellent oxidation stability. Additionally, sunflower biodiesel met the international biodiesel specifications, with the exception of increased Ca concentration within the biodiesel, as a result of CaO/Al_2O_3 catalyst use in the biodiesel synthesis. This soft metal, along with Mg, K were introduced in the biodiesel through the synthesis process. While soil, seed, fertiliser, and contamination in the vegetable oils, may have contributed to the high content of P, and trivial Fe, Al, and Zn. The use of ICP - OES allowed for the determination of these metals.

To commercialise biodiesel, optimisation can be performed in reducing the cost and time necessary to produce biodiesel. After optimising sunflower biodiesel using response surface methodology and central composite design, the optimal reaction conditions observed were 5 h for reaction time, 60 °C for temperature and 2.5wt% for catalyst weight. With the use of a linear regression model that had 95 % confidence, the predicted and experimental yields were confirmed to be comparable.

In accessing fuel quality of biodiesel and the biodiesel-petrol blends, analysis of the viscosity, acidity, oxidation, density, volatility, moisture content, cetane number, metal contamination and particulate matter were conducted. Palm biodiesel had an increased thermal stability which rendered the palm biodiesel-petrol blended fuels superiority over the sunflower biodiesel-petrol blends. The blended fuels were observed to have enhanced fuel characteristics, better than pure petrol, increasing with increase in biodiesel content with 75% petrol 25% biodiesel (PB25) showing quality like petrodiesel. The addition of petrol into the biodiesel diminished the Ca concentrations, and obstructed moisture absorption, while improving low temperature fluidity loads, air-fuel mixing, and characteristics of good performance with high efficiency. Sunflower biodiesel-petrol blends were observed to be less acidic, have more energy content and subsequently more power. While palm biodiesel-petrol blends had more thermal stability and better cold start. Moreover, addition of petrol reduced particulate matter of sulphates.

In the final part of this study, the effect of Cu, Fe and Zn on the characteristics of fuel quality were evaluated for the purpose of the storage and transportation of biodiesel and the biodiesel-petrol blends. From the results obtained for pure biodiesel, the highest degradation was caused by exposure to Fe concentrations, while degradation in the biodiesel-petrol blends was caused by exposure to Cu. Sunflower biodiesel-petrol blends degraded in order of Fe > Cu > Zn, while palm biodiesel-petrol blends were degraded by Cu > Fe > Zn, and with Cu affecting pure palm biodiesel the most. Increase in oxidation instability for biodiesel-petrol blends was due to rise in Cu concentrations. The fuel quality was observed to decrease the most in palm biodiesel and palm biodiesel-petrol blends.

Graphical Abstract



Acknowledgement

I wish to convey my deepest gratitude to all the people that made enormous support in my pursuit of this degree successfully:

- First and foremost, to the almighty creator for his wisdom, strength, courage, and grace to undertake this task.
- To my supervisor, Dr. Otolorin Adelaja Osibote who has accepted me as her student and gave me relentless diligence, constructive and meticulous critique, great inspiration, and warm encouragements throughout this research.
- To my co-supervisor, Prof. Oluwaseun Oyekola for his fatherly love, guidance, prodigious patience, prompt communication and constant uplifting spirit throughout.
- To my assistant supervisor, Dr. Uyiosa Osagie Aigbe for his tremendous, continued mentorship, meticulous insights, instantaneous communication, and enthusiasm at every stage of this research.
- I am extremely grateful particularly for the laboratory assistance given by Dr. O. Oputu, Mrs H. Small, Mrs Z. Mthembu during my experimental phase.
- Thanks to my colleagues S. Chakawa, P. Dyosile L. Maina, J. Mulamba, J. Shabani, CPUT staff, non-teaching staff, A. Rabiu; for their constant courage, advice, and love in this process
- Special recognition to my family for their endless love, faith, and support. My parents, Emile and Christine Nzanana for their sincere encouragement, tremendous guidance, relentless prayers, sacrifice and care they provided throughout my entire life. My siblings, Iris, Boris, and Sandy-Lisa Nzanana for their enormous belief in me, giving me selfless love and constant good spirit.
- Special thanks to extended relatives and close friends especially J. Amoko, K. Chinyanga, M. Ilunga, J. Iradukunda, V. Iribagiza, M. Kanyange, B. Kumordzie, S. Madela, K. Mjuleni, D. Ndazivunnye, M. Nyangezi, S. Scheler, C. Umutesi.
- I am forever indebted to CPUT's Chemical Engineering, Analytical Chemistry and Food Science and Technology departments, and their staffs for all the necessary materials, resources and infrastructures provided for me to be able to carry on all experiments.
- Warm thanks to Suppa Oils, for donating all the waste oils used through-out this research, Oilwatch and iThemba Laboratories, Analytical laboratories at UCT under the Chemical Engineering Department. All these laboratories allowed me to carry out specific catalyst, biodiesel and biodiesel-petrol blends samples characterizations and emission tests.

- Finally, special thanks to the Albert Einstein German Academic Refugee Initiative (DAFI) under United Nations High Commissioner for Refugees (UNHCR) administrated by StudyTrust, and the Centre of Postgraduate Studies (CPGS) at CPUT for their financial support throughout my studies.

Dedication

I am dedicating this thesis to these departed souls, that even though they are no longer with me, their memories will continue to guide my life.

To my auntie, Maureen Elms for her angelic spirit and guidance throughout my life, her faith and credulity in every stage of my studies.

To my maternal grandmother, Dative Mukankubana, whom I've cherished from my childhood, I will never forget your constant teachings to wisdom, unconditional love and advice to always be a kind, humble and hard worker.

To my paternal grandfather, Canisius Munyabarame for his infinite love, prayers, protection and support.

I hope I have made you all proud.

May your souls rest in peace

Amen.

Table of Contents

List of Figures

List of Tables

List of Acronyms

ANOVA: Analysis of variance

ASTM: American Society for Testing and Material

BET: Brunauer Emmett Teller

BBLD: Barrels of Oil per Day

BOE: Barrels of Oil Equivalent

BXX: Biodiesel blends

CCD: Central Composition Design

CPUT: Cape Peninsula University of Technology

DoE: Design of experiment

EIA: Energy Information Administration

EN: European Standard

ETA-AAS: Electrothermal Atomization-Atomic Absorption Spectroscopy

FAME: fatty acid methyl esters

FBO: Final Boiling Point

FFA: free fatty acid

FPO: Fresh Palm Oil

FSO: Fresh Sunflower Oil

FTIR: Fourier Transform Infrared

GC: Gas Chromatography

IBP: Initial Boiling Point

ICP-MS: Inductively Coupled Plasma Mass Spectrometer

ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometer

ISO: International Organisation for Standardization

MES: Diglycerides

MB/D: Million Barrels per Day

MBOE/D: Million Barrels of Oil Equivalent per Day

MGS: Monoglycerides

OECD: Organization for Economic Co-operation and Development

OPEC: Organization of Petroleum Exporting Countries

OSI: Oxidation Stability Index

P-B100: Palm Biodiesel

P-PBXX: Palm Biodiesel-petrol blends

PPM: Parts Per Million

PLS: Partial Least Squares

R^2: Coefficient of determination

RSM: Response Surface Methodology

S-B100: Sunflower Biodiesel

SEM: Scanning Electron Microscope

S-PBXX: Sunflower Biodiesel-petrol blends

STP: Standard Temperature and Pressure

TAN: Total Acid Number

TGS: Triglycerides

WOs: Waste Oils

WCOs: Waste Cooking Oils

WVOs: Waste Vegetable Oils

WPO: Waste Palm Oil

WSO: Waste Sunflower Oil

XRD: X-ray Diffraction

Nomenclature

Symbol	Description	Unit
ρ	Density	kg/m^3
%	Percentage	
Q	British Thermal	Btu
T_c	Degree Celsius	^0C
T_F	Degree Fahrenheit	^0F
m	Mass	g
x	Magnification	
t	Time	h
HV	Accelerating Voltage for electrons	Kv
T_k	Degree Kelvin	^0K
	Relative emission Intensity	a. u
IP	Induction Period	h
P_d	Pore Diameter	nm
P_v	Pore Volume	cm^3/g
P	Pressure	kPa
Sg	BET surface area	m^2/g
V	Volume	mL
η	Kinematic Viscosity	mm^2/s
	Relative Pressure	p/p^o
	Resolution	µm
%T	Transmittance	
2θ	2Thetha	
wt%	Weight Percent	
λ	Wavelength	Å
WD	Working distance	mm
$CaCO_3$	Calcium carbonate	
CaO	Calcium Oxide	
Al_2O_3	Aluminium Oxide	
$Ca(OH)_2$	Calcium Hydroxide	
$(H_3O)_2Al_{22}O_3$	Oxonium Aluminium Oxide	
Cu	Copper	mg/L

Zn	Zinc	mg/L
Fe	Iron	mg/L
Na	Sodium	mg/L
Mg	Magnesium	mg/L
K	Potassium	mg/L
Ca	Calcium	mg/L
P	Phosphorus	mg/L
Al	Aluminium	mg/L
S	Sulfur	mg/L

Chapter 1: **Introduction**

"The use of vegetable oils for engine fuels may seem insignificant today but such oils may become, over time, as important as petroleum and the coal-tar products of the present time". ~ (Nieuwenhuis & Wells, 2009)

1.1 Background

OECD (2012) stated that global energy demand is on the rise as advanced industrialization and total population growth sways the resources of petroleum-based fuels. This has adverse effects on the environment and people, as found by Magsi (2015), and Muhammad et al., (2018). A more significant sustainable movement led by advancement towards environmental conservation, feasible economy and equity has prompted a search for substitutes of fossil fuels that are eco-friendly and viable energy generating (Carraretto et al., 2004). In this regard, the direct use of vegetable oil in diesel engine was initially attempted (Capuano et al., 2017), and owing to its high viscosity, acid composition, and free fatty acid (FFA) characteristics, it was reported unsuitable for such engine (Mondal et al., 2008). However, after modification of the viscosity by reduction through transesterification reaction, so-called "biodiesel fuel" can be produced (Elkady et al., 2015). Biodiesel (methyl or ethyl ester of fatty acid) produced from edible or non-edible oils of vegetable and animal fat was found to be excellent alternative fuels due to its renewability, and environmental friendliness, and reduction in greenhouse effect (Rocha & Corrêa, 2018). De Araújo et al., (2013), reported that burning of biodiesel will release 48% less carbon monoxide; 47% less particulate material and 67% less hydrocarbon. According to Nelson et al. (2007), the significant factors that affect biodiesel's cost are feedstock cost, plant size, raw materials, and the value of the glycerine by-product.

Awogbemi et al. (2019) reported that there is an annual vast amount of waste oils and animal fats that are generated by restaurants worldwide, with South Africa reaching up to 200000 tonnes, Canada 120 000 to 135 000 tonnes, USA 0.6 million tonnes, UK 700000 to 1000000 tonnes and European union 200000 tonnes. This creates a disposal issue as disposal methods used can contaminate environmental water resulting in pollution (Boadu et al., 2019). Thus, producing biodiesel from waste cooking oil rather than food-grade vegetable oil is one of the better ways to efficiently and economically minimize pollution (Kulkarni & Dalai, 2006). Biodiesel could be synthesised through chemical processes such as transesterification, thermal cracking or hydrotreating. According to Mathiyazhagan & Ganapathi, (2011), factors that affect transesterification reaction are molar ratio of alcohol and oil, catalyst type, alcohol type, time, temperature, and speed are critical. Additionally, when raw materials contain high content of FFA, they need to be pre-treated with an acid catalyst to form esters of FFA to eliminate saponification reaction (Allah & Alexandru, 2016).

Quality of oils is negatively affected by presence of heavy metals especially on taste and smell, they accelerate the process of the rancidification of oils and cause a threat to human health (Szyczewski et al., 2016). Their determination is very critical due to their harmful effect on vegetable oil's oxidative stability and plays a role in clogging vehicle fuel lines and leaving an undesirable residuum of metal oxides in engine's parts (Pillay et al., 2012). Therefore, every biodiesel needs to be carefully checked for quality before its commercialization, including the determination of several metallic species. It is believed that certain metals found in biodiesel are brought either through manufacture, storage or transport processes (Chaves et al., 2011; Isis et al., 2012). Those found in feedstocks are assumed to be delivered from the seeds or soil, while the mineral composition of the seeds varies according to the presence and availability of metals in the soil where the plant was grown, pesticides and fertilizers used to grow that plant (Chaves et al., 2010).

Metals in biodiesel result in many mechanical problems in the engine like corrosion of some parts and the deactivation of catalysts, which will lead to environmental harm (Sánchez et al., 2015). They can corrode rubber hosing and tubes in vehicles, also, they can leave unwanted deposits that could clog fuel lines. Therefore, quality control and qualitative assessment are needed. Trace metal emissions from the use of biodiesel could lead to air pollution (Pillay et al., 2012).

Several studies have reported the storage and oxidative stability of biodiesel synthesised from edible oils (Moser, 2009; Kumar et al., 2015 & Verma et al., 2016), but only recently few studies were conducted on effect of blending of biodiesel with petrol on the combustion and emission characteristics of that blend, in compression ignition engines (Adams et al., 2013; Putrasari & Lim, 2017; Das et al., 2018; Kanti et al., 2018; Thongchai & Lim, 2018; Vu & Lim, 2019; Zhang et al., 2019; Gad et al., 2020; & Zhong et al., 2021). Further, to the knowledge of the authors of this work, no research has yet been reported on the effect of metal contaminants on fuel the qualities and performances of non-edible biodiesel and petrol blend. Raw materials, process and storage of biodiesel production can influence engine performance and emissions (Kumar et al., 2018) due to the presence of metal contents from different feedstocks. In this research, metal contents in waste cooking oils, biodiesel produced from sunflower and palm waste oils using CaO/Al_2O_3 bi-functional catalyst, and their blends will be analyzed for their effect on quality and performance.

1.2 Problem Statement

There is a huge depletion of petroleum resources globally, causing an increase in the cost of petro-derived fuels as time passes and having negative impacts on our planet. A need

for cleaner alternative fuels has led to the exploration of a mixture of mono-alkyl esters derived from vegetable oils and animal fats as biodiesel. Biodiesel is well-positioned to be a replacement of some petroleum fuels. However, there are still issues regarding its lifespan, the effect of metal contents on its quality and performance. This research intends to evaluate the influence of metal contents on the characteristics of biodiesel and biodiesel-petrol blends as a transportation fuel.

1.3 Research Questions

In this study, the following questions will be used in analyzing results and drawing a conclusion.

a) What are the appropriate reaction conditions and the suitable catalyst required to produce biodiesel from waste cooking oils (WCOs)?
b) What are the metals found in WCOs and in the biodiesel and what are their origin? What are the effects of metal contents on characteristics of biodiesel fuels produced from solid bi-functional catalyst?
c) How does adding Fe, Cu and Zn metal contents in different concentrations affect the characteristics of the biodiesel-petrol blended fuels and engine performance?

1.4 Aim and Objectives

This study aims to investigate the influence of metal contents on biodiesel and its blends with petrol (PBXX fuel) and the suitability of biodiesel blends as a replacement for petrodiesel as transportation fuels, particularly as it relates to the retention of its fuel properties with time and storage in car engines. In realizing this aim, the objectives of the project are as follows:

a) Produce biodiesel from waste sunflower and waste palm cooking oils over CaO-Al_2O_3 catalyst.
b) Investigate the origin of metals in waste palm oil (WPO), waste sunflower oil (WSO) and their respective biodiesels.
c) Evaluate the effects of blending petrol with biodiesels produced, on their characteristics of fuels' quality and performance.
d) Explore the effects of adding Cu, Fe, Zn, metal contents in different mg/l on petrol and biodiesel blended fuels' characteristics and oxidation stability.

1.5 Significance of the Study

Petroleum-based fuel is at explosive growth, and as energy demand keeps increasing comprehensively, it causes massive concern to the environment and people. Consequentially, studies have been conducted globally for alternative energy production methods and focus on conservation of the environment, a feasible economy, and equity leading to biodiesel. The use of waste feedstocks such as waste cooking oil in the processing stage of biodiesel brings out improved production through cheaper raw materials and reduction in pollution. Bi-functional catalyst helps in fastening the process with its high activity and stability, improved yield percentages, and the reusability of the catalyst. The blending petrol and biodiesel improves fuel's quality, engine performance, thermal efficiency, and reduced emissions; thus, biodiesel's longer lifespan brings out engine protection.

1.6 Delineation of the Study

A detailed study on biodiesel production by transesterification using a bi-functional catalyst with methanol then testing the effect of metal contents on the quality of petrol and biodiesel blends as well as performance and efficiency. However, other methods of production of biodiesel, use of other alcohols and cost will not be investigated in this study

1.7 Thesis Outline

Chapter 1: Introduction

This chapter deals with the introduction to energy, fossil fuels and the focus on alternative fuels describing how waste oils can be used to our advantage in finding renewable fuel called biodiesel, bringing about sustainable energy. It also brings in present issues found on this fuel. This chapter includes a problem statement detailing the global energy issue in terms of declining petrodiesel and their effects on biodiesel and how this research will be conducted through more explanation through aim, objectives, and research questions.

Chapter 2: Literature Review

This chapter consists of a literature review that discusses what Fatty Acid Methyl Esters (FAME) is, the current methodology used in the production, and more details on waste oils, alcohols, and types of catalysts. It discusses the advantages, disadvantages and blending of this fuel with petrodiesel, ethanol and petrol. Necessary quality tests per

ASTM or EN standards are seen that describes the performance. It discusses the effect of storage and oxidation as well as metal contamination.

Chapter 3: Catalyst and Biodiesel Production

This chapter focuses on catalyst preparations and biodiesel production from both waste palm and waste sunflower oils. Methods and results on feedstocks, biodiesel and catalyst characterizations and detailed synthesis of fatty acid methyl ester (FAME) are seen.

Chapter 4: Sunflower Biodiesel Optimisation

This chapter focuses on the optimization of the biodiesel produced from waste sunflower oil. The optimisation was conducted using Design of Experiment (DoE) and effects of the different parameters on yield were analysed using ANOVA. The fuel quality of optimized biodiesel evaluated.

Chapter 5: Biodiesel-Petrol Blending

This chapter deals with blending biodiesel with petrol, discussion on blended fuel's characteristics with respect to quality, performance, elemental contents and other fuel properties are in more details. Methods used in the analyses were discussed.

Chapter 6: Metal Content Analysis in Biodiesel and its Blends

This chapter focuses on the effect of adding Cu, Fe, and Zn metal contents in the biodiesel and its blends, accessing quality and performance, especially oxidation stability and how it was conducted

Chapter 7: Conclusion and Recommendation

This chapter concludes the overall study and gives recommendations. It summarises all results obtained and how they impact the significance of the study, it concludes on how the research questions were answered and to what degree they were in achieving set objectives**.**

1.8 References

Adams, C.A., Loeper, P., Krieger, R., Andrie, M.J. & Foster, D.E. 2013. Effects of biodiesel – gasoline blends on gasoline direct-injection compression ignition (GCI) combustion. *Fuel*, 111: 784–790. http://dx.doi.org/10.1016/j.fuel.2013.04.074

Allah, F.U.M. & Alexandru, G. 2016. Waste cooking oil as source for renewable fuel in Romania. *IOP Conf. Ser.: Mater. Sci. Eng*, 147(1): 1–6. http://dx.doi.org/10.1088/1757-899X/147/1/012133

Boadu, K.O., Joel, O.F., Essumang, D.K. & Evbuomwan, B.O. 2019. A Review of Methods for Removal of Contaminants in Used Lubricating Oil. *Chemical Science International Journal*, 26(2): 1–11. http://dx.doi.org/10.9734/csji/2019/v26i430101

Capuano, D., Costa, M., Di Fraia, S., Massarotti, N. & Vanoli, L. 2017. Direct use of waste vegetable oil in internal combustion engines. *Renewable and Sustainable Energy Reviews*, 69: 759–770. http://dx.doi.org/10.1016/j.rser.2016.11.016

Carraretto, C., Macor, A., Mirandola, A., Stoppato, A. & Tonon, S. 2004. Biodiesel as alternative fuel: Experimental analysis and energetic evaluations. *Energy*, 29: 2195–2211. http://dx.doi.org/10.1016/j.energy.2004.03.042

Chaves, E.S., José, E., Araujo, R.G.O., Vladimir, J., Lúcia, V., Frescura, A. & Curtius, A.J. 2010. Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS. *Microchemical Journal*, 96(1): 71–76. http://dx.doi.org/10.1016/j.microc.2010.01.021

Chaves, E.S., Loos-vollebregt, M.T.C. De, Curtius, A.J. & Vanhaecke, F. 2011. Spectrochimica Acta Part B Determination of trace elements in biodiesel and vegetable oil by inductively coupled plasma optical emission spectrometry following alcohol dilution. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 66: 733–739. http://dx.doi.org/10.1016/j.sab.2011.09.006

Das, S.K., Kim, K. & Lim, O. 2018. Experimental study on non-vaporizing spray characteristics of biodiesel-blended gasoline fuel in a constant volume chamber. *Fuel Processing Technology*, 178: 322–335. https://doi.org/10.1016/j.fuproc.2018.05.009

Elkady, M.F., Zaatout, A. & Balbaa, O. 2015. Production of Biodiesel from Waste Vegetable Oil via KM Micromixer. *Journal of Chemistry*, 2015: 2–9. https://doi.org/10.1155/2015/630168

Gad, M.S., EL-Seesy, A.I., Radwan, A. & He, Z. 2020. Enhancing the combustion and emission parameters of a diesel engine fueled by waste cooking oil biodiesel and gasoline additives. *Fuel*, 269: 2–11. https://doi.org/10.1016/j.fuel.2020.117466

Isis, A., Oliveira, A.P. De, Magalhães, M.R.L. De & Villa, R.D. 2012. Determination of sodium and potassium in biodiesel by flame atomic emission spectrometry, with dissolution in ethanol as a single sample preparation step. *Fuel*, 93: 381–384. http://dx.doi.org/10.1016/j.fuel.2011.08.060

Jain, S. & Sharma, M.P. 2014. Effect of metal contents on oxidation stability of biodiesel/diesel blends. *Fuel*, 116: 14–18. http://dx.doi.org/10.1016/j.fuel.2013.07.104

Kanti, S., Kim, K. & Lim, O. 2018. Experimental study on non-vaporizing spray characteristics of biodiesel- blended gasoline fuel in a constant volume chamber. *Fuel Processing Technology*, 178: 322–335. https://doi.org/10.1016/j.fuproc.2018.05.009

Kulkarni, M.G. & Dalai, A.K. 2006. Waste cooking oil - An economical source for biodiesel: A review. *Industrial and Engineering Chemistry Research*, 45(9): 2901–2913. https://doi.org/10.1021/ie0510526

Kumar, A., Shukla, S.K. & Tierkey, J. V. 2015. A Review of Research and Policy on Using Different Biodiesel Oils as Fuel for C.I. Engine. *Energy Procedia*, 90: 292–304. http://dx.doi.org/10.1016/j.egypro.2016.11.197

Kumar, S., Yadav, K. & Dwivedi, G. 2018. Impact analysis of Oxidation Stability for Biodiesel & its Blends. *Materials Today: Proceedings*, 5(9): 19255–19261. https://doi.org/10.1016/j.matpr.2018.06.283

Magsi, H. 2015. Industrialization, Environment and Pollution. *Dipl. insight*, 7: 24-26. Available online: https://www.researchgate.net/publication/270899735 [accessed on 02 August 2021].

Mandolesi De Araújo, C.D., De Andrade, C.C., De Souza E Silva, E. & Dupas, F.A. 2013. Biodiesel production from used cooking oil: A review. *Renewable and Sustainable Energy Reviews*, 27: 445–452. http://dx.doi.org/10.1016/j.rser.2013.06.014

Mondal, P., Basu, M., & Balasubramanian, N. 2008. Direct use of vegetable oil and animal fat as alternative fuel in internal combustion engine. Reviewed in *Biofuels, Bioproducts and Biorefining*, 2(2): 155–174. Available online: https://onlinelibrary.wiley.com/doi/pdf/10.1002/bbb.61 [accessed 10 July 2021].

Moser, B.R. 2009. Biodiesel production, properties, and feedstocks. *In Vitro Cellular & Developmental Biology - Plant*, 45(3): 229–266. http://link.springer.com/10.1007/s11627-009-9204-z

Muhammad, M.B., Aziz, R.A. & Yew, V.W.C. 2018. Socio - Economic Effects of Industrialization in the Society, 8(4): 23-30. Available online: https://www.researchgate.net/publication/327966349_Socio_-_Economic_Effects_of_Industrialization_in_the_Society/citations [accessed on 02 August 2021].

Nieuwenhuis, P., Wells, P. 2003. *The Automotive Industry and the Environment.* Cambridge, UK. Woodhead publishing: 73-86

OECD see Organisation for Economic Co-operation and Development

Organisation for Economic Co-operation and Development. 2012. OECD Green Growth Studies. *OECD Publishing*: 104. https://doi.org/10.1787/9789264115118-en

Pillay, A.E., Elkadi, M., Fok, S.C., Stephen, S., Manuel, J., Khan, M.Z. & Unnithan, S. 2012. A comparison of trace metal profiles of neem biodiesel and commercial biofuels using high performance ICP-MS. *Fuel*, 97: 385–389. http://dx.doi.org/10.1016/j.fuel.2012.02.040

Putrasari, Y & Lim, O. 2017. A study on combustion and emission of GCI engines fueled with gasoline-biodiesel blends. *Fuel*, 189: 141–154. https://doi.org/10.1016/j.fuel.2016.10.076

Rocha, L.D.S. & Corrêa, S.M. 2018. Determination of size-segregated elements in diesel-biodiesel blend exhaust emissions. *Environmental Science and Pollution Research*, 25(18): 18121–18129. https://doi.org/10.1007/s11356-018-1980-8

Sánchez, R., Sánchez, C., Lienemann, C.-P. & Todolí, J.-L. 2015. Metal and metalloid determination in biodiesel and bioethanol. *J. Anal. At. Spectrom*, 30(1): 64–101. http://pubs.rsc.org/en/content/articlehtml/2015/ja/c4ja00202d

Thongchai, S. & Lim, O. 2018. Investigation of the combustion characteristics of gasoline compression ignition engine fueled with gasoline-biodiesel blends. *Journal of Mechanical Science and Technology*, 32(2): 959–967. https://doi.org/10.1007/s12206-018-0146-9

Vu, D.N. & Lim, O. 2019. Experimental study on ignition characteristic of gasoline-biodiesel blended fuel in a constant-volume chamber. *Journal of Mechanical Science and Technology*, 33(10): 5073–5083. https://doi.org/10.1007/s12206-019-0946-1

Zhang, Y., Zhan, L., He, Z., Jia, M., Leng, X., Zhong, W., Qian, Y. & Lu, X. 2019. An investigation on gasoline compression ignition (GCI) combustion in a heavy-duty diesel engine using gasoline/hydrogenated catalytic biodiesel blends. *Applied Thermal Engineering*, 160: 2–12. https://doi.org/10.1016/j.applthermaleng.2019.113952

Zhong, W., Xiang, Q., Pachiannan, T., Mahmoud, N.M., Li, B., He, Z., Wang, Q. & Sun, J. 2021. Experimental study on in-flame soot formation and soot emission characteristics of gasoline/hydrogenated catalytic biodiesel blends. *Fuel*, 289: 2–11. https://doi.org/10.1016/j.fuel.2020.119813

Chapter 2: **Literature Review**

The petroleum-based fuel has become the main source of power for engines due to its low production cost over the past century. However, with the predictions based on Hubert's curve that the peak oil may occur within this decade, the price of oil would continue to rise until no longer affordable as world oil reserves approach depletion. ~ Hubbert,1959

2.1 Introduction

The transportation sector is one of the highest energy consumers due to the development of motorization industry, with equivalence share of 63% in global liquid fuel consumption as from 2010 to 2014 (Hade et al., 2017). Furthermore, in 2016 a 43 million barrels per day (mb/d) was used by this sector where Organisation for Economic Co-operation and Development region (OECD) accounted for 55% and developing countries used 40% (OPEC, 2017). The use of fossil fuel within transport vehicles once combusted will results in severe ecological changes, including an increase in global surface temperature which will result in global warming (Knittel, 2012), changes in rainfall patterns, and in the frequency of extreme weather events. A study by Torres-Garcia (2019), reported that in 2007 and 2008 the transportation sector resulted in roughly 23% and 22% global total world CO_2 emissions, respectively (Torres-García et al., 2019).

Substantial effort is being exerted globally to explore renewable energy sources that can replace fossil fuels by creating clean combustion (Kohse-Höinghaus, 2018). Biomass-based fuels or biofuels are advantageous over fossil fuels used for liquid fuels in the transportation sector (Balat, 2011). The energy crisis of the 1970s led to vigorous investigations about the use of biodiesel as an alternative fuel (Canakci et al., 2001; Demirbas, 2005). Conventionally, Biodiesel is derived from vegetable oils or animal fats using a homogeneous or heterogeneous catalyst (Atadashi et al., 2011).

Nabi et al., (2009) and Lee et al., (2015), used non-edible oils to produce biodiesel, while Ito et al., (2012) and Alptekin et al., (2014), studied use of waste animal fats, and waste cooking oil were conducted in making biodiesel; (Saydut et al., 2010; Thanh et al., 2010; Budiman & Putra, 2018). More than 350 oil-bearing crops, including sunflower, safflower, soybean, cottonseed, castor, palm, grape seed, and peanut oils, are considered potential feedstocks for the biodiesel production. However, only some are suitably used, due to their specific productivity and local climate (Demirbas, 2005; Torres et al., 2013). The use of biodiesel in fuel blending can significantly reduce pollution as De Araújo et al., (2013) suggested, that the blended methyl esters of 10 % biodiesel 90% petrodiesel and 20% biodiesel 80% petrodiesel (B10 and B20) respectively, will result in reductions from 40 to 60 % in emissions corresponding to pure petrodiesel.

2.2 Biodiesel Production

Over the past two centuries, the rise in anthropogenic carbon dioxide (CO_2) emissions have been gradual primarily due to the burning of fossil fuels (Garrido et al., 1994; Woods

& Fryer, 2007). CO_2 traps solar radiation causing a rise in global temperatures hence, the need for reduction in the use of fossil fuels (Garrido et al., 1994). The fact that biodiesel can be produced from vegetable favours the reduction of CO_2 (Elkadi et al., 2014). This is crucial as the world is on a pathway to net-zero CO_2 emissions by 2050 in order to limit global rise to 1.5 °C as reported by International Energy Agency (IEA, 2021). According to Climate Works report, there is a huge negative impact on sea, animals and plants as well as humans if the world had to have 2°C warming instead of 1.5 °C as projected by the Intergovernmental Panel on Climate Change (IPCC) (Lynskey et al., 2020).

Biodiesel is a fuel that is synthesised from either vegetable oils or animal fats and is described theoretically as a fuel contained of monoalkyl esters of long-chain fatty acids formed with a notation in its 100% pure state as biodiesel (B100), meeting the requirements of the American Society for Testing and Material D-67651 or European standard EN14214 (Lu et al., 2008 & Knothe, 2010). Biodiesel is composed of 14-24 carbon chains (C14-C24) and can be formulated as $C_{15\text{-}25}H_{28\text{-}48}O_2$. The term biodiesel has been coined around 1988 (Wang, 1988), with the first initiatives reported to be in South African in 1981 followed by Austria, Germany and New Zealand. Its first small pilot plant was built in 1985 in Austria (Körbitz, 1999). Ever since then many other countries such as Brazil, United States, Australia, Italy and Malaysia have been producing this renewable energy (Songstad et al., 2009; Chin, 2011; Yusuf et al., 2011). While Nelson et al. (2007), stated that the significant factors which affect the cost of biodiesel are feedstock cost, plant size, and the value of the glycerine by-product. In a review on economic and sustainability of biodiesel production conducted by Mizik & Gyarmati, raw material is the major variable that affect the cost of biodiesel which by use of free or cheap resources such as waste and residues is essential (Mizik & Gyarmati, 2021).

There is an annual vast amount of waste oils and animal fats that are generated by retailers and wholesalers, for instance according to World Economic Forum (WEF), approximately 50 billion chickens alone are slaughtered each year for human consumption (Thornton, 2019). Additionally, over 16.54 million tons per year of waste cooking oils are generated from major producing countries such as United States, China, Canada, Taiwan and Japan (Don et al., 2013; Loizides et al., 2019; De Feo et al., 2020). This creates an environmental issue and economic loss as their waste can contaminate landfill, drains water systems and animals. Thus, producing biodiesel from waste cooking oils rather than food or first-grade oils such as canola and soybean oils is one of the better ways to reduce the cost of biodiesel (Sirisomboonchai et al., 2015), and subsequently minimise waste disposal treatment costs and avoiding the use of land used in growing

the feedstocks (Bautista et al., 2009). This then produce an efficient, economical fuel (Kulkarni & Dalai, 2006), that controls pollution (Bamankar et al., 2015), and reducing greenhouse gas emissions (Atabani et al., 2012). The global market of used cooking oil in 2019 was USD 5.5 billion and is estimated to grow to USD 8.48 billion by 2027 (Polaris market research, 2020).

2.2.1 Biodiesel Advantages

Although Biodiesel cannot entirely replace petroleum-based petrodiesel fuel, there are at least six reasons that justify its development.

1. It provides a market for excess production of vegetable oils and animal fats (Yusuf et al., 2011)
2. It decreases, although it will not eliminate the country's dependence on imported petroleum (Khatlar et al, 2009).
3. Biodiesel is a renewable fuel and does not contribute much to global warming due to its closed carbon cycle. A life cycle analysis of Biodiesel showed that overall CO_2 emissions were reduced by 78% compared with petroleum-based petrodiesel fuel (Lai, 2014).
4. The exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from Biodiesel are lower than those of regular petrodiesel fuel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NOx) (Yusuf et al., 2011).
5. When added to regular petrodiesel fuel in an amount equal to 1–2 %, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur petrodiesel fuel, into an acceptable fuel (Gerpen, 2005)
6. When added to petrol, the blended fuel possess better low temperature fluidity and evaporation than pure biodiesel due to enhanced properties (Chen et al., 2018 & Gad & Mohamed A. Ismail, 2021)

2.2.2 Biodiesel Disadvantages

Biodiesel tends to have high viscosity, lower energy content, high cloud point and pour point, higher nitrogen oxides emissions, lower engine speed and power, injector coking engines compatibility (Demirbas, 2009). Biodiesel production using virgin feedstock requires increased demand for vegetable oil; thus, a high agricultural landscape with synthesis will lead to high cost (Huang et al., 2011), and a reduction in food security since 1 billion people suffer from malnourishment (Azócar et al., 2010). In the USA biodiesel

with 99-100% purity cost around 15–30% higher than that of petrodiesel, (Zahan & Kano, 2018). Biodiesel can absorb moisture causing high corrosive wear in an engine (Fazal et al., 2011a), 12% lower energy content and higher oxidation stability than petrodiesel (Yusuf et al., 2011).

At current production levels, biodiesel requires a subsidy to compete directly with petroleum-based fuels. According to Sarin (2012), federal and state governments are providing incentives that encourage the biodiesel industry's rapid growth. In South Africa, the cost of subsidy in biofuels is estimated at R800 million per year, equivalent to 3.5c/litre on fuel used in the country (South Africa, 2020). The national biodiesel board stated that biodiesel has an annual production capacity of 60-80 million gallons and has the potential of producing about 200 million gallons if produced from oleochemicals (Sadeghinezhad et al., 2014). Current production levels are 20–25 million gallons/year but achieving current European levels of 500 million to 1 billion gallons/year should be feasible (Gerpen, 2005).

2.3 Methods of Biodiesel Production

2.3.1 Dilution (blending)

This method which doesn't require any chemical process involves blending crude vegetable oils directly or diluted with petrodiesel fuels to improve their viscosity (Atabani et al., 2012). Dilution reduces the viscosity and engine performance problems such as injector coking and carbon deposits creation (Sarin, 2012).

2.3.2 Micro-emulsification

Described as colloidal equilibrium dispersion of an optically isotropic fluid microstructure with measurements generally in the 1-150 nm range formed instinctively from two normally immiscible liquids and one or more ionic amphiphiles (Abbaszaadeh et al., 2012).it has three constituents, an oil, an aqueous and surfactant phase with a solvent such as methanol, ethanol, or other alcohols (Sarin, 2012).

2.3.3 Pyrolysis (thermal cracking)

Meaning heat or by heat with the aid of a catalyst. This method is a thermal decomposition of organic matter in the absence or limited supply of oxygen and the presence of a catalyst (Abbaszaadeh et al., 2012; Pushparaj & Ramabalan, 2012; Ito et al., 2012).

2.3.4 Transesterification

Shifting of alcohol with another from an ester known as alcoholysis is the reaction of a triglyceride molecule with short-chain alcohol in the presence of a catalyst yielding a product called biodiesel which has a substantially lower viscosity compared to vegetable oil (Meher et al., 2006). This is the most used method and is regarded as the best method among all others due to its economic feasibility and simplicity (Vyas et al., 2010; Atadashi et al., 2011; Endalew et al., 2011; Lin et al., 2011; Atabani et al., 2012). In the production of biodiesel, it is so far, the most approved viscosity reduction method. According to (Sarin, 2012), Glycerin is consequently a by-product of biodiesel production.

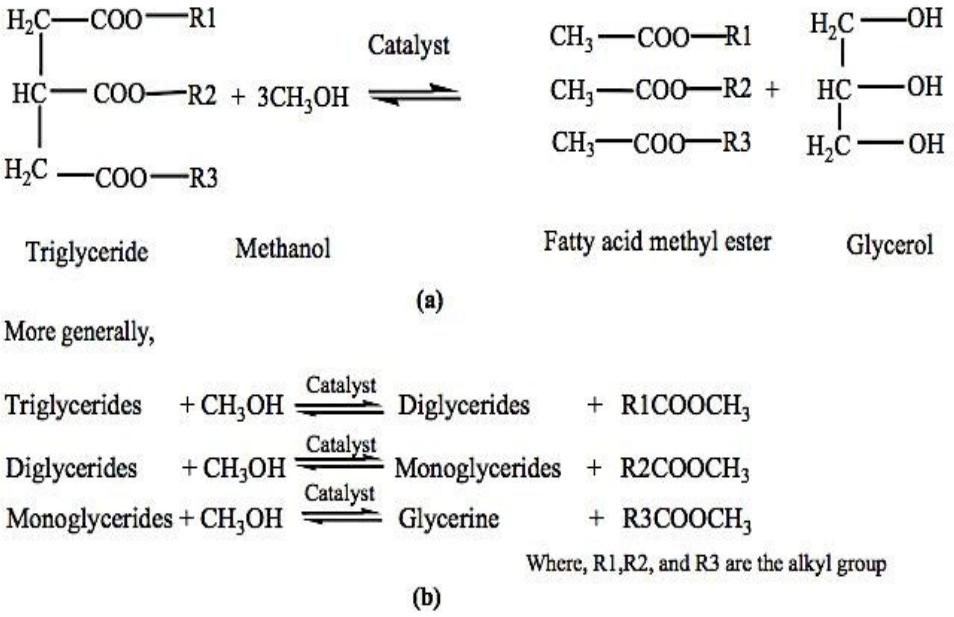


Figure 2-1. Transesterification of triglycerides (a) and the steps in transesterification (b) adapted from Ramadhas et al., 2005

2.4 Factors Affecting Transesterification

The transesterification reaction is affected by various parameters (Demirbas, 2005; Mathiyazhagan & Ganapathi, 2011; Atabani et al., 2012), which include the following.

2.4.1 Type of Alcohol

In the transesterification reaction, either primary or secondary alcohols can be used (Koval et al., 2008). In other words, these must be open chains alcohols that contain one hydroxyl group (Romero et al., 2007). The number of carbon atoms must be between 1 and 8, as Romero and his co-workers (2007) also established. The synthesis of biodiesel via both homogeneous and heterogeneous catalysis has been successfully achieved using methanol, ethanol, propanol, isopropanol, butanol and pentanol (Fukuda et al., 2001;

Demirbas, 2005). The viscosity of biodiesel obtained is also lower by using methanol (Allah & Alexandru, 2016).

2.4.2 Alcohol to Oil Molar Ratio.

Leung and Guo, 2006; Zhang et al., 2003; Ma and Hanna, 1999; Freedman et al., 1986 concluded that 3:1 ratio in general alcohol to triglycerides needed for the conversion to three moles of alkyl esters, however, increase in the alcohol up to specific concentration will drive the reaction to completion within a shorter time. Further increase in alcohol content does not increase biodiesel yield but also increases the cost of alcohol recovery (Leung and Guo, 2006). In alkali catalyst, the reaction will require a 6:1 ratio of alcohol to catalyze the transesterification of oils or fats (Freedman et al., 1986; Zhang et al., 2003) while waste cooking oils will require a higher ratio of alcohol, i.e., 15:1 when subjected to acid catalyst reaction (Ali et al., 1995; Zhang, 1994; Leung and Guo, 2006).

2.4.3 Catalyst Choice and Concentration

Choice of catalyst is the first step for designing a transesterification process, since it's used to raise the reaction rate (Lee et al., 2009; Sirisomboonchai et al., 2015). Many researchers have reported that homogenous catalysts are the most commonly used types of catalysts as a result of their availability and affordability. However, they have tendency to form soap, the catalyst will be difficult to recover and longer reaction time (Abbaszaadeh et al., 2012). Where else heterogeneous are quickly recovered but there are concerning issues regarding their activity and selectivity (Leung et al., 2010; Thangaraj et al., 2019). A supported bimetallic catalyst has been demonstrated to enhance the catalytic activity, product selectivity, and catalytic stability over supported monometallic catalysts for a range of catalytic reactions. According to Agarwal et al., 2012, Wang et al., 2012, Biodiesel produced from waste cooking oils with methanol on the bifunctional catalyst with Al_2O_3 as support had a good yield varying between 94,8 to 97,7%.

2.4.4 Reaction Temperature and Time

An increase in temperature increases the biodiesel yield and reaction rate (Allah & Alexandru, 2016). However, Leung and Guo, (2006) and Eevera et al. (2009) found that an increase in reaction temperature beyond the optimal level leads to a decrease of biodiesel yield because higher reaction temperature accelerates the saponification of triglycerides (Mathiyazhagan & Ganapathi, 2011).

Allah & Alexandru, (2016) found that the maximum ester conversion was achieved in less than 90 minutes. An increase in reaction time does not increase the yield product, i.e., in the study by Phan & Phan (2008), a decrease in conversion of waste cooking oils to biodiesel was observed, when 70 °C was used instead of 50 °C, in the transesterification.

2.4.5 Rate of Mixing, Intensity and Stirring Mode

Speed is vital in the formation of products; mixing and improved speed rate help in the time taken for reactants and catalyst to diffuse onto each other, therefore better yield. Allah & Alexandru, (2016) found that at 400 rpm, higher conversion of the end product was obtained while Knothe et al., (2005); Demirbas, (2008); Eevera et al., (2009); Rashid and Anwar, (2008) concluded that higher stirring speed favours the formation of soap due to the reverse behaviour of transesterification reaction.

2.4.6 The Purity of the Reactants.

Ester conversion is highly affected by the impurities present in the vegetable oils (Pandey, 2008). The presence of FFA in oils will have a significant impact on biodiesel fuel properties, its yield as well as its quality (Varma et al, 2016).

2.5 Biodiesel Feedstocks

2.5.1 Waste Vegetable Oil Usage

Biodiesel production cost about 1,5 to 3 times more as compared to petrodiesel (Zhang et al., 2003), because 95% of biodiesel produced is from edible oils such as rapeseed, palm, canola, mustard, peanut and soybean Mardhiah et al., (2017), and raw materials makes the highest portion in biodiesel production as reported by Kulkarni & Dalai, (2006), accounting about 70 to 95% of the total production cost (Azócar et al., 2010). Amongst many edible oils, palm oil is a popular feedstock that grows in hot and humid weather such as Malaysia and Indonesia which supply about 80-85% of global capacity (Habibullah et al., 2014). In order to replace 5% of the petrodiesel used in transportation 13% and 15% of farmlands in the USA and Europe would be needed respectively (Azócar et al., 2010). When one compares palm biodiesel with other vegetable oils and petrodiesel fuels, its associated with better engine performance, higher specific fuel consumption, shorter ignition delay, higher viscosity which improves its lubricating properties and anti-wear characteristics (Mosarof et al., 2015, Samanta & Sahoo, 2020). It reduces exhaust emission of hydrocarbon, carbon monoxide, carbon dioxide, and smoke by 50 to 70%, but not oxide of nitrogen emissions (Zahan & Kano, 2018). It is a relatively sustainable, environment-friendly, less expensive, and economically beneficial potential source of

energy (Mosarof et al., 2015). However, researchers have shown that biofuels production from non-edible biomass is more economical and more compatible with regular petrodiesel fuel Elkadi et al., (2014), where residual oils and fat from domestic commercial and industrial activities such as the ones used for frying food, can be employed for biodiesel production (Chaves et al., 2010, Awogbemi et al., 2019). Since, WCO is two and three times less pricy than that of fresh vegetable oil in terms of cost (Sirisomboonchai et al., 2015), the use of waste oils will lead to a significant reduction in the total processing cost of biodiesel resulting in economic and waste management solutions (De Araújo et al., 2013, Elkady et al., 2015).

2.5.2 Importance of Vegetable Oils

Waste Vegetable oils (WVO) or Waste Cooking Oils (WCO) are oils that is no longer suitable for their original purpose and can be collected from industries and restaurants (Ali & Khartoum, 2001). It was reported that vegetable oil motor fuels of E DIN 51605 quality can be used directly in utility vehicles, trucks, agricultural machines, buses, and stationary engines without problems (Mondal et al., 2008). Waste vegetable/ cooking oils in the production of liquid fuels such as biodiesel has several advantages over other alternative fuel options (Soetaert, 2009):

- The technologies for extraction and processing are easy and simple, as conventional equipment with low energy input is needed.
- Their fuel properties are close to petrodiesel fuel with high heat content close to 90% of petrodiesel (Mondal et al., 2008).
- Vegetable oils are renewable in nature (Hade et al., 2017).
- They are liquid, stable and have no handling hazards.
- The by-products left over after the extraction of oil is rich in protein and can be used as animal feed or solid fuel.
- The farming of their seeds is adaptable in different climate conditions and geographic locations.
- Biodiesel has proved to be appropriate for direct use in compression ignition engines without any substantial modifications to the engine.
- Biodiesel contains an absence of sulphur thus and no production of oxides of sulphur.

2.5.3 Fatty Acids in Different Vegetable Oil

Oil and fats are constituent of mostly triglycerides which make 90-98% of total mass (Giakoumis, 2018). Vegetable oils from variety of sources possess different fatty acids (FA) compositions, which aids in selecting efficient biodiesel production method (Mahmudul et

al., 2017), and their chain size, degree of saturation, and presence of other chemical functions helps in choosing production parameters (Chaves et al., 2010, Folayan et al., 2019). The most frequent fatty acids in triglycerides of vegetable oils are stearic (18:0), palmitic (16:0), oleic (18:1), linoleic (18:2) and linolenic (18:3) acids. Vegetable oils have high viscosities and have other disadvantages such as low volatility, coking on the injectors, carbon deposits, oil ring sticking, and thickening of lubricating oils (Manivannan et al., 2017). Hence, it can be used in petrodiesel engines once modified by transesterification (Nabi et al., 2009).

Table 2-1. Fatty acids compositions of various vegetable oil in wt.% extracted from (Yaşar, 2020)

Fatty acids	**C:D**	**Closed formula**	**Palm**	**Sunflower**	**Canola**	**Soybean**
Lauric	**C 12:0**	$C_{12}H_{24}O_2$	0.2	-	-	-
Myristic	**C 14:0**	$C_{14}H_{28}O_2$	1.1	0.08	0.05	0.07
Palmitic	**C 16:0**	$C_{16}H_{32}O_2$	44	5.93	6.23	11.43
Palmioleic	**C 16:1**	$C_{16}H_{30}O_2$		0.14	0.23	0.07
Stearic	**C 18:0**	$C_{18}H_{36}O_2$	4.5	3.44	2.49	4.03
Oleic	**C 18:1**	$C_{18}H_{34}O$	39.2	36.22	61.46	24.85
Linoleic	**C 18:2**	$C_{18}H_{32}O_2$	10.1	52.95	22.12	55.33
Linolenic	**C 18:3**	$C_{18}H_{30}O_2$	0.4	0.38	5.11	3.34
Arachidic	**C 20:0**	$C_{20}H_{40}O_2$	0.1	0.23	1.43	0.25
Gadoleic	**C 20:1**	$C_{20}H_{38}O_2$	-	-	-	-
Behenic	**C 22:0**	$C_{22}H_{44}O_2$	-	0.46	0.37	0.57
Erucic	**C 22:1**	$C_{22}H_{42}O_2$	-	-	-	-
Total saturated fatty acids			**49.9**	**10.14**	**10.43**	**10.35**
Total monosaturated fatty acids			**39.2**	**36.37**	**61.80**	**24.92**
Total polysaturated fatty acids			**10.5**	**53.33**	**27.23**	**58.67**

As illustrated in Table 2.1 above, fatty acids compositions of different oils will determine fuel properties like cetane number, oxidation stability, distillation characteristics, the composition varies according to the conditions of soil and moisture present (Pandey, 2009). Vegetable oils have molecular structures which are made of 90-98% triglycerides and have a high energetic capacity which is essential to fuels, they have free fatty acids, generally between 1 and 5% weight by weight (w/w), small amounts of monoglycerides, diglycerides, phospholipids, phosphatides, carotenes and tocopherols, and water traces (Torres-García et al., 2019). Waste cooking oils contain more free fatty acids Allah & Alexandru, (2016), as a result in high unsaturated bonds which cause oxidation when they react with oxygen Dwivedi & Sharma, (2014). They will cause formation of sludge

(Pandey, 2008). It will require a more alkaline catalyst for the transesterification of oils that have Free Fatty Acids (FFA) of ≥1% such as waste oils (Mathiyazhagan & Ganapathi, 2011).

Ramos et al. (2009), examined FA compositions of different oils for biodiesel synthesis and compared them to fuel properties; it was found that cetane number and oxidation stability values improved with increasing carbon chain length and decreasing level of poly-unsaturated fatty acids as well as higher iodine values and lower CFPPs. Mono-unsaturated fatty acids present in almond, olive, corn, rapeseed, and high oleic sunflower oils resulted in better biodiesel properties such as kinematic viscosity, density, flash point, and heating value. After analyzing correlations between properties and FFA compositions i.e., Table 2.1 and Table 2.2, it was concluded that fuel properties strongly depend on the feedstock type and marginally affected by reaction parameters. Therefore, there is a strong positive correlation between these fuel features as they increased with increasing carbon chain length and degree of saturation (Elangovan, 2017).

2.5.4 Physical and Chemical Properties of Different Oils

Table 2-2. Physical and chemical properties of different vegetable oils extracted from (Torres-García et al., 2019)

Vegetable Oils	LHV (kJ/kg)	Viscosity (mm^2/s)	PP (°C)	FP (°C)	Density (kg/m^3)	Sulphur (%)	Carbone residue (%)	Cetane number
Palm	36.55	39.6(38°C)	-	267	920	0.01	-	37.1
Sunflower	39.58	37.1(38°C)	-15	274	920	0.01	0.23	41.1
Soybean	39.63	32.6(38°C)	-12	254	910	0.01	0.27	37.9

2.6 Alcohols

2.6.1 Methanol

Methanol is mainly known as wood alcohol with a toxic, colourless liquid, a very faint odour which is produced as liquid thus stored and handed like gasoline (Methanol Institute, 2010). It was initially discovered in 1661 by Robert boyle (Yasin et al., 2013), formed from natural gas or wide range of renewable sources such as wood or paper (Aasberg-petersen et al., 2008). Its use began in the 1800s by steam-reforming of natural gas and CO_2 using copper-based catalysts (Blumberg et al., 2019; Ott et al., 2012). When 85% of methanol was blended with 15%gasoline, carbon monoxide (CO) emissions were reduced by 25% and nitrogen oxides (NOx) emissions by 80% (Rifal & Sinaga, 2016). Pure (100%) Methanol has low vapor pressure and cold starts therefore blending with 15%

gasoline in will improve it, since gasoline has 20% presence of aromatic (Nichols, 2003). Using methanol causes a reduction in vehicle range by 40%, since 1.77 gallons of methanol is required to produce equivalent energy in one gallon of gasoline (Yacobucci, 2004). It is mostly used as feedstock in formaldehyde, acetic acid, chloromethane and methyl tertiary butyl ether, 70% of its production is used in chemical process (Dalena et al., 2018). It can be used as solvent for paint strippers, paints, carburettor cleaners, plastics, and automobile wind solid water. Since 1965 it has been used as fuel for certain vehicles such as race cars (Thipse, 2008).

2.6.2 Ethanol

Ethanol (CH_3CH_2OH) is a clear colourless liquid known as ethyl alcohol (Foundation, 2007). Ethanol can be produced from many different raw materials that contain sugar, which is classified into starches, sugars and cellulose due to the type of carbohydrates they contain (Lin & Tanaka, 2006). It is used as a biodegradable additive (Pimentel & Patzek, 2005). It is a clean-burning, high octane fuel and used as a cleaning solvent (Ramadhas, 2006). Ethanol mixes well with water in most organic liquids and has been used as a fuel in the United States since 1908 with the Ford Model T, which has been modified to run on either gasoline or pure alcohol (Thipse, 2008).

2.6.3 Butanol

Butanol is an alcohol that is produced by fermentation from corn, grass, leaves, agricultural waste and other biomass (Yacobucci, 2004). Butanol, compared to ethanol, is less volatile and explosive, and has a higher flash point, and lower vapour pressure, making it safer to handle. Butanol contains more energy as it has a higher number of carbon atoms. It is less hygroscopic and easily miscible with gasoline in any proportion. Also, the air to fuel ratio and the energy content of butanol are close to gasoline (Biswas et al., 2017). Bio-butanol can be produced through fermentation of lignocellulosic materials (agricultural or paper waste) or non-cellulosic materials (corn or molasses) (Kumar & Gayen, 2011 & Kolesinska et al., 2019). Moreover, it is less corrosive and can be distributed within an existing pipeline. Due to the presence of four hydrogen atoms and its high energy output production, it is regarded as safe and suitable for use in fuel cells (Thipse, 2008)

2.7 Choice of Alcohol

In the transesterification reaction, either primary or secondary alcohols can be used (Koval et al., 2008). In other words, these must be open chains alcohols that contain one

hydroxyl group. The number of carbon atoms must be between 1 and 8 (Romero et. al., 2007). The synthesis of biodiesel through both homogeneous and heterogeneous catalysis has been successfully achieved using methanol, ethanol, propanol, isopropanol, butanol and pentanol (Fukuda et. al., 2001; Demirbas, 2005). However, for the transesterification processes, methanol has been reported to be favourable due to its rapid reaction with triglycerides along being relatively inexpensive. This rapid reaction is mainly due to three factors: polarity, alcohol chain length (Romero et. al., 2007; Lee et. al., 2011). Not only is methanol a polar compound but it is the shortest chained alcohol. Due to these properties, the reaction time during methanolysis is shortened as compared to alcoholysis with another alcohol such as propanol and butanol (Koval et. al., 2008; Malhotra et. al., 2015; Shah et. al., 2015).

The conversion of palm kernel oil to alkyl esters using P. *cepacia* lipase and, ethanol gave the highest conversion rate of 72%, while only 15% (MEs) was obtained with methanol (Abigor et al 2018). Effect of methanol, ethanol and butanol on yield by use of alkaline catalyst in transesterification of waste canola oil resulted in methanol having the highest yield followed by ethanol and butanol (Hossain et al., 2010). Generally, the efficiency of transesterification of triglycerides with methanol is likely to be less than ethanol with or without a solvent (Soetaert, 2009). It was found that methanol was both practical and cost-effective with regard to the transesterification of sunflower oil using alkaline and acid catalyst while ethanol and 2- propanol was not feasible and acid catalyst needs to be used (Sanli & Canakci, 2008). Butanol provides better interaction with gasoline than ethanol and a higher energy content (Sauer, 2016); its fuel benefits the environment in that when consumed in an internal engine, it does not yield sulfur oxides (SOx), NOx or CO but carbon dioxide (CO_2). Navas et al. (2020), suggested butanol should be favored over other short-chain alcohols such as methanol or ethanol due to the more extended chain properties of the final biodiesel and its blending with conventional diesel. Further, butyl ester has a higher energy value and superior cloud point than equivalents methyl or ethyl esters (Hájek et al., 2017). However, Gerpen et al., (2004), argued that natural of alcohol in the transesterification does not have any chemical modification to the produced biodiesel and that long-chained alcohols are usually avoided due to steric hindrance effect and cost (Yusuf et al., 2011). Therefore, short chained alcohol was chosen due to better conversion of triglycerides to alkyl esters under the same reaction thus reducing energy cost (Wen et al., 2009).

2.8 Catalysts

They are substances that provide an alternative pathway for a reaction to occur as they speed it up when breaking and making bonds, The importance and economic significance of catalysis are enormous (Deutschmann et al., 2009).

2.8.1 Homogeneous Catalysts

These catalysts exist in the same phase as the reactants, in the production of biodiesel, they are of two kinds: acid and basic (Romero et al., 2007; Zabeti et al., 2010). They both have high producing yields in terms of fatty acid methyl esters (FAME). Preference is given to basic catalysts, they have the ability to complete the reaction faster, they require lower temperatures, and they have higher conversion efficiency (Sanli & Canakci, 2008)(Sarin, 2012). However, in cases where feedstocks contain high FFA, basic homogeneous catalysts are rendered ineffective due to their intolerance to high FFA (Changmai et al., 2020). Even though, alkaline catalysts (NaOH, KOH, NaOMe, KOMe) are widely used to convert refined edible oils into biodiesel, several limitations are present when they are used in waste cooking oils (De Araújo et al., 2013; Sanli & Canakci, 2008). The acid values of most non-edible oils are higher than the functioning range of base catalysts. To avoid soap formation, which is inevitable in such instances, both types of homogeneous are used consecutively (Thanh et. al., 2010). Although in the presence of homogeneous catalysts, the reaction rate is rapid, separating the products, catalyst and impurities requires additional steps in the production phase (Vázquez et. al., 2011). This dramatically increases the production cost, and due to the non-reusability of the catalysts, it results in a great hindrance to commercializing biodiesel produced though homogeneous basic catalysts to make it competitive with conventional petrodiesel (Thangaraj et al., 2019). Additionally, there is a large quantity of wastewater produced and low-grade glycerol Liao & Chung, (2013), which then result in a disposal issue and environment pollution (Aransiola et al., 2013).

2.8.2 Heterogeneous Catalysts

Heterogeneous catalysts can overcome issues presented by homogeneous catalyst since they can improve the economy of biodiesel production by introducing a solid base catalyst which can be used for continuous process (Moradi et al., 2014). For instance, The production of 8000 tons of biodiesel will require approximately 88 tons of sodium hydroxide (NaOH), while only 5.6 tons of magnesium oxide (MgO) will suffices production of 100 000 tons of biodiesel Romero et al., (2007), therefore less amount of heterogenous catalyst will required per tons of biodiesel. Another point is the potential of reusability of

the catalyst for the next cycle, which is better than that of homogeneous. Also, these catalyst eliminate the neutralization salts in glycerol, which will reduce the number of separation steps and besides, they can be retained in the reactor by filtration (Kawashima et al., 2009), since methanol and ethanol do not mix with solid heterogeneous catalyst (Chouhan & Sarma, 2011a). Additionally, there no or less wastewater (De Araújo et al., 2013) and they are less corrosive compared to homogeneous catalysts (Dossin et. al., 2006).

2.8.3 Enzyme Catalyst

They are known as biocatalysts; they have properties of both homogeneous and heterogeneous catalysts. In recent years, enzymatic reactions using lipase have attracted growing attention due to its advantages over chemical catalysts: it has easy product recovery, environmental-friendly properties, high selectivity and a require low alcohol-to-oil molar ratio (Vyas et al., 2010; Zhao et al., 2013). Enzyme catalysts tolerate FFA and water content, facilitating biodiesel and glycerol's easy purification (Zhao et al., 2013). However, Enzyme catalysts are expensive and residual enzymes can contaminate biodiesel. While enzymes can be easily deactivated, a long reaction time is required and these significant drawbacks limit the industrial application of biodiesel production using enzymes (Boey et al., 2011; Endalew et al., 2011; Zhao et al., 2013).

To minimize some of these limitations, immobilized enzymes are employed which facilitate multiple uses and consequent cost reduction. However, glycerol's build-up limits the number of their reusability cycles (Vyas et al., 2010). Recent studies though have been directed at using enzymes in the transesterification reaction, whether immobilized or otherwise (Avhad & Marchetti, 2015). In these processes, it was found that transesterification through enzymatic catalysis had several advantages (Tan et al., 2010). There was no by-product formation in some instances (Lam et al., 2010) and when there was for some cases, the products were easily separated (Robles-Medina et al., 2009). Furthermore, the enzymes could be reused without any separation step, and the operating conditions were found to be lower (Aarthy et. al., 2014). However, enzymes' current cost, for their use as catalysts in transesterification is very high which is the main hindrance to its commercialization (Talebian-Kiakalaieh et al., 2013).

2.9 Choice of Catalyst

Transesterification of triglycerides needs to be carried out in acid and base catalysed reaction (Baskar & Aiswarya, 2016). One of the concerns in catalyst development is the ability to convert feedstocks with high FFA to FAME. High FFA content (>15%) causes

catalyst deactivation and biodiesel contamination with soaps (Loe et al., 2019; Knothe, 2010). Since, heterogenous catalyst has mass transfer limitation as a result of the formation of three phases with oil and alcohol (Baskar & Aiswarya, 2016). In order to eliminate this issue, the use of structural promoters which tend to have the more specific surface area and the active site has been studied (Wen et al., 2009). Since Nanda et al., (2017), elaborated on the functions of appropriate promoter as one that would need to increase the catalyst surface area and be able to create dispersion of catalyst particles through stopping the accumulation, sintering of metals and improving the catalyst's mechanical strength. Furthermore, the addition of a second metal to a traditional single one in the heterogeneous catalyst may lead to the formation of an alloy with enhanced catalytic activity, selectivity, and stability compared to its single-metal counterparts (Yang et al., 2013).

Solid acid catalyst has the potential to both esterify and transesterify feedstocks of high FFA (Thangaraj et al., 2019). A solid base catalyst such as alkaline earth metal oxide is insoluble in methanol and has low noxiousness (Changmai et al., 2020). They have a high catalytic activity which increases with regards to the atomic number and decrease in polarizing power of MgO < CaO < SrO < BaO due to basicity (Kwong & Yung, 2015). According to their basicity and availability, the activity of calcium oxide (CaO) which has been widely studied can be improved through calcination Chouhan & Sarma, (2011b), Since calcined CaO was reported as a highly active catalyst in the transesterification of sunflower oil (Cho et al., 2009). However, specific surface area of CaO is usually small Wu et al., (2013), therefore porous materials such as alumina, carbon, clay, zeolite or silica are impregnated to produce high specific surface area metal oxides (Małecka et al., 2015). Aluminium oxide (Al_2O_3) has high specific surface area, large pore size and pore volume, and as a support it has drawn attention in catalysis processes (Zabeti et al., 2009).

There is a huge effect of two complementary functional groups in terms of reactivity and stereo-control in a reaction which eliminates challenges that were presented previously by single functional group catalysts (Dixon, 2016). In the review of the catalytic activity of of several solid base and acid catalyst for biodiesel production especially metal oxides and supported metal oxides, it was found that the activity depended on the active site concentration and the catalyst support(Zabeti et al., 2009). According to (Agarwal et al., 2012, Wang et al., (2012), biodiesel produced from waste cooking oils (WCOs) using methanol and the bi-functional catalyst with Al_2O_3 as support the yield varied 94,8 to 97,7%. Investigation of biodiesel production from WCOs with methanol over solids acid catalysts and the capacity of porous supports for waste oils (WOs) based on FAME yield,

was reported that the highest yield was in this order Al_2O_3 > SiO_2 > SnO_2 > ZnO where Al_2O_3 yielding of 97.5% FAME (Komintarachat & Chuepeng, 2009).

In conclusion, a supported bimetallic catalyst has been demonstrated to enhance the catalytic activity, product selectivity, and catalytic stability over supported monometallic catalysts for a range of catalytic reactions. Bimetallic nanoparticles have shown major technological applications in heterogeneous catalysis, they have distinctive properties, often a better reactivity, because the core metal particle could modify the lattice strain of the shell metal, resulting in a shift of the shell metal's electronic band structure (Banerjee et al, 2017

2.10 Biodiesel Characteristics

Biodiesel needs to be analyzed and evaluated for its chemical and physical properties for use in petrodiesel engines. These properties are usually analyzed against standards like those of the American Society for Testing Materials (ASTM), European Union (EN 14214), Germany (DIN 51606), Austria (ON) and Czech Republic (CSN) standards for biodiesel fuel, However, the preferred international standard specifications used are the American Standard for Testing Materials and European Standard (Atabani et al., 2012) as seen in Table 2.3.

2.10.1 Physical and Chemical Properties

Biodiesel is characterized by different physical and chemical properties depending on the feedstock used in the manufacturing process such as acid number, cetane number, oxidative stability, viscosity, flash point, cloud point, pour point, density, free and total glycerol moisture content, phosphorus content, calorific value, sulphated ash test and carbon residue. Qualitative characteristics of biofuels follow the legislation set for environmental safety purpose, this complex assessment is becoming progressively restrictive therefore the choice of raw material is a decisive factor (Chaves et al., 2010; Ruzinska, 2015).

Table 2-3. American Society of Testing and Material and European Standards Specification for Biodiesel (Adapted from Atabani et al., 2012)

Fuel properties	**Petrodiesel**	**Biodiesel**	
		ASTM	**EN**
Density(kg/m^3)	7.1(850)	7.3	7.3(880)

Carbon (wt%)	84-87	77	77
Hydrogen (wt%)	12-16	12	12
Oxygen (wt%)	0-0.31	11	11
Sulfur (wt%)	0.0-0.0024	0.0015 max	0.02 max
Boiling point °C	180-340	325-350	315-350
Flash point °C	60-80	100-170	100-170
Cloud point °C	-35 to 5	-3 to 15	-3 to 12
Pour point °C	35-55	-5 to 10	-5 to 10
Cetane number	40-55	48-65	48-65
Viscosity at 40°C(cSt)	2.6	1.9-6.0	3.5-5.0
Acid value (mg KOH/g)	0.062	Max 0.50	Max 0.50
Oxidation	3min	-	6min

2.10.2 Acid Number

The acid number is an indicator of FFA content. In biodiesel, it needs to be kept low which according to ASTM D664 and EN 14104 the approved maximum acid value in the biodiesel is 0.5 mg KOH/g (Atabani et al., (2012), to ensure no residual free fatty acids or processing acids are present in the fuel. The presence of excess acids can lead to corrosion and deposits in the fuel system (Alleman et al., 2013). This acid value can be elevated if the fuel is not properly manufactured or if it has undergone oxidative degradation. According to Sarin al., (2012), the acid level and viscosity may increase as biodiesel ages in storage, and it was found that high acidity (> 3%) in the oil results in lower conversion efficiency and may cause severe corrosion in the fuel supply system (Meher et al., 2006; Atabani et al., 2012). Pure biodiesel can be contaminated with water during storage, which will lead to FFA formation.

