

**INVESTIGATION OF POTENTIAL OF A BIFUNCTIONAL
CATALYST FOR THE SIMULTANEOUS ESTERIFICATION AND
TRANSESTERIFICATION OF HIGH FREE FATTY ACID
FEEDSTOCK**

by

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Abstract

There has been growing concern around the depletion of the world's oil reserves as well as the negative environmental impacts fossil fuels pose. Therefore, there has been a crucial demand in the exploration of clean, sustainable, and alternative fuels/ fuel sources. Biodiesel, which can be derived from edible plant oils, waste oils as well as animal fats has been regarded as a clean, renewable and feasible substitute for diesel compression ignition engines without the need for modification.

This study aimed to investigate the simultaneous esterification and transesterification of various feedstocks using bi-functional catalysts. Four catalysts consisting of varying ratios of CaO and Al₂O₃ were synthesised through co-precipitation in order to ensure their bifunctionality where CaO provided basic sites and Al₂O₃ provided acidic sites. The four catalysts (CaO: Al₂O₃ ratios of 80:20, 70:30, 60:40, and 50:50) were calcined at a temperature of 600 °C. Catalysts were characterised using Brunauer Emmet Teller (BET), Scanning Electron Microscope (SEM) and X-Ray diffraction (XRD). They exhibited adequate morphological and catalytic characteristics where pore sizes were ≥ 209 Å, surface areas ≥ 11 m²/g and pore volumes ≥ 0.072 cm³/g.

Seven feedstock samples were used: 3 virgin oils (canola (VCO), sunflower (VSO) and palm (VPO)), 4 non-edible oils (waste canola (WCO), waste sunflower (WSO), waste palm (WPO) and neem oil (NO)). Free fatty acid contents ranged from 0.22 to 3.25%. Feedstocks were pre-treated through filtration, to eliminate solid particles and dehydrated to reduce moisture. Thereafter, each feedstock underwent simultaneous esterification and transesterification using the four catalysts. These experiments were carried out at temperature of 65 °C, agitation rate of 1200 rpm, 2.5 wt% catalyst loading and a methanol to oil molar ratio of 12:1 at a reaction time of 4 hours under reflux as the optimised conditions stipulated by (Zabeti *et al.*, 2009).

The results showed that feedstocks with low FFA content required catalysts with less acidic sites to produce the highest yield of biodiesel. In contrast, feedstock with a high FFA content (>1 wt%) favoured a catalyst with a higher quantity of acidic sites. This was evident as VPO, VCO and VSO, which had FFA contents of 0.67%, 0.33% and 0.22% respectively, performed optimally through the use of 80% CaO:20%Al₂O₃ with yields of 97.85%, 98.95% and 95.6% respectively. Neem oil, which had the highest FFA content of 3.25% achieved the highest yield

(97.63%) with the use of a catalyst with more acidic sites (60% CaO: 40%Al₂O₃). Therefore, the relationship between FFA and acid site quantity was evident.

The effect of feedstock saturation on catalyst performance was also investigated. The highly saturated feedstocks (WPO and NO) had a saturated fatty acid (SFA) content of 46.79 and 44.06%, respectively, where the highly unsaturated feedstocks (SO and WSO) had a polyunsaturated fatty acid (PUFA) content of 67.8 and 64.0%, respectively. Monounsaturated fatty acids (MUFA) were dominant in WCO and CO at values of 66.6 and 71.2%, respectively. There were negligible differences in yields between PUFA, MUFA and SFA dominant feedstocks. It was evident that the degree of unsaturation of the feedstock had no significant effect on catalyst performance.

Transportation fuel characteristics of the biodiesel synthesised were also determined. These included oxidation stability, density, kinematic viscosity, flash point, sulphur content, total acid number (TAN) and water content in accordance with the ASTM reference test methods (D4502, D 664, D 445, D 93, D 5453 and D 2709). Biodiesel density values ranged from 0.88 to 0.889 g/m³, viscosity from 0.4 to 30.4 cSt, flash point from 130 to 170 °C, sulphur content from 0 to 334 ppm, TAN from 0.17 to 0.88 mgKOH/g and water content from 0.02 to 0.19 wt%. The RANCIMAT procedure was also utilised for the measurement of induction time/oxidation stability. The fuels adhered to the ASTM and EU restrictions with the exception to neem oil biodiesel (NB100). This was attributed to the physio-chemical nature of the corresponding feedstock used. Catalyst robustness was also investigated. It was found that all four catalysts maintained excellent catalytic activity for up to 8 runs. Loss of catalytic activity thereafter was attributed to loss of mass during the cleaning and drying process as well as exposure to moisture and air. The current study provided evidence for the need to synthesise tailor-made bifunctional catalysts with robust nature for the E and TE of low-cost feedstocks.

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Table of Contents

Declaration	2
Abstract	i
Acknowledgements.....	iii
Table of Contents.....	iv
Glossary.....	ix
Terms and Definitions.....	x
Chapter 1 : Introduction	1
1.1. Background	2
1.2. Problem Statement.....	4
1.3. Aim and objectives.	4
1.4. Research Motivation and Significance	4
1.5. Delineation of Research.....	5
Chapter 2 : Literature Review	7
2.1. Biodiesel.....	7
2.1.1. Advantages of FAME.....	7
2.1.2. Disadvantages of FAME	8
2.2. FAME Production Technologies.....	9
2.2.1. Direct Use and Blending of Oils.....	9
2.2.2 Thermal Cracking (Pyrolysis).....	9
2.2.3. Transesterification of Triglycerides	10
2.2.4. Esterification of Free Fatty Acids (FFA).....	11
2.3. FAME Feedstock.....	12
2.3.1. Non-edible Oil feedstock.....	12
2.3.2. Waste Vegetable oil (WVO).....	13
2.3.3. Animal Fats and Other Sources	13
2.3.4. Alcohol	14
2.4. Parameters Affecting FAME Production.....	14
2.4.1. FFA Content	14
2.4.2. Alcohol Type and Alcohol to Oil Molar Ratio	15
2.4.3. Catalyst Size and Loading	16
2.4.3.1. Catalyst Loading.....	16
2.4.3.2. Catalyst Particle Size	17
2.4.4. Temperature.....	18
2.4.4.1. Reaction Temperature.....	18
2.4.4.2. Calcination Temperature.....	18

2.4.5. Water Content	19
2.5. Catalysts	19
2.5.1. Homogenous Catalysts	20
2.5.2. Heterogeneous Catalysts	21
2.5.3. Bio-Catalysts	22
2.5.4. Bi-functional Catalysts	23
2.5.4.1. Impregnation Methods for Catalyst Preparation	24
2.5.4.2. Precipitation Methods for Catalyst Preparation	25
2.6. Transportation Fuel Characteristics	25
2.6.1. Oxidation Stability	25
2.6.2. Saturation and Iodine Number/ Value (IV)	26
2.6.3. Carbon Residue, Emissions and Particulate Matter	27
2.6.4. Density and Specific Gravity	28
2.6.5. Kinematic Viscosity	29
2.6.6. Heating Value/ Calorific Value	30
2.6.7. Lubricity	30
2.6.8. Cetane Number	31
2.6.9. Flash Point	32
2.6.10. Cold Flow Properties	32
2.6.10.1. Cold filter plugging point	32
2.6.10.2. Cloud Point (CP)	32
2.6.10.3. Pour Point (PP)	33
2.6.11. Acid Number	33
2.6.12. Glycerol Content	33
2.7. Effect of Fatty Acid Constituents on Crucial Fuel Characteristics	35
2.7.1. Lubricity	35
2.7.2. Cetane Number	36
2.7.3. Oxidation Stability and Iodine Value	36
2.7.4. Cold Filter Plugging Point	37
Chapter 3 : Methodology	39
3.1. Materials	39
3.2. Catalyst Preparation	39
3.2.1. Co-precipitation	39
3.2.2. Wet Impregnation	40
3.2.3. Catalyst Reusability	41
3.3. Catalyst Characterisation and Analysis	41
3.3.1. X-Ray Diffraction	41

3.3.2. Brunauer-Emmett-Teller	42
3.3.3. Scanning Electron Microscope	42
3.4. Fatty Acid Methyl Esters Production.....	43
3.4.1. Feedstock Pre-treatment	43
3.4.2. Feedstock Analysis	43
3.4.2.1. Gas Chromatography Mass Spectroscopy (GC-MS).....	43
3.4.2.2. Chemical Titration.....	44
3.5. Experimental Set Up and Procedure.....	44
3.5.1. Experimental Set Up	44
3.5.2. Experimental Procedure.....	45
3.5.3. Product Estimation.....	47
3.6. Fuel Characteristic Analysis.....	47
Chapter 4 Results and Discussion.....	50
4.1. Catalyst Analysis and Characterisation	50
4.1.1. Catalyst Composition	50
4.1.2. Catalyst Structure, Surface Area and Pore Volume	51
4.1.3. Catalyst Morphology.....	52
4.2. Feedstock Composition and Analysis.....	55
4.2.1. Free Fatty Acid Content	55
4.2.2. Fatty Acid Profile.....	55
4.3. Biodiesel Characterisation	57
4.3.1. Biodiesel Yield.....	58
4.3.1.1. Effect of FFA and Catalyst Composition on Sunflower Oil FAME	58
4.3.1.2. Effect of FFA and Catalyst Composition on Palm Oil FAME.....	59
4.3.1.3. Effect of FFA and Catalyst Composition on Canola Oil FAME.....	60
4.3.1.4. Effect of FFA and Catalyst Composition on Neem Oil FAME	61
4.3.1.5. Overall Biodiesel Yields of Feedstock	62
4.3.1.6. Catalyst Reusability	63
4.3.2. Biodiesel Transportation Fuel Characteristics.....	64
4.3.2.1. Total Acid Number	66
4.3.2.2. Density	66
4.3.2.3. Kinematic Viscosity.....	67
4.3.2.4. Flash Point.....	67
4.3.2.5. Sulphur Content.....	68
4.3.2.6. Water Content.....	68
4.3.4.7. Oxidation Stability.....	68
4.3.3. Effect of Feedstock Unsaturation on Catalyst Performance.....	69
4.4. Summary	70

Chapter 5 Conclusion and Recommendations.....	73
5.1. Conclusion.....	73
5.2. Recommendations	74
References	76
Appendices	83
Appendix A: Sample Calculations on Biodiesel Production	83
A.1 Acid Number and Free Fatty Acid Determination.....	83
A.2 Catalyst Preparation	83
A.3 Biodiesel Yield Calculations	85

List of Figures

Figure 2-1: FAME molecular structure.....	7
Figure 2-2: Petroleum diesel molecular structure.....	7
Figure 2-3: Transesterification of triglycerides. Where R1, R2 and R3 are the corresponding long saturated carbon chains.	10
Figure 2-4: Intermediate reactions in the transesterification process	11
Figure 2-5: Esterification of FFAs.....	12
Figure 2-6: Biodiesel catalysts	20
Figure 2-7: General mechanism for simultaneous esterification and transesterification reactions on bi-functional heterogenous catalyst (Ramli <i>et al.</i> , 2016)	24
Figure 2-8: Example of Bis-allylic carbons adapted from (Chuah <i>et al.</i> , 2016)	26
Figure 3-1: Calcination process of catalyst (CaO/Al ₂ O ₃)	41
Figure 4-1 Cumulative Composition of catalysts (XRD)	51
Figure 4-2a: 80% CaO morphology (SEM).....	53
Figure 4-3a: Effect of catalyst on virgin sunflower FAME yield.....	59
Figure 4-7: Catalyst Reusability	64

List of Tables

Table 2-1: Feedstock sources with corresponding oil content.	13
Table 2-2: Transportation fuel characteristic specification (ASTM & EU)	34
Table 2-3: Fatty acid constituent (%) of various edible oils.	35
Table 2-4: Lubricity in different methyl esters.....	36
Table 2-5: Cetane number trend in different fatty acids	36
Table 4-1: Physiochemical properties of compounds in catalysts.....	50
Table 4-2: Predicted and actual catalyst ratios	51
Table 4-3: Catalyst structure, surface area and pore volume	52
Table 4-4: FFA content of feedstocks.....	55
Table 4-5: Fatty acid composition of feedstocks.....	56
Table 4-6: Saturation and unsaturation composition of feedstocks.....	57
Table 4-7: Catalyst labelling	58
Table 4-9: Transportation fuel characteristics of FAME produced.....	65
Table 4-10: Induction times of FAME produced.	69
Table A-1: Sunflower Biodiesel Yields	85
Table A-2: Palm Oil Biodiesel Yields	85
Table A-3: Canola oil Biodiesel Yields	86

Table A-4: Neem Biodiesel Yields.....	86
Table A-5: Waste palm oil yields (Catalyst reusability).....	86

Glossary

Abbreviations

BET	Brunauer-Emmett-Teller
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC-MS	Gas Chromatography Mass Spectroscopy
SEM	Scanning Electron Microscopy
TAN	Total Acid Number
TG	Triglyceride
DG	Diglyceride
MG	Monoglyceride
PUFA	Polyunsaturated Fatty Acids
MUFA	Monosaturated Fatty acids
SFA	Saturated Fatty Acids
VCO	Virgin Canola oil
VSO	Virgin Sunflower Oil
VPO	Virgin palm oil
WPO	Waste Palm Oil
WSO	Waste Sunflower Oil
WVO	Waste Vegetable Oil
XRD	X-Ray Diffraction
E	Esterification
TE	Transesterification

Terms and Definitions

Acid number: a measurement/ indication of acidity in a fuel or feedstock (Tshizanga, 2015)

Ash content: a measure of the amount of non-combustible matter present in a fuel (Tshizanga, 2015)

Biodiesel: a fuel that consists of fatty acid methyl/alkyl esters or long chain mono alkyl esters (Tshizanga, 2015)

Cetane number: is a dimensionless number that denotes the self-ignitability of a fuel (Giakoumis and Sarakatsanis, 2018)

Density: as the ratio of a substance's mass per unit volume (Giakoumis 2016).

Esterification: the conversion of FFA into methyl esters in the presence of an alcohol with the aid of an acid catalyst (Antolín *et al.*, 2015)

Flash point: the temperature at which the biodiesel ignites when exposed to a flame or a spark at the atmospheric pressure of 101.325 kPa (Mo *et al.*, 2016).

Reflux: the process of boiling reactants whilst continuously cooling the vapour, returning it back into the reactor as a liquid (Tshizanga, 2015)

Transesterification: the reaction between an alcohol and triglyceride to form methyl, ethyl or butyl esters (Meher *et al.* 2016)

Kinematic viscosity: a measure of the resistance of a fluid which is being deformed by either shear or tensile stress (Giakoumis, 2016)

CHAPTER 1

INTRODUCTION

Chapter 1 : Introduction

1.1. Background

Energy is the most lucrative and precious resource since the dawn of humanity itself. While various methods have been formulated to produce it, an exponentially increasing population has heightened its demand. Moreover, the depletion of natural resources such as petroleum and coal has contributed to the strain on energy production due to the increase in fuel costs. Climate change has become a major factor in motivating and perpetuating the importance of environmentally friendly and renewable energy sources (Rehan and Arabia, 2017).

Due to the rapid increase of the human population, the vehicle industry has experienced a surge in production (Mofijur, Rasul, Hyde, Azad, 2016). Consequently, vehicular emissions such as particulate matter (PM), hydrocarbons (HC) carbon dioxides (CO₂), carbon monoxide (CO) and nitrogen oxides (NO_x) have increased as well.

Biodiesel, also known as FFAE (Fatty acid alkyl esters) can be produced from both used and unused edible oils. Fatty alkyl methyl esters (FAME) is the biodiesel produced when methanol is used to react with the triglyceride containing feedstock in the transesterification process. South Africa requires ~400 times more diesel than it produces. Hence, it is imperative to investigate and construct alternative diesel production methods that are feasible for sustainability and renewability, as well as in cost (Nahman, 2013).

The use of waste edible oils as biodiesel production feedstock in South Africa is a potential advantage. Bio green, a renewable fuels energy company, has estimated that South Africa produces a total of 28 million tons of waste cooking oil. Only 3 million tons are reused and repurposed leaving a total of 25 million tons of untapped waste oil which could potentially be converted to biodiesel (Frost and Sullivan, 2016).

The synthesis of biodiesel from triglycerides containing feedstock through the transesterification process has attracted immense attention over the past decades as a biodegradable, renewable and sustainable fuel (Alaba *et al.* 2016). Currently, biodiesel production faces several limitations, and the main production route is expensive at approximately 1.3 USD/ litre according to the International Renewable Energy Agency. For example, the most common production method is through base catalysis with sodium hydroxide. Major advantages of using homogeneous base catalysts such as sodium or

potassium hydroxide include high efficiency as well as easy, inexpensive procurement. However, the use of these chemical catalysts enable a saponification reaction, This side reaction proves to be highly undesired as the separation and purification process of biodiesel from the soap formed proves to be both tedious and costly (Sebastian, Muraleedharan and Santhiagu 2016).