2.10.3 Cetane Number

The cetane number of biodiesels depend on its fatty acid profile and increases as fatty acid proportions are elevated (Azad et al,2016). Long chains and more saturated fatty acid lead to high cetane number but lower volatility, while unsaturated fatty acids have low cetane numbers and reduced oxidation stability (Anitescu & Bruno, 2012). According to ASTM D613 and EN ISO 5165, cetane number of a biodiesel varies between 48-65 while petrodiesel is 40-55 (Atabani et al., 2012, Ong et al., 2013). Therefore, biodiesel has a higher cetane number than petrodiesel fuel, and since biodiesel contains 10-11% oxygen by weight (Canakci et al., 2001& Alleman et al., 2016). These characteristics reduce the emissions of carbon monoxide (CO) and hydrocarbon (HC) as compared to petroleum-based petrodiesel fuel, which subsequently reduce engine noise (Canakci et al., 2001).

2.10.4 Cloud Point

This is the temperature where the fuel first begins to form crystals, its used to predict cold weather operability. Therefore, the most commonly used in the measurement of low-temperature operability is the cloud point (CP), as fuels are generally expected to operate at temperatures as low as their cloud point. Biodiesel made from waste oil or animal fats has higher cloud point of 7 °C and 2 °C for Mohua and waste soybean biodiesels (Chaudhari, 2017) while palm biodiesels have 16 °C (Benjumea et al., 2008), which is relative to that made from refined oil (Saydut et al., 2010). Conventional petrodiesel cloud point is typically lower than that of biodiesel which is evident in (Table 2-3) and starts to get colder as soon as the temperature drops. CP depends mostly on the type and quality of impurities in the fuel, such as monoglycerides. The values range between -3 and 15 °C for biodiesel and -35 to 5 °C for conventional diesel, according to ASTM standard (Atabani et al., 2012). In biodiesel, the CP is particularly important because biodiesel is usually blended with petrodiesel, and the CP of the biodiesel will have a significant impact on the final blend properties (Alleman et al., 2013)

2.10.5 Density

Density which is defined as mass per volume can be measured by ASTM D94 or EN ISO 3675 and 12185, it plays a role in fuel consumption (Siraj, 2017). Additionally, this fuel has a major effect on performance characteristics such as cetane number and heating value (Ateeq, 2019). The density of biodiesel depends on the feedstock used in the production process. Biodiesel produced from saturated fats tends to have a higher density than biodiesel from unsaturated fats Ong et al., (2013), due to shorter chains and double bonds (Ghoreishi & Moein, 2013). Furthermore, denser oils contain more energy Atadashi et al., (2011), because of high mass used which is injected resulting in more heat (Canesin et al., 2014). Density in biodiesel depends on time and increase as time goes (Lima et al., 2010).

2.10.6 Distillation

This property is important as it shows fuel volatility, and is used to examine combustion and engine emissions (Hassan & Kalam, 2013; Lapuerta et al., 2015), distillation curves illustrate the percentage of hydrocarbons and their temperatures as it boils over time. Distillation curves will be vary according to the difference in the chemical compositions of the fuel (Aleme & Barbeira, 2012; Anitescu & Bruno, 2012). T10 (10% distilled volume), T50 and T90 temperatures are the most crucial points on the curves, they are used for calculate cetane index (Benjumea et al., 2008), and together with initial and final boiling

points (IBP and FBP, respectively), they are associated with engine performance and emissions (Lapuerta et al., 2015). When a fuel has a low T10, the cold start will be easier due to enough fuel evaporation while T50 is related to engine warm up and therefore should be low to ensure quick power gain without stalling (Kheiralla et al., 2011). High T90 shows heavy compounds which plays a role in increased particulate matter and subsequently deposit built up inside combustion chamber, it shows crankcase dilution (Lapuerta et al., 2015). According to ASTM 975 and EN 590, the set limits for distilled fraction and temperature are shown in the figure below:

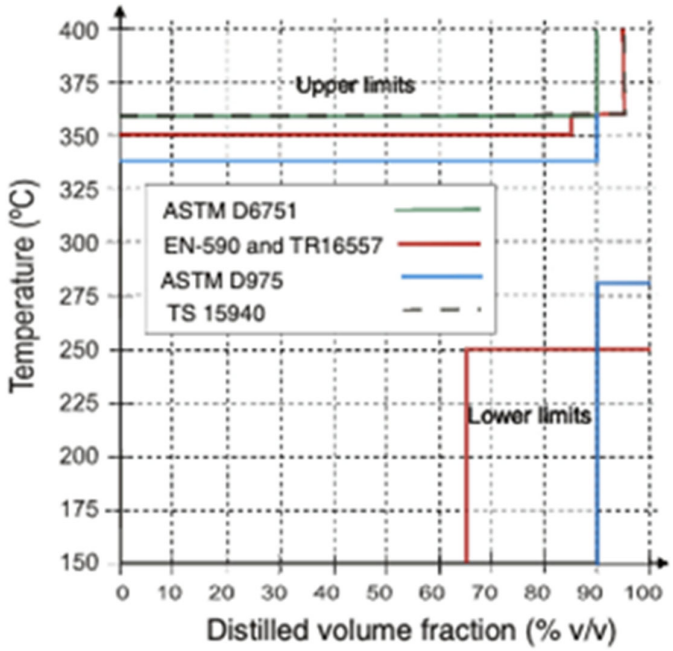


Figure 2-2. Limits Of Temperature And Distillate Volumes Adapted From (Lapuerta et al., 2015).

2.10.7 Flashpoint

Flash point indicate the minimum temperature to which the fuel will start to ignite, a minimum limit of 130 °C flash point has been set in order for safety in case of biodiesel handling (Alleman et al., 2013). As the temperature at which the fuel inflames due to the formation of a homogeneous mixture of fuel vapour and air above the fuel surface. Flash point, an important parameter to be considered in fuel storage and handling is influenced by the methanol content (Hamamre et al., 2014). Biodiesel has a relatively high flash point, which makes it less volatile and safer to transport than petrodiesel (Buasri, 2009; Atabani et al., 2012). ASTM specifies that biodiesel flash point must be in the range 100-170 °C while EN 14124 compliant is over 110 °C (Lai, 2014). A study by Hamamre et al.

(2014), demonstrated that an increase of 0.5% in methanol content led to a 50 °C decrease of biodiesel flash point.

2.10.8 Free and Total Glycerol

Glycerol is essentially insoluble in biodiesel; free glycerol may remain as suspended droplets in biodiesel. Free glycerol is the amount of glycerol left in the final biodiesel product and therefore the free glycerol content is dependent on the production process (Atabani et al., 2012). Accumulation of glycerol may damage the fuel injection and increases mass transfer difficulty (Atabani et al., 2012; Zhao et al., 2013). Avoiding inadequate separation in the washing stage of the methyl ester product is crucial as it will create high yields of glycerol in biodiesel. EN 14105 specify a free glycerol limit of 0.02% while ASTM requires that total glycerol be less than 0.24% of the final biodiesel production (Atabani et al., 2012).

2.10.9 Nitration

Nitration indicates excessive blow-by from cylinder walls, compression and accelerates oxidation, as nitration increases total acid number and viscosity increases simultaneously. In addition to causing oil thickening and some of these products being acidic, nitration products are the major cause of varnish or lacquer buildup. It can also reflect operating conditions, such as high loads and low operating temperature, as well as piston ring blow-by.

2.10.10 Oxidation

Oxidation can increase wear, retard performance, and shorten equipment life. Oxidation is worsened when temperatures are elevated, some oil molecules may form complex and corrosive organic acids (Haider et al., 2013). Biodiesel is susceptible to oxidation, a phenomenon that can cause the fuel to become acidic, form insoluble gums, sediments and that can plug fuel filters, as well as increase viscosity. Factors influencing the oxidation process of biodiesel are light, temperature, heat, traces of metal, fatty acid structure i.e., presence of double bond, and presence of air (Kapilan et al., 2009; Ong et al., 2013). Most biodiesel contains significant amounts of oleic, linoleic, or linolenic acid, which influence the oxidative stability of the fuel (Knothe, 2005). Oxidation occurs due to the presence of unsaturated fatty acid chains and double bonds in the oil reacting with oxygen in the presence of air (Atabani et al., 2012). biodiesel made from feedstock high in saturated fat such as palm oil or tallow tends to oxidize slower, this is due to the presence of high oleic acids (Robles-Medina et al., 2009).

2.10.11 Pour point

Pour point is the lowest temperature at which the fuel begins to be semi-solid under specific conditions (Boshui et al., 2010), a characteristic directly proportional to the viscosity of the feedstock. Biodiesel made from different feedstock may have different pour points, making it suitable over conventional petrodiesel. Biodiesel has a pour point in the range of -5 to 10 °C above conventional petrodiesel, which is -35 to -15 °C (Atabani et al., 2012).

2.10.12 Soot

Soot is the impure carbon particles generated from the incomplete combustion of a hydrocarbon. It is partially burnt fuel, which results in a heterocyclic hydrocarbon particle. It is also a non-classical abrasive that will erode boundary-lubricated surfaces at high concentrations. This will cause severe engine wear. An increase in the soot content of the oil indicates combustion problems or that the drain period may have been extended.

2.10.13 Sulfate

Sulfate compounds increase the production of varnish and sludge, which generally degrade the oil. They also react with the water formed during combustion to produce powerful inorganic acids such as sulfuric acid (H_2SO_4). They give a better idea of mistuned engines and ring failures.

2.10.14 Viscosity

Viscosity is a measure of the internal flow resistance of a liquid i.e. the thickness of the oil, this is an intrinsic property of vegetable oils affecting the fuel's fluidity (Aworanti et al., 2012; Jiang et al., 2019). Being one of the specifications for compliance in the production of biodiesel. The product with less viscosity is the one with higher total FAME content (Babajide et al., 2010). The presence of water and FFA increase the formation of soap and frothing resulting in high viscosity (Ramadhas et al., 2005). The main reason of the use of transesterification process is to lower the viscosity of oil (Sureshkumar & Muralidharan, 2014). Fuel with high viscosity especially at low temperatures will cause mechanical problems due to increase in viscosity as temperature drops (Hassan & Kalam, 2013), i.e. for temperatures below or at -20 C, viscosity should be below 48 mm^2/s (Barabas & Todoru, 2011). High viscosity result in poor atomisation which tends to form large droplets on the injection pump, which causes poor combustion and increased smoke and emission (Sahu et al., 2013, Hamamre et al., 2014). The viscosity of biodiesel is 10-15 times greater than that of petrodiesel due to its large molecular mass and chemical

structure (Atabani et al., 2012). The maximum limit of viscosity in biodiesel, according to ASTM D445 varies between 1.9 and 6.0 mm^2/s, and in the range of 3.5-5 mm^2/s in EN ISO 3104.

2.10.15 Water Content

The presence of water within biodiesel is due to the washing phase or contact with moisture, Karl Fischer measurement is usually used to test this property base of reaction between components and reagent moisture (Quveon, 2014; Matějovský et al., 2018; Aisyah et al., 2019). The hydroscopic nature in the biodiesel can cause the increase of water content within storage causing hydrolysis (Lin & Lin, 2012; Fregolente et al., 2015) This will lead to reducing heat of combustion and degrade the fuel more (Leung et al., 2006; Cursaru et al., 2014). According to ASTM D2709 and EN ISO 12937 specifications, the limit of water withing biodiesel should be 0.05% or 500ppm (Mahmudul et al., 2017; Cavalheiro et al., 2020). Additionally, it is an important property for the determining of fuel in sale, taxation and custody transfer (Srivastava & Prasad, 2000).

2.11 Fuel Blending

Emission regulations and over rising energy demand have created need for novel technologies. Compression ignition engines running on petrodiesel have high thermal efficiencies but produces huge amount of emissions as a result of high combustion temperature and limited fuel/air mixing (Zhang et al., 2019). Contrary to petrodiesel, which is a high reactivity fuel, petrol is a low reactivity fuel used in spark ignition engines, which operates at low compression ratios, offering lower engine efficiencies but extremely low emissions (Putrasari & Lim, 2017). Additionally, compression ignition engines do not offer knocking at high loads, they have reduced amount of fuel injected, and during compression stroke only air is compressed (Putrasari & Lim, 2018). Therefore, researchers were driven by the goal to combine advantages of high efficiency of petrodiesel engines and low emissions of petrol engines as well as considering innovation, energy conservation and enhancing combustions to develop engine systems that uses high volatile fuels and alternative fuels for compression ignition engines (Adams et al., 2013; Putrasari & Lim, 2018). It was addressed by using alcohol as additives to petrodiesel or biodiesel fuel and low- temperature combustions (LTC) (Misra & Murthy, 2011; Chen et al., 2018; Zhong et al., 2019).

The low temperature combustion approach was more attractive and is classified into homogeneous charge compression ignition (HCCI), partially premixed compression

ignition (PPCI), reactivity-controlled compression ignition (RCCI) and petrol or gasoline compression ignition (GCI) (Gad et al., 2020). Since HCCI and PPCI are good under low to medium load conditions but face great difficulty at high loads and RCCI has cost issue as well as high carbon monoxide and unburned hydrocarbons at low loads, petrol or gasoline compression ignition (GCI) has shown to possess greater potential amongst others (Putrasari & Lim, 2017b; Zhang et al., 2019). It offers high thermal efficiencies, low NOx and soots, low combustion temperatures as well as no requirement for high exhaust gas recirculation and engine modification (Putrasari & Lim, 2017a; Xuan et al., 2020). It also similar to petrodiesel engines offering lower fuel cost, produces high torque than petrol engines and allows for more broader ranges of fuels (Rose et al., 2013). This low temperature combustion method uses petrol/gasoline like fuel instead of petrodiesel (Zhang et al., 2019; Xuan et al., 2020). The use of petrol was found to enhance efficiency by improved air and fuel mixing and reduces NOx and soot (Gad et al., 2020) but had its downfall as it requires high intake temperature and high compression ratio, low lubricity, low viscosity, cold start difficulty (Vu & Lim, 2019).

2.11.1 Alcohol - Petrol Blends

Ethanol added into petrol spark ignition engines is more preferred (Kheiralla et al., 2011), while using ethanol-petrol blends in compression ignition engines resulted in good reduction emission and high efficiency, however double injection is preferred (Manente et al., 2009; Kaiadi et al., 2013; Noh & No, 2017). Even though NOx decreases, CO and HC emission increases with dilution ratio (Peng, 2017; Ngo, 2020). Additionally, bioethanol is prone to high moisture absorption, acidity, corrosion, dissolved oxygen and presence of chlorides, acetate ions and sulfate (Khuong et al., 2017; Matěǰovsky et al., 2017; Rocabruno-valdés et al., 2020)

2.11.2 Biodiesel - Petrodiesel Blends

When blending biodiesel with petrodiesel for compression ignition engines, these biodiesel blends are usually referred to as BXX with XX indicating percentage loading (El-Kassaby & Nemit-Allah, 2013). Lower blending from B6 to B20 is required for better engine performance but mostly B20 (Shamim et al., 2017), while it was found that high blended biodiesel will cause a solvency effect in the petrodiesel engine (Kadam & Kale, 2015). There is a significant decrease in particulate matter emission with an increase in biodiesel blends (Demshemino et al., 2013). Contrastingly, Kumar et al. (2014), reported that increased biodiesel in blends results in increased emissions of CO_2 at a lower compression ratio and increased NOx emissions (Can, 2014; Kumar et al., 2014). Additionally, increase in biodiesel content increased NOx, due to higher cetane number and oxygen content found

in biodiesel which favour operations at low heating value (Can et al., 2017; Mickevičius et al., 2014; Raman et al., 2019; Wu et al., 2020). Also, the molecular structure such as high degree of unsaturation leads to high flame temperature during premixed combustion and consequently increased NOx (Al-lwayzy & Yusaf, 2017 & Sharma et al., 2020).

Nevertheless, biodiesel blends have more heat release rate than petrodiesel due to the presence of more oxygen content leading to more complete combustion Ramesha et al., (2015), and auto-ignition delay which increases with the increase in blending percentage (Mickevičius et al., 2014). However, the brake thermal efficiency of the engine decreases with an increase in biodiesel blends due to low caloric value, high density and viscosity (Sharma et al., 2020). Moreover, there is a decrease in engine power from 1.2% to 0.7% for B95 and B5 respectively with biodiesel produced WCO, even though there is low emission and high flashpoint (>148 °C) when blending biodiesel with petrodiesel (Nair, 2013). A review by Misra and Murthy, (2011), concluded that when considering improving cold flow properties of biodiesel for enhanced performance and emission control, additives are required. High density and viscosity of biodiesel makes is problematic in cold areas and long-time storage affecting process atomization and engine performance as well as increased NOx emissions in compression ignition engines, meanwhile alcohol additives are LTC are suggested (Razzaq et al., 2020). Moreover, biodiesel is more prone moisture and oxidation than petrodiesel fuel leading to corrosion and degradation (Karavalakis et al., 2010; Almeida et al., 2011; Fazal et al., 2012; Z. Yang et al., 2013; Yaakob et al., 2014; Kumar, 2017; M. A. Fazal et al., 2018; Chandran, 2020).

2.11.3 Petrol - Petrodiesel Blends

High volatility and low cetane number fuels like petrol are good in reducing soot and NOx as they are more resistant to auto-ignition, have better air-mixing and longer ignition delay (Han et al., 2010). The low temperature combustion is preferred. Han, et al. (2011) Shi, et al. (2010), Torregrasa et al., (2017), conducted experiments blending petrol with petrodiesel for compression ignition engines under different conditions and compared it to diesel fuels, they found that gasoline or petrol like fuels are promising for heavy duty compression ignition as a result of reduced NOx, soot emissions, improved mixing rates, improved engines performance and higher economy as compared to conventional petrodiesel fuels (Shi & Reitz, 2010; Han et al., 2011; Torregrosa et al., 2017). However, when low temperature combustion was conducted increase in carbon monoxide and unburned hydrocarbons were observed Han et al., (2012), and petrol blends greater than 50% would be required for GCI engines (Al-Abdullah et al., 2015).

2.11.4 Petrol - Biodiesel Blends

In improving ignition characteristics of petrol, studies conducted by Putrasari & Lim (2017), Thongchai & Lim (2018), Das et al. (2018), Adam et al (2013). concluded that blending biodiesel with petrol improved its thermal efficiency, reduced ignition delay and reduced emissions significantly where 20% of biodiesel blending to petrol having similarities to that of pure petrodiesel (Das et al., 2018; Thongchai & Lim, 2018). High oxygen content, cetane number and viscosity of biodiesel improves air-fuel mixture, spray, fuel injection system and auto ignition (Putrasari & Lim, 2017; Gad & Ismail, 2021). Blending petrol with biodiesel will achieve fuel properties needed for GCI, solving those issues as compared to pure petrodiesel (Adams et al., 2013; Thongchai & Lim, 2018; Zhong, et al., 2019). Moreover, blends of biodiesel with petrol or kerosene has been proven acceptable for usage in petrodiesel engines as they possess improved performance, combustion and emission reduction (Gad & Ismail, 2021). Biodiesel-petrol blended fuel possesses enhanced low temperature fluidity, vaporisation and performance than pure biodiesel because addition of petrol reduces smoke emissions at low, medium and high loads (Chen et al., 2018). Furthermore, biodiesel has been used as alternative renewable fuel in petrodiesel engines without engine modification with great interest of its availability, sustainability, pollution reduction, superior lubricity and free sulfur as well as aromatics (Palash et al., 2013; Bhangale & Kulkarni, 2017; Vu & Lim, 2019).

2.12 Metal Contaminants

The presence of inorganic constituents in biodiesel is important such as Na, K and P (Korn et al., 2010). As a result of catalysts and hard water used in the process Ca and Mg concentrations should be monitored (Nogueira & Lucio, 2011). Metals in diesel/biodiesel blends can cause illness (Rocha & Corrêa, 2018). The occurrence of trace metals in biodiesel can be detrimental to the environment and equipment such as clogging engines and undesirable residue of metal oxides in its part (Elkadi et al., 2014). Ulrich et al 2014 reported that the origins of these metals are various, while Garrido et al., 1994 and Sánchez et al., 2015 state their occurrence is mainly due to their content in the starting raw materials such as seeds or contact with the manufacturing or storage equipment while some metals are believed to have been brought in during transport process (Isis et al., 2012). Mendil et al., (2009) established that the concentration of heavy metals in oil plants depends on many factors, such as plant species, soil types, anthropogenic pressure, fertilization, and hydrological conditions. Rocha & Corrêa, (2018) demonstrated that 0.1-10 gm/L of Cr, Ni, Cu and Pb can originate from abrasion in piston rings, cylinder liners,

valve cams and bearing. Those found in feedstocks are assumed to be delivered from the seeds or soil while the mineral composition of the seeds varies according to the presence and availability of metals in the soil where the plant was grown, pesticides and fertilizers used to grow that plant, (Chaves et al., 2010). The concentration of trace elements allows for the knowledge regarding the geographic origin as well as disclose of oil contamination (Chaves et al., 2011).

2.12.1 Effect on Biodiesel Quality

Exposure of metal surface to biodiesel at a high rate results in a corrosive state which is a great concern in the automotive sector (Sorate & Bhale, 2018). Induced corrosion happens firstly by the deterioration of the biodiesel as due to contaminants and the second is the degradation due to engine wear or fuel delivery system (Yeşilyurt et al., 2019). The quality of biodiesel is affected by the presence of microorganisms during storage which increases corrosion due to the deterioration of metallic tanks (Baena & Calderón, 2020), They form hydroperoxides during oxidation leading to an increase in acidity and thus corroding the vehicle system (De Carvalho et al., 2016). Since some of the metals are used for building parts of storage containers, there is an importance in the studying of their effect as they are contacted with biodiesel over time (Fazal et al., 2012). Evaluation carried out to study the corrosion behaviours of aluminium (Al), carbon steel (CS), stainless steel (SS) and copper (Cu) on biodiesel and petrodiesel at 43°C showed that Cu and CS showed the highest corrosion (Hu et al., 2012), while a corrosion test was conducted for magnesium (Mg) and Al influence on biodiesel showing that Mg resulted in higher corrosion (Chew et al., 2013). Studies show that the presence of certain metals such as Cu, Fe, Ni, Sn, and brass (a copper-rich alloy) can increase the oxidization of fatty oils. The presence of Cu, at 70 ppm in rapeseed oil greatly increased its oxidation. Copper has also been found to reduce the oxidation stability (OS) of methyl oleate more than either Fe or Ni while iron is a very effective hydroperoxides decomposer and its effect on rapeseed oil methyl esters was more pronounced at 40°C than at 20°C, (Sarin, 2012). Biodiesel stability depends on temperature, light and the presence of metals and other elements that can accelerate the oxidation process (Chaves et al., 2010).

2.12.2 Effect on Human Health

Pollution from biodiesel is not near that of petro-diesel yet, but toxic metals from biodiesel can find their way into the environment in different ways. Elkadi et al., (2014), studied influence of metal uptake during biodiesel production when acid and base catalyst were used, he found that low levels of Be, Se, Ti, Pb, Bi were produced when NaOH was used while using KOH presented low Sb. It was concluded that these deleterious elements can

be released into the atmosphere as exhaust fumes from biodiesel combustion then migrate into the soil and water table. Heavy metals present in biomass can be toxic to human health and consequently the quality of the environment (Ruzinska et al., 2015). An estimation of 80% of the daily dose of heavy metals enter the human body through the consumption of food (Szyczewski et al., 2016). Metals are usually emitted as oxides and other minor compounds such as sulphates, nitrates and peroxides (Health Effects Institute, 2002). The smaller the particle size the greater particles can reach vital parts of the human body such as the lungs, liver and brain (Rainho et al., 2013). In urban aerosols, the abundance of Na, K, Al, Pb, Ni, Cr, Ti, V and Zn and less U and Ce were reported (Sanderson et al., 2014). Particle matter under 10 μm have an impact on human health (Health Effects Institute, 2002). Copper poisoning symptoms in humans include renal failure, liver failure and coma, abdominal pain, dizziness, tachycardia, and digestive haemorrhage (Anant et al., 2018).

2.12.3 Effect on Emission and Engine Performance

Heavy metal has a negative influence on the quality of oils (especially taste and smell), they can accelerate the rancidification process of oils Szyczewski et al., (2016), resulting in many mechanical problems in the engine like corrosion of parts which consequently leads to environmental harm (Sánchez et al., 2015). These metals can form unwanted deposits in the vehicles causing corrosion within rubber hosing, tubes and ultimately clog fuel lines (Pillay et al., 2012). Their determination is very critical in the characterization of biodiesel since they possess many harmful effects, i.e. decreased oxidative stability of vegetable oils, deactivation of catalysts and clogging engine parts with their undesirable residuum of metal oxides (Pillay et al., 2012). Some metals such as Al and Sn are characterized by low catalytic activity while Cu and Fe accelerate oxidation reaction Garrido et al., (1994), as well as Ca and Mg (Mendil et al., 2009). Korn et al., (2010), found that phosphorous (P) can poison the catalytic converters within the engine causing the release of CO, CO_2 and SO_2 emissions, while Cd and Zn may be partially lost by volatilization (Black, 1975). Garrido et al., (1994), reported that the most concerning elements are catalyst residues and sulfur.

2.13 Storage of Biodiesel

Storage instability is the time at which a liquid fuel once interacted with hindering factors and conditions such as temperature will cause unacceptable physical and chemical changes (Tamsma & Pallansch, 1964; Lushinga et al., 2020). Additionally, if a liquid fuel or biodiesel interact with contaminants and water causing oxidation Bhandarkar & Nijagunappa, (2011), this happens due exposure to light and temperature as reported by

Varatharajan & Pushparani, (2018) and other stress factors which accelerate the oxidation degradability of the fuel and reduce the cleanliness of the fuel (McCormick & Westbrook, 2010). The resistance of biodiesel to oxidation degradation during storage is an important issue for its viability and sustainability as an alternative fuel (Kivevele & Huan, 2015). Several studies related to the storage stability of biodiesel derived from less common tree-borne non-edible oil seeds under different conditions have been reported in the literature. The nature of storage of biodiesel container can affect the rate of oxidation (Farahani et al., 2009). For instance, a study conducted by Sarin et al., (2012), evaluated the influence of contact between metal contaminants and jatropha biodiesel over 6 months on the oxidation stability and results indicated that copper contamination had the strongest detrimental and catalytic effect on the oxidation stability of biodiesel. This was previously reported by Jain & Sharma, (2010), and Leung et al., (2006) investigated of degradation characteristics of biodiesel stored at 4°C, 20 °C and 40 °C for 52 weeks showed that there was less than 10% purity decrease for sample kept at 4 °C and 20 °C and nearly 40% degradation at (40 °C). A conclusion that storage conditions such as high temperature with air exposure will increase the rate of degradation in biodiesel significantly. Furthermore, water content as a result of organic acidity will promote hydrolysis and consequent degradation (Bondioli et al., 1995). Komariah et al., (2017), suggested that if a fuel (pure or blended) is kept longer than 6 months, an antioxidant should be added.

2.14 References

Aarthy, M., Saravanan, P., Gowthaman, M.K., Rose, C. & Kamini, N.R. 2014. Enzymatic transesterification for production of biodiesel using yeast lipases: An overview. *Chemical Engineering Research and Design*, 92(8): 1591–1601. http://dx.doi.org/10.1016/j.cherd.2014.04.008

Aasberg-petersen, B.K., Nielsen, C.S., Dybkjær, I. & Perregaard, J. 2008. Large Scale Methanol Production from Natural Gas. *Haldor Topsøe*: 2–13. Available online: https://www.researchgate.net/profile/Rick_Manner/post/CO2_Hydrogenation_to_produce_methanol_model_simulation/attachment/59d650a279197b80779a963d/AS%3A503928378884096%401497157296471/download/Topsoe_large_scale_methanol_prod_paper.pdf [accessed on 25 March 2021]

Abbaszaadeh, A., Ghobadian, B., Omidkhah, M.R. & Najafi, G. 2012. Current biodiesel production technologies: A comparative review. *Energy Conversion and Management*, 63: 138–148. http://dx.doi.org/10.1016/j.enconman.2012.02.027

Adams, C.A., Loeper, P., Krieger, R., Andrie, M.J. & Foster, D.E. 2013. Effects of biodiesel-gasoline blends on gasoline direct-injection compression ignition (GCI) combustion. *Fuel*, 111: 784–790. http://dx.doi.org/10.1016/j.fuel.2013.04.074

Agarwal, M., Chauhan, G., Chaurasia, S.P. & Singh, K. 2012. Journal of the Taiwan Institute of Chemical Engineers Study of catalytic behavior of KOH as homogeneous and

heterogeneous catalyst for biodiesel production. *Journal of the Taiwan Institute of Chemical Engineers*, 43(1): 89–94. http://dx.doi.org/10.1016/j.jtice.2011.06.003

Aisyah, L., Bethari, S.A., Wibowo, C.S., Hermawan, N., Alwi, D.U., Rulianto, D. & Anggarani, R. 2019. Water content in biodiesel for diesel fuel blends: Measurement using centrifuge and coulometric titration method. *IOP Conference Series: Material Science Engineering*, 494(1): 1–4. http://dx.doi.org/10.1088/1757-899X/494/1/012082

Al-Abdullah, M.H., Kalghatgi, G.T. & Babiker, H. 2015. Flash points and volatility characteristics of gasoline/diesel blends. *Fuel*, 153: 2–9. http://dx.doi.org/10.1016/j.fuel.2015.02.070

Al-lwayzy, S.H. & Yusaf, T. 2017. Diesel engine performance and exhaust gas emissions using Microalgae Chlorella protothecoides biodiesel. *Renewable Energy*, 101: 690–701. http://dx.doi.org/10.1016/j.renene.2016.09.035

Aleme, H.G. & Barbeira, P.J.S. 2012. Determination of biodiesel content in diesel using distillation curves and multivariate calibration. *Energy and Fuels*, 26(9): 5769–5774. http://dx.doi.org/10.1021/ef3008757

Allah, F.U.M. & Alexandru, G. 2016. Waste cooking oil as source for renewable fuel in Romania. *IOP Conf. Ser.: Mater. Sci. Eng.*, 147(1): 1–6. http://dx.doi.org/10.1088/1757-899X/147/1/012133

Alleman, T.L., Fouts, L. & Chupka, G. 2013. Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011. *National Renewable Energy Laboratory*: 1–35. Available online: http://www.osti.gov/bridge [accessed on 02 August 2021]

Alleman, T.L., Mccormick, R.L., Christensen, E.D., Fioroni, G., Moriarty, K. & Yanowitz, J. 2016. *Biodiesel handling and use guide*. 5th ed. United states: n. p. Available online: https://www.osti.gov/servlets/purl/1347103 [accessed 31 July 2021]

Almeida, E.S., Portela, F.M., Sousa, R.M.F., Daniel, D., Terrones, M.G.H., Richter, E.M. & Muñoz, R.A.A. 2011. Behaviour of the antioxidant tert-butylhydroquinone on the storage stability and corrosive character of biodiesel. *Fuel*, 90(11): 3480–3484. http://dx.doi.org/10.1016/j.fuel.2011.06.056

Alptekin, E., Canakci, M. & Sanli, H. 2014. Biodiesel production from vegetable oil and waste animal fats in a pilot plant. *Waste Management*, 34(11): 2146–2154. http://dx.doi.org/10.1016/j.wasman.2014.07.019

Anant, J.K., Inchulkar, S.R., Bhagat, S. 2018. An overview of Copper Toxicity Relevance to public Health. *European Journal of Pharmaceutical and Medical Research*, 5(11): 232–237. http://dx.doi.org/10.5694/j.1326-5377.1978.tb131528.x

Anitescu, G. & Bruno, T.J. 2012. Biodiesel fuels from supercritical fluid processing: Quality evaluation with the advanced distillation curve method and cetane numbers. *Energy and Fuels*, 26(8): 5256–5264

Aransiola, E.F., Ojumu, T. V, Oyekola, O.O. & Madzimbamuto, T.F. 2013. ScienceDirect A review of current technology for biodiesel production : State of the art. *Biomass and Bioenergy*, 61: 276–297. http://dx.doi.org/10.1016/j.biombioe.2013.11.014

De Araújo, M.C.D., De Andrade, C.., De Souza, E.. & Dupas, F.A. 2013. Biodiesel production from used cooking oil: A review. *Renewable and Sustainable Energy Reviews*, 27: 445–452. http://dx.doi.org/10.1016/j.rser.2013.06.014

Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H. & Mekhilef, S. 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, 16(4): 2070–2093. http://dx.doi.org/10.1016/j.rser.2012.01.003

Ateeq, E.A. 2015. Biodiesel Viscosity and Flash Point Determination. *Paper presented at The Eight palestinian Internatioonal Chemistry Conference (PICC), Nablus, Palestine, 22 April 2015*: 101–109. Available online: https://www.researchgate.net/publication/275526328_Biodiesel_Viscosity_and_Flash_Point_Determination. [Accessed on 31 July 2021]

Avhad, M.R. & Marchetti, J.M. 2015. A review on recent advancement in catalytic materials for biodiesel production. *Renewable and Sustainable Energy Reviews*, 50: 696–718. http://dx.doi.org/10.1016/j.rser.2015.05.038

Awogbemi, O., Onuh, E.I. & Inambao, F.L. 2019. Comparative study of properties and fatty acid composition of some neat vegetable oils and waste cooking oils. *International Journal of Low-Carbon Technologies*, 14(3): 417–425. http://dx.doi.org/10.1093/ijlct/ctz038

Aworanti, O.A., Agarry, S.E. & Ajani, A.O. 2012. A Laboratory Study of the Effect of Temperature on Densities and Viscosities of Binary and Ternary Blends of Soybean Oil, Soy Biodiesel and Petroleum Diesel Oil. *Advances in Chemical Engineering and Science*, 2: 444–452. http://dx.doi.org/10.4236/aces.2012.24054

Azócar, L., Ciudad, G., Heipieper, H.J. & Navia, R. 2010. Biotechnological processes for biodiesel production using alternative oils. *Applied Microbiology and Biotechnology*, 88(3): 621–636. http://dx.doi.org/10.1007/s00253-010-2804-z

Baena, L.M. & Calderón, J.A. 2020. Effects of palm biodiesel and blends of biodiesel with organic acids on metals. *Heliyon*, 6(5): 2–13. http://dx.doi.org/10.1016/j.heliyon.2020.e03735

Bamankar, P.B., Shubham, J. & Ruturaj, P.M. 2015. A Review on Emission Analysis of Waste Vegetable Oil Methyl Ester on IC Engine. *International Journal for Scientific research &* Development, 3(08): 473–475. Available online: http://ijsrd.com/Article.php?manuscript=IJSRDV3I80346 [accessed on 25 July 2020]

Barabas, I. & Todoru, I.-A. 2011. Biodiesel Quality, Standards and Properties. In *Montero, G.,* (Ed.). *Biodiesel Quality, Emission and By-Products*. Rijeka, Croatia: InTech: 1–28. http://dx.doi.org/10.5772/25370

Baskar, G. & Aiswarya, R. 2016. Trends in catalytic production of biodiesel from various feedstocks. *Renewable and Sustainable Energy Reviews*, 57: 496–504. http://dx.doi.org/10.1016/j.rser.2015.12.101

Bautista, L.F., Vicente, G., Rodríguez, R. & Pacheco, M. 2009. Optimisation of FAME production from waste cooking oil for biodiesel use. *Biomass and Bioenergy*, 33(5): 862–872. http://dx.doi.org/10.1016/j.biombioe.2009.01.009

Benjumea, P., Agudelo, J. & Agudelo, A. 2008. Basic properties of palm oil biodiesel-diesel blends. *Fuel*, 87: 2069–2075. http://dx.doi.org/10.1016/j.fuel.2007.11.004

Bhandarkar, S. & Nijagunappa, R. 2011. Use of bio-diesel as an alternative fuel for sustainable development of transport in Gulbarga bus depots. In Institution of mechanical Engineers. *Innovations in Fuel Economy and Sustainable Road Transport*. Cambridge, UK: Woodhead publishing: 149–160. http://dx.doi.org/10.1533/9780857095879

Bhangale, J.H. & Kulkarni, A.B. 2017. Effects of biodiesel from different feedstocks on engine performance and emissions: A review. *International research Journal of Engineering and Technology*, 4(7): 3273–3279. http:https://doi.org/10.1016/j.rser.2015.06.031

Biswas, S., Katiyar, R., Gurjar, B.R. & Pruthi, V. 2017. Biofuels and their Production Through Different Catalytic Routes. *Chem Biochem. Eng. Q*, 31(1): 47–62. https://doi.org/10.15255/CABEQ.2016.897

Black, L.T. 1975. Comparison of three atomic absorption techniques for determining metals in soybean oil. *Journal of the American Oil Chemists Society*, 52 (3): 88–91. http://dx.doi.org/10.1007/BF02633044

Blumberg, T., Lee, Y.D., Morosuk, T. & Tsatsaronis, G. 2019. Exergoenvironmental analysis of methanol production by steam reforming and autothermal reforming of natural gas. *Energy*, 181: 1273–1284. https://doi.org/10.1016/j.energy.2019.05.171

Bondioli, P., Gasparoli, A., Lanzani, A., Fedeli, E., Veronese, S. & Sala, M. 1995. Storage stability of biodiesel. *Journal of the American Oil Chemists' Society*, 72(6): 699–702. http://dx.doi.org/10.1007/BF02635658

Boshui, C., Yuqiu, S., Jianhua, F., Jiu, W. & Jiang, W. 2010. Effect of cold flow improvers on flow properties of soybean biodiesel. *Biomass and Bioenergy*, 34(9): 1309–1313. http://dx.doi.org/10.1016/j.biombioe.2010.04.001

Budiman, Y. & Putra, Z.A. 2018. Biodiesel production from waste cooking oil: A review. In *Recycled Cooking Oil: Processing and Uses*. Hauppauge, NY: Nova Science Publishers, Inc.: 89–109. Available online: https://www.scopus.com/inward/record.uri?eid=2-s2 [accessed on 12 June 2020]

Can, Ö. 2014. Combustion characteristics, performance and exhaust emissions of a diesel engine fueled with a waste cooking oil biodiesel mixture. *Energy Conversion and Management*, 87: 676–686. http://dx.doi.org/10.1016/j.enconman.2014.07.066

Can, Ö., Öztürk, E. & Yücesu, H.S. 2017. Combustion and exhaust emissions of canola biodiesel blends in a single cylinder DI diesel engine. *Renewable Energy*, 109: 73–82. http://dx.doi.org/10.1016/j.renene.2017.03.017

Canesin, E.A., de Oliveira, C.C., Matsushita, M., Felicidade Dias, L., Reghiany Pedrão, M. & de Souza, N.E. 2014. Characterization of residual oils for biodiesel production. *Electronic Journal of Biotechnology*, 17(1): 39–45. http://dx.doi.org/10.1016/j.ejbt.2013.12.007

De Carvalho, A.L., Cardoso, E.A., Da Rocha, G.O., Teixeira, L.S.G., Pepe, I.M. & Grosjean, D.M. 2016. Carboxylic acid emissions from soybean biodiesel oxidation in the

EN14112 (Rancimat) stability test. *Fuel*, 173: 29–36. http://dx.doi.org/10.1016/j.fuel.2015.12.067

Cavalheiro, L.F., Misutsu, M.Y., Rial, R.C., Viana, L.H. & Oliveira, L.C.S. 2020. Characterization of residues and evaluation of the physico chemical properties of soybean biodiesel and biodiesel: Diesel blends in different storage conditions. *Renewable Energy*, 151: 454–462. https://doi.org/10.1016/j.renene.2019.11.039

Chandran, D. 2020. Compatibility of diesel engine materials with biodiesel fuel. *Renewable Energy*, 147: 89–99. https://doi.org/10.1016/j.renene.2019.08.040

Changmai, B., Vanlalveni, C., Ingle, A.P., Bhagat, R. & Rokhum, L. 2020. Widely used catalysts in biodiesel production: A review. *RSC Advances*, 10: 41625–41679. http://dx.doi.org/10.1039/d0ra07931f

Chaudhari, J.C, Seth, P.C. 2017. A Review Paper on Investigation on Diesel Engine using Smart Biodiesel. International Journal for innovative Research in Science & Technology, 3(11): 218–222. Available online: http://www.ijirst.or/articles/IJIRSTV3I11145.pdf. [accessed on 31 July 2021]

Chaves, E.S., José, E., Araujo, R.G.O., Vladimir, J., Lúcia, V., Frescura, A. & Curtius, A.J. 2010. Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS. *Microchemical Journal*, 96(1): 71–76. http://dx.doi.org/10.1016/j.microc.2010.01.021

Chaves, E.S., Loos-vollebregt, M.T.C. De, Curtius, A.J. & Vanhaecke, F. 2011. Spectrochimica Acta Part B Determination of trace elements in biodiesel and vegetable oil by inductively coupled plasma optical emission spectrometry following alcohol dilution. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 66: 733–739. http://dx.doi.org/10.1016/j.sab.2011.09.006

Chen, H., He, J., Chen, Y. & Hua, H. 2018. Performance of a common rail diesel engine using biodiesel of waste cooking oil and gasoline blend. *Journal of the Energy Institute*, 91(6): 856–866. https://doi.org/10.1016/j.joei.2017.10.003

Chew, K. V., Haseeb, A.S.M.A., Masjuki, H.H., Fazal, M.A. & Gupta, M. 2013. Corrosion of magnesium and aluminum in palm biodiesel: A comparative evaluation. *Energy*, 57: 478–483. http://dx.doi.org/10.1016/j.energy.2013.04.067

Chin, M. 2011. Biofuels in Malaysia: An analysis of the legal and institutional framework. *Center for International Forestry Research*: 2-23. https://doi.org/10.17528/cifor/003470

Cho, Y.B., Seo, G. & Chang, D.R. 2009. Transesterification of tributyrin with methanol over calcium oxide catalysts prepared from various precursors. *Fuel Processing Technology*, 90(10): 1252–1258. http://dx.doi.org/10.1016/j.fuproc.2009.06.007

Chouhan, A.P.S. & Sarma, A.K. 2011a. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 15(9): 4378–4399. http://dx.doi.org/10.1016/j.rser.2011.07.112

Chouhan, A.P.S. & Sarma, A.K. 2011b. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 15(9): 4378–4399. http://dx.doi.org/10.1016/j.rser.2011.07.112

Cursaru, D.L., Brănoiu, G., Ramadan, I. & Miculescu, F. 2014. Degradation of automotive materials upon exposure to sunflower biodiesel. *Industrial Crops and Products*, 54: 149–158. https://doi.org/10.1016/j.indcrop.2014.01.032

Dalena, F., Senatore, A., Basile, M., Knani, S., Basile, A. & Iulianelli, A. 2018. Advances in methanol production and utilization, with particular emphasis toward hydrogen generation via membrane reactor technology. *Membranes*, 8(4): 2-27. https://doi.org/10.3390/membranes8040098

Das, S.K., Kim, K. & Lim, O. 2018. Experimental study on non-vaporizing spray characteristics of biodiesel-blended gasoline fuel in a constant volume chamber. *Fuel Processing Technology*, 178: 322–335. https://doi.org/10.1016/j.fuproc.2018.05.009

Demirbas, A. 2005. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31(5–6): 466–487. https://doi.org/10.1016/j.pecs.2005.09.001

Demirbas, A. 2007. Importance of biodiesel as transportation fuel. *Elsevier*, 35: 4661–4670. https://doi.org/10.1016/j.enpol.2007.04.003

Demshemino, S.I., Sylvester, P.O., Yahaya, M.F., Nwadike, I. & Okoro, L.. 2013. Comparative analysis of Biodiesel and Petroleum Diesel. *International Journal of Education and Research*, 1(8): 1–8. Available oniline: https://www.researchgate.net/publication/301552040 [accessed on 31 July 2021]

Deutschmann, O., Knözinger, H., Kochloefl, K. & Turek, T. 2009. Heterogeneous catalysis and solid catalysts. *Ullmann's Encyclopedia of Industrial Chemistry*, 1: 2–110. https://doi.org/10.1002/14356007.a05_313.pub2

Dixon, D.J. 2016. Bifunctional catalysis. *Beilstein Journal of Organic Chemistry*, 12: 1079–1080. https://doi.org/10.3762/bjoc.12.102

Don, T., Sinks, D. & Other, O.R. 2013. Available Technologies and Materials for Waste Cooking Oil Recycling. *Processes*, 8(366): 1–13. https://doi.org/10.3390/pr8030366

Dossin, T.F., Reyniers, M.F., Berger, R.J. & Marin, G.B. 2006. Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. *Applied Catalysis B: Environmental*, 67(1–2): 136–148. https://doi.org/10.1016/j.apcatb.2006.04.008

Dwivedi, G. & Sharma, M.P. 2014. Impact of antioxidant and metals on biodiesel stability-a review. *Journal of Materials and Environmental Science*, 5(5): 1412–1425.

El-Kassaby, M. & Nemit-Allah, M.A. 2013. Studying the effect of compression ratio on an engine fueled with waste oil produced biodiesel/diesel fuel. *Alexandria Engineering Journal*, 52(1): 1–11. https://doi.org/10.1016/j.aej.2012.11.007

Elangovan, T. 2017. Biodiesel and its Properties from Various Feedstocks. *International Journal for Trends in Engineering & Technology*, 1(2): 1–7. Available online: https://www.researchgate.net/publication/313106496 [accessed on 13 September 2019]

Elkadi, M., Pillay, A., Manuel, J., Khan, M.Z., Stephen, S. & Molki, A. 2014. Sustainability study on heavy metal uptake in neem biodiesel using selective catalytic preparation and hyphenated mass spectrometry. *Sustainability*, 6(5): 2413–2423. https://doi.org/10.3390/su6052413

Elkady, M.F., Zaatout, A. & Balbaa, O. 2015. Production of Biodiesel from Waste Vegetable Oil via KM Micromixer. *Journal of Chemistry*, 2015: 2–9. https://doi.org/10.1155/2015/630168

Farahani, M., Pagé, D.J.Y.S., Turingia, M.P. & Tucker, B.D. 2009. Storage stability of biodiesel and ultralow sulfur diesel fuel blends. *Journal of Energy Resources Technology, Transactions of the ASME*, 131(4): 0418011–0418016. https://doi.org/10.1115/1.4000177

Fazal, M.A., Haseeb, A.S.M.A. & Masjuki, H.H. 2011. Biodiesel feasibility study: An evaluation of material compatibility; Performance; emission and engine durability. *Renewable and Sustainable Energy Reviews*, 15(2): 1314–1324. http://dx.doi.org/10.1016/j.rser.2010.10.004

Fazal, M.A., Haseeb, A.S.M.A. & Masjuki, H.H. 2012. Degradation of automotive materials in palm biodiesel. *Energy*, 40(1): 76–83. http://dx.doi.org/10.1016/j.energy.2012.02.026

Fazal, M.A., Suhaila, N.R., Haseeb, A.S.M.A., Rubaiee, S. & Al-Zahrani, A. 2018. Influence of copper on the instability and corrosiveness of palm biodiesel and its blends: An assessment on biodiesel sustainability. *Journal of Cleaner Production*, 171: 1407–1414. https://doi.org/10.1016/j.jclepro.2017.10.144

De Feo, G., Di Domenico, A., Ferrara, C., Abate, S. & Osseo, L.S. 2020. Evolution of waste cooking oil collection in an area with long-standing waste management problems. *Sustainability (Switzerland)*, 12(20): 1–16. https://doi.org/10.3390/su12208578

Folayan, A.J., Anawe, P.A.L., Aladejare, A.E. & Ayeni, A.O. 2019. Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass. *Energy Reports*, 5: 793–806. https://doi.org/10.1016/j.egyr.2019.06.013

Foundation, U.N. 2007. Biofuels for our future: a primer. *Energy Future Coalition*: 1-59. Available online: http://energyfuturecoalition.org/biofuels_faq. [accessed on 25 March 2021]

Fregolente, P.B.L., Wolf Maciel, M.R. & Oliveira, L.S. 2015. Removal of water content from biodiesel and diesel fuel using hydrogel adsorbents. *Brazilian Journal of Chemical Engineering*, 32(4): 895–901. https://doi.org/10.1590/0104-6632.20150324s20140142

Fukuda, H., Kondo, A. & Noda, H. 2001. Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*, 92(5): 405–416. https://doi.org/10.3390/su6052413

Gad, M.S., EL-Seesy, A.I., Radwan, A. & He, Z. 2020. Enhancing the combustion and emission parameters of a diesel engine fueled by waste cooking oil biodiesel and gasoline additives. *Fuel*, 269: 2–11 . https://doi.org/10.1016/j.fuel.2020.117466

Gad, M. S. & Ismail, M.A. 2021. Effect of waste cooking oil biodiesel blending with gasoline and kerosene on diesel engine performance, emissions and combustion characteristics. *Process Safety and Environmental Protection*, 149: 1–10. https://doi.org/10.1016/j.psep.2020.10.040

Garrido, M.D., Frías, I., Díaz, C. & Hardisson, A. 1994. Concentrations of metals in vegetable edible oils. *Food Chemistry*, 50(3): 237–243. https://doi.org/10.1016/0308-8146(94)90127-9

Ghoreishi, S.M. & Moein, P. 2013. Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. *Journal of Supercritical Fluids*, 76: 24–31. http://dx.doi.org/10.1016/j.supflu.2013.01.011

Giakoumis, E.G. 2018. Analysis of 22 vegetable oils' physico-chemical properties and fatty acid composition on a statistical basis, and correlation with the degree of unsaturation. *Renewable Energy*, 126: 403–419. https://doi.org/10.1016/j.renene.2018.03.057

Habibullah, M., Masjuki, H.H., Kalam, M.A., Rizwanul Fattah, I.M., Ashraful, A.M. & Mobarak, H.M. 2014. Biodiesel production and performance evaluation of coconut, palm and their combined blend with diesel in a single-cylinder diesel engine. *Energy Conversion and Management*, 87: 250–257. http://dx.doi.org/10.1016/j.enconman.2014.07.006

Hájek, M., Skopal, F., Vávra, A. & Kocík, J. 2017. Transesterification of rapeseed oil by butanol and separation of butyl ester. *Journal of Cleaner Production*, 155: 28–33. http://dx.doi.org/10.3390/su6052413

Han, D., Ickes, A.M., Assanis, D.N., Huang, Z. & Bohac, S. V. 2010. Attainment and load extension of high-efficiency premixed low-temperature combustion with edieseline in a compression ignition engine. *Energy and Fuels*, 24(6): 3517–3525. http://dx.doi.org/10.1021/ef100269c

Han, D., Ickes, A.M., Bohac, S. V., Huang, Z. & Assanis, D.N. 2012. HC and CO emissions of premixed low-temperature combustion fueled by blends of diesel and gasoline. *Fuel*, 99: 13–19. http://dx.doi.org/10.1016/j.fuel.2012.04.010

Han, D., Ickes, A.M., Bohac, S. V., Huang, Z. & Assanis, D.N. 2011. Premixed low-temperature combustion of blends of diesel and gasoline in a high speed compression ignition engine. *Proceedings of the Combustion Institute*, 33(2): 3039–3046. http://dx.doi.org/10.1016/j.proci.2010.07.045

Hassan, M.H. & Kalam, M.A. 2013. An overview of biofuel as a renewable energy source: Development and challenges. *Procedia Engineering*, 56: 39–53. http://dx.doi.org/10.1016/j.proeng.2013.03.087

Health Effects Institute. 2002. Understanding the Health Effects of Components of the Particulate Matter Mix: Progress and Next Steps. *HEI Perspectives*: 1–20. Available online: https://www.healtheffects.org/publication/understanding-health-effects-components-particulate-matter-mix-progress-and-next-steps [accessed on 02 August 2021].

Hossain, A.B.M.S., Boyce, A.N., Salleh, A. & Chandran, S. 2010. Impacts of alcohol type, ratio and stirring time on the biodiesel production from waste canola oil. *African Journal of Agricultural Research*, 5(14): 1851–1859. http://dx.doi.org/10.5897/AJAR09.135

Hu, E., Xu, Y., Hu, X., Pan, L. & Jiang, S. 2012. Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol. *Renewable Energy*, 37(1): 371–378. http://dx.doi.org/10.1016/j.renene.2011.07.010

Huang, D., Zhou, H. & Lin, L. 2011. Biodiesel: An alternative to conventional fuel. *Energy Procedia*, 16: 1874–1885. http://dx.doi.org/10.1016/j.egypro.2012.01.287

International Energy Agency. 2021. Net Zero by 2050 A Roadmap for the Global Energy Sector. 2-222. Available online: https://iea.blob.core.windows.net/assets/4719e321-6d3d-41a2-bd6b-461ad2f850a8/NetZeroby2050-ARoadmapfortheGlobalEnergySector.pdf. [accessed on 31 July 2021]

Institute, M. 2010. MethanolFact: About Methanol. *Methanol.Org*. Available online: http://www.methanol.org/wp-content/uploads/2016/06/About-Methanol-FS.pdf. [accessed 02 August 2021]

Isis, A., Oliveira, A.P. De, Magalhães, M.R.L. De & Villa, R.D. 2012. Determination of sodium and potassium in biodiesel by flame atomic emission spectrometry , with dissolution in ethanol as a single sample preparation step. *Fuel*, 93: 381–384. http://dx.doi.org/10.1016/j.fuel.2011.08.060

Ito, T., Sakurai, Y., Kakuta, Y., Sugano, M. & Hirano, K. 2012. Biodiesel production from waste animal fats using pyrolysis method. *Fuel Processing Technology*, 94(1): 47–52. http://dx.doi.org/10.1016/j.fuproc.2011.10.004

Jabade, S., Sakthivel, M. & Chavan, S. 2020. Bio-diesel as an alternative fuel for compression ignition engine: A review. *International Journal Advanced Science Technology*, 29(1): 18–28. Available online: http://sersc.org/journals/index.php/IJAST/article/view/2975 [accessed on 13 January 2020]

Jain, S. & Sharma, M.P. 2010a. Review of different test methods for the evaluation of stability of biodiesel. *Renewable and Sustainable Energy Reviews*, 14(7): 1937-1947. http://dx.doi.org/10.1016/j.rser.2010.04.011

Jain, S. & Sharma, M.P. 2010b. Thermal stability of biodiesel and its blends: A review. *Renewable and Sustainable Energy Reviews*, 14: 667-687. http://dx.doi.org/10.1016/j.rser.2010.08.022

Jiang, S., Qi, J., Hu, Y., Ren, C., Jiang, Y. & Zhao, Z. 2019. Predicting the Density and Viscosity of Biodiesels and Biodiesel Blends by the Regular-Solution Theory. *Industrial and Engineering Chemistry Research*, 58(36): 17038–17048. http://dx.doi.org/10.1021/acs.iecr.9b03046

Kaiadi, M., Johansson, B., Lundgren, M. & Gaynor, J.A. 2013. Experimental Investigation on different Injection Strategies for Ethanol Partially Premixed Combustion. *SAE Technical Paper*: 2–19. https://doi.org/10.4271/2013-01-0281

Karavalakis, G., Stournas, S. & Karonis, D. 2010. Evaluation of the oxidation stability of diesel / biodiesel blends. *Fuel*, 89(9): 2483–2489. http://dx.doi.org/10.1016/j.fuel.2010.03.041

Kadam, P.M, & Kale, P.T. 2015. Performance Analysis of Biodiesel Blend in Diesel Engine - A review. Global Journal of Engineering Science and Researches, 2(3): 99–104. Available online: https://www.researchgate.net/publication/313439676. [accessed on 13 January 2021]

Kawashima, A., Matsubara, K. & Honda, K. 2009. Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresource Technology*, 100(2): 696–700. https://doi.org/10.1016/j.biortech.2008.06.049

Kheiralla, A.F., El-Awad, M., Hassan, M.Y., Hussen, M.A. & Osman, H.I. 2011. Effect of Ethanol−Gasoline Blends on Fuel Properties Characteristics of Spark Ignition Engines. *University of Khartoum Engineering Journal,* 1(2): 22–28. Available online: https://www.researchgate.net/publication/263773714. [accessed on 20 June 2021]

Khuong, L.S., Masjuki, H.H., Zulkifli, N.W.M., Mohamad, E.N., Kalam, M.A., Alabdulkarem, A., Arslan, A., Mosarof, M.H., Syahir, A.Z. & Jamshaid, M. 2017. Effect of gasoline-bioethanol blends on the properties and lubrication characteristics of commercial engine oil. *RSC Advances*, 7: 15005–15019. https://doi.org/10.1039/c7ra00357a

Kivevele, T. & Huan, Z. 2015. Review of the stability of biodiesel produced from less common vegetable oils of African origin. *South African Journal of Science*, 111(9/10): 1–7. https://doi.org/10.17159/sajs.2015/20140434

Knittel, C.R. 2012. Reducing Petroleum Consumption Transportation. *Journal of Economic Perspectives*, 26(1): 93–118. Available online: https://pubs.aeaweb.org/doi/pdf/10.1257/jep.26.1.93 [accessed on 23 March 2020]

Knothe, G. 2010. Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3): 364–373. http://dx.doi.org/10.1016/j.pecs.2009.11.004

Kohse-Höinghaus, K. 2018. Clean combustion: Chemistry and diagnostics for a systems approach in transportation and energy conversion. *Progress in Energy and Combustion Science*, 65: 1–5. https://doi.org/10.1016/j.pecs.2017.10.001

Kolesinska, B., Fraczyk, J., Binczarski, M., Modelska, M., Berlowska, J., Dziugan, P., Antolak, H., Kaminski, Z.J., Witonska, I.A. & Kregiel, D. 2019. Butanol synthesis routes for biofuel production: Trends and perspectives. *Materials*, 12(3): 2–22 https://doi.org/10.3390/ma12030350

Komintarachat, C. & Chuepeng, S. 2009. Solid Acid Catalyst for Biodiesel Production from Waste Used Cooking Oils. *Ind. Eng. Chem Res,* 48(20): 9350–9353. https://doi.org/10.1021/ie901175d

Korn, M.G.A, Santos, D.C.M.B., Guida, M.A.B., Barbosa, I.S. & Passos, M.L.C. 2010. Evaluation of Digestion Proceures for Simultaneous Determination of Ca, P, Mg, K and Na in Biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry. *J. Braz. Chem. Soc*, 21(12): 2278–2284. https://doi.org/10.1590/S0103-50532010001200015

Körbitz, W. 1999. Biodiesel production in Europe and North America, an encouraging prospect. *Renewable Energy*, 16: 1078–1083. https://doi.org/10.1016/s0960-1481(98)00406-6

Koval, L.I., Dzyuba, V.I., Ilnitska, O.L. & Pekhnyo, V.I. 2008. Efficient transesterification of ethyl acetoacetate with higher alcohols without catalysts. *Tetrahedron Letters*, 49(10): 1645–1647. https://doi.org/10.1016/j.tetlet.2008.01.018

Kulkarni, M.G. & Dalai, A.K. 2006. Waste cooking oil - An economical source for biodiesel: A review. *Industrial and Engineering Chemistry Research*, 45(9): 2901–2913. https://doi.org/10.1021/ie0510526

Kumar, M. & Gayen, K. 2011. Developments in biobutanol production: New insights. *Applied Energy*, 88(6): 1999–2012. https://doi.org/10.1016/j.apenergy.2010.12.055

Kumar, N. 2017. Oxidative stability of biodiesel: Causes, effects and prevention. *Fuel*, 190: 328–350. http://dx.doi.org/10.1016/j.fuel.2016.11.001

Kumar, P., Sharma, M.P. & Dwivedi, G. 2014. Impact of biodiesel on Combustion , Performance and Exhaust Emissions of Diesel Engines. *J Integr Sci Technol*, 2(2): 57–63. Available online: https://www.researchgate.net/publication/263088964 [accessed on 03 May 2021]

Kwong, T.L. & Yung, K.F. 2015. Heterogeneous alkaline earth metal-transition metal bimetallic catalysts for synthesis of biodiesel from low grade unrefined feedstock. *RSC Advances*, 5(102): 83748–83756. http://dx.doi.org/10.1039/c5ra13819a

Lai, E.P.C. 2014. Biodiesel: Environmental friendly Alternative to Petrodiesel. *Journal of Petroleum & Environmental Biotechnology*, 4(1): 1–2. http://dx.doi.org/10.4172/2157-7463.1000e122

Lam, M.K., Lee, K.T. & Mohamed, A.R. 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances*, 28(4): 500–518. https://doi.org/10.1016/j.biotechadv.2010.03.002

Lapuerta, M., Rodríguez-Fernandez, J., García-Contreras, R. & Bogarra, M. 2015. Molecular interactions in blends of alcohols with diesel fuels: Effect on stability and distillation. *Fuel*, 139: 171–179. http://dx.doi.org/10.1016/j.fuel.2014.08.055

Lee, H. V., Juan, J.C. & Taufiq-Yap, Y.H. 2015. Preparation and application of binary acid-base CaO-La2O3 catalyst for biodiesel production. *Renewable Energy*, 74: 124–132. https://doi.org/10.1016/j.renene.2014.07.017

Lee, S., Posarac, D. & Ellis, N. 2011. Process simulation and economic analysis of biodiesel production processes using fresh and waste vegetable oil and supercritical methanol. *Chemical Engineering Research and Design*, 89(12): 2626–2642. https://doi.org/10.1016/j.cherd.2011.05.011

Leung, D.Y.C., Koo, B.C.P. & Guo, Y. 2006. Degradation of biodiesel under different storage conditions. *Bioresource Technology*, 97(2): 250-256. https://doi.org/10.1016/j.biortech.2005.02.006

Leung, D.Y.C., Wu, X. & Leung, M.K.H. 2010. A review on biodiesel production using catalyzed transesterification. *Applied Energy*, 87(4): 1083–1095. http://dx.doi.org/10.1016/j.apenergy.2009.10.006

Liao, C.C. & Chung, T.W. 2013. Optimization of process conditions using response surface methodology for the microwave-assisted transesterification of Jatropha oil with KOH impregnated CaO as catalyst. *Chemical Engineering Research and Design*, 91(12): 2457–2464. http://dx.doi.org/10.1016/j.cherd.2013.04.009

Lima, L.S., Barbosa, T.P., da Silva, L.F.B., Santo, F.D.M., Castro, C.S.C., Siqueira, J.R.R., Barbosa, A.P.F., Marteleto, P.R., Rodrigues, C.R.C & Pereira, R.G. 2010. Biodiesel Density Characterization Using a Pycnometer. *Metrologia*: 1–8. Available

online: https://www.cenam.mx/sm2010/info/pmiercoles/sm2010-mp06a.pdf [accessed on 10 May 2021]

Lin, C.Y. & Lin, Y.W. 2012. Fuel characteristics of biodiesel produced from a high-acid oil from soybean soapstock by supercritical-methanol transesterification. *Energies*, 5(7): 2370–2380. http://dx.doi.org/10.3390/en5072370

Lin, M.Y. & Tanaka, S. 2006. Ethanol fermentation from biomass resources : current state and prospects. *Appl Microbiol Biotechnol*, 69: 627–642. http://dx.doi.org/10.1007/s00253-005-0229-x

Loizides, M.I., Loizidou, X.I., Orthodoxou, D.L. & Petsa, D. 2019. Circular bioeconomy in action: Collection and recycling of domestic used cooking oil through a social, reverse logistics system. *Recycling*, 4(2): 2–10. http://dx.doi.org/10.3390/recycling4020016

Lu, X., Vora, H. & Khosla, C. 2008. Overproduction of free fatty acids in E. coli: Implications for biodiesel production. *Metabolic Engineering*, 10(6): 333–339. http://dx.doi.org/10.1016/j.ymben.2008.08.006

Lushinga, N., Cao, L., Dong, Z. & Assogba, C.O. 2020. Improving storage stability and physicochemical performance of styrene-butadiene-styrene asphalt binder modified with nanosilica. *Sustainability (Switzerland)*, 12(21): 1–22. http://dx.doi.org/10.3390/su12218968

Lynskey, R., Graham, S., Li, M. & Stock, P. 2020. Moving to zero: Accelerating the transition to zero-emissions transport. *Climate Works Australia*, (June): 11-51. Available online: https://www.climateworksaustralia.org/resource/moving-to-zero/ [accessed on 02 September 2020]

Maca, J., Posp, M., Baros, P., Stas, M. & Krausova, A. 2017. Study of Corrosion of Metallic Materials in Ethanol − Gasoline Blends : Application of Electrochemical Methods. *Energy Fuels*, 31: 10880–10889. http://dx.doi.org/10.1021/acs.energyfuels.7b01682

Mahmudul, H.M., Hagos, F.Y., Mamat, R., Adam, A.A., Ishak, W.F.W. & Alenezi, R. 2017. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review. *Renewable and Sustainable Energy Reviews*, 72: 497–509. http://dx.doi.org/10.1016/j.rser.2017.01.001

Małecka, B., Łącz, A., Drozdz, E. & Małecki, A. 2015. Thermal decomposition of d-metal nitrates supported on alumina. *Journal of Thermal Analysis and Calorimetry*, 119(2): 1053–1061. http://dx.doi.org/10.1007/s10973-014-4262-9

Malhotra, D., Mukherjee, J. & Gupta, M.N. 2015. Lipase catalyzed transesterification of castor oil by straight chain higher alcohols. *Journal of Bioscience and Bioengineering*, 119(3): 280–283. https://doi.org/10.1016/j.jbiosc.2014.08.005

Manente, V., Johansson, B. & Tunestal, P. 2009. Partially Premixed Combustion at High Load using Gasoline and Ethanol, a Comparison with Diesel. In *SAE Technical Paper*: 1–11. https://doi.org/10.4271/2009-01-0944

Manivannan, D., Manimaran, K., Elavarasan, K., balaji, R. & Karthik, V. 2017. Performance and Emission Analysis of Single Cylinder Diesel Engine Using Honge Oil Blends With 1,4 Dioxen Additive. *International Journal of Engineering and Applied Sciences*, 4(5): 91–95. Available online:

https://www.neliti.com/id/publications/257460/performance-and-emission-analysis-of-single-cylinder-diesel-engine-using-honge-o. [accessed on 13 January 2021]

Mardhiah, H.H., Ong, H.C., Masjuki, H.H., Lim, S. & Lee, H. V. 2017. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews*, 67: 1225–1236. http://dx.doi.org/10.1016/j.rser.2016.09.036

Mata, T.M. & Martins, A.A. 2015. Biodiesel Production Processes. In Delgado, J.M.P.Q (Ed.). *Current Trends in Chemical Engineering*. New Delhi, Delhi: Studium Press: 314–340 Available online: https://www.researchgate.net/publication/280728855 [accessed on 25 March 2021]

Mateĭjovský, L., Macák, J., Pospíšil, M., Baroš, P., Staš, M & Krausova, A. 2017. Study of Corrosion of Metallic Materials in Ethanol − Gasoline Blends: Application of Electrochemical Methods. *Energy and Fuels*, 31: 10880–10889. http://dx.doi.org/10.1021/acs.energyfuels.7b01682

Matějovský, L., Macák, J., Pospíšil, M., Staš, M., Baroš, P. & Krausová, A. 2018. Study of Corrosion Effects of Oxidized Ethanol-Gasoline Blends on Metallic Materials. *Energy and Fuels*, 32(4): 5145–5156. http://dx.doi.org/10.1021/acs.energyfuels.7b04034

Mathiyazhagan, M. & Ganapathi, A. 2011. Factors Affecting Biodiesel Production. *Research in Plant Biology,* 1(2): 1–5. Available: https://updatepublishing.com/journal/index.php/ripb/article/download/2566/2544 [accessed on 23 March 2020]

McCormick, R.L. & Westbrook, S.R. 2010. Storage stability of biodiesel and biodiesel blends. *Energy and Fuels*, 24(1): 690–698. http://dx.doi.org/10.1021/ef900878u

Meher, L.C., Sagar, D.V. & Naik, S.N. 2006. Technical aspects of biodiesel production by transesterification — a review. *Renewable and Sustainable Energy Reviews*, 10: 248–268. http://dx.doi.org/10.1016/j.rser.2004.09.002

Mendil, D., Uluözlü, Ö.D., Tüzen, M. & Soylak, M. 2009. Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry. *Journal of Hazardous Materials*, 165: 724–728. http://dx.doi.org/10.1016/j.jhazmat.2008.10.046

Mickevičius, T., Slavinskas, S., Wierzbicki, S. & Duda, K. 2014. The effect of diesel-biodiesel blends on the performance and exhaust emissions of a direct injection off-road diesel engine. *Transport*, 29(4): 440–448. http://dx.doi.org/10.3846/16484142.2014.984331

Misra, R.D. & Murthy, M.S. 2011. Blending of additives with biodiesels to improve the cold flow properties, combustion and emission performance in a compression ignition engine - A review. *Renewable and Sustainable Energy Reviews*, 15(5): 2413–2422. http://dx.doi.org/10.1016/j.rser.2011.02.023

Mizik, T. & Gyarmati, G. 2021. Economic and Sustainability of Biodiesel Production—A Systematic Literature Review. *Clean Technologies*, 3(1): 19–36. http://dx.doi.org/10.3390/cleantechnol3010002

Moradi, G., Mohadesi, M. & Hojabri, Z. 2014. Biodiesel production by CaO/SiO2 catalyst synthesized by the sol–gel process. *Reaction Kinetics, Mechanisms and Catalysis*, 113(1): 169–186. http://dx.doi.org/10.1007/s11144-014-0728-9

Mosarof, M.H., Kalam, M.A., Masjuki, H.H., Ashraful, A.M., Rashed, M.M., Imdadul, H.K. & Monirul, I.M. 2015. Implementation of palm biodiesel based on economic aspects, performance, emission, and wear characteristics. *Energy Conversion and Management*, 105: 617–629. http://dx.doi.org/10.1016/j.enconman.2015.08.020

Nabi, M.N., Rahman, M.M. & Akhter, M.S. 2009. Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. *Applied Thermal Engineering*, 29: 2265–2270. http://dx.doi.org/10.1016/j.applthermaleng.2008.11.009

Nair, J.N. 2013. Study of Biodiesel Blends and Emission Characteristics of Study of Biodiesel. International Journal of Innovative Research in Science Engineering and Technology, 2(8): 3710–3715. Available online: https://www.researchgate.net/publication/281430011 [accessed on 13 January 2021]

Nanda, M.R., Yuan, Z., Shui, H. & Xu, C. 2017. Selective Hydrogenolysis of Glycerol and Crude Glycerol (a By-Product or Waste Stream from the Biodiesel Industry) to 1,2-Propanediol over B_2O_3 Promoted Cu/Al_2O_3 Catalysts. *Catalysts*, 7(196): 1–16. http://dx.doi.org/10.3390/catal7070196

Navas, M.B., Ruggera, J.F., Lick, I.D. & Casella, M.L. 2020. A sustainable process for biodiesel production using Zn/Mg oxidic species as active , selective and reusable heterogeneous catalysts. *Bioresources and Bioprocessing*, 7(4): 2-13. https://doi.org/10.1186/s40643-019-0291-3

Ngo, V.T. 2020. Experimental investigations on combustion and emission characteristic of GCI engine fuelled E20 blend. *Cogent Engineering*, 7(1): 1-11. https://doi.org/10.1080/23311916.2020.1826078

Nichols, R.J. 2003. The Methanol Story : A Sustainable Fuel for the Future. *Journal of Scientific & Industrial Research*, 62(February): 97–105. http://hdl.handle.net/123456789/17582

Nogueira, T. & Lucio, C. 2011. Determination of Ca , K , Mg , Na , sulfate , phosphate , formate , acetate , propionate , and glycerol in biodiesel by capillary electrophoresis with capacitively coupled contactless conductivity detection. *Microchemical Journal*, 99(2): 267–272. http://dx.doi.org/10.1016/j.microc.2011.05.014

Noh, H.K. & No, S.Y. 2017. Effect of bioethanol on combustion and emissions in advanced CI engines: HCCI, PPC and GCI mode – A review. *Applied Energy*, 208(September): 782–802. http://dx.doi.org/10.1016/j.apenergy.2017.09.071

Komariah, N.L., Marwani, Aprisah, S. & Rosa, Y.S.L. 2017. Storage tank materials for biodiesel blends; The analysis of fuel property changes. *MATEC Web of Conferences*, 101: 1–6. http://dx.doi.org/10.1051/matecconf/201710102012

OPEC see Organization of Petroleum Exporting Countries

Organization of Petroleum Exporting Countries. 2017. *World Oil Outlook 2040*. Vienna, Austria: OPEC: 61–161. http://dx.doi.org/10.1190/1.1439163.

Ott, J., Gronemann, V., Pontzen, F., Fiedler, E., Grossman, G., Burkhard Kersebohm, K., Weiss, G. & Witte, C. 2012. Methanol. *Ullmann's Encyclopedia of Industrial Chemistry*: 2–23. Available online: https://vdocument.in/methanol-in-ullmanns-encyclopedia-of-industrial-chemistry.html [accessed on 25 March 2021]

Palash, S.M., Kalam, M.A., Masjuki, H.H., Masum, B.M., Rizwanul Fattah, I.M. & Mofijur, M. 2013. Impacts of biodiesel combustion on NOx emissions and their reduction approaches. *Renewable and Sustainable Energy Reviews*, 23: 473–490. http://dx.doi.org/10.1016/j.rser.2013.03.003

Pandey, A. 2008. *Handbook of plant-based biofuels*. Boca Raton, CRC Press: 3–281. https://doi.org/10.1201/9780789038746

Peng, D.X. 2017. Effect of unleaded gasoline blended with biofuels on gasoline injector wear and exhaust emissions. *Industrial Lubrication and Tribology*, 69(2): 208–214. http://dx.doi.org/10.1108/ILT-09-2016-0217

Phan, A.N. & Phan, T.M. 2008. Biodiesel production from waste cooking oils. *Fuel*, 87(17–18): 3490–3496. http://dx.doi.org/10.1016/j.fuel.2008.07.008

Pillay, A.E., Elkadi, M., Fok, S.C., Stephen, S., Manuel, J., Khan, M.Z. & Unnithan, S. 2012. A comparison of trace metal profiles of neem biodiesel and commercial biofuels using high performance ICP-MS. *Fuel*, 97: 385–389. http://dx.doi.org/10.1016/j.fuel.2012.02.040

Pimentel, D. & Patzek, T.W. 2005. Ethanol Production Using Corn , Switchgrass , and Wood ; Biodiesel Production Using Soybean and Sunflower. Natural Resources Research, 14(1): 65–75 http://dx.doi.org/10.1007/s11053-005-4679-8

Polaris Market Search. 2020. Used Cooking Oil Market. *Fortune Business Insights*, (January): 2016–2027. Available online: https://www.alliedmarketresearch.com/used-cooking-oil-UCO-market [accessed on 02 September 2020]

Pushparaj, T & Ramabanan, S. 2012. Influence of CNSL Biodiesel with Ethanol Additive on Diesel Engine Performance and Exhaust Emission. *International Journal of Mechanical Engineering and Technology*, 3(2): 665-642. Available online: https://www.academia.edu/19970853 [accessed on 13 January 2021]

Putrasari, Y. & Lim, O. 2017. A study on combustion and emission of GCI engines fueled with gasoline-biodiesel blends. *Fuel*, 189: 141–154. http://dx.doi.org/10.1016/j.fuel.2016.10.076

Putrasari, Y. & LIM, O. 2018. A study of a GCI engine fueled with gasoline-biodiesel blends under pilot and main injection strategies. *Fuel*, 221(January): 269–282. https://doi.org/10.1016/j.fuel.2018.01.063

Quveon: Basics of Karl Fischer Titration: *Advance Analytical Technology*. 2014, 1-15. Avalaible online: http://www.quveon.com/wp-content/pdf/KF Titration by Quveon.pdf [accessed on 19 April 2021]

Rainho, C.R., Velho, A.M.A., Corrêa, S.M., Mazzei, J.L., Aiub, C.A.F. & Felzenszwalb, I. 2013. Prediction of health risk due to polycyclic aromatic hydrocarbons present in urban air in Rio de Janeiro, Brazil. *Genetics and Molecular Research*, 12(3): 3992–4002. https://doi.org/10.4238/2013.February.28.6

Ramadhas, A.S. 2006. Alternative fuels for transportation. *Energy Exploration & Exploitation*, 24(1): 45–54. https://doi.org/10.1201/b16260

Ramadhas, A.S., Jayaraj, S. & Muraleedharan, C. 2005. Biodiesel produced from high rubber seed oil. *Fuel*, 84:335–340. http://dx.doi.org/10.1016/j.fuel.2004.09.016

Raman, L.A., Deepanraj, B., Rajakumar, S. & Sivasubramanian, V. 2019. Experimental investigation on performance, combustion and emission analysis of a direct injection diesel engine fuelled with rapeseed oil biodiesel. *Fuel*, 246: 69–74. https://doi.org/10.1016/j.fuel.2019.02.106

Ramesha, D.K; Kumara, G.P; Abhishek Jain, C.N; Akash, B; BabuReddy, R; Kammara, K.M. 2015. Experimental investigation on combustion, performance and Emission characteristics of blends of Plastic oil and Biodiesel as a substitute fuels in Diesel Engine. *European International Research Journal of Engineering and Technology*, 2(2): 1057–1062. Available online: https://www.researchgate.net/publication/352480014 [accessed on 13 January 2021]

Ramos, M.J., Fernández, C.M., Casas, A., Rodríguez, L. & Pérez, Á. 2009. Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*, 100(1): 261–268. https://doi.org/10.1016/j.biortech.2008.06.039

Ravuri, m., Harsha vardhan, D., Ajay, V., Rajasekharreddy, M.. 2013. Experimental Invesstigations and comparison of DI Diesel Engine Working on Jatropha Bio-Diesel and Jatropha Crude Oil. *International Journal of Mechanical Engineering and Technology*, 4(3): 24–31. Available online: https://www.researchgate.net/publication/239318950 [accessed on 13 January 2021]

Razzaq, L., Farooq, M., Mujtaba, M.A., Sher, F., Farhan, M., Hassan, M.T., Soudagar, M.E.M., Atabani, A.E., Kalam, M.A. & Imran, M. 2020. Modeling viscosity and density of ethanol-diesel-biodiesel ternary blends for sustainable environment. *Sustainability (Switzerland)*, 12(12): 24–31. https://doi.org/10.3390/su12125186

Rifal, M. & Sinaga, N. 2016. Impact of methanol-gasoline fuel blend on the fuel consumption and exhaust emission of a SI engine. *AIP Conference Proceedings*, 1725: 020070-1–020070-6. https://doi.org/10.1063/1.4945524

Robles-Medina, a., González-Moreno, P. a., Esteban-Cerdán, L. & Molina-Grima, E. 2009. Biocatalysis: Towards ever greener biodiesel production. *Biotechnology Advances*, 27(4): 398–408. https://doi.org/10.1016/j.biotechadv.2008.10.008

Rocabruno-valdés, C.I., Escobar-jiménez, R.F., Díaz-blanco, Y. & Gómez-aguilar, J.F. 2020. Corrosion evaluation of Aluminum 6061-T6 exposed to sugarcane bioethanol-gasoline blends using the Stockwell transform, 878: 2–11. https://doi.org/10.1016/j.jelechem.2020.114667

Rocha, L.D.S. & Corrêa, S.M. 2018. Determination of size-segregated elements in diesel-biodiesel blend exhaust emissions. *Environmental Science and Pollution Research*, 25(18): 18121–18129. https://doi.org/10.1007/s11356-018-1980-8

Romero, R., Martínez, S.L. & Natividad, R. 2011. Biodiesel Production by Using Heterogeneous Catalysts. In Manzanera, M (Ed.). *Alternative Fuel*. Rijeka, Croatia: InTech: 2–21. https://doi.org/10.5772/23908

Rose, K.D., Ariztegui, J., Cracknell, R.F., Dubois, T., Hamje, H.D.C., Pellegrini, L., Rickeard, D.J., Heuser, B., Schnorbus, T. & Kolbeck, A.F. 2013. Exploring a gasoline compression ignition (GCI) engine concept. *Concave*, 2(13): 2–27. https://doi.org/10.4271/2013-01-0911

Ruzinska, E., Stollmann, V., Hagara, V. & Jablonski, M. 2015. Analysis of selected heavy metals in biomass for preparation of biofuels – Part II. Determination of heavy metals content. *Annals of Warsaw University of Life Sciences - SGGW. Forestry and Wood Technology*, 92: 383–389. Available online: http://agro.icm.edu.pl/agro/element/bwmeta1.element.agro-c1690cab-9853-4775-93fd-d790b418cc8d/c/383__Annals92.pdf [accessed on 23 March 2020]

Sadeghinezhad, E., Kazi, S.N., Sadeghinejad, F., Badarudin, A., Mehrali, M., Sadri, R. & Reza Safaei, M. 2014. A comprehensive literature review of bio-fuel performance in internal combustion engine and relevant costs involvement. *Renewable and Sustainable Energy Reviews*, 30: 29–44. http://dx.doi.org/10.1016/j.rser.2013.09.022

Sahu, I.P., Shrivastava, N., Shrivastava, V. & Singh, A.P. 2013. Experimental Investigation of Performance Parameters of Four. Stroke Single Cylinder Direct Injection Diesel Engine Operating On Rice Bran Oil & Rice Bran Oil Methyl Ester. *Ijmer*, 3(1): 509–513. Available online: http://www.ijmer.com/papers/Vol3_Issue1/DI31509513.pdf [accessed 13 January 2021]

Samanta, S. & Sahoo, R.R. 2020. Waste Cooking (Palm) Oil as an Economical Source of Biodiesel Production for Alternative Green Fuel and Efficient Lubricant. *Bioenergy Research,* 14: 163–174. http://dx.doi.org/10.1007/s12155-020-10162-3

Sánchez, R., Sánchez, C., Lienemann, C.-P. & Todolí, J.-L. 2015. Metal and metalloid determination in biodiesel and bioethanol. *J. Anal. At. Spectrom*, 30(1): 64–101. http://dx.doi.org/10.1039/C4JA00202D

Sanderson, P., Delgado-Saborit, J.M. & Harrison, R.M. 2014. A review of chemical and physical characterisation of atmospheric metallic nanoparticles. *Atmospheric Environment*, 94: 353–365. http://dx.doi.org/10.1016/j.atmosenv.2014.05.023

Sanli, H. & Canakci, M. 2008. Effects of different alcohol and catalyst usage on biodiesel production from different vegetable oils. *Energy and Fuels*, 22(4): 2713–2719. http://dx.doi.org/10.1021/ef700720w

Sarin, A. 2016. *Biodiesel: Production and Properties*. Cambridge, UK: RSC Publishing: 41-80. https://doi.org/10.1520/mnl11645m

Sauer, M. 2016. Industrial production of acetone and butanol by fermentation — 100 years later. *FEMS Microbiology Letters*, 363(13): 1–4. http://dx.doi.org/10.1093/femsle/fnw134

Saydut, A., Kafadar, A.B., Tonbul, Y., Kaya, C., Aydin, F. & Hamamci, C. 2010. Comparison of the biodiesel quality produced from refined sunflower (Helianthus annuus L) oil and waste cooking oil. *Energy Exploration and Exploitation*, 28(6): 499–512. http://dx.doi.org/10.1260/0144-5987.28.6.499

Shah, M., Poudel, J., Kwak, H. & Oh, S.C. 2015. Kinetic analysis of transesterification of waste pig fat in supercritical alcohols. *Process Safety and Environmental Protection*, 98: 239–244. https://doi.org/10.1016/j.psep.2015.08.002

Shamim, M., Aalam, C.S., Manivannan, D. & Kumar, P. 2017. Combustion and Emission Analysis of Mahua and Jujube Biodiesel Blends as Fuel in a CI Engine. *International Journal of Advanced Engineering Research and Science*, 4(2): 116–123. http://dx.doi.org/10.22161/ijaers.4.2.24

Sharma, A.K., Sharma, P.K., Chintala, V., Khatri, N. & Patel, A. 2020. Environment-friendly biodiesel/diesel blends for improving the exhaust emission and engine performance to reduce the pollutants emitted from transportation fleets. *International Journal of Environmental Research and Public Health*, 17(11). http://dx.doi.org/10.3390/ijerph17113896

Shi, Y. & Reitz, R.D. 2010. Optimization of a heavy-duty compression-ignition engine fueled with diesel and gasoline-like fuels. *Fuel*, 89(11): 3416–3430. http://dx.doi.org/10.1016/j.fuel.2010.02.023

Siraj, S. 2017. Effects of Thermal, Physical, and Chemical Properties of Biodiesel and Diesel Blends. *American Journal of Mechanical and Industrial Engineering*, 2(1): 24. http://dx.doi.org/10.11648/j.ajmie.20170201.14

Sirisomboonchai, S., Abuduwayiti, M., Guan, G., Samart, C., Abliz, S., Hao, X., Kusakabe, K. & Abudula, A. 2015. Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. *Energy Conversion and Management*, 95: 242–247. http://dx.doi.org/10.1016/j.enconman.2015.02.044

Songstad, D.D., Lakshmanan, P., Chen, J., Gibbons, W., Hughes, S. & Nelson, R. 2009. Historical perspective of biofuels: Learning from the past to rediscover the future. *In Vitro Cellular and Developmental Biology - Plant*, 45(3): 189–192. http://dx.doi.org/10.1007/s11627-009-9218-6

Sorate, K.A. & Bhale, P. V. 2018. Corrosion Behavior of Automotive Materials with Biodiesel: A Different Approach. *SAE International Journal of Fuels and Lubricants*, 11(2): 147–162. http://dx.doi.org/10.4271/04-11-02-0007

South Africa. 2020. Department of Miniral Resources and Energy. *Government Gazette*, 656(43003): 1–44, February 02. Available online: http://www.greengazette.co.za/pages/national-gazette-37230-of-17-january-2014-vol-583_20140117-GGN-37230-003. [accessed 02 August 2021]

Sureshkumar, K. & Muralidharan, K. 2014. Exhaust Emission Characteristics of Diesel Engine Operating on Biodiesel and its Blends at Elevated Temperature of Air. *International Journal of Engineering Sciences & Research Technology*, 3(10): 69–78. Available online: https://www.academia.edu/9170267/Exhaust_Emission_Characteristics_of_Diesel_Engine_Operating_on_Biodiesel_and_its_Blends_at_Elevated_Temperature_of_Air [accessed on 13 January 2021]

Szyczewski, P., Frankowski, M., Zioła-Frankowska, A., Siepak, J., Szyczewski, T. & Piotrowski, P. 2016. A comparative study of the content of heavy metals in oils: Linseed oil, rapeseed oil and soybean oil in technological production processes. *Archives of Environmental Protection*, 42(3): 37–40. http://dx.doi.org/10.1515/aep-2016-0029

Talebian-Kiakalaieh, A., Amin, N.A.S. & Mazaheri, H. 2013. A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104: 683–710. https://doi.org/10.1016/j.apenergy.2012.11.061

Tamsma, A. & Pallansch, M.J. 1964. Factors Related to the Storage Stability of Foam-Dried Whole Milk. IV. Effect of Powder Moisture Content and In-Pack Oxygen at Different Storage Temperatures. *Journal of Dairy Science*, 47(9): 970–976. https://doi.org/10.3168/jds.S0022-0302(64)88821-4

Tan, T., Lu, J., Nie, K., Deng, L. & Wang, F. 2010. Biodiesel production with immobilized lipase: A review. *Biotechnology Advances*, 28(5): 628–634. http://dx.doi.org/10.1016/j.biotechadv.2010.05.012

Thangaraj, B., Solomon, P.R., Muniyandi, B., Ranganathan, S. & Lin, L. 2019. Catalysis in biodiesel production - A review. *Clean Energy*, 3(1): 2–23. http://dx.doi.org/10.1093/ce/zky020

Thanh, L.T., Okitsu, K., Sadanaga, Y., Takenaka, N., Maeda, Y. & Bandow, H. 2010. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: A practical and economical approach to produce high quality biodiesel fuel. *Bioresource Technology*, 101(14): 5394–5401. https://doi.org/10.1016/j.biortech.2010.02.060

Thongchai, S. & Lim, O. 2018. Investigation of the combustion characteristics of gasoline compression ignition engine fueled with gasoline-biodiesel blends. *Journal of Mechanical Science and Technology*, 32(2): 959–967. http://dx.doi.org/10.1007/s12206-018-0146-9

Torregrosa, A.J., Broatch, A., Novella, R., Gomez-Soriano, J. & Mónico, L.F. 2017. Impact of gasoline and Diesel blends on combustion noise and pollutant emissions in Premixed Charge Compression Ignition engines. *Energy*, 137: 58–68. http://dx.doi.org/10.1016/j.energy.2017.07.010

Torres-García, M., García-Martín, J.F., Jiménez-Espadafor Aguilar, F.J., Barbin, D.F. & Álvarez-Mateos, P. 2019. Vegetable oils as renewable fuels for power plants based on low and medium speed diesel engines. *Journal of the Energy Institute*, 93(x). http://dx.doi.org/10.1016/j.joei.2019.08.006

Varatharajan, K. & Pushparani, D.S. 2018. Screening of antioxidant additives for biodiesel fuels. *Renewable and Sustainable Energy Reviews*, 82(Part3): 2017–2028. https://doi.org/10.1016/j.rser.2017.07.020

Vázquez, A.M., Montero, G. & Sosa, J.F. 2011. Economic Analysis of Biodiesel Production from Waste Vegetable Oil in Mexicali, Baja California. *Energy Science and Technology*, 1(1): 87–93. http://dx.doi.org/10.3968/j.est.1923847920110101.007

Vu, D.N. & Lim, O. 2019. Experimental study on ignition characteristic of gasoline-biodiesel blended fuel in a constant-volume chamber. *Journal of Mechanical Science and Technology*, 33(10): 5073–5083. http://dx.doi.org/10.1007/s12206-019-0946-1

Wang, R. 1988. Development of biodiesel fuel. *Taiyangneng Xuebao*, 9: 434–436.

Wang, Y., Ma, S., Wang, L., Tang, S., Riley, W.W. & Reaney, M.J.T. 2012. Solid superacid catalyzed glycerol esterification of free fatty acids in waste cooking oil for biodiesel production. *European Journal of Lipid Science and Technology*, 114(3): 315–324. https://doi.org/10.1002/ejlt.201100111

Wen, D., Jiang, H. & Zhang, K. 2009. Supercritical fluids technology for clean biofuel production. *Progress in Natural Science*, 19(3): 273–284. http://dx.doi.org/10.1016/j.pnsc.2008.09.001

Woods, G.D. & Fryer, F.I. 2007. Direct elemental analysis of biodiesel by inductively coupled plasma – mass spectrometry. *Anal Bioanal Chem*, 389: 753–761. http://dx.doi.org/10.1007/s00216-007-1439-0

Wu, G., Ge, J.C. & Choi, N.J. 2020. A comprehensive review of the application characteristics of biodiesel blends in diesel engines. *Applied Sciences*, 10(22): 1–31. http://dx.doi.org/10.3390/app10228015

Wu, H., Zhang, Junhua, Wei, Q., Zheng, J. & Zhang, Jianan. 2013. Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. *Fuel Processing Technology*, 109: 13–18. http://dx.doi.org/10.1016/j.fuproc.2012.09.032

Xuan, T., EL-Seesy, A.I., Mi, Y., Lu, P., Zhong, W., He, Z. & Wang, Q. 2020. Effects of an injector cooling jacket on combustion characteristics of compressed-ignition sprays with a gasoline-hydrogenated catalytic biodiesel blend. *Fuel*, 276: 2–10. https://doi.org/10.1016/j.fuel.2020.117947

Yaakob, Z., Narayanan, B.N., Padikkaparambil, S., Unni K., S. & Akbar P., M. 2014. A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews*, 35: 136–153. http://dx.doi.org/10.1016/j.rser.2014.03.055

Yacobucci, B.D. 2004. Alternative Fuel Vehicle Tax Incentive and CLEAR ACT. *Congressional Research Services*: 1–6. Available online: https://www.everycrsreport.com/files/20041217_RS21277_20c20b960097c887fdd6f5b7352ded2be17488ca.pdf [accessed on 23 March 2020]

Yang, F., Yao, Y., Yan, Z., Min, H. & Goodman, D.W. 2013. Applied Surface Science Preparation and characterization of planar Ni – Au bimetallic model catalysts. *Applied Surface Science*, 283: 263–268. http://dx.doi.org/10.1016/j.apsusc.2013.06.099

Yang, Z., Hollebone, B.P., Wang, Z., Yang, C. & Landriault, M. 2013. Factors affecting oxidation stability of commercially available biodiesel products. *Fuel Processing Technology*, 106: 366–375. http://dx.doi.org/10.1016/j.fuproc.2012.09.001

Yaşar, F. 2020. Comparision of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel*, 264: 2–7. http://dx.doi.org/10.1016/j.fuel.2019.116817

Yasin, M.H.M., Mamat, R., Yusop, A.F., Rahim, R., Aziz, A. & Shah, L.A. 2013. Fuel physical characteristics of biodiesel blend fuels with alcohol as additives. *Procedia Engineering*, 53: 701–706. http://dx.doi.org/10.1016/j.proeng.2013.02.091

Yeşilyurt, M.K., Öner, İ.V. & Yılmaz, E.Ç. 2019. Biodiesel Induced Corrosion and Degradation: A Review. *Pamukkale University Journal of Engineering Sciences*, 25(1): 60–70. http://dx.doi.org/10.5505/pajes.2018.01885

Yusuf, N.N.A.N., Kamarudin, S.K. & Yaakub, Z. 2011. Overview on the current trends in biodiesel production. *Energy Conversion and Management*, 52(7): 2741–2751. http://dx.doi.org/10.1016/j.enconman.2010.12.004

Zabeti, M., Daud, W.M.A.W. & Aroua, M.K. 2010. Biodiesel production using alumina-supported calcium oxide: An optimization study. *Fuel Processing Technology*, 91(2): 243–248. http://dx.doi.org/10.1016/j.fuproc.2009.10.004

Zabeti, M., Wan Daud, W.M.A. & Aroua, M.K. 2009. Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, 90(6): 770–777. http://dx.doi.org/10.1016/j.fuproc.2009.03.010

Zahan, K.A. & Kano, M. 2018. Biodiesel production from palm oil, its by-products, and mill effluent: A review. *Energies*, 11(8): 1–25. http://dx.doi.org/10.3390/en11082132

Zhang, Y., Dubé, M.A., McLean, D.D. & Kates, M. 2003. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresource Technology*, 90(3): 229–240. http://dx.doi.org/10.1016/S0960-8524(03)00150-0

Zhang, Y., Zhan, L., He, Z., Jia, M., Leng, X., Zhong, W., Qian, Y. & Lu, X. 2019. An investigation on gasoline compression ignition (GCI) combustion in a heavy-duty diesel engine using gasoline/hydrogenated catalytic biodiesel blends. *Applied Thermal Engineering*, 160: 2–12. https://doi.org/10.1016/j.applthermaleng.2019.113952

Zhong, W., Li, B., He, Z., Xuan, T., Lu, P. & Wang, Q. 2019. Experimental study on spray and combustion of gasoline / hydrogenated catalytic biodiesel blends in a constant volume combustion chamber aimed for GCI engines. *Fuel*, 253(301): 129–138. https://doi.org/10.1016/j.fuel.2019.04.114.

Chapter 3: **Catalyst and Elemental Analysis Involving Biodiesel from Various Feedstocks**

To be a catalyst is the ambition most appropriate for those who see the world as being in constant change, and who, without thinking that they control it, wish to influence its direction. ~ Theodore Zeldin

Published in the Catalysts 2021, 11 (8) 2-17

Title: "Catalyst and Elemental Analysis Involving Biodiesel from Various Feedstocks"

Authors: Ines Simbi, Uyiosa Osagie Aigbe, Oluwaseun Oyekola, Otolorin Adelaja Osibote

Objectives of thesis addressed in present chapter

Part of objectives (a) and (b) were addressed, a bifunctional catalyst ($CaO\text{-}Al_2O_3$) was produced through wet impregnation and analysed for its functionality through variety of characterisations. The obtained catalyst was utilised in the transesterification of waste sunflower and waste palm oils to biodiesels which were analysed for physicochemical properties. Also, an evaluation of the presence of metal contents within sunflower and palm waste oils and their respective biodiesels were conducted with regards to their sources.

Abstract

The world is currently faced with the depletion of fossil fuel energy sources and their use is associated with environmental pollution. This has triggered the need to seek alternative energy sources that are renewable, sustainable, and environmentally benign. Biodiesel, an alternative fuel of interest, is obtainable from biomass feedstocks. However, in existing biodiesel fuel, contamination of elemental contents is a concern, which over time will affect the quality. This study aimed to investigate the influence of a bifunctional catalyst on the conversion of free fatty acids and the elemental composition of biodiesel obtained from waste oils of sunflower and palm feedstocks. The synthesised catalyst was characterised using BET, XRD, FTIR and SEM while ICP-OES and Rancimat were used for elemental contents and oxidation in feedstocks and biodiesels. The effect of Cu, Zn and Fe metals on the stability of synthesised biodiesel was further studied. The produced catalyst showed characteristics of bifunctionality, with improved textural properties necessary for the conversion of feedstocks with high free fatty acids to biodiesel, though an increasing Ca content within the produced biodiesel was observed. Sunflower biodiesel showed characteristics of a superior fuel, while palm biodiesel had more oxidation stability. An increase in the concentration of metals decreased the induction period, with Cu and Fe being more effective than Zn metal.

Keywords: bifunctional catalyst; biodiesel; elemental content; degradation; metals; oxidation stability; transesterification; waste cooking oils

3.1 Introduction

Global primary energy demand is set to experience an annual increase of 1.46% from 2009 to 2035 [1]. This is not surprising, as industrialisation has grown significantly with a rise in the global population to 7.3 billion in 2015, which is projected to further grow to 9.2 billion in 2040 [2]. The enormous use of fossil fuels has put the environment and human health at risk [3,4], with energy utilisation especially high in the transportation sector, which is expected to make up about 63% of total global fuel consumption from 2010 to 2040 [5,6].

In 2008, it was reported that the transportation sector contributed to about 23% of total CO_2 emissions globally [7,8], with 73% of this contribution made by road transport [9], while the contribution from fuel combustion increases by 1.6% per year [1]. This will lead to severe ecological impacts, namely air and noise pollution, an increase in global surface temperatures (excess of 6 °C), changes in rainfall patterns and subsequently extreme weather events [1,10–12].

Apart from the potential exhaustion of petroleum reserves over time [13], fuel prices have increased [14] due to oil reserves being concentrated in specific regions in the world [15], giving rise to some political conflicts. Therefore, a more significant sustainable movement led by advancement towards environmental conservation, a feasible economy and equity has prompted a search for substitutes for fossil fuels. The substitute must be eco-friendly and a viable energy-generating fuel [16].

The quest for green energy fuel led to the discovery of biodiesel, which is chemically defined as monoalkyl esters of long-chained fatty acids, having physicochemical characteristics similar to that found in petrodiesel [17]. Biodiesel is believed to release on average 48% less carbon monoxide, 47% less particulate material and 67% less hydrocarbon than petrodiesel [18]. However, producing biodiesel has cost implications attached to it, since it can be synthesised from vegetable oils and animal fats through chemical processes such as transesterification [19]. The raw materials account for about 70-95% of its production costs [20]. Therefore, to minimise costs, the use of waste cooking oils rather than food-grade oils is suggested for economic efficiency [21] and pollution reduction resulting from improper waste oil disposal to the environment [22].

Waste oils are mainly composed of free fatty acids (FFA), which are highly unsaturated [23] and would require acid and base-catalysed reaction to convert the high FFA feedstocks into fatty acid methyl esters [5]. This is despite the fact that heterogeneous catalysts are easily separated after the transesterification reaction [24], which promotes their reusability [25]. They also can overcome saponification, in contrast to homogeneous catalysts [26]. However, heterogeneous catalysts have mass transfer limitations associated with reduced rate of reaction as a result of the formation of three phases with oil and alcohol [5], and the leaching of active phases may occur in the reaction medium [27]. To overcome this diffusion problem, structurally promoting the catalyst can be performed [28]. This improved structure will stimulate a catalyst with enhanced stability against dissolution by forming a bifunctional catalyst with a potential for increased activity and selectivity [29], along with enhanced stability compared to the monometallic counterpart due to more active sites [30], which can esterify and transesterify feedstock of high FFA.

It is believed that in biodiesel, metals are brought in either during syntheses by the use of hard water during washing, by the catalyst used [31,32], or during the storage and transport process [33]. Chaves et al. [34] reported that they can exist within feedstocks due to soil types and fertilisers used, along with hydrological conditions according to geographical origins [35,36]. These metals may cause many mechanical problems within engines if their contents are excessive [35]. Some of the issues caused by the presence of

metals are the corrosion of certain engine parts and the deactivation of catalysts, leading to environmental harm [32,37]. A study conducted by Waynick [38] showed that the presence of Cu, Fe, Ni, Sn and Cu-Zn (a copper-rich alloy) metals can increase the oxidisation of fatty oils [8,38]. They reported that in biodiesel, Cu reduces oxidation stability more than Fe and Ni, while Fe is an effective hydroperoxide decomposer. Copper is the most corrosive element in palm biodiesel [39]. Meanwhile, Al and Sn are characterised by low catalytic activity and Cu, Fe, Ca, and Mg were found to accelerate oxidation reaction [35,40]. While some metals such as phosphorus (P) can poison the catalytic converters, causing high release of CO, CO_2 and SO_2 emissions [41]. This subsequently has an effect on human health through emission of particulate matters of oxides, nitrates, sulphates, or peroxides [42]. In combination with polluted air, these pollutants can also migrate into the soil and water table [43]. Even though Cd and Zn can partially be lost by volatilisation [44], the most concerning elements are catalyst residues and sulphur [40].

Corrosion within metallic tanks is due to microorganism growth within tanks, which leads to degradation of the fuel. Therefore, as the fuel is stored over time, there is a need to evaluate the effects of metals that come in contact with the fuel [39]. This study presents the production of a CaO/Al_2O_3 catalyst using the wet impregnation method using a ratio of 75% of CaO and 25% of Al_2O_3 (calcined), which was characterised using FTIR, SEM, XRD and BET. The catalyst was used in the production of biodiesel from waste cooking oils of palm and sunflower. Evaluation of the elemental contents of the feedstocks and biodiesel was performed by ICP-OES. Analysis of fuel properties were conducted by density meter, flash tester, viscometer and FTIR spectrometer. Additionally, the effect of Cu, Zn and Fe on oxidation stability and other fuel properties of the produced biodiesels was also studied.

3.2 Results

This section gives an overview of the bi-functional CaO/AI_2O_3 catalyst synthesised using wet impregnation method, as well as the characterisation of the synthesised catalyst using SEM, XRD, FTIR and BET to determine the surface morphology, crystalline structure, functional groups and surface area, pore volume and diameter respectively. Also discussed in this section is the fatty acids composition of each feedstock and the fuel properties determined using the gas chromatography (GC), viscometer, density meter, flash tester, color-indicator titrator and FTIR.

3.2.1 Bi-functional Catalyst Characterisation

The FTIR spectrum of CaO, Al_2O_3 and CaO/Al_2O_3 catalyst is shown in Figure 3-1, with absorption bands in the range of 400-4000 cm^{-1}. Figure 3-1a shows all characteristic peaks of CaO with a broad CO_3 stretch at 1409.32 cm^{-1} and a smaller CaO band [45], while the presence of water molecules in the uncalcined catalyst was observed with a strong hydroxyl (H-O) band appearing at 3640.79 cm^{-1} [46]. Intense peaks at 636.06 cm^{-1}, 554.55 cm^{-1} and 485.48 cm^{-1} are presented in Figure 3-1b, with dominancy of Al-O, normally found in the region of 1000-400 cm^{-1} [47]. The synthesised CaO/Al_2O_3 catalyst was confirmed by the co-existence of Ca-O and Al-O within the CaO/Al_2O_3 catalyst as shown in Figure 3-1c, by the presence of CaO absorption bands at 875 cm^{-1} and 713 cm^{-1} corresponding to C-O and Ca-O bonding and by a broader $CaCO_3$ band at 1469.80 cm^{-1}. The H-bonded hydroxyl group appeared due to moisture and the presence of CO_2 [48]. Furthermore, Table 3-1 re-affirms these compositions within the synthesised catalyst.

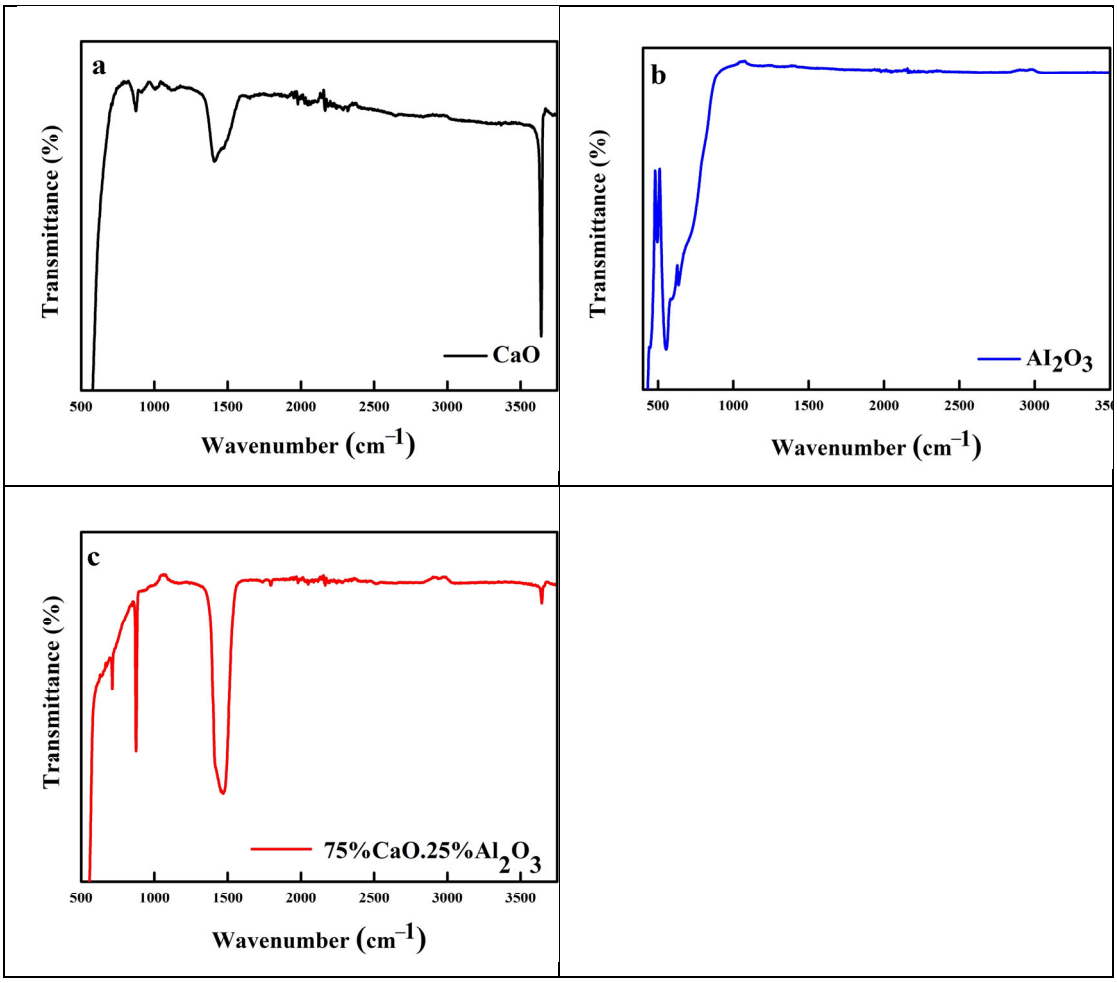
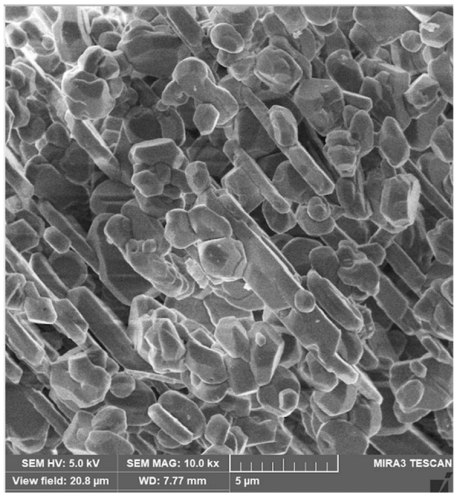


Figure 3-1. FTIR curves for the (**a**) CaO, (**b**) Al_2O_3 and (c) synthesised CaO/Al_2O_3 catalyst.

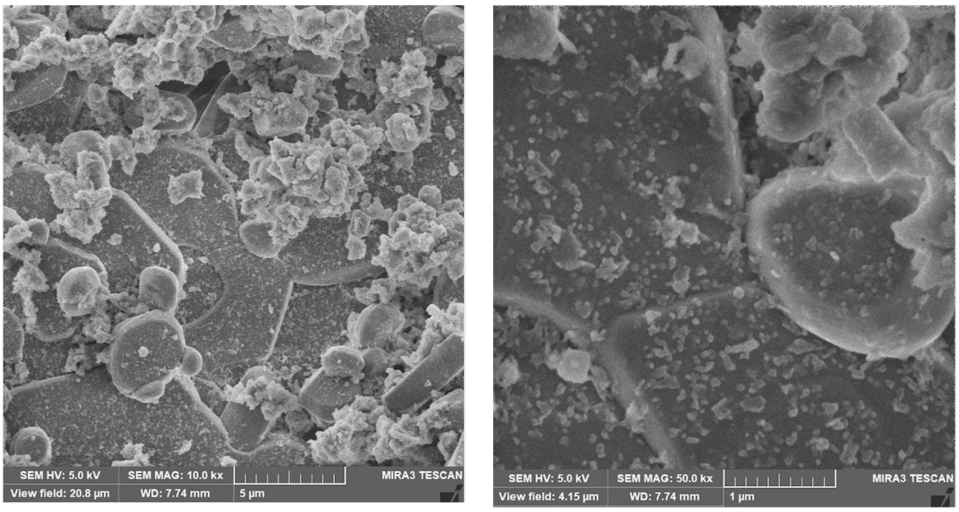
Table 3-1. Composition of compounds within the catalyst.

Material	Compound	Formula	Composition (%)
CaO	Portlandite	$Ca(OH)_2$	50
	Lime	CaO	50
Al_2O_3	Aluminium Oxide	Al_2O_3	0.69
	Oxonium Aluminium Oxide	$H_3O_2Al_{22}O_{34}$	75
75CaO-25 Al_2O_3	Portlandite	$Ca(OH)_2$	92.08
	Lime	CaO	63.79
	Calcite	$CaCO_3$	8.73
	Aluminium Oxide	Al_2O_3	22.92

The external morphological characteristics of Al_2O_3 and synthesised CaO/Al_2O_3 catalyst after calcination at 475 °C were studied by SEM. Figure 3-2a, b illustrate the morphology of commercial Al_2O_3 particles appearing as crystals of corundum, normally found to promote densification of corundum shape-like composites which help in enhancing performance [49]. After thermal treatment with high temperature (475 °C) for 5 h and impregnation of CaO, a modification of Al_2O_3 into irregularly shaped clusters due to the breakage of large particles into smaller pieces [50], with the intensification of CaO particle agglomeration on the support, can be observed in Figure 3-2c. This is due to the huge percentage of metal oxide which normally has an irregular shape even after thermal treatment [25], and the presence of impurities and unconverted $Ca(OH)_2$ [51]. The micrographs are in agreement with the results shown in Table 3-2, where the supported oxide in Figure 3-2c,d showed the increased surface area and increased pore size distribution as was also reported by Young et al. [52], which increases activity due to the formation of more active sites on the surface area and has an effect on the reaction rates and selectivity [53].



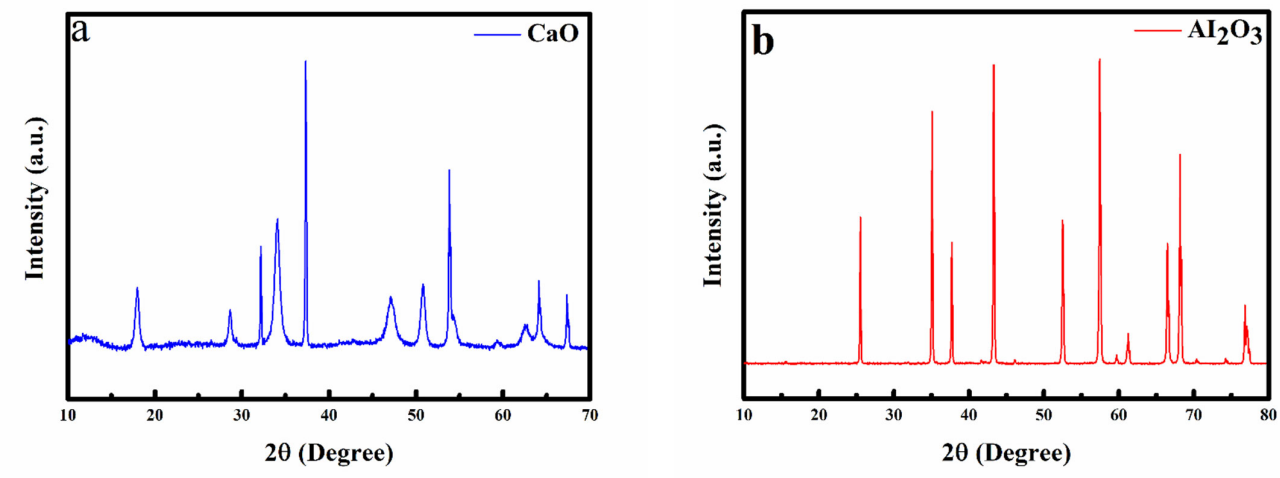
(**a**) (**b**)



(**c**) (**d**)

Figure 3-2. Scanning electron microscopy (SEM) images of (**a**, **b**) Reference Al_2O_3 and (**c**, **d**) 75%CaO/25%Al_2O_3.

Figure 3-3 displays the XRD patterns of CaO and Al_2O_3 materials prior to calcination and after the catalyst was synthesised. The results confirmed the characteristic peaks of 2θ ranging from 18° to 80°. Table 3-1 shows that there was an even distribution of lime and portlandite for CaO while in Figure 3-3b, Al_2O_3 support can be seen to have appeared at intensified peaks of 25.55°, 35.11°, 43.30°, 52.49°, 57.43° and 68.13°. These peaks reaffirmed the presence of rhombohedral Al_2O_3. Face-centered cubic CaO peak was found at 32.20°, 37.35°, 54° and 64.15°. As seen in Figure 3-3a, these peaks correspond to the crystal planes of CaO and its cubic shape [54,55]. The CaO/Al_2O_3 pattern also indicated small peaks of rhombohedral $CaCO_3$, hexagonal Ca $(OH)_2$ and $(H3O)_2Al_{22}O_{34}$, which were spread through with intense peaks of Ca (OH), CaO and Al_2O_3 in that order.



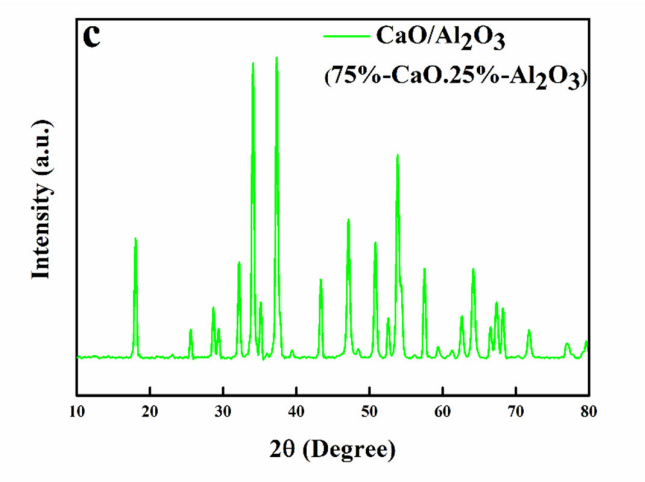


Figure 3-3. XRD patterns of (a) CaO, (b) Al_2O_3 and (c) CaO/Al_2O_3.

The specific surface area and pore volume were determined by the nitrogen adsorption-desorption technique summarised in Table 3-2, using Brunauer-Emmett-Teller (BET). The nitrogen isotherms recorded in Figure 3-4 for CaO/Al_2O_3 showed hysteresis over the relative pressure. The N_2 isotherms exhibited a typical s-shaped behaviour of type IV with a type H1 desorption hysteresis loop as categorised by IUPAC [56–58], indicating a potential presence of relatively wide cylindrical pores [59,60], which shows characteristics of a mesoporous material [61,62].

The calculated specific area, pore volume and pore diameter for pure Al_2O_3 and calcined 75% CaO supported on 25% Al_2O_3 are presented in Table 3-2. Synthesised catalyst had a surface area of 13.0006 m^2/g and Al_2O_3 had 0.6239 m^2/g, while pore volumes and diameters were 0.079732 cm^3/g, 0.000857 cm^3/g, 24.0371 nm and 5.9147 nm for prepared catalyst and alumina, respectively. An increase in surface area of CaO/Al_2O_3 catalyst was observed after impregnating 75 wt% metal oxides onto alumina and thermal treatment. There was a significant increase in pore volume and pore size after the addition of CaO, which contributed to the liquid-solid heterogeneous phase reaction and offered enough of a reaction surface area for the transformation of waste oil into biodiesel.

Recent studies showed that CaO calcined at low temperature (500 °C) possesses a surface area of 5.2 m^2/g and mean pore diameter of 11.9 nm [63], while the corresponding properties of the catalyst samples calcined at high temperatures (700–950 °C) changed but not to a substantial extent [61,63]. It seems that the textural characteristics of CaO used in the experiment (from CaO-500 °C to CaO-900 °C) are favourable for a liquid-solid

heterogeneous phase reaction and provide a sufficient reaction surface area for the conversion of large triglyceride molecules. Significantly, the structural properties of CaO catalyst in the production of biodiesel effectively reduce greenhouse gas emissions. Nevertheless, in the study by Stankovic [64], the effect of calcination temperatures (425 °C, 450 °C, 475 °C, 500 °C) on the yield of biodiesel was evaluated with an inference that 475 °C gave the highest yield. After applying the same calcination temperature (475 °C), the pore diameter in this study increased to 24 nm, which is superior by showing better permeability with an increased surface area as shown in Table 3-2. This assisted in the transesterification of sunflower waste oil to biodiesel yielding a maximum 98% conversion using a lower base catalyst weight (2.5 wt%) and ratio (75% CaO: 25%Al_2O_3). Such yield was similarly obtained by Elias et al. (2020), in transesterification of waste sunflower oil yet using 80% CaO: 20% Al_2O_3 catalyst loading [65]. Additionally, the yield found was a lot more than that reported by Marinkovic et al. where a high catalyst amount of 5.5 wt% was used prepared at high calcination of 700 °C [66].

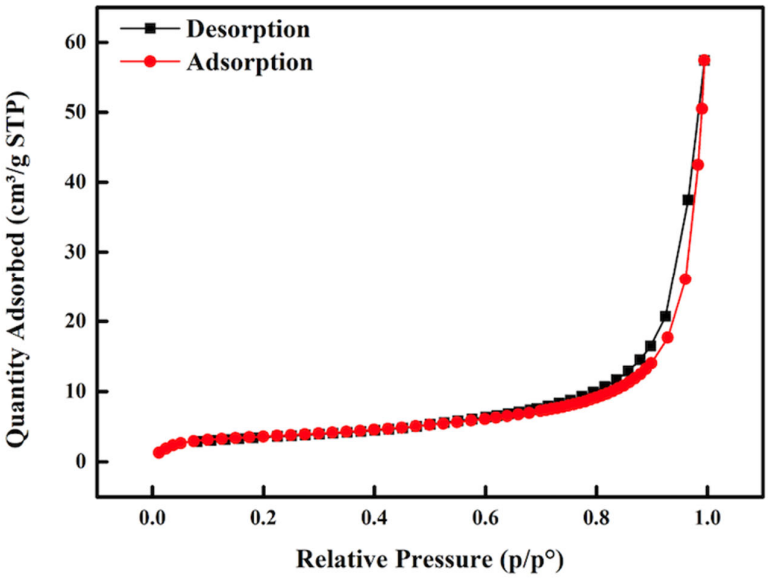


Figure 3-4. Nitrogen Adsorption-desorption isotherm of CaO/Al_2O_3.

Table 3-2. Textural properties and surface area analysis of Al_2O_3 and 75%CaO/25%Al_2O_3 catalyst calcined at 475 °C

Catalyst	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
Al_2O_3	0.6239	0.000857	5.9147
75%CaO/25%Al_2O_3	13.0006	0.079732	24.0371

3.2.2 Feedstock and Biodiesel Composition Characterisation

The estimation of fatty acids content within each feedstock and the determination of fuel properties shown in Table 3-3 were determined by employing gas chromatography. Double bonds are less stable than single bonds, their presence in the fatty acids will affect the iodine number, viscosity, melting point, the efficiency of combustion and particulate matter formation relating to soot [67]. Increased average unsaturation enhanced low-temperature performance but also decreases the cetane number and results in poor oxidation stability [68]. On the other hand, saturated fatty acids play a huge role in the cold flow properties relating to viscosity [69]. ASTM recommend viscosity of 1.9–6 mm^2/s at 40 °C for biodiesel [70], and the high viscosity of vegetable oils prevents its direct usage in petrodiesel engines [69] since this leads to the formation of deposits in the engine due to incomplete combustion [71]. As illustrated in Table 3-4, waste palm oil (WPO) had high viscosity value of 47.5 cSt followed by waste sunflower oil (WSO) with 37.1 cSt, which corresponds to fatty acid compositions i.e. degree of saturation (Table 3-3). The density of WSO and WPO in this study were found to be 0.9212 and 0.9168 g/cm^3, respectively. The flashpoints reported in this study were above the minimum requirement supported by the findings by Bukkarapu et al., and Yaşar, who reported flash point of sunflower to be higher (178 °C), than 172 °C of palm biodiesel [72–75]. It was also observed that contaminants of acid, nitrates, sulphates, and glycol were lower in virgin oils than in their respective waste oils. This is due to degradation and contaminations resulting from over usage through cooking and contact with other chemicals. This creates FFA and accelerates the oxidation process.

Table 3-3. Fatty Acids Compositions in waste cooking oils.

FFA Acid Types	Carbon Chain	WPO (wt%)	WSO (wt%)
Lauric	C12:0	0.42	-
Myrisitc	C14:0	0.53	--
Palmitic	C16:0	16.25	4.36
Stearic	C18:0	1.50	3.39
Oleic	C18:1	13.82	9.45
Linoleic	C18:3	3.04	27.25

FFA: Free Fatty Acids, WPO: Waste Palm Oil, WSO: Waste Sunflower Oil.

Table 3-4. Physico-chemical properties of waste oils and respective biodiesels produced.

Properties	WPO	PB100	WSO	SB100	ASTM	EN&SA
Flash Point (°C)	-	170	200	175	>93	>120
Oxidation Stability (h)	-	17.43	-	4.20	>3	>6
Density at 15°C (g/cm3)	0.9168	0.892	0.9212	0.8871	0.9	0.86-0.9
Viscosity at 40°C (cSt)	47.5	11.1	37.1	6	1.9-6	3.5-5

Acid Value (mg of KOH/g of oil)	3.23	0.55	1.26	0.25	<0.5	<0.5
Nitrates	3	11	4	11	-	-
Sulphates	153	118	160	121	-	-
Glycol	0	10	12	11	-	-
Soot	11	11	11	12	-	-

WPO: Waste Palm Oil, PB100: 100% Palm biodiesel, WSO: Waste Sunflower Oil, SB100: 100% Sunflower biodiesel, ASTM: American standard, EN: European standard, SA: South African Standard.

3.2.3 Feedstocks and Biodiesel Quality Analysis

Table 3-4 shows the properties of biodiesels (PB100) and (SB100) produced from waste palm oil (WPO) and waste sunflower oil (WSO) respectively. Most of the properties of the biodiesels produced were within the biodiesel standard specifications. These properties are crucial in fuel quality, performance, transportation, and storage [76]. Notably, they depend on the feedstock used in the synthesis, which subsequently relates to the degree of saturation as seen in Table 3-3. Sunflower biodiesel is less flammable as indicated by a higher flashpoint of 175 °C, while palm biodiesel had 170 °C, which is preferred for handling and storage purposes [77]. These values are lower than that of petroleum diesel, which is usually above 150 °C [78]. Palm biodiesel was characterised by a high density, which will have consequent high mass of injected fuel, resulting in higher heat, creating more carbon, and subsequently more power in the engine [79]. Additionally, P100 was observed to possess higher oxidation stability due to less polyunsaturated fatty acids in WPO, this characteristic will confer on it a long-time stability at harsh conditions [17]. On the other hand, for degradation during storage as indicated by acid number [72], sunflower biodiesel was the better fuel with a lower acid rate of 0.25 mg KOH/g which was below the standard limit and low compared to 0.55 mg KOH/g for palm biodiesel. A characteristic of fuel atomisation i.e. viscosity was better in sunflower biodiesel, as indicated by reduced viscosity which meets standard specification [80]. Contaminants as indicated by the particulate matter of sulphates decreased in biodiesel from waste oils while nitrates increased as a result of more oxygen found in biodiesel [13,81]. Indication of chances for incomplete combustion were observed by properties such as soot and glycol which were higher in sunflower biodiesel. Overall, sunflower biodiesel showed preferred fuel qualities. However, it also showed the possibility of lower oxidation stability under harsh conditions over longer storage time, as well as the possibility of incomplete combustion.

3.2.4 Elemental Content Analysis

3.2.4.1 ICP-OES Analysis in Virgin, Waste Sunflower and Palm Oil and Their Biodiesels

The compositions of the feedstocks and their corresponding biodiesels, with respect to major and minor elements are shown in (Table 3-5). P, S and Zn are present in feedstocks since they are taken from the soil and are a result of fertilisers used during cultivation [82], while Ca, K, Mg, Na and P are usually introduced through the production process [83] and can lead to undesirable combustion if present at high concentrations. A report by Sánchez et al. [37] found that Al, Fe, Mn, and Zn are minor elements that relate to the soil characteristics, which explains their presence in the virgin oils. There was an increase in phosphorus from 17.625 mg/L and 31.937 mg/L for virgin sunflower and palm oils to 21.264 mg/L and 44.455 mg/L for waste sunflower and palm oils respectively. The absence of Mg and K in both sunflower and palm virgin oils were observed, while less than 0.068 mg/L of Mg and 0.012 mg/L of K was seen in WPO. This can be attributed to salts used during cooking [37]. A report by Avila Orozco et al. [83] showed that Na, K, Ca, S and P came from raw material or chemical reagents. Lyra et al. [84] reported that their presence could have been incorporated due to the washing process with water. In this study, Ca was observed to be 0.025 mg/L and 0.345 mg/L in waste oils, after biodiesel production a huge increase to 27.559 mg/L and 23.401 mg/L in their respective biodiesels were found. This can be explained by the use of CaO/Al_2O_3 in synthesising the biodiesels. This significant increase might result in the sticking of injection or deposit on parts [85]. Sunflower methyl esters produced had lower elemental contaminates than palm methyl esters, which relate to better fuel quality but in terms of Ca, SB100 was higher, which would increase the rate of oxidation [35]. According to standard requirements set by ASTM D6751 and EN 14214, Ca+Mg should have a maximum concentration of 5 mg/L [86]. Both the SB100 and PB100 failed this test which is a great concern considering that high levels of Ca and Mg will form deposits [87], which accelerate oxidation reaction [40]. Nevertheless, elements of Na, Fe, P and Al were reduced after the conversion of waste feedstocks to biodiesel meeting specifications requirements. Operational problems caused by high levels of Na and K through corrosion [88], the poisoning of catalytical converters and the ability of the after-treatment system were eliminated, due to deterioration caused by high P in fuel [89,90] and because sulphur is amongst the most undesirable elements [40]. A high S content can adversely affect the performance of engines [91], and the maximum limit set for sulphur in biodiesel is 10 mg/L [70,92]. It was observed that both biodiesels passed this test, which reduces corrosion in fuel containers [12].

Table 3-5. Elements content in virgin oils, waste oils and biodiesels produced.

Elements (mg/L)	VSO	WSO	SB100	VPO	WPO	PB100
Na	0.971	1.133	0.333	1.648	2.399	0.383
Mg	0	0	0.125	0	0.068	0.266
K	0	0	0	0	0.012	0
Ca	0.024	0.025	27.692	0.206	0.345	23.534
Fe	3.654	4.054	2.686	5.199	6.229	2.810
P	17.625	21.264	8.239	31.937	44.453	8.913
Al	1.682	1.969	0.870	2.861	4.109	0.921
Cu	0	0	0	0	0	0
Zn	1.185	1.216	1.623	1.407	1.601	1.666
S	-	-	4	-	-	6

VSO: Virgin Sunflower oil; WSO: Waste Sunflower Oil; VPO: Virgin Palm oil; WPO: Waste Palm Oil: SB100: 100% Sunflower Biodiesel; PB100: 100% Palm Biodiesel.

3.2.4.2 Effect of Metals on the Oxidation Stability of Biodiesels Produced from Waste Sunflower and Palm Oils

The presence of inorganic constituents in biodiesel can affect the quality of the fuel and cause the malfunctioning of engines [87]. Since different materials are used for storage containers and engine parts, there is an issue with compatibility [93]. The main source of metals contaminants in vegetable oil is either its presence in raw material or the contact with the manufacturing process and storage [40]. This subsequently leads to degradation and contamination in the engine [31]. Corrosion in biodiesel is mainly due to the component nature and composition of biodiesel, as well as the environment [12,94]. Metallic storage tanks such as stainless steel and Al are normally used for storage [95], while in automobiles, the fuel is in direct contact with various parts of the engine like the fuel pump, fuel injector, pistons, and piston rings, which are made of Cu, Al, brass-Br (copper-rich alloy) and bronze [93]. Meanwhile, Cu has a huge effect in increasing the oxidation within biodiesel [96]. Therefore, assessing Cu, Fe, and Zn along with Ni, Sn, and brass is very crucial since they can affect stability through oxidation [97].

Figure 3-5 and Figure 3-6 illustrate the degradation of metal contents in biodiesel with different fatty acids composition by the Rancimat method of EN 14112 specification, with samples held at a temperature of 110 °C. It is clear that all metal contaminants promoted oxidation in both palm and sunflower biodiesels, with a greater effect in palm biodiesel. These metals initiate the formation of free radicals [98]. As the concentration of metals added were increased, the oxidation stability in the fuels decreased. However, after the concentration of 2 ppm, the induction period was not constant, as was previously reported by [99]. The results obtained from biodiesels indicate that oxidation instability was greatly affected by Fe, more than Cu or Zn. This was strongly pronounced from 300 ppm while Cu

showed a significant influence at 100 ppm onward in palm biodiesel. Meanwhile in sunflower biodiesel, a gradual reduction was observed through to 700 ppm. Contrarily, Cu was reported to reduce oxidation stability more than Fe or Zn according to literature [91,100,101] and the induction period became constant after 2 ppm [99,102]. In the current study, Fe has the most catalytic effect in reducing the induction period and it became constant after 500 ppm of metal concentration for both biodiesels. Additionally, palm biodiesel showed higher level of degradation and more corrosiveness [12].

Sunflower biodiesel showed the highest corrosiveness impact of metals with Fe followed by Zn and Cu. However, at a concentration of 700 ppm, Cu was the most degraded metal. For PB100, the addition of metal concentrations lower than 100 ppm resulted in Cu having more corrosiveness followed by Zn and Fe but after 300 ppm, Fe was more corrosive than Cu and Zn. This was supported by the studies of Baena and Calderón and Sentanuhady et al. [103,104], who found the metal that was most prone to corrosion in biodiesel to be Cu. Shiotani and Goto [100] reported in their study that in PB100, Cu was found to have more degradation of oxidation followed by tin, iron, zinc, and aluminium. Additionally, Thangavelu et al. [105] reported that copper had a higher corrosion rate than aluminium and stainless steel in that order. The investigation by Hu et al. [106] also reported that corrosion in biodiesel from rapeseed oil was in the order of stainless Cu > carbon steel > Al > stainless steel, while in the study by Fazal et al. [39], it was discovered that palm biodiesel degraded in the order of Cu > brass (Br) > Al > cast iron (CFe). Furthermore, in the experiment by Komariah et al. [107], where they investigated the corrosive behaviour of different steel materials which are mainly iron found in stainless steel, corrosion was localised while mild and galvanised steels were generalised.

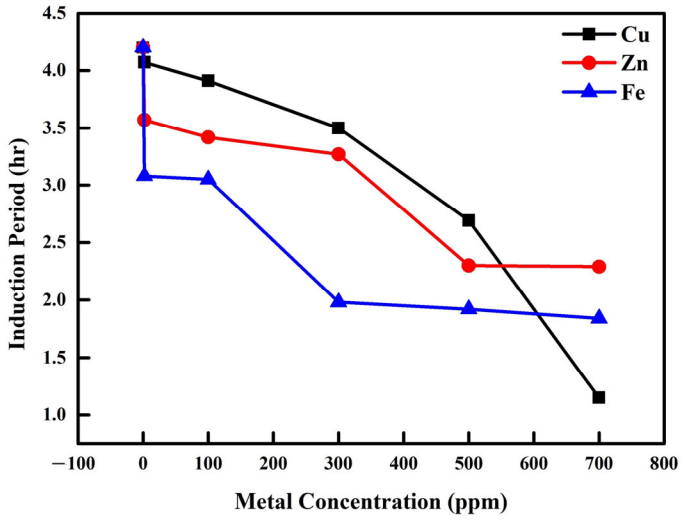


Figure 3-5. Oxidation stability in sunflower biodiesel before and after exposure to metals.

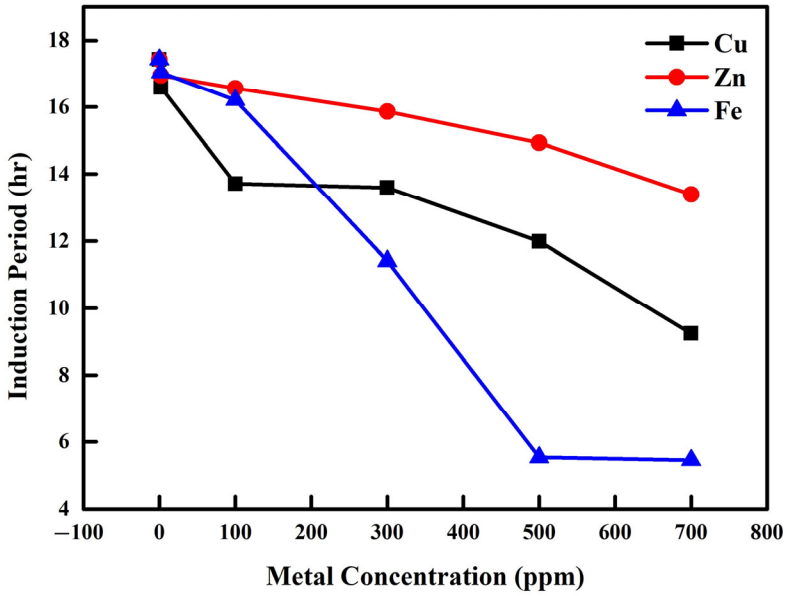


Figure 3-6. Oxidation stability in palm biodiesel before and after exposure to metals.