Due to the saponification reaction caused by using a strong chemical base in the presence of a feedstock with high FFA, solid catalysis has become increasingly popular as it eliminates this side reaction. An alternative method to using base catalysis in the presence of high FFA feedstock includes the use of lipids and enzymes (enzymatic catalysis). However, enzymes are relatively expensive to procure which further compounds the already high cost of biodiesel production (Alaba *et al.* 2016). Therefore, special attention has been directed to applying heterogeneous catalysis for biodiesel production due to the green and recyclable catalytic properties of heterogeneous catalysts (Ramli *et al.*, 2016). The use of heterogeneous catalysts resulted in reduced reactor corrosion, decreased FFA and moisture sensitivities as well as simplified separation and purification downstream (Ramli *et al.*, 2016).

The use of supported solid catalysts such as calcium oxide or magnesium oxide ensures the eradication of saponification reactions (Singh, Yadav and Sharma, 2017). The most prominent advantage is that the transesterification and esterification processes occur simultaneously. Other than that, such catalysts have proved to be reusable while still producing high yields of biodiesel (Frost and Suliman, 2016).

Bi-functional solid catalysis involves the combination of both acid and base solid catalysts during the production of biodiesel. The use of bi-functional catalysts was initiated by the limitations and difficulties experienced by only using either acid or base catalysts (Rehan and Arabia., 2017). Even though base catalysts have higher activity and shorter reaction times, they fail to produce the optimal yield of FAME as compared to a bi-functional catalyst. In addition, the use of only solid acid catalysts requires more extreme conditions with regards to temperature and pressure catalysts (Rehan and Arabia., 2017).

The use of bi-functional catalysts is associated with efficient biodiesel production from a variety of feedstock as they exhibit both acidic and basic characters. Consequently, with the aid of these catalysts, simultaneous esterification of free fatty acids and transesterification of triglycerides take place. This results in cleaner and more economical processes for biodiesel production. More importantly, a bi-functional catalyst can easily be modified and altered to

introduce the desired properties and yield so that the presence of FFAs or water does not affect the reaction steps during the transesterification process. Ultimately due to the simultaneous esterification and transesterification processes that occur as a result of the use of bi-functional catalysts, a higher conversion is achieved (Rehan *et al.*, 2017).

1.2. Problem Statement

The synthesis of biodiesel using edible oils in the presence of a homogeneous base catalyst has been the conventional route at the industrial level. Nevertheless, the high cost of edible oils is a constraint to the production process as the feedstock accounts for over 70% of the total production cost. South Africa produces ~ 28 million tons of waste cooking oil which has potential as a ubiquitous feedstock supplement. Its use is however associated with challenges of washing, saponification, high water consumption and catalyst separation in the presence of conventional homogenous catalysts. Hence, there is a need to employ robust solid catalysts that can simultaneously mediate esterification and transesterification in biodiesel. This approach promises to improve biodiesel production and reduce potential pollution from waste vegetable oil.

1.3. Aim and objectives.

To develop bi-functional catalyst with the view to convert high FFA feedstock in one-step simultaneous esterification (E) and transesterification (TE) reaction

1. To synthesise and characterise a variety of bifunctional catalysts based on acid/base ratios (50% CaO, 60% CaO, 70% CaO and 80% CaO)
2. To characterise selected FFA containing feedstocks.
3. To investigate the production of biodiesel using the feedstocks and bi-functional catalysts in a single-step esterification and transesterification reaction,
4. To investigate the effect of fatty acid saturation on the effectiveness of the catalyst.

1.4. Research Motivation and Significance

Fossil fuels remain unsustainable, and their use is associated with problems caused by global warming and climate change. It is imperative to find a cleaner, more sustainable, and more environmentally friendly alternative source of energy. Feedstock cost plays a critical role in determining the competitiveness of biodiesel. Disposal of waste cooking oil has been reported to be challenging (Chuah *et al.*, 2016). The synthesis of biodiesel using high FFA feedstock

with the use of a bi-functional heterogeneous catalyst promises to address the elevated production costs observed in current industrialised methods. The use of waste oil has the potential to reduce production costs as well as decrease waste oil dumping which is environmentally challenging. The bi-functional heterogeneous catalyst is a combination of calcium oxide and alumina (aluminium oxide) which consists of compounds that are affordable and/or readily available. Calcium oxide can be derived from the thermal decomposition of calcium carbonate, which is abundant and naturally occurring in sea shells, egg shells, bones as well as limestone (Vargas *et al.*, 2019). Further exploitation of such materials includes dolomite rock, which provides a low-cost sustainable source of solid catalysts (Vargas *et al.*, 2019). Alumina, due to its good physical and chemical properties is widely consumed in various chemical industries and is manufactured from bauxite, a naturally occurring ore. Large reserves of bauxite are found in both West Africa and Australia. Bauxite undergoes the Bayer process which produces alumina (Barry *et al.*, 2019). In addition, alumina can be produced from the waste material generated from the industrial aluminium process (slag milling operations) (López-Andrés *et al.*, 2011). Boehmite, which consists of aluminium nitride, carbide and sulphide, is extracted from raw aluminium waste through acid digestion and alkalisation. Boehmite is subjected to thermal treatment to produce aluminium oxide (López-Andrés *et al.*, 2011).

The use of a bi-functional catalyst optimises the production of biodiesel from high FFA feedstock through the conversion of both triglycerides and free fatty acids. These simultaneous reactions accompanied by the elimination of saponification should contribute to the reduction of production costs. Investigation of the effect of certain reaction parameters as well as product robustness will contribute to a better understanding of the process and ultimately pave the way for biodiesel as a feasible alternative to fossil fuels.

1.5. Delineation of Research

This study investigates the production of biodiesel from varying high FFA feedstock through bi-functional heterogeneous catalysis. Different operation parameters will be imposed namely the ratio of acid to base present in the catalyst and varying FFA levels in the oil feedstock. The transportation fuel characteristics of the biodiesel produced from the above varying parameters will be investigated. The effect of water content, as well as production costs, were not covered in this study.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 : Literature Review

2.1. Biodiesel

FAME (biodiesel from methanolysis) has a structure that contains a long carbon chain and an ester functional group. Diesel engines can burn biodiesel fuel with no modifications (except for some rubber tube replacement to combat oxidation and corrosion). This is possible because biodiesel is chemically very similar to conventional diesel. The only difference in structure is the lack of an active ester group. Furthermore, the sizes of the molecules in biodiesel and petroleum diesel are about the same, but they differ in chemical structure (Devi *et al.*, 2017). Biodiesel molecules consist almost entirely of fatty acid alkyl esters, which contain unsaturated “olefin” components. Low-sulphur petroleum diesel, on the other hand, consists of 95% saturated hydrocarbons and 5% aromatic compounds (Devi *et al.*, 2017). Even though the chemical structures of bio and petroleum diesel do not vary immensely, different noticeable structural properties can be observed (Figures 2-1 and 2-2).

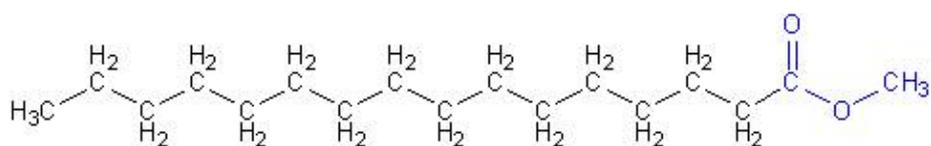


Figure 2-1: FAME molecular structure

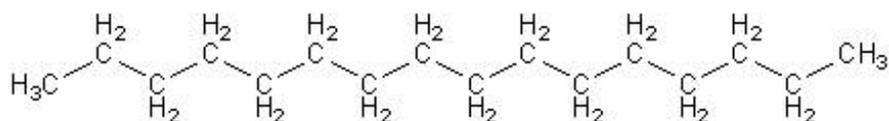


Figure 2-2: Petroleum diesel molecular structure

2.1.1. Advantages of FAME

According to Hassan and Kalam, (2013), the opportunities and advantages of biodiesel are as follows

- Production of biodiesel compared to petroleum diesel is much easier and less time-consuming.
- Emissions present in petroleum diesel such as CO₂, CO, SO₂, and particulate matter are significantly higher compared to biodiesel.

- Due to its elevated lubricity and cetane number, the use of biodiesel reduces engine wear and increases engine performance. This results in the reduction of engine maintenance and prolonged engine performance compared to petroleum diesel.
- Biodiesel proves to be more cost-efficient as it can be produced locally. As a result, it holds great potential in the stimulation of local and rural development generating both energy and financial security.
- Biodiesel does not need to be mined/drilled and transported from reservoirs like oil and natural gas. This poses a major environmental advantage due to the decrease in pollutants associated with these processes.
- Biodiesel trumps fossil diesel in certain transportation characteristics namely flash point, aromatic content as well as biodegradability
- Due to the above-mentioned higher flash point, it is less volatile and safer to transport. Moreover, it is less toxic and biodegradable which further improves the safety in transportation and handling.
- Engine modification is not required for blends up to B20, that is 20% biodiesel and 80% fossil diesel.
- Its nontoxic and non-flammable nature reduces fumes, tailpipe emissions and unpleasant odours.
- Has a higher combustion efficiency compared to petroleum diesel.

2.1.2. Disadvantages of FAME

Although FAME production and use poses numerous advantages, it is also associated with certain challenges (Altaie, (2020) and Hassan and Kalam, (2013))

- Due to its corrosive nature, it damages copper and brass components which would cause internal mechanical issues.
- A higher cloud point and pour point challenges in vehicle and ignition start-up in cold climates.
- Although it is observed to emit less numerous greenhouse gasses such as carbon monoxide and carbon dioxide, biodiesel does have a slightly higher level of NO_x emissions.
- Decreased oxidation stability causes degradation in storage over prolonged periods of time.

- Due to the molecular structure of biodiesel, it has a viscosity up to 17 times greater than petro-diesel. This leads to difficulties and problems in injector systems, atomisation, pumping as well as combustion in the engine.
- In addition, long-term high viscosity operation effects include the formation of injector deposits, rig sticking, filter plugging, gumming formation and incompatibility of standard conventional lubrication oils.
- Carbon deposits on the head of the engine and pistons cause excessive engine wear.
- Due to expensive raw materials needed to synthesise FAME i.e., methanol, biodiesel proves to be less cost-competitive compared to fossil diesel.

2.2. FAME Production Technologies

There are numerous accepted procedures involved in the synthesis of biodiesel that have been well established over the years with the preference for vegetable oils and animal fats as the main source of feedstock. These feedstocks can be modified to rectify properties such as viscosity in order to produce biodiesel consisting of physical properties suitable for diesel engines (Abbaszaadeh *et al.*, 2019). Many procedures can be implemented to produce a better-quality biodiesel namely micro emulsions, pyrolysis, (trans)esterification, direct use and blending.

2.2.1. Direct Use and Blending of Oils

The inventor of the diesel engine, Dr Rudolph Diesel, was the first to use direct use and blending of oils where he tested peanut oil in diesel engines. This process proved to be problematic as the structural and molecular make-up of these oils did not coincide with combustion engine specifications in terms of physical properties such as viscosity. However, due to extensive research over the past century, crude vegetable oils can be mixed or diluted with petro diesel to improve such physical properties (Thoai *et al.*, 2017).

In terms of energy consumption, vegetable oils blended with diesel are found to be less than adequate for both direct and indirect diesel engines. In addition, the high viscosity, FFA content, acid composition and gum formation due to oxidation during both storage and combustion cause carbon deposits (Thoai *et al.*, 2017).

2.2.2 Thermal Cracking (Pyrolysis)

Pyrolysis is a process that involves the thermal decomposition of the feedstock or biomass with the absence of oxygen (Goyal *et al.*, 2008). Thermal decomposition in an oxygen-deficient environment can also be considered as true pyrolysis with the condition that the primary

products are either in solid or liquid form. One major advantage of biofuels produced through pyrolysis has a low oxygen concentration. The decreased oxygen content allows for lower polarity and as a result, better compatibility with traditional hydrocarbon fuels (Tariq *et al.*, 2012).

2.2.3. Transesterification of Triglycerides

FAME can be synthesised using an array of oils and fat such as palm oil, sunflower oil, Jatropha oil and various other seed oils (both used and unused). Chemically, these oils/fats consist of triglyceride molecules of three long-chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Thus biodiesel refers to lower alkyl esters of long-chain fatty acids, which are synthesised either by transesterification with lower alcohols or by esterification of fatty acids (Meher *et al.*, 2016).

Transesterification otherwise known as alcoholysis is the reaction between an alcohol and triglyceride (Meher *et al.*, 2016). It has been widely used to decrease the viscosity of triglycerides. In biodiesel production, these triglycerides are reacted with a basic alcohol, usually methanol to produce FAME and glycerol as a by-product (Figure 2-3).

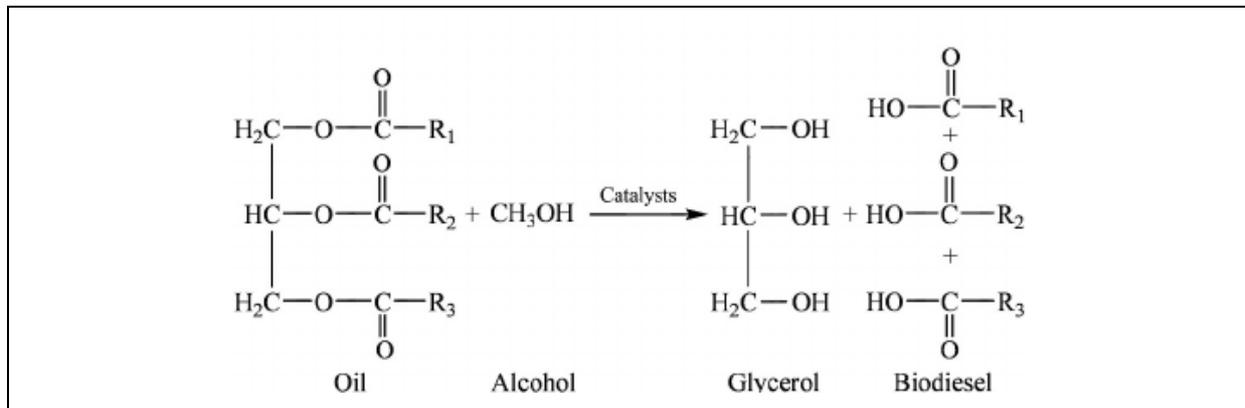


Figure 2-3: Transesterification of triglycerides. Where R1, R2 and R3 are the corresponding long saturated carbon chains (Meher *et al.*, 2016)

This process takes place in the presence of a basic catalyst and excess alcohol to shift the intermediate reactions toward the formation of esters (Meher *et al.*, 2016).

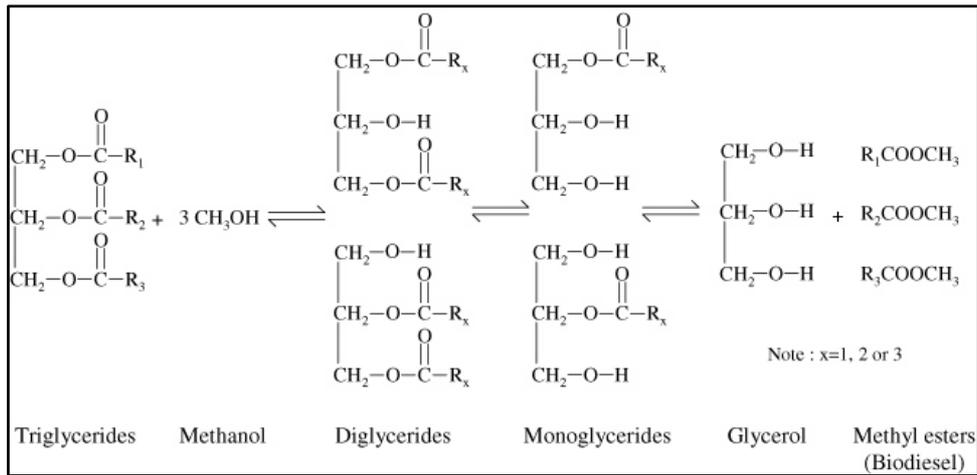


Figure 2-4: Intermediate reactions in the transesterification process (Meher *et al.*, 2016)

Transesterification takes place in three successive and reversible intermediate reactions which are highly influenced by the amount of alcohol introduced to the reaction as seen in Figure 2-4. Even though excess alcohol proves to drive the forward reaction, in some conditions where the operating temperature is higher than the alcohol's boiling point, a lower biodiesel yield is observed.

2.2.4. Esterification of Free Fatty Acids (FFA)

Apart from the presence of triglycerides, many oils contain free fatty acids (FFA). FFA content varies depending on the source of oil as well as whether it has been used or not. Waste cooking oil (WCO) usually has a high FFA content due to the exposure to animal fats and high temperatures. Non-edible plant-based oils such as neem, castor, coconut, Karanja and jatropha also contain higher levels of free fatty acids (Banković *et al.*, 2012). A high FFA content poses a great disadvantage to this process as they undergo a saponification reaction in the presence of a basic catalyst. This side reaction is highly undesirable as a lower yield of biodiesel is achieved (Ramadhas, *et al.*, 2015). The by-product (soap) also proves to be tedious and costly to separate from the biodiesel. However, the presence of an acid catalyst aids in the conversion of FFA into methyl esters in the presence of methanol (Figure 2-5) and this process is known as esterification (Antolín *et al.*, 2015).

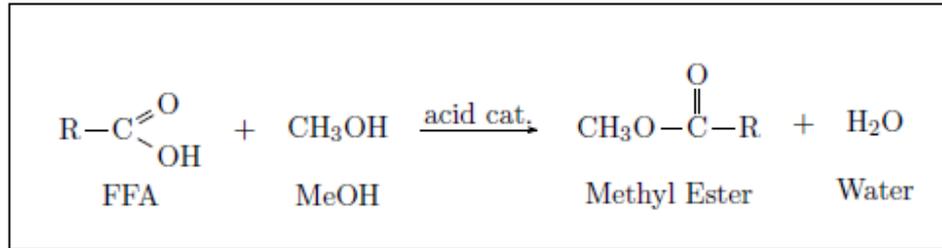


Figure 2-5: Esterification of FFA (Meher *et al.*, 2016)

2.3. FAME Feedstock

Oil crops are the main feedstock for biodiesel production. It is imperative to choose a suitable feedstock for the production of biodiesel as it constitutes 75% of production expenses. At present, up to 350 oil-bearing crops have been identified as potential feedstock. These can be characterised as edible or non-edible/waste oils. The most common sources of edible feedstock include peanut oil, soybean oil, sunflower oil, safflower oil, coconut oil, rapeseed oil, coconut oil, olive oil, castor oil, milkweed seed oil, palm oil, rice bran oil and linseed oil (Mahmudul *et al.*, 2017). Once the above-mentioned oils are used or fried, then they become waste oil feedstocks. Even though edible oils are currently the main source of biodiesel production, there are viable reasons to stray from it as the dominant feedstock of choice. One of these includes the influence and imbalance to the market as it will consequently decrease available food sources. As a result of high demand, the feedstock price is bound to experience constant increment (Mo *et al.*, 2016).

2.3.1. Non-edible Oil feedstock

Non-edible oils signify a potential future energy supply as they are readily available in many parts of the world. Furthermore, they can be grown in barren and degraded lands which would otherwise be unable to support the growth and production of food crops. It can also be observed that large amounts of non-edible plants oil are readily available in nature. Due to this, they are more efficient, environmentally favourable and more economical. Non-edible feedstocks include rubber seed oil, jojoba oil, fish oil, apricot seed oil, cottonseed oil and *Jatropha curcas* as seen in Table 2-1 (Mishra and Goswami, 2018).

However, non-edible oils are known to contain high FFA contents which might ultimately increase the cost of production of biodiesel due to a separation and purification stage needed if a homogenous base catalyst is used (Mo *et al.*, 2016).

Table 2-1: Feedstock sources with corresponding oil content adapted from Mishra and Goswami (2018).

Feedstock	Oil content (%)
Jatropha seed	35-40
Kernel	50-60
Linseed	40-44
Neem	20-30
Pongamia pinnata (karanja)	27-39
Soybean	15-20
Calophyllum inophyllum L	65
35 Moringa oleifera	40
Uphorbia lathyris L.	12-29
Sapium sebiferum L.	12-29

2.3.2. Waste Vegetable oil (WVO)

Waste vegetable oil, especially produced from restaurants, has gained popularity in being a source of feedstock for biodiesel production (Bhuiya *et al.* 2016). This is due to the high cost of edible oil feedstock (Bhuiya *et al.* 2016). Waste vegetable oils pose a great disadvantage, namely a high FFA and water content which increases the cost of biodiesel production while using conventional homogenous catalysts. However, the use of WVO presents an advantage in the form of minimized waste/disposal and is resultantly environmentally favourable (Sajjadi *et al.*, 2016).

2.3.3. Animal Fats and Other Sources

Another potential non-edible oil feedstock source is algae oil (both micro and macro) which is one of the most efficient sources for biodiesel synthesis. This biomass plays an important role in solving the dilemma between competitive food production and biofuels. Microalgae may be the potential and economical source for biofuel production because of their high oil yield as well as rapid biomass production. This is a result of elevated photosynthetic efficiency which results in higher biomass as well as faster growth. Moreover, microalgae have simple structures and can be procured and cultured throughout the year. They reside and grow well in water/aquatic environments and take up less capacity compared to plants that provide non-edible oil feedstock (Guldhe *et al.*, 2017). Biodiesel synthesised from microalgae poses numerous environmental advantages as they are non-toxic and carbon emissions can be regulated depending on where they are grown. Ultimately, biodiesel produced from micro algae has zero sulphur content and can reduce wear and tear on engines due to better oxidation stability values (Mishra and Goswami 2018).

Animal fats are also an acceptable feedstock source for biodiesel production, where the most commonly used animal fat feedstocks include pork lard, beef tallow, poultry fat, fish oil as well as chicken fat (Atabani *et al.*, (2012). These feedstocks pose a monetary advantage as they are low cost and often unwanted waste products readily available for use. However, animal fats tend to have elevated free fatty acid and water content compared to other feedstocks (Goyal, *et al.*, 2018). Both of these factors are disadvantageous during the conventional production of biodiesel.

2.3.4. Alcohol

Alcohol and alcohol type plays a vital role in the production of biodiesel. Different alcohols synthesise different alkyl esters. Methanol alcohol feedstock produces FAME. Similarly, ethanol, propanol and butanol produce FAEE, FAPE and FABE respectively where

FAEE – Fatty Acid Ethyl Ester

FAPE – Fatty Acid Propyl Ester

FABE – Fatty Acid Butyl Ester

Commonly, methanol and ethanol are the alcohols of choice due to availability and cost. Moreover, the reaction time required is less and the biodiesel produced is of high performance (Tshizanga *et al.*, 2016). Methanol is mostly used in production is obtained from mineral oil or is produced from non-renewable resources such as natural gas (Thoai *et al.*, 2017). Alternatively, the use of methyl acetate is also possible for the synthesis of FAME. The reaction requires supercritical conditions or the presence of an enzymatic catalyst. However enzymatic catalysis proves to be costly, hence the use of methanol is more widely preferred (Mishra and Goswami, 2018).

Ethanol is widely produced from renewable sources such as sugar cane, orange peels and elephant grass and it harbours a lower toxicity level compared to methanol (Hassan and Kalam, 2013). However, the production of FAEE requires an extended reaction time and more energy compared to FAME. Resultantly, it is less cost-efficient (Tshizanga *et al.*, 2016).

2.4. Parameters Affecting FAME Production

2.4.1. FFA Content

Currently, the conventional feedstock in biodiesel production is edible (non-waste) oils using a simple alcohol such as methanol and basic catalysts (Tariq *et al.*, 2012). However, a large amount of waste cooking oils and fats are available today and in growing numbers due to both

the fast-food phenomena and the food processing industry (Ramadhas *et al.*, 2015). Waste cooking oils come with several challenges, a major one being that of purity, another being the high FFA content compared to refined edible oil. This is because used oils were previously exposed to high temperatures (mostly for cooking purposes). These high temperatures cause triglycerides present in the oil to break down and form FFA. Moreover, waste oils will likely contain animal fats obtained from the cooking process (Chuah *et al.*, 2016). Animal fats are known to have very high free fatty acid content (8 - 40%) (Srinivasan and Jambulingam, 2018). The difficulty with basic transesterification of these oils is the inhibition of separation of products downstream and cause a consequent decrease in the yield of biodiesel (Ramadhas *et al.*, 2015). Due to the high temperatures in the heating and cooking process, waste cooking oils often contain high FFA contents (> 1 wt%) as well as a high water content (> 0.5 wt%) due to the hydrolysis of the triglyceride during the coking process (Mansir *et al.*, 2018; Díaz and Borges, 2012). Different feedstocks used for biodiesel production inhibit different FFA contents which influence biodiesel yield. Other properties that are influenced by FFA content include kinematic viscosity, cetane number acid value, cloud point, flash point, oxidation stability, cold filter and plugging point (Mansir *et al.*, 2018). Yellow grease (waste cooking oil or used frying oil from restaurants or industrial/commercial cooking operations) have been reported to have an FFA content of up to 15 wt% which, this varies depending on the cooking process as well as the storage and collection conditions (Gaurav *et al.*, 2019). A high FFA content facilitates saponification in the presence of a basic catalyst which hampers FAME production, therefore, these challenges must be taken into consideration with the use of a basic catalyst (Mansir *et al.*, 2018).

2.4.2. Alcohol Type and Alcohol to Oil Molar Ratio

The type of alcohol used in the synthesis of biodiesel affects reaction kinetics as well as the cost of production. Methanol and ethanol are the most commonly used alcohols in biodiesel production where ethanol is mainly procured from agricultural products and methanol can be obtained through wood distillation as well as atmospheric gasses at high temperatures and pressures. Compared to ethanol, methanol costs less and is the most used in the esterification and transesterification processes (Khedri *et al.*, 2019). Furthermore, methanol exhibits a lower sensitivity to water which proves to be advantageous as it has a lower tendency to react with any water potentially existing in the feedstock oil (Wilson *et al.*, 2019). The use of ethanol has major advantages as well (Toledo Arana *et al.*, 2019). Ethanol makes a more environmentally friendly biodiesel (FAEE), which produces lower CO₂, particulate matter and NO_x compared

to FAME. In addition, the fuel characteristics such as cetane number and cloud point are better compared to FAME which makes it better suited for current diesel combustion engines (Toledo Arana *et al.*, 2019).

The molar ratio of alcohol to oil is one of the most influential factors affecting the yield as well as the conversion efficiency of FAME production and overall process. The theoretical stoichiometric ratio is 3:1 alcohol to oil. However, due to the high reaction reversibility rates, a higher ratio is required in order to achieve desired yields of biodiesel. A higher alcohol to oil molar ratio increases the miscibility and enhances contact between the two feedstocks. Moreover, excess alcohol enables the breaking down of glycerine fatty linkages during the transesterification of triglycerides. Consequently, a greater alkyl ester conversion is achieved in a shorter time with an added advantage of higher biodiesel purity. Virgin edible oils such as sunflower and palm oil require a lower ratio compared to plant-based non-edible feedstocks such as pongamia and neem. This might be due to the higher viscosities as well as higher amounts of free fatty acids observed in non-edible oils (Wilson *et al.*, 2019). As a result, it is widely observed that the overall alkyl ester yield is lower in non-edible oils compared to edible oils, and therefore, the optimal ratios should range from 6:1 to 30:1 (Khedri *et al.*, 2019).

2.4.3. Catalyst Size and Loading

Several types of catalysts exist in the production of biodiesel. The two most commonly used are homogenous and heterogeneous catalysts with homogenous catalysts currently being the more conventional option. This is due to their availability and low cost of procurement (Khedri *et al.*, 2019). Alkoxides such as sodium hydroxide and potassium hydroxide are widely used and are observed in producing high yields of biodiesel with a shorter reaction time compared to heterogeneous catalysts. However, heterogeneous catalysts are slowly gaining stride as low-cost alternatives, like calcium oxide, which can be derived from eggshells or readily available limestone (Marwaha *et al.*, 2018).

2.4.3.1. Catalyst Loading

This variable is vital because it determines the reaction rate and, in the case of a homogenous catalyst, can cause hydrolysis and saponification as a loading value too high or too low favours the reverse reaction (Al-Jammal, *et al.*, 2019). Homogenous acid catalysts can be used for feedstocks with elevated acid values however the rate of reaction is extremely slow and ultimately proves to be very costly and inefficient (Ramadhas *et al.*, 2015).

This similarly applies to non-bi-functional heterogeneous catalysts. However, an extra advantage is present with bi-functional catalysts as they consist of both an acid and base constituent. Basic catalysts are extensively used in oils containing a lower free fatty acid content (Hanif *et al.*, 2017). Feedstocks that consist of a high FFA content cause saponification to occur and therefore the introduction of acidic catalysts prevents that to some degree (Leung *et al.*, 2015). Due to the existence of both catalytic capabilities found in bi-functional catalysts, it is imperative to find the optimal ratio between acid and base. This is largely influenced by the acid value in the feedstock used. A lower acid value would require a higher basic to acidic catalytic ratio whilst feedstock with a high FFA content would require a lower ratio to achieve the desired biodiesel yield. Therefore, catalyst loading and ratios are feedstock specific and the ultimate goal is to hinder the reverse reaction as much as possible.

Catalyst loading is a crucial factor that contributes to the conversion of biodiesel. Studies have shown that a loading ratio between 0.5 wt% and 2 wt% are optimal for the achievement of high biodiesel yields. However, a catalyst loading higher than 2 wt% results in a decrease in yield. By adding excess catalyst, adsorption of some produced biodiesel is noticeable and consequently, the amount of biodiesel obtained will be less. Furthermore, an excess amount of catalyst can result in the deactivation of activated molecules through the collision with ground state molecules (Kamel *et al.*, 2017). Another disadvantage of excess catalyst loading includes the formation of a slurry which inhibits the production of more biodiesel (Buchori *et al.*, 2019). Catalyst loading greater than 5 wt% results in the formation of other compounds which are not methyl esters and as a result, the biodiesel obtained has a high viscosity and density (approximately 6.52 cP and 0.89 g/cm³ respectively) which does not adhere to both EN and ASTM standards (Buchori *et al.*, 2019).

2.4.3.2. Catalyst Particle Size

Vital catalytic properties which affect reaction yield and rate include activity, surface area and porosity where particle size dictates the nature of these properties (Al-Jammal *et al.*, 2019). A smaller particle size is desired as it increases the porosity which results in a higher number of active sites. In addition, the surface area gets larger as the particle size decreases which results in better catalytic activity and therefore higher yields and faster reaction rates (Wilson *et al.*, 2019). However in some cases, if the particle size is too small, it can increase the internal diffusion resistance to the reactant molecules which results in a lower conversion (Al-Jammal *et al.*, 2019).

2.4.4. Temperature

2.4.4.1. Reaction Temperature

The effect of temperature is always a major influence in all reactions including the transesterification of oils to biodiesel. Temperature affects the yield of biodiesel as it alters the reaction kinetics. It is further elaborated that the increase of temperature results in an increase in feedstock conversion due to the enhancement of mass transfer by the improvement of the oil – alcohol miscibility and therefore, the rate of reaction is also improved and increased (Tiwari *et al.*, 2018). The transesterification reaction is endothermic hence it favours high temperature conditions. The effect of temperature on reaction rate is explained by the theory of chemical reaction kinetics where an increase in temperature results in an increase of high speed molecules and therefore a high kinetic rate. However, different optimal reaction temperatures vary depending on the feedstock used. Feedstocks such as neem oil have been found to have optimal reaction temperatures between 55 and 63 °C under heterogenous catalysis, producing yield values between 84 and 94% (Abbah *et al.*, 2016). In the case of waste cooking oils, an average rate of yield increase is reported as 5% per 5 °C with 64 °C being the optimal temperature which facilitates a yield of 96% (Istiningrum, Aprianto and Pamungkas, 2017).

Many studies are done with reaction temperatures below the boiling point of the feedstock alcohol. It is found that reactions performed with higher temperatures result in a decrease in yield. Operating reaction temperatures above the boiling point of the alcohol causes the saponification of the triglycerides which is accelerated by the catalyst before complete alcoholysis occurs (Al-Jammal *et al.*, 2019). In addition, feedstock alcohol mass is lost due to evaporation. However, operating temperatures higher than the boiling point of the alcohol under reflux conditions have the ability to produce high yields of biodiesel (Bilgin *et al.*, 2015). Hence it is imperative to operate the reaction at the optimal temperature in order to achieve the highest and desired yield.