3.3 Materials and methods

3.3.1 Chemical and Reagents

Waste cooking oils of palm and sunflower were supplied by Suppa Oils (Cape Town, South Africa) and transesterification was conducted by the use of methanol (99.5% Sigma-Aldrich, Johannesburg, South Africa) with the catalyst prepared using CaO (>68%, Sigma-Aldrich, MO, United States) and Al_2O_3 (99.95% Labchem, Johannesburg, South Africa). For elemental analysis by ICP, digestion was performed by utilising Nitric Acid (57.2%), sulphuric acid (98.08%) from KIMIX (Cape Town, South Africa) and Hydrogen Peroxide from 35% Labchem (Johannesburg, South Africa). To evaluate the effect of added metal powders in biodiesel, Iron (> 99,9% Sigma-Aldrich, Johannesburg, South Africa), Zinc (98% Merck, Gauteng, South Africa) and Cu (99,3% AERONTEC, Cape Town, South Africa) were used.

3.3.2 Preparation of Bi-functional Catalyst (CaO/Al_2O_3)

The bifunctional (CaO/Al_2O_3) catalyst was synthesised by preparing an aqueous solution made of 37.5 g primary reagent grade of calcium oxide and 12.5 Aluminium oxide support. The wet impregnation method was utilised [108]. However, a minor modification was done by using precursor salt of commercial CaO, which was dissolved in distilled water. Thereafter, the introduction of alumina onto the precursor was carried out in a 100 mL flask. The mixture was vigorously stirred at room temperature for 4 h using an

overhead stirrer (SCIENTECH inc, Boulder, United States) set at 600 rpm, as reported in the study by Zabeti et al. [109]. The mixture was filtered under vacuum with grade 1 Whatman filter paper (Merch, Darmstadt, Germany). Thereafter, drying was accomplished in a static oven (Scientific, Kyalami, South Africa) set to 120 °C for 18 h. Prior to activation, the dried paste was crushed into fine powders by the use of pestle and mortar. To calcine the catalyst, a muffle furnace which was set at 475 °C, was used for 5 h. with a ramping rate of 5 °C/min [64,108]. After calcination, the catalyst was left to cool down at room temperature and was then transferred to a closed glass vial for storage.

3.3.3 Transesterification

In this study, the 75%CaO/25%Al_2O_3 catalyst was used to investigate the effect of conversion rate per catalyst (rate of yield) through a transesterification reaction and its contribution towards the elemental content within biodiesel. The reaction was carried out in a 250 mL round glass flask connected to a condenser, which avoided evaporation by having inlet and outlet systems to cool down the temperature. Waste cooking oil was added into the round glass flask with a thermometer placed inside it. The oil was pre-heated to 40 °C and the flask was slowly introduced into a water bath on a hotplate. A total of 100 g of methanol to oil ratio was mixed with 2.5 wt% of catalyst synthesised and poured into a 250 mL round-flask which had a stirrer; the mixture was then stirred vigorously. The hotplate was roughly set at 110 °C and as the temperature reading on the thermometer increased to 60 °C, the reaction was kick-started. The inlet and outlet flow of water that was connected to the condenser assisted in maintaining a constant temperature throughout the reaction and the mixing speed was set at 1300 rpm. After the reaction was completed, the products were poured into centrifuge tubes with equal masses and were centrifuged at 2200 rpm using Ohaus Multi Centrifuge for 10 min. Thereafter, samples were poured into separatory funnels for the separation of biodiesel and glycerol into phases, while solids were left in the centrifuge tubes. Distilled water used in the biodiesel washing was heated to a temperature of 50 °C. During the washing stage, three times the amount of water to biodiesel was used. This allowed for clean biodiesel, as the washed water was clear. The biodiesel was thereafter placed on a hotplate in a beaker and a small amount of Na_2SO_4 was used to dry any trace amount of water that might have been left in the biodiesel. The product was then left to cool and stored for analysis.

3.3.4 Characterisation Techniques

The Infrared spectral was performed using a spectrum high performance TWO LITA FTIR instrument (PerkinElmer, Inc., Walthan, MA, USA) equipped with a lithium tantalate

detector ($LiTaO_3$) and Spectrum 10™ software. All spectra were collected at a range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} using an average of 10 scans.

The morphology of the catalyst was assessed using a Field-Emission Scanning Electron Microscope (The Nova NanoSEM 230, Hillsboro, OR, USA) equipped with an in-lens secondary electron and backscattered electron detectors. The element was operated at an accelerating voltage of 5 kV using TESCAN MIRA.

The crystalline phases present were identified using a multipurpose X-ray diffractometer (XRD), D8-Advance (BRUKER AXS, Karlsruhe, Germany), which was operating in a continuous scan in locked coupled-mode using Cu-Kα radiation with a wavelength (λ) of 1.5406 Å at 40 kV and 40 mA. The measurements were run within a range in 2θ (0.5° to 80°) with a typical step size of 0.034°. A position-sensitive detector, Lyn-Eye, was used to record diffraction data at a screening speed of 0.5 sec/step, which is equivalent to an effective time of 92 sec/step for a scintillation counter. The XRD phases were identified using an Internal Center for Diffraction Data (ICDD) PDF database 1999 using EVA software from BRUKER.

The Brunauer-Emmett-Teller (BET) was employed to determine the surface area, pore volume and pore size distribution of the synthesised catalysts using TriStar II 3020 Analyser version 2.00 (Micromeritics, Instruments Corporation, GA, U.S.A) at a liquid nitrogen and operation bath temperature of 77.350 K. The BJH method was used for calculating pore volume distribution and average pore diameter while for the surface area, BET analysis was used. The sample was degassed overnight at 200 °C, while the reference Al_2O_3 was degassed at 300 °C for 3 h to obtain reasonable adsorption-desorption isotherms.

The fatty acids concentration was obtained using GC 7890A (Agilent Technologies, Inc, Waldbronn, Germany) detailing components within feedstocks, as materials were separated from each other by the number of their constituent atoms. This follows ASTM 6584 and EN 14214 standardisation.

Physico-chemical properties of feedstock and biodiesel were analysed for properties such as acid number, density, viscosity, oxidation stability, flash point and total contamination using conventional methods according to ASTM and EN methods.

3.4 Conclusions

A highly active bi-functional catalyst of CaO/Al_2O_3 was prepared by the wet impregnation method and used for its transesterification reaction. The catalyst was found to be suitable for the conversion of oils with high FFA contents (>15% FFA) such as waste cooking oils to FAME. However, it influenced the increase of concentration of Ca within biodiesel.

Biodiesel properties were evaluated according to ASTM and EN methods. The quality was highly influenced by the molecular structure, the chain length, and the degree of saturation in the feedstock used for biodiesel production. From the results obtained, it was determined that biodiesels produced from waste palm oil had longer oxidation stability than those produced from waste sunflower oil. This was attributed to the high degree of saturation in palm oil. Additionally, with the evaluation of the oxidation stability through the addition of Fe, Cu and Zn metal powders to biodiesels at concentrations of 2–700 ppm, results showed that all metals had an impact on reducing the induction time at the studied concentration range. The intensification in the oxidation instability was influenced by the increase in metal concentrations and the type of biodiesel produced. In both biodiesels, Fe decreased oxidation stability and significantly failed EN specifications in PB100 from 500–700 ppm and in all concentrations of SB100. Furthermore, a remarkable decrease of Cu in induction period for SB100 at a concentration of 700 ppm was also observed and the order of overall corrosiveness of metals in sunflower biodiesel was Fe > Zn > Cu and the equivalent in palm biodiesel was Fe > Cu > Zn, with most metals impacting on induction time reductions.

3.5 References

1. Organization for Economic Co-operation and Development. OECD Green Growth Studies. *OECD Publishing* **2012**, 9–104. http://dx.doi:10.1787/9789264115118-en.

2. Organization of Petroleum Exporting Countries (OPEC). *World Oil Outlook 2040*; OPEC: Vienna, Austria, 2017; pp. 61–161. http://dx.doi:10.1190/1.1439163. ISBN 978-3-9503936-4-4.

3. Magsi, H. Industrialization, Environment and Pollution. *Dipl. Insight* **2015**, *7*, 24–26. Available online: https://www.researchgate.net/publication/270899735_Industrialization_Environment_and_Pollution (accessed on 02 August 2021).

4. Muhammad, M.B.; Aziz, R.A.; Yew, V.W.C. Socio—Economic Effects of Industrialization in the Society. *Int. J. Environ. Ecol. Fam. Urban. Stud.* **2018**, *8*, 24–29. Available online: https://www.researchgate.net/publication/327966349_Socio_-_Economic_Effects_of_Industrialization_in_the_Society/citations (accessed on 02 August 2021).

5. Baskar, G.; Aiswarya, R. Trends in catalytic production of biodiesel from various feedstocks. *Renew. Sustain. Energy Rev.* **2016**, *57*, 496–504. http://dx.doi:10.1016/j.rser.2015.12.101.

6. Jabade, S.; Sakthivel, M.; Chavan, S. Bio-diesel as an alternative fuel for compression ignition engine: A review. *Int. J. Adv. Sci. Technol.* **2020**, *29*, 18–28. Available online: http://sersc.org/journals/index.php/IJAST/article/view/2975 [accessed on 13 January 2020]

7. Torres-García, M.; García-Martín, J.F.; Jiménez-Espadafor Aguilar, F.J.; Barbin, D.F.; Álvarez-Mateos, P. Vegetable oils as renewable fuels for power plants based on low and medium speed diesel engines. *J. Energy Inst.* **2019**, *93*, 953–961. http://dx.doi:10.1016/j.joei.2019.08.006.

8. Atabani, A.E.; Silitonga, A.S.; Badruddin, I.A.; Mahlia, T.M.I.; Masjuki, H.H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2070–2093. http://dx.doi:10.1016/j.rser.2012.01.003.

9. Alhindawi, R.; Nahleh, Y.A.; Kumar, A.; Shiwakoti, N. Projection of greenhouse gas emissions for the road transport sector based on multivariate regression and the double exponential smoothing model. *Sustainability* **2020**, *12*, 9152, http://dx.doi:10.3390/su12219152.

10. Abbaszaadeh, A.; Ghobadian, B.; Omidkhah, M.R.; Najafi, G. Current biodiesel production technologies: A comparative review. *Energy Convers. Manag.* **2012**, *63*, 138–148. http://dx.doi:10.1016/j.enconman.2012.02.027.

11. Harfoot, M.B.J.; Tittensor, D.P.; Knight, S.; Arnell, A.P.; Blyth, S.; Brooks, S.; Butchart, S.H.M.; Hutton, J.; Jones, M.I.; Kapos, V.; et al. Present and future biodiversity risks from fossil fuel exploitation. *Conserv. Lett.* **2018**, *11*, 1–13. doi:10.1111/conl.12448.

12. Nguyen, X.P.; Vu, H.N. Corrosion of the metal parts of diesel engines in biodiesel-based fuels. *Int. J. Renew. Energy Dev.* **2019**, *8*, 119–132, doi:10.14710/ijred.8.2.119-132. http://dx.doi:10.14710/ijred.8.2.119-132.

13. Nair, J.N. Study of Biodiesel Blends and Emission Characteristics of Study of Biodiesel Blends and Emission Characteristics of Biodiesel. (ISO 3297: 2007). *Int. J. Innov. Rev. Sci. Eng. Technol.* **2013**, *2*, 3710–3715. Available online https://www.researchgate.net/publication/281430011_STUDY_OF_BIODIESEL_BLENDS_AND_EMISSION_CHARACTERISTICS_OF_BIODIESEL (accessed on 02 August 2021).

14. Borugadda, V.B.; Paul, A.K.; Chaudhari, A.J.; Kulkarni, V.; Sahoo, N.; Goud, V.V. Influence of Waste Cooking Oil Methyl Ester Biodiesel Blends on the Performance and Emissions of a Diesel Engine. *Waste Biomass Valorization* **2018**, *9*, 283–292. http://dx.doi:10.1007/s12649-016-9749-0.

15. Peng, D.X. Effect of unleaded gasoline blended with biofuels on gasoline injector wear and exhaust emissions. Ind. Lubr. Tribol. **2017**, *69*, 208–214. http://dx.doi:10.1108/ILT-09-2016-0217.

16. Carraretto, C.; Macor, A.; Mirandola, A.; Stoppato, A.; Tonon, S. Biodiesel as alternative fuel: Experimental analysis and energetic evaluations. *Energy* **2004**, *29*, 2195–2211. http://dx.doi:10.1016/j.energy.2004.03.042.

17. Moser, B.R.; Bryan, R. Moser: Biodiesel production, properties, and feedstocks. *Vitr. Cell. Dev. Biol. Plant.* **2009**, *45*, 229–266, http://dx.doi:10.1007/s11627-009-9204-z.

18. Mandolesi de Araújo, C.D.; de Andrade, C.C.; de Souza, E.; Silva, E.; Dupas, F.A. Biodiesel production from used cooking oil: A review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 445–452. http://dx.doi:10.1016/j.rser.2013.06.014.

19. Rocha, L.D.S.; Corrêa, S.M. Determination of size-segregated elements in diesel-biodiesel blend exhaust emissions. Environ. Sci. Pollut. Res. **2018**, *25*, 18121–18129. http://dx.doi:10.1007/s11356-018-1980-8.

20. Zhang, Y.; Dubé, M.A.; McLean, D.D.; Kates, M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresour. Technol.* **2003**, *90*, 229–240. http://dx.doi:10.1016/S0960-8524(03)00150-0.

21. Kulkarni, M.G.; Dalai, A.K. Waste cooking oil—An economical source for biodiesel: A review. *Ind. Eng. Chem. Res.* **2006**, *45*, 2901–2913. doi:10.1021/ie0510526.

22. Boadu, K.O.; Joel, O.F.; Essumang, D.K.; Evbuomwan, B.O. A Review of Methods for Removal of Contaminants in Used Lubricating Oil. *Chem. Sci. Int. J.* **2019**, *26*, 1–11. http://dx.doi:10.9734/csji/2019/v26i430101.

23. Allan, F.; Alexandru, G. Waste cooking oil as source for renewable fuel in Romania. In Proceedings of the 7th International Conference on Advanced Concept in Mechanical Engineering, Iasi, Romania, 9–10 June 2016; Volume 146, pp. 1–6. http://dx.doi:10.1088/1757-899X/147/1/012133.

24. Agarwal, M.; Chauhan, G.; Chaurasia, S.P.; Singh, K. Journal of the Taiwan Institute of Chemical Engineers Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. *J. Taiwan Inst. Chem. Eng.* **2012**, *43*, 89–94. http://dx.doi:10.1016/j.jtice.2011.06.003.

25. Zhu, H.; Wu, Z.; Chen, Y.; Zhang, P.; Duan, S.; Liu, X.; Mao, Z. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. *Chin. J. Catal.* **2006**, *27*, 391–396. http://dx.doi:10.1016/S1872-2067(06)60024-7.

26. Calero, J.; Luna, D.; Sancho, E.D.; Luna, C.; Bautista, F.M.; Romero, A.A.; Posadillo, A.; Verdugo, C. Development of a new biodiesel that integrates glycerol, by using CaO as heterogeneous catalyst, in the partial methanolysis of sunflower oil. *Fuel* **2014**, *122*, 94–102. http://dx.doi:10.1016/j.fuel.2014.01.033.

27. Alba-Rubio, A.C.; Santamaría-González, J.; Mérida-Robles, J.M.; Moreno-Tost, R.; Martín-Alonso, D.; Jiménez-López, A.; Maireles-Torres, P. Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts. *Catal. Today* **2010**, *149*, 281–287. http://dx.doi:10.1016/j.cattod.2009.06.024.

28. Wen, D.; Jiang, H.; Zhang, K. Supercritical fluids technology for clean biofuel production. *Prog. Nat. Sci.* **2009**, *19*, 273–284. http://dx.doi:10.1016/j.pnsc.2008.09.001.

29. Banerjee, M.; Dey, B.; Talukdar, J.; Chandra, M. Production of biodiesel from sunflower oil using highly catalytic bimetallic gold e silver core e shell nanoparticle. *Energy* **2014**, *69*, 695–699. http://dx.doi:10.1016/j.energy.2014.03.065.

30. Changmai, B.; Vanlalveni, C.; Ingle, A.P.; Bhagat, R.; Rokhum, L. Widely used catalysts in biodiesel production: A review. *RSC Adv.* **2020**, *10*, 41625–41679. http://dx.doi:10.1039/d0ra07931f.

31. Nogueira, T.; Lucio, C. Determination of Ca, K, Mg, Na, sulfate, phosphate, formate, acetate, propionate, and glycerol in biodiesel by capillary electrophoresis with capacitively coupled contactless conductivity detection. *Microchem. J.* **2011**, *99*, 267–272. http://dx.doi:10.1016/j.microc.2011.05.014.

32. Elkadi, M.; Pillay, A.; Manuel, J.; Khan, M.Z.; Stephen, S.; Molki, A. Sustainability study on heavy metal uptake in neem biodiesel using selective catalytic preparation and hyphenated mass spectrometry. *Sustainability* **2014**, *6*, 2413–2423. http://dx.doi:10.3390/su6052413.

33. Isis, A.; de Oliveira, A.P.; de Magalhães, M.R.L.; Villa, R.D. Determination of sodium and potassium in biodiesel by flame atomic emission spectrometry, with dissolution in ethanol as a single sample preparation step. *Fuel* **2012**, *93*, 381–384. http://dx.doi:10.1016/j.fuel.2011.08.060.

34. Chaves, E.S.; de Loos-vollebregt, M.T.C.; Curtius, A.J.; Vanhaecke, F. Spectrochimica Acta Part B Determination of trace elements in biodiesel and vegetable oil by inductively coupled plasma optical emission spectrometry following alcohol dilution. *Spectrochim. Acta Part B At. Spectrosc.* **2011**, *66*, 733–739. http://dx.doi:10.1016/j.sab.2011.09.006.

35. Mendil, D.; Uluözlü, Ö.D.; Tüzen, M.; Soylak, M. Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry. *J. Hazard. Mater.* **2009**, *165*, 724–728. http://dx.doi:10.1016/j.jhazmat.2008.10.046.

36. Pillay, A.E.; Elkadi, M.; Fok, S.C.; Stephen, S.; Manuel, J.; Khan, M.Z.; Unnithan, S. A comparison of trace metal profiles of neem biodiesel and commercial biofuels using high performance ICP-MS. *Fuel* **2012**, *97*, 385–389. http://dx.doi:10.1016/j.fuel.2012.02.040.

37. Sánchez, R.; Sánchez, C.; Lienemann, C.P.; Todolí, J.L. Metal and metalloid determination in biodiesel and bioethanol. *J. Anal. At. Spectrom.* **2015**, *30*, 64–101, http://dx.doi:10.1039/C4JA00202D.

38. Waynick, J.A. Characterization of biodiesel oxidation and oxidation products. *Tech. Lit. Rev.* **2005**, 1–51. http://dx.doi:10.2172/909194.

39. Fazal, M.A.; Haseeb, A.S.M.A.; Masjuki, H.H. Degradation of automotive materials in palm biodiesel. *Energy* **2012**, *40*, 76–83. http://dx.doi:10.1016/j.energy.2012.02.026.

40. Garrido, M.D.; Frías, I.; Díaz, C.; Hardisson, A. Concentrations of metals in vegetable edible oils. *Food Chem.* **1994**, *50*, 237–243. http://dx.doi:10.1016/0308-8146(94)90127-9.

41. Santos, D.C.M.B.; Guida, M.A.B.; Barbosa, I.S.; Passos, M.L.C. Evaluation of Digestion Procedures for Simultaneous Determination of Ca, P, Mg, K and Na in Biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry. *J. Braz. Chem. Soc.* **2010**, *21*, 2278–2284. http://dx.doi:10.1590/S0103-50532010001200015.

42. Health Effects Institute: Understanding the Health Effects of Components of the Particulate Matter Mix: Progress and Next Steps. *HEI Perspect.* **2002**, 1–20. Available online: https://www.healtheffects.org/publication/understanding-health-

effects-components-particulate-matter-mix-progress-and-next-steps (accessed on 02 August 2021).

43. Ruzinska, E.; Stollmann, V.; Hagara, V.; Jablonski, M. Analysis of selected heavy metals in biomass for preparation of biofuels—Part II. Determination of heavy metals content. *Ann. Wars. Univ. Life Sci. SGGW. For. Wood Technol.* **2015**, *92*, 383–389. Available online: http://agro.icm.edu.pl/agro/element/bwmeta1.element.agro-c1690cab-9853-4775-93fd-d790b418cc8d/c/383__Annals92.pdf [accessed on 23 March 2020]

44. Black, L.T. Comparison of three atomic absorption techniques for determining metals in soybean oil. *J. Am. Oil Chem. Soc.* **1975**, *52*, 88–91. doi:10.1007/BF02633044.

45. Sompech, S.; Dasri, T.; Thaomola, S. Preparation and characterization of amorphous silica and calcium oxide from agricultural wastes. *Orient. J. Chem.* **2016**, *32*, 1923–1928. http://dx.doi:10.13005/ojc/320418.

46. Aitlaalim, A.; Ouanji, F.; Benzaouak, A.; El Mahi, M.; Lotfi, E.M.; Kacimi, M.; Liotta, L.F. Utilization of waste grooved razor shell (Grs) as a catalyst in biodiesel production from refined and waste cooking oils. *Catalysts* **2020**, *10*, 703. http://dx.doi:10.3390/catal10060703.

47. Hosseini, S.A.; Niaei, A.; Salari, D. Production of γ-Al_2O_3 from Kaolin. *Open J. Phys. Chem.* **2011**, *1*, 23–27. http://dx.doi:10.4236/ojpc.2011.12004.

48. Kesserwan, F.; Ahmad, M.N.; Khalil, M.; El-Rassy, H. Hybrid CaO/Al_2O_3 aerogel as heterogeneous catalyst for biodiesel production. *Chem. Eng. J.* **2020**, *385*, 2–11. http://dx.doi:10.1016/j.cej.2019.123834.

49. Ruan, G.; Zhang, Z.; Yin, M.; Xu, G. Effect of aluminum powder on the synthesis of corundum-mullite composites. *Ceram. Silikaty.* **2013**, *57*, 133–137.

50. Granados-Correa, F.; Bonifacio-Martínez, J.; Hernández-Mendoza, H.; Bulbulian, S. Capture of CO2 on γ-Al2O3 materials prepared by solution-combustion and ball-milling processes. *J. Air Waste Manag. Assoc.* **2016**, *66*, 643–654. http://dx.doi:10.1080/10962247.2016.1161673.

51. Mirghiasi, Z.; Bakhtiari, F.; Darezereshki, E.; Esmaeilzadeh, E. Preparation and characterization of CaO nanoparticles from Ca $(OH)_2$ by direct thermal decomposition method. *J. Ind. Eng. Chem.* **2014**, *20*, 113–117. http://dx.doi:10.1016/j.jiec.2013.04.018.

52. Yang, W.; Feng, Y.; Chu, W. Promotion Effect of CaO Modification on Mesoporous Al_2O_3-Supported Ni Catalysts for CO2 Methanation. *Int. J. Chem. Eng.* **2016**, *2016*, 2041821. http://dx.doi:10.1155/2016/2041821.

53. Intarasiri, S.; Ratana, T.; Sornachamni, T.; Tungkamani, S.; Phongaksorn, M. Pore size effect of mesoporous support on metal particle size of Co/SiO2 catalyst in Fischer-Tropsch synthesis. *Int. J. Adv. Appl. Sci.* **2018**, *5*, 80–85. http://dx.doi:10.21833/ijaas.2018.11.011.

54. Imtiaz, A.; Farrukh, M.A.; Khaleeq-Ur-Rahman, M.; Adnan, R. Micelle-assisted synthesis of Almiddot; CaO nanocatalyst: Optical properties and their

applications in photodegradation of 2,4,6-trinitrophenol. *Sci. World J.* **2013**, *2013*, 641420. http://dx.doi:10.1155/2013/641420.

55. Teo, S.H.; Taufiq-Yap, Y.H.; Rashid, U.; Islam, A. Hydrothermal effect on synthesis, characterization, and catalytic properties of calcium methoxide for biodiesel production from crude Jatropha curcas. *RSC Adv.* **2015**, *5*, 4266–4276. http://dx.doi:10.1039/c4ra11936c.

56. Nayebzadeh, H.; Saghatoleslami, N.; Haghighi, M.; Tabasizadeh, M. Catalytic Activity of KOH–CaO–Al2O3 Nanocomposites in Biodiesel Production: Impact of Preparation Method. *Int. J. Self Propagating High Temp. Synth.* **2019**, *28*, 18–27. http://dx.doi:10.3103/S1061386219010102.

57. Marinković, D.M.; Avramović, J.M.; Stanković, M.V.; Stamenković, O.S.; Jovanović, D.M.; Veljković, V.B. Synthesis and characterization of spherically shaped CaO/Γ-Al2O3 catalyst and its application in biodiesel production. *Energy Convers. Manag.* **2017**, *144*, 399–413. http://dx.doi:10.1016/j.enconman.2017.04.079.

58. Wacharasindhu, S.; Likitmaskul, S.; Punnakanta, L.; Chaichanwatanakul, K.; Angsusingha, K.; Tuchinda, C. Serum IGF-I and IGFBP-3 Levels for Normal Thai Children and their Usefulness in Clinical Practice. *J. Med. Assoc. Thail.* **1998**, *81*, 420–430.

59. Yang, F.; Ning, Z.; Liu, H. Fractal characteristics of shales from a shale gas reservoir in the Sichuan Basin, China. *Fuel* **2014**, *115*, 378–384. http://dx.doi:10.1016/j.fuel.2013.07.040.

60. Xu, L.; Zhang, J.; Ding, J.; Liu, T.; Shi, G.; Li, X.; Dang, W.; Cheng, Y.; Guo, R. Pore structure and fractal characteristics of different shale lithofacies in the dalong formation in the western area of the lower yangtze platform. *Minerals* **2020**, *10*, 2–20. http://dx.doi:10.3390/min10010072.

61. Zhu, L.; Cao, M.; Zhou, H.; Zhang, N.; Zheng, J.; Li, Y.; Chen, B.H. A highly stable and active CaO/Al_2O_3 base catalyst in the form of calcium aluminate phase for oxidation of cyclohexanone to ε-caprolactone. *Catal. Lett.* **2014**, *144*, 1188–1196. http://dx.doi:10.1007/s10562-014-1277-6.

62. Huang, B.; Bartholomew, C.H.; Woodfield, B.F. Improved calculations of pore size distribution for relatively large, irregular slit-shaped mesopore structure. *Microporous Mesoporous Mater.* **2014**, *184*, 112–121. http://dx.doi:10.1016/j.micromeso.2013.10.008.

63. Ljupković, R.B.; Radulović, N.S.; Bojić, A.L.; Zarubica, A.R.; Mićić, R.D.; Tomić, M.D. Značaj strukturnih karakteristika CaO katalizatora za proizvodnju biodizela: Uticaj na smanjenje emisije gasova staklene bašte. *Hem. Ind.* **2014**, *68*, 399–412. http://dx.doi:10.2298/HEMIND130612063L.

64. Stankovic, M. Preparation of CaO/γ -Al_2O_3 catalyst for biodiesel fuels. The catalytic activity in relation to thermal. In Proceedings of the 12th International Conference on Fundamental and Applied Aspects of Physical Chemistry. Belgrade, Serbia, 22–26 September 2014; pp. 2–3. http://dx.doi:10.13140/2.1.4772.9927.

65. Elias, S.; Rabiu, A.M.; Okeleye, B.I.; Okudoh, V.; Oyekola, O. Bifunctional heterogeneous catalyst for biodiesel production from waste vegetable oil. *Appl. Sci.* **2020**, *10*, 2–11. http://dx.doi:10.3390/app10093153.

66. Marinkovic, D.; Stankovic, M.; Velickovic, A.; Avramovic, J.; Cakic, M.; Veljkovic, V. The synthesis of CaO loaded onto Al2O3 from calcium acetate and its application in transesterification of the sunflower oil. *Savrem. Tehnol.* **2015**, *4*, 26–32. http://dx.doi:10.5937/savteh1501026m.

67. Capuano, D.; Costa, M.; Di Fraia, S.; Massarotti, N.; Vanoli, L. Direct use of waste vegetable oil in internal combustion engines. *Renew. Sustain. Energy Rev.* **2017**, *69*, 759–770. http://dx.doi:10.1016/j.rser.2016.11.016.

68. Mahmudul, H.M.; Hagos, F.Y.; Mamat, R.; Adam, A.A.; Ishak, W.F.W.; Alenezi, R. Production, characterization, and performance of biodiesel as an alternative fuel in diesel engines—A review. *Renew. Sustain. Energy Rev.* **2017**, *72*, 497–509. http://dx.doi:10.1016/j.rser.2017.01.001.

69. Chhetri, A.; Watts, K.; Islam, M. Waste Cooking Oil as an Alternate Feedstock for Biodiesel Production. *Energies* **2008**, *1*, 3–18. http://dx.doi:10.3390/en1010003.

70. Knothe, G. Analyzing biodiesel: Standards and other methods. *JAOCS J. Am. Oil Chem. Soc.* **2006**, *83*, 823–833. http://dx.doi:10.1007/s11746-006-5033-y.

71. Axelsson, L.; Franzén, M.; Ostwald, M.; Berndes, G.; Lakshmi, G.; Ravindranath, N.H. Perspective: Jatropha cultivation in southern India: Assessing farmers' experiences. *Biofuels Bioprod. Biorefining* **2012**, *6*, 246–256. http://dx.doi:10.1002/bbb.

72. Yasin, M.H.M.; Mamat, R.; Yusop, A.F.; Rahim, R.; Aziz, A.; Shah, L.A. Fuel physical characteristics of biodiesel blend fuels with alcohol as additives. *Procedia Eng.* **2013**, *53*, 701–706. http://dx.doi:10.1016/j.proeng.2013.02.091.

73. Bukkarapu, K.R.; Rahul, T.S.; Kundla, S.; Vardhan, G.V. Effects of blending on the properties of diesel and palm biodiesel. *IOP Conf. Ser. Mater. Sci. Eng.* **2018**, *330*, 012092. http://dx.doi:10.1088/1757-899X/330/1/012092.

74. Giakoumis, E.G. Analysis of 22 vegetable oils' physico-chemical properties and fatty acid composition on a statistical basis, and correlation with the degree of unsaturation. *Renew. Energy.* **2018**, *126*, 403–419. http://dx.doi:10.1016/j.renene.2018.03.057.

75. Yaşar, F. Comparision of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel* **2020**, *264*, 2–7. http://dx.doi:10.1016/j.fuel.2019.116817.

76. Barabas, I.; Todoru, I.A. *Biodiesel Quality, Standards and Properties*; Montero, G., Ed.; Technical University of Cluj-Napoca: Cluj-Napoca, Romania, 2011; pp. 1–28, ISBN 978-953-307-784-0. http://dx.doi:10.5772/25370.

77. Al-Abdullah, M.H.; Kalghatgi, G.T.; Babiker, H. Flash points and volatility characteristics of gasoline/diesel blends. *Fuel* **2015**, *153*, 67–69. http://dx.doi:10.1016/j.fuel.2015.02.070.

78. Senthil, R.; Silambarasan, R. Annona: A new biodiesel for diesel engine: A comparative experimental investigation. *J. Energy Inst.* **2015**, *88*, 459–469. http://dx.doi:10.1016/j.joei.2014.09.011.

79. Canesin, E.A.; de Oliveira, C.C.; Matsushita, M.; Felicidade Dias, L.; Reghiany Pedrão, M.; de Souza, N.E. Characterization of residual oils for biodiesel production. *Electron. J. Biotechnol.* **2014**, *17*, 39–45. http://dx.doi:10.1016/j.ejbt.2013.12.007.

80. Ghoreishi, S.M.; Moein, P. Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. *J. Supercrit. Fluids* **2013**, *76*, 24–31. http://dx.doi:10.1016/j.supflu.2013.01.011.

81. Palash, S.M.; Kalam, M.A.; Masjuki, H.H.; Masum, B.M.; Rizwanul Fattah, I.M.; Mofijur, M. Impacts of biodiesel combustion on NOx emissions and their reduction approaches. *Renew. Sustain. Energy Rev.* **2013**, *23*, 473–490. http://dx.doi:10.1016/j.rser.2013.03.003.

82. Sadeghzadeh, B. A review of zinc nutrition and plant breeding. *J. Soil Sci. Plant Nutr.* **2013**, *13*, 907–927. http://dx.doi:10.4067/S0718-95162013005000072.

83. Avila Orozco, F.D.; Kovachev, N.; Aguirre Pastor, M.Á.; Domini, C.E.; Fernández Band, B.S.; Hernández, A.C. Analysis of metals and phosphorus in biodiesel B100 from different feedstock using a Flow Blurring multinebulizer in inductively coupled plasma-optical emission spectrometry. *Anal. Chim. Acta.* **2014**, *827*, 15–21. http://dx.doi:10.1016/j.aca.2014.04.016.

84. Lyra, F.H.; Tereza, M.; Dias, W.; Brandão, G.P.; Pessoa, H.M.; de Castro, E.V. Determination of Na, K, Ca, and Mg in biodiesel samples by flame atomic absorption spectrometry (FAAS) using microemulsion as sample preparation. *Microchem. J.* **2010**, *96*, 180–185. http://dx.doi:10.1016/j.microc.2010.03.005.

85. Vieira, M.A.; Castro, C.; Ara, R. Determination of As in Vegetable Oil and Biodiesel by Graphite Furnace Atomic Absorption Spectrometry. *Energy Fuels* **2009**, *23*, 5942–5946. http://dx.doi:10.1021/ef900709q.

86. Hoekman, S.K.; Broch, A.; Robbins, C.; Ceniceros, E.; Natarajan, M. Review of biodiesel composition, properties, and specifications. *Renew. Sustain. Energy Rev.* **2012**, *16*, 143–169. http://dx.doi:10.1016/j.rser.2011.07.143.

87. Iqbal, J.; Carney, W.A.; Lacaze, S.; Theegala, C.S. Metals Determination in Biodiesel (B100) by ICP-OES with Microwave Assisted Acid Digestion. *Open Anal. Chem. J.* **2010**, *4*, 18–26. http://dx.doi:10.2174/1874065001004010018.

88. Woods, G.D.; Fryer, F.I. Direct elemental analysis of biodiesel by inductively coupled plasma—mass spectrometry. *Anal. Bioanal. Chem.* **2007**, *389*, 753–761. http://dx.doi:10.1007/s00216-007-1439-0.

89. Szyczewski, P.; Frankowski, M.; Zioła-Frankowska, A.; Siepak, J.; Szyczewski, T.; Piotrowski, P.; Pillay, A.E.; Elkadi, M.; Fok, S.C.; Stephen, S.; et al. Metals Determination in Biodiesel (B100) by ICP-OES with Microwave Assisted Acid Digestion. *Microchem. J.* **2010**, *96*, 18121–18129. http://dx.doi:10.2174/1874065001004010018.

90. Henrique Lyra, F.; Weitzel Dias Carneiro, M.T.; Pedrini Brandão, G.; Moura Pessoa, H.; Ribeiro De Castro, E.V. Direct determination of phosphorus in biodiesel samples by graphite furnace atomic absorption spectrometry using a solid sampling accessory. *J. Anal. At. Spectrom.* **2009**, *24*, 1262–1266. http://dx.doi:10.1039/b907071k.

91. Ramadhas, A.S.; Jayaraj, S.; Muraleedharan, C. *Biodiesel: Production and Properties*; The Royal Society of Chemistry: Cambridge, UK, 2016; pp. 41–80. ISBN 978-1-84973-470-7.

92. de Goede, S.; Wilken, C.; Ajam, M.; Roets, P.; Engelbrecht, P.; Woolard, C. A Comparison of the Stability Performance of Blends of Paraffinic Diesel and Petroleum-Derived Diesel, with RME Biodiesel Using Laboratory Stability Measurement Techniques. *J. Fuels* **2015**, *2015*, 528497. http://dx.doi:10.1155/2015/528497.

93. Zuleta, E.C.; Baena, L.; Rios, L.A.; Calderón, J.A. The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: A review. *J. Braz. Chem. Soc.* **2012**, *23*, 2159–2175. http://dx.doi:10.1590/S0103-50532012001200004.

94. Qiu, F.; Li, Y.; Yang, D.; Li, X.; Sun, P. Biodiesel production from mixed soybean oil and rapeseed oil. *Appl. Energy* **2011**, *88*, 2050–2055. http://dx.doi:10.1016/j.apenergy.2010.12.070.

95. Komariah, L.N.; Dewi, T.K.; Ramayanti, C. Study on corrosion behavior of storage tanks filled with biodiesel and the blends. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *543*, 1–7. http://dx.doi:10.1088/1757-899X/543/1/012033.

96. Yeşilyurt, M.K.; Öner, İ.V.; Yılmaz, E.Ç. Biodiesel Induced Corrosion and Degradation: A Review. *Pamukkale Univ. J. Eng. Sci.* **2019**, *25*, 60–70. http://dx.doi:10.5505/pajes.2018.01885.

97. Chaves, E.S.; José, E.; Araujo, R.G.O.; Vladimir, J.; Lúcia, V.; Frescura, A.; Curtius, A.J. Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS. *Microchem. J.* **2010**, *96*, 71–76. http://dx.doi:10.1016/j.microc.2010.01.021.

98. Kivevele, T. Storage and thermal stability of biodiesel produced from manketti nut oil of Southern Africa origin with the influence of metal contaminants and antioxidants. *SN Appl. Sci.* **2020**, *2*, 930. http://dx.doi:10.1007/s42452-020-2743-y.

99. Jain, S.; Sharma, M.P. Effect of metal contents on oxidation stability of biodiesel/diesel blends. *Fuel* **2014**, *116*, 14–18. http://dx.doi:10.1016/j.fuel.2013.07.104.

100. Shiotani, H.; Goto, S. Studies of fuel properties and oxidation stability of biodiesel fuel. *SAE Tech. Pap.* **2007**, *116*, 70–75. http://dx.doi:10.4271/2007-01-0073.

101. Knothe, G.; Steidley, K.R. The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition. *Fuel Process. Technol.* **2018**, *177*, 75–80. http://dx.doi:10.1016/j.fuproc.2018.04.009.

102. Sarin, A.; Arora, R.; Singh, N.P.; Sarin, R.; Sharma, M.; Malhotra, R.K. Effect of metal contaminants and antioxidants on the oxidation stability of the methyl

ester of pongamia. *JAOCS J. Am. Oil Chem. Soc.* **2010**, *87*, 567–572. http://dx.doi:10.1007/s11746-009-1530-0.

103. Baena, L.M.; Calderón, J.A. Effects of palm biodiesel and blends of biodiesel with organic acids on metals. *Heliyon* **2020**, *6*, 2–13. http://dx.doi:10.1016/j.heliyon.2020.e03735.

104. Sentanuhady, J.; Saputro, W.; Muflikhun, M.A. Metals and chemical compounds contaminants in diesel engine lubricant with B20 and B100 biofuels for long term operation. *Sustain. Energy Technol. Assess.* **2021**, *45*, 101161. http://dx.doi:10.1016/j.seta.2021.101161.

105. Thangavelu, S.K.; Ahmed, A.S.; Ani, F.N. Impact of metals on corrosive behavior of biodiesel-diesel-ethanol (BDE) alternative fuel. *Renew. Energy* **2016**, *94*, 1–9. http://dx.doi:10.1016/j.renene.2016.03.015.

106. Hu, E.; Xu, Y.; Hu, X.; Pan, L.; Jiang, S. Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol. *Renew. Energy* **2012**, *37*, 371–378. http://dx.doi:10.1016/j.renene.2011.07.010.

107. Komariah, N.L.; Arita, S.; Prianda, B.E.; Dewi, T.K. Engineering Sciences Technical assessment of biodiesel storage tank; A corrosion case study. *J. King Saud Univ. Eng. Sci.* **2021**, *33*, 1–6. http://dx.doi:10.1016/j.jksues.2021.03.016.

108. Marinković, D.M.; Miladinović, M.R.; Avramović, J.M.; Krstić, I.B.; Stanković, M.V.; Stamenković, O.S.; Jovanović, D.M.; Veljković, V.B. Kinetic modeling and optimization of sunflower oil methanolysis catalyzed by spherically shaped CaO/Γ-Al2O3 catalyst. *Energy Convers. Manag.* **2018**, *163*, 122–133. http://dx.doi:10.1016/j.enconman.2018.02.048.

109. Zabeti, M.; Daud, W.M.A.W.; Aroua, M.K. Optimization of the activity of CaO/Al_2O_3 catalyst for biodiesel production using response surface methodology. *Appl. Catal. A Gen.* **2009**, *366*, 154–159. http://dx.doi:10.1016/j.apcata.2009.06.047.

Chapter 4: **Optimisation of Biodiesel Produced from Waste Sunflower Cooking Oil over CaO/Al_2O_3**

Biofuels are the future of energy in this nation and around the world ~ Rod Blagojevish

Abstract

In the current global climate emergency and with the interesting environmental advantages of biodiesel, a look into the commercialisation of such greener fuel is essential. While raw materials account for the most production cost, time and energy can be economised through the use of statistical models. The optimisation of free methyl esters (FAME) synthesised from waste sunflower oil over CaO/Al_2O_3, and methanol was carried out at a methanol oil ratio of 12:1. The aim was to investigate the effect of operation parameters on the yield of sunflower biodiesel, with the use central composite response surface methodology. The chosen variables were catalyst loading, temperature, and time while the response was the yield. The catalyst weight had the most significant effect on yield. The linear regression model was obtained to predict responses given by these variables, with 95% confidence. The predicted and experimental yields were comparable having 92.773% and 95.665% respectively. A significant yield of 98.23% was obtained at optimal operating conditions of catalyst loading (2.5 wt%), time (5 h) and temperature (60 °C). The properties of optimised FAME were within the international standard limits set for biodiesel except for the increased Ca+Mg concentrations.

Keywords: Variance analysis; biodiesel; interaction; operation parameters; optimisation; yield; response surface methodology

4.1 Introduction

Since the petroleum resource crisis in 1970 (Sadeghinezhad et al., 2014), there is a 1.6% annual expectation growth in primary energy demand worldwide, as energy consumption mainly originates from fossil fuel (88%), while nuclear and renewable energy make 7% and 5% respectively (Thangaraj et al., 2019). The global fossil fuels production is about 934 million tonnes of diesel annually (Kulkarni & Dalai, 2006) and the transportation sector makes about 97.6% use of oil resources (Baskar & Aiswarya, 2016). All these contribute to the potential exhaustion of petroleum reserves (Nair, 2013), increase in fuel prices (Borugadda et al., 2018) and global warming (Saxena et al., 2013). More focus has been given to renewable energy studies which are capable of environmental preservation, economic and social sustainability.

According to the Kyoto protocol clean energy development mechanism is driven by energy security and environmental sustainability, with biodiesel, a potential replacement of fossil

fuel in the future gaining huge research interest since the 1990s. It is an alternative fuel characterised with appreciable reduction of greenhouse gases or extender of petrodiesel for combustion in diesel engine (Moser, 2009). It is not economically feasible when high-quality feedstock is used (Atabani et al., 2012) since 70-95% of production cost is due to the raw material used (Zhang et al., 2003). With the increasing use of non-edible feedstocks such as waste cooking oils, there is a reduction in production costs (Fadhil et al., 2017) and a need for subsidy (Robles-Medina et al., 2009).

The American Society for Testing and Materials (ASTM) has defined this fuel as mono-alkyl esters produced from either vegetable oils or animal fats (Saydut et al., 2010; Santos et al., 2013). Different oil sources such as corn, and grapeseed can be used in its production, however, sunflower oil has proved to have better fuel quality as compared to other oil sources (Bhangale & kulkarni, 2017; Yaşar, 2020). Furthermore, Simbi et al. (2021), reported enhanced fuel quality of biodiesel produced from waste sunflower oil as compared to waste palm oil.

As a result of the availability of edible oils such as sunflower oil in certain regions like Europe and the USA, there is more advancement of this type of renewable energy development (Jain & Sharma, 2014). Although edible oils can be used, their availability (Atabani et al., 2012), price and food vs fuel dilemma cause them to be less economical (Kumar et al., 2015). Therefore, the use of non-edible and waste oils in biodiesel synthesis is a much more valuable way to potentially reduce the production cost, however the presence of high free fatty acids (FFA) within feedstocks is a slight issue (Sirisomboonchai et al., 2015; Giakoumis, 2018). Therefore, high FFA feedstocks would require acid-catalysis in order to esterify oils before transesterification process (Rizwanul Fattah et al., 2020), or a two-step reaction consisting of an acid-base process (Shohaimi & Marodzi, 2018). Bi-functional catalysts have been shown to mediate the conversion of high FFA feedstocks to fatty acids methyl esters (FAME) due to their possession of Lewis or Bronsted basic functionality and hydrogen bond donor (Li, 2010; Lee et al., 2015; Dixon, 2016). Additionally, they have the ability to enhance biodiesel production (Changmai et al., 2020).

The process of transesterification is commonly used in the conversion of oils to biodiesel using an alcohol and catalyst yielding methyl or ethyl esters (Rao et al., 2017). This process has shown impressive results in reducing the viscosity of the oils (Nabi et al., 2009). Factors influencing the yield can be varied from feedstock compositions, alcohol type to the operation conditions such as time, temperature, and catalyst weight (Nabi et al., 2009; Azócar et al., 2010; Sirisomboonchai et al., 2015). To save time and energy as well as

complex processes, a statistical experimental design can be performed. All relevant factors necessary can be evaluated through response surface methodology (RSM), in finding optimum reaction conditions (Zabeti, Daud, et al., 2009; Worapun et al., 2012; Hamze et al., 2015; Sánchez et al., 2019).

Such a robust mathematical modelling tool has been reliable in finding the optimum reaction conditions for biodiesel production. RSM optimization model is preferably used when a response is dependent on a variety of independent variables. It uses a statistical experimental design central composite design (CCD) to optimize responses, minimizing the number of experiments (Sugashini & Begum, 2013)(Ahmadi et al., 2005). This method is used to avoid the limitations caused by conventional methods where one factor is studied at the time while other variables are kept constant, which results in a large number of unnecessary experiments and waste of resources (Ani et al., 2019)(Ani et al., 2016).

In this present work, the production of biodiesel from sunflower waste cooking oil was studied, to investigate the relationships between selected parameters of time, temperature and catalyst loading to obtain maximum yield and optimum reaction conditions for the transesterification process. Response surface methodology composed of the central composite design was employed, in the design of experiments providing empirical equations for biodiesel conversion prediction. Finally, the produced biodiesel was tested for fuel quality (viscosity, flash point, density, oxidation stability, acid value, water content, distillation, and contaminations).

4.2 Statistical Analysis Using Response Surface Methodology

Design of Experiment and Optimization

This study used applications of central composite design (CCD) and response surface methodology (RSM) techniques in the optimisation of sunflower biodiesel since these methods are conventionally used for chemical and environmental processes such as the transesterification of FAME (Hojjat et al., 2017). This has the capability of generating a model equation and calculating the optimum conditions (Zabeti et al., 2009).

The experimental design applied was 2^3 factorial response surface methodology using Design-Expert Software version 12.0.9.0 (STAT-EASE Inc., Minneapolis, USA). In order to investigate the effects of time (A), temperature (B) and catalyst loading (C) on the yield of biodiesel, regression and analysis of experimental data were employed. These variables had ranges of time 3-5 h, temperature 60-70 °C and catalyst loading 2.5-5.5 wt%. A randomised order was followed with a combination of each variable at either its lowest (-

1) or highest (1) level in 20 experimental runs. Analysis of variance (ANOVA) was used in the statistical analysis of the model and check for adequacy of the empirical model; model fit was evaluated using coefficients determination (R^2) and a linear polynomial equation from regression analysis was developed to plot response surface. Table 4-1 lists the experimental design layout of ranges and levels of those independent variables in the study with the response obtained. The conversion to biodiesel ranged from 87.567% to 98.23% in yield with design points 2 and 4 respectively, at minimum operation condition at 65.95 °C, with 3.75673 wt% for 3.07 h and maximum conditions of 64.5 °C, with 4.15 wt% for 4.96 h.

Table 4-1. Experimental design layout of 3 parameters with results of the response

	Factor 1	**Factor 2**	**Factor 3**	**Response 1**
Run	**A: Time (hrs)**	**B: Temperature (°C)**	**C: Catalyst loading (wt%)**	**Yield (%)**
1	4.9	69.5	4	97.5
2	3.07	65.95	3.75673	87.567
3	3	60	3.61	93.5
4	4.96	64.5	4.15	98.23
5	4.25	60	5.5	89.267
6	5	60	2.5	95.667
7	3	60.0299	5.49306	95
8	3	70	2.5	95.83
9	3.9	64.5	2.56	94.93
10	3.9	64.5	2.56	95.567
11	4.96	64.5	4.15	93.93
12	3	66.3	5.5	91.167
13	5	70	5.5	89.23
14	4.96	64.5	4.15	95.4
15	3.9	64.5	2.56	95.73
16	3.9	69.85	4.15	94.63
17	5	70	2.5	96
18	4.17	65.85	5.485	89.93
19	4.17	60.25	3.745	95.8
20	3.9	69.85	4.15	95.167

4.3 Confirming the Mathematical Model

The accuracy of the model was checked with residual analysis plots (Hamze et al., 2015), in Figure 4-1, Figure 4-2 and Figure 4-3**,** where good conformity was seen in Figure 4-1 since the line was linear. While the graphical comparison between experimental and predicted values of the response variable is illustrated in Figure 4-2. There is a reasonable

data fit along the line of unit slope (Hojjat et al., 2017). Colour indicators starting from dark blue to red on the graph indicate the lowest to highest yield. An adequate model is shown in Figure 4-3, indicated by the random patterns of residuals, where all points were within limits which is good (Anderson et al., 2017). To find optimum conditions in the synthesis of biodiesel, a numerical optimisation was conducted by minimizing all 3 independent variables to maximise the yield. The corresponding responses were 3 h for reaction time, 2.5 wt% for catalyst loading and 60 °C for reaction the temperature, a conversion of 95.129% was achieved with highest desirability of 0.918. While maximising the yield to a higher conversion of 97.014% was achieved when all variances were kept in range. However, the desirability was 0.886, the conditions given were temperature of 60 °C, 2.5 wt% catalyst loading for 5 h. Different variable ranges were assessed for good yield and optimisation. It was concluded for this study that for the transesterification of waste cooking oil (WCO) with 12:1 methanol to oil ratio at speed of 1100 rpm, optimum reaction parameters chosen for this model were catalyst weight of 2.5 wt%, reaction temperature of 60 °C and reaction time of 5 h for, this was desirable in comparison to those reported in the literature by Kesić et al., (2016).

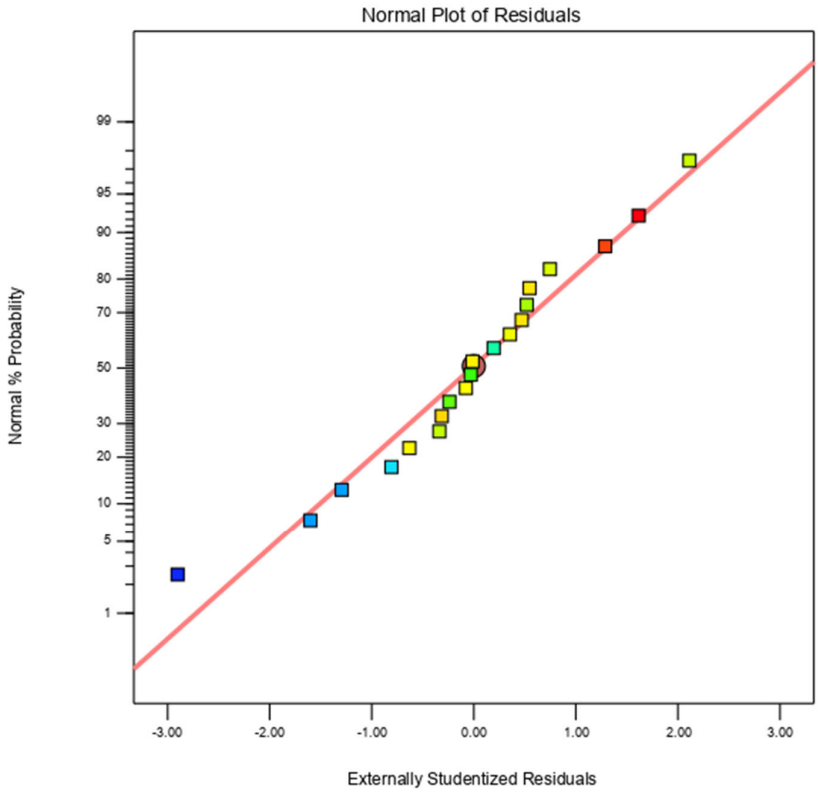


Figure 4-1. Normal distribution of Residuals

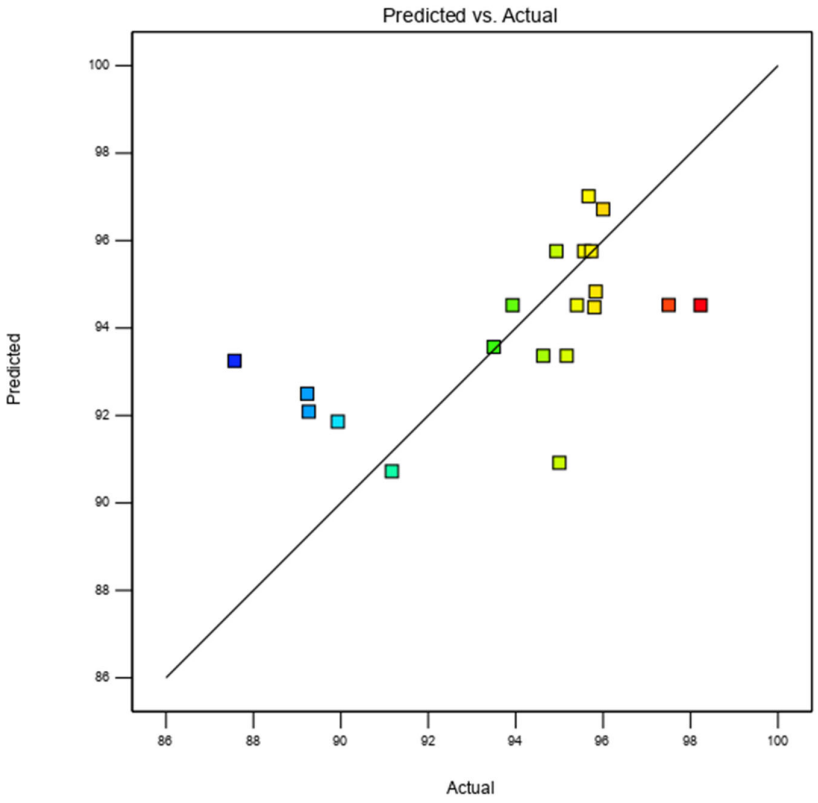


Figure 4-2. Predicted vs actual plot of the response variable

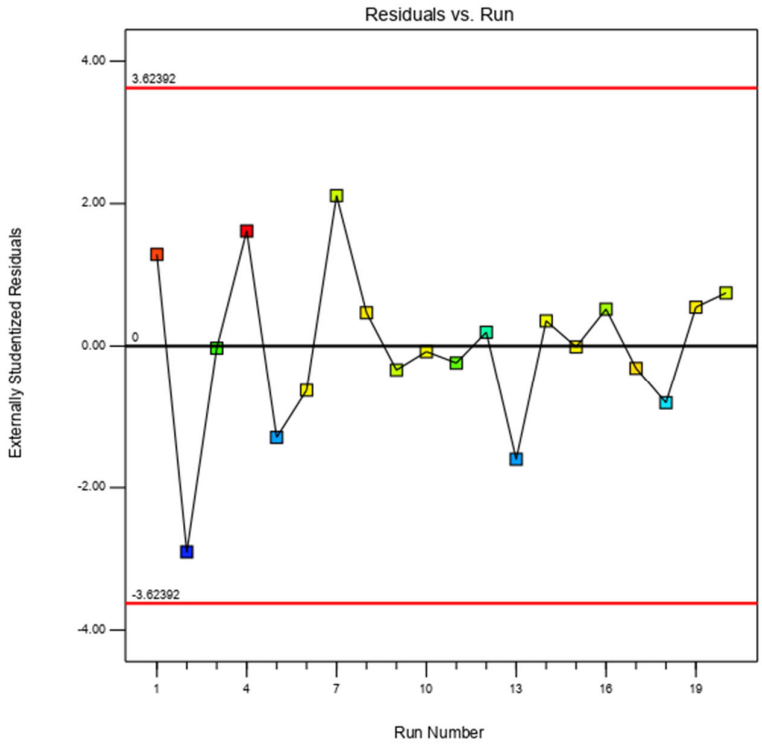


Figure 4-3. Residuals vs run orders

4.4 Effects of Operating Parameters on Yield

4.4.1 Interaction of Reaction Time and Temperature on Yield

An increase in the temperature of the reaction will increase the reaction rate by decreasing the viscosity of oils and reducing reaction time (Ramadhas et al., 2005). In Figure 4-4, the effect of temperature and time on the yield of FAME when catalyst loading was kept at optimum (2.5 wt%), a high yield was found as compared to using 5.5 wt%. Increase catalyst weight from 2.5-5.5 wt% reduced yield significantly from 96-89.23%. An increased catalyst loading, resulted in the mass transfer challenge, which reduces the accessibility of reactants to the active sites. When the temperature was kept at 60 °C and time was maximized to 5 h, a 95.667% yield was found, while 95.830% yield was obtained when the maximum temperature of 70 °C was applied and minimum time of 3 h. However, this appeared above the surface design, and consequently in maximizing both time and temperature to 5 h and 70 °C, a 96% yield was found which was below the surface design. This was supported by literature (Hamze et al., 2015), that at low catalyst loading, elevating temperatures increased the yield. While keeping the temperature constant at a maximum of 70 °C and increasing the time from 3-5 h resulted in increased yield from 95.83-96%, as the bulk of WCO was converted to biodiesel over a longer reaction time. This observation was supported by a previous study by Kesserwan et al., (2020).

On the other hand, keeping time constant at 5 h and having an increase in temperature from 60 to 70 °C resulted in a yield of 95.667-96% which is in agreement with a previous report by Phan & Phan, (2008), an increase in temperature of the reaction from 30 to 50 °C increased yield from 88 to 99%, While a high increase in temperature up to 70 °C reduced the conversion of WCO. This was in contrast with the results obtained for the current study. Additionally, there is a need to obtain a reaction temperature that will consume less energy, facilitating a high yield while reducing the cost of production (Fadhil et al., 2017). Leung et al., (2010), found optimum reaction temperatures to be between 50 °C and 60 °C, while Knothe, (2010), reported that a typical temperature of 60-65 °C should be used in transesterification in presence of methanol. Therefore, from the results obtained, employing a reaction temperature of 60 °C with reaction time of 5 h was considered ideally more cost effective by saving energy as opposed to using 70 °C for 5 h.

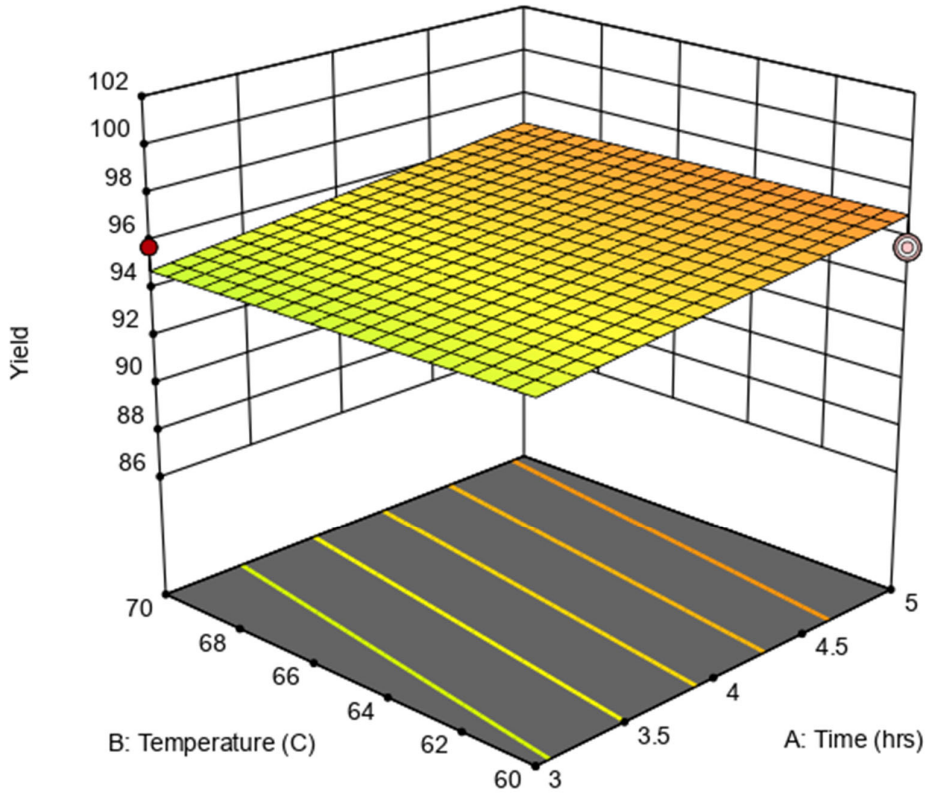


Figure 4-4. Interaction of reaction temperature and time on biodiesel yield

4.4.2 Interaction of Reaction Time and Catalyst Loading of Yield

The interaction between time and catalyst loading is illustrated in Figure 4-5. This is more significant than other interactions, since all the design points appeared within the surface. A decrease in catalyst loading with an increase in reaction time increased the yield, therefore a maximum of 5 h reaction time with catalyst loading of 2.5 wt% is expected to have the highest desirability and yield which was 95.83%. This was also true when the reaction was kept at 60 °C, while in increasing the temperature there was a significant decrease in the design points. Moreover, when the time was decreased to 3 h and catalyst loading was increased from 2.5 to 5.5 wt%, a 93.5 % yield was observed for reaction of 3 h and 3.61 wt% while elevating time and catalyst loading to 4.25 h and 5.5 wt%, the yield was reduced to 89.296%. The significance of catalyst loading, and time is supported by p-values in Table 4-2. Here, catalyst weight was observed to have the lowest p-value which showed that it was the most important factor followed by time and then lastly temperature.

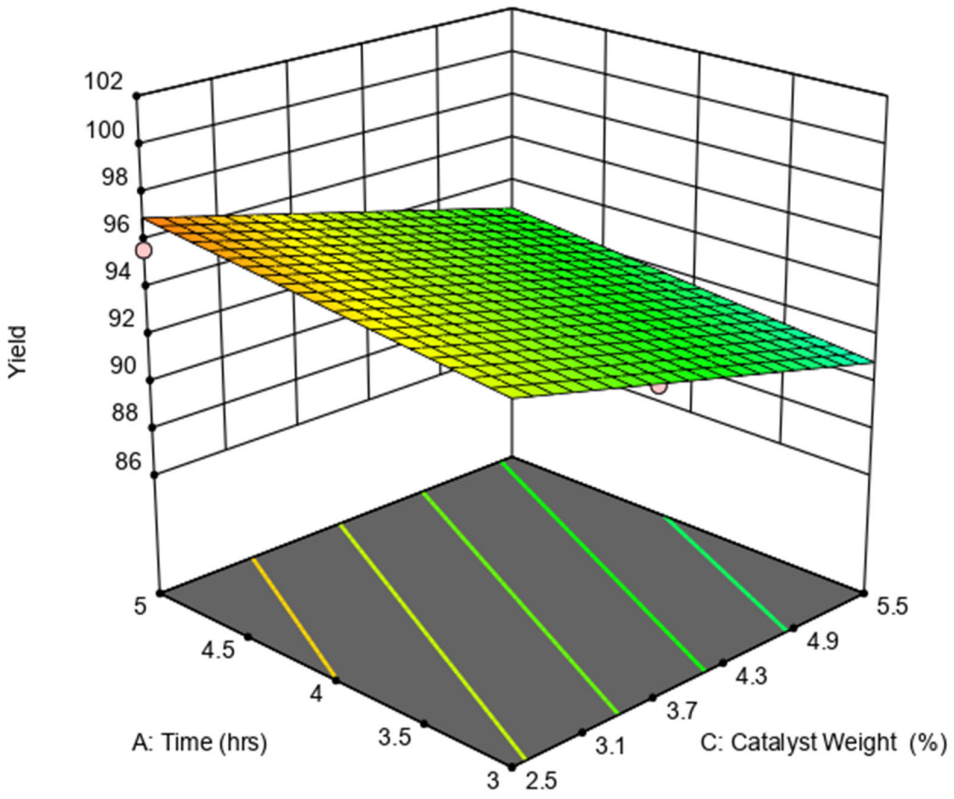


Figure 4-5. Interaction between time and catalyst loading

4.4.3 Interaction of Reaction Temperature and Catalyst Loading on Yield

Figure 4-6 illustrates the interaction between temperature and catalyst loading, with reaction time kept constant at 5 h. When the reaction time was decreased, the desirability and most of the design points were above the surface, only one point was below the surface design, which had a yield of 93.5% using reaction conditions of temperature and time of 60 °C and 3 h respectively. In the figure below, when conducted at a temperature of 70 °C, and with catalyst loading of 2.5-5.5 wt%, the yield obtained was 96-89.23%. However, a 95.667% yield was achieved when the temperature was decreased to 60 °C and catalyst loading of 2.5 wt%. It is noticeable from the below results, that low catalyst loading with either low or high temperatures should be considered. However, according to interaction between temperature, time and catalyst loading, there is a clear observation that high temperature is not desirable. The use of low temperature, low catalyst loading, and high reaction time should be used for experiments to obtain optimum yield with high desirability.

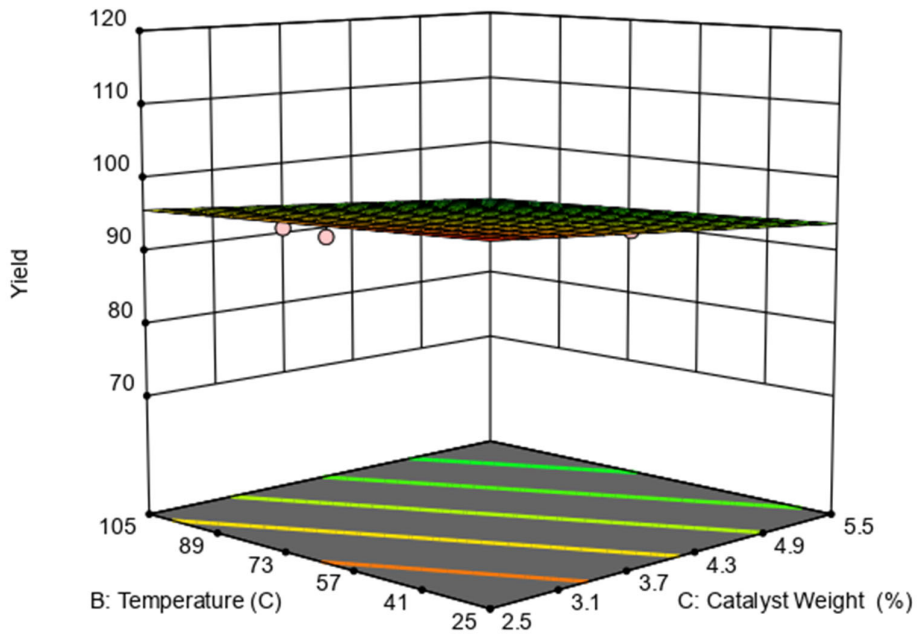


Figure 4-6. Interaction of reaction temperature and catalyst loading on yield of biodiesel.