2.4.4.2. Calcination Temperature

Calcination temperature plays a crucial role in the catalyst synthesis and resultant biodiesel yield. This is because it affects major catalytic attributes such as pore volume, surface area, basic/acidic site densities as well as crystalline and molecular structure. While undergoing the catalytic process, high temperatures cause the exposure of catalytic sites due to the elimination of water and loosely bound carbon dioxide. Furthermore, the calcination process rearranges the

bulk atoms on the surface of the catalyst as a result of molecular structure change (e.g. α -alumina to γ -alumina). A study showed an increase in FAME yield from 62% to 90% when the calcination temperature was changed from 250 to 350 °C for 4 hours. The increase in calcination temperature enhanced catalytic performance in the transesterification process however, an excessive increase in temperature could result in low FAME yield which would indicate decreased catalytic performance. This is explained by the gaseous diffusion out of the pores during thermal treatment. This results in a surface pore limitation as well as partial removal of binding water molecules from the catalyst structure leading to catalyst damage and consequently the formation of an unknown species (Mansir *et al.*, 2018).

2.4.5. Water Content

Alkaline catalysts are sensitive to the water content in the feedstock and the occurrence of a saponification side reaction, which forms catalyst soap, hinders the main desired reaction. This is because the presence of water and the relatively high reaction temperature causes the hydrolysis of the triglyceride which consequently increases the FFA content of the oil. Ultimately, a higher water content results in a lower biodiesel yield. Therefore, the water content (by weight) in the feedstock should be less than 1% (Khedri *et al.*, 2019).

2.5. Catalysts

Catalysts can be mainly classified into two main groups namely homogenous and heterogeneous, where the heterogeneous catalyst can be either mono, bi-functional or bio catalysts (Figure 2-6). The choice of catalyst in FAME production depends on numerous parameters that include among others the type of oil as well as the alcohol to oil molar ratio used to synthesise biodiesel.

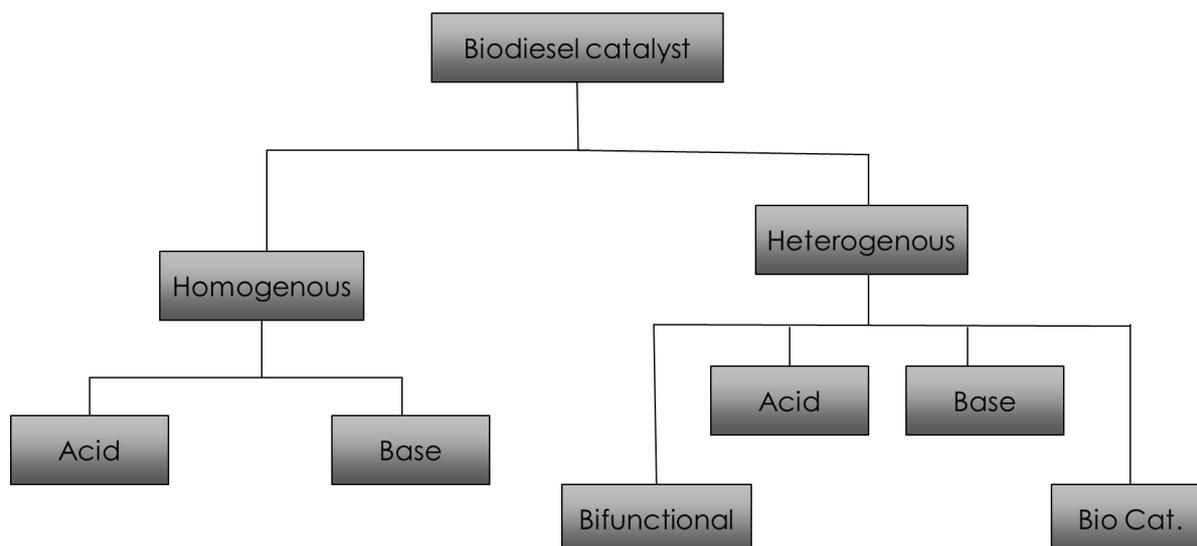


Figure 2-6: Biodiesel catalysts

2.5.1. Homogenous Catalysts

Homogenous catalysts, which can be basic or acidic, are catalysts that exist in the same phase as the feedstock and reactants (Hanif *et al.*, 2017). Homogenous base catalysts are extensively used for biodiesel production because of their high rate of reaction as they favour the transesterification of triglycerides due to their reduced mass transfer effect which facilitates faster reaction efficiency (Mansir *et al.*, 2018). The most commonly used homogenous catalysts on an industrial scale are alkoxides and hydroxides of alkali metals such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (CH₃ONa) (Mansir *et al.*, 2018). However, a problem arises when the feed stock has a high FFA content (>1 wt%) and other impurities (Chuah *et al.*, 2016). An elevated FFA content results in the high formation of soap which is undesired as previously mentioned. The use of just an acid catalyst hinders this saponification reaction as it favours the esterification of free fatty acids. However, acid catalysts have a much slower rate of reaction compared to basic catalysts and prove to be time consuming (Leung *et al.*, 2015). Moreover, the use of homogenous catalysts proves to be expensive as the separation process is very extensive and difficult. Although conventional homogeneous catalysts offer high yields, they are associated with several drawbacks such as an extra neutralization step, tedious purification process and wastewater generation which result in increased production costs of biodiesel (Guldhe *et al.*, 2017).

2.5.2. Heterogeneous Catalysts

Heterogeneous catalysts are defined as catalysts that are in different phases from the reacting medium in a reaction process. In the production of biodiesel, the feedstock and reaction medium are in liquid phase and the heterogeneous catalyst for the reaction is in solid phase (Gaurav *et al.*, 2019). These catalysts could be acidic or basic in nature and can be utilised in the alcoholysis process depending on the feedstock's FFA content (Mansir *et al.*, 2018). Heterogeneous catalysts are gaining interest for conversion of oils to biodiesel due to their advantage of easy separation from the reaction mixture and reuse (Ramli *et al.*, 2016). These catalysts have also shown potential to overcome the challenges posed by the use of homogeneous catalysts and replacing them at an industrial scale (Guldhe *et al.*, 2017). However, the use of heterogeneous catalysts comes with a fair share of disadvantages. One of the major hurdles associated with the use of solid heterogeneous catalysts for biodiesel production is their very high cost (Tabatabaei *et al.*, 2019). The cost of most solid heterogeneous catalysts is significantly higher than that of homogeneous catalysts. Therefore, the use of solid heterogeneous catalysts at an industrial scale is limited. Furthermore, heterogeneous catalysts require some preparatory processes for their synthesis which can be time-consuming. In addition, atmospheric exposure for a prolonged period of time might deter the activity and stability of the catalyst (Mansir *et al.*, 2018)

Moreover, the efficiency of heterogeneous catalysts is not as good as that of homogeneous catalysts (Tariq *et al.*, 2012). Higher efficiency of any catalytic processes can be achieved by improving the activity and selectivity of the catalyst. Both these features depend on the catalytic material designed with the dispersion of the active sites and desired structure. Heterogeneous catalysts used for biodiesel production have two different constituents: one is the active constituents and the other is the catalytic support (Rehan and Arabia, 2017). Heterogeneous catalysts such as metal oxides derived from alkaline earth metals such as barium, calcium and magnesium have been utilised in previous studies due to their high activity and long lifespan (Elias *et al.*, 2020). The choice of supportive material depends on the conditions of reaction and the nature of the feedstock used and therefore, the quality of the feedstock strongly affects the properties of supportive material (Adedoyin *et al.*, 2019). Hence it is imperative to design the catalyst taking into consideration these aspects.

2.5.3. Bio-Catalysts

A more environmentally friendly method for the production of biodiesel is enzymatic transesterification which involves the use of lipases under mild reaction conditions and low energy consumption by exploiting a variety of feedstocks. The use of enzymatic catalysts, otherwise known as biocatalysts have added benefits such as high yield and product purity (Gihaz *et al.*, 2016). Moreover, they have been shown to achieve better conversion and selectivity and are able to catalyse both the transesterification and esterification reactions at relatively low temperatures. This facilitates catalyst recovery as well as the purification of glycerol. Biocatalysts do have their fair share of disadvantages, the primary one being the presence of water in the reaction which can lead to the hydrolysis of esters (Sánchez-Bayo *et al.*, 2019). Enzymatic catalysis in biodiesel production is also constrained by short-chain alcohols such as methanol (Gihaz *et al.*, 2016). This limited stability is caused by the stripping of structural water molecules by the feedstock alcohol which consequently alters conformational flexibility and leads to catalyst deactivation. Several approaches have been developed to combat these shortcomings, one of them being enzyme immobilisation (Gihaz *et al.*, 2016).

Enzyme immobilisation can be defined as the confinement of enzyme molecules onto a support either physically, chemically or both in such a way that it retains its full or most of its activity while improving catalytic stability. There are different types of immobilisation techniques namely cross-linking, adsorption and covalent immobilization. Cross-linking immobilization involves the attachment of an enzyme to another using a multifunctional reagent. The enzyme is precipitated from aqueous solutions by the addition of non-ionic polymers, salts or organic solvents (Kim, Lee and Lee, 2018). However, it is hard to control the cross-linking reaction and therefore, some loss in catalytic activity is evident. Adsorption immobilization involves a physical binding mechanism such as dipole-dipole, hydrogen bonding, van der Waals interaction or hydrophobic bonding. This process does not provide high stability and a loss of enzyme molecules may occur due to the weak binding forces between the enzyme and support. The covalent immobilisation of a biocatalyst is the attachment of the enzyme to a nano matrix through covalent bonding between the support and enzyme (Kim, Lee and Lee, 2018). This strong bond facilitates high stability however, this technique may result in catalyst deactivation due to the conformational restriction of the enzyme by covalent bonding (Kim, Lee and Lee, 2018).

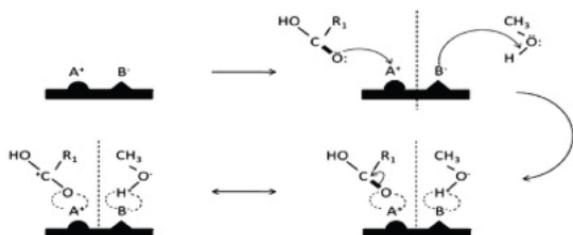
2.5.4. Bi-functional Catalysts

Bi-functional heterogenous catalysts are catalysts that are both acidic and basic in nature (solid acidic – solid basic character) (Figure 2-7) which have the ability to simultaneously esterify and transesterify the feedstock (Elias *et al.*, 2020). The use of bi-functional catalysts was sparked by the limitations and difficulties experienced by only using either acid or base catalysts (Rehan and Arabia 2017). Though basic catalysts have higher activity and shorter reaction times, they fail to produce the optimal yield of FAME as compared to a bi-functional catalyst (Rehan and Arabia 2017). In addition, the use of only solid acid catalysts requires more extreme conditions with regards to temperature and pressure (Marwaha *et al.*, 2018).

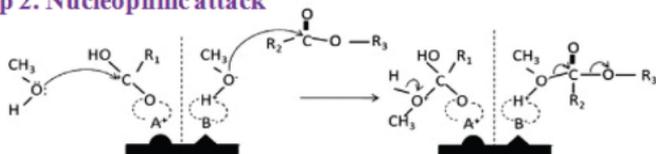
This flexibility proves to be advantageous as the catalyst can be designed according to the FFA content of the raw material in order to achieve a high yield. For example, any oil with a high FFA (> 2 wt. %) content will require a larger acid to base ratio in order to favour the esterification reaction. Whereas for any oil with a relatively low FFA content (< 1 wt. %) a higher conversion to biodiesel will be achieved if a higher ratio of basic to acidic catalyst is used (Sánchez-Bayo *et al.*, 2019). Furthermore, heterogenous bi-functional catalysts can be reused, recycled and regenerated with minimal energy consumption and inhibit soap formation during the synthesis of methyl esters. This process requires very little and simple purification and does not require catalyst recovery or aqueous treatment stages. Solid bi-functional catalysts give better FAME yields as they are more tolerant to feedstocks containing high FFA and water content due to their heterogenous nature. Moreover, they are not soluble in the feedstock which facilitates easy and cheap separation (Elias *et al.*, 2020).

Although the use of bi-functional catalysts provides many advantages, these catalysts are prone to accelerated deactivation, i.e. their catalytic performance and efficiency decreased per reaction (Hanif *et al.*, 2017). This poses a major concern as heterogeneous catalysts are already quite costly to procure. Hence it is imperative to design an efficient bi-functional catalyst with a precise acid-base ratio to achieve both maximum yields as well as good catalytic performance over a number of consecutive cycles.

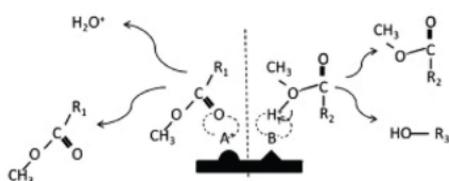
Step 1. Methanol and FFA adsorption on basic acid sites respectively.



Step 2. Nucleophilic attack



Step 3. Desorption



A*: Acid site on the catalyst surface
B*: Basic site on the catalyst surface
R₁: Alkyl group of fatty acid
R₂: Alkyl group of fatty acid on triglyceride
R₃: alkyl group of triglyceride

Figure 2-7: General mechanism for simultaneous esterification and transesterification reactions on bi-functional heterogeneous catalyst (Ramli *et al.*, 2016)

2.5.4.1. Impregnation Methods for Catalyst Preparation

Impregnation methods remain the most popular of choices in catalyst preparation. Impregnation consists of two different types namely wet impregnation and dry impregnation (Mehrabadi *et al.*, 2017). Using an amount of the precursor solution in excess of the support pore volume resulting in a thin slurry is termed as wet impregnation (WI) whereas limiting the solution amount just enough to fill the pore volume is known as dry or insipient wetness impregnation (DI). The use of WI requires a need to recycle the excess liquid in order to limit wastage. However, with the use of dry impregnation, there is little to no excess liquid which eliminates the need for filtration. Catalysts synthesised through impregnation methods do not usually produce particles with high dispersion due to the lack of induced interaction between the support and the precursor, which allows mobility of the precursor during the drying process. Consequently, this lack of strong interaction causes moisture mitigation to the external surface of the support during the drying process. As a result, the precursor particles agglomerate together. This causes the above-mentioned major disadvantage where there is a lack of particle size control and distribution, especially with metal particles. It is however the fastest and simplest method in catalyst preparation (Mehrabadi *et al.*, 2017).

2.5.4.2. Precipitation Methods for Catalyst Preparation

The two main types of precipitation methods are deposit precipitation and reductive deposition. Deposit precipitation (DP) is defined as a method that involves the conversion of a highly soluble metal salt precursor into a less soluble substance which only precipitates on the support and not in the solution. In many cases, this is achieved by a change in pH of the solution, the addition of a reducing agent, the addition of a precipitation agent or the change in the concentration of a complexation agent. In order for this to be successfully achieved, two conditions must be met. Firstly, there needs to be a strong interaction between the soluble metal and the precursor. Secondly, spontaneous precipitation needs to be avoided through controlling the concentrations of the precursor in solution. This method however comprises of one major drawback; it is widely observed that there is poor control of both surface composition as well as poor metal distribution. Reductive deposition is one amongst various methods used to prepare nanometre sized particles. The first step in order to synthesise these metallic nano particles involves dissolving precursor metal salts in an organic or aqueous medium. Thereafter, there is an addition of a reducing agent solution which results in metal particles being selectively deposited on supports. Similarly to DP, reductive deposition is achieved through induced precipitation. The metal precursors are usually reduced through thermal decomposition (the use of high temperatures), electrochemically or by the use of highly reductive agents such as hydrazine and ethylene glycol. The use of these reductive agents, however, are undesired due to their toxic nature and the use of electro-chemicals requires costly equipment. Hence the more environmentally friendly route is through thermal decomposition (Mehrabadi *et al.*, 2017).

2.6. Transportation Fuel Characteristics

2.6.1. Oxidation Stability

Oxidation stability is the measure of a compound's ability to easily undergo oxidation (Devi *et al.* 2017). The oxidation stability of biodiesel is important during storage as it yields products that degrade biodiesel quality and consequently affects the combustion engine performance (Pullen and Saeed, 2012). Fatty wastes are more susceptible to oxidation due to the presence of double bonds (high unsaturation) which prove to be very reactive (Devi *et al.* 2017). Consequently, biodiesel produced by unsaturated FFA oils or waste oils are more inclined to oxidation. Even though the number of double bonds, otherwise known as the level of saturation does play a role, the major cause of biodiesel oxidation is the number of bis-allylic carbon sites

present Bis allylic sites, or rather bis allylic carbon is a carbon atom bonded to a carbon atom that is in turn bonded to another carbon atom by a double bond.