Table 4-3 to 4-5, show the summary of the analysis of different models, the possibility of their significance in evaluating the most effective parameters on the yield of biodiesel. While a detailed summary of the suggested model, with a significant of 95% confidence intervals is shown in Table 4-2. Normally, when p-values of parameters are greater > 0.05, models are called insignificant (Sulochana & Bhatti, 2018). Hence, the list of variables that were significant at $p < 0.05$ of each catalyst loading was 0.0159, with the highest F-value of 7.26 among the other variables, while time and temperature had 0.2378, 0.8536 and 1.50, 0.0352 of p-values and F-values respectively. From these data observation, it is confirmed that catalyst loading was the most important variable for the production of biodiesel from WCO (Hamze et al., 2015). Therefore, time and temperature could not be disregarded since they were necessary for the support of the model hierarchy.

The selected model had an insignificant lack of fit since its p-value was 0.0589 which was slightly greater than 0.05 (Ghoreishi & Moein, 2013). This was better compared to 0.0258 for the quadratic model and 0.0432 for the two-factor interaction (2FI) model as seen in Table 4-5. The p-value > 0.05 implies that there was no significance relating to pure error, which is good as it indicates that the model is fitted to all data (Zabeti, Daud, et al., 2009). F-value found for the suggested model was 3.02, implying that there is a 6.03% (0.0603 p-value) chance that this occurred due to noise which is in agreement with the literature reported by Worapun et al., (2012). The adequate precision which measures signal to noise

ratio was found to be 5.468, which indicated adequate signal since it was above 4 (Zabeti et al., 2009). Based on actual parameters, a linear regression model equation which is shown below, can be used to make predictions of the response for each factor given:

$$Y = 97.60355 + 0.942336A - 0.029759B - 1.40628C \quad (4.1)$$

Here, Y is the response variable which is the yield of biodiesel and A, B, and C are actual values of predictors, namely time, temperature and catalyst loading respectively. The positive sign in front of a term is pro linearity while the negative sign shows an antagonistic effect on Y (Liao & Chung, 2013). This shows that an increase in reaction time will have a positive effect on yield while a decrease in temperature and catalyst loading will increase the yield, this is further supported by the interaction of parameters shown in Figure 4-4, 4-5 and 4-6. The quality of the model fit was evaluated using R-squared (R^2), where predicted R^2 measures how good the model predicts values for response (Table 4-3) (Zabeti et al., 2009). According to Worapun et al., (2012), a good statistical model should be closer to 1, since the R^2 value is always between 0 and 1. The linear model had an R^2 value of 0.3618 and negative predicted R^2 (-0.0352) while the cubic model had better R^2 and adjusted R^2 results of 0.9394 and 0.7697 respectively. Even though the cubic model had good R^2 values as compared to other models, the predicted R^2 was not calculated due to some missing data which is evident in Table 4-3 to 4-5, therefore, making it aliased. When the predicted R^2 is negative, it implies that the overall mean, which was 94 for the suggested model might be a better predictor. Nevertheless, the adjusted R^2 for the suggested model was 0.2422 (24.22%), which was within 0.2 confirming no problem with experimental data or the model (Zabeti et al., 2009). Therefore, since the sum of squares was 60.04 for linear vs mean, a polynomial order was suggested where other terms are significant and not aliased.

Table 4-2. ANOVA for the linear model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	60.04	3	20.01	3.02	0.0603	Not significant
A-Time	9.95	1	9.95	1.50	0.2378	Not significant
B-Temperature	0.2328	1	0.2328	0.0352	0.8536	Not significant
C-Catalyst Weight	48.05	1	48.05	7.26	0.0159	Significant
Residual	105.89	16	6.62			
Lack of Fit	95.84	11	8.71	4.33	0.0589	Not significant
Pure Error	10.05	5	2.01			
Cor Total	165.93	19				

Table 4-3. Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	**2.57**	**0.3618**	**0.2422**	**-0.0352**	**171.77**	**Suggested**
2FI	2.68	0.4368	0.1768	-1.2950	380.79	
Quadratic	2.84	0.5132	0.0750	-4.7170	948.60	
Cubic	1.42	0.9394	0.7697		*	Aliased

Table 4-4. Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	1.767E+05	1	1.767E+05			
Linear vs Mean	**60.04**	**3**	**20.01**	**3.02**	**0.0603**	**Suggested**
2FI vs Linear	12.43	3	4.14	0.5765	0.6406	
Quadratic vs 2FI	12.68	3	4.23	0.5231	0.6761	
Cubic vs Quadratic	70.73	5	14.15	7.03	0.0258	Aliased
Residual	10.05	5	2.01			
Total	1.769E+05	20	8844.69			

Table 4-5. Lack of fit tests

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Linear	**95.84**	**11**	**8.71**	**4.33**	**0.0589**	**Suggested**
2FI	83.40	8	10.43	5.18	0.0432	
Quadratic	70.73	5	14.15	7.03	0.0258	
Cubic	0.0000	0				Aliased
Pure Error	10.05	5	2.01			

4.5 Properties of Optimised Sunflower Biodiesel

Table 4-6 shows the properties of optimised biodiesel from sunflower waste cooking oil. Most of the results found falls within the limits specified by the International standard for biodiesel ASTM or EN.

4.5.1 Viscosity

The viscosity is a property that has an important role in biodiesel, contributing highly in the fuel atomisation as reported by Borugadda et al., (2018), and there is need for the reduction of viscosity in the vegetable oil (Borges et al., 2011). Through the process of transesterification reduction of viscosity in oils is achievable (Elkady et al., 2015). The process transforms triglycerides which are highly unsaturated fatty acids and very susceptible to oxidation Domingos et al., (2007), into mixtures of long-chained fatty acid esters, which are more saturated (Jain and Sharma, 2011). The decrease of the viscosity

in biodiesel is observed in an order of magnitude than that of its source oil (Gopinath et al., 2015). The viscosity of the produced biodiesel was 5.33 mm^2/s (Table 4-6), from 29.8 mm^2/s of sunflower waste cooking oil. In studies conducted by Knothe, (2005), and Gopinath et al., (2015), viscosity was reported to increase according to molecular structure, chain length of hydrocarbons and degree of saturation. Produced biodiesel from waste sunflower cooking oil, in this study was found to have a good viscosity which meet the ASTM standardisation, as compared to those found by Hossain and Boyce, (2009). For pure sunflower cooking oil and waste sunflower cooking oil the determined viscosity of their biodiesels were 5.8 mm^2/s and 9.5 mm^2/s respectively.

4.5.2 Density

The density of the fuel quality affects its performance, engine emissions, production, transportation and distributions (Jiang et al., 2019). The produced biodiesel had a density of 0.8811 g/cm^3 as shown in Table 4-6, The density will improve from the oil to the biodiesel, a reduction was reported by Samanta & Sahoo, (2020), since density increases with decreasing chain length and increasing number of double bonds (Ghoreishi & Moein, 2013). However, the density does not decrease much when oils are converted to biodiesel is usually not much as previously reported by Simbi et al., (2021), this is due to the similarity within feedstocks. In this study, methanol (0.792 g/cm^3) which was used in the process of converting waste sunflower oil (0.9225 g/cm^3) into biodiesel, have very close values to the actual alkyl methyl esters. The high density resulted in the high mass of injected fuel, causing increased heat and carbon, and consequently increasing power in diesel engines (Canesin et al., 2014). The density of biodiesel is usually between 0.86 g/cm^3 and 0.90 g/cm^3 which is higher than that of diesel fuel (Alptekin & Canakci, 2008; Yasin et al., 2013).

4.5.3 Oxidation

As shown in Table 4-6, The oxidation stability was measured by induction periods of methyl esters produced from waste sunflower using the Rancimat method as described in (Schober & Mittelbach, 2004). According to a report by Yaşar, (2020), feedstocks with more polyunsaturated fatty acids will oxidize more than those with saturated fatty acids. Therefore, resulting in low oxidation stability as reported by Moser (2009), waste sunflower oil possess high linoleic acid causing low stability as compared to other biodiesel i.e. palm biodiesel (Simbi et al., 2021). The studies conducted by Can, (2014) and Cursaru et al., (2014) found the oxidation stability of biodiesel produced from waste sunflower oil to be extremely low with 0.43 h and 1.81 h. However, this study recorded an improved oxidation stability of 4.2 h (Simbi et al., 2021).

4.5.4 Flashpoint

This is an important measure that determines the handling and transportation safety (Al-Abdullah et al., 2015), indicating the flammability of the fuel as it measures the lowest temperature at which heated vapor and the air above the fuel will ignite (Ishida & Iwama, 1986). This guides against contamination of highly volatile impurities (Saxena et al., 2013). In this study flashpoint for sunflower biodiesel was 170 °C as seen in Table 4-6 which according to Yasin et al., (2013) was found safe. The flashpoint of biodiesel is different to mineral petrodiesel by 85% according to Senthil and Silambarasan, (2015), adding that normally its above 150 °C. Similarly, in a study by Sirisomboonchai et al., (2015), in biodiesel produced from waste cooking oil (WCO), flashpoint of 179 °C was reported. Therefore, in this study sunflower biodiesel produced is regarded safe.

4.5.5 Water

The water content test was carried out using the European standards, since the test was done separately from sediments (Hassan & Kalam, 2013). The extremely hygroscopic nature of the biodiesel promotes biological growth within biodiesel storage and which subsequently leads to further corrosion of metals such as copper (Cu), iron (Fe), chromium (Cr) and zinc (Zn) (Fregolente et al., 2015). Additionally, the presence of water will cause low heating value in biodiesel (Aisyah et al., 2019), and together with the FFA within feedstock, formation of soap will occur during transesterification as a result of the reduction in catalytic effectiveness, subsequently reducing the yield (Thangaraj et al., 2019). According to Table 4-6, the produced sunflower biodiesel had a water content of 0.03 wt% which was below the maximum limits allowed by international standards. This was lower than those found in literature for biodiesel produced from sunflower and waste cooking oils (Cursaru et al., 2014; Hamze et al., 2015).

4.5.6 Acid Number

The produced sunflower biodiesel had an acid number of 0.2 mg KOH/g which was below the standard limit as seen in Table 4-6. A similar value was found for biodiesel produced from clean sunflower oil (Cursaru et al., 2014), This property indicates the presence of FA in the biodiesel, the increase in acid number is caused by organic acids and oxidation. High acid can lead to severe corrosion of fuel supply system in petrodiesel engines (Yang et al., 2016). From the study by Avila Orozco et al., (2014), it was reported that various biodiesels produced from different sunflower oils and others oils had acid values ranging from 0.3 to 0.6 mg KOH/g. Acid value is important for controlling degradation during storage and needs to be kept low (Yasin et al., 2013). Therefore, there was an improvement with the produced biodiesel. The acid value of this study was lower than those found in

literatures, where alkaline catalyst was used for conversion of both pure and waste sunflower oils to biodiesel (Hossain & Boyce, 2009; Saydut et al., 2010).

4.5.7 Metal Content

According to Table 4-6, Sunflower biodiesel had 27.559 mg/L of calcium and magnesium (Ca + Mg), 0.333 mg/L of sodium and potassium (Na + K), 8.913 mg/L of phosphorus (P) and 4 mg/L of sulfur (S). Additionally, contaminants of sulphates were extremely higher in SB100 while nitrates, soot and glycol were low. According to Lyra et al., (2010), The presence of these metals could have been incorporated into the biodiesel during the cleaning and washing process, and the feedstock used (Sánchez et al., 2015), or left in by the catalyst used (Simbi et al., 2021). Contamination by soot, nitrates, sulphates and glycol indicate chances for incomplete combustion, engine failure and operating condition issues, therefore are undesirable, Furthermore, the presence of elemental compounds in the biodiesel are usually due to degradation or contamination, by harmful compounds in the engine (Nogueira & Lucio, 2011). According to standard requirements for the total contaminants in biodiesel, the produced sunflower biodiesel failed with Ca + Mg metals, and sulphates as they were higher than the standards limit. These compounds are of a greater concern considering their impact on emission.

4.5.8 Distillation

Distillation is crucial in terms of safety and behavior of the fuel as it measures the percentage of vaporized fuel as temperature increases (de Coro et al., 2016). The presence of components in the fuel with high boiling points will affect the formation grade solid deposit during combustion (Encinar et al., 2005). Therefore, the maximum recommended temperature for biodiesel distillation at 90% distilled volume (T90) is 360 °C, and since the sunflower biodiesel was completely evaporated at T90 point, its final boiling point was 335.59°C at 80% distilled volume (T80). High boiling points at T90 indicates the presence of heavy compounds and therefore deposits build-up and engine problems (Lapuerta et al., 2015). However, the 10 vol% distillation residues for the optimised biodiesel was 24%. This was above the 0.3% standard limit set for biodiesel. High carbon residues indicate the presence of impurities and deposits in the biodiesel i.e. methanol, glycerol, catalyst residues, which will decrease the flashpoint and cetane number and subsequently lead to corrosion and blockage of nozzles (Graboski & Mccormick, 1998; Phan & Phan, 2008; Barabas & Todoru, 2011).

Table 4-6. Physico-chemical properties of optimised sunflower biodiesel

	Biodiesel			
Properties	**Sunflower biodiesel**	**ASTM D6751**	**EN 14214**	**Unit**
Kinematic Viscosity @40°C	5.33	**1.9 - 6**	**3.5 ~ 5**	mm^2/s
Density @15°C	0.8811	**0.80 – 0.90**	**0.875 ~ 0.90**	g/cm^3
TAN	0.2	**<0.5**	**<0.5**	mg KOH/g
Oxidation stability @110 °C	4.20	**3**	**>6**	hrs
Water content (ppm)	0.03	**Max 0.08**	**<0.05**	wt%
Flash point	170	**>130**	**>120**	°C
Distillation 90%	335.59 (@80%)	**<360**		°C
10%dist. Residue	24	**-**		% mass
Ca + Mg by ICP-OES	27.559	**Max 5**		mg/L
Na + K by ICP-OES	0.333	**Max 5**		mg/L
Phosphorus	8.239	**Max 10**	**Max 10**	mg/L
Sulfur	4	**-**	**Max 10**	mg/L
Nitrates	10			
Sulphates	111			
Glycol	0			
Sool	1			
Total contaminant	>40	**-**	**<20**	mg/L

4.6 Conclusions

Response surface methodology was conducted in an investigation for the optimisation of biodiesel produced from waste sunflower oil, with the use of methanol to oil ratio of 12:1 and a bi-functional catalyst. The method studied, the effect of time, temperature and catalyst loading for the transesterification of waste sunflower oil. As shown by the ANOVA results, catalyst loading was the most significant parameter affecting yield and linear model was used. In order to obtain the maximum yield of 98.23%, the optimised catalyst loading was 2.5 wt% with a reaction temperature of 60 °C and reaction time of 5 h. The predicted value of the yield using linear regression model was 92.773% which was comparable with the experimental yield of 95.667%, showing a good relationship and an agreement with data fit of the selected model. The model was statistically significant at 95% confidence, with catalyst affecting the yield the most, followed by time and then temperature. Additionally, the properties of the sunflower biodiesel produced were within the biodiesel standard specifications, except for the Ca + Mg content and sulphates.

4.7 References

Aisyah, L., Bethari, S.A., Wibowo, C.S., Hermawan, N., Alwi, D.U., Rulianto, D. & Anggarani, R. 2019. Water content in biodiesel for diesel fuel blends: Measurement using centrifuge and coulometric titration method. *IOP Conference Series: Materials Science and Engineering*, 494(1): 1–4. http://dx.doi.org/10.1088/1757-899X/494/1/012082

Al-Abdullah, M.H., Kalghatgi, G.T. & Babiker, H. 2015. Flash points and volatility characteristics of gasoline/diesel blends. *Fuel*, 153: 2–9. http://dx.doi.org/10.1016/j.fuel.2015.02.070

Alptekin, E. & Canakci, M. 2008. Determination of the density and the viscosities of biodiesel-diesel fuel blends. *Renewable Energy*, 33(12): 2623–2630. http://dx.doi.org/10.1016/j.renene.2008.02.020

Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H. & Mekhilef, S. 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, 16(4): 2070–2093. http://dx.doi.org/10.1016/j.rser.2012.01.003

Avila Orozco, F.D., Kovachev, N., Aguirre Pastor, M.Á., Domini, C.E., Fernández Band, B.S. & Hernández, A.C. 2014. Analysis of metals and phosphorus in biodiesel B100 from different feedstock using a Flow Blurring multinebulizer in inductively coupled plasma-optical emission spectrometry. *Analytica Chimica Acta*, 827: 15–21. http://dx.doi.org/10.1016/j.aca.2014.04.016

Azócar, L., Ciudad, G., Heipieper, H.J. & Navia, R. 2010. Biotechnological processes for biodiesel production using alternative oils. *Applied Microbiology and Biotechnology*, 88(3): 621–636. http://dx.doi.org/10.1007/s00253-010-2804-z

Bhangale, J.H. & Kulkarni, A.B. 2017. Effects of biodiesel from different feedstocks on engine performance and emissions: A review. *International research Journal of Engineering and Technology*, 4(7): 3273–3279. http:https://doi.org/10.1016/j.rser.2015.06.031

Borges, M.E., Díaz, L., Gavín, J. & Brito, A. 2011. Estimation of the content of fatty acid methyl esters (FAME) in biodiesel samples from dynamic viscosity measurements. *Fuel Processing Technology*, 92(3): 597–599. http://dx.doi.org/10.1016/j.fuproc.2010.11.016

Borugadda, V.B., Paul, A.K., Chaudhari, A.J., Kulkarni, V., Sahoo, N. & Goud, V. V. 2018. Influence of Waste Cooking Oil Methyl Ester Biodiesel Blends on the Performance and Emissions of a Diesel Engine. *Waste and Biomass Valorization*, 9(2): 283–292

Can, Ö. 2014. Combustion characteristics, performance and exhaust emissions of a diesel engine fueled with a waste cooking oil biodiesel mixture. *Energy Conversion and Management*, 87: 676–686. http://dx.doi.org/10.1016/j.enconman.2014.07.066

Canesin, E.A., de Oliveira, C.C., Matsushita, M., Felicidade Dias, L., Reghiany Pedrão, M. & de Souza, N.E. 2014. Characterization of residual oils for biodiesel production. *Electronic Journal of Biotechnology*, 17(1): 39–45. http://dx.doi.org/10.1016/j.ejbt.2013.12.007

Changmai, B., Vanlalveni, C., Ingle, A.P., Bhagat, R. & Rokhum, L. 2020. Widely used catalysts in biodiesel production: A review. *RSC Advances*, 10(68): 41625–41679. http://dx.doi.org/10.1039/d0ra07931f

de Coro, F.M., Sánchez, L.R. & Sánchez, B. 2016. Distillation: Basic Test in Quality Control of Automituve Fuels. In Mendes, M. (Ed.). *Distillation- Innovative Applications and Modelling*. London, UK: Intech: 78–96. http://dx.doi.org/10.5772/67140

Cursaru, D.L., Brănoiu, G., Ramadan, I. & Miculescu, F. 2014. Degradation of automotive materials upon exposure to sunflower biodiesel. *Industrial Crops and Products*, 54: 149–158. https://doi.org/10.1016/j.indcrop.2014.01.032

Dixon, D.J. 2016. Bifunctional catalysis. *Beilstein Journal of Organic Chemistry*, 12: 1079–1080. https://doi.org/10.3762/bjoc.12.102

Domingos, A.K., Saad, E.B., Vechiatto, W.W.D., Wilhelm, H.M. & Ramos, L.P. 2007. The influence of BHA, BHT and TBHQ on the oxidation stability of soybean oil ethyl esters (biodiesel). *Journal of the Brazilian Chemical Society*, 18(2): 416–423

Elkady, M.F., Zaatout, A. & Balbaa, O. 2015. Production of Biodiesel from Waste Vegetable Oil via KM Micromixer. *Journal of Chemistry*, 2015: 2–9. https://doi.org/10.1155/2015/630168

Encinar, J.M., González, J.F. & Rodríguez-Reinares, A. 2005. Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. *Industrial and Engineering Chemistry Research*, 44(15): 5491–5499. http://dx.doi.org/10.1021/ie040214f

Fadhil, A.B., Al-Tikrity, E.T.B. & Albadree, M.A. 2017. Biodiesel production from mixed non-edible oils, castor seed oil and waste fish oil. *Fuel*, 210: 721–728. http://dx.doi.org/10.1016/j.fuel.2017.09.009

Fregolente, P.B.L., Wolf Maciel, M.R. & Oliveira, L.S. 2015. Removal of water content from biodiesel and diesel fuel using hydrogel adsorbents. *Brazilian Journal of Chemical Engineering*, 32(4): 895–901. https://doi.org/10.1590/0104-6632.20150324s20140142

Ghoreishi, S.M. & Moein, P. 2013b. Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol. *Journal of Supercritical Fluids*, 76: 24–31. http://dx.doi.org/10.1016/j.supflu.2013.01.011

Giakoumis, E.G. 2018. Analysis of 22 vegetable oils' physico-chemical properties and fatty acid composition on a statistical basis, and correlation with the degree of unsaturation. *Renewable Energy*, 126: 403–419. https://doi.org/10.1016/j.renene.2018.03.057

Graboski, S.M. & Mccormick, R.L. 1998. Combustion of fat and vegetable oil derived fuels in diesel engines. *Progress in Energy and Combustion Science*, 24(97): 125–164. https://doi.org/10.1016/S0360-1285(97)00034-8

Hamze, H., Akia, M. & Yazdani, F. 2015. Optimization of biodiesel production from the waste cooking oil using response surface methodology. *Process Safety and Environmental Protection*, 94: 1–10. http://dx.doi.org/10.1016/j.psep.2014.12.005

Hassan, M.H. & Kalam, M.A. 2013. An overview of biofuel as a renewable energy source: Development and challenges. *Procedia Engineering*, 56: 39–53. http://dx.doi.org/10.1016/j.proeng.2013.03.087

Hojjat, M., Nayebzadeh, H., Khadangi-Mahrood, M. & Rahmani-Vahid, B. 2017. Optimization of process conditions for biodiesel production over $CaO\text{-}Al_2O_3/ZrO_2$ catalyst using response surface methodology. *Chemical Papers*, 71(3): 689–698. http://dx.doi.org/10.1007/s11696-016-0096-1

Hossain, A.B.M.S. & Boyce, A.N. 2009. Biodiesel production from waste sunflower cooking oil as an environmental recycling process and renewable energy. *Bulgarian Journal of Agricultural Science*, 15(4): 312–317. Available online: https://www.researchgate.net/publication/236236066 [accessed on 16 April 2021]

Ishida, H. & Iwama, A. 1986. Some Critical Discussions on Flash and Fire Points of Liquid Fuels. *Proceedings of the first International symposium,Tokyo, Japan. Fire Safety Science*, 1: 217–226. http://dx.doi.org/10.3801/iafss.fss.1-217

Jain, S. & Sharma, M.P. 2014. Effect of metal contents on oxidation stability of biodiesel/diesel blends. *Fuel*, 116: 14–18. http://dx.doi.org/10.1016/j.fuel.2013.07.104

Jain, S. & Sharma, M.P. 2011. Thermal stability of biodiesel and its blends : A review. *Renewable and Sustainable Energy Reviews*, 15(1): 438–448. http://dx.doi.org/10.1016/j.rser.2010.08.022

Jiang, S., Qi, J., Hu, Y., Ren, C., Jiang, Y. & Zhao, Z. 2019. Predicting the Density and Viscosity of Biodiesels and Biodiesel Blends by the Regular-Solution Theory. *Industrial and Engineering Chemistry Research*, 58(36): 17038–17048. http://dx.doi.org/10.1021/acs.iecr.9b03046

Kesić, Ž., Lukić, I., Zdujić, M., Mojović, L. & Skala, D. 2016. Calcium Oxide Based Catalysts For Biodiesel Production: A Review. *Chemical Industry and Chemical Engineering Quarterly*, 22(4): 391–408. https://doi.org/10.2298/CICEQ160203010K

Kesserwan, F., Ahmad, M.N., Khalil, M. & El-Rassy, H. 2020. Hybrid CaO/Al_2O_3 aerogel as heterogeneous catalyst for biodiesel production. *Chemical Engineering Journal*, 385: 2–13. https://doi.org/10.1016/j.cej.2019.123834

Knothe, G. 2010. Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, 36(3): 364–373. http://dx.doi.org/10.1016/j.pecs.2009.11.004

Knothe, G. 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. , 86: 1059–1070. http://dx.doi.org/10.1016/j.fuproc.2004.11.002

Kraber, S.L., Whitcomb, P.J., & Anderson, M.J. 2000. *Handbook for Experimenters: A concise collection of handy tips to help you set up and analyse your designed experiments*. Minneapolis, MN: Stat-Ease,Inc: 4–73. Available online: https://www.statease.com/pubs/handbk_for_exp_sv.pdf [accessed on 25 July 2020]

Kumar, A., Shukla, S.K. & Tierkey, J. V. 2015. A Review of Research and Policy on Using Different Biodiesel Oils as Fuel for C.I. Engine. *Energy Procedia*, 90: 292–304. http://dx.doi.org/10.1016/j.egypro.2016.11.197

Lapuerta, M., Rodríguez-Fernandez, J., García-Contreras, R. & Bogarra, M. 2015. Molecular interactions in blends of alcohols with diesel fuels: Effect on stability and distillation. *Fuel*, 139: 171–179. http://dx.doi.org/10.1016/j.fuel.2014.08.055

Lee, H. V., Juan, J.C. & Taufiq-Yap, Y.H. 2015. Preparation and application of binary acid-base CaO-La2O3 catalyst for biodiesel production. *Renewable Energy*, 74: 124–132. https://doi.org/10.1016/j.renene.2014.07.017

Leung, D.Y.C., Wu, X. & Leung, M.K.H. 2010. A review on biodiesel production using catalyzed transesterification. *Applied Energy*, 87(4): 1083–1095. http://dx.doi.org/10.1016/j.apenergy.2009.10.006

Li, J. 2010. Chemistry 535: Bifunctional Asymmetric Catalysts: Design and Applications. Ames: Iowa State University of Science and Technology.

Liao, C.C. & Chung, T.W. 2013. Optimization of process conditions using response surface methodology for the microwave-assisted transesterification of Jatropha oil with KOH impregnated CaO as catalyst. *Chemical Engineering Research and Design*, 91(12): 2457–2464. http://dx.doi.org/10.1016/j.cherd.2013.04.009

Lyra, F.H., Tereza, M., Dias, W., Brandão, G.P., Pessoa, H.M. & Castro, E.V. De. 2010. Determination of Na , K , Ca and Mg in biodiesel samples by fl ame atomic absorption spectrometry (F AAS) using microemulsion as sample preparation. *Microchemical Journal*, 96(1): 180–185. http://dx.doi.org/10.1016/j.microc.2010.03.005

Moser, B.R. & Bryan R. Moser. 2009. Biodiesel production, properties, and feedstocks. *In Vitro Cellular & Developmental Biology - Plant*, 45(3): 229–266. http://link.springer.com/10.1007/s11627-009-9204-z

Nabi, M.N., Rahman, M.M. & Akhter, M.S. 2009. Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. *Applied Thermal Engineering*, 29: 2265–2270. http://dx.doi.org/10.1016/j.applthermaleng.2008.11.009

Rao, M.S., Venkatesh, N. & Naidu, A.L. 2017. A Review on Performance of Diesel Engines by using Biodiesel blends from Different oils A Review on Performance of Diesel Engines by using Biodiesel blends from Different oils. *International Journal of Research & Development Technology*, 7(6)134–143. Avaiable online: https://www.researchgate.net/publication/318128352 [accessed on 13 January 2021]

Nogueira, T. & Lucio, C. 2011. Determination of Ca , K , Mg , Na , sulfate , phosphate , formate , acetate , propionate , and glycerol in biodiesel by capillary electrophoresis with capacitively coupled contactless conductivity detection. *Microchemical Journal*, 99(2): 267–272. http://dx.doi.org/10.1016/j.microc.2011.05.014

Phan, A.N. & Phan, T.M. 2008. Biodiesel production from waste cooking oils. *Fuel*, 87(17–18): 3490–3496. http://dx.doi.org/10.1016/j.fuel.2008.07.008

Ramadhas, A.S., Jayaraj, S. & Muraleedharan, C. 2005. Biodiesel production from high FFA rubber seed oil. , 84: 335–340. http://dx.doi.org/10.1016/j.fuel.2004.09.016

Rizwanul Fattah, I.M., Ong, H.C., Mahlia, T.M.I., Mofijur, M., Silitonga, A.S., Ashrafur Rahman, S.M. & Ahmad, A. 2020. State of the Art of Catalysts for Biodiesel Production. *Frontiers in Energy Research*, 8: 2-18. http://dx.doi.org/10.3389/fenrg.2020.00101

Samanta, S. & Sahoo, R.R. 2020. Waste Cooking (Palm) Oil as an Economical Source of Biodiesel Production for Alternative Green Fuel and Efficient Lubricant. *Bioenergy Research*: 163–174. http://dx.doi.org/10.1007/s12155-020-10162-3

Sánchez, N., Encinar, J.M., Nogales, S. & González, J.F. 2019. Biodiesel production from castor oil by two-step catalytic transesterification: Optimization of the process and economic assessment. *Catalysts*, 9(10). http://dx.doi.org/10.3390/catal9100864

Sánchez, R., Sánchez, C., Lienemann, C.-P. & Todolí, J.-L. 2015. Metal and metalloid determination in biodiesel and bioethanol. *J. Anal. At. Spectrom.*, 30(1): 64–101. http://dx.doi.org/10.1039/C4JA00202D

Santos, B.S., Capareda, S.C. & Capunitan, J.A. 2013. Sunflower Methyl Ester as an Engine Fuel: Performance Evaluation and Emissions Analysis. *ISRN Renewable Energy*, 2013: 1–12. http://dx.doi.org/10.1155/2013/352024

Saxena, P., Jawale, S. & Joshipura, M.H. 2013. A review on prediction of properties of biodiesel and blends of biodiesel. *Procedia Engineering*, 51: 395–402. http://dx.doi.org/10.1016/j.proeng.2013.01.055

Saydut, A., Kafadar, A.B., Tonbul, Y., Kaya, C., Aydin, F. & Hamamci, C. 2010. Comparison of the biodiesel quality produced from refined sunflower (Helianthus annuus L) oil and waste cooking oil. *Energy Exploration and Exploitation*, 28(6): 499–512. http://dx.doi.org/10.1260/0144-5987.28.6.499

Schober, S. & Mittelbach, M. 2004. The impact of antioxidants on biodiesel oxidation stability. *European Journal of Lipid Science and Technology*, 106(6): 382–389. http:https://doi.org/10.1002/ejlt.200400954

Senthil, R. & Silambarasan, R. 2015. Annona: A new biodiesel for diesel engine: A comparative experimental investigation. *Journal of the Energy Institute*, 88(4): 459–469. http:https://doi.org/10.1016/j.joei.2014.09.011

Shohaimi, N.A.M. & Marodzi, F.N.S. 2018. Transesterification Of Waste Cooking Oil In Biodiesel Production Utilizing CaO/Al_2O_3 Heterogeneous Catalyst. *Malaysian Journal of Analytical Sciences*, 22(1): 157–165. http://dx.doi.org/10.17576/mjas-2018-2201-20

Simbi, I., Aigbe, U.O., Oyekola, O. & Osibote, O.A. 2021. Catalyst and Elemental Analysis Involving Biodiesel from Various Feedstocks. *Catalysts 2021,* 11(8): 2–17. http:https://doi.org/10.3390/CATAL11080971

Sirisomboonchai, S., Abuduwayiti, M., Guan, G., Samart, C., Abliz, S., Hao, X., Kusakabe, K. & Abudula, A. 2015. Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. *Energy Conversion and Management*, 95: 242–247. http://dx.doi.org/10.1016/j.enconman.2015.02.044

Sulochana, G & Bhatti, S.K. 2018. Performance and Emission Characteristics of a Twin Cylinder Diesel Engine Blended Biodiesel With Nano Aditives Using Response Surface Methodolody. *International Journal of Mechanical and Production Engineering Research and Development,* 8(3): 635–646. Available online: https://www.researchgate.net/publication/342314578 [accessed on 13 January 2021]Thangaraj, B., Solomon, P.R., Muniyandi, B., Ranganathan, S. & Lin, L. 2019. Catalysis in biodiesel production - A review. *Clean Energy*, 3(1): 2–23. http://dx.doi.org/10.1093/ce/zky020

Worapun, I., Pianthong, K. & Thaiyasuit, P. 2012. Optimization of biodiesel production from crude palm oil using ultrasonic irradiation assistance and response surface methodology. *Journal of Chemical Technology and Biotechnology*, 87(2): 189–197. http://dx.doi.org/10.1002/jctb.2679

Yang, J., Caldwell, C., Corscadden, K., He, Q.S. & Li, J. 2016. An evaluation of biodiesel production from Camelina sativa grown in Nova Scotia. *Industrial Crops and Products*, 81: 162–168. http://dx.doi.org/10.1016/j.indcrop.2015.11.073

Yaşar, F. 2020. Comparision of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel*, 264. 2–7. http://dx.doi.org/10.1016/j.fuel.2019.116817.

Yasin, M.H.M., Mamat, R., Yusop, A.F., Rahim, R., Aziz, A. & Shah, L.A. 2013. Fuel physical characteristics of biodiesel blend fuels with alcohol as additives. *Procedia Engineering*, 53: 701–706. http://dx.doi.org/10.1016/j.proeng.2013.02.091

Zabeti, M., Daud, W.M.A.W. & Aroua, M.K. 2009. Optimization of the activity of CaO/Al2O3 catalyst for biodiesel production using response surface methodology. *Applied Catalysis A: General*, 366(1): 154–159. http://dx.doi.org/10.1016/j.apcata.2009.06.047

Chapter 5: **Chemical and Thermal Stability of Biodiesel and Petrol blends**

A transition to cleaner energy is about making an investment into the future. ~ Gloria Reuben

Abstract

The development of an appropriate fuel to run on a petrol compression ignition engine conceptualises a low-temperature combustion strategy which faces challenges. With the high intake temperatures, low lubricity and need for high compression ratio for this engine, the use of petrol-biodiesel blend as a fuel addresses such issues. This study aimed to evaluate characteristics of fuel quality and performance of blended fuels with biodiesel additives (5%, 15%, and 25%) to petrol (95%, 85%, and 75%) compared to neat petrol and biodiesel. The analysis of petrol blended with biodiesel produced from waste sunflower and palm oil was carried out, with respect to acid number, density, distillation, cetane number, metal contents, oxidation stability, viscosity, and water content. Results showed that the blended fuels possessed improved fuel quality compared with pure petrol and met international standards. Comparing the biodiesel-petrol blends with pure biodiesel, the values of these properties were lowered, while oxidation stability was enhanced. The two types of fuel blends portrayed different fuel qualities, with sunflower biodiesel-petrol blends having more energy content and lower acid number, while palm biodiesel-petrol blends had an exceptional thermal stability and characteristics of a better cold start. The high degree of unsaturation was reported in sunflower biodiesel, which led to increased carbon residues, reduced cetane number and subsequently difficulty in cold start. An increase in petrol percentage in the blends reduced concentrations of calcium and magnesium (Ca and Mg) significantly and hindered the absorption of moisture content. The produced biodiesel-petrol blends were comparable with petrodiesel.

Keywords: biodiesel-petrol blends; compression ignition engine; emissions; low temperature combustion, performance; thermal efficiency

5.1 Introduction

The Paris Climate Accord COP21 globally signed by many countries was aimed at reducing the 21st-century global rise in temperature below 2 °C, with a commitment that by 2030 the greenhouse gases (GHG) should be below 40% (European Union, 2019). The feasibility of such a goal would require huge changes in the traditional way of energy productions, since most of the world's energy comes from fossil fuels and possess the greatest of today's emissions (Kulkarni & Dalai, 2006).

Globally, it is estimated that there are 1.2 billion passenger cars and 380 million commercial vehicles, and these numbers are expected to grow mostly in non- Organization for Economic Co-operation and Development (OECD) nations such as India and China (Kalghatgi, 2018). Generally, the world's primary energy consumption mainly originate from fossil fuel (88%), while nuclear and renewable energy accounts for 7% and 5% respectively (Thangaraj et al., 2019). The transportation sector holding the highest share in energy consumption, release about 23% of CO_2 discharges and 14% of greenhouse gases (GHG). Transport is mainly power-driven by the internal combustion engines using petrodiesel and petrol (> 99.9 %). While the global demand for transport fuel continue to rise with an expected annual growth of 1%, there is a need for 4.9 billion litres of petrol and 1.3 billion litres of jet fuel daily. These changes in the transport sector are occurring owing to the growing need driven by population and prosperity growth, the need to guarantee energy security, controlling GHG released and enhancing the community air quality in reaction to consumers desire and demand (Kalghatgi, 2018; Kalghatgi, 2019).

Perhaps, the rise in fuels prices is understandable (Borugadda et al., 2018). Additionally, fossil fuels being finite as petroleum reserves have the potential of exhaustion, with a great damage to the earth's biodiversity (Nair, 2013; Harfoot et al., 2018), leading to serious global warming phenomenon (Saxena et al., 2013). Therefore, the need to look for other ways of generating energy is necessary even if energy demand in 2020 declined by 4% and the use of the transportation sector went down by 14% as a result of less mobility and restrictions set, in preventing the spread of covid-19 pandemic (International Energy Agency, 2021).

The growth in global energy demand is still expected to increase by 40% in 2030 and the transportation sector rising by 1.1% annually (Mahmudul et al., 2017). Kalghatgi, (2019), reported that due to air pollution caused by internal combustion engines, 14% of GHG is released by this sector. In combating this, greener fuels which are renewable energy are being developed, to solve the issue of the global climate change. With that, fascinating fuels such as biodiesel with the capacity of preserving the environment, bringing a feasible economy and creating social sustainability are being produced (Singh et al., 2011). Besides this, the developments of new engine combustion systems that can produce less emissions while maintaining high efficiency are underway (Zhong et al., 2019).

Traditionally, petrodiesel fuel has been used to power compression ignition (CI) engines which produces high thermal efficiencies but possess a drawback such as the use of high

combustion temperatures and limited fuel/air mixtures, which produce a huge amount of emissions (Han et al., 2010; Zhang et al., 2019). Nevertheless, using biodiesel or its blends in CI engines have proven to possess a good combustion performance similar to petrodiesel with a significantly reduced emissions of carbon monoxide (CO), and unburned hydrocarbon (HC), but has an increased amount of nitrogen oxide (NOx) emissions (Qi et al., 2010; Senthil & Silambarasan, 2015; Ashok et al., 2016). The presence of high oxygen content within biodiesel is advantageous (Dwivedi et al., 2013). Although, a decrease in efficiency has been reported (Bhangale & Kulkarni, 2017; Thanigaivelan & Loganathan, 2019). Additional studies by Singh et al., (2012); Yusoff, (2015); and Wu et al., (2020)., reported that biodiesel has a greater tendency to corrosion within the engine as compared to petrodiesel and consequently forming oxides (Kumar et al., 2018; Cavalheiro et al., 2020).

Furthermore, in the combustion chamber of the petrodiesel CI engine, fuel injection is greatly affected by the viscosity of the fuel, and biodiesel being significantly less viscous than petrodiesel and more than vegetable oil (Yasin et al., 2013), and according to the study by Nair, (2013), which reported that the use of 100% biodiesel (B100) would result in maintenance and performance issues. Therefore, blending with petrodiesel was suggested, since the blended fuel will produce enhanced properties, better viscosity, cold flow, combustion, lubricity, oxidation stability, cetane number and exhaust emissions as compared to neat biodiesel properties (Moser, 2009; Bukkarapu et al., 2018). Also, El-Kassaby & Nemit-Allah, (2013), reported that there is no need for car engine modification when 2-30% biodiesel-petrodiesel blends are being used. However, prior to blending there is a need for biodiesel to meet the requirement set by the American Society of Testing and Material (ASTM) and European Union (EN) fuel standardisation (Moser, 2014). In practice, before blending the biodiesel, there is a need of warming it at a temperature of -3.9 -1.1 °C above its cloud point (NREL. 2012).

A study conducted by Bukkarapu et al., (2018), evaluated the effect of blending palm biodiesel with different ratios of petrodiesel, and the fuel properties. They reported that increasing biodiesel content within the blends improved the fuel properties such as viscosity, density, flash point and fire point but deteriorated the fuel properties of petrodiesel, with the 90% petrodiesel 10% biodiesel (B10) ratio showing the best viscosity for atomization. While in the study conducted by Al-Dawody & Al-Farhany (2018), where they investigated the effect of blending methyl esters from waste cooking oil with petrodiesel in ratios of B10, 80% petrodiesel 20% biodiesel (B20) and B100 and the performance and emissions characteristics. They reported that B20 was the preferred

blending ratio and that a higher blend will cause a significant reduction in performance. This was also confirmed in the study conducted by Kumar & Singh, (2015), where the performance of biodiesel produced from waste cooking oil and its blends in petrodiesel engines was assessed. They concluded that the blend of B20 had similar properties to petrodiesel especially the thermal efficiency. While Iortyer et al., (2017), found contradicting results in their biodiesel produced from cashew nut seed oil and its blends. They found that B10-B40 have satisfactory performance similar to that of petrodiesel. Also, Hafizil et al., (2017), investigated the biodiesel and petrodiesel blend of B20 and reported that a significant decrease in viscosity and density close to petrodiesel was obtained, with improved fuel qualities where the acid number was within limits set by international standards. Also, the flashpoint and moisture content were noticed to increase from petrodiesel to blends which were good for handling purposes. Furthermore, Sharma et al., (2020), concluded that as the blending ratio of biodiesel increased, there is a decrease in engine efficiency, all carbon-based and smoke emissions but increase in NOx emissions.

Contrary to diesel, which has a high reactivity fuel, petrol is a low reactivity fuel which is used to power spark ignition engines that operate at low compression ratios and produce low engine efficiencies but extremely low emissions. Therefore, to produce high efficiency and low emissions, different combustion methods are proposed, to the reduced combustion temperatures and improved fuel-air mixing (Chaichan, 2014). Using petrol, which has high volatility and poor self-ignition, the air-fuel mixing is increased thereby creating a more volatile petrol-like fuel with a low cetane number (CN), which can be the solution for CI engines (Das et al., 2018). These engines rely on the concept of using low-temperature combustions strategies such as gasoline compression ignition (GCI), partially pre-mixed compression ignition (PPCI), homogenous charge compression ignition (HCCI) and reactivity controlled compression ignition (RCCI) (Zhong, et al., 2019). Amongst these combustion strategies, GCI has proven to show more advantageous compared to others (Putrasari & LIM, 2018). However, ignition at low-temperature conditions is a challenge for GCI (Cory A. Adams et al., 2013), and by adding biodiesel, ignition will be enhanced (Vu & Lim, 2019). Therefore, studies were conducted in order to improve the ignition characteristics of petrol, after their observations Adam et al. (2013), Putrasari & Lim (2017), Das et al. (2018), Thongchai & Lim (2018), reported that blending biodiesel with petrol improved thermal efficiency, reduced ignition delay and emissions significantly. They also added that 20% of biodiesel blended to 80% petrol (PB20) showed similarities with the pure petrodiesel. High oxygen content, cetane number and viscosity of biodiesel improves air-fuel mixture, spray, fuel injection system and auto ignition (Putrasari & Lim,

2017; Gad & Ismail, 2021), while low-cetane number of petrol helps in reducing intake temperature (Adams et al., 2013). The qualities of these fuels put together render the blended fuel superior auto-ignition characteristics and less combustion emissions (Lee et al., 2017; Kanti et al., 2018). Additionally, blending biodiesel with petrol will achieve enhanced fuel properties needed for GCI, in solving emission issues as compared to using pure petrodiesel (Adams et al., 2013; Thongchai & Lim, 2018; Zhong et al., 2019). Although, certain studies have been conducted on performances, emission and combustion characteristics of petrol-alcohol blends, petrol-diesel blends and petrol-biodiesel blends to be used in petrodiesel engines (Abedin et al., 2014; Khuong et al., 2017; Peng, 2017; Torregrosa et al., 2017; Liu et al., 2019; Gad & Ismail, 2021), there is dearth of literature on blending biodiesel with petrol and the assessment of the properties of these blended fuels (Putrasari & Lim, 2017; Das et al., 2018; Kanti et al., 2018; Thongchai & Lim, 2018). Also, no research has been recorded in evaluating numerous physical and chemical fuel properties of biodiesel-petrol blended fuel.

The current study presents blending biodiesels produced from waste sunflower and waste palm oils with commercial petrol and evaluating the properties of the blending fuels to assess how their chemical and physical properties will be affected in relation to the fuel quality, performance, and unwanted metals in the petrodiesel engine. Elemental analysis and other tests were performed according to ASTM D6751 and EN 14214, D974 for acid number, D979 and D4737 for cetane number, EN ISO 3675 for density, D86 for distillation, EN 14112 for oxidation stability, D445 for viscosity and D6304 for moisture content.

5.2 Materials and Methods

5.2.1 Materials

Mineral acids and oxidising agents (57.2% nitric acid and 98.08% sulfuric acids) were purchased from KIMIX Chemical Lab Supplies South Africa. 35% hydrogen peroxide was purchased from Labchem South Africa, while biodiesel and deionised water of 18.2 MΩcm (Milli-Q) were obtained from Chemical Engineering Oil and Gas Laboratory Cape Peninsula University of Technology (CPUT) Bellville, South Africa. Petrol was purchased from Sasol fuel garage South Africa.

5.2.2 Biodiesel and Petrol Blends Preparation

For this study, the palm, and sunflower biodiesels produced were mixed with commercial petrol in three different proportions of PB5, PB15, and PB25, which were made on a

volume basis of (5% biodiesel, 95% petrol), (15% biodiesel, 85% petrol), and (25% biodiesel, 75% petrol) respectively. The P stands for petrol, B stands for biodiesel, and the numeric value stands for the percentage of biodiesel content. Splash blending (Joshi & Pegg, 2007), was used for blending since it was an effective and accurate technique. This was conducted at constant temperatures of 22 to 24 °C with continuous stirring using 400 rpm for a minimum time of 30 minutes, using an overhead stirrer (Scientech inc, Boulder, US) to ensure homogeneity (Moser, 2014; Azahari et al., 2016; Putrasari & Lim, 2017a; Gad & Ismail, 2021).

5.2.3 Characterisation of Biodiesel and Petrol Blends

To check the quality of the biodiesel and its blends various tests were conducted at Oilwatch laboratories in South Africa, while oxidation stability and elemental analysis were done at Food Science & Technology and Analytical Chemistry laboratories at Cape Peninsula University of Technology, Bellville, South Africa.

5.2.3.1 Measurement of Acid Value

Acid number test used colour indicator non-aqueous titration as detailed in ASTM D974 (Knothe, 2006). The petrol and biodiesel blends with acid levels ranging from 0.1 to 0.55 mg KOH/g were examined by adding 10 mL isopropanol into 1 mg sample, then adding 2 to 3 drops of phenolphthalein and neutralising the solution with 0.1 M of KOH. Calculation of acid number was done as follows:

$$\text{Acid value (mg KOH/g)} = \frac{56.1 \text{ X } 0.1 \text{ M X V}}{\text{g}} \quad (5.1)$$

where 56.1 = constant molecular mass for KOH, 0.1 M = concentration of KOH, V = volume of final value - volume of initial value and g = weight of sample in grams.

5.2.3.2 Measurement of Density

The density of the fuel was measured by using the modern high-precision density meter DMA40 (Anton Paar GmbH, Graz, Austria) operating at 15 °C according to EN 14214 (Knothe, 2006). 2 mL of sample was injected into the measuring cell and each sample measurement was repeated three times to ensure accuracy and the average value was recorded. The density of a material is determined by the mass per volume measures compactness within a substance (Dwivedi & Sharma, 2016) as follows:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{kg}}{\text{m}^3} = \frac{\text{g}}{\text{cm}^3} \quad (5.2)$$

5.2.3.3 Measurement of Cetane Number

The calculated cetane index (CCI) was calculated by using of density reported in equation 5.2 with recovery temperature at 50% distillation (T50) according to ASTM D979-91 in equation 5.3 (Khadka, 2017), or with using distillation temperatures of 10%, 50% and 90% (T10, T50,T90) according to D4737-09 in equation 5.4 (Fidyayuningrum et al., 2020) as follows:

$$\text{Cetane Index} = 454.74 - 1641.416\,\rho + 774.74 \times \rho^2 - 0.554\,T_{50} + 97.803\,(\log T_{50})^2 \quad (5.3)$$

where ρ = Density in g/cm^3 at 15 °C, T_{50} = Mid boiling point temperature in °C (The temperature at which 50% of the sample by volume has evaporated).

$$CCI = 45.2 + 0.0892\,T_{10N} + [0.131 + 0.901\,B]\,T_{50N} + [0.0523 - 0.420\,B]\,T_{90N} + 0.00049\,[(T_{10N})2 - (T_{90N})^2 + 107\,B + 60\,B^2 \quad (5.4)$$

where CCI = Calculated Cetane Index, D = Density in g/cm^3 at 15 ^{0}C, DN = D – 0.85, B = e $^{(-3.5)\,(DN)) - 1}$, T_{10} = Distillation temperature at 10% distillates (^{0}C), T_{10N} = T10 – 215, T_{50} = Distillation temperature at 50% distillates (^{0}C), T_{50N} = T50 – 260, T_{90} = Distillation temperature at 90% distillates (^{0}C), and T_{90N} = T90 – 310.

$$CN = CCI - 2 \quad (5.5)$$

Where CN = Cetane Number and CCI = Calculated Cetane Index

5.2.3.1 Measurement of Elemental Content

5.2.3.4.1 Standards Preparation

All glassware used were soaked in 10% volume per volume (v/v) nitric acid overnight and were rinsed with deionised water before usage. Multielement standard solutions containing (Ca, Sn, As, Cr, Mn, Pb, P, Al, Ni, Cd, Se, Sb, Zn, Cu, Co, K, Ba, Mg, Fe, Na, Si) were prepared in concentrations 0.05, 0.01, 0.5, 0.1, 1, 5, 10, and 20 ppm, in 8 volumetric flasks of 100 mL using dilution method by decreasing concentration from 1000 mg/L stock solution using deionised water.

5.2.3.4.2 Sample Digestion

Biodiesel has a high viscosity and therefore requires dilution before ICP analysis is carried out. An open system with conventional heating was used for digesting of the samples by first weighing 1 g of 100% biodiesel (B100) or petrol-biodiesel blend (PBXX) sample into a

borosilicate tube. 5 mL of HNO_3, 2 mL of H_2SO_4 and 1 mL of H_2O_2 were added and heated on a hot plate which was set at 90 ^{0}C for 2 hours. Thereafter, 3 mL of HNO_3 and 1 mL of H_2O_2 were measured and transferred into the beaker holding the sample, and the hot plate temperature was subsequently adjusted to 220 ^{0}C and left for 40 min. Then 2 mL HNO_3 and 4mL H_2O_2 were added to the beaker, when the sample color did not turn colorless by this step, the procedures were repeated (from the first step) until the solution turned colorless. Finally, the sample was diluted to a volume of 10 mL with denoised water. The accuracy was checked by spiking the blank sample with the same digestion procedure (Korn et al., 2010).

5.2.3.4.3 ICP-OES Sample Procedure

An Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES) ARCOS HFS12 (Ametek Inc., Pennsylvania, United states) was used to measure elemental content and argon (Afrox Ltd., Gauteng, South Africa) used as carry gas. Wavelengths were selected to measure emission intensities of analytes were 324.745 nm for Cu, 396.847 nm for Ca, 167.078 nm for Al, 259.941 nm for Fe, 766.491 nm for K, 279.553 nm for Mg, 589.592 nm for Na, 213.856 nm for Zn, and 177.495 nm for P.

The smart analyser vision was initialised after switching on the auto sampler on the computer connected to the ICP and the extractor fan on ICP switched on. Argon gas in the non-flammable gas room was allowed to flow and while the system was flushed twice. The plasma was left to stabilise for 20 to 30 min while the needle in the auto sampler was in its original position. Thereafter, calibration was conducted three times before standards containing organometallic standard solutions of 0.05, 0.01, 0.5, 0.1, 1, 5, 10, and 20 ppm could be run through the ICP. After generating calibration curves for the analytes, organic samples were continuously introduced into the ICP through the nozzle and allowed to be analysed on the computer. 5% nitric acid was used in flushing the nozzle in between each sample.

5.2.3.4.4 Measurement of Water Content

The water content was measured using the Karl Fischer Titration method according to the most reliable D6304 technique (Quveon, 2014; Anon, 2020). An appropriate amount of sample was weighed, poured into a vial, sealed, and heated under vacuum in an oven to evaporate water. The vaporised water was carried into a conditioned titration cell (hydranal Coulomat-AG) which was titrated with Karl Fischer reagent, until the endpoint was reached.

5.3 Results and Discussions

5.3.1 Effect of Acid Number

As observed in Figure 5-1, Petrol (P100) had an acid number value of 0.1 mg KOH/g and an increase in blending percentage of biodiesel increased total acid number (TAN) from 0.23 mg KOH/g and 0.28 mg KOH/g in 5% biodiesel-petrol blend (PB5) of sunflower biodiesel and palm biodiesel to 0.46 and 0.55 mg KOH/g in 100% sunflower biodiesel and palm biodiesel (S-B100 and P-B100), respectively. Also, the figure illustrates a higher acid value for palm biodiesel as compared to sunflower biodiesel, with a decrease in the TAN as percentage of petrol added in blends increase which was comparable to a conclusion drawn by Jain & Sharma, (2011), when petrodiesel and biodiesel were blended. According to Phan & Phan, (2008) and Gopinath et al., (2015), these acid values were indicative of fatty acid or acid moieties content in the fuel, which were found to fall within set limits of ASTM D974 and EN 14104 standards with a maximum limit of 0.8 mg KOH/g and 0.5 mg KOH/g respectively (Barabas & Todoru, 2011; Tyson & McCormick, 2009). Except for a slight deviation of 0.05 mg KOH/g in palm biodiesel which was above EN specification. Similarly, close values were reported by Hossain & Boyce, (2009), after producing biodiesel from waste sunflower oil and the TAN obtained was 0.44 mg KOH/g while 0.43 mg KOH/g was found for waste cooking oils by Phan & Phan, (2008). Also, in a study conducted by Saydut et al., (2010), when comparing biodiesel fuel quality produced from different oil sources, acid values reported were 0.50, and 0.52 mg KOH/g for refined sunflower oil and 0.56 and 0.57 mg KOH/g for waste cooking oil. Comparing those studies with current study, an improvement in the acid value was obtained.

On other hand, according to ASTM D467-08 a maximum limit of 0.3 mg KOH/g was set for biodiesel blends of 6% biodiesel 94% petrodiesel to 20% biodiesel 80% petrodiesel (B6-B20) (Hoekman et al., 2012). Therefore, all the sunflower biodiesel-petrol blends (S-PBXX) had values that met the specification set for a blended fuel, while in palm biodiesel-petrol blends (P-PBXX), only P-PB5 met the specification. The high acid value is problematic with regards to the fuel supply to the engine (Hassan & Kalam, 2013), which would result in the increased viscosity, cloud point (Kubičková et al., 2005), and subsequently leading to the corroding of rubber parts within the engine causing deposits and these impurities are created by heavy molecular weight as reported by Kumar, (2016), and Kumar et al., (2018). Also, a study by Matějovský et al., (2018), further concluded that an increase in corrosion rate was greatly affected by increased TAN of the fuels. Additionally, the value of acid number indicates the degree of degradation upon storage in time (Anguebes-Franseschi et al., 2019). Therefore, it is clear that in sunflower biodiesel-petrol blends, the

acid value is lower than the palm biodiesel-petrol blends. All sunflower biodiesel-petrol blends (S-PB5, S-PB15, S-PB25) could be considered for the use in compression ignition engine without modification, since the acid number values for S-PB5, S-PB15, S-PB25 were 0.23 mg KOH/g, 0.26 mg KOH/g and 0.30 mg KOH/g respectively. However, in palm biodiesel-petrol blends (P-PB5, P-PB15, P-PB25) only P-PB5 can qualify for use.

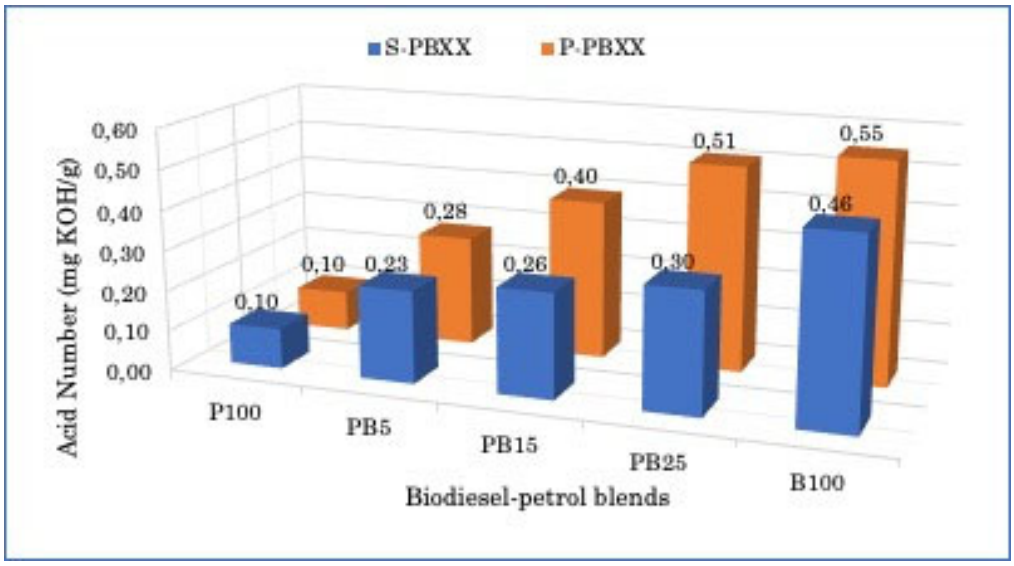


Figure 5-1. Acid values in palm and sunflower biodiesel-petrol blends

5.3.2 Effect of Density

Figure 5-2 illustrates the density of palm and sunflower biodiesel-petrol blends ranging between 762-763 kg/m^3 to 887.1-882 kg/m^3 for 5% biodiesel-petrol blend (PB5) to 100% biodiesel of sunflower and palm (S-B100, P-B100) respectively. It was observed from these results, that the obtained densities did not surpass the ASTM and EN specifications standard limits set that range between 860-900 kg/m^3 in biodiesel, petrodiesel of range between 815-840 kg/m^3 and petrol of range between 715-780 kg/m^3 (Pandey, 2008; Worldwide Fuel Charters, 2019). The density of biodiesel produced from waste oils were high especially from waste sunflower biodiesel according to studies by Borugadda et al., (2018); Ilkilic & Öner, (2017) and Phan & Phan, (2008). Even biodiesel produced from neat sunflower oil possessed higher density than the waste palm oil as reported by Alptekin & Canakci, (2008), obtaining 884.5 kg/m^3 and 874.6 kg/m^3 respectively. In the study of Hoekman et al., (2012), it was reported that the increase in density was caused by the high degree of unsaturated alkyl esters which is indicated by the presence of double bonds. Also, Folayan et al., (2019), reported a decrease in density due to the presence of a longer chain length. This is in agreement with the previous results obtained by Simbi et al., (2021), where there was less linoleic (polyunsaturated) acids but more palmic and oleic

acids in the palm waste oil, while in sunflower waste oils more linoleic acids was observed. Also, since high density increases nitrogen oxide (NOx) emissions (Nallusamy, 2010; Yogeeswara et al., 2020), causing poor vaporization which leads to incomplete combustion (Silitonga et al., 2013). Blending biodiesel with petrol will produce a fuel that has a reduced density as shown in Figure 5-2 since petrol had a low density of 739.2 kg/m^3. Considering the low density of petrol, it varies around also 712.7 kg/m^3 , 737 kg/m^3 and 762 kg/m^3 and this is supported by literature by Agarwal, (2007); Putrasari & Lim, (2017); Thongchai & Lim, (2019); Zhong, (2019).

When petrol was blended with biodiesel, enhancement in density of blended fuel in comparison with original density of pure petrol was achieved, and density was directly proportional to the biodiesel content. This affects the amount of fuel injected, with more biodiesel per volume pumped into the engine (Giakoumis, 2018), which influences the air-fuel ratio and energy content in combustion chambers (Saxena et al., 2013), and consequently relates to the of performance characteristics (Jiang et al., 2019). Moreover, Das et al., (2018), and Thongchai & Lim, (2019), reported that density relates to spray mass flow rate, and since biodiesel-petrol blends have low density than petrodiesel, but higher than pure petrol the characteristics of spray combustion will differ. Consequently, more energy is given by S-B100 and S-PB25 as compared to P-B100 and P-PB25, while in lower biodiesel-petrol blends of PB5 and PB15 palm biodiesel-petrol blends had more energy than sunflower biodiesel-petrol blends.

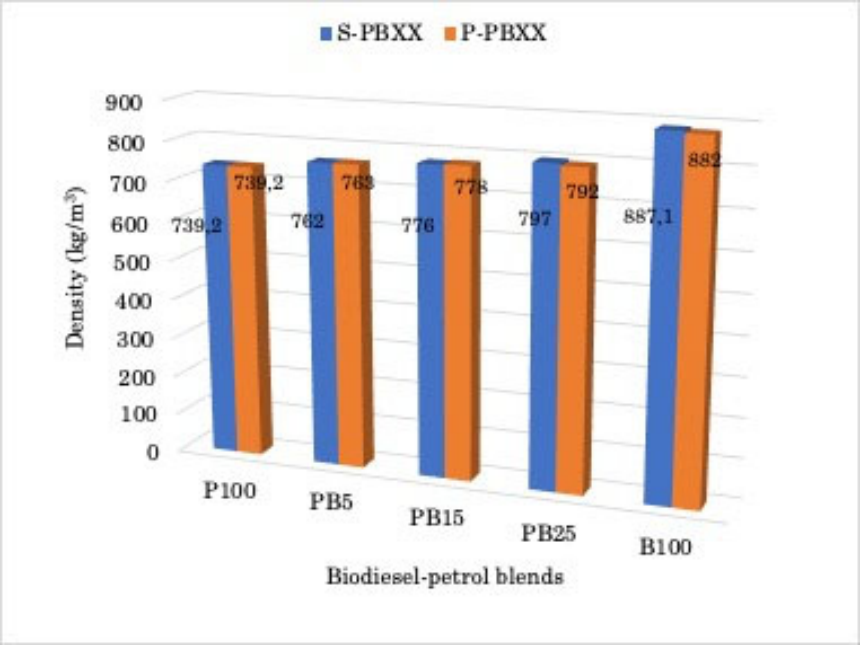


Figure 5-2. Density in palm and sunflower biodiesel-petrol blends.

5.3.3 Effect of Distillation

Distillation or volatility of the fuel can be determined by the use of the D86 method with an advanced distillation curve, which measures the percentage of the fuel vaporized as temperature increases (Anitescu & Bruno, 2012). This property relates to combustion processes and engine emissions, and therefore will influence the performance, safety and long-term usage of the fuel (Qi et al., 2010; Qi & Lee, 2014). Furthermore, Knothe, (2006), recognised a great correlation of volatility with other properties such as viscosity, heating value and average molecular weight. Therefore, by interpreting various points obtained on the curve will provide information on the behaviour of individual fuel and conclusions drawn from it (Qi & Lee, 2014; de Coro et al., 2016).

As shown in Figure 5-3 and Figure 5-4 are distillation curves for sunflower (S) and palm (P) biodiesel-petrol blends (PBXX) where XX indicates the percentage of biodiesel content. Typically, the initial boiling point (IBP) of biodiesel from distillation is higher than petrodiesel (Valente et al., 2011; Aleme & Barbeira, 2012), and certainly much higher than petrol (Rodriguez & Cheng, 2016). IBP for pure biodiesel (B100) of sunflower and palm obtained were 299 ^{0}C and 238 ^{0}C respectively, indicative of the purity of biodiesel while the blended fuels had extremely low IBP as compared to pure biodiesel.

Similarly, studies by Benjumea et al., (2008) and Phan & Phan, (2008), reported temperatures of 300 ^{0}C and 213 ^{0}C as IBP of biodiesel produced from palm and waste cooking oils respectively. The difference found in their boiling points was attributed to their fatty methyl esters (Knothe, 2005 Lin & Lin, 2012). Also, Graboski & Mccormick, (1998), suggested that a low IBP in biodiesel could have been resulted from methanol and glycerol left in biodiesel after the transesterification process. Normally, according to ASTM D6751, the temperature of B100 at 90 percent distilled volume per volume (90% v/v) should not exceed 360 ^{0}C (Lapuerta et al., 2015). This limitation is necessary for the prevention of deposits in combustion chambers and sparks plugs (Silva et al., 2021), therefore biodiesel produced met the standard specified since at 90% v/v of palm biodiesel (P-B100) approximately 338 ^{0}C was obtained. This is fairly close to the 340 ^{0}C, the maximum limit set for petrodiesel (Worldwide Fuel Charters, 2019). Initial points on the curve are crucial, lower temperatures of IBP and 10% v/v would allow for the easy start of an engine while a lower temperature at 50% v/v would allow for faster warm-up (Kheiralla et al., 2011). Temperatures obtained at 10% and 50% v/v for S-B100 were 327.4 ^{0}C and 335.5 ^{0}C while P-B100 had 319.3 ^{0}C and 327.4 ^{0}C respectively. Also, high density of sunflower biodiesel due to a higher degree of unsaturation as seen in Figure 5-2 played a

role in increased temperatures of distillation. Benjumea et al., (2011), supports this as they noticed that high temperatures at 50% and 90% v/v correlate to a high density found in fuel. A further observation was noticed when high temperature is obtained at 90% v/v, emissions of total hydrocarbon (THC) will increase (Benjumea et al., 2011).

Overall, distillation temperatures across boiling points had a narrow range with a boiling point difference of 7.1 ^{0}C - 11.1 ^{0}C as observed in S-B100 and P-B100 from 20% v/v to 70% v/v. Occurrence of such a narrow range was majorly influenced by closeness in the boiling points of alkyl esters (Phan & Phan, 2008; Qi et al., 2010; Qi & Lee, 2014). However, a gradual decrease was obtained for S-B100 at 80% v/v, which thereafter was depleted. While in P-B100 a constant increase was observed from the IBP and a subsequently depletion at 80 % v/v. The depletion could be caused by the presence of high unsaturated esters i.e. methyl linoleate (Aleme & Barbeira, 2012; Anitescu & Bruno, 2012), which was expected in sunflower biodiesel for this current study. Considering IBP, 10% and 50% points, P-B100 showed a better ignition characteristic in terms of cold start and warm-up since obtained results were lower than S-B100.

On the other hand, distillation temperatures of petrol was 50% lower than petrodiesel (Kook & Pickett, 2012; Kanti et al., 2018). In sunflower blended biodiesel (S-PBXX), the IBP obtained for 5% biodiesel 95% petrol (PB5), 15% biodiesel 85% petrol (PB15) and 25% biodiesel 75% petrol (PB25) were 39.4 ^{0}C, 38.4 ^{0}C and 29 ^{0}C while 37.2 ^{0}C, 41.2 ^{0}C and 42.3 ^{0}C were obtained for palm blended biodiesel (P-PBXX). The low IBP reported in blended fuel was due to the use of high volatile fuel petrol (P100), which normally has an IBP value ranging between 25 ^{0}C and 30 ^{0}C and final boiling point (FBP) of approximately 210 ^{0}C (Ott et al., 2012; de Coro et al., 2016; Rodriguez & Cheng, 2016; Peng, 2017). Therefore, temperatures at IBP in blended fuels will have lower values that are closer to the petrol (Aleme & Barbeira, 2012; de Coro et al., 2016). In blends of S-PB5, S-PB15 and S-PB25 at 10% v/v, temperatures of 57.7 ^{0}C, 66.9 ^{0}C, 52.3 ^{0}C were obtained while in P-PB5, P-PB15 and P-PB25 corresponding temperatures of 52.5 ^{0}C, 55.1 ^{0}C, and 59.2 ^{0}C were found. Meanwhile, temperatures obtained at 50 % v/v for S-PB5, S-PB15 and S-PB25, were 119.2 ^{0}C, 126 ^{0}C, 99.4 ^{0}C and for P- PB5, P-PB15 and P-PB25, temperature obtained were 101.5 ^{0}C, 106.4 ^{0}C and 117.6 ^{0}C respectively.

In a study by Gomes et al., (2013), for petrol fuel to have a good cold-start at 20% v/v the fuel must have vaporised below 70 ^{0}C. Therefore, in the distillation curves below, at 20% v/v P-PB5, P-PB15 and P-PB25 had 62.7 ^{0}C, 64.9 ^{0}C and 71.5 ^{0}C. While S-PB5, S-PB15 and S-PB25 had values of 70.4 ^{0}C, 82.2 ^{0}C and 65.9 ^{0}C respectively. This shows that palm

blended fuels have the potential of a better cold start. Overall, broader boiling point ranges were observed for blended fuels with a sharp increase in temperatures from 70% v/v onwards approaching that of biodiesel. This occurred as a result of the presence of ester quantity in the biodiesel according to Aleme & Barbeira, (2012). Evidently, an increase in biodiesel percentage within the blends increased the distillation temperatures from 10% v/v to FBP, with more effect observed from middle and final distillation points as clearly shown by Figure 5-3 and Figure 5-4. This was also reported by Paulauskiene et al., (2019).

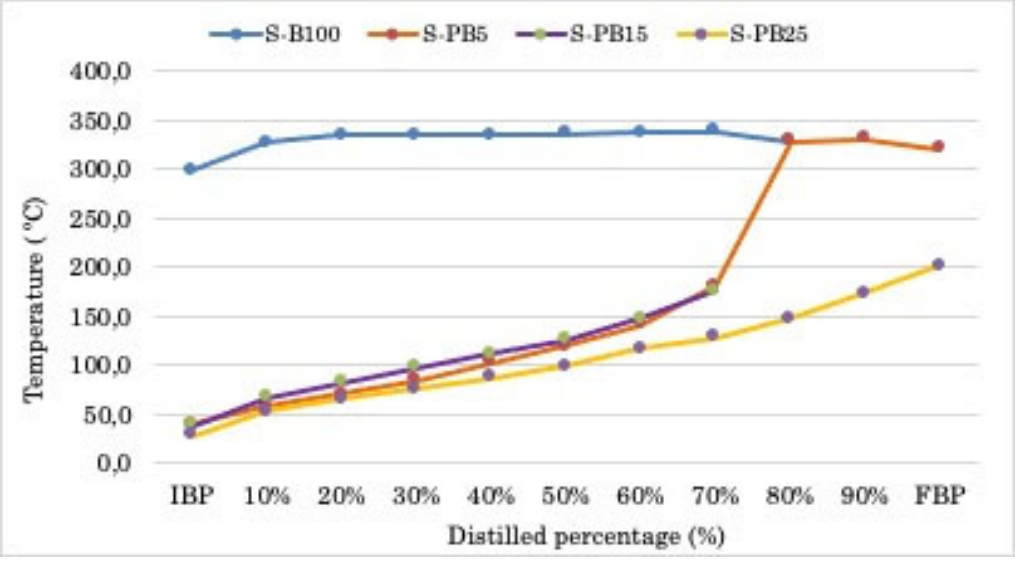


Figure 5-3. Distillation curves for sunflower biodiesel and petrol blends

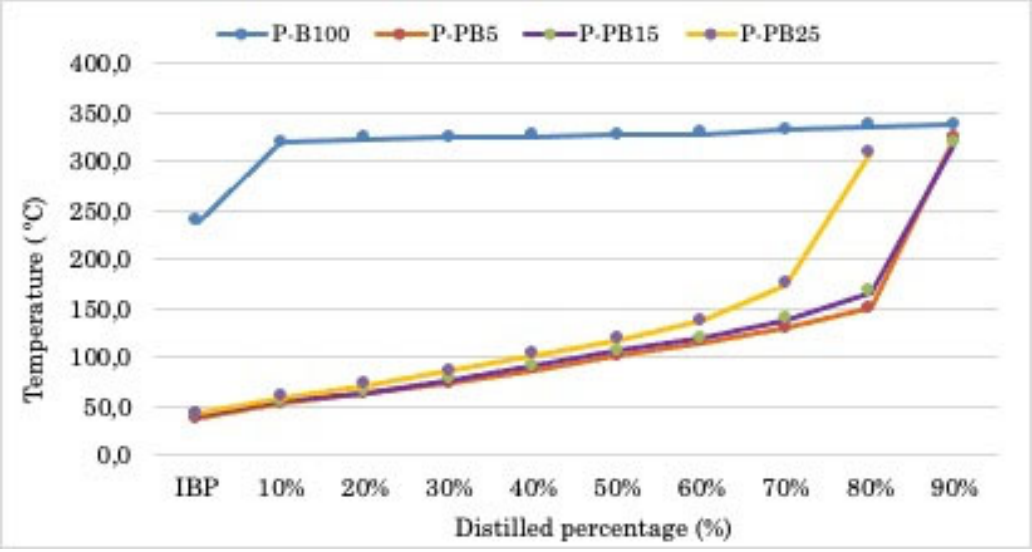


Figure 5-4. Distillation curves for palm biodiesel and petrol blends.

Table 5-1 shows the carbon residues and recovery rate percentages for S-B100, P-B100) and the blended fuels (PBXX). Carbon residues obtained for S-B100 and P-B100 were 25% and 4% respectively, while in S-PB5, S-PB15 and S-PB25 had carbon residues values of 0.5, 20, and 9.2%, and P-PB5, P-PB15 and P-PB25 had carbon residue values of 0.5, <0.5 and 0.5%. Standardisation by ASTM D6751 and EN 14213 specify the level of carbon residue in biodiesel at 10% should not exceed 0.05% and 0.30% respectively, while in blends of B5-B20, ASTM D6751 and EN 14213 standardisation allow 0.35 maximum for ASTM D524 (McCormick & Westbrook, 2010; Barabas & Todoru, 2011). Therefore, results show that if palm biodiesel-petrol blended fuels are to be used in the engine and thermal conditions are applied, there will be a less tendency for the formation of carbonaceous deposits as compared to the sunflower biodiesel-petrol blended fuels. This will result in carbon residue which will increase with an increase in biodiesel content (Patel et al., 2017; Phan & Phan, 2008), as a result of degradation of glycerides/polymerisation of unsaturated fatty acids at high temperatures which will cause in engine problems (Fernando et al., 2007; Candeia et al., 2009). For this study, the produced S-B100 had more unsaturated fatty acids in the parental oil than P-B100 (Simbi et al., 2021), However, blending S-B100 and P-B100 with petrol reduced the carbon residue significantly, with better recovery rate shown in palm biodiesel and its biodiesel-petrol blends.

Table 5-1. Residue of distillation

PBXX	Carbon Residue % (m/m) (In 10% distillation residue)	Recovery rate (%)
S-B100	25	70
S-PB5	0.5	95
S-PB15	20	70
S-PB25	9.2	90.4
P-B100	4	92
P-PB5	0.5	96
P-PB15	< 0.5	96
P-PB25	0.5	80

5.3.4 Effect of Cetane Number

Cetane number (CN) is a fuel property that indicates ignition characteristics (Benjumea et al., 2008), and fuel's aromaticity (Graboski & Mccormick, 1998). A very low CN will reduce thermal performance (Sanjid et al., 2013), as a result of longer ignition delay which causes knocking and subsequently incomplete combustion and increased particular exhaust emission (PM) (Bhangale & kulkarni, 2017).

Conversely, a higher cetane number makes combustion easier (Paulauskiene et al., 2019), thereby reducing the release of hydrocarbons, carbon monoxide (CO), nitrogen oxides (NOx), and sulfur oxides (SOx), which play a role in pollution reduction (Moradi et al., 2013; Fidyayuningrum et al., 2020). Measuring CN can be expensive to conduct since Cooperative Fuel Research (CFR) engine, ignition Quality Tester (IQT) or Fuel Ignition Tester (FIT) would be required (Santos et al., 2013; Khadka, 2017).

Therefore, a simple and reliable method using distillation temperatures and density was utilised (Fidyayuningrum et al., 2020). Such methods use equations 5.3 or 5.4 to obtain the Calculated Cetane Index (CCI) as shown in Table 5-2. S-B100 and P-B100 had CCI of 46.35 and 46.98 according to ASTM D976 method in equation 5.3 which considers the middle distillation temperatures at 50% v/v and density. Therefore, the predicted CN were 44.35 and 44.98 for S-B100 and P-B100 respectively.

When the ASTM D4737 method presented in equation 5.4, the distillation temperatures at 10% v/v and 90% v/v were used, the obtained CCI and CN for P-B100 were 53.87 and 51.87. As seen in Figure 5-3, there was a depletion of S-B100 at 90% v/v, therefore CCI and CN for S-B100 could not be calculated. The D4737 method showed more reliable values with regard to S-B100 and P-B100, since more temperature points of distillation curves were considered which were relatable to the values reported (Bamgboye & Hansen, 2008; Benjumea et al., 2008; Saydut et al., 2010; Kumar et al., 2018). However, Hoekman et al., (2012), argued that no valid computerized method for reliable correlation between cetane index to CN was found. Nevertheless, engine fuels such as biodiesel need to auto-ignite alone otherwise it will have poor running and difficulty during starting (Anitescu & Bruno, 2012). For that reason biodiesel normally has a good cetane number which is above 40 (Bamgboye & Hansen, 2008; Abbaszaadeh et al., 2012; Hoekman et al., 2012), and according to American and European standards, the minimum CN should be 47 and 51 respectively (Knothe, 2006; Saydut et al., 2010; Gopinath et al., 2015; Yogeeswara et al., 2020).

In the current study, produced biodiesel (P-B100) met the requirements set for CN according to ASTM D4737 method rather than D976 method. Some errors were encountered when calculating the CN for the blended fuels using D976 method, while in pure biodiesel this method gave the same CN values with petrodiesel fuel (40-55) (Tyson & McCormick, 2009). For this reason, D4737 technique was a preferred method of predicting CN through CCI, and was also found to be a reliable analysis technique by

Benjumea et al., (2008). In pure esters, it is expected that a high degree of unsaturated esters such as linoleic acid will reduce the CN while longer chains will increase the CN (Giakoumis, 2018). Therefore, palm biodiesel or methyl palmitate was expected to have a higher cetane number due to more carbon chain in fuel (Knothe, 2005; Rao & Chary, 2018), while sunflower biodiesel with more methyl linoleate will have a lower CN (Anitescu & Bruno, 2012; Folayan et al., 2019; Yaşar, 2020). This was confirmed in Table 5-2 where CN obtained from either D976 or D4737 methods were higher in palm biodiesel than sunflower biodiesel. Furthermore, biodiesel is composed of longer chained hydrocarbons (C14-C24) allowing the CN of biodiesel to be higher than petroleum fuels, which has shorter hydrocarbons i.e. petrol (C4-C12) (Saxena et al., 2013; Peng, 2017).

Considering a study conducted by Zhong, et al., (2019), which reported the CN for petrol to be 14 while hydrogenated catalytic biodiesel CN of had 103.3. Adding petrol to biodiesel, with such high volatile fuel will reduce the CN in biodiesel blends. Normally, blends of biodiesel and petrodiesel up to B20 need to meet the minimum cetane index or CN of 40 according to ASTM 7467 (Moser, 2009; Alleman et al., 2016). However, since petrol was blended with biodiesel as a new alternative fuel for petrol compression ignition engines, all blended fuels had values below the standard set for biodiesel and petrodiesel blends. Even if, these values obtained were low, they were still higher than that of pure petrol for instance, in P-PB5 and P-PB15 CN, the CN were 14.39 and 16.67 respectively. Also, the CN increased as the percentage of biodiesel added to the blends increased. Although, CN calculations can be carried out using methods mentioned above, Valente et al., (2011), suggested that since ASTM D4737 was established for petrodiesel, the method of calculating cetane index in biodiesel blended fuels should be further investigated. Moreover, a recommendation was given Chaichan, (2014), to use CN ignition improver in order to enhance the CN in the petrodiesel-biodiesel blends, since petrodiesel have CN of 17. Overall, P-B100 will ignite quicker and easier than S-B100, and the lower CN in S-B100 will cause higher carbon residue due to incomplete combustion is which evident in Table 5-1.

Table 5-2. Calculated cetane index and predicted cetane number for biodiesel blends

	ASTM D976-91		**ASTM D4737-09**	
BXX	**CCI**	**CN-Predicted**	**CCI**	**CN-Predicted**
S-B100	46.35	44.35	-	-
S-PB5	9.41	7.41	23.22	21.22
S-PB15	9.19	7.19	-	-
S-PB25	-26.22	-28.22	12.87	10.87

P-B100	46.98	44.98	53.87	51.87
P-PB5	-9.12	-11.12	16.39	14.39
P-PB15	-10.47	-12.47	18.67	16.67
P-PB25	-5.20	-7.20	-	-

5.3.5 Presence of Elemental Content

As shown in Table 5-3 is analytical figures of important evaluation indicating a good correlation coefficient value (R2) for all elements for the set of standard solutions in the range of 0-24 mg/L was used. The R^2 for all analytes were above 0.99 while Zn had 0.97. The high coefficient of determination (R^2) represented good linearity (Chaves et al., 2010). This confirms that analytical calibration curves correlate the measured emission signal with the concentration of analytes standards (Avila Orozco et al., 2014). Also, a good R^2 show satisfactory standard calibration curves for analyzing the digested samples (Iqbal et al., 2010).

Table 5-3. Analytical figures of merit for determination of elements by ICP-OES

Analytes	Line range (mg/L)	Std.Error (mg/L)	Correlation Coefficient
Al	0-24	0.169	0.99961
Ca		0.375	0.99809
Cu		0.0797	0.99991
Fe		0.374	0.99821
K		0.184	0.99954
Mg		0.139	0.99974
Na		0.184	0.99954
Zn	0.00288 - 24	1.43	0.97194

5.3.5.1 Presence of Group I metal

The concentrations of sodium (Na) in S-B100, P-B100 and P100 were 0.372 mg/kg, 0.430 mg/kg, and 0.392 mg/kg respectively, while potassium (K) was absent in all samples as shown in Table 5-4. An increase in the concentration of Na in biodiesel-petrol blends (PBXX) was noticed with 0.800 mg/kg, 1.057 mg/kg, and 0.804 mg/kg in S-PB5, S-PB15, S-PB25. The concentration of Na in palm biodiesel-petrol blends (PBXX) in P-PB5, P-PB15, P-PB25 was also determined to be and 0.917 mg/kg, 0.784 mg/kg, and 1.224 mg/kg respectively. According to standards set by ASTM D6751 and EN 14214 a maximum set limit for Na+K and Ca+Mg is 5 mg/kg (Hoekman et al., 2012). All biodiesel and the blended fuels in this study met the Na+K specification. With an increase in biodiesel content the concentrations of Na were observed to increase in all blends, having a concave downward shape for S-PBXX and concave upwards shape in P-PBXX. According to Table 5-4, Na was present in both biodiesel and petrol, and with studies by De Jesus et al., (2008) and Avila

Orozco et al., (2014), reporting that Na, K, Ca, and Mg will appear in the biodiesel during the production phase, it was evident that blending increased the concentration of Na. It is important for these metals to be kept below standards set for biodiesel and its blends since a high concentration of these metals can results in the formation of deposits within the engine which is undesirable (Iqbal et al., 2010).

Table 5-4. Content of K and Na in biodiesel and its blends

	Sunflower biodiesel-petrol blends				**Palm biodiesel-petrol blends**				**Petrol**
Elements	S-B100	S-PB5	S-PB15	S-PB25	P-B100	P-PB5	P-PB15	P-PB25	P100
K (mg/kg)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na (mg/kg)	0.372	0.800	1.057	0.803	0.430	0.917	0.784	1.224	0.392
K+Na (mg/kg)	**0.372**	**0.800**	**1.057**	**0.803**	**0.430**	**0.917**	**0.784**	**1.224**	**0.392**

5.3.5.2 Presence of Group II metal

In Table 5-5, the concentration of calcium (Ca) with magnesium (Mg) in S-B100 and P-B100 were observed to be 31.357 mg/kg and 26.683 mg/kg respectively. For the blended fuels, a linear increase in the concentrations of Ca was observed as biodiesel content in S-PB5, S-PB15, and S-PB25 increased with values of 23.178 mg/kg, 27.491 mg/kg, and 34.657 mg/kg. While P-PB5, P-PB15 and P-PB25 had a linear increase in the Ca concentration with increased biodiesel content of 33.309 mg/kg, 35.571 mg/kg and 34.314 mg/kg. This linear increase was also obtained for Mg across all biodiesel-petrol blends. The presence of these metals did not occur in petrol, it was therefore evident that blending petrol with biodiesel led to a significant reduction in both Ca and Mg concentrations. The limits set for Ca and K concentration in biodiesel was 5 mg/kg and as observed in Table 5-5. Below, as all PBXX were above the specified limit set in EN 14213 and ASTM D6751 (Barabas & Todoru, 2011; Alleman et al., 2013). This could have been attributed by the (CaO/Al_2O_3) catalyst used in the synthesis of biodiesel or some left during the purification stage and hence, having an increase in Ca and Mg concentrations in the biodiesel and the blended fuels (Nogueira & Lucio, 2011). Also, Ca and Mg could have been absorbed during the cleaning process (Lyra et al., 2010). A high concentration of Ca cause pollution in the air once combusted (Chaves et al., 2011), which then may form undesirable compounds leading to engine malfunctioning and reducing fuel stability (Avila Orozco et al., 2014).

Table 5-5. Content of Ca and Mg in biodiesel and its blends

	Sunflower biodiesel-petrol blends				**Palm biodiesel-petrol blends**				**Petrol**
Elements	S-B100	S-PB5	S-PB15	S-PB25	P-B100	P-PB5	P-PB15	P-PB25	P100
Ca (mg/kg)	31.216	23.178	27.491	34.657	26.683	33.309	35.571	34.314	0.000
Mg (mg/kg)	0.141	0.019	0.063	0.132	0.302	0.043	0.199	0.247	0.000
Ca+Mg (mg/kg)	**31.357**	**23.197**	**27.554**	**34.789**	**26.985**	**33.352**	**35.770**	**34.561**	**0.000**

5.3.5.3 Presence of Phosphorus

Figure 5-5 shows phosphorus (P) concentrations in biodiesel-petrol blends, S-B100, P-B100 and petrol (P100) had concentrations of 9.29 mg/kg and 10.10 mg/kg and 9.75 mg/kg respectively. The EN 14107 and ASTM D4951 set the P limit in biodiesel to be 10 mg/kg (Knothe, 2006; Alleman et al., 2016), S-B100 passed the test while P-B100 was slightly above the specified limit. In biodiesel-petrol blends, the lower value was only noticed in SB25, while in other blends there was an increase in P concentration as the biodiesel content was increased. Since there was P present in P100 and B100, blending these two fuels resulted in an increased concentration of P in the blended fuels. The P level amongst blended fuels of PB5 and PB15 did not change much except in PB25, this can be supported by a conclusion drawn by a research of Southwest Research Institute which reported that no significant change was found in P for biodiesel blends (Fernando et al., 2007). Nevertheless, it was reported by Iqbal et al., (2010), that the presence of P was due to its initial feedstock, which showed that waste palm oil had more P concentration than waste sunflower oil (Simbi et al., 2021). The high presence of P has a negative impact on the engine, it can cause the formation of deposits within the engine which can damage the ability of after-treatment systems (Lyra et al., 2009). Also, studies by Iqbal et al., (2010) and Korn et al., (2010), reported that presence of high P can be poisonous to catalytic the converters of petrodiesel engines, which will emit high level of CO, CO_2 and SO_2.

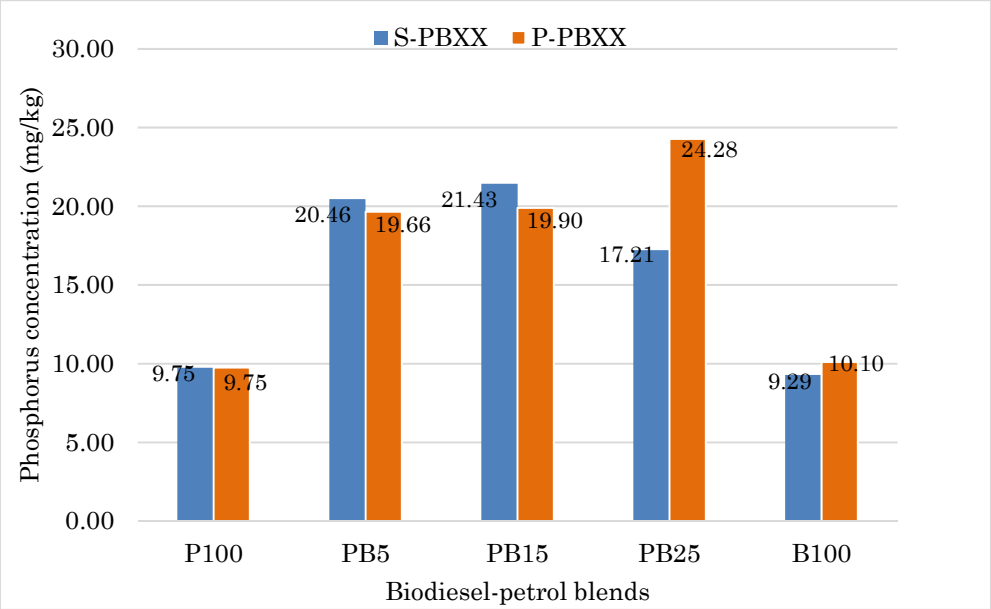


Figure 5-5. Phosphorus concentration in biodiesel and petrol blends

5.3.5.4 Presence of Sulfur

Figure 5-6 illustrates sulfur (S) content in PBXX, 4 mg/kg and 6 mg/kg concentrations were obtained in S-B100 and P-B100, and in S-PB5, S-PB15, and S-PB25 various S concentrations of 14.50 mg/kg, 18.70 mg/kg and 20.90 mg/kg were determined respectively. While in P-PB5, P-PB15, and P-PB25, S concentration of 18.60 mg/kg, 34.30 mg/kg and 17.90 mg/kg were also determined. Also, decrease in the S concentration was observed in P-PBXX as the biodiesel content was increased in P-PB5 to P-B100 except in P-PB15. On other hand, in S-PBXX, S content increased linearly from in S-PB5, S-PB15, and S-PB25, with a subsequent decreased in S-B100. Normally, in biodiesel-petrodiesel blends, S content decrease with an increase in biodiesel content (Qi & Lee, 2014). This was achieved in P-PBXX with slight deviation in P-PB15. In biodiesel, a maximum limit set for sulfur was 10 mg/kg according to EN ISO 20884 and ASTM D5453 (Knothe, 2006; de Goede et al., 2015), while for biodiesel-petrodiesel blends, up to 20% of biodiesel (B20) a maximum 15 mg/kg of S was allowed (McCormick & Westbrook, 2010).

Both biodiesels met the standard specifications with low S content obtained, and in PBXX, only S-PB5 met standard set for blended biodiesel while other blends failed this test because of higher content of S in petrol as compared to biodiesel. Even though, S found in petrol was below 10 mg/kg which was supported by a similar finding by Han et al., (2011), and in the study by Zhong (2019), they reported increased S content in blended fuels.

However, blended fuels showed characteristics of fuels needed for ultra-low emission vehicle (ULEV) and low emission vehicle (LEV) in the United States which are under category 3 of gasoline and petrodiesel. The specification for this category is a maximum S concentration of 50 mg/kg and 30 mg/kg for petrol and petrodiesel respectively (Worldwide Fuel Charters, 2019). High S content can negatively affect emission-control system performance and the environment (Ramadhas et al., 2006). Therefore, the low S content in the biodiesel helps in reducting engine wear and exhaust emissions (Valente et al., 2011).

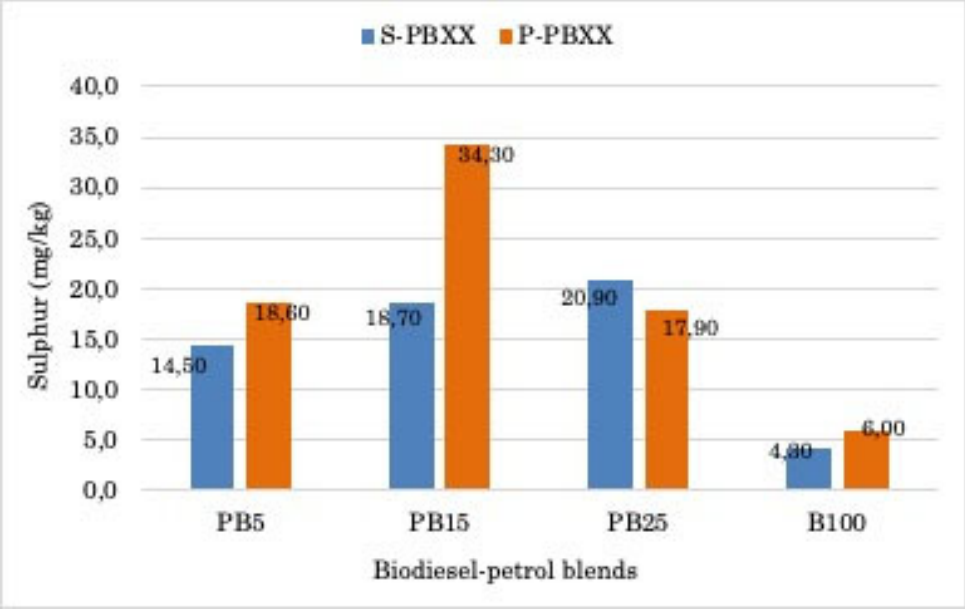


Figure 5-6. Sulfur concentration in biodiesel and petrol blends

5.3.5.5 Presence of Minor Elements (Al, Cu, Fe and Zn)

As observed in Figure 5-7, Copper (Cu) was absent in all B100 and PBXX, but only 0.212 mg/kg of Cu was noticed in PB25. Also, it was noticed that the concentration of iron (Fe) in the PBXX was the highest amongst other elements followed by zinc (Zn) then finally aluminium (Al) as depicted by Figure 5-7. Although, all these trivial concentrations were below the standard limit allowed in biodiesel, blending increased the elemental content. Metals in fuel can lead to mechanical problems within the engine due to deposits cause by corrosion (Pillay et al., 2012), and they can result in environmental pollution (Sánchez et al., 2015). Moreover, it was reported that oxidation stability of alkyl esters was reduced by the increased in Cu, Fe, Ni, and Sn, with Fe being a very effective hydroperoxides decomposer (Lobo et al., 2009). This can be explained by the catalytic effects of these metals in the auto-oxidation of oils as a result of rancidity (Garrido et al., 1994).

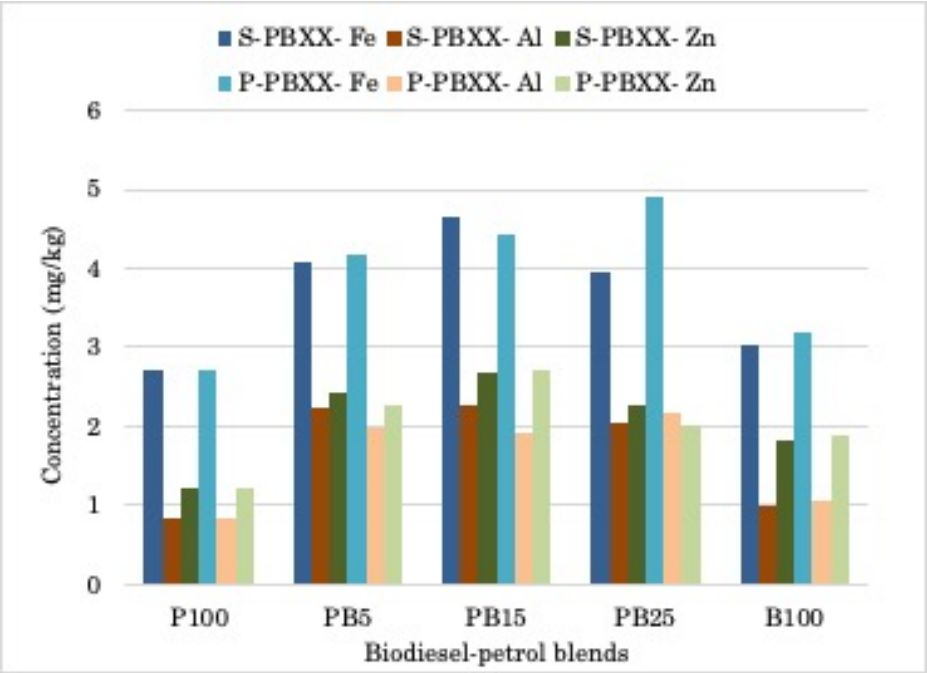


Figure 5-7. Minor elements in biodiesel and petrol blends

5.3.6 Effect of Oxidation Stability

Figure 5-8 shows the obtained oxidation stability (OS) of B100 and PBXX as indicated by induction period (IP) in hour (h). The IP values for S-PB5, S-PB15, S-PB25 and S-B100 were observed to be 7.19 h, 6.5 h, 3.98 h and 4.2 h respectively. While in P-PB5, P-PB15, P-PB25 and P-B100, the IP values of 24.09 h, 21.45 h, 17.22 h and 17.43 h were also observed. Increase in biodiesel content within blended biodiesels resulted in decreased IP which indicated a drop of OS and by increasing petrol content, OS was enhanced. Low OS in biodiesel is caused by the presence of unsaturated fatty acids found in biodiesel as compared to petrodiesel. These acids facilitate the increased chance of the fuel reacting with air, temperature, metal ions. Furthermore, the storage time and exposure to ultraviolet or visible light in biodiesel can increase the oxidation (Ng et al., 2010; Abedin et al., 2014; Lanjekar & Deshmukh, 2016). Also, natural antioxidants found in vegetable oils play a role in varying OS of different oils (McCormick & Westbrook, 2010).

Karavalakis et al., (2010), reported an increase in biodiesel blends with decreased OS, because of the increased presence of linolenic and linoleic acids. However, both biodiesels met the 3 h minimum requirement set by the ASTM D5761, with P-B100 exceptionally surpassing the 6 h minimum set by EN 14112 (Ramadhas et al., 2006; Karavalakis et al., 2010; Sanjid et al., 2013). In the study conducted by de Goede et al., (2015), they reported

that the number of double bonds and the position influence the rate of oxidation, with OS decreasing in order of oleic >> linoleic > linolenic. This was the reason palm biodiesel was highly saturated with more OS than sunflower biodiesel which has more double bonds. This was also confirmed by Simbi et al., (2021), with an expected superior OS of methyl esters in palm biodiesel (Giakoumis, 2018). Similarly, in the reports by Benjumea et al., (2011) and Baena & Calderón, (2020), they noticed a higher oxidation stability of 12.83 h in palm biodiesel in their various studies. Also, Sarin et al., (2007), reported oxidation stability of 18 h in palm biodiesel when Rancimat equipment was used with heating to temperature of 100 ^{0}C and with a further increase in the temperature to 110 ^{0}C, a decrease in OS was obtained at 13.37 h with palm biodiesel from 18 h. According to ASTM D525, a minimum OS of 8 h must be met for petrol (Worldwide Fuel Charters, 2019). Therefore, by adding biodiesel to petrol, an increment in OS of biodiesel-petrol blends was observed. Since oxidation is inversely proportional to an increase in the percentage of biodiesel (Jain & Sharma, 2011), due to the presence of high unsaturated fatty acids (Jain & Sharma, 2010b). A minimum of 20 h OS was required according to IS 15607 D590 for biodiesel blends (Dwivedi & Sharma, 2014; Jain & Sharma, 2014), while in EN14112 specification 6 h minimum is required in biodiesel blended fuels (Hoekman et al., 2012; Silitonga et al., 2013). Therefore, biodiesel-petrol blends of S-PB5 and S-PB15 met the EN 14112 standardisation, while all P-PBXX met the EN 14112, with P-PB5 and P-PB15 passing the IS 15607 standard for blended fuels.

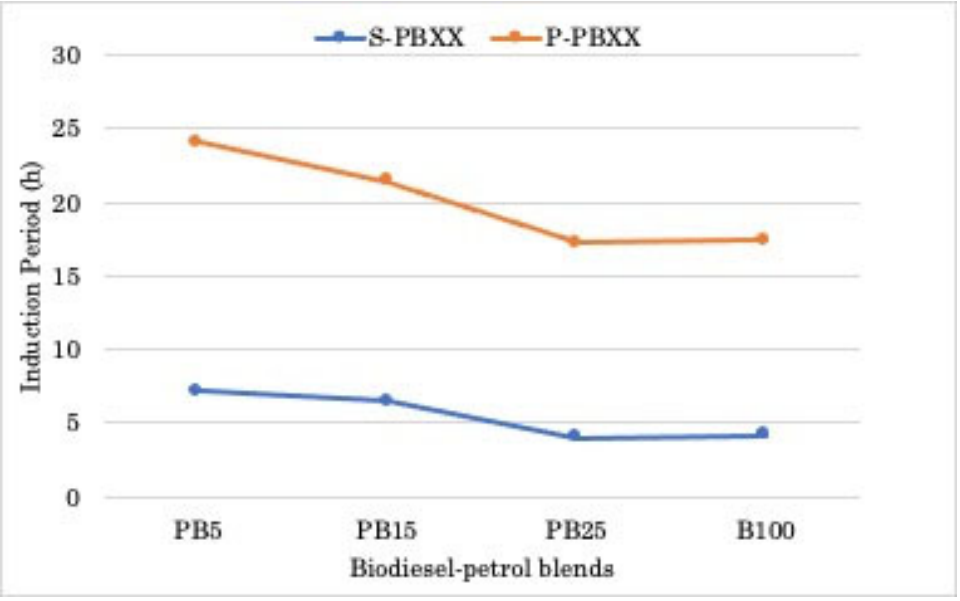


Figure 5-8. Change in oxidation stability in biodiesel and petrol blends

5.3.7 Effect of Viscosity

According to Figure 5-9, the viscosity of P-B100 was found to be 11.1 mm^2/s and S-B100 was 6 mm^2/s. The viscosity obtained for P-B100 was higher than 7.7 mm^2/s from the results of the study by Yogeeswara et al., (2020), in biodiesel produced form waste frying palm oil, and with the 6.01 mm^2/s reported by Bukkarapu et al., (2018), for biodiesel produced from neat palm oil. While an improvement in the viscosity of S-B100 in this study when compared with the results reported by Hossain & Boyce, (2009), when biodiesel was produced from pure and waste sunflower oil having 5.8 mm^2/s and 9.5 mm^2/s respectively. Additionally, a study by Santos et al., (2013), reported a high viscosity of 6.3 mm^2/s in sunflower methyl ester. Even though, S-B100 did not meet the specification set for EN 14214 as it is greater than the range of 3.5-5 mm^2/s, the obtained viscosity was in range of 1.9-6 mm^2/s limit set in ASTM D7651 (Yang et al., 2016).

Also, Knothe, (2006), suggested that the maximum limit of 5 mm^2/s should exclude biodiesels produced from frying oils since they have a high amount of trans fatty acids and which less unsaturated. Hence, waste palm oil has more saturated fatty acids than waste sunflower oil (Simbi et al., 2021), which justifies their high viscosity. There is a huge relationship between viscosity and density, as the viscosity increases with increased volume fraction of biodiesel (Ghazanfari et al., 2017; Moradi et al., 2013). The relationship between density and viscosity was supported by Parikh, (2014), in palm biodiesel having a density of 0.876 g/cm^3 corresponded with 4.8 mm^2/s as it increased to 0.882 g/cm^3 the viscosity changed to 7.01 mm^2/s (Kumar & Sharma, 2016). Also, noticeably problems at lower temperature conditions such as cold start issues can appear since it increases with a decrease in temperature (Joshi & Pegg, 2007; Hoekman et al., 2012).

In Figure 5-9, it was observed below that petrol had an extremely low viscosity of 0.7 mm^2/s as compared to biodiesel. Similar, Chaichan, (2014), reported the viscosity of petrol to be as low as 0.44 mm^2/s and Bao et al., (2014), reported 0.735 mm^2/s as the viscosity of petrol. Therefore, with the blending of petrol and biodiesel, it is expected that the viscosity of the blends will be less than that of pure biodiesel. Also noticed was the petrol decrease in viscosity when the percentage of biodiesel in the blends was decreased and petrol percentage was increased. This is preferred in compression ignition engines since it renders easier fuel movements allowing faster atomization and lower ignition delay (Alptekin & Canakci, 2008; Giakoumis, 2018; Gad & Ismail, 2021).

According to D455 of ASTM D7467, viscosity of biodiesel-petrol blends up to 20% biodiesel content should range between 1.9-4.1 mm²/s (Moser, 2009), while no limit has been set for biodiesel-petrol blends of low viscosity, which is necessary for better atomization (Chen et al., 2018). Viscosity values of PB5, PB15, and PB25 are in order of magnitude with increased viscosity than original pure petrol. PB25 representing a better blend with 1.2 mm²/s and 1.6 mm²/s for S-PB25 and P-PB25 respectively which is close to the limit set in ASTM D7467 (Moser, 2009; Jain & Sharma, 2014).

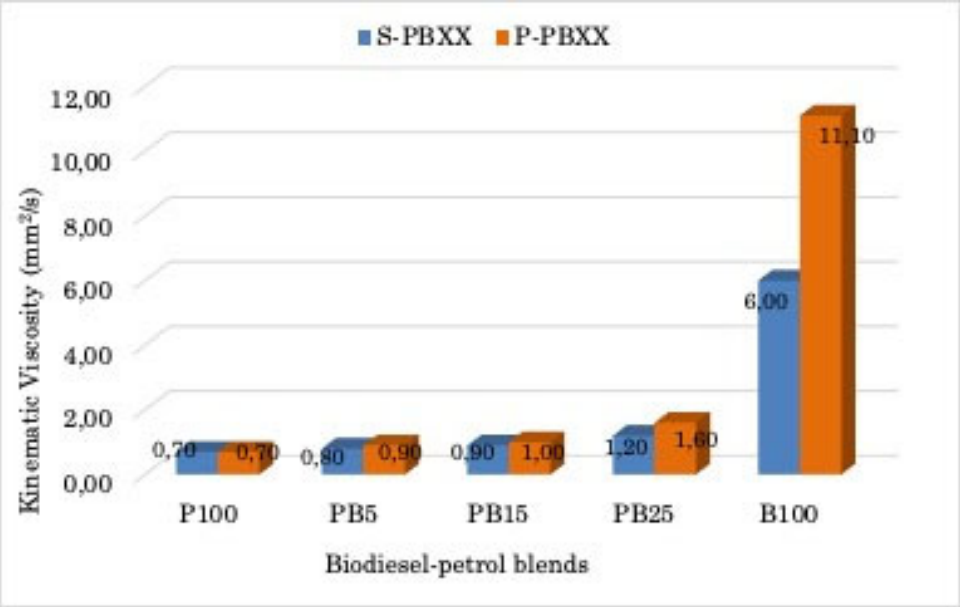


Figure 5-9. Viscosity at 40 ^{0}C of biodiesel and petrol blends

5.3.8 Effect of Moisture Content

As shown in Figure 5-10 is the determined moisture content in S-B100 and P-B100 which were 0.050 and 0.055 % volume (vol.%) respectively. Also, the determined moisture content for S-PBXX of S-PB5, S-PB15, and S-PB25 were 0.020, 0.030 and 0.040 vol.% while in P-PBXX of P-PB5, P-PB15, and P-PB25, the moisture content observed were 0.031, 0.035 and 0.050 vol.% respectively. According to EN 14214 and ASTM D6751 standards, the maximum moisture limit for pure biodiesel is 500 mg/kg or 0.05 vol.% (Joshi & Pegg, 2007 Alptekin & Canakci, 2008; Aisyah et al., 2019), and in biodiesel blends the limit set at 0.05 vol.% according to ASTM D7467 or EN ISO 12937 standards (Moser, 2009). Gumahin et al., (2019), reported that the chances of biodiesel absorbing moisture is 6.5 times higher than petrodiesel even if there is constant relative humidity, this is due to the presence of ester bonds within biodiesel. Therefore, when comparing the moisture contents of petrol and biodiesel, it is clear that that biodiesel moisture content was approximately 5.5 times

higher than that of petrol. Another way to evaluate the presence of moisture content in biodiesel is the indication of its high acidity (Cavalheiro et al., 2020). Observation of the high acidity in P-B100 and P-PBXX as seen in Figure 5-1 correspond with the higher moisture contents of P-PBXX as compared to S-PBXX in Figure 5-10, which shows a correlation of moisture content and acidity. In reducing the moisture content of biodiesel, blending it with petrol will reduce the hydrophilicity of biodiesel since petrol had a moisture content of 0.01 vol.% (McCormick & Westbrook, 2010). Even though, P-B100 had a moisture content that was above the limit set for biodiesel, the addition of petrol led to a lowered moisture content, therefore improvement with the blended fuels were observed (P-PBXX and S-PBXX), meeting specifications set for blends. As reported by Baena & Calderón, (2020), blending created mixtures with a lower absorption capacity. It is essential to evaluate moisture content within fuels in order to avoid microbial growth during storage as this enhances degradation (Knothe, 2006), causing low heating value (Aisyah et al., 2019), and would result in re-processing of the fuel (Fregolente et al., 2015).

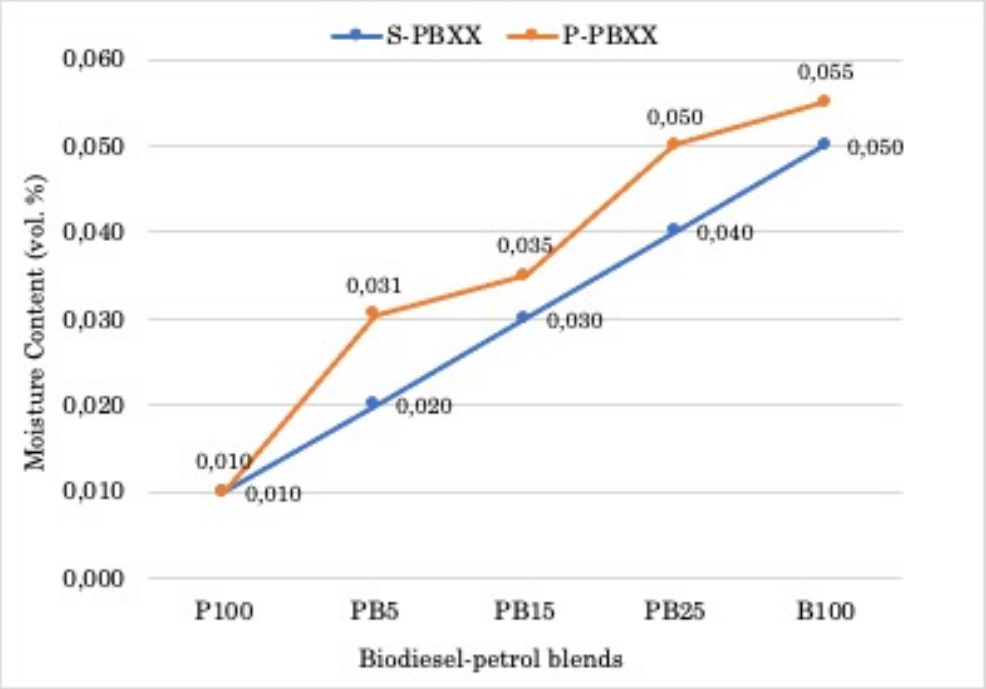


Figure 5-10. Moisture content in biodiesel and petrol blends

5.4 Conclusions

In conclusion, blending sunflower and palm biodiesel with petrol resulted in blended fuels that have improved characteristics compared to pure biodiesel or petrol which met standard specifications set for biodiesel and petrodiesel blends. By adding petrol, the acid

number, density, volatility, cetane number, viscosity, moisture content, carbon residue and harmful metals were lowered while oxidation stability was enhanced. S-PBXX showed lower acid number and more energy due to higher density and were more viscous than P-PBXX. While these properties seemed to correlate with each other i.e., acidity and moisture content, density and viscosity, an increase in values were observed for these properties as the percentage of biodiesel content is elevated within the blends, owing to the structural properties of esters present. High degree of unsaturation found in S-B100 resulted in more chances for the formation of total hydrocarbons, depletion at 80% v/v, with more carbon residues, and subsequently longer ignition delay for S-PBXX. On other hand, P-B100 portrayed a quicker and easier cold start and warm up after ASTM D4737-09 was found to be a reliable method for obtaining cetane number. Therefore, P-PBXX showed better performance with characteristics of a good cold start, with an exceptional oxidation stability as compared to S-PBXX due to the longer chain length of esters in P-B100. Addition of petrol to biodiesel was noticed to increase the concentration of S, P, and some minor elements. Blending biodiesel with petrol, Ca+Mg metals and moisture content were reduced significantly.

5.5 References

Abbaszaadeh, A., Ghobadian, B., Omidkhah, M.R. & Najafi, G. 2012. Current biodiesel production technologies: A comparative review. *Energy Conversion and Management*, 63: 138–148. http://dx.doi.org/10.1016/j.enconman.2012.02.027

Abedin, M.J., Masjuki, H.H., Kalam, M.A., Varman, M., Arbab, M.I., Fattah, I.M.R. & Masum, B.M. 2014. Experimental investigation of a multicylinder unmodified diesel engine performance, emission, and heat loss characteristics using different biodiesel blends: Rollout of B10 in Malaysia. *Scientific World Journal*, 2014: 2–9. http://dx.doi.org/10.1155/2014/349858

Adams, C.A., Loeper, P., Krieger, R., Andrie, M.J. & Foster, D.E. 2013. Effects of biodiesel-gasoline blends on gasoline direct-injection compression ignition (GCI) combustion. *Fuel*, 111: 784–790. http://dx.doi.org/10.1016/j.fuel.2013.04.074

Agarwal, A.K. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science*, 33(3): 233–271. http://dx.doi.org/10.1016/j.pecs.2006.08.003

Aisyah, L., Bethari, S.A., Wibowo, C.S., Hermawan, N., Alwi, D.U., Rulianto, D. & Anggarani, R. 2019. Water content in biodiesel for diesel fuel blends: Measurement using centrifuge and coulometric titration method. *IOP Conference Series: Materials Science and Engineering*, 494(1)): 1–4. http://dx.doi.org/10.1088/1757-899X/494/1/012082

Al-Dawody, M.F. & Al-Farhany, A.K. 2018. A Comparative Analysis of Diesel Engine Fuelled with Diesel Fuel and Methyl Ester of Waste Cooking Oil. *International Journal*

of Applied Engineering Research, 13(1): 14–20. Available online: https://www.researchgate.net/publication/322950888 [accessed on 13 January 2021]

Aleme, H.G. & Barbeira, P.J.S. 2012. Determination of biodiesel content in diesel using distillation curves and multivariate calibration. *Energy and Fuels*, 26(9): 5769–5774. http://dx.doi.org/10.1021/ef3008757

Alleman, T.L., Fouts, L. & Chupka, G. 2013. Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011. *National Renewable Energy Laboratory*: 1–35. Available online: http://www.osti.gov/bridge [accessed on 02 August 2021]

Alleman, T.L., Mccormick, R.L., Christensen, E.D., Fioroni, G., Moriarty, K. & Yanowitz, J. 2016. *Biodiesel handling and use guide*. 5th ed. United states: n. p. Available online: https://www.osti.gov/servlets/purl/1347103 [accessed 31 July 2021]

Alptekin, E. & Canakci, M. 2008. Determination of the density and the viscosities of biodiesel-diesel fuel blends. *Renewable Energy*, 33(12): 2623–2630. http://dx.doi.org/10.1016/j.renene.2008.02.020

Anguebes-Franseschi, F., Bassam, A., Abatal, M., May Tzuc, O., Aguilar-Ucán, C., Wakida-Kusunoki, A.T., Diaz-Mendez, S.E. & San Pedro, L.C. 2019. Physical and Chemical Properties of Biodiesel Obtained from Amazon Sailfin Catfish (Pterygoplichthys pardalis) Biomass Oil. *Journal of Chemistry*, 2019: http://dx.doi.org/10.1155/2019/7829630

Anitescu, G. & Bruno, T.J. 2012. Biodiesel fuels from supercritical fluid processing: Quality evaluation with the advanced distillation curve method and cetane numbers. *Energy and Fuels*, 26(8): 5256–5264. http://dx.doi.org/10.1021/ef300615r

Anon. 2020. Determining Water in Oil: Basics of Oil. *Petroleum Technology Group*: 1–4. Available online: https://assets.ctfassets.net/jqmtaofwvr9e/7wW4tQc4pI22wKScrw90jo/859ceb3e27cc650ac7fd8ac923996135/Water_In_Oil.pdf [accessed on 19 April 2021]

Ashok, B., Thundil Karuppa Raj, R., Nanthagopal, K., Tapaswi, A., Jindal, A. & Hari Subbish Kumar, S. 2016. Animal fat methyl ester as a fuel substitute for DI compression ignition engine. *International Journal of Thermodynamics*, 19(4): 206–212. http://dx.doi.org/10.5541/ijot.5000191582

Avila Orozco, F.D., Kovachev, N., Aguirre Pastor, M.Á., Domini, C.E., Fernández Band, B.S. & Hernández, A.C. 2014. Analysis of metals and phosphorus in biodiesel B100 from different feedstock using a Flow Blurring multinebulizer in inductively coupled plasma-optical emission spectrometry. *Analytica Chimica Acta*, 827: 15–21. http://dx.doi.org/10.1016/j.aca.2014.04.016

Azahari, S.R., Salahuddin, B.B., Noh, N.A.M., Nizah, R. & Rashid, S.A. 2016. Physico-chemical and emission characterization of emulsified biodiesel/diesel blends. *Biofuels*, 7(4): 337–343. http://dx.doi.org/10.11113/jt.v78.8007

Bamgboye, A. & Hansen, A. 2008. Prediction of Cetane Number of biodiesel fuel from fatty acid ethyl ester (FAEE) composition. *International Agrophysics*, 22(1). http://dx.doi.org/10.17485/ijst/2015/v8i35/78272

Baena, L.M. & Calderón, J.A. 2020. Effects of palm biodiesel and blends of biodiesel with organic acids on metals. *Heliyon*, 6(5): 2–13. http://dx.doi.org/10.1016/j.heliyon.2020.e03735

Bao, Y., Chan, Q.N., Kook, S. & Hawkes, E. 2014. Spray Penetrations of Ethanol, Gasoline and Iso-Octane in an Optically Accessible Spark-Ignition Direct-Injection Engine. *SAE International Journal of Fuels and Lubricants*, 7(3): 1010–1026. https://doi.org/10.4271/2014-01-9079

Barabas, I. & Todoru, I.-A. 2011. Biodiesel Quality, Standards and Properties. *Biodiesel-Quality, Emissions and By-Products*. Rijeka, Croatia: InTech: 1–28. http://dx.doi.org/10.5772/25370

Benjumea, P., Agudelo, J. & Agudelo, A. 2008. Basic properties of palm oil biodiesel-diesel blends. *Fuel*, 87(10–11): 2069–2075. http://dx.doi.org/10.1016/j.fuel.2007.11.004

Benjumea, P., Agudelo, J.R. & Agudelo, A.F. 2011. Effect of the degree of unsaturation of biodiesel fuels on engine performance, combustion characteristics, and emissions. *Energy and Fuels*, 25(1): 77–85. http://dx.doi.org/10.1021/ef101096x

Bhangale, J.H. & Kulkarni, A.B. 2017. Effects of biodiesel from different feedstocks on engine performance and emissions: A review. *International research Journal of Engineering and Technology*, 4(7): 3273–3279. http:https://doi.org/10.1016/j.rser.2015.06.031

Borugadda, V.B., Paul, A.K., Chaudhari, A.J., Kulkarni, V., Sahoo, N. & Goud, V. V. 2018. Influence of Waste Cooking Oil Methyl Ester Biodiesel Blends on the Performance and Emissions of a Diesel Engine. *Waste and Biomass Valorization*, 9(2): 283–292. http://dx.doi.org/10.1007/s12649-016-9749-0

Bukkarapu, K.R., Rahul, T.S., Kundla, S. & Vardhan, G.V. 2018. Effects of blending on the properties of diesel and palm biodiesel. *IOP Conference Series: Materials Science and Engineering*, 330(1). http://dx.doi.org/10.1088/1757-899X/330/1/012092

Candeia, R.A., Silva, M.C.D., Carvalho Filho, J.R., Brasilino, M.G.A., Bicudo, T.C., Santos, I.M.G. & Souza, A.G. 2009. Influence of soybean biodiesel content on basic properties of biodiesel-diesel blends. *Fuel*, 88(4): 738–743. http://dx.doi.org/10.1016/j.fuel.2008.10.015

Cavalheiro, L.F., Misutsu, M.Y., Rial, R.C., Viana, L.H. & Oliveira, L.C.S. 2020. Characterization of residues and evaluation of the physico chemical properties of soybean biodiesel and biodiesel: Diesel blends in different storage conditions. *Renewable Energy*, 151: 454–462. https://doi.org/10.1016/j.renene.2019.11.039

Chaichan, M.T. 2014. Combustion and Emissions Characteristics for DI Diesel Engine Run by Partially-Premixed (PPCI) Low Temperature Combustion (LTC) Mode. *International Journal of Mechanical Engineering*, 2(10): 7–16. Available online: https://www.researchgate.net/publication/269165788 [accessed on 19 April 2021]

Chaves, E.S., José, E., Araujo, R.G.O., Vladimir, J., Lúcia, V., Frescura, A. & Curtius, A.J. 2010. Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS. *Microchemical Journal*, 96(1): 71–76. http://dx.doi.org/10.1016/j.microc.2010.01.021

Chaves, E.S., Loos-vollebregt, M.T.C. De, Curtius, A.J. & Vanhaecke, F. 2011. Spectrochimica Acta Part B Determination of trace elements in biodiesel and vegetable oil by inductively coupled plasma optical emission spectrometry following alcohol dilution. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 66(9–10): 733–739. http://dx.doi.org/10.1016/j.sab.2011.09.006

Chen, H., He, J., Chen, Y. & Hua, H. 2018. Performance of a common rail diesel engine using biodiesel of waste cooking oil and gasoline blend. *Journal of the Energy Institute*, 91(6): 856–866. https://doi.org/10.1016/j.joei.2017.10.003

de Coro, F.M., Sánchez, L.R. & Sánchez, B. 2016. Distillation: Basic Test in Quality Control of Automituve Fuels. In Mendes, M. (Ed.). *Distillation- Innovative Applications and Modelling*. London, UK: Intech: 78–96. http://dx.doi.org/10.5772/67140

Das, S.K., Kim, K. & Lim, O. 2018. Experimental study on non-vaporizing spray characteristics of biodiesel-blended gasoline fuel in a constant volume chamber. *Fuel Processing Technology*, 178: 322–335. https://doi.org/10.1016/j.fuproc.2018.05.009

Dwivedi, G., Jain, S. & Sharma, M.P. 2013. Diesel engine performance and emission analysis using biodiesel from various oil sources - Review. *Journal of Materials and Environmental Science*, 4(4): 434–447. Available online: https://www.jmaterenvironsci.com/Document/vol4/vol4_N4/65-JMES-371-2013-Dwivedi.pdf [accessed on 13 January 2021]

Dwivedi, G. & Sharma, M.P. 2016. Experimental investigation on thermal stability of Pongamia Biodiesel by thermogravimetric analysis. *Egyptian Journal of Petroleum*, 25(1): 33–38. http://dx.doi.org/10.1016/j.ejpe.2015.06.008

Dwivedi, G. & Sharma, M.P. 2014. Impact of antioxidant and metals on biodiesel stability-a review. *Journal of Materials and Environmental Science*, 5(5): 1412–1425. Available online: https://www.researchgate.net/publication/264006609 [accessed on 05 August 2018]

El-Kassaby, M. & Nemit-Allah, M.A. 2013. Studying the effect of compression ratio on an engine fueled with waste oil produced biodiesel/diesel fuel. *Alexandria Engineering Journal*, 52(1): 1–11. https://doi.org/10.1016/j.aej.2012.11.007

European Union. 2019. Worldwide Emission Standards and Related Regulations - Passenger Cars / Light and Medium Duty Vehicles. *Continental: The Future in Motion*, (May): 2–210. Available online: https://www.continental-automotive.com/getattachment/8f2dedad-b510-4672-a005-3156f77d1f85/EMISSIONBOOKLET_2019.pdf [accessed on 09 September 2021]

Fernando, S., Karra, P., Hernandez, R. & Jha, S.K. 2007. Effect of incompletely converted soybean oil on biodiesel quality. *Energy*, 32(5): 844–851. http://dx.doi.org/10.1016/j.energy.2006.06.019

Fidyayuningrum, H., Fatoni, R. & Harismah, K. 2020. Characteristics of Cetane index of traditional diesel oil in Wonocolo district, Bojonegoro. *AIP Conference Proceedings*, 2223(April). http://dx.doi.org/10.1063/5.0000823

Folayan, A.J., Anawe, P.A.L., Aladejare, A.E. & Ayeni, A.O. 2019. Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic

and high-linoleic vegetable oil biomass. *Energy Reports*, 5:793–806. https://doi.org/10.1016/j.egyr.2019.06.013

Fregolente, P.B.L., Wolf Maciel, M.R. & Oliveira, L.S. 2015. Removal of water content from biodiesel and diesel fuel using hydrogel adsorbents. *Brazilian Journal of Chemical Engineering*, 32(4): 895–901. https://doi.org/10.1590/0104-6632.20150324s20140142

Gad, M. S. & Ismail, M.A. 2021. Effect of waste cooking oil biodiesel blending with gasoline and kerosene on diesel engine performance, emissions and combustion characteristics. *Process Safety and Environmental Protection*, 149: 1–10. https://doi.org/10.1016/j.psep.2020.10.040

Garrido, M.D., Frías, I., Díaz, C. & Hardisson, A. 1994. Concentrations of metals in vegetable edible oils. *Food Chemistry*, 50(3): 237–243. https://doi.org/10.1016/0308-8146(94)90127-9

Ghazanfari, J., Najafi, B., Faizollahzadeh Ardabili, S. & Shamshirband, S. 2017. Limiting factors for the use of palm oil biodiesel in a diesel engine in the context of the ASTM standard. *Cogent Engineering*, 4(1): 1–16. http://doi.org/10.1080/23311916.2017.1411221

Giakoumis, E.G. 2018. Analysis of 22 vegetable oils' physico-chemical properties and fatty acid composition on a statistical basis, and correlation with the degree of unsaturation. *Renewable Energy*, 126: 403–419. https://doi.org/10.1016/j.renene.2018.03.057

de Goede, S., Wilken, C., Ajam, M., Roets, P., Engelbrecht, P. & Woolard, C. 2015. A Comparison of the Stability Performance of Blends of Paraffinic Diesel and Petroleum-Derived Diesel, with RME Biodiesel Using Laboratory Stability Measurement Techniques. *Journal of Fuels*, 2015: 1–15. http://dx.doi.org/10.1155/2015/528497

Gopinath, A., Sairam, K., Velraj, R. & Kumaresan, G. 2015. Effects of the properties and the structural configurations of fatty acid methyl esters on the properties of biodiesel fuel: A review. *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, 229(3): 357–390. http://dx.doi.org/10.1177/0954407014541103

Graboski, S.M. & Mccormick, R.L. 1998. Combustion of fat and vegetable oil derived fuels in diesel engines. *Progress in Energy and Combustion Science*, 24(97): 125–164. https://doi.org/10.1016/S0360-1285(97)00034-8

Gumahin, A.C., Galamiton, J.M., Allerite, M.J., Valmorida, R.S., Laranang, J.R.L., Mabayo, V.I.F., Arazo, R.O. & Ido, A.L. 2019. Response surface optimization of biodiesel yield from pre-treated waste oil of rendered pork from a food processing industry. *Bioresources and Bioprocessing*, 6(1):2–13 https://doi.org/10.1186/s40643-019-0284-2

Hafizil, M., Yasin, M., Mamat, R., Majeed, O., Fitri, A., Adnin, M., Yusri, M. & Rasul, M. 2017. Study of diesel-biodiesel fuel properties and wavelet analysis on cyclic variations in a diesel engine. *Energy Procedia*, 110: 498–503. http://dx.doi.org/10.1016/j.egypro.2017.03.175

Han, D., Ickes, A.M., Assanis, D.N., Huang, Z. & Bohac, S. V. 2010. Attainment and load extension of high-efficiency premixed low-temperature combustion with edieseline in a compression ignition engine. *Energy and Fuels*, 24(6): 3517–3525. http://dx.doi.org/10.1021/ef100269c

Han, D., Ickes, A.M., Bohac, S. V., Huang, Z. & Assanis, D.N. 2011. Premixed low-temperature combustion of blends of diesel and gasoline in a high speed compression ignition engine. *Proceedings of the Combustion Institute*, 33(2): 3039–3046. http://dx.doi.org/10.1016/j.proci.2010.07.045

Harfoot, M.B.J., Tittensor, D.P., Knight, S., Arnell, A.P., Blyth, S., Brooks, S., Butchart, S.H.M., Hutton, J., Jones, M.I., Kapos, V., Scharlemann, J.P.W. & Burgess, N.D. 2018. Present and future biodiversity risks from fossil fuel exploitation. *Conservation Letters*, 11(4): 1–13. http://dx.doi.org/10.1111/conl.12448

Hassan, M.H. & Kalam, M.A. 2013. An overview of biofuel as a renewable energy source: Development and challenges. *Procedia Engineering*, 56: 39–53. http://dx.doi.org/10.1016/j.proeng.2013.03.087

Hoekman, S.K., Broch, A., Robbins, C., Ceniceros, E. & Natarajan, M. 2012. Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews*, 16(1): 143–169. http://dx.doi.org/10.1016/j.rser.2011.07.143

Hossain, A.B.M.S. & Boyce, A.N. 2009. Biodiesel production from waste sunflower cooking oil as an environmental recycling process and renewable energy. *Bulgarian Journal of Agricultural Science*, 15(4): 312–317. Available online: https://www.researchgate.net/publication/236236066 [accessed on 16 April 2021]

Ilkilic, C. & Öner, C. 2017. Biodiesel Fuel Obtained from Sunflower Oil as an Alternative Fuel for Diesel Engines. *The Online Journal of Science and Technology*, 7(3): 12–18. Available online: https://tojsat.net/journals/tojsat/articles/v07i03/v07i03-03.pdf [accessed on 17 April 2021]

International Energy Agency. 2021. Global Energy Review 2021. *Global Energy Review 2020*: 1–36. Available online: https://iea.blob.core.windows.net/assets/d0031107-401d-4a2f-a48b-9eed19457335/GlobalEnergyReview2021 [accessed on 09 September 2021]

Iortyer, H.A., Adoga, F.I. & Tuleun, L.. 2017. Performance Of A CI Engine Fuelled With Cashew Nut Seed Oil Biodiesel-Effect Of Load. *Global Journal of Engineering Science and Research Management*, 4(7): 104–113. http://dx.doi.org/10.5281/zenodo.836623

Iqbal, J., Carney, W.A., Lacaze, S. & Theegala, C.S. 2010. Metals Determination in Biodiesel (B100) by ICP-OES with Microwave Assisted Acid Digestion. *The Open Analytical Chemistry Journal*, 4: 18–26. http://dx.doi.org/10.5281/zenodo.836623

Jain, S. & Sharma, M.P. 2014. Effect of metal contents on oxidation stability of biodiesel/diesel blends. *Fuel*, 116: 14–18. http://dx.doi.org/10.1016/j.fuel.2013.07.104

Jain, S. & Sharma, M.P. 2011. Oxidation stability of blends of Jatropha biodiesel with diesel. *Fuel*, 90(10): 3014–3020. http://dx.doi.org/10.1016/j.fuel.2011.05.003

Jain, S. & Sharma, M.P. 2010b. Thermal stability of biodiesel and its blends: A review. *Renewable and Sustainable Energy Reviews*, 14: 667–687. http://dx.doi.org/10.1016/j.rser.2010.08.022

De Jesus, A., Silva, M. & Vale, M.G.R. 2008. The use of microemulsion for determination of sodium and potassium in biodiesel by flame atomic absorption spectrometry.*Talanta*, 74: 1378–1384. http://dx.doi.org/10.1016/j.talanta.2007.09.010

Jiang, S., Qi, J., Hu, Y., Ren, C., Jiang, Y. & Zhao, Z. 2019. Predicting the Density and Viscosity of Biodiesels and Biodiesel Blends by the Regular-Solution Theory. *Industrial and Engineering Chemistry Research*, 58(36): 17038–17048. http://dx.doi.org/10.1021/acs.iecr.9b03046

Joshi, R.M. & Pegg, M.J. 2007. Flow properties of biodiesel fuel blends at low temperatures. *Fuel*, 86(1–2): 143–151. http://dx.doi.org/10.1016/j.fuel.2006.06.005

Kalghatgi, G. 2019. Development of Fuel/Engine Systems—The Way Forward to Sustainable Transport. *Engineering*, 5(3): 510–518. https://doi.org/10.1016/j.eng.2019.01.009

Kalghatgi, G. 2018. Is it really the end of internal combustion engines and petroleum in transport? *Applied Energy*, 225: 965–974. https://doi.org/10.1016/j.apenergy.2018.05.076

Kanti, S., Kim, K. & Lim, O. 2018. Experimental study on non-vaporizing spray characteristics of biodiesel- blended gasoline fuel in a constant volume chamber. *Fuel Processing Technology*, 178: 322–335. https://doi.org/10.1016/j.fuproc.2018.05.009

Karavalakis, G., Stournas, S. & Karonis, D. 2010. Evaluation of the oxidation stability of diesel / biodiesel blends. *Fuel*, 89(9): 2483–2489. http://dx.doi.org/10.1016/j.fuel.2010.03.041

Khadka, C.B. 2017. How Much Money Can an Equation Really Save? Standard Test Method for Calculating Cetane Index via Four Variable Equation. *Economic Journal of Development Issues*, 19(1): 60–76. http://dx.doi.org/10.3126/ejdi.v19i1-2.17702

Kheiralla, A.F., El-Awad, M., Hassan, M.Y., Hussen, M.A. & Osman, H.I. 2011. Effect of Ethanol−Gasoline Blends on Fuel Properties Characteristics of Spark Ignition Engines. *University of Khartoum Engineering Journal*, 1(2): 22–28. Available online: https://www.researchgate.net/publication/263773714. [accessed on 20 June 2021]

Khuong, L.S., Masjuki, H.H., Zulkifli, N.W.M., Mohamad, E.N., Kalam, M.A., Alabdulkarem, A., Arslan, A., Mosarof, M.H., Syahir, A.Z. & Jamshaid, M. 2017. Effect of gasoline-bioethanol blends on the properties and lubrication characteristics of commercial engine oil. *RSC Advances*, 7(25): 15005–15019. https://doi.org/10.1039/c7ra00357a

Knothe, G. 2006. Analyzing biodiesel: Standards and other methods. *JAOCS, Journal of the American Oil Chemists' Society*, 83(10): 823–833. http://dx.doi.org/10.1007/s11746-006-5033-y

Knothe, G. 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel processing technology*, 86: 1059–1070. http://dx.doi.org/10.1016/j.fuproc.2004.11.002

Kook, S. & Pickett, L.M. 2012. Liquid length and vapor penetration of conventional, Fischer-Tropsch, coal-derived, and surrogate fuel sprays at high-temperature and high-pressure ambient conditions. *Fuel*, 93: 539–548. http://dx.doi.org/10.1016/j.fuel.2011.10.004

Korn, M.G.A, Santos, D.C.M.B., Guida, M.A.B., Barbosa, I.S. & Passos, M.L.C. 2010. Evaluation of Digestion Proceures for Simultaneous Determination of Ca, P, Mg, K and Na in Biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry. *J. Braz. Chem. Soc*, 21(12): 2278–2284. https://doi.org/10.1590/S0103-50532010001200015

Kubičková, I., Snåre, M., Eränen, K., Mäki-Arvela, P. & Murzin, D.Y. 2005. Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. *Catalysis Today*, 106(1–4): 197–200. http://dx.doi.org/10.1016/j.cattod.2005.07.188

Kulkarni, M.G. & Dalai, A.K. 2006. Waste cooking oil - An economical source for biodiesel: A review. *Industrial and Engineering Chemistry Research*, 45(9): 2901–2913. https://doi.org/10.1021/ie0510526

Kumar, K. & Sharma, M.P. 2016. Performance and emission characteristics of a diesel engine fuelled with biodiesel blends. *International Journal of Renewable Energy Research*, 6(2): 658–662. Available online: https://www.ijrer.org/ijrer/index.php/ijrer/article/view/3827 [accessed on 13 January 2021]

Kumar, P. & Singh, I. 2015. Performance Evaluation of Waste Cooking Biodiesel and its blends on Diesel Engine. *Advances in power generation from renewable energy sources:* 68–273. Available online: https://www.researchgate.net/publication/304167515 [accessed on 13 January 2021]

Kumar, R. 2016. Experimental Comparison of Performance Characteristics of a Single Cylinder Diesel Engine Fueled With Jatropha Biodiesel-Diesel and Kerosene Oil-Jatropha Biodiesel-Diesel Blends. *International Journal of Mechanical Engineering and Technology*, 7(5): 321–329. Available online: http://www.iaeme.com/ijmet/issues.asp?JType=IJMET&VType=7&IType=5 [accessed on 16 April 2021]

Kumar, S., Yadav, K. & Dwivedi, G. 2018. ScienceDirect Impact analysis of Oxidation Stability for Biodiesel & its Blends. *Materials Today: Proceedings*, 5(9): 19255–19261. https://doi.org/10.1016/j.matpr.2018.06.283

Lanjekar, R.D. & Deshmukh, D. 2016. A review of the effect of the composition of biodiesel on NOx emission, oxidative stability and cold flow properties. *Renewable & sustainable energy reviews*, 54: 1401–1411. http://dx.doi.org/10.1016/j.fuel.2013.07.104

Lapuerta, M., Rodríguez-Fernandez, J., García-Contreras, R. & Bogarra, M. 2015. Molecular interactions in blends of alcohols with diesel fuels: Effect on stability and distillation. *Fuel*, 139: 171–179. http://dx.doi.org/10.1016/j.fuel.2014.08.055

Lee, C., Ahmed, A., Nasir, E.F., Badra, J., Kalghatgi, G., Sarathy, S.M., Curran, H. & Farooq, A. 2017. Autoignition characteristics of oxygenated gasolines. *Combustion and Flame*, 186: 114–128. http://dx.doi.org/10.1016/j.combustflame.2017.07.034

Lin, C.Y. & Lin, Y.W. 2012. Fuel characteristics of biodiesel produced from a high-acid oil from soybean soapstock by supercritical-methanol transesterification. *Energies*, 5(7): 2370–2380. http://dx.doi.org/10.3390/en5072370

Liu, H., Wang, X., Zhang, D., Dong, F., Liu, X., Yang, Y., Huang, H., Wang, Y., Wang, Q. & Zheng, Z. 2019. Investigation on blending effects of gasoline fuel with n-butanol, DMF, and ethanol on the fuel consumption and harmful emissions in a GDI vehicle. *Energies*, 12(10): 2–21. http://dx.doi.org/10.3390/en12101845

Lyra, F.H.., Weitzel Dias Carneiro, M.T., Pedrini Brandão, G., Moura Pessoa, H. & Ribeiro De Castro, E.V. 2009. Direct determination of phosphorus in biodiesel samples by graphite furnace atomic absorption spectrometry using a solid sampling accessory.