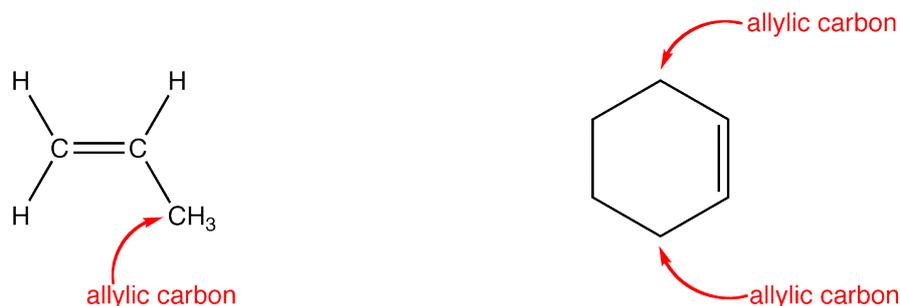


Figure 2-8: Example of Bis-allylic carbons adapted from (Chuah *et al.*, 2016)

The oxidation of biodiesel takes place in several stages. The initiation step is the formation of a free radical that can react directly with oxygen. This leads to the formation of a peroxide or hydro peroxide. The most reactive site is the bis-allylic site where radicals formed from the bis-allylic site isomerise to form a more stable conjugated structure that reacts with oxygen to form hydrogen peroxide. The presence of these molecules is an early indication of oxidation. Peroxide value is a measure of the level of oxidation of a fat or oil containing poly unsaturated fatty acids (which are the main cause of rancidity) (Chuah *et al.*, 2016). The final stage of biodiesel degradation is that due to the free peroxides, ketones and aldehydes are formed. This results in their polymerization where resins are formed which ultimately make the fuel unstable (Devi *et al.*, 2017).

Due to the chemical structure of FAME, oxidation rates depend on many variables such as temperature, light, radiation intensity and naturally occurring antioxidants. Oxidation of FAME can be prevented by adding antioxidants. Synthetic antioxidants are preferred to natural antioxidants due to their level of efficiency (Pullen and Saeed, 2012).

2.6.2. Saturation and Iodine Number/ Value (IV)

The degree of unsaturation of a feedstock is a very influential parameter in biodiesel quality (Giakoumis., 2013). The iodine number or iodine value is defined as a parameter used to determine the degree of unsaturation. This number indicates the mass of iodine (I_2) that is needed to completely saturate 100 g of feedstock through stoichiometric reaction (Giakoumis., 2013). The iodine number ranges from 7.8, for the most saturated methyl ester (synthesised from coconut oil) to a high of 184.5 for the most unsaturated being linseed (Chuah *et al.*, 2016). An overall average of ~ 80 is observed for the range of biodiesel produced by the current feedstocks used to synthesise it. A value of less than 120 is required to operate an average

combustion engine with no modifications or alterations (Giakoumis and Sarakatsanis, 2018). The higher the iodine number, the more likely the biodiesel has elevated instability due to the increased double bonds and level of unsaturation (Mahmudul *et al.* 2017).

2.6.3. Carbon Residue, Emissions and Particulate Matter

Carbon residue and particulate matter of a fuel indicates the extent of carbon and various solid deposits resulting from the combustion of a fuel (Bhuiya *et al.*, 2016). The carbon residue produced by biodiesel is more significant to that of petroleum diesel as it is influenced by factors such as FFA content, glycerides, polymers of higher unsaturated fatty acids and inorganic impurities. However, carbon residue and particulate matter is caused by the subsequent pyrolysis of the fuel components that may clog the fuel injectors (Hoekman *et al.* 2012).

Emissions from a diesel engine exhaust is typically composed of nitrogen oxides (NO_x) with the prominent oxide being nitrogen oxide, NO. NO formation has 3 mechanisms namely Fenimore (prompt formation of NO), Zeldovitch (thermal production of NO) and the fuel NO mechanism. A non-premixed combustion engine is the main cause of the Fenimore and Zeldovich mechanisms. The presence of high temperatures greater than 1800K as well as a mixture equivalence ratio less than 1 at the periphery of the diffusion flame are optimal conditions in the increased production of thermal NO_x (Lanjekar and Deshmukh, 2016). Thus, any parameter that influences combustion temperature, fuel to air ratio and equivalence ratio directly affects the formation of NO_x emissions. In the case of biodiesel however, NO_x emissions are mostly caused by advanced injection timing. Injection timing is the timing at which a fuel is injected inside the cylinder which ultimately has a significant effect on combustion efficiency. Due to the higher density of biodiesel, advanced injection is necessary because a higher modulus of biodiesel is needed and injected compared to petroleum diesel (Lanjekar and Deshmukh, 2016). The density of biodiesel is directly proportional to the level of unsaturation in the fuel. Hence the more unsaturated the fuel, the more likely it is to experience advanced fuel injection and consequently produce higher NO_x emissions.

NO_x emissions, especially in petroleum diesel are largely caused by high combustion temperatures that range from 148 to 252 °C (Altaie, 2020). In the case of biodiesel, long unsaturated chains in elevated temperatures produce higher emissions. Long chain saturated esters however produce lower emissions compared to short chain saturated esters (Altaie, 2020). Ultimately, biodiesel with an iodine value of 38, which is equivalent to a ratio of 1.5

double bonds per molecule would be a NO_x neutral fuel relative to standard petroleum diesel (Lanjekar and Deshmukh, 2016).

Although Biodiesel produces slightly higher NO_x emissions (~ 12% higher than petroleum diesel), its carbon monoxide emissions are significantly lower (~ 63% lower than petroleum diesel) (Altaie, 2020). This is due to the extra oxygen found in biodiesel that ultimately facilitates complete combustion (Balat 2017). However, these emissions vary and are subject to combustion temperature and oxygen saturation in the feedstock used (Altaie, 2020). Sulphur oxide and dioxide emissions are next to nil compared to petroleum diesel due to the minuscule sulphur content of biodiesel (0.0000-0.0024 wt%) versus petroleum diesel (0.04-0.01 wt%). Due to this, biofuels have the potential to reduce up to 80% of greenhouse gas emissions. A lower percentage of biodiesel-diesel blends emit very low amounts of carbon dioxide in comparison with standard fossil diesel (Mo *et al.*, 2016).

2.6.4. Density and Specific Gravity

The density of a material or fluid is defined as the ratio of its mass per unit volume and the dimensionless term specific gravity (SG), is defined as the ratio of the density of a substance relative to the density of a reference substance, which is commonly water (Giakoumis, 2013). Biodiesel fuels in general are known to exhibit a higher density than that of petroleum diesel. Petroleum diesel densities range from 745 to 832 kg/m³ which is almost 5% lower than the standard EU acceptable methyl ester range of 860 – 900 kg/m³. Due to this comparatively elevated density, it is found that a greater mass of biodiesel will be volumetrically injected as an operating fuel compared to conventional petroleum diesel (Mahmudul *et al.*, 2017). The density of the fuel directly affects engine performance. A higher density will increase fuel particle size in the combustion chamber which in turn increases the air to fuel ratio. In addition, fuels with lower density are found to be more efficient with regard to air-fuel ratio and atomization (Altaie, 2020). The density of the fuel is directly proportional to the engine emissions therefore a fuel of higher density causes higher emissions (Hassan and Kalam, 2013). This is a result of the above-mentioned higher air to fuel ratio which consequently causes high particulate matter and NO_x production.

The density of petroleum diesel is influenced by the type of crude as well as refinery specifications. Similarly, the density of biodiesel is determined by the feedstock used to synthesise it. Thus, the less dense the feedstock, the denser the fatty acid alkyl esters produced.

2.6.5. Kinematic Viscosity

Viscosity is a measure of the resistance of a fluid that is being deformed by either shear or tensile stress (Giakoumis, 2013) . In the case of transportation fuels, less viscous fuels are favoured. This is because the less viscous the fuel, the greater the ease of its movement or fluidity, which reduces the ignition delay period. Increased viscosity proves to be problematic as it affects engine efficiency. Similarly, to the effect of high density, higher kinematic viscosity leads to less than accurate fuel injection and results in poor atomization of the fuel. These inefficiencies are further exacerbated during cold starting. In addition, higher kinematic viscosity leads to higher injection pressures and hence mass of the injected fuel and consequently higher emissions such as NO_x. The viscosity of biodiesel heavily relies on the type of reactants used, more specifically the feedstock oil. Vegetable oils have a high viscosity (up to 121 mm²/s at 40 °C), which is higher than the current acceptable petroleum diesel value of 2.6 mm²/s (Giakoumis, 2013). Due to this, vegetable oils cannot be used safely in a compression engine without prior heating. Thus, the process of transesterification to produce alkyl esters is imperative. Although the transesterification process reduces the viscosity of FAME and FAEE, the levels are still slightly higher than those of conventional petroleum diesel (Devi *et al.*,2017).

The European specifications strictly dictate that the acceptable viscosity range of biodiesel be between 3.5 and 5 mm²/s (Adedoyin *et al.*, 2019). This range is achieved by using waste oils such as sunflower oil, palm oil and olive oil which produce a product with an average viscosity range of 4.55 – 5.06 mm²/s (Sundus *et al.*, 2017). Biodiesel produced from feedstocks like castor oil however exhibit an average kinematic viscosity value of 14.5 mm²/s which exceeds the stipulated and acceptable range. This is due to the fact that castor is rich in ricinoleic acid which contains OH and as a result, biodiesel produced from castor oil feedstock exhibits a high viscosity value (Chuah *et al.*, 2016). Hence castor biodiesel is often blended with petroleum diesel in order to achieve acceptable viscosity. On the other side of the spectrum, however, biodiesel produced from coconut oil, which has a very low viscosity, has an average kinematic viscosity value of 2.55 mm²/s and needs to be blended with a heavier diesel in order to achieve the standard acceptable operating range (Devi *et al.*,2017).

Viscosity is known to increase with increasing chain length, whereas branching plays a more secondary role. The existence of double bonds also reduces viscosity. More specifically, *cis* double bonds cause lower viscosity than *trans* double bonds, which are commonly found in cooking oils (Giakoumis, 2013).

2.6.6. Heating Value/ Calorific Value

The lower heating value (LHV) and the higher heating value (HV) are defined as the measure of a fuel's heat of combustion, with the difference between them being the water's heat of vaporization (Giakoumis and Sarakatsanis, 2018). Heating value is one of the most important parameters and fuel characteristics as it affects both the thermal efficiency and combustion characteristics of an engine since it ultimately measures the energy content of the fuel. The heating value, also known as the calorific value is further defined as the heat of combustion of fuel, or rather the thermal energy released per unit quantity of fuel when the fuel undergoes complete combustion (Mahmudul *et al.*, 2017). A higher calorific value (CV) is more desirable for a combustion engine because the higher the value, the higher the fuel's energy content and therefore the higher the fuel efficiency (Bhuiya *et al.*, 2016). The calorific value increases with the number of carbon atoms or rather chain length. It also increases as the ratio of carbon and hydrogen to nitrogen and oxygen increases. This ratio is more efficient whilst dealing with lower carbon chain lengths within the range of c8 and c14 (Sajjadi *et al.*, 2016). Due to the increased oxygen content, biodiesel has a relatively lower calorific value compared to normal petroleum diesel (Yadav *et al.*, 2019). One of the main factors that affect HV is the level of saturation in the fuel. It is observed that the heating value of FAME and FAEE decreases as the number of double bonds increases. The effect of unsaturation is greater compared to the effect of carbon chain length. The higher heating value decreases by approximately 0.21 MJ/Kg for each increase in the degree of unsaturation of fatty acid methyl esters. The average heating value of petroleum diesel is 46 MJ/Kg which is 12% higher than that of biodiesel estimated at a range of 39.57 – 41.33 MJ/Kg (Sajjadi *et al.*, 2016).

2.6.7. Lubricity

Lubricity refers to the reduction of friction between surfaces in relative motion. There are two factors and mechanisms that influence and contribute to overall lubricity. These factors include boundary lubrication and hydrodynamic lubrication (Hoekman *et al.* 2012). In the case of hydrodynamic lubrication, a liquid layer, in this case, being diesel or biodiesel within a fuel injector, inhibits contact between two opposing surfaces hence decreasing surface friction significantly, whereas boundary lubricants are compounds that adhere to surfaces, usually metal surfaces. Boundary lubricants form a thin, protective anti-wear layer which becomes extremely significant especially when the hydrodynamic lubricant has been worn out or removed from the abovementioned opposing surfaces. Boundary lubrication alone may not be ideal as it causes high wear, generated heat as well as increased friction (Sundus *et al.*, 2017).

It is therefore imperative to have mixed lubrication as the asperities in this lubrication still allow for contact with each other although they are separated by a lubricating film.

The high frequency reciprocating rig method (HFRR) is the standard mode of lubricity testing (ASTM D6079 and ISO 12156). The HFRR test is a ball on disk method where the wear scar is an average of the major and minor axes of an elliptical contact area. The maximum allowable wear scar is 460 μm and 520 μm at 60 °C as described by the European petrodiesel standard (EN 590) and American petrodiesel standard (ASTM D975) respectively (Liu *et al.*, 2019).

Good lubricity in a transportation fuel is critical to protect fuel injection systems. Moreover, in many cases, it is found that the fuel itself is the only lubricant in the system. Maintaining good lubrication is crucial as operational demands are increasing. Modern injection systems now operate under higher pressure, higher injection rates as well as multiple and increased injections per cycle (Hoekman *et al.* 2012). It is found that petroleum diesel has relatively lower lubricity (~380 μm) compared to biodiesel (<200 μm) at 25 °C (Xiao *et al.*, 2019). This is because petroleum diesel is previously hydrotreated to remove hetero-atom containing molecules namely oxygen, nitrogen and sulphur (Balat, 2017). These molecules significantly increase lubricity. Biodiesels are esters hence they contain an extra molecule of oxygen compared to standard petroleum diesel and as a result, the presence of this molecule results in a higher lubricity in FAME and FAEE compared to petroleum diesel. In general, lubricity effectiveness decreases in the order O>N>S>C (Hoekman *et al.*, 2012).

In addition, biodiesel's elevated lubricity is also contributed to the higher degree of impurities in biodiesel, more specifically the free fatty acids and monoglycerides which were introduced in the feedstock and prove to be highly effective lubricants. Although the free fatty alkyl esters have improved lubricity characteristics due to these impurities, they can also contribute to the pugging of filters as a result of the formation of deposits (Bhuiya *et al.*, 2016). Ultimately, the high lubricity of biodiesel fuel results in reduced friction loss which ultimately improves brake effective power (Hoekman *et al.*, 2012).

2.6.8. Cetane Number

The cetane number is one of the most crucial parameters in transportation fuel. It is a dimensionless number that denotes the self-ignitability of a fuel, or other words, it is a measure of a fuel's ability to auto-ignite after being injected into the combustion chamber (Giakoumis, 2013). Thus a higher cetane number indicates a shorter ignition delay, which is the time passed between ignition and initiation of the fuel injection into the combustion chamber (Sajjadi *et al.*,

2016). Cetane number (CN) increases with an increase in saturation and chain length of fatty acids. A decreased CN causes an increase in gaseous emissions and particulate matter (Bhuiya *et al.*, 2016). Furthermore, low CN causes knocking as well as excessive engine deposits due to incomplete combustion. Due to the fact that biodiesel is mostly composed of long-chain non-aromatic hydrocarbons, it typically has a higher CN than petroleum diesel (Hoekman *et al.*, 2012). Hence it is observed that biodiesels with low amounts of unsaturates will have higher CN and vice versa. A cetane number from the 25 most popular biodiesel feedstocks range from 50.4 to 61.2, which is 8-10% higher than that of petroleum diesel (Giakoumis, 2013).

2.6.9. Flash Point

Flash point (FP) is the temperature at which the biodiesel ignites when exposed to a flame or a spark at the atmospheric pressure of 101.325 kPa. Biodiesel typically has a flash point of 150 °C whilst petro diesel has a flash point range of 55 -66 °C (Mo *et al.*, 2016). Flash point is a key safety property that is evaluated in order to consider aspects like handling, transportation and storage conditions (Sajjadi *et al.* 2016). Consequently, due to the higher flash point of biodiesel, it is safer to store and transport compared to petroleum diesel. Flashpoint is often found to be directly proportional to a fuel's volatility (Mo *et al.*, 2016).

2.6.10. Cold Flow Properties

The three most significant cold flow properties include cold filter plugging point (CFPP) cloud point (CP) and pour point (PP)

2.6.10.1. Cold filter plugging point

Cold filter plugging point is an important low-temperature property of a fuel and is defined as the minimum or lowest temperature at which 20 mL of fuel passes through a standard filtration apparatus within 60 s, i.e., it is used as an indicator of how well a fuel can operate under very low temperatures. CFPP is critical especially in regions prone to very low temperatures. Furthermore, the CFPP is the temperature at which fuel starts to gel, resulting in the clogging/plugging of the fuel filter (Sajjadi *et al.*, 2016). CFPP is known as one of the most critical parameters in biodiesel as it determines the crystallisation/ gelling/ solidification temperature of the fuel in order to avoid the plugging of filters (Chuah *et al.*, 2016). The specifications of this temperature vary worldwide due to differing climates.

2.6.10.2. Cloud Point (CP)

The temperature at which a fuel starts to get 'cloudy' and form a solidified wax. The presence of this wax or rather bio wax in the case of biodiesel clogs the injectors and ultimately the

engine. A higher CP is not desirable as it indicates that the fuel will crystallise easier and ultimately cause engine wear due to impaired lubricity (Lanjekar and Deshmukh, 2016).

2.6.10.3. Pour Point (PP)

Pour point is defined as the measure of the fuel's gelling point, a temperature at which the fuel cannot be pumped (Lanjekar and Deshmukh 2016). Biodiesel has a higher pour point than petroleum diesel. The average range of biodiesel PP is -15 – 13 °C whereas that of petroleum diesel ranges from -36 to -30 °C (Sajjadi *et al.*, 2016).

2.6.11. Acid Number

The acid number is the most used parameter to evaluate and monitor the degradation of biodiesel. It is an important parameter that quantifies the amount of free fatty acids (FFA), accompanied by other various acids originating from the degradation reactions of biodiesel during the production process and storage. These degradation reactions include hydrolysis and the oxidation of TGs and monoesters formed during the production and storage of biodiesel. This parameter is heavily influenced by the amount of humidity absorbed during storage, the presence of water/ the water content in the biodiesel, peroxides, and carboxylic acids of low molecular mass caused by oxidative degradation. The conversion of esters into alcohols and carboxylic acids leads to the reduction of the flash point and the increase of the acid number respectively. FFAs are the main cause of elevated acid values in biodiesel and a high acid number proves to be highly disadvantageous because it indicates that the fuel is relatively volatile and unsafe for extended transportation. Moreover, fuels with high acid numbers trigger saponification reactions which could result in corrosion. Ultimately, this leads to engine operational problems caused by fuel degradation such as filter clogging and the occurrence of engine deposits (Santos *et al.*, 2018).

2.6.12. Glycerol Content

The total glycerol content is a vital parameter whilst evaluating the properties of biodiesel and is defined as the total amount of glycerol present in the produced biodiesel (Thoai *et al.* 2017). In the production of biodiesel one mole of triglycerides reacts with three moles of alcohol to produce three moles of esters and a mole of glycerol. The transesterification reaction, in reality, consists of a sequence of three successive and reversible reactions where mono (MG) and diglycerides (DG) are the intermediate products. Therefore, the calculation for the total glycerol content (GT) is as follows:

$$\% G_T = \% G_F + 0.255(\% MG) + 0.146(\% DG) + 0.013(\% TG) \quad 2-1$$

where

% G_F – weight percentage of free glycerol in biodiesel

% MG – weight percentage of monoglycerides

% DG – weight percent of diglycerides

% TG – weight percent of triglycerides

It is deduced from the above equation that the total glycerol content has a close relationship with the ester content which are both determined by the remaining quantities of the intermediate compounds (mono and di glycerides). Therefore, a high glycerol content indicates a decreased ester content in biodiesel (Thoai *et al.*, 2017). A high ester content results in a high and stable functioning fuel, hence an elevated glycerol content in biodiesel is highly undesirable.

The accepted values and ranges of the abovementioned fuel characteristics are tabulated below. According to Yadav *et al.* (2019), the American (ASTM) and European (EN) standards are as follow:

Table 2-2: Transportation fuel characteristic specification (ASTM & EU) adapted from (Yadav *et al.*, 2019)

Transportation Fuel characteristics	Biodiesel		Diesel
	ASTM	EN	
Density (Kg.m ⁻³)	880	860-900	850
Viscosity at 40 °C (cSt)	1.9 – 6.0	3.5 – 5.0	2.6
Boiling point (°C)	315 - 350	315 – 350	180 – 340
Flash point (°C)	100 - 170	100 – 170	60 – 80
Cloud point (°C)	-3 – 15	-3 – 12	-35 – 5
Pour point (°C)	-5 – 10	-5 – 10	-35 – 15
Cetane Number	48 – 65	48 – 65	40 – 55
Water and sediment content (%vol)	≤ 0.05	≤ 0.05	≤ 0.05
Acid value (Mg KOH/g)	≤ 0.5	≤ 0.5	0.062
Oxidation (hrs)	≥ 3	≥ 6	≥ 3
Carbon (wt%)	77	77	84 – 87
Sulphur (wt%)	≤ 0.0015	≤ 0.0015	0 – 0.0025
Oxygen (wt%)	11	11	0 – 0.31
Hydrogen (wt%)	12	12	12 – 16

2.7. Effect of Fatty Acid Constituents on Crucial Fuel Characteristics

Feedstocks contain different fatty acids which vary in chain length as well as the number of double bonds. However, it is observed that even-numbered carbon atoms are more commonly found and are the more dominant fatty acids. These carbon chains range between C12 and C20 with the most popular, in vegetable oil, being stearic acid (C18:0), palmitic acid (C16:0), linoleic acid (C18:2), linolenic (C18:3) and oleic acid (C18:1) (Mata and Martins, 2017). The transportation fuel characteristics of biodiesel are largely influenced and depend on the fatty acid distribution of the feedstocks used in its production. The main characteristic influenced being cetane number, lubricity and oxidation stability/ iodine value and cold filter plugging point. The following table includes various feedstocks and their fatty acid constituents.

Table 2-3: Fatty acid constituent (%) of various edible oils. Adapted from (Yaşar, 2020)

Fatty acid	C : D	Molecular formula	Palm oil	Sunflower oil	Canola oil	Soybean oil
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
Palmitoleic	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

2.7.1. Lubricity

Free fatty acids, monoglycerides and glycerol possess better lubricity compared to neat esters because of the existing free OH groups (Mishra and Goswami, 2018). Lubricity increases with longer carbon chains as well as the presence of double bonds therefore FAME formulated from oils with hydroxylated fatty acids (HFA) have elevated lubricity (Leung and Leung, 2015). However, lubricity is enhanced more by the presence of double bonds compared to chain

length. This is because sterically unhindered (i.e. exposed) electrons in the form of free electron pairs or free double bonds are the most effective for the increase of lubricity (Mehrabadi *et al.*, 2017).

Table 2-4: Lubricity in different methyl esters

Methyl Ester	Lubricity
Linolenic	
Linoleic	
Oleate	
Stearate	

2.7.2. Cetane Number

The longer the fatty acid carbon chain and the more saturated the molecules, the higher the cetane number of the corresponding biodiesel produced (Hansen *et.al* 2015). This is seen in the table below

Table 2-5: Cetane number trend in different fatty acids (Hansen *et.al* 2015)

Fatty Acid	Average Cetane Number of derived Fuel
Stearic	
Palmitic	
Myristic	
Lauric	
Oleic	
Palmitoleic	
Laprylic	
Linoleic	

Different feedstocks however contain a mixture of these fatty acids. Therefore, it is found that feedstocks containing long-chained higher saturated FA such as stearic, palmitic and myristic as the predominant acids have higher cetane numbers.

2.7.3. Oxidation Stability and Iodine Value

It is reported that the more unsaturated the fatty acid is, the higher the iodine value and hence the more unstable the resultant methyl ester is. The lower the iodine value, the higher the cetane number and consequently, the lower the NO_x emissions (Chuah *et al.*, 2016). Feedstocks with less percentages of stearic and palmitic acid such as coconut and neem oil are reported to have elevated iodine values. Oxidation in biodiesel is induced by ester polymerisation which forms insoluble gums that often clog fuel filters and this occurs when there is unsaturated fatty acids

in the feedstock used to synthesise the biodiesel. The oxidation stability of biodiesel is important during storage as it yields products that degrade biodiesel quality and consequently affects the combustion engine performance. Therefore, feedstocks that contain elevated levels of fatty acids such as linoleic and linolenic are likely to produce a more unstable biodiesel (Chuah *et al.*, 2016).

2.7.4. Cold Filter Plugging Point

The specification of this temperature varies world wide due to differing climates. Poor low-temperature cold flow properties could be attributed to the precipitation of saturated fatty acids such as palmitic and stearic which results in clogged fuel filters (Chuah *et al.*, 2016). Another major contributor is the availability of stearyl glucosides which facilitate the precipitation. Overall, low-temperature properties heavily depend on the saturated fatty acid composition (Na-Ranong and Kitchaiya, 2014). Unsaturated fatty acids play little or no role as they are considered and act as solvents (Chuah *et al.*, 2016).

CHAPTER 3

METHODOLOGY

Chapter 3 : Methodology

3.1. Materials.

The feedstock for FAME production included methanol, virgin palm oil (VPO), virgin sunflower oil (VSO), waste palm oil (WPO), waste sunflower oil (WSO), virgin canola oil (VCO), waste canola Oil (WCO) and neem oil. The virgin and waste oils were procured and bought from an oil manufacturing company SupaOil (Cape Town, South Africa). Methanol (>99.9% purity) was procured from Merck Millipore.

Catalyst synthesis required the use of Calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%, AceChem), aluminium nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%, AceChem) and sodium hydroxide (NaOH) pellets (Merck, 98%), as the initial reagents for co-precipitation. Calcium oxide (99%, Merk) and recalcined aluminium oxide (98%, Merk) were utilised in the impregnation method for catalyst preparation.

3.2. Catalyst Preparation

Solid heterogeneous catalysts purposed for the simultaneous esterification and transesterification reactions for FAME production can be prepared in two ways, namely impregnation and co-precipitation. Co-precipitation was the method of choice as catalysts synthesised through impregnation deactivated after 48 hours.

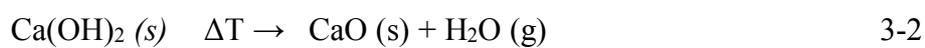
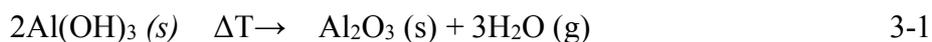
3.2.1. Co-precipitation

The heterogeneous bi-functional catalyst of choice was a mixture of calcium oxide (CaO) and alumina (Al_2O_3) with the basic catalyst being CaO, and alumina acting as the acidic. The basic to acidic ratios were 50:50, 60:40, 70:30 and 80:20. Respective to these ratios, on a weight basis, the corresponding amounts of calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were mixed well in enough deionised (MilliQ) water in a 2L flask to dissolve the salts but also to avoid splashing during stirring. The solution was then heated with a Heidolph MR 3001K hot plate fitted with a thermocouple (Heidolph EKT 3001), under atmospheric pressure until boiling or slight bubbling was visible. Simultaneously, 4M NaOH solution was brought to a boil in a 2L flask.

Thereafter, the two solutions were mixed under a stirrer and instantaneous precipitation took place. The very viscous suspension/solution was then continuously stirred for 45 minutes at

1500 rpm by the Dragon Lab OS20-S overhead stirrer and was kept at a temperature of 100 °C in order to promote the nucleation dissolution process. The milky solution was then taken off the hot plate and was allowed to cool down for 30 minutes.

The precipitate, which consisted of mostly calcium oxide and alumina was then transferred into a Buckner filter set up and was washed with hot distilled water to eliminate impurities such as sodium nitrate (NaNO₃) while being filtered. The purified filter cake was transferred to a ceramic plate and dried in an oven overnight at a temperature of 100 °C. The dried filter cake was ground to smaller particles with the use of a pestle and mortar. Thereafter, it was transferred to a furnace (SNOL 8.2/1100 LHM01 fitted with an Omron E5CC-T controller) and calcined at 600 °C at a rate of 5 °C/ min for 800 minutes as illustrated in Figure 3-1. This was done to remove residual H₂O and CO₂ in order to reveal basic sites. Moreover, the calcination process was necessary for the thermal reduction of calcium and aluminium hydroxides (Equations 3-1 and 3-2) to the desired calcium and aluminium oxides (CaO/Al₂O₃)



After calcination, the catalyst was then further milled to maximise surface area for increased reaction contact.

3.2.2. Wet Impregnation

Respective ratios of reactive CaO (80,70,60 and 50) and recalcined alumina (20,30,40 and 50) were mixed in distilled water. The solution was then stirred (1500 rpm) and heated (100 °C) for 1 hour to allow effective mixing. Thereafter, the sludge was filtered, and the catalyst filter cakes were subjected to oven drying overnight at a temperature of 95 °C in order to eliminate any excess moisture. Thereafter, the catalysts were calcined at a temperature of 600 °C for 6 hours with a ramp temperature increase of 5 °C per minute (Figure 3-1). The calcination process was followed by grinding the catalyst into a fine powder to maximise surface area. Finally, the catalyst was stored in an airtight container to prevent any atmospheric moisture contact as this can cause catalyst deactivation.

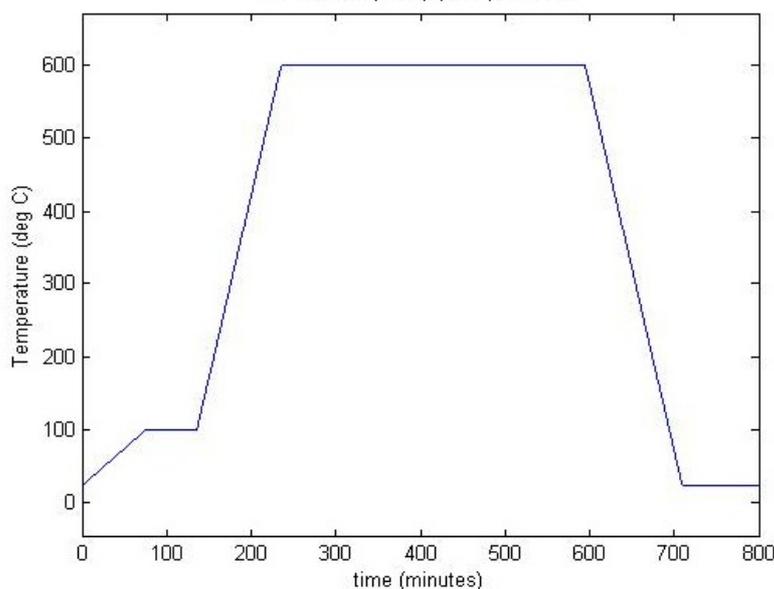


Figure 3-1: Calcination process of catalyst (CaO/Al₂O₃)

3.2.3. Catalyst Reusability

The bi-functional catalysts were removed from the product after undergoing centrifugation, thereafter, they were washed with methanol and dried at room temperature (~20 °C) for 24 hours. The catalysts were reused for 12 cycles with waste palm oil as the feedstock of choice due to the relatively high FFA content. This proved optimal in the determination of catalyst robustness.

3.3. Catalyst Characterisation and Analysis

In order to predict the reactivity and efficiency of the catalyst made, various methods were used to analyse various parameters. Firstly, the pH of the catalyst was measured to determine alkalinity. The higher the alkalinity, the more favourable the catalyst is to the transesterification process. Other processes included XRD, BET and SEM.

3.3.1. X-Ray Diffraction

X-ray diffraction (XRD) is an analytical procedure used to evaluate metal oxides and bulk phases present in the calcined samples as well as the determination of average particle sizes (Elias *et al.*, 2020). A sample of the calcined catalysts with various ratios were analysed to determine the respective morphologies and compound peaks. XRD also reveals different compositions of the catalysts to discover any impurities present which might hinder the reaction.

Measurements were performed using a multi-purpose X-ray diffractometer D8-Advance from BRUKER AXS (Germany) operated in a continuous θ - θ scan in locked coupled mode with Cu-K α radiation ($\lambda K\alpha_1=1.5406 \text{ \AA}$). The sample was mounted in the centre of the sample holder on a glass slide and levelled up to the correct height. The measurements ran within a range in 2θ defined by the user with a typical step size of 0.034° in 2θ . A position-sensitive detector, Lyn-Eye, was used to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter.

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

3.3.2. Brunauer-Emmett-Teller

The different catalysts were subjected to BET analysis to characterise them for surface area pore size and pore volume.

The samples were dried through nitrogen purging. The volume of the gas absorbed to the surface of the particles was measured at the boiling point of nitrogen (-196°C). Thereafter, the amount of absorbed gas was correlated to the pores and surface area of the sample. Nitrogen was used as the adsorbate gas which enabled the determination of volume and size distribution of the catalyst micropores between the measurements of 0.35 – 2.0 nm. The catalyst samples were degassed at a temperature of 200°C and p/p^0 ranged between 0.05 and 0.3.

3.3.3. Scanning Electron Microscope

Hitachi S-3000N Standard VP-SEM (Hitachi High Technologies, USA) was used in the analysis of the sample catalysts. The model specifications include four quadrant solid-state BSED (back scatter electron detector). Imaging of compositional 3D and topographic modes were made possible by the thermo-ionic electron source. The S-3000N with the PCI Data Management Interface and the patented Hitachi dual-bias system permitted easy attainment of high-resolution images down to 300 V.

The different samples of catalysts were subjected to SEM analysis where the morphological aspects of the catalysts were scrutinised. The SEM also provided information and clarity on surface areas, particle sizes as well as agglomeration.

Catalysts were prepared by pressing the dry powder onto a graphite glue coated aluminium sample holder. The graphite coating allowed for the conduction of electrons which eliminated charge build-up. A Denton vacuum desk II cold sputtering unit (Denton Vacuum, USA) fitted with a gold sputter cathode was used to clean the surface of the sample and to deposit an ultra-thin layer of Au (gold) conductive coating. The morphology and homogeneity of the catalysts were characterised under room temperature conditions and an accelerating voltage of 20kV.

3.4. Fatty Acid Methyl Esters Production

3.4.1. Feedstock Pre-treatment

Oil pre-treatment was conducted as follows:

- **Filtration:** the waste cooking oils were filtered in order to remove debris and undesirable particles that might hinder the reaction process.
- **Drying and dehydration:** the oils were kept in an oven overnight (14 hrs) at 100 °C to eliminate water content.

There was no pre-treatment involved with the virgin oils as they did not consist of any impurities.

3.4.2. Feedstock Analysis

The feedstock samples were analysed for free fatty acids (FFA) composition. Fatty acid (FA) profiles and constituents were also analysed. Both gas chromatography (GC) and chemical titration methods were used to ensure accuracy in FFA determination. However, only GC was used to calibrate triglyceride/ fatty acid content.

3.4.2.1. Gas Chromatography Mass Spectroscopy (GC-MS)

Gas chromatography was selected for the analysis of Fatty acid constituents, FFA and TG content. A standard sample with known concentration is injected into the instrument. The standard sample peak retention time (appearance time) and area are compared to the test sample to calculate the concentration and/or content of interest. The GC-MS used in this study was fitted with a FAMEWAX column (30 m) with an inner diameter of 0.32 mm and film thickness of 0.25 µm.

This method was carried out by firstly dissolving 500 mg of feedstock oil in 2 ml of butylated hydroxytoluene (BHT) and chloroform solution. Thereafter, 50 µl of heptadecanoic acid was added as an internal standard and then evaporated. A solution of 2 ml in volume consisting of 0.005% BHT, 5% sulphuric acid and 95% methanol was then added after evaporation. This

was followed by an incubation period of 2 hours at a temperature of 70 °C. The solution was then cooled after incubation followed by the addition of 2 ml of distilled water and a similar amount of n-hexane. The new solution was then vortexed as the individual layers were allowed to separate. After phase separation, sodium carbonate and a concentrate were added to the hexane only layer under a nitrogen stream to 100 µl. The fatty acid mass was obtained by multiplying the peak of the internal standard by the FA ratio peak. FA constituents in the respective feedstocks were determined.

3.4.2.2. Chemical Titration

Fatty acid concentrations equal to or higher than 1 mM may be easily determined through titration. Titrimetry was used to determine the acid value or otherwise known as the free fatty content of vegetable oils and fats.

A solution of ethanol and diethyl ether was made at a ratio of 1:1 on a volume basis. Thereafter 0.1M KOH (>99%, Sigma-Aldrich) in ethanol (95%, Merk) was standardised by 0.1M HCl (99%, Merk). An indicator solution containing 1% phenolphthalein and ethanol was also be prepared. Thereafter, 0.1 to 10 g of feedstock was measured and mixed in a glass container containing 50 g of solvent mixture (ethanol and diethyl ether (98%, Merk)). The indicator solution was then added and the mixture was then be titrated by the KOH solution until a pink colour is visible and persisted for at least 10 seconds. The acid number (AN) was be calculated using the following formula:

$$AN = \frac{56.1(N)(V)}{M} \quad 3-3$$

where N is the exact normality, V is the volume of KOH solution used and M is the feedstock mass.

FFA was calculated as per appendix A1

3.5. Experimental Set Up and Procedure

The simultaneous esterification and transesterification of high FFA feedstock occurred in four 500 ml, stirred batch reactors situated in temperature-controlled water bath

3.5.1. Experimental Set Up

The transesterification and esterification reactions occurred in the figure below where the configuration included four 500 ml reactor flasks with overhead stirrers, 4 condensers and a water bath (Figure 3-2).

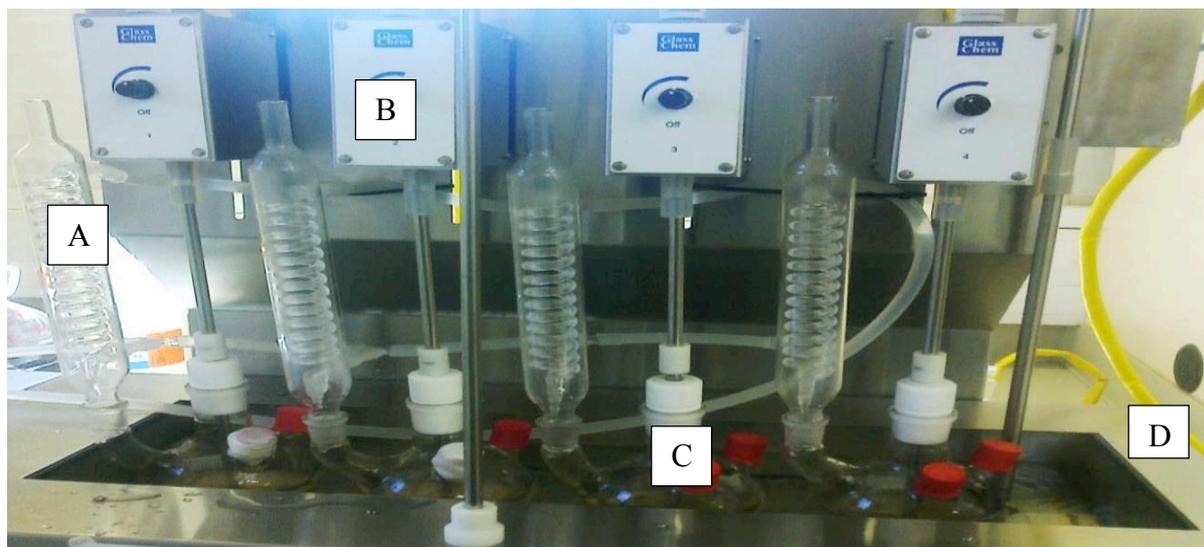


Figure 3-2: Biodiesel production unit

A: Condenser; B: Overhead stirrer; C: 500 ml 3 neck reaction flask; D: Water bath

3.5.2. Experimental Procedure

In order to investigate the effect of FFA, FA constituents and the differently modified catalysts on the production of biodiesel and its corresponding characteristics, 28 experiments were conducted. Each oil feedstock was converted to biodiesel using all the catalyst ratios.

Firstly, the 12:1 molar ratio of methanol (>99%) was prepared. The cumulative volume in each flask was approximately 200 ml. The catalyst was then added at a quantity and loading of 2.5 wt%. Thereafter, the flasks were placed inside the temperature-controlled water bath which was operating at 65 °C. The condensers were then attached in series to the four reactor flasks. This was followed by the attachment of a cooling water pipe which sustained the condensers. The cooling water was set to an approximate temperature of 15°C. Once the cooling water was circulating, the reactors, water baths and stirrers were turned on and the synthesis process commenced. The reaction took 4.5 hours to complete with an agitation rate of 1200 rpm. These optimal reaction conditions were derived from (Zabeti *et al.*, 2009). The reaction apparatus was then turned off and the flasks were allowed to cool down for 5 min. this was followed by the sieving out of the catalyst and the decanting of the now synthesised FAME and by-product mixture into a separating funnel. It was observed that different layers formed where the top layer consisted of methyl esters whereas the bottom layer predominantly consisted of glycerol with visible traces of unreacted methanol and water. These by-products were then drained out after 1 hour. The biodiesel was then subjected to a centrifuge operating at 6000 rpm for further separation of intermediates and glycerol present.

After being subjected to centrifugation, further purification was achieved by cleaning the biodiesel with hot distilled water. This was done by washing the FAME with 30% v/v distilled water. This was done to dissolve any remnants of glycerol or methanol in the crude biodiesel. The mixture was then slightly agitated and left for an hour in the separation funnel where the water layer was then drained out. This washing procedure was repeated until the water drained was colourless which indicated that the various impurities were completely removed. In order to ensure minimal water content, the biodiesel was subjected to a drying agent (Na_2SO_4 , >90%, Sigma-Aldrich) and was heated up until no bubbling was present, indicating complete water absorption and evaporation. All the experiments conducted followed this procedure with varying chosen reaction parameters. Figure 3-3 shows the step-by-step approach.

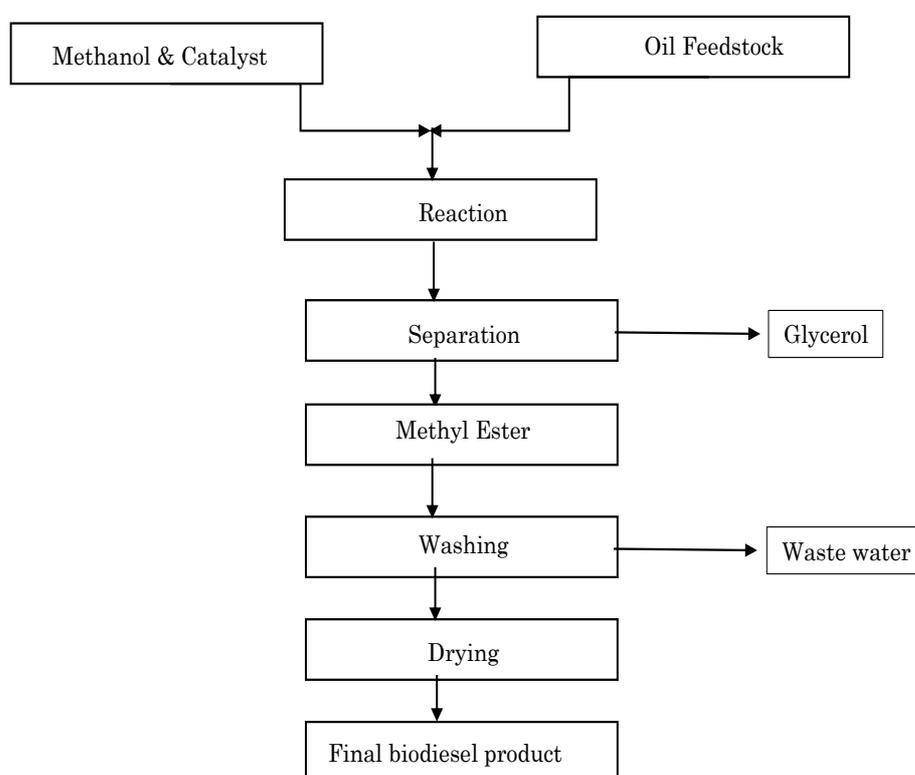


Figure 3-3: Experimental flow diagram

The synthesised FAME samples were then taken for analysis where they were subjected to a GC after sample preparation. The GC then produced information on important compound constituents and their corresponding quantities. These compounds included free fatty acids and fatty acids. Similarly, an identical set of samples were analysed through Rancimat after sample preparation. The oxidation stability of the FAME samples was then determined. Other fuel characteristics such as density, kinematic viscosity, flash point, acid number and water content

was be sent to OILWATCH for analysis in accordance with the ASTM reference analytical methods.

3.5.3. Product Estimation

In order to determine the various conversion and yields of the product made, the following equations were used:

$$\% \text{ Conversion} = \frac{Mass_{oil} - Mass_{BD}}{Mass_{oil}} \times 100 \quad 3-4$$

$$\% \text{ Yield} = \frac{Mass_{BD}}{Mass_{oil}} \times 100 \quad 3-5$$

Where BD is the purified biodiesel.

3.6. Fuel Characteristic Analysis

The transportation fuel characteristics of various samples of FAME produced under varying conditions were analysed through the Rancimat method. The Rancimat or oxidative stability instrument determined the oxidative stability index (OSI) of the products at elevated temperatures ranging from 100 to 130 °C while exposing the sample to a stream of air. The results obtained were used to estimate the product shelf life. The higher the OSI value, the more stable the product. The Rancimat method is an accelerated ageing test. In this process, fatty acids were oxidized and at the end of the test, volatile, secondary reaction products were formed, which were then transported into the measuring vessel by the air stream and absorbed in the measuring solution (deionised water). The continuously recorded electrical conductivity of the measuring solution increased due to the absorption of the reaction products. Thus, their appearance was detected. The time until secondary reaction products are detected is called induction time. The different induction times of the corresponding fuels were recorded as they characterise the oxidation stability of oils and fats.

Transportation fuel characteristics were also analysed. Similar samples were sent to OILWATCH Laboratories situated in Cape Town, where these properties were determined using standard methods and procedures approved by the American Society for Testing and Materials (ATSM). The characteristics were tested as follows:

- Viscosity at 40 °C with ASTM D445 test method to indicate the resistance of the fuel to flow.
- Density at 20 °C with ASTM D4052 test method.
- Flash point with ASTM D93 test method.

- Appearance and colour
- Sulphur content obtained using ASTM D5493 test method.
- Acid number with ASTM D664 test method to determine the acidity of the fuel.
- Water content with ASTM D2709 test method.

These results were then compared to both the acceptable American and European standards of biodiesel characterisation.

CHAPTER 4

RESULTS AND DISCUSSION

Chapter 4 Results and Discussion

4.1. Catalyst Analysis and Characterisation

The different catalysts were analysed and characterised through XRD (for composition determination), BET (for structural definition) and SEM (to show the morphology of the catalyst and its various compounds).

4.1.1. Catalyst Composition

Analysis was done on the four different catalysts 1, 2, 3 and 4 with CaO/ Al₂O₃ ratios as 80:20, 70:30, 60:40 and 50:50 respectively under the 2 θ range. These ratios were chosen in order to evaluate catalyst bi-functionality effectiveness where CaO and Al₂O₃ were the basic and acidic catalyst components respectively. The variance of basic and acidic ratios was done to aid in the synthesis of biodiesel from feedstocks with varying FFA levels, where a more acidic catalyst is predicted to be more effective on higher FFA feedstocks as it drives the esterification reaction. Similarly, feedstock containing low FFA and high TG levels would produce a higher yield of biodiesel as the transesterification reaction would be favoured by a higher quantity/ ratio of basic catalyst (Mansir *et al.*, 2018).

The XRD analysis on the catalyst samples indicated two predominant compounds namely calcium oxide and aluminium oxide which indicated adequate catalyst synthesis as they were the two desired catalyst components. Small amounts of calcium hydroxide and calcium carbonate were also present. This is attributed to the incomplete calcination of both elements (Table 4-1).

Spectroscopic analysis also indicated trace amounts of impurities: <0.1% Sr; <0.01%Ba, <0.001% Al, B, Cs, Cu, K, Mg, Na, Si, Sn; <0.0001% Ag, Cr, Fe, Li, Mn

Table 4-1: Physiochemical properties of compounds in catalysts

	Lattice	Mol. Weight	Volume [CD]	Dx	a	Z
CaO	Face centred cubic	56.08	111.33	3.346	4.81059	4
CaCO₃	Rhombohedral	100.09	367.78	2.711	4.989	6
Al₂O₃	Rhombohedral	101.96	254.81	3.987	4.75870	6
Ca(OH)₂	Hexagonal	74.09	54.88	2.242	3.593	1

Figure 4-1 shows the cumulative XRD analytical graphs on all four catalysts. All four graphs follow the same trend in compound composition with a deviation in compound concentrations which is to be expected as the ratios vary per catalyst.

Table 4-2: Predicted and actual catalyst ratios

Catalyst no.	Compound	Predicted composition wt%	Actual composition wt%
1 (80% CaO)	CaO	80	81.02
	Al ₂ O ₃	20	18.68
2 (70% CaO)	CaO	70	68.97
	Al ₂ O ₃	30	30.06
3 (60% CaO)	CaO	60	59.54
	Al ₂ O ₃	40	36.82
4 (50% CaO)	CaO	50	51.07
	Al ₂ O ₃	50	47.98

Slight deviations in catalyst concentrations and ratios can be attributed to factors such as unprecise measurements of weighted catalysts in the process of catalyst preparation as well as impurities present in the raw catalyst reactants.