Journal of Analytical Atomic Spectrometry, 24(9): 1262–1266. http://dx.doi.org/10.1039/b907071k

Lyra, F.H., Tereza, M., Dias, W., Brandão, G.P., Pessoa, H.M. & Castro, E.V. De. 2010. Determination of Na , K , Ca and Mg in biodiesel samples by fl ame atomic absorption spectrometry (F AAS) using microemulsion as sample preparation. *Microchemical Journal*, 96(1): 180–185. http://dx.doi.org/10.1016/j.microc.2010.03.005

Mahmudul, H.M., Hagos, F.Y., Mamat, R., Adam, A.A., Ishak, W.F.W. & Alenezi, R. 2017. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review. *Renewable and Sustainable Energy Reviews*, 72: 497–509. http://dx.doi.org/10.1016/j.rser.2017.01.001

Matějovský, L., Macák, J., Pospíšil, M., Staš, M., Baroš, P. & Krausová, A. 2018. Study of Corrosion Effects of Oxidized Ethanol-Gasoline Blends on Metallic Materials. *Energy and Fuels*, 32(4): 5145–5156. http://dx.doi.org/10.1021/acs.energyfuels.7b04034

McCormick, R.L. & Westbrook, S.R. 2010. Storage stability of biodiesel and biodiesel blends. *Energy and Fuels*, 24(1): 690–698. http://dx.doi.org/10.1021/ef900878u

Moradi, G.R., Karami, B. & Mohadesi, M. 2013. Densities and kinematic viscosities in biodiesel-diesel blends at various temperatures. *Journal of Chemical and Engineering Data*, 58(1): 99–105. http://dx.doi.org/10.1021/je3008843

Moser, B. 2009. Biodiesel production, properties, and feedstocks. *Vitro Cell Dev. Biol.* 45:230–265. http://dx.doi.org/10.1007/978-1-4419-7145-6

Moser, B.R. 2014. Impact of fatty ester composition on low temperature properties of biodiesel-petroleum diesel blends. *Fuel*, 115: 500–506. http://dx.doi.org/10.1016/j.fuel.2013.07.075

Moser, B.R. & Bryan R. Moser. 2009. Biodiesel production, properties, and feedstocks. *In Vitro Cellular & Developmental Biology - Plant*, 45(3): 229–266. http://link.springer.com/10.1007/s11627-009-9204-z

Nair, J.N. 2015. Study of Biodiesel Blends and Emission Characteristics of Study of Biodiesel Blends and Emission Characteristics of. , 2(8): 3710–3715. Available online: http://www.ijirset.com/upload/august/43_STUDY.pdf [accessed on 13 January 2021]

Nallusamy, N. 2010. Relationships among the physical properties of biodiesel and engine fuel system design requirement. *International Journal of Energy and Environment*, 1(5): 919–926. Available online: https://www.researchgate.net/publication/44848825 [accessed on 17 April 2021]

NREL see National Renewable Energy Laboratory

National Renewable Energy Laboratory. 2012. *Biodiesel Handling and Use Guide. 4th ed.* Ohio, United States: Bibliogov: 1-98. Available online: https://www.canr.msu.edu/uploads/files/Fuels/Handling%20and%20Use%20Guidelines.pdf [accessed on 07 August 2018]

Ng, J.H., Ng, H.K. & Gan, S. 2010. Advances in biodiesel fuel for application in compression ignition engines. *Clean Technologies and Environmental Policy*, 12(5): 459–493. http://dx.doi.org/10.1007/s10098-009-0268-6

Nogueira, T. & Lucio, C. 2011. Determination of Ca , K , Mg , Na , sulfate , phosphate , formate , acetate , propionate , and glycerol in biodiesel by capillary electrophoresis with capacitively coupled contactless conductivity detection. *Microchemical Journal*, 99(2): 267–272. http://dx.doi.org/10.1016/j.microc.2011.05.014

Ott, J., Gronemann, V., Pontzen, F., Fiedler, E., Grossman, G., Burkhard Kersebohm, K., Weiss, G. & Witte, C. 2012. Methanol. *Ullmann's Encyclopedia of Industrial Chemistry*: 2–23. Available online: https://vdocument.in/methanol-in-ullmanns-encyclopedia-of-industrial-chemistry.html [accessed on 25 March 2021]

Pandey, A. 2008. *Handbook of plant-based biofuels*. Boca Raton, CRC Press: 3–281. https://doi.org/10.1201/9780789038746

Parikh, H. 2014. Emission Characteristics of Palm Biodiesel And Its Blends in The Single Cylinder Diesel Engine. , 4(02): 1–5. Available online: https://www.academia.edu/25760939/Emission_Characteristics_of_Palm_Biodiesel_and_Its_Blends_in_the_Single_Cylinder_Diesel_Engine [accessed on 16 April 2021]

Patel, A., Arora, N., Mehtani, J., Pruthi, V. & Pruthi, P.A. 2017. Assessment of fuel properties on the basis of fatty acid profiles of oleaginous yeast for potential biodiesel production. *Renewable and Sustainable Energy Reviews*, 77: 604–616. http://dx.doi.org/10.1016/j.rser.2017.04.016

Paulauskiene, T., Bucas, M. & Laukinaite, A. 2019. Alternative fuels for marine applications: Biomethanol-biodiesel-diesel blends. *Fuel*, 248: 161–167. https://doi.org/10.1016/j.fuel.2019.03.082

Peng, D.X. 2017. Effect of unleaded gasoline blended with biofuels on gasoline injector wear and exhaust emissions. *Industrial Lubrication and Tribology*, 69(2): 208–214. http://dx.doi.org/10.1108/ILT-09-2016-0217

Phan, A.N. & Phan, T.M. 2008. Biodiesel production from waste cooking oils. *Fuel*, 87(17–18): 3490–3496. http://dx.doi.org/10.1016/j.fuel.2008.07.008

Pillay, A.E., Elkadi, M., Fok, S.C., Stephen, S., Manuel, J., Khan, M.Z. & Unnithan, S. 2012. A comparison of trace metal profiles of neem biodiesel and commercial biofuels using high performance ICP-MS. *Fuel*, 97: 385–389. http://dx.doi.org/10.1016/j.fuel.2012.02.040

Putrasari, Yanuandri & Lim, O. 2017. A study on combustion and emission of GCI engines fueled with gasoline-biodiesel blends. *Fuel*, 189: 141–154. http://dx.doi.org/10.1016/j.fuel.2016.10.076

Putrasari, Y. & LIM, O. 2018. A study of a GCI engine fueled with gasoline-biodiesel blends under pilot and main injection strategies. *Fuel*, 221(January): 269–282. https://doi.org/10.1016/j.fuel.2018.01.063

Putrasari, Y. & Lim, O.T. 2017. Performance and Emission of Gasoline Compression Ignition Engine Fueled with 5 and 20% Gasoline-Biodiesel Blends under Single Injection Strategy. *Energy Procedia*, 105: 1743–1750. http://dx.doi.org/10.1016/j.egypro.2017.03.501

Qi, D.H., Chen, H., Geng, L.M. & Bian, Y.Z. 2010. Experimental studies on the combustion characteristics and performance of a direct injection engine fueled with

biodiesel/diesel blends. *Energy Conversion and Management*, 51(12): 2985–2992. http://dx.doi.org/10.1016/j.enconman.2010.06.042

Qi, D.H. & Lee, C.F. 2014. Influence of soybean biodiesel content on basic properties of biodiesel-diesel blends. *Journal of the Taiwan Institute of Chemical Engineers*, 45(2): 504–507. http://dx.doi.org/10.1016/j.jtice.2013.06.021

Quveon: Basics of Karl Fischer Titration: *Advance Analytical Technology*. 2014, 1–15. Avalaible online: http://www.quveon.com/wp-content/pdf/KF Titration by Quveon.pdf [accessed on 19 April 2021]

Ramadhas, A.S. 2006. Alternative fuels for transportation. *Energy Exploration & Exploitation*, 24(1): 45–54. https://doi.org/10.1201/b16260

Ramadhas, A.S., Jayaraj, S. & Muraleedharan, C. 2005. Biodiesel produced from high rubber seed oil. *Fuel*, 84:335–340. http://dx.doi.org/10.1016/j.fuel.2004.09.016

Rao, P.V. & Chary, D.P. 2018. Characteristics comparison of Biodiesel-Diesel Blend (B20) Fuel with Alcohol Additives. *International Journal of Advanced Engineering Research and Science*, 5(8): 128–132. http://dx.doi.org/10.22161/ijaers.5.8.17

Rizwanul Fattah, I.M., Kalam, M.A., Masjuki, H.H. & Wakil, M.A. 2014. Biodiesel production, characterization, engine performance, and emission characteristics of Malaysian Alexandrian laurel oil. *RSC Advances*, 4(34): 17787–17796. http://dx.doi.org/10.1016/j.enconman.2014.07.006

Rodriguez, J.F. & Cheng, W.K. 2016. Reduction of Cold-Start Emissions through Valve Timing in a GDI Engine. *SAE International Journal of Engines*, 9(2):1–10. http://dx.doi.org/10.4271/2016-01-0827

Sánchez, R., Sánchez, C., Lienemann, C.-P. & Todolí, J.-L. 2015. Metal and metalloid determination in biodiesel and bioethanol. *J. Anal. At. Spectrom.*, 30(1): 64–101. http://dx.doi.org/10.1039/C4JA00202D

Sanjid, A., Masjuki, H.H., Kalam, M.A., Rahman, S.M.A., Abedin, M.J. & Palash, S.M. 2013. Impact of palm, mustard, waste cooking oil and Calophyllum inophyllum biofuels on performance and emission of CI engine. *Renewable and Sustainable Energy Reviews*, 27: 664–682. http://dx.doi.org/10.1016/j.rser.2013.07.059

Santos, B.S., Capareda, S.C. & Capunitan, J.A. 2013. Sunflower Methyl Ester as an Engine Fuel: Performance Evaluation and Emissions Analysis. *ISRN Renewable Energy*, 2013: 1–12. http://dx.doi.org/10.1155/2013/352024

Santos, D.C.M.B., Guida, M.A.B., Barbosa, I.S. & Passos, M.L.C. 2010. Evaluation of Digestion Proceures for Simultaneous Determination of Ca, P, Mg, K and Na in Biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry. *J. Braz. Chem. Soc*, 21(12): 2278–2284. https://doi.org/10.1590/S0103-50532010001200015

Sarin, R., Sharma, M., Sinharay, S. & Malhotra, R.K. 2007. Jatropha-Palm biodiesel blends: An optimum mix for Asia. *Fuel*, 86(10–11): 1365–1371. https://doi.org/10.1016/j.fuel.2006.11.040

Saxena, P., Jawale, S. & Joshipura, M.H. 2013. A review on prediction of properties of biodiesel and blends of biodiesel. *Procedia Engineering*, 51: 395–402. http://dx.doi.org/10.1016/j.proeng.2013.01.055

Saydut, A., Kafadar, A.B., Tonbul, Y., Kaya, C., Aydin, F. & Hamamci, C. 2010. Comparison of the biodiesel quality produced from refined sunflower (Helianthus annuus L) oil and waste cooking oil. *Energy Exploration and Exploitation*, 28(6): 499–512. http://dx.doi.org/10.1260/0144-5987.28.6.499

Senthil, R. & Silambarasan, R. 2015. Annona: A new biodiesel for diesel engine: A comparative experimental investigation. *Journal of the Energy Institute*, 88(4): 459–469. http://dx.doi.org/10.1016/j.joei.2014.09.011

Sharma, A.K., Sharma, P.K., Chintala, V., Khatri, N. & Patel, A. 2020. Environment-friendly biodiesel/diesel blends for improving the exhaust emission and engine performance to reduce the pollutants emitted from transportation fleets. *International Journal of Environmental Research and Public Health*, 17(11): 2–18 http://dx.doi.org/10.3390/ijerph17113896

Silitonga, A.S., Masjuki, H.H., Mahlia, T.M.I., Ong, H.C., Chong, W.T. & Boosroh, M.H. 2013. Overview properties of biodiesel diesel blends from edible and non-edible feedstock. *Renewable and Sustainable Energy Reviews*, 22: 346–360. http://dx.doi.org/10.1016/j.rser.2013.01.055

Silva, J.B., Almeida, J.S., Barbosa, R. V, Fernandes, G.J.T., Coriolano, A.C.F., Fernandes, V.J. & Araujo, A.S. 2021. Pressurized Differential Scanning Calorimetry and Its Calculated Cetane Index, *Processes*. 9(1): 2–11. https://doi.org/10.3390/pr9010174

Simbi, I., Aigbe, U.O., Oyekola, O. & Osibote, O.A. 2021. Catalyst and Elemental Analysis Involving Biodiesel from Various Feedstocks. *Catalysts 2021,* 11(8): 2–17. http:https://doi.org/10.3390/CATAL11080971

Singh, A., Nigam, P.S. & Murphy, J.D. 2011. Renewable fuels from algae: An answer to debatable land based fuels. *Bioresource Technology*, 102(1): 10–16. http://dx.doi.org/10.1016/j.biortech.2010.06.032

Singh, B., Korstad, J. & Sharma, Y.C. 2012. A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition. *Renewable and Sustainable Energy Reviews*, 16(5): 3401–3408. http://dx.doi.org/10.1016/j.rser.2012.02.042

Thangaraj, B., Solomon, P.R., Muniyandi, B., Ranganathan, S. & Lin, L. 2019. Catalysis in biodiesel production - A review. *Clean Energy*, 3(1): 2–23. http://dx.doi.org/10.1093/ce/zky020

Thanigaivelan, V. & Loganathan, M. 2019. Investigational analysis of performance characteristics and emission of cashew nut shell biodiesel on DI diesel engine. *International Journal of Advanced Research in Engineering and Technology*, 10(1): 45–54. http://dx.doi.org/10.34218/IJARET.10.1.2019.005

Thongchai, S. & Lim, O. 2019. Combustion and Emission Characteristics of Wood Pyrolysis Oil-Butanol Blended Fuels in a Di Diesel Engine. *International Journal of Automotive Technology*, 20(4): 701–711. http://dx.doi.org/10.1007/s12239

Thongchai, S. & Lim, O. 2018. Investigation of the combustion characteristics of gasoline compression ignition engine fueled with gasoline-biodiesel blends. *Journal of Mechanical Science and Technology*, 32(2): 959–967. http://dx.doi.org/10.1007/s12206-018-0146-9

Torregrosa, A.J., Broatch, A., Novella, R., Gomez-Soriano, J. & Mónico, L.F. 2017. Impact of gasoline and Diesel blends on combustion noise and pollutant emissions in Premixed Charge Compression Ignition engines. *Energy*, 137: 58–68. http://dx.doi.org/10.1016/j.energy.2017.07.010

Tyson, K.S & McCormick, R.L. 2009. *Biodiesel Handling and Use Guidelines, 3rd ed.* Collingdale, PA: Diane Publishing: 2–60. http://dx.doi.org/10.2172/893000

Valente, O.S., Pasa, V.M.D., Belchior, C.R.P. & Sodré, J.R. 2011. Physical-chemical properties of waste cooking oil biodiesel and castor oil biodiesel blends. *Fuel*, 90(4): 1700–1702. http://dx.doi.org/10.1016/j.fuel.2010.10.045

Vu, D.N. & Lim, O. 2019. Experimental study on ignition characteristic of gasoline-biodiesel blended fuel in a constant-volume chamber. *Journal of Mechanical Science and Technology*, 33(10): 5073–5083. http://dx.doi.org/10.1007/s12206-019-0946-1

World Fuel Charters. 2019. Gasoline and diesel fuel, 6th ed. *The European Automobile Manufacurers Association:* 4–96. Available online: https://www.acea.auto/publication/worldwide-fuel-charter-2019-gasoline-and-diesel-fuel/ [accessed on 29 April 2021]

Wu, G., Ge, J.C. & Choi, N.J. 2020. A comprehensive review of the application characteristics of biodiesel blends in diesel engines. *Applied Sciences (Switzerland)*, 10(22): 1–31. http://dx.doi.org/10.3390/app10228015

Yang, J., Caldwell, C., Corscadden, K., He, Q.S. & Li, J. 2016. An evaluation of biodiesel production from Camelina sativa grown in Nova Scotia. *Industrial Crops and Products*, 81: 162–168. http://dx.doi.org/10.1016/j.indcrop.2015.11.073

Yaşar, F. 2020. Comparision of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel*, 264. 2–7. http://dx.doi.org/10.1016/j.fuel.2019.116817

Yasin, M.H.M., Mamat, R., Yusop, A.F., Rahim, R., Aziz, A. & Shah, L.A. 2013. Fuel physical characteristics of biodiesel blend fuels with alcohol as additives. *Procedia Engineering*, 53: 701–706. http://dx.doi.org/10.1016/j.proeng.2013.02.091

Yogeeswara, T., Devendra, U. & Kalaisselvane, A. 2020. Physical and chemical characterization of waste frying palm oil biodiesel and its blends with diesel. *AIP Conference Proceedings*, 2225(March). http://dx.doi.org/10.1063/5.0005584

Yusoff, Z. 2015. An overview of current issues on the fabrication, application and metalic corrosion of biodiesel. *Journal of Petrochemical Engineering Department*, 2(1): 25–55. Available online: https://www.researchgate.net/publication/283044634 [accessed on 16 June 2021]

Zhang, Y., Zhan, L., He, Z., Jia, M., Leng, X., Zhong, W., Qian, Y. & Lu, X. 2019. An investigation on gasoline compression ignition (GCI) combustion in a heavy-duty diesel engine using gasoline/hydrogenated catalytic biodiesel blends. *Applied Thermal Engineering*, 160: 2–13. https://doi.org/10.1016/j.applthermaleng.2019.113952

Zhong, W., Li, Bei, He, Z., Xuan, T., Lu, P. & Wang, Q. 2019. Experimental study on spray and combustion of gasoline / hydrogenated catalytic biodiesel blends in a constant volume combustion chamber aimed for GCI engines. *Fuel*, 253(301): 129–138. https://doi.org/10.1016/j.fuel.2019.04.114

Zhong, W., Tamilselvan, T., Li, Z., Qian, Y., Zhang, Y., Wang, Q., He, Z. & Lu, X. 2019. Combustion and emission characteristics of gasoline/hydrogenated catalytic biodiesel blends in gasoline compression ignition engines under different loads of double injection strategies. *Applied Energy*, 251: 2–12. https://doi.org/10.1016/j.apenergy.2019.05.099

Chapter 6: **Metal Content Analysis on The Characteristics of Biodiesel and Petrol Blends**

Copper continues to be unstoppable, ~ Leonardo Suuarez

Abstract

The fundamental nature of biodiesel makes it more susceptible to degradation over time, than petroleum fuels. Apart from light, temperature and exposure to air, the fuel's contact with metals is one great factor used to access the corrosiveness so as to evaluating the effectiveness and sustainability of the fuel. The present study aims at investigating the behaviour effect of copper, iron, and zinc in both sunflower and palm biodiesels and their blends with petrol. Various metal powders of these metals in concentrations of 2, 100, 300, 500, and 700 ppm were immersed into the biodiesel and the blended fuel at temperatures of 25-27 °C for 24-48 h. Results show that the biodiesel type played a role in varying corrosiveness. Metals were observed to decrease the fuel quality of viscosity and oxidation stability, while density, acidity, volatility, and particulate were increased. Corrosion was increased with increase in metal concentration intensification, with Fe oxidised pure biodiesels the most, while Cu had a huge influenced on the blended fuels. Other properties such as viscosity, flash point, density was generally negatively affected the sequential order of Cu > Fe > Zn in palm blended fuels and in sunflower blended fuels Fe > Cu > Zn

Keywords: copper; corrosion; exposure; immersion; Rancimat; iron; zinc

6.1 Introduction

The international energy agency estimated that, by 2025 that the global energy utilisation will grow nearly by 42% (Aalam & Saravanan, 2017). Currently, the major issue for the transportation sector is fossil fuels energy supply and the overall global energy consumption share from 20120-2040 will be equivalent to 63% (Mahmudul et al., 2017). It is not surprising that the demand is excepted to have an annual rise of 1.1% in response to the escalation of the motor industry (Jabade et al., 2020; Subramaniam et al., 2013) and population growth (Verma & Sharma, 2015). Moreover, petroleum reserves, are finite (Peng, 2017). Upsurge in fuel prices are foreseeable (Bergthorson & Thomson, 2015) as these reserves are predicted to last for 218, 41 and 63 years for coal, oil and natural gas respectively (Rao & Ramakrishna , 2015).

The exploitation of fossil fuels has destructive impact on humans, the environment as well as causing air and noise pollution in addition to climate change. The survey and extraction of these fossil fuels cause physiological impacts and disrupt species' behaviour, directly

and indirectly affecting biodiversity via conversion, degradation, contamination, or disruption of the environment at sites of extraction, increase right to use for hunters, loggers, farmers, and settlements. The increasing energy demand, rising crude oil price, worldwide warming owing to greenhouse gases (GHG) release, ecological contamination and the swift decreasing fossil fuel supply are the key reasons why there is a huge search for unconventional energy sources which are ecofriendly, feasible and readily available. Some of these outstanding unconventional energy sources which are efficient to substitute for fossil fuels are solar, biofuel, energy from wind and water. Also, due to the decreasing petroleum resources and the environmental impact of petroleum-fueled engines emission, the development of other fuels for petrodiesel engines are ever more important (Meher et al., 2006; Abbaszaadeh et al., 2012; Harfoot et al., 2018; Nguyen & Vu, 2019).

The use of biomass in generating energy has potential for environmental conservation and future energy security (Börjesson et al., 2014; Malvade & Satpute, 2013). Renewable energy makes about 11% of total final energy consumption of which the transport sector holds 3.3% (REN21, 2017). In line with sustainable development, for a rapid growth to occur, biofuels production for the transportation sector should have an annual growth of at least 10% by 2030 (Ersson et al., 2013). Even though, biodiesel plants cost less than petrodiesel refinery plants, in 2018, the biodiesel production cost was 3.77 $/gallon in the US, while petrodiesel was 2.56 $/gallon (El-gharabawy, 2017), hence, setting constant production cost higher than market prices (Amigun, 2008; Huang, 2016). Therefore, in securing their economic feasibility and market competitiveness there is a need for considerable incentives through subsidy mechanisms and biodiesel policies are necessary (South Africa, 2020).

Based on the similarities in fuel properties between biodiesel and petrodiesel, biodiesel is a promising and suitable biofuel in replacing petroleum fuels, with the increased oxygen contents of 11% which will allow for a smoother combustion, reduced energy content and polarity (Abbaszaadeh et al., 2012; Prabakaran & Vijayabalan, 2018). Furthermore, enhanced fuel quality is produced when blended with petrol, by achieving complete combustion subsequently lowering CO, HC, NOx emissions and intake temperature requirements on petrol compression ignition engines (Peng, 2017; Zhong, et al., 2019). Blending biodiesel with petrol improves its atomization behaviour by promoting better air-fuel mixing (Lee et al., 2017; Kanti et al., 2018).

In the work of Adam et al., (2013), they investigated the combustion effects of adding 5 and 10% biodiesel to petrol, used in a single-cylinder, direct injection, light-duty

petrodiesel engine. The study showed a reduction in ignition delay as indicated by increased cetane number and a reduced intake temperature was required, as compared to pure petrol. Moreover, high nitrogen oxides and particulate matter were emitted by compression ignition engines due to high combustion temperature, fuel-rich of oxygen, and reaction time (Hellier & Ladommatos, 2015; Sharma et al., 2020). By blending petrol with biodiesel, a low temperature compression can be achieved solving ignition problems (Zhong, et al., 2019; Zhong et al., 2021).

Nevertheless, petrol, petrodiesel and stationary combustion processes release high levels of particulate matter into the atmosphere when ignited, these discharged metals are responsible for various diseases (Rocha & Corrêa, 2018), some are devastating to the environment, and others trigger engine malfunctioning (Elkadi et al., 2014). Therefore, to avoid engine failure or environmental pollution, a continuous evaluation and examination of sediments within fuels whether in pure biodiesel or in the blended fuel is essential (Iqbal et al., 2010; Ruzinska et al., 2015). Corrosion within biodiesel is mainly caused by its component nature, compositions and place of growth of the feedstock (Qiu et al., 2011; Nguyen & Vu, 2019). Metals and metalloids are taken up in raw materials used for the manufacturing process or will accumulate overtime during storage (Garrido et al., 1994; Sánchez et al., 2015). Also, metallic tanks and containers such as stainless steel and aluminium are normally used for storage (Zuleta et al., 2012; Komariah et al., 2019), and fuel will be in direct contact with engine parts made of copper (Cu), aluminium (Al) or brass such as the fuel pump, fuel injector, pistons and piston rings (copper-rich alloy) and bronze (Zuleta et al., 2012). Nogueira & Lucio, (2011), reported that undesired compounds such as copper (Cu) will eventually contribute to degradation and contamination within engines while Iqbal et al., (2010), observed a lower fuel quality and engine, caused by exposure to these compounds. Also, Yeşilyurt et al. (2019), reported presence of Cu in biodiesel resulted in oxidation and consequent degradation. Furthermore, a study conducted by Chaves et al., (2010), reported that the stability of biodiesel through oxidation was affected by Cu, Fe, Zn along with Ni and Sn.

Studies conducted by Jain & Sharma (2014), confirmed that an increase in the concentration of metals decreased oxidation stability of non-edible biodiesel and its blends which was impacted by Fe, Ni, Mn, Co, and Cu metals. It was also reported that oxidation stability became constant after 2 ppm of metal concentration was added to the biodiesel and metals of less influence in the oxidation instability were in order of Fe < Ni < Mn < Co < Cu in both pure and blended biodiesel (Jain & Sharma, 2014). This was also supported by Dwivedi & Sharma, (2014) study, where it was reported that exposure of Cu

to biodiesel decreased oxidation stability suggesting that Al and cast-iron containers were best for storage and transportation use. While, Fazal et al (2018), concluded that lower blends of biodiesel are more sustainable than high blends or pure biodiesel with high corrosiveness caused by Cu in biodiesel and blends than in petrodiesel, reducing oxidation stability and density significantly. In a review by Singh et al (2012), biodiesel was reported to be associated with more corrosion than petrodiesel and blends in compression ignition (CI) engines which is stimulated by contact with temperature, water content, microbial growth or presence of unsaturated fatty acids in feedstocks. Luis et al., (2021), thereafter concluded that Cu was more receptive to corrosion and degradation in biodiesel-petrodiesel blends as compared to steel or Al. Consequently, storage conditions play a huge role in contamination and corrosion and lead to reduced efficiency (Komariah et al., 2021), with Cu and lead (Pb) being the most effective metals (Sentanuhady et al., 2021).

On the other hand, the corrosiveness of metallic materials made of steel, Al, Zn and Cu exposed to ethanol-petrol blends have a relation with acidity and absorption of moisture which decreases with an increase in ethanol content (Mateĭovsky et al., 2017; Rocabruno-valdés et al., 2020). Additionally, the use of petrol combustion ignition engines reduces pollution while maintaining high thermal efficiencies (Putrasari & Lim, 2017b). Therefore, the use of blended petrol-biodiesel on petrol compression ignition engines will have a significant role in combustion and emissions characteristics (Cory A. Adams et al., 2013; Zhang et al., 2019). Although some studies have evaluated the effect of metal corrosiveness on biodiesel-petrodiesel blends and ethanol-petrol blends, to the author's knowledge, there are no previous investigations reported in literature, dealing with the effect of metal contents on the long-time storage and the qualities of biodiesel-petrol blended fuels i.e., viscosity, density, flash point (FP)

6.2 Materials and Methods

6.2.1 Materials

100% biodiesel (B100) of palm, sunflower, and their blends with petrol in different ratios of 5 % biodiesel 95% petrol, 15% biodiesel 85% petrol, and 25% biodiesel 75% petrol (PB5, PB15, PB25) were prepared at Cape Peninsula University of Technology oil and gas laboratory (Bellville, Cape Town), demineralised water (MillQ, Molsheim, France) was obtained at food science and technology laboratory at Cape Peninsula University of Technology (Bellville, Cape Town). While acetone and ethanol were purchased ((> 99,5%)) from Sigma-Aldrich, South Africa. Metals such as iron (> 99,9%), zinc (98%) and Cu

(99,3%) added to the biodiesel and biodiesel-petrol blends were obtained from Merck, South Africa; and AERONTEC, South Africa).

6.2.2 Methodology

Before testing, samples were exposed to metal powders of Cu, Fe and Zn for 24 hours (h) for proper mixing. A Rancimat 743 (Metrohm, Hersau, Switzerland) was utilised in this study to determine the effect of metals on the oxidation stability of biodiesel and its blends with petrol as described in EN 14112 (NREL, 2005; Karavalakis et al., 2010). The equipment was heated at a constant temperature of 110 °C. The air tubing connected with O-ring was placed inside the reaction vessel containing 4 g of sample and a measuring vessel with 60 mL of demineralised water, which was linked together with FEP tubing adapters and properly inserted in the instrument. With the heating unit suitable temperature stable at 111.6 °C, the system was initiated, and air at rate flowing at rate of 10 L h^{-1} was bubbled into the first cell containing the sample. Thereafter, air and vapours liberated from the first cell were transported to the second cell which was closely fitted with an electrode that measured conductivity. Over time, as a rapid increase in conductivity was observed, and the induction period was reached which was indicative of oxidation stability.

6.3 Results and Discussions

6.3.1 Effect of Cu, Zn and Fe Metals on the Oxidation Stability of Palm and Sunflower Biodiesel-Petrol Blends

Figure 6-1 shows the degradation of metal contents in biodiesel with different fatty acids composition by Rancimat method of EN 14112 specification with sample held at a temperature of 110 °C. From the obtained result, it is clear that all metal contaminants influenced and promoted oxidation in palm and sunflower biodiesels (P-B100, S-B100), with a greater pronounced effect for the palm biodiesel, these metals initiate the formation of free radicals (Kivevele, 2020). The oxidation was drastically increased by Fe than by Cu or Zn in both biodiesels. This was strongly pronounced at concentrations >100 ppm, while Cu showed a significant influence at >2 ppm in palm biodiesel. In sunflower biodiesel a gradual reduction in the induction period was observed all through to 700 ppm. In contrast to the results reported in this study, Cu was reported to reduce oxidation stability more than Fe or Zn from previous researchers and the induction period was constant after 2 ppm (Shiotani & Goto, 2007; Sarin et al., 2010; Jain & Sharma, 2014; Knothe & Steidley, 2018).

In the current study Fe was observed to have the most harmful effect and appeared constant only after 500 ppm for both biodiesels, this constant after 500 ppm was also observed for Zn in S-B100. In studies by Shiotani & Goto, (2007); Fazal et al., (2018) and Nguyen & Vu, (2019), P-B100 proved to degrade more and was found to have the most corrosiveness. It was also observed that metals corrosiveness in S-B100 was mostly impacted by Fe followed by Zn and Cu. However, at concentration of 700 ppm, Cu surpassed other metals in terms of reducing the oxidation stability (Figure 6-1). For P-B100, the addition of concentration of metal (< 100 ppm) resulted in Cu having more degradation followed by Zn and Fe, but with further increase in metal the concentration above 300 ppm, Fe was found to be more fuel degrading followed by Cu and Zn. This is supported by previous studies (Baena & Calderón, 2020; Sentanuhady et al., 2021), which reported that Cu was the most metal prone to corrosion in biodiesel from other metals. While Shiotani & Goto, (2007), also found Cu had more oxidisation degradation followed by tin (Sn), Fe, Zn and Al in palm biodiesel. Thangavelu et al., (2016), reported in their study that Cu had a higher corrosion rate than Al and stainless steel in that order. Investigation by Hu et al, (Hu et al., 2012) also reported that corrosion in biodiesel from rapeseed oil was in the order of stainless Cu > carbon steel > Al > stainless steel. In the study by Fazal et al., (2012), it was discovered that palm biodiesel degraded in the order of Cu > brass > Al > cast Fe. Furthermore, a study by Komariah et al., (2021) who investigated the corrosive behaviour of different steel materials for 30 days, which are mainly Fe, and found that in stainless steel corrosion was localised while mild and galvanised steels were generalised.

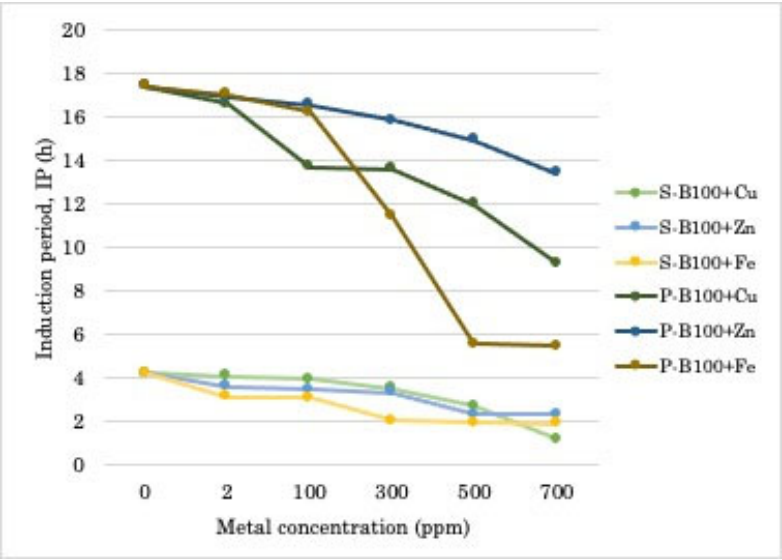


Figure 6-1. Changes in oxidation stability on sunflower and palm biodiesel at different concentrations of metal-contamination.

Figure 6-2 to Figure 6-4 depict the influence of Cu, Fe and Zn on metals oxidation stability of sunflower biodiesel-petrol blends (S-PBXX) and palm biodiesel-petrol blends (P-PBXX) namely S-PB5, S-PB15, S-PB25, P-PB5, P-PB15 and P-PB25. The reduction of the induction period and consequent oxidation instability was in the order of magnitude with increased metal concentrations and biodiesel contents. Cu demonstrated surpassing depletion in induction period for almost all metal concentrations in both biodiesel-petrol blends (PBXX) with stronger influence within P-PBXX from as low as 2 ppm. Cu was observed to reduce the oxidation stability from 24.09 h, 21.45 h and 17.22 h to 5.14 h, 4.98 h and 9.61 h in P-PB5, P-PB15 and P-PB25 respectively. This decrease continued gradually as the concentration of Cu metal increased and not attaining the minimum requirement of 20 h set for biodiesel blends. However, as the biodiesel content within the blends increases, the effect in reduction was lessened. Although, S-PBXX portrayed gradual depletion in induction period as metal content increased, the oxidation stability decreased the higher the biodiesel content got (Figure 6-4). The next element that had a significant impact on the oxidation as biodiesel content increased was Zn in P-PBXX and Fe in S-PBXX (Figure 6-2 and Figure 6-4). Nevertheless, their influence was below that of Cu with relative steadiness after the concentrations were increased from 2 ppm to 500 ppm which was as specifically noticed in Fe (Figure 6-2 and Figure 6-3) and with the exception of Zn from 300 ppm onwards.

Moreover, in PB5 and PB15, it was observed that as the metal concentration approached 700 ppm, the effect of reduced induction period became constant in P-PBXX and S-PBXX while in PB25 they continued to decrease (Figure 6-4). According to Jain & Sharma, (2014) study, in biodiesel-petrodiesel blends, it was reported that Cu metal had the most impact in decreasing induction period, with corrosion of metals increasing with increasing order of biodiesel content and as a result, biodiesel was more prone to oxidation than petrodiesel (Cursaru et al., 2014; Nguyen & Vu, 2019). On the other hand, in ethanol-petrol blends, increased oxidation corrosion was observed to be more in Al, than in mild steel, Cu and brass (Matějovský et al., 2018 & Brito-Franco et al., 2020). Setiyo et al., (2018), after studying the effect of ethanol on fuel tanks, suggested that fuel tanks made of steel (Fe_U100) have good corrosion resistance. While Thangavelu et al., (2016), reported that the corrosiveness was in order of Al < mild steel < Cu in biodiesel-petrodiesel-ethanol blends. In conclusion, oxidation was greatly influenced by Fe in pure biodiesel, while Cu was very effective in reducing oxidation stability in biodiesel-petrol blends. In P-PBXX, the order of corrosiveness was Cu > Zn > Fe and in S-PBXX Cu > Fe > Zn was obtained.

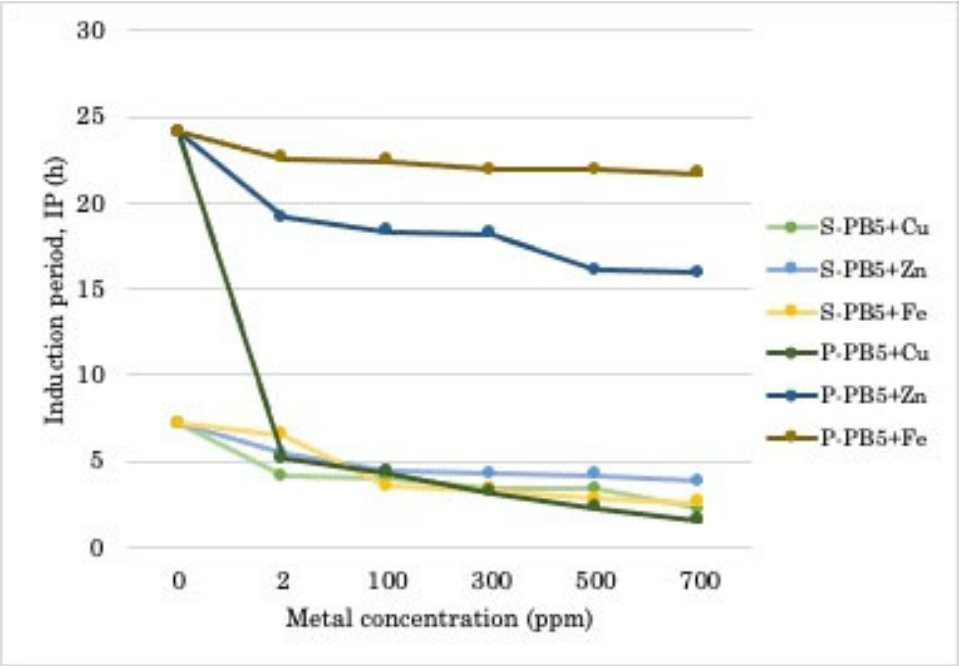


Figure 6-2. Changes in oxidation stability of PB5 sunflower and palm blends at different concentration of metal-contamination

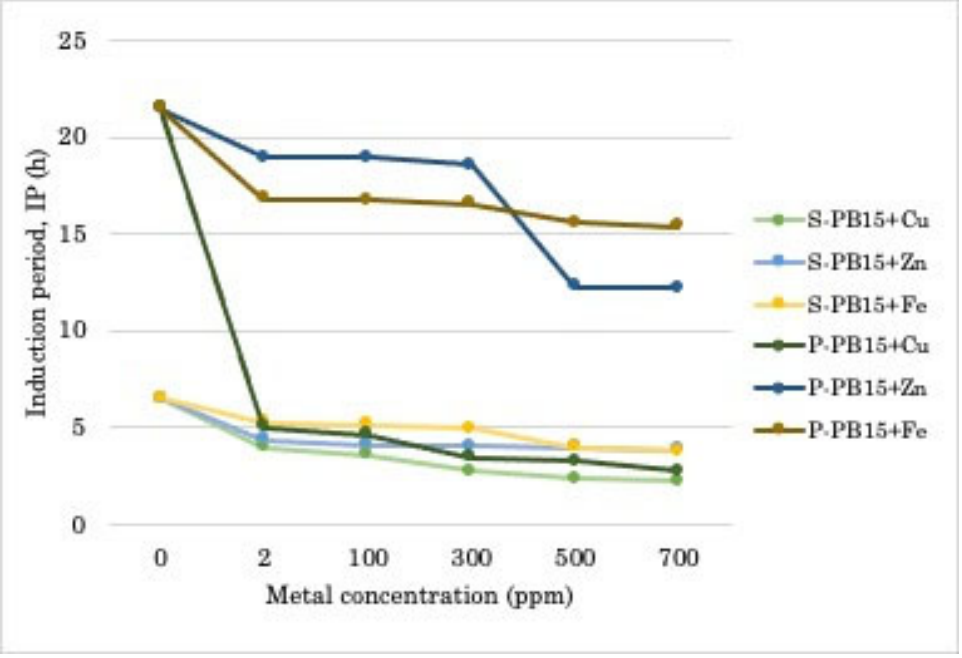


Figure 6-3. Changes in oxidation stability of PB15 sunflower and palm blends at different concentration of metal-contamination

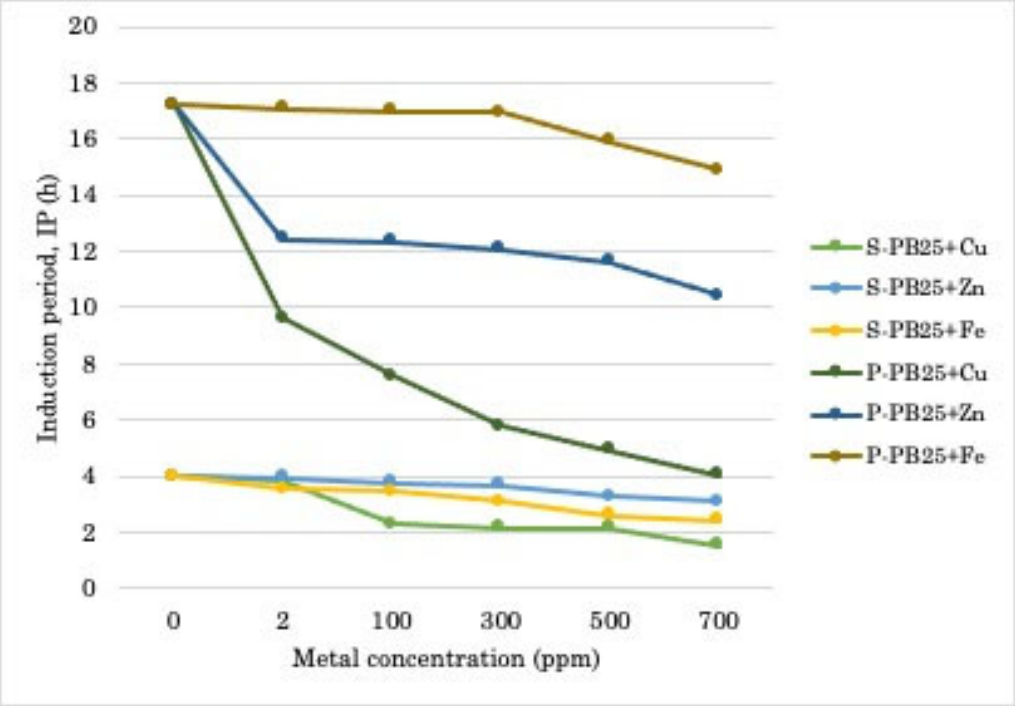


Figure 6-4. Changes in oxidation stability of PB25 sunflower and palm blends at different concentration of metal-contamination

6.3.2 Effect of Cu, Zn and Fe Metals on the Volatility of Palm and Sunflower Biodiesel

Flash point (FP) reduced from 170 °C in P-B100 to 110 °C, 150 °C and 140 °C when 2pp of Cu, Zn and Fe were added. While in S-B100, with the addition of 2 ppm of Fe, the FP was reduced to 150 °C from 175 °C (Figure 6-5). Thereafter, the results show that as the intensification in the concentration of metals lead to reduced FP, which fluctuates between 100 °C and 180 °C. Furthermore, it was noticeable that Cu and Fe effectively increased flammability by reducing FP than by Zn. Typically, the FP of biodiesel is high, which allow for the safe storage and transportation (Folayan et al., 2019).

The FP as described to be the lowest temperature necessary for ignition, was indicated by the fuel giving off enough vapours which mixes with air (Ateeq, 2019; Rao & Chary, 2018). According to ASTM D93, the FP of biodiesel should be above 130 °C (Alleman et al., 2013). Therefore, Zn was a preferred metal that had less effect on increasing the volatility of biodiesel than Cu and Fe, as it hardly reduced the FP below the standard limits set. Adding Cu, Zn and Fe metals concentration in the fuel reduced the FP, except at 700 ppm of Cu in P-B100, here FP increased. A study by Yusof et al., (2015), reported that that this high FP which represented low auto-ignition, less volatile and subsequently safer.

Additionally, the effect of Fe in S-B100 was tolerable as compared to the Fe reduction in P-B100. In previous work by Thangavelu et al., (2016), on evaluating the behaviour of biodiesel-petrodiesel-ethanol blends, they reported that there was no change observed in FP when the fuel was exposed to Cu, mild steel and Al. However, this study illustrates that there were changes in FP with the addition of various metals, with a reducing effect in the FP in the following order of Cu > Fe > Zn

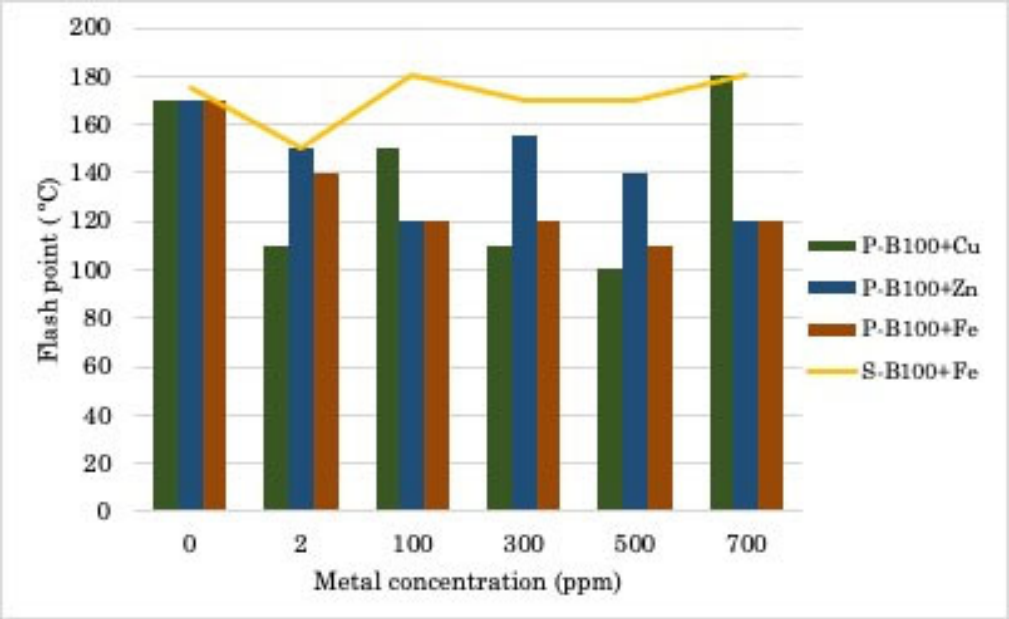


Figure 6-5. effect of Cu, Fe and Zn on the flash point of palm and sunflower biodiesels

6.3.3 Effect of Cu and Zn Metals on the Water Content of Sunflower Biodiesel-Petrol Blends

Results from Figure 6-6 illustrates exposure of Zn and Cu in S-PBXX. Increase in the concentrations of metals and biodiesel content, increased the water content within S-PBXX. Zn metal facilitated the absorption of moisture in the fuels. This is detected from concentrations as low as 2 ppm while biodiesel without metal addition had 0.03% moisture content. After the exposure of the S-B100 to 2 ppm of Zn, the value of water content increased to 1.05% and which gradually increased up to 1.99% after the addition of 700 ppm of Zn (Figure 6-6). Similarly, high water content was recorded when Cu and brass were added to biodiesel at 55 °C (Ziółkowska & Wardzińska, 2013). Fazal et al., (2010), assessed effect of stainless steel, Al, and Cu in palm biodiesel and petrodiesel at 80 °C for 1200 h and findings show that stainless steel increased water content followed by Cu and Al. The study further investigated the impact of mild steel in biodiesel at temperatures of

27, 50 and 80 °C. It was shown that an increase in temperature and duration of storage time elevated water percentage from 0% in unexposed biodiesel to 0.36% at 80 °C (Fazal et al., 2011b). Also, it was reported that Cu corrosion led to more water percentage than mild steel (Fazal et al., 2014).

In this study, Zn and Cu were added to biodiesel blends at a temperature approximately 27 °C. After about 48 h, it was observed that Zn had more effect in the absorption of moisture content than Cu and which increased with biodiesel content within the blends. This was supported by results reported by Haseeb et al., (2010), where the high water content in biodiesel-rich blends (B80, B100) was caused by bronze rather than Cu. The maximum limit for water content in biodiesel and petrodiesel is 0.05% according to EN 14214 and ASTM D975 (Alleman et al., 2013; Worldwide Fuel Charters, 2019). The addition of Zn metal at all concentrations in S-B100 and from 300 ppm to 700 ppm in S-PB25 failed to meet this standard limit (Figure 6-6). The presence of water in biodiesel will stimulate microbial growth, enhance corrosion within the tank, leading to hydrolysis of esters and triglycerides when exposed to temperature and subsequently causing more corrosion (Knothe, 2006; Thomas et al., 2007). The presence of water in biodiesel can also decrease the heat of combustion (Cursaru et al., 2014). Moreover, the hygroscopic nature of biodiesel makes it easy to draw up moisture during storage over a long period (Fazal et al., 2010; Fazal et al., 2014). Furthermore, it is clear that the type of metals biodiesel and blends are exposed to, led to the absorption of moisture. In the current study, S-PBXX exposed to Zn metal resulted in a huge draw of moisture content, even at a low water content of 1%, biofilms can form. Therefore, in designing materials compatibility for storage and transportation, brass should be avoided. (Cursaru et al., 2014; Baena & Calderón, 2020). Another reason to avoid the use of brass is due to its ability to degrade biodiesel more as a result of release of Cu^{2+} and Zn^{2+} ions which have high catalytic effect (Aquino et al., 2012). Also, the high oxygen content of biodiesel cause the formation of CuO, $CuCO_3$ and Cu_2O layers when exposed to Cu at different temperatures (Tabish, 2018; Zuleta et al., 2012)

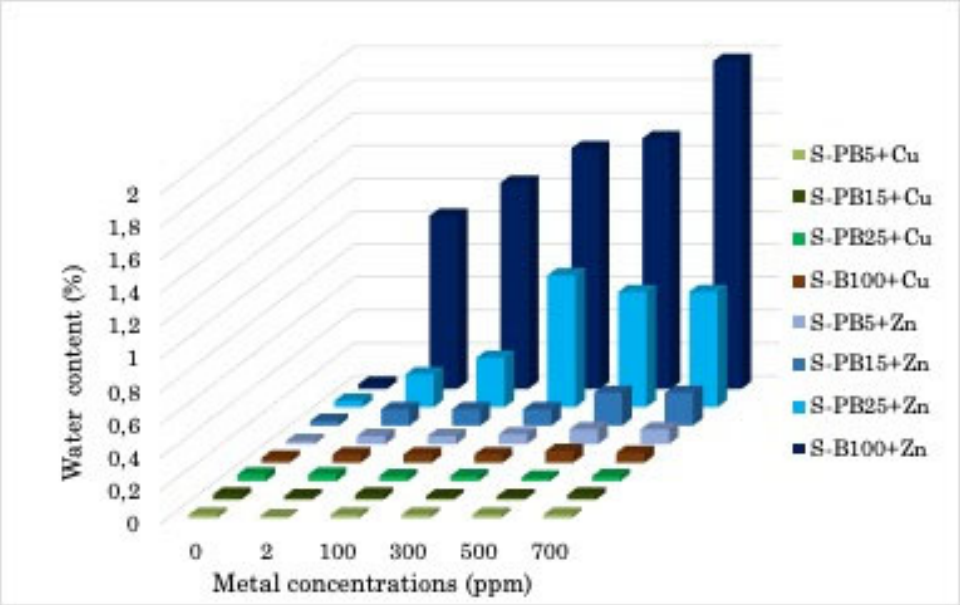


Figure 6-6. Water content changes in sunflower biodiesel-petrol blends before and after exposure to Cu and Zn metals

6.3.4 Effect of Cu, Zn and Fe Metals on the Acidity within Palm and Sunflower Biodiesel-Petrol Blends

The total acid values of biodiesel before (at 0 ppm) and after being exposed to metals (at 2, 100, 300, 500, and 700 ppm) are presented in Figure 6-7. Before the immersion of metals in the biodiesels, it was observed that unexposed S-B100 had an acid number of 0.46 mgKOH/g, which was below the standard limit (0.5 mgKOH/g) set by ASTM D6751, while unexposed P-B100 had an acid value of 0.55 mgKOH/g, which was slightly above the limit set. With the immersion of the metals in the biodiesel at room temperature, Cu and Zn marginally affected the S-B100, while Fe had a significant influence in promoting acidity at all concentrations elevating the acid number from 0.46 mgKOH/g to 2.02, 2.13 and 1.9 mgKOH/g at 2, 100, and 300 ppm respectively. In P-B100, the immersion of all metals increased the acid number, resulting in values above-set limits, with nearly similar values fluctuating between 1.46 to 1.79 mgKOH/g for Cu and 1.68 to 1.9 mgKOH/g for Zn. With the immersion of Fe into the biodiesel, a magnitude of increased concentration was observed. However, after 300 ppm it became constant.

High acid number values in the fuel will result in residual free fatty acid, which will lead to the formation of deposits and corrosion (Alleman et al., 2013). Cu was been found to increase corrosion effects in biodiesel, leading to more acid value than in other metals like stainless steel, mild steel and Al (Fazal et al., 2010; Hu et al., 2012; Fazal et al., 2014), as well as brass and cast Fe (Fazal et al., 2012). Interestingly, in this study reports high acid values in S-B100 which were observed in the order of Fe > Zn > Cu. In P-B100, it was in

the order of Zn > Cu > Fe at low concentrations (2 to 300 ppm) and in the order of Cu > Zn > Fe at high concentrations (500 to 700 ppm). Presumably, the higher effect by Fe observed to increase the acidity of S-B100 was caused by presence of fatty acids after oxidation i.e. linoleic acids (Tsuchiya et al., 2006). Also, Cu has been reported to have a slow rate of corrosion, which was intensified at higher temperatures and longer time (Fazal et al., 2010; Haseeb et al., 2010; Ziółkowska & Wardzińska, 2013). Additionally, when Figure 6-7 and Figure 6-1 are compared, a direct correlation between acid value number and oxidation is observed, therefore affirming to the high acid number value in S-B100 and P-B100.

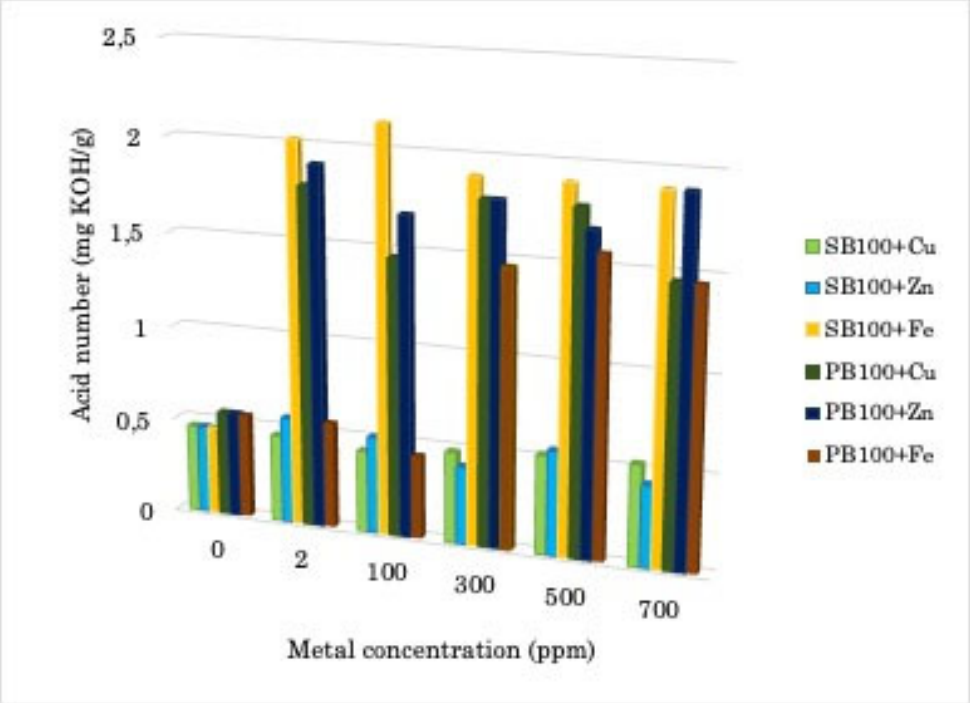


Figure 6-7. Change in totatl acid number after immersion of Cu, Fe and Zn in palm and sunflower biodiesels

The total acid number (TAN) (Figure 6-8 to Figure 6-10) decreased in PBXX as compared to B100, since biodiesel was blended with petrol, especially in S-BPXX. It was also evident that exposure to metals barely affected the S-PBXX when compared to the increase in the acidity observed for P-PBXX. In S-PBXX, it was observed that an increase in TAN was impacted by these metals in order of Fe > Cu > Zn and with the increase in metal concentrations and biodiesel content. The decrease in the TAN was observed in the order of Zn > Cu at lower concentrations (2-100 ppm) and Cu > Zn in the higher concentrations (300-700 ppm) of S-PB15 and SPB25, while Fe increased the TAN. In P-PBXX, the trend of increased acidity was Fe > Zn > Cu and with an increase in biodiesel content. Overall,

Fe had the most significant effect in increasing acidity within both blends as the biodiesel content increases. Similarly, Baena & Calderón, (2020), showed that carbon steel (Fe alloy) and Cu showed high corrosiveness in biodiesel blends after studying the corrosion behaviour of those metals together with stainless steel, Sn and Al. A report by Matějovský et al., (2018), demonstrated that oxidised steel, Al, brass and Cu in ethanol-petrol blends, and the highest increase in TAN was caused by steel and Al. Cu was also reported to be more susceptible to corrode in biodiesel and biodiesel-petrodiesel-bioethanol blends at room temperature (Cursaru et al., 2014; Thangavelu et al., 2015). Therefore, we can conclude that in biodiesel-petrol blends, Fe triggered most acidity or increase in TAN regardless of the type of biodiesel blended. Moreover, Cu will promote acidity in the biodiesel-petrol blends as the content of biodiesel increase within blends Figure 6-10, while in a lower blend (PB5), Zn showed a more pronounced effect (Figure 6-8).