Figure 4-1 indicates a peak in CaO and alumina. Studies done by Hashmi *et al.*, (2016) show that the XRD pattern suggests that the catalysts have a basic centred cubic structure.

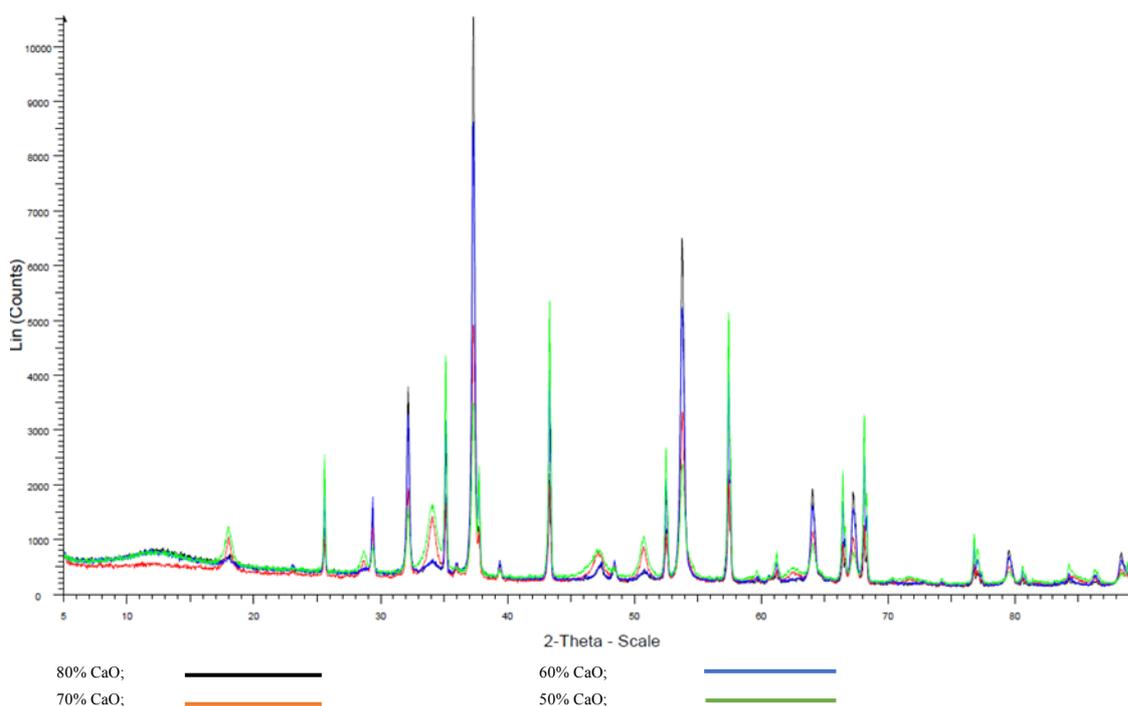


Figure 4-1 Cumulative Composition of catalysts (XRD)

4.1.2. Catalyst Structure, Surface Area and Pore Volume

The catalyst surface areas were in the range of 11 – 13.5 m²/g (Table 4-3). An adequate surface area required for good catalytic activity on a heterogeneous catalyst in the transesterification

of oils is $>8 \text{ m}^2/\text{g}$ (Chingakham *et. al.*, 2019). Hence the catalyst surface areas were adequate and effective. Pore diameters of $>209.5 \text{ \AA}$ were measured. Similarly, a high pore volume is crucial in the activity of a catalyst as it assists in the efficient diffusion as well as an increased rate of absorption of reactants (Tshizanga, 2015). High pore volumes in the range 0.72 to 0.91 cm^3/g were observed. The catalysts are considered to be very porous as a high pore diameter and volume are considered to be above 100 \AA and 0.07 cm^3/g respectively (Chingakham *et. al.*, 2019).

High surface area, porosity and pore volumes are crucial as they enhance overall catalytic activity and catalyst performance. Good catalytic activity might reduce catalyst loading, improve biodiesel yield and ultimately, biodiesel production costs (Ngoie *et al.*, 2019)

Table 4-3: Catalyst structure, surface area and pore volume

Catalyst	CaO:Al ₂ O ₃ ratio	Surface Area (m ² /g)	Pore Diameter (\AA)	Pore Volume (cm ³ /g)
1	80:20	13.4701	227.086	0.090
2	70:30	13.3020	233.820	0.091
3	60:40	11.1145	231.763	0.076
4	50:50	11.0414	209.508	0.072

4.1.3. Catalyst Morphology

A scanning electron microscope was used to identify the shape and morphology of the catalysts with a range varying from 1 μm -5 μm (Figures 4-2 a-d). 80% CaO had the highest surface area value (13.4701 m^2/g) followed by 70% CaO (13.3020 m^2/g). The morphology of these two catalysts further shows that 80% CaO is less dense compared to 70% CaO. 70% CaO however had a larger pore volume and pore diameter of 0.091 cm^3/g and 233.820 \AA respectively, which was the highest of the 4 catalysts. Surface area, pore diameter and pore volume are three major characteristics that influence catalyst activity. The higher these values, the higher the catalytic effectiveness (Vyas *et. al.*, 2017). A significant reduction in surface area and pore volume was observed with 60% CaO and 50% CaO relative to 80% CaO and 70% CaO. CaO is more porous than alumina hence a decrease in CaO content in the catalyst leads to a decrease in pore volume and surface area

Figures 4-2 (a-d, ii) showed the formation of mesoporous aggregated particles with irregular shapes and pore sizes varying in different surfaces. This morphology is similar to the bi-functional catalyst synthesised under the same conditions as reported by (Elias *et al.*, 2020). Moreover, calcium particles are visibly present and are seen to be distributed on aluminium

(Figures 4-2 a-d, i). Hence it can be concluded that the potential catalytic activity in the E and TE of the feedstocks was improved by the presence of Al_2O_3 .

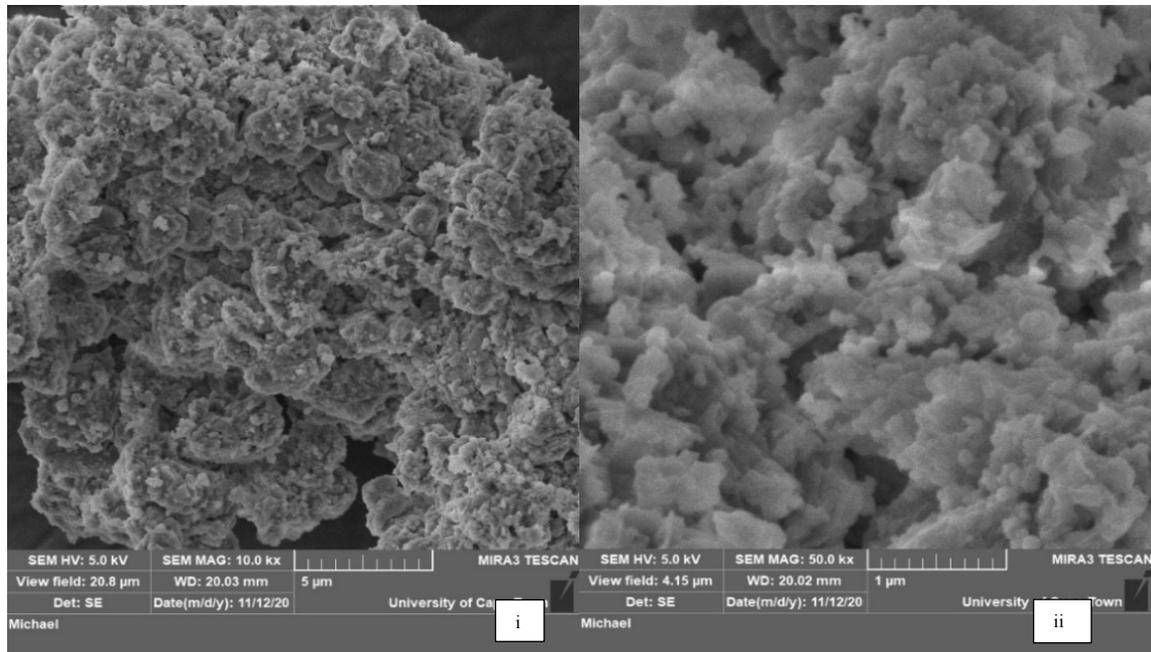


Figure 4-2a: 80% CaO morphology (SEM); (i: 5 μm; ii: 1 μm)

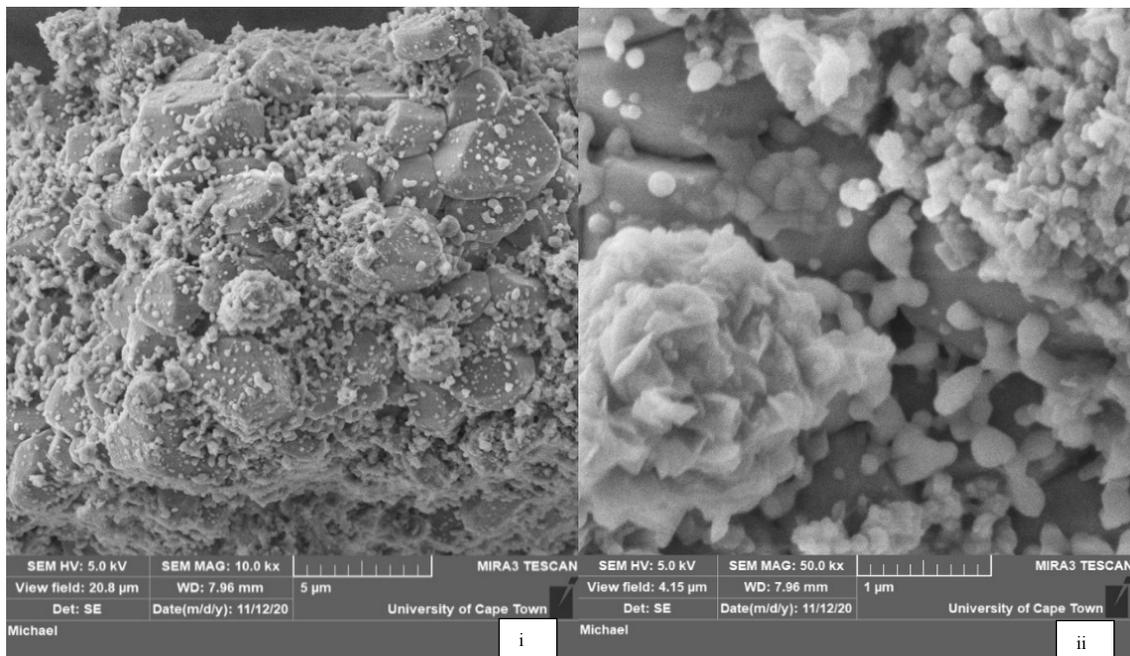


Figure 4-2b: 70% CaO morphology (SEM); (i: 5 μm; ii: 1 μm)

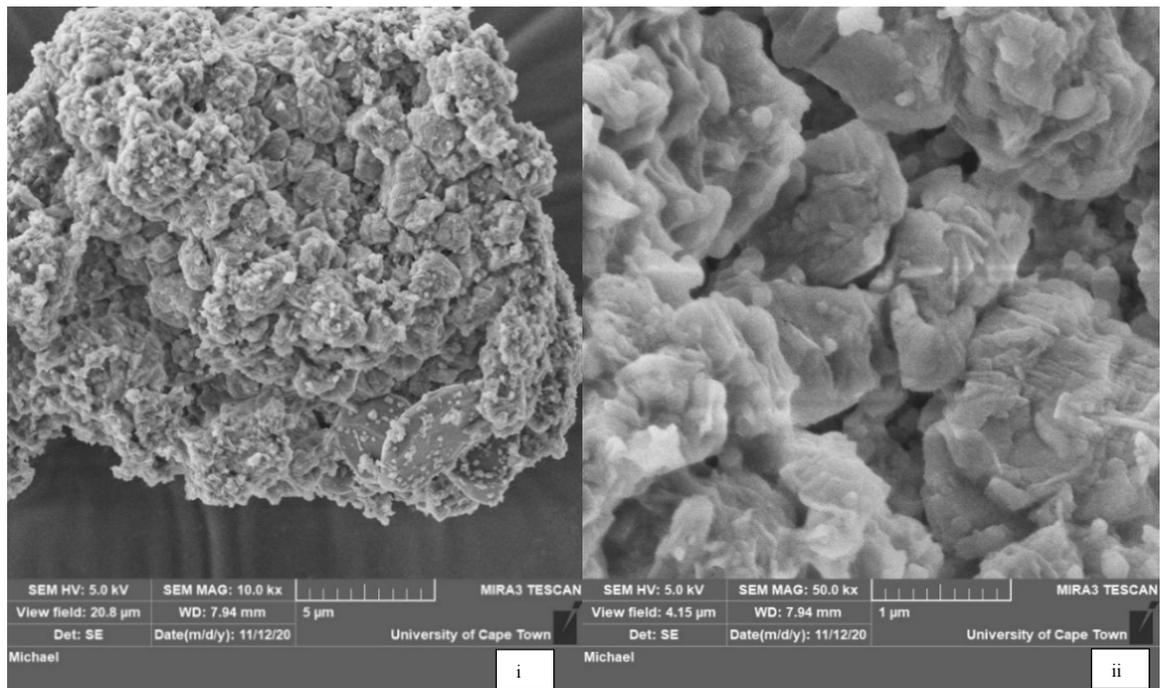


Figure 4-2c: 60% CaO morphology (SEM); (i: 5 μm; ii: 1 μm)

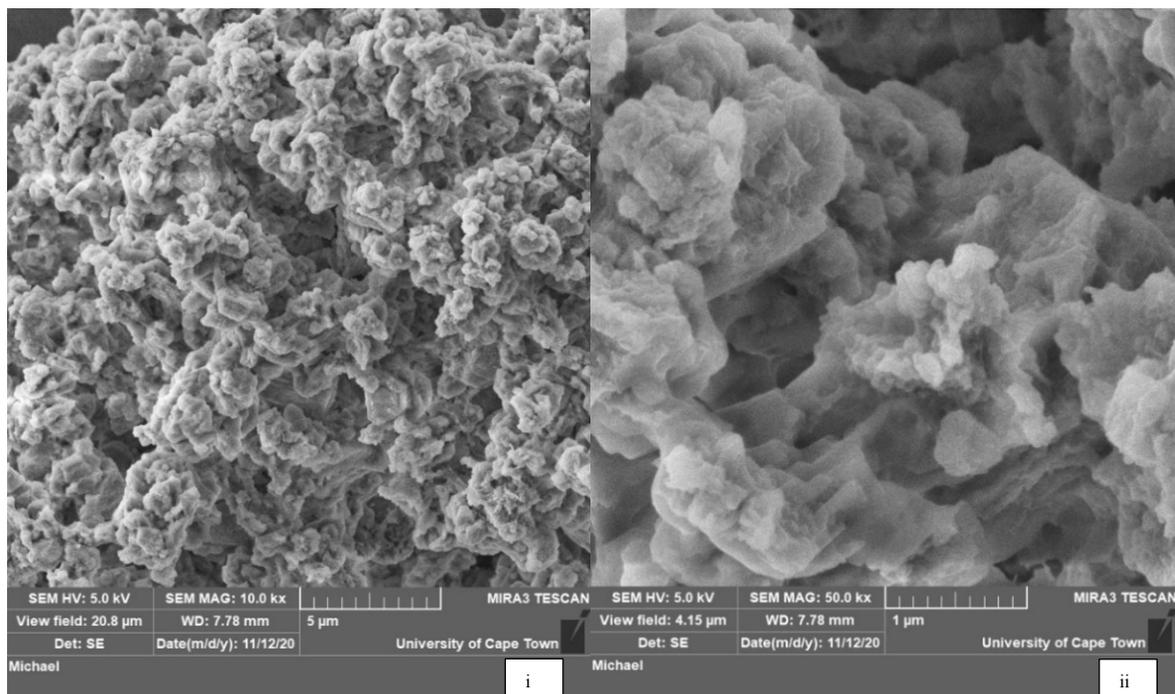


Figure 4-2d: 50% CaO morphology (SEM), (i: 5 μm; ii: 1 μm)

4.2. Feedstock Composition and Analysis

Seven different feedstocks were utilised in the syntheses of biodiesel. These feedstocks composed of three virgin oils (palm, sunflower and canola), three waste oils (palm, sunflower and canola) as well as one non-edible oil (Neem oil). Fatty acid profiles were derived