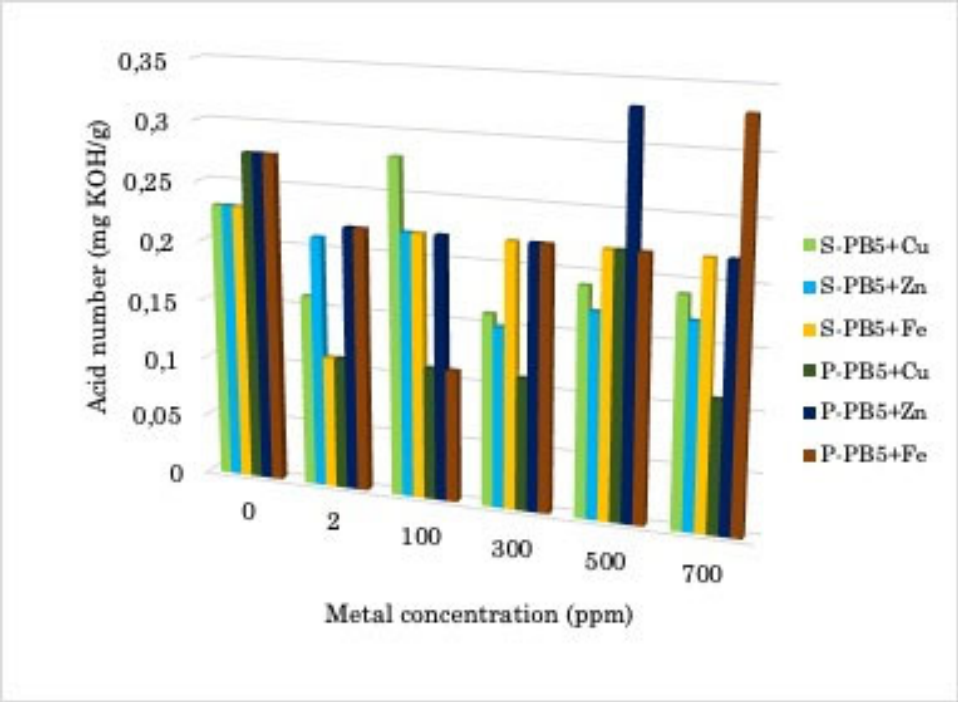


Figure 6-8. Change in total acid number after immersion of Cu, Fe and Zn in palm and sunflower PB5 blends

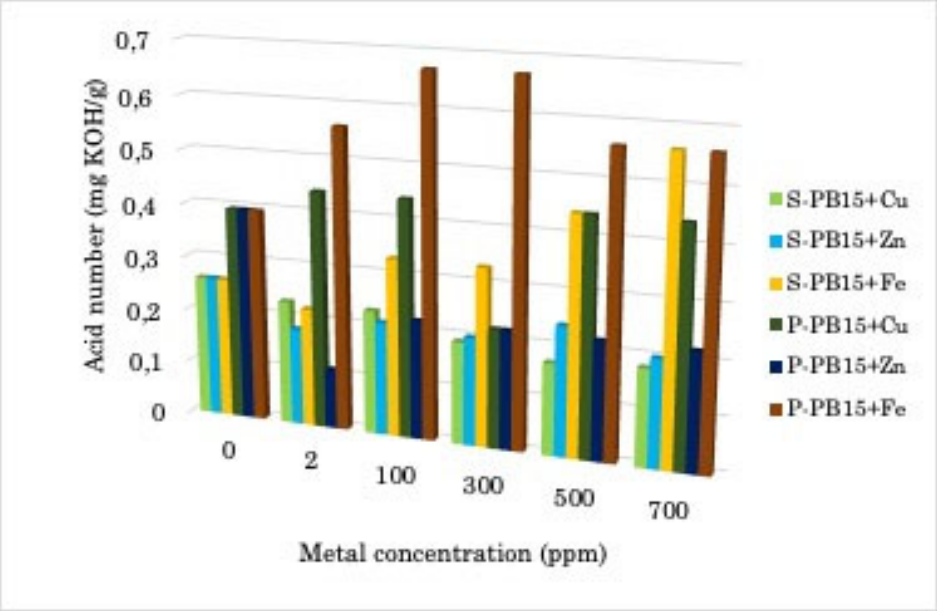


Figure 6-9. Change in total acid number after immersion of Cu, Fe and Zn in palm and sunflower PB15 blends

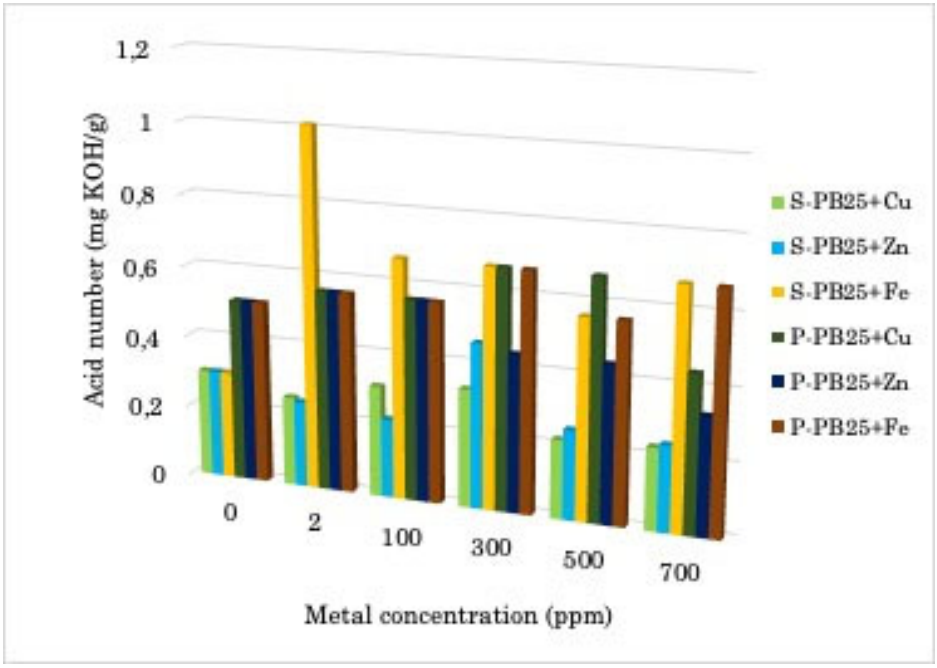


Figure 6-10. Change in total acid number after immersion of Cu, Fe and Zn in palm and sunflower PB25 blends

6.3.5 Effect of Cu, Zn and Fe Metals on the Viscosity within Palm and Sunflower Biodiesel-Petrol Blends

Figure 6-11 shows the change in viscosity of S-B100 and P-B100 without metal exposure (0 ppm) and after being exposed to different concentrations of Cu, Zn and Fe metals. In S-

B100, there is a slight reduction in viscosity values for S-B100 in all metal concentrations, this shows the viscosity was minimally affected after being exposed to metals. Meanwhile, in P-B100, it was observed that exposure to Cu decreased viscosity significantly followed by Zn and Fe. In the study conducted by Aquino et al., (2012), a contradictory observation was reported, when they assessed the influence of brass and Cu metals in biodiesel in light, darkness and darkness with increased temperature (55 °C). They concluded that immersing those metals in biodiesel elevated viscosity, the highest increase in the viscosity was recorded as the biodiesel was exposed to metals at 55 °C, and while lowest viscosity was observed in the absence of light, with similar close values for the unexposed biodiesel (Aquino et al., 2012). In the study by Fazal et al., (2010), which evaluated stainless steel, Al and Cu effects in biodiesel and petrodiesel at 80 °C for 1200 h were evaluated, they found out that the viscosity values were nearly similar to that of unexposed in petrodiesel, while Cu increased the viscosity in biodiesel.

Presence of fatty acids in biodiesel makes it more susceptible to reaction with metals (Haseeb et al., 2010). External factors such as light and temperature will promote more corrosion (Aquino et al., 2012). In this study, the corrosion reduced viscosity, where Cu was effective in P-B100, while Fe was observed to have more influence in reducing the viscosity of S-B100

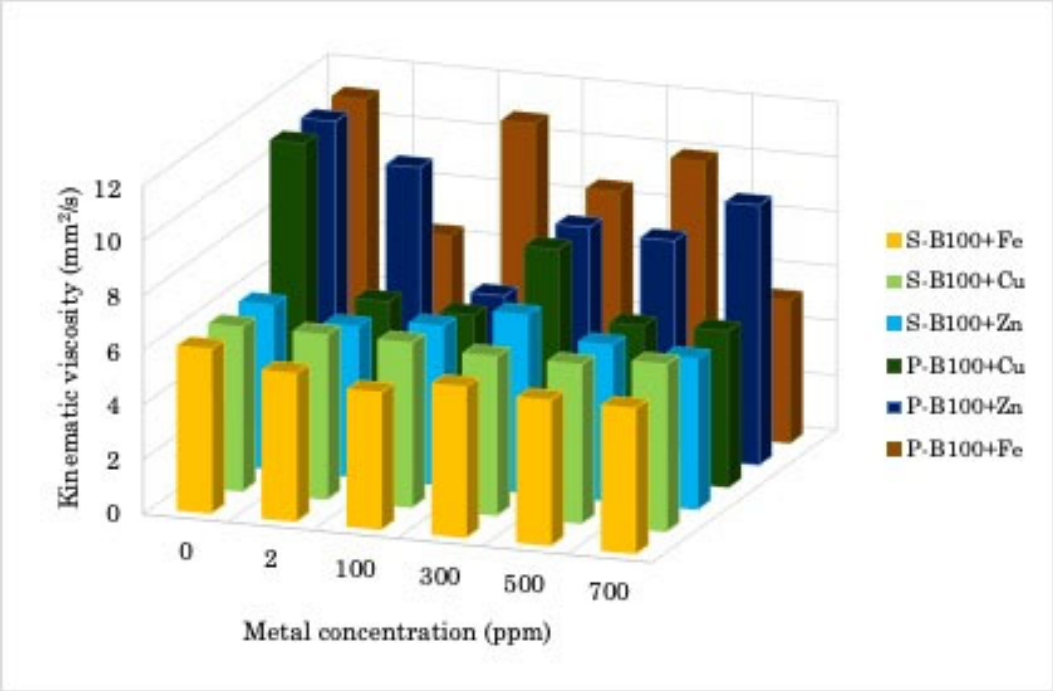


Figure 6-11. Change in viscosity of sunflower and palm biodiesels before and after exposure to metals

As both biodiesel blends were exposed to metals, changes in their viscosities are shown (Figure 6-12 to Figure 6-14). As observed increase in viscosity led by an increase in biodiesel content and with subsequent decrease of petrol, was caused by the presence of hydrogen bonding in biodiesel (Azahari et al., 2016; Gad & Ismail, 2021). By adding metals in both blended fuels, viscosities were reduced, especially in P-PBXX. It is clear that Fe was most effective in the viscosity reduction in S-PBXX, and while in P-PBXX, Zn showed the highest impact on viscosity reduction at lower blends of PB5 and PB15. With increased blending (PB25) in P-PBXX, Cu and Fe had similar effects in reducing the viscosity, with the same values observed at metal concentrations of 300 ppm onwards (Figure 6-14). In S-PB15 (700 ppm), a huge increase in viscosity caused by Cu was noticed. This was not surprising as Cu has been shown to cause a high corrosion effect in biodiesel blends (Norouzi et al., 2012; Cursaru et al., 2014). Very high viscosity is undesirable as it will increases the frictional loss (Agarwal, 2007). While extremely low viscosity can lead to excessive wear of bearing within the engine causing more corrosion as a result of more asperity contact between the surfaces (Carden et al., 2013; Zhang et al., 2021). Therefore, the viscosity needs to be high enough, within the standard limit, to prevent internal flow and low enough to stop energy loss (Khuong et al., 2017).

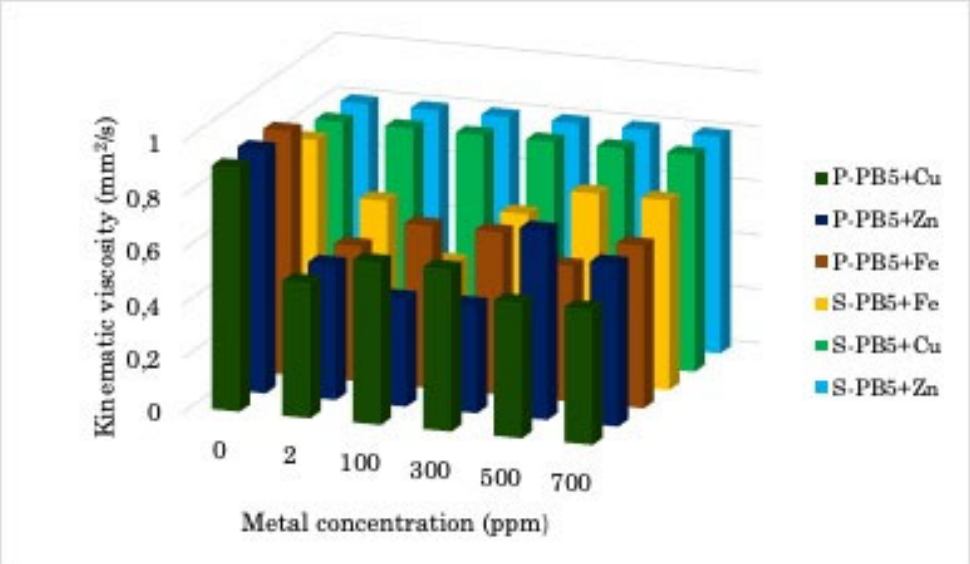


Figure 6-12. Change in viscosity of sunflower and palm biodiesel-petrol blends of PB5 before and after exposure to metals

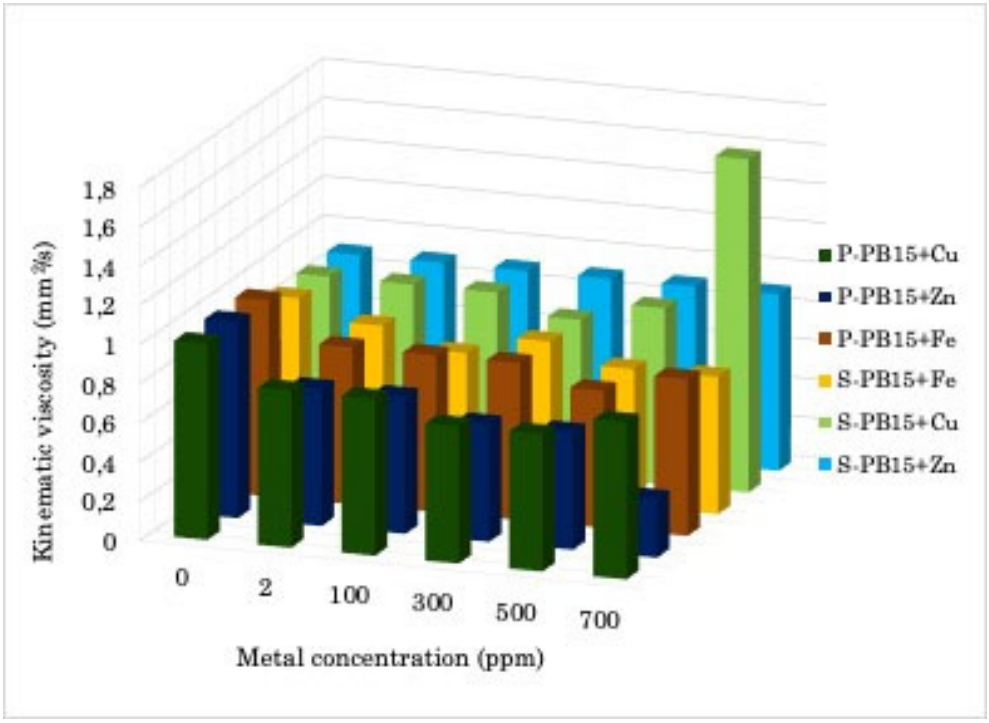


Figure 6-13. Change in viscosity of sunflower and palm biodiesel-petrol blends of PB15 before and after exposure to metals

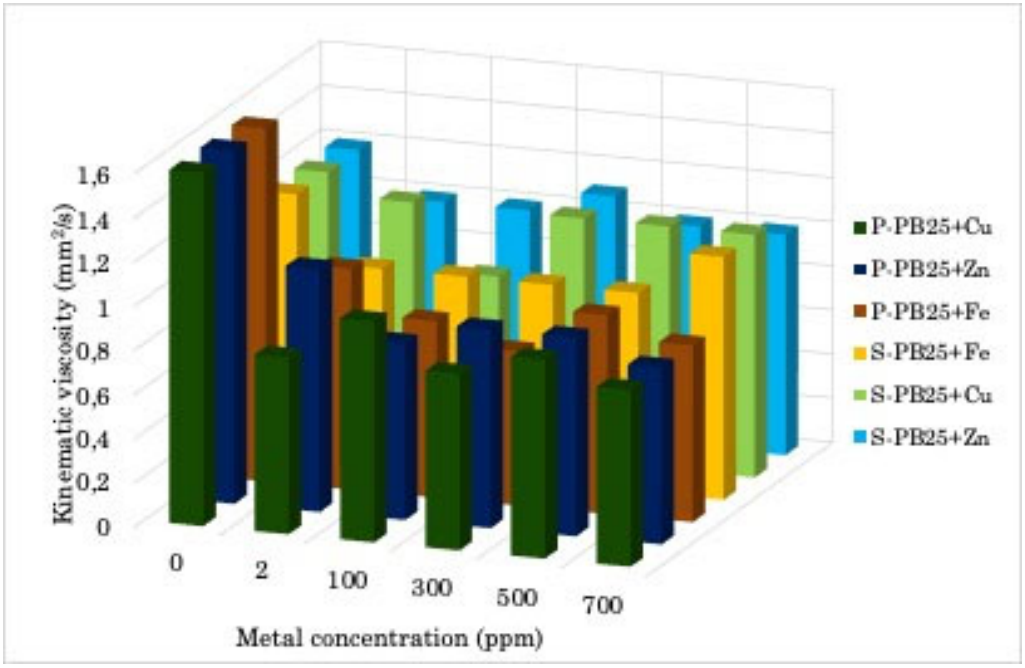


Figure 6-14. Change in viscosity of sunflower and palm biodiesel-petrol blens of PB25 before and after exposure to metals

6.3.6 Effect of Cu, Zn and Fe Metals on the Density in Palm Biodiesel Blends

Figure 6-15 shows the effects of metal concentrations on the density of biodiesel. It is evident that exposure of Cu, Zn and Fe metals at 2 ppm, increased the density of the fuel from 882 kg/m^3 in P-B100 to 886, 886 and 844 kg/m^3 for Cu, Zn and Fe respectively. It was worth noticing that the addition of 2 ppm of Cu concentration, the density was observed to be 844 kg/m^3, which failed to meet the international standard set for biodiesel. Subsequently, an increase in the concentration of metals above 2 ppm, led to increased density. The metal with the most significant impact on increasing density was observed to be Fe, followed by Zn and Cu. However, these densities were still within limits set by EN 14214 standard (< 890 kg/m^3). Similar findings were reported when biodiesel was exposed to mild steel (Fazal et al., 2011b). However, Cu was found to surpass the given standard limit of density in biodiesel. While stainless steel and Al met the specification after their exposure to biodiesel (Fazal et al., 2010). However, from the observations in the current study, Cu had the least effect in increasing the density of biodiesel at low (2-100 ppm) and to high (700 ppm) concentrations (Figure 6-15).

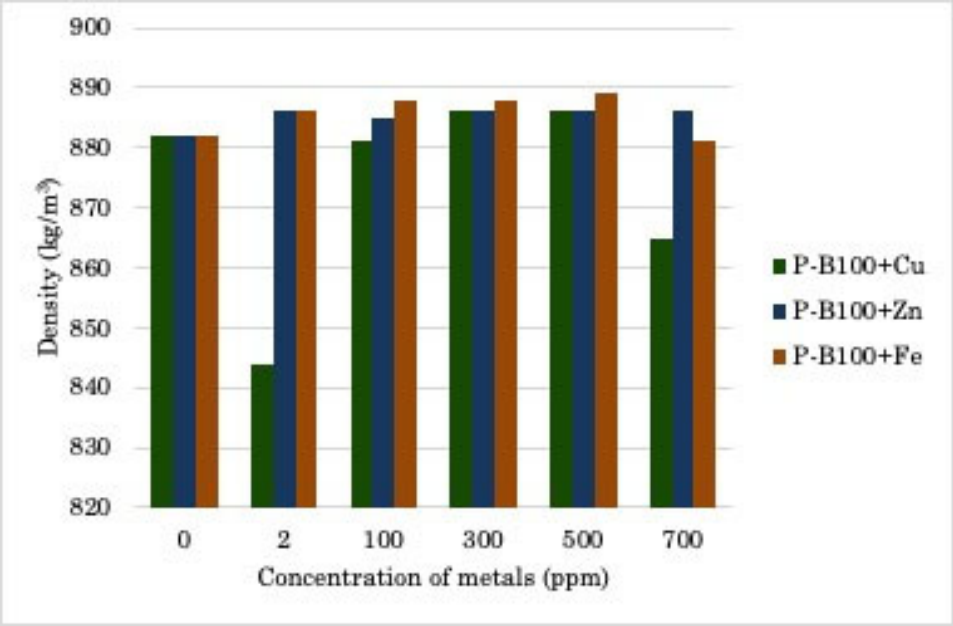


Figure 6-15. Change in density for palm biodiesel before and after exposure to metals

An increase in density was also observed for unexposed relative to exposed biodiesel blends (Figure 6-16 to Figure 6-18). In PB5, as the concentrations increased the density increased, while in PB15 and PB25 there was a decrease in the density of the exposed PBXX. Cu was shown to be more harmful in lower biodiesel blend (PB5) leading to an extreme increase in density followed by Fe and as biodiesel content increased in the blends (PB15), Zn had the most significant impact by reducing the density significantly, followed by Cu and Fe

(Figure 6-17). It was also noticeable that as biodiesel blending increased (PB25), the Cu effect increased by reducing the density (Figure 6-18), which was similarly found by Fazal et al. (2018). Generally, the corrosion rate caused by Cu is the highest although it differs with material and biodiesel under study (Baena & Calderón, 2020; Cursaru et al., 2014; Sylvester et al., 2015). Additionally, Al, Zn, brass and bronze are not compatible with biodiesel (Zuleta et al., 2012; Yeşilyurt et al., 2019). This was observed by the huge decrease in the density caused by Zn and Cu (Figure 6-17 to Figure 6-18). In conclusion, Fe was more harmful in pure biodiesel and Cu showed the most significant effect in increasing the density of biodiesel and biodiesel blend of PB5. While a significant decrease in the density of PB15 and PB25 was caused by Zn and Cu respectively.

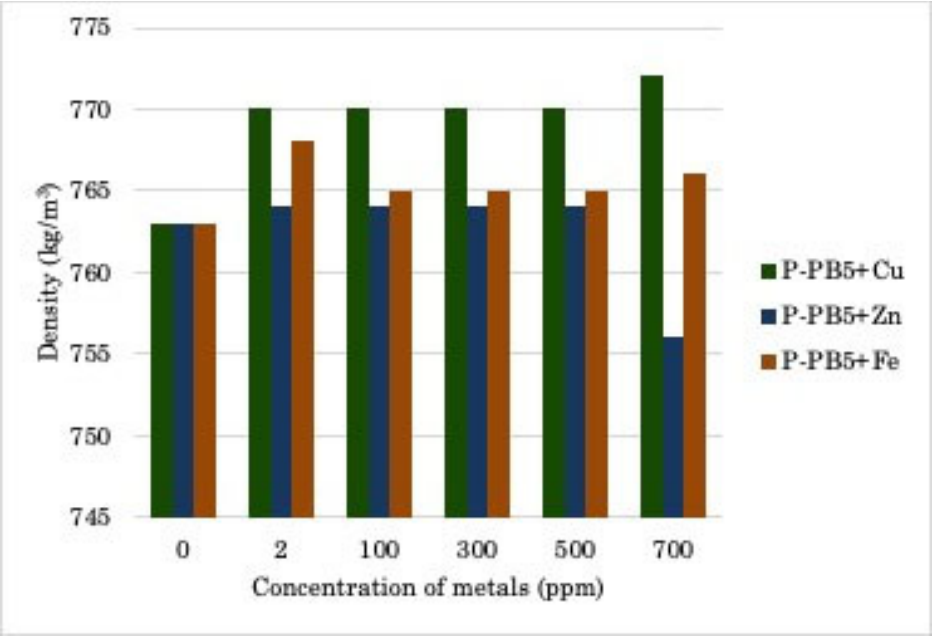


Figure 6-16. Change in density for palm biodiesel blends of PB5 before and after exposure to metals

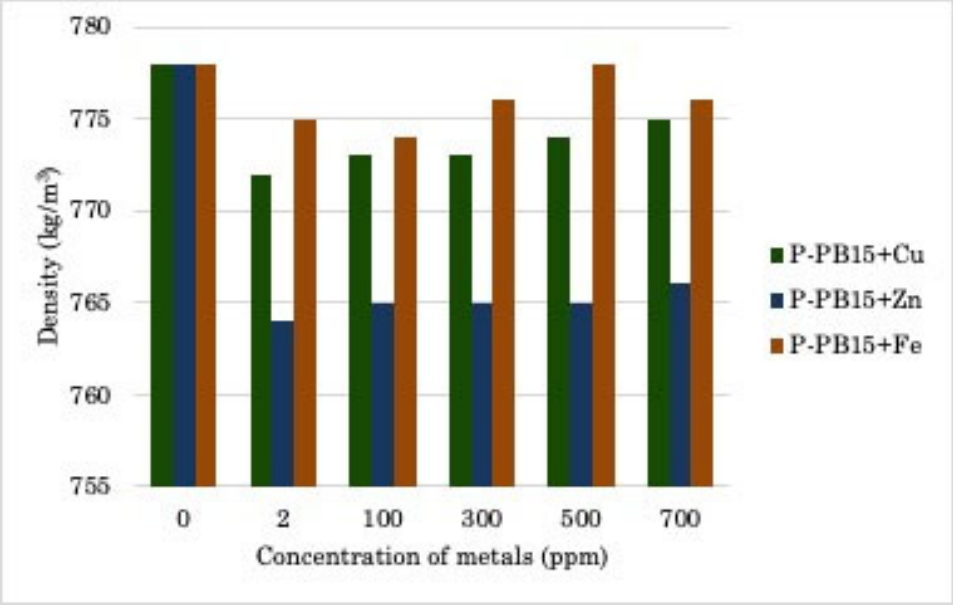


Figure 6-17. Change in density for palm biodiesel blends of PB15 before and after exposure to metals

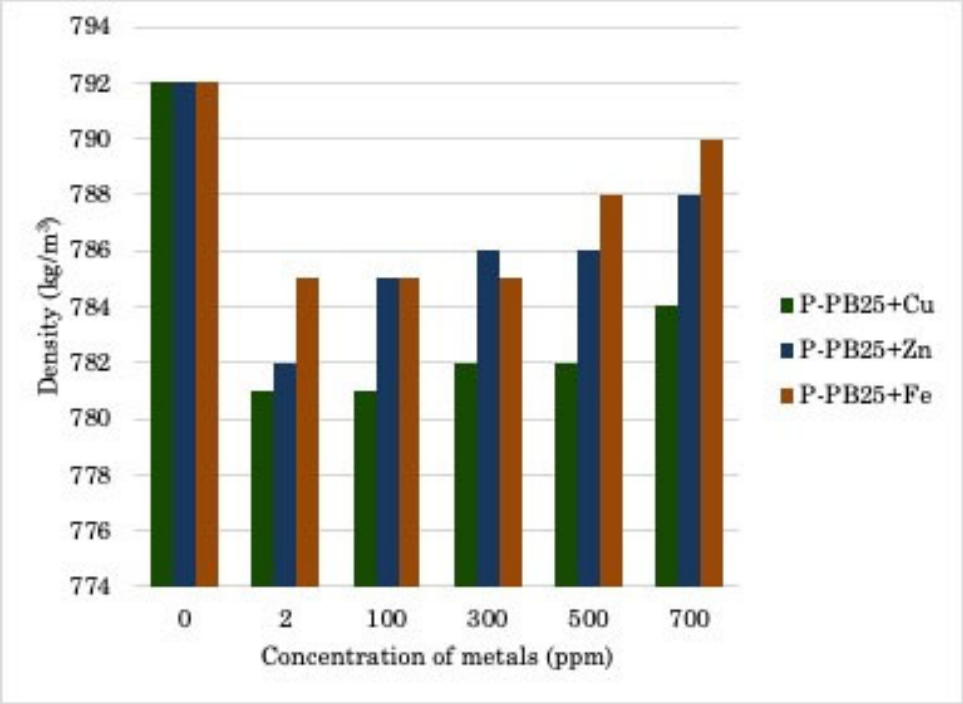


Figure 6-18. Change in density for palm biodiesel blends of PB25 before and after exposure to metals

6.3.7 Effect of Cu and Zn Metals on Nitrates and Sulphates in Sunflower Biodiesel Blends

Changes in nitrate contents as biodiesel blends were exposed to metals at different concentrations is evident (Figure 6-19). Biodiesel without metals had nitrates of 10 ppm, as biodiesel was blended. An increase in nitrate contents were observed for PB5, PB15 and

PB25 having 15, 14 and 14 ppm for respectively. Fe and Zn did not affect nitrate composition. While exposure to Cu in S-PB15, increased nitrates concentrations from 14 ppm to 15 ppm and from 100 to 700 ppm was observed. The formation of nitrates could have resulted from a prompt mechanism where series of hydrocarbon fragments react with oxygen (Palash et al., 2013). High nitrates are one of many problems that can lead to potential cooling failure.

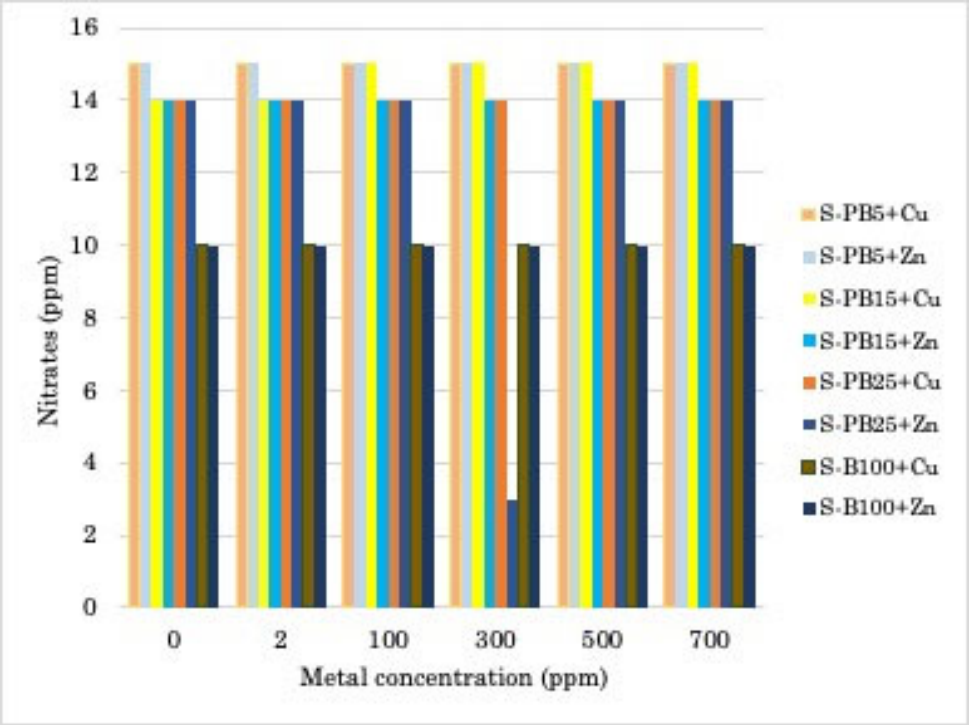


Figure 6-19. Changes in nitrates for sunflower biodiesel blends before and after exposure to metals

Biodiesel samples without metals had sulphates of 111 ppm, as a result of sulfur-based acids reacting with oils. With blending biodiesel with petrol, in the proportion of PB5, PB15 and PB25, sulphate concentrations decreased to 24, 34 and 49 ppm respectively (Figure 6-20). It is worthy of note that, there was a significant reduction in sulphate concentrations when petrol was added to the biodiesel. Sulphates are produced from combustion. An increase in sulphates is observed when there is incomplete combustion, with subsequently high residue indication. Therefore, pure biodiesel had more sulphates which was observed to decrease as petrol was added. However, Cu had an influence on a slight increase in sulphates particularly for PB15, where it increased from 34 ppm of unexposed blends to 37 ppm at concentration of 100 to 700 ppm. While in PB25, in unexposed blends the sulphate concentration was observed to be 49 ppm, which increased

to 52 ppm at concentration of 2 ppm. Overall, Cu slightly increased the sulphates concentration, while Zn seemed to decrease it.

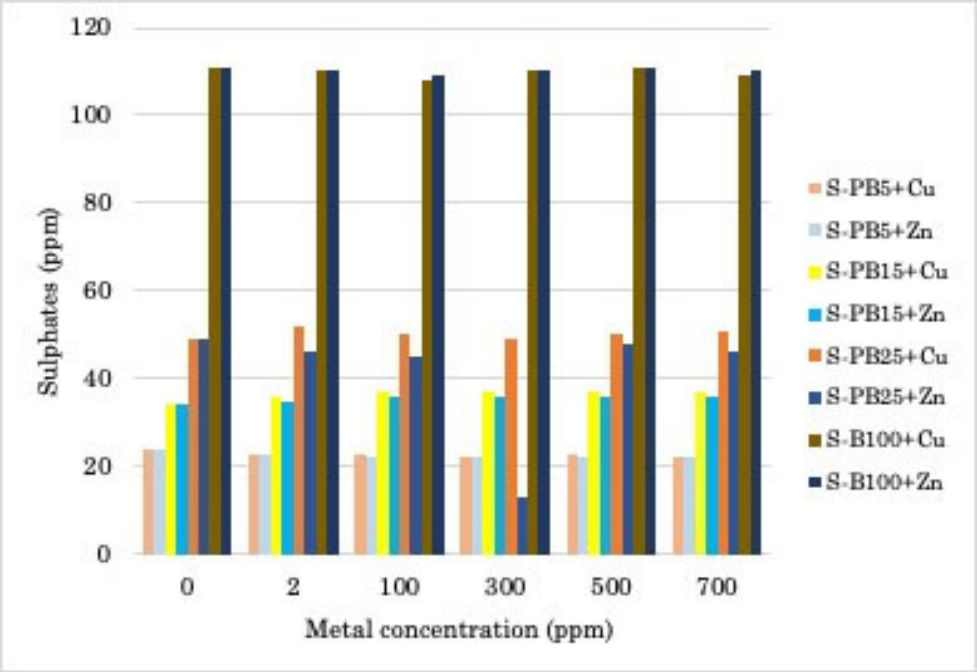


Figure 6-20. Changes in sulphates for sunflower biodiesel blends before and after exposure to metal

6.4 Conclusions

Corrosion of metals caused during storage and transportation of fuels is a serious issue in the automotive industry. The use of biodiesel as an alternative fuel has been widely studied and many studies are finding ways of blending it with petroleum fuels in order to reduce pollution. However, due to its nature, storage conditions and materials which are normally used in storing fuels, it is very crucial to continuously evaluate biodiesel and its blends since contaminated fuels can lead to many problems within fuel, engine, environment, and efficiency. After studying the effect of Cu, Zn and Fe on the characteristics of petrol blended with biodiesel made from waste sunflower and palm oils, the following conclusions were made:

- Aggravation in the oxidation of the PBXX was influenced by the increase in metal concentration and type of biodiesel produced. In both biodiesels, Fe significantly decreased oxidation stability, failing European standard specification set for biodiesel, in P-B100 from 500 ppm onward, and in all the concentrations of S-B100. Moreover, Cu in S-B100 notably decreased oxidation stability at a high concentration of 700 ppm. The overall corrosiveness of metals in sunflower

biodiesel was Fe > Zn > Cu, and Zn, which promoted increased moisture absorption. While in palm biodiesel the corrosiveness was caused by Cu > Zn > Fe.

- In biodiesel-petrol blends, Cu was very effective in reducing oxidation stability followed by Zn and Fe, Also, Cu slightly increased particulate matter of nitrates and sulphates.
- All metals decreased viscosity with the most significant effect caused by Cu and Fe. Fe negatively affected acid number and density. Density was increased the most when Cu was exposed in pure biodiesel, while in biodiesel-petrol blends Cu and Zn also had a negative influence.
- Overall, Fe and Cu portrayed the worst and most negative effects in most properties tested. Therefore, these metals and their alloys would be undesirable for use in manufacturing storage or transportation facilities of biodiesel and biodiesel-petrol blends, since they would jeopardise the fuel quality and consequently have negative impacts on the engine and environment.

6.5 References

Aalam, C.S. & Saravanan, C.G. 2017. Effects of nano metal oxide blended Mahua biodiesel on CRDI diesel engine. *Ain Shams Engineering Journal*, 8(4): 689–696. https://doi.org/10.1016/j.asej.2015.09.013

Abbaszaadeh, A., Ghobadian, B., Omidkhah, M.R. & Najafi, G. 2012. Current biodiesel production technologies: A comparative review. *Energy Conversion and Management*, 63: 138–148. http://dx.doi.org/10.1016/j.enconman.2012.02.027

Adams, C.A., Loeper, P., Krieger, R., Andrie, M.J. & Foster, D.E. 2013. Effects of biodiesel-gasoline blends on gasoline direct-injection compression ignition (GCI) combustion. *Fuel*, 111: 784–790. http://dx.doi.org/10.1016/j.fuel.2013.04.074

Agarwal, A.K. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science*, 33(3): 233–271. http://dx.doi.org/10.1016/j.pecs.2006.08.003

Alleman, T.L., Fouts, L. & Chupka, G. 2013. Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011. *National Renewable Energy Laboratory*: 1–35. Available online: http://www.osti.gov/bridge [accessed on 02 August 2021]

Amigun, B. 2008. Processing Cost Analysis of the African Biofuels Industry with Special Reference to Capital Cost Estimation Techniques. Unpublished PhD Thesis, University of Cape Town, Cape Town., South Africa. 2008.

Aquino, I.P., Hernandez, R.P.B., Chicoma, D.L., Pinto, H.P.F. & Aoki, I. V. 2012. Influence of light, temperature and metallic ions on biodiesel degradation and corrosiveness to copper and brass. *Fuel*, 102: 795–807. http://dx.doi.org/10.1016/j.fuel.2012.06.011

Ateeq, E.A. 2015. Biodiesel Viscosity and Flash Point Determination. *European Journal of Advances in Engineering and Technology*,: 9–14. Available online: https://www.researchgate.net/publication/275526328_Biodiesel_Viscosity_and_Flash_Point_Determination. [Accessed on 31 July 2021]

Azahari, S.R., Salahuddin, B.B., Noh, N.A.M., Nizah, R. & Rashid, S.A. 2016. Physico-chemical and emission characterization of emulsified biodiesel/diesel blends. *Biofuels*, 7(4): 337–343. http://dx.doi.org/10.1080/17597269.2015.1135374

Baena, L.M. & Calderón, J.A. 2020. Effects of palm biodiesel and blends of biodiesel with organic acids on metals. *Heliyon*, 6(5): 2–13. http://dx.doi.org/10.1016/j.heliyon.2020.e03735

Bergthorson, J.M. & Thomson, M.J. 2015. A review of the combustion and emissions properties of advanced transportation biofuels and their impact on existing and future engines. *Renewable and Sustainable Energy Reviews*, 42: 1393–1417. http://dx.doi.org/10.1016/j.rser.2014.10.034

Börjesson, M., Ahlgren, E.O., Lundmark, R. & Athanassiadis, D. 2014. Biofuel futures in road transport - A modeling analysis for Sweden. *Transportation Research Part D: Transport and Environment*, 32(2014): 239–252. http://dx.doi.org/10.1016/j.trd.2014.08.002

Brito-Franco, A., Uruchurtu, J., Rosales-Cadena, I., Lopez-Sesenes, R., Serna-Barquera, S.A., Hernandez-Perez, J.A., Rocabruno-Valdes, C. & Gonzalez-Rodriguez, J.G. 2020. Corrosion behavior of al in ethanol-gasoline blends. *Energies*, 13(2.1): 2–17. http://dx.doi.org/10.3390/en13215544

Carden, P., Pisani, C., Andersson, J., Field, I., Lainé, E., Bansal, J. & Devine, M. 2013. The effect of low viscosity oil on the wear, friction and fuel consumption of a heavy-duty truck engine. SAE Technical Papers, 2(2): 311–319. http://dx.doi.org/10.4271/2013-01-0331

Castellini, M., Ubertini, S., Barletta, D., Baffo, I., Buzzini, P. & Barbanera, M. 2021. Techno-Economic Analysis of Biodiesel Production from Microbial Oil Using Cardoon Stalks as Carbon Source. 14: 1–21. https://doi.org/10.3390/en14051473

Chaves, E.S., José, E., Araujo, R.G.O., Vladimir, J., Lúcia, V., Frescura, A. & Curtius, A.J. 2010. Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS. *Microchemical Journal*, 96(1): 71–76. http://dx.doi.org/10.1016/j.microc.2010.01.021

Cursaru, D.L., Brănoiu, G., Ramadan, I. & Miculescu, F. 2014. Degradation of automotive materials upon exposure to sunflower biodiesel. *Industrial Crops and Products*, 54: 149–158. https://doi.org/10.1016/j.indcrop.2014.01.032

Dwivedi, G. & Sharma, M.P. 2014. Impact of antioxidant and metals on biodiesel stability-a review. *Journal of Materials and Environmental Science*, 5(5): 1412–1425. Available online: https://www.researchgate.net/publication/264006609 [accessed on 05 August 2018]

El-gharabawy, Allah, A.S.A. 217. Cost Analysis for Biodiesel Production from Waste Cooking Oil Plant in Egypt. *International Journal of Smart Grid*, 1(1): 17–25. Available online: https://www.researchgate.net/publication/343166924 [accessed on 16 April]

Elkadi, M., Pillay, A., Manuel, J., Khan, M.Z., Stephen, S. & Molki, A. 2014. Sustainability study on heavy metal uptake in neem biodiesel using selective catalytic preparation and hyphenated mass spectrometry. *Sustainability*, 6(5): 2413–2423. https://doi.org/10.3390/su6052413

Ersson, C., Ammenberg, J. & Eklund, M. 2013. Biofuels for transportation in 2030: Feedstock and production plants in a Swedish county. *Biofuels*, 4(4): 379–395. https://doi.org/10.4155/bfs.13.23

Fazal, M.A., Haseeb, A.S.M.A. & Masjuki, H.H. 2010. Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials. *Fuel Processing Technology*, 91(10): 1308–1315. http://dx.doi.org/10.1016/j.fuproc.2010.04.016

Fazal, M.A., Haseeb, A.S.M.A. & Masjuki, H.H. 2012. Degradation of automotive materials in palm biodiesel. *Energy*, 40(1): 76–83. http://dx.doi.org/10.1016/j.energy.2012.02.026

Fazal, M.A., Haseeb, A.S.M.A. & Masjuki, H.H. 2011. Effect of temperature on the corrosion behavior of mild steel upon exposure to palm biodiesel. *Energy*, 36(5): 3328–3334. http://dx.doi.org/10.1016/j.energy.2011.03.028

Fazal, M.A., Jakeria, M.R. & Haseeb, A.S.M.A. 2014. Effect of copper and mild steel on the stability of palm biodiesel properties: A comparative study. *Industrial Crops and Products*, 58: 8–14. http://dx.doi.org/10.1016/j.indcrop.2014.03.019

Fazal, M.A., Suhaila, N.R., Haseeb, A.S.M.A., Rubaiee, S. & Al-zahrani, A. 2018. In fl uence of copper on the instability and corrosiveness of palm biodiesel and its blends : An assessment on biodiesel sustainability. *Journal of Cleaner Production*, 171: 1407–1414. https://doi.org/10.1016/j.jclepro.2017.10.144

Folayan, A.J., Anawe, P.A.L., Aladejare, A.E. & Ayeni, A.O. 2019. Experimental investigation of the effect of fatty acids configuration, chain length, branching and degree of unsaturation on biodiesel fuel properties obtained from lauric oils, high-oleic and high-linoleic vegetable oil biomass. *Energy Reports*, 5: 793–806. https://doi.org/10.1016/j.egyr.2019.06.013

Gad, M.S. & Ismail, M.A. 2021. Effect of waste cooking oil biodiesel blending with gasoline and kerosene on diesel engine performance, emissions and combustion characteristics. *Process Safety and Environmental Protection*, 149: 1–10. https://doi.org/10.1016/j.psep.2020.10.040

Garrido, M.D., Frías, I., Díaz, C. & Hardisson, A. 1994. Concentrations of metals in vegetable edible oils. *Food Chemistry*, 50(3): 237–243. https://doi.org/10.1016/0308-8146(94)90127-9

Harfoot, M.B.J., Tittensor, D.P., Knight, S., Arnell, A.P., Blyth, S., Brooks, S., Butchart, S.H.M., Hutton, J., Jones, M.I., Kapos, V., Scharlemann, J.P.W. & Burgess, N.D. 2018. Present and future biodiversity risks from fossil fuel exploitation. *Conservation Letters*, 11(4): 1–13. http://dx.doi.org/10.1111/conl.12448

Haseeb, A.S.M.A., Masjuki, H.H., Ann, L.J. & Fazal, M.A. 2010. Corrosion characteristics of copper and leaded bronze in palm biodiesel. *Fuel Processing Technology*, 91(3): 329–334. http://dx.doi.org/10.1016/j.fuproc.2009.11.004

Hellier, P. & Ladommatos, N. 2015. The influence of biodiesel composition on compression ignition combustion and emissions. *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 229(7): 714–726. http://dx.doi.org/110.1177/0957650915598424

REN21. 2017. Renewables 2027 Global Status Report. 2017. *Ren21*: 26–262. Available online: https://abdn.pure.elsevier.com/en/publications/ren21-renewables-2017-global-status-report [accessed on 02 may 2021]

Hu, E., Xu, Y., Hu, X., Pan, L. & Jiang, S. 2012. Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol. *Renewable Energy*, 37(1): 371–378. http://dx.doi.org/10.1016/j.renene.2011.07.010

Huang, H. 2016. Techno-economic analysis of biodiesel and ethanol co-production from lipid-producing sugarcane: 299–315.

Iqbal, J., Carney, W.A., Lacaze, S. & Theegala, C.S. 2010. Metals Determination in Biodiesel (B100) by ICP-OES with Microwave Assisted Acid Digestion. *The Open Analytical Chemistry Journal*, 4: 18–26. http://dx.doi.org/10.5281/zenodo.836623

Jabade, S., Sakthivel, M. & Chavan, S. 2020. Bio-diesel as an alternative fuel for compression ignition engine: A review. *International Journal of Advanced Science and Technology*, 29(1): 18–28. Available online: http://sersc.org/journals/index.php/IJAST/article/view/2975 [accessed on 13 January 2020]

Jain, S. & Sharma, M.P. 2014. Effect of metal contents on oxidation stability of biodiesel/diesel blends. *Fuel*, 116: 14–18. http://dx.doi.org/10.1016/j.fuel.2013.07.104

Kanti, S., Kim, K. & Lim, O. 2018. Experimental study on non-vaporizing spray characteristics of biodiesel- blended gasoline fuel in a constant volume chamber. *Fuel Processing Technology*, 178: 322–335. https://doi.org/10.1016/j.fuproc.2018.05.009

Karavalakis, G., Stournas, S. & Karonis, D. 2010. Evaluation of the oxidation stability of diesel / biodiesel blends. *Fuel*, 89(9): 2483–2489. http://dx.doi.org/10.1016/j.fuel.2010.03.041

Khuong, L.S., Masjuki, H.H., Zulkifli, N.W.M., Mohamad, E.N., Kalam, M.A., Alabdulkarem, A., Arslan, A., Mosarof, M.H., Syahir, A.Z. & Jamshaid, M. 2017. Effect of gasoline-bioethanol blends on the properties and lubrication characteristics of commercial engine oil. *RSC Advances*, 7(25): 15005–15019. https://doi.org/10.1039/c7ra00357a

Kivevele, T. 2020. Storage and thermal stability of biodiesel produced from manketti nut oil of Southern Africa origin with the influence of metal contaminants and antioxidants. *SN Applied Sciences*, 2(5): 1–10. https://doi.org/10.1007/s42452-020-2743-y

Knothe, G. 2006. Analyzing biodiesel: Standards and other methods. *Journal of the American Oil Chemists' Society*, 83(10): 823–833. http://dx.doi.org/10.1007/s11746-006-5033-y

Knothe, G. & Steidley, K.R. 2018. The effect of metals and metal oxides on biodiesel oxidative stability from promotion to inhibition. *Fuel Processing Technology*, 177: 75–80. https://doi.org/10.1016/j.fuproc.2018.04.009

Komariah, N.L, Dewi, T.K. & Ramayanti, C. 2019. Study on corrosion behavior of storage tanks filled with biodiesel and the blends. *IOP Conference Series: Materials Science and Engineering*, 543(1). https://doi.org/10.1088/1757-899X/543/1/012033

Lee, C., Ahmed, A., Nasir, E.F., Badra, J., Kalghatgi, G., Sarathy, S.M., Curran, H. & Farooq, A. 2017. Autoignition characteristics of oxygenated gasolines. *Combustion and Flame*, 186: 114–128. http://dx.doi.org/10.1016/j.combustflame.2017.07.034

Luis, C., Roberto, M., Luiz, V., Alberto, C., Rovere, D., Luis, R.W. & Code, Z. 2021. Corrosion behavior of carbon steel, stainless steel, aluminum and copper upon exposure to biodiesel blended with petrodiesel. *Energy*, 226: 2–15 https://doi.org/10.1016/j.energy.2021.120344

Matěǰovský, L., Macák, J., Pospíšil, M., Baroš, P., Staš, M & Krausova, A. 2017. Study of Corrosion of Metallic Materials in Ethanol − Gasoline Blends: Application of Electrochemical Methods. *Energy and Fuels*, 31: 10880–10889. http://dx.doi.org/10.1021/acs.energyfuels.7b01682

Mahmudul, H.M., Hagos, F.Y., Mamat, R., Adam, A.A., Ishak, W.F.W. & Alenezi, R. 2017. Production, characterization and performance of biodiesel as an alternative fuel in diesel engines – A review. *Renewable and Sustainable Energy Reviews*, 72(January): 497–509. http://dx.doi.org/10.1016/j.rser.2017.01.001

Malvade, A.V. & Satpute, S.T. 2013. Production of palm fatty acid distillate biodiesel and effects of its blends on performance of single cylinder diesel engine. *Procedia Engineering*, 64: 1485–1494. http://dx.doi.org/10.1016/j.proeng.2013.09.230

Matějovský, L., Macák, J., Pospíšil, M., Staš, M., Baroš, P. & Krausová, A. 2018. Study of Corrosion Effects of Oxidized Ethanol-Gasoline Blends on Metallic Materials. *Energy and Fuels*, 32(4): 5145–5156. http://dx.doi.org/10.1021/acs.energyfuels.7b04034

Meher, L.C., Sagar, D.V. & Naik, S.N. 2006. Technical aspects of biodiesel production by transesterification — a review, 10: 248–268. http://dx.doi.org/10.1016/j.rser.2004.09.002

NREL see National Renewable Energy Laboratory.

National Renewable Energy Laboratory. 2005. Characterization of biodiesel oxidation and oxidation products. United States: N.P. Available online: https://doi.org/10.2172/909194 [accessed on 11 May 2021]

Nguyen, X.P. & Vu, H.N. 2019. Corrosion of the metal parts of diesel engines in biodiesel-based fuels. *International Journal of Renewable Energy Development*, 8(2): 119–132. http://dx.doi.org/10.14710/ijred.8.2.119-132

Nogueira, T. & Lucio, C. 2011. Determination of Ca, K, Mg, Na, sulfate, phosphate, formate , acetate , propionate , and glycerol in biodiesel by capillary electrophoresis with capacitively coupled contactless conductivity detection. *Microchemical Journal*, 99(2): 267–272. http://dx.doi.org/10.1016/j.microc.2011.05.014

Norouzi, S., Eslami, F., Wyszynski, M.L. & Tsolakis, A. 2012. Corrosion effects of RME in blends with ULSD on aluminium and copper. *Fuel Processing Technology*, 104: 204–210. http://dx.doi.org/10.1016/j.fuproc.2012.05.016

Komariah, N.L., Arita, S., Prianda, B.E. & Dewi, T.K. 2021. Technical assessment of biodiesel storage tank; A corrosion case study. Journal of King Saud University -

Engineering Sciences, Saudi Arabia, 30 March. https://doi.org/10.1016/j.jksues.2021.03.016

Palash, S.M., Kalam, M.A., Masjuki, H.H., Masum, B.M., Rizwanul Fattah, I.M. & Mofijur, M. 2013. Impacts of biodiesel combustion on NOx emissions and their reduction approaches. *Renewable and Sustainable Energy Reviews*, 23: 473–490. http://dx.doi.org/10.1016/j.rser.2013.03.003

Peng, D.X. 2017. Effect of unleaded gasoline blended with biofuels on gasoline injector wear and exhaust emissions. *Industrial Lubrication and Tribology*, 69(2): 208–214. http://dx.doi.org/10.1108/ILT-09-2016-0217

Prabakaran, B. & Vijayabalan, P. 2018. Influence of zinc oxide nano particles on performance, combustion and emission characteristics of butanol-diesel-ethanol blends in DI CI engine. *IOP Conference Series: Materials Science and Engineering*, 377(1). http://dx.doi.org/10.1088/1757-899X/377/1/012069

Putrasari, Y. & Lim, O. 2017. A study on combustion and emission of GCI engines fueled with gasoline-biodiesel blends. *Fuel*, 189: 141–154. http://dx.doi.org/10.1016/j.fuel.2016.10.076

Qiu, F., Li, Y., Yang, D., Li, X. & Sun, P. 2011. Biodiesel production from mixed soybean oil and rapeseed oil. *Applied Energy*, 88(6): 2050–2055. http://dx.doi.org/10.1016/j.apenergy.2010.12.070

Rao, P.V. & Chary, D.P. 2018. Characteristics comparison of Biodiesel-Diesel Blend (B20) Fuel with Alcohol Additives. *International Journal of Advanced Engineering Research and Science*, 5(8): 128–132. http://dx.doi.org/10.22161/ijaers.5.8.17

Rao, K.S & Ramakrishna, A. 2015. Cost Estimation Analysis of Biodiesel Production from Waste Chicken Fat. *International Journal of Applied Engineering Research*, 10(4): 8864–8870. Available online: https://www.researchgate.net/publication/274831997 [accessed on 16 June 2021]

Rocabruno-valdés, C.I., Escobar-jiménez, R.F., Díaz-blanco, Y. & Gómez-aguilar, J.F. 2020. Corrosion evaluation of Aluminum 6061-T6 exposed to sugarcane bioethanol-gasoline blends using the Stockwell transform, 878. http://dx.doi.org/10.1016/j.jelechem.2020.114667

Rocha, L.D.S. & Corrêa, S.M. 2018. Determination of size-segregated elements in diesel-biodiesel blend exhaust emissions. *Environmental Science and Pollution Research*, 25(18): 18121–18129. http://dx.doi.org/10.1007/s11356-018-1980-8

Ruzinska, E., Stollmann, V., Hagara, V. & Jablonski, M. 2015. Analysis of selected heavy metals in biomass for preparation of biofuels – Part II. Determination of heavy metals content. *Annals of Warsaw University of Life Sciences - SGGW. Forestry and Wood Technology*, 92(x): 383–389. Available online: http://agro.icm.edu.pl/agro/element/bwmeta1.element.agro-c1690cab-9853-4775-93fd-d790b418cc8d/c/383__Annals92.pdf [accessed on 23 March 2020]

Sánchez, R., Sánchez, C., Lienemann, C.-P. & Todolí, J.-L. 2015. Metal and metalloid determination in biodiesel and bioethanol. *J. Anal. At. Spectrom.*, 30(1): 64–101. http://dx.doi.org/10.1039/C4JA00202D

Sentanuhady, J., Saputro, W. & Muflikhun, M.A. 2021. Metals and chemical compounds contaminants in diesel engine lubricant with B20 and B100 biofuels for long term operation. *Sustainable Energy Technologies and Assessments*, 45: 101161. https://doi.org/10.1016/j.seta.2021.101161

Setiyo, M., Saifudin, S., Jamin, A.W., Nugroho, R. & Karmiadji, D.W. 2018. the Effect of Ethanol on Fuel Tank Corrosion Rate. *Jurnal Teknologi*, 80(6): 20–25 https://doi.org/10.11113/jt.v80.1232

Sharma, A.K., Sharma, P.K., Chintala, V., Khatri, N. & Patel, A. 2020. Environment-friendly biodiesel/diesel blends for improving the exhaust emission and engine performance to reduce the pollutants emitted from transportation fleets. *International Journal of Environmental Research and Public Health*, 17(11). 2–18 http://dx.doi.org/10.3390/ijerph17113896

Shiotani, H. & Goto, S. 2007. Studies of fuel properties and oxidation stability of biodiesel fuel. *SAE Technical Papers*, 116: 70–75. http://dx.doi.org/10.4271/2007-01-0073

Singh, B., Korstad, J. & Sharma, Y.C. 2012. A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition. *Renewable and Sustainable Energy Reviews*, 16(5): 3401–3408. http://dx.doi.org/10.1016/j.rser.2012.02.042

South Africa. 2020. Department of Miniral Resources and Energy. *Government Gazette*, 656(43003): 1–44, February 02. Available online: http://www.greengazette.co.za/pages/national-gazette-37230-of-17-january-2014-vol-583_20140117-GGN-37230-003 [accessed 02 August 2021]

Subramaniam, D., Murugesan, A., Avinash, A. & Kumaravel, A. 2013. Bio-diesel production and its engine characteristics - An expatiate view. *Renewable and Sustainable Energy Reviews*, 22: 361–370. http://dx.doi.org/10.1016/j.rser.2013.02.002

Sylvester, O.D., Adams, F. V & Okoro, L.N. 2015. Impact of Biodiesel on the Corrosion of Zinc and Copper Strips. *International Journal of Scientific & Engineering Research*, 6(2): 546–549. Available online: https://www.ijser.org/paper/Impact-of-Biodiesel-on-the-Corrosion-of-Zinc-and-Copper-Strips.html [accessed on 16 June 2021]

Tabish, A. 2018. Corrosion Behaviour of Biofuel. *Petroleum and Chemical Industry International*, 1(2): 2–19. Available online: https://www.researchgate.net/publication/340684219 [accessed on 25 October 2021]

Thangavelu, S.K., Ahmed, A.S. & Ani, F.N. 2016. Impact of metals on corrosive behavior of biodiesel-diesel-ethanol (BDE) alternative fuel. *Renewable Energy*, 94: 1–9. http://dx.doi.org/10.1016/j.renene.2016.03.015

Thangavelu, S.K., Piraiarasi, C., Ahmed, A.S. & Ani, F.N. 2015. Corrosion Behavior of Copper in Biodiesel-Diesel-Bioethanol (BDE). *Advanced Materials Research*, 1098: 44–50. Available online: https://www.scientific.net/AMR.1098.44

Thomas, E.W., Fuller, R.E. & Terauchi, K. 2007. Fluoroelastomer compatibility with biodiesel fuels. *SAE Technical Papers*, 116: 947–956. http://dx.doi.org/10.4271/2007-01-4061

Tsuchiya, T., Shiotani, H., Goto, S., Sugiyama, G. & Maeda, A. 2006. Japanese Standards for Diesel Fuel Containing 5% FAME: Investigation of Acid Generation in

FAME Blended Diesel Fuels and Its Impact on Corrosion. *SAE Technical Papers*. Available online: https://www.sae.org/publications/technical-papers/content/2006-01-3303/ [accessed on 25 October 2021]

Verma, P. & Sharma, M.P. 2015. Performance and emission characteristics of biodiesel fuelled diesel engines. *International Journal of Renewable Energy Research*, 5(1): 245–250. http://dx.doi.org/10.20508/ijrer.32087

Worldwide Fuel Charters. 2019. Gasoline and diesel fuel, 6th ed. *The European Automobile Manufacurers Association:* 4–96. Available online: https://www.acea.auto/publication/worldwide-fuel-charter-2019-gasoline-and-diesel-fuel/ [accessed on 29 April 2021]

Yeşilyurt, M.K., Öner, İ.V. & Yılmaz, E.Ç. 2019. Biodiesel Induced Corrosion and Degradation: A Review. *Pamukkale University Journal of Engineering Sciences*, 25(1): 60–70. http://dx.doi.org/10.5505/pajes.2018.01885

Yusof, H., Tamaldin, N., Abdollah, M.F.B. & Khalid, A. 2015. Evaluation of the storage effect on the fuel properties for variety biodiesel blends. *ARPN Journal of Engineering and Applied Sciences*, 10(17): 7701–7707. Available online: https://www.researchgate.net/publication/283354271 [accessed on 16 April 2021]

Zhang, Y., Ma, Z., Feng, Y., Diao, Z. & Liu, Z. 2021. The Effects of Ultra-Low Viscosity Engine Oil on Mechanical Efficiency and Fuel Economy. *Energies*, 14(8): 2–20. https://doi.org/10.3390/en14082320

Zhang, Y., Zhan, L., He, Z., Jia, M., Leng, X., Zhong, W., Qian, Y. & Lu, X. 2019. An investigation on gasoline compression ignition (GCI) combustion in a heavy-duty diesel engine using gasoline/hydrogenated catalytic biodiesel blends. *Applied Thermal Engineering*, 160: 2–13. https://doi.org/10.1016/j.applthermaleng.2019.113952

Zhong, Wenjun, Li, B., He, Z., Xuan, T., Lu, P. & Wang, Q. 2019. Experimental study on spray and combustion of gasoline / hydrogenated catalytic biodiesel blends in a constant volume combustion chamber aimed for GCI engines. *Fuel*, 253(301): 129–138. https://doi.org/10.1016/j.fuel.2019.04.114

Zhong, W., Pachiannan, T., Li, Z., Qian, Y., Zhang, Y. & Wang, Q. 2019. Combustion and emission characteristics of gasoline / hydrogenated catalytic biodiesel blends in gasoline compression ignition engines under di ff erent loads of double injection strategies. *Applied Energy*, 251: 113296. https://doi.org/10.1016/j.apenergy.2019.05.099

Zhong, W., Xiang, Q., Pachiannan, T., Mahmoud, N.M., Li, B., He, Z., Wang, Q. & Sun, J. 2021. Experimental study on in-flame soot formation and soot emission characteristics of gasoline / hydrogenated catalytic biodiesel blends. *Fuel*, 289: 2–11. https://doi.org/10.1016/j.fuel.2020.119813

Ziółkowska, M. & Wardzińska, D. 2013. Corrosiveness of Fuels During Storage Processes. *Intech*, 32: 137–144. http://dx.doi.org/10.5772/59803

Zuleta, E.C., Baena, L., Rios, L.A. & Calderón, J.A. 2012. The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: A review. *Journal of the Brazilian Chemical Society*, 23(12): 2159–2175. http://dx.doi.org/10.1590/S0103-50532012001200004

Chapter 7: **General Conclusions and Recommendations**

7.1 Conclusions

This research laid a prospective view on the potential use of green fuels, biodiesel, and biodiesel-petrol blends, on their use as transportation fuels in the fight against the global climate crisis. Even though, there is a great significance in the use of waste oils to produce biodiesel, this fuel is susceptible to degradation, increased NOx, and low thermal efficiencies. With the blending of biodiesel and petrol, these issues were minimised. Undesirable metal contents in the fuel and engine were evaluated, their presence and effects on the quality of the biodiesel and the blended fuel and possible engine emission were accessed.

Synthesised CaO/Al_2O_3 bi-functional catalyst used in transesterification process which had enhanced properties and provided a high biodiesel yield. Even though, the produced catalyst portrayed high activity, evident with increased active sites on high surface area which aided in the liquid-solid reaction by selecting and subsequently converting of high free fatty acids to biodiesel. This catalyst was observed to increase the Ca concentration in biodiesel, this subsequently degraded fuel quality of the biodiesel i.e., lower oxidation stability.

The characterisation of elemental content in the biodiesel, before and after production, showed that P, Fe, Al, Zn were present in feedstocks while Ca, Mg, K were introduced in the biodiesel through production process. Also, Transesterification reduced Na, Fe, P and Al concentrations, meeting standard limit set.

The structure of methyl esters played a major role in fuel quality in this study. The fatty acid compositions of waste cooking oils were observed to have a major effect on the fuel quality. Waste sunflower oil was had more linoleic acids while waste palm oils were more palmitic and oleic. High unsaturation degree in sunflower biodiesel resulted in lower oxidation stability, cetane number, more density, and a better storage temperature. While the high saturation of palm biodiesel rendered it characteristics of a better cold flow property, thermal and long-time stability. Higher acidity observed in palm biodiesel promoted degradation and low viscosity of sunflower biodiesel indicates the fuel would allow for better atomisation.

In the optimisation of sunflower biodiesel, the use of response surface methodology gave the linear regression model with 95% confidence, which predicted the yield that was found to be comparable with the experimented yield. While catalyst loading was the most significant parameter and the highest yield obtained was 98.23 %, optimised parameters were 5 h, 2.5 wt% at 60 °C. Also, optimisation improved fuel quality particularly the characteristic of fuel atomisation i.e., viscosity. Also, contaminants of nitrates, sulphates, soot were reduced meeting all standard set for biodiesel.

Blending biodiesel with petrol, enhanced fuel qualities were achieved. The blended fuels were recorded to have enhanced fuel characteristics compared with pure petrol, with 25 % biodesel-75% petrol showing similarities nearly of the petrodiesel. The high degree of unsaturation in sunflower biodiesel, resulted in sunflower biodiesel- petrol blends possessing high formation of high carbon deposits and total hydrocarbons. While palm biodiesel-petrol blends were observed to have excellent stability, potential for good cold start engine warm up. Also, blending biodiesel with petrol reduced the concentration of Ca, along with Mg and the absorption of the moisture content.

Overall, the influence of metals on quality of the sunflower biodiesel-petrol blends was observed as Fe > Cu > Zn, while in palm biodiesel-petrol blends it was observed to be Cu > Fe > Zn. It was observed that low oxidation, high acidity, high density and low a viscosity in pure biodiesel was caused by increase in Fe concentration, while Cu affected the blended fuel the most followed by Fe and Zn. Results showed that Fe had a huge impact in degradation of pure biodiesels while Cu was observed to decrease the fuel quality of biodiesel-petrol blends. Cu also increased flammability and particulate matter of nitrates and sulphates. While Zn promoted the absorption of water content in sunflower biodiesel blends.

7.2 Recommendations

The following further research can be conducted to better understand and support the findings of this thesis.

It was observed that the use of 75%CaO/25%Al_2O_3 for biodiesel synthesis, aided the transesterification of high free fatty acids. However, it was associated with increased concentration of Ca in biodiesel (Simbi et al., 2021). Further investigation on functionality and effect of varying acid: base ratios of the synthesised catalyst and accessing the concentration of Ca in produced biodiesel is recommended.

It was well known that the nature of feedstocks i.e. fatty acids compositions is the main cause in varying biodiesel quality of different oil origins (Baskar & Aiswarya, 2016; Rao et al., 2017; Yaşar, 2020). Therefore, the ranged quality of biodiesel could result in different biodiesel-petrol blends. A recommendation is suggested to produced various biodiesels with different feedstock origins and blend them with petrol, to access possible fuel quality of blended fuels.

The present study established characteristics of fuel quality of blended sunflower and palm biodiesel-petrol blends in proportions of PB5, PB15 and PB25, a further look into testing the combustion characteristics of these blended fuels on compression ignition engine could provide a strong foundation for emission, performance and efficiencies of these fuels. This will support ongoing research on the use of oxygenated petrol, in compression ignition engines, promoting reduction of emissions (Xuan et al., 2020 Gad & Ismail, 2021).

After analysing effect Cu, Fe and Zn, and with Cu reported to have the highest corrosive rates (Cursaru et al., 2014; Sylvester et al., 2015; Baena & Calderón, 2020). It was observed that Fe is not compatible with biodiesel while Cu degrade biodiesel-petrol blends. It is strongly recommended that, in designing fuel tanks, alloys of Fe and Cu be avoided, it was observed that fuel degradation is mainly contributed by these metals.

7.3 References

Baena, L.M. & Calderón, J.A. 2020. Effects of palm biodiesel and blends of biodiesel with organic acids on metals. *Heliyon*, 6(5): 2–13. http://dx.doi.org/10.1016/j.heliyon.2020.e03735

Baskar, G. & Aiswarya, R. 2016. Trends in catalytic production of biodiesel from various feedstocks. *Renewable and Sustainable Energy Reviews*, 57: 496–504. http://dx.doi.org/10.1016/j.rser.2015.12.101

Cursaru, D.L., Brănoiu, G., Ramadan, I. & Miculescu, F. 2014. Degradation of automotive materials upon exposure to sunflower biodiesel. *Industrial Crops and Products*, 54: 149–158. https://doi.org/10.1016/j.indcrop.2014.01.032

Gad, M.S. & Ismail, M.A. 2021. Effect of waste cooking oil biodiesel blending with gasoline and kerosene on diesel engine performance, emissions and combustion characteristics. *Process Safety and Environmental Protection*, 149: 1–10. https://doi.org/10.1016/j.psep.2020.10.040

Rao, M.S., Venkatesh, N. & Naidu, A.L. 2017. A Review on Performance of Diesel Engines by using Biodiesel blends from Different oils A Review on Performance of Diesel Engines by using Biodiesel blends from Different oils. *International Journal of Research & Development Technology*, 7(6)134–143. Avaiable online: https://www.researchgate.net/publication/318128352 [accessed on 13 January 2021]

Simbi, I., Aigbe, U.O., Oyekola, O. & Osibote, O.A. 2021. Catalyst and Elemental Analysis Involving Biodiesel from Various Feedstocks. *Catalysts 2021*, 11(8): 2–17. http:https://doi.org/10.3390/CATAL11080971

Sylvester, O.D., Adams, F. V & Okoro, L.N. 2015. Impact of Biodiesel on the Corrosion of Zinc and Copper Strips. *International Journal of Scientific & Engineering Research*, 6(2): 546–549. Available online: https://www.ijser.org/paper/Impact-of-Biodiesel-on-the-Corrosion-of-Zinc-and-Copper-Strips.html [accessed on 16 June 2021]

Xuan, T., EL-Seesy, A.I., Mi, Y., Lu, P., Zhong, W., He, Z. & Wang, Q. 2020. Effects of an injector cooling jacket on combustion characteristics of compressed-ignition sprays with a gasoline-hydrogenated catalytic biodiesel blend. *Fuel*, 276: 2–10. https://doi.org/10.1016/j.fuel.2020.117947

Yaşar, F. 2020. Comparision of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type. *Fuel*, 264: 2–7. http://dx.doi.org/10.1016/j.fuel.2019.116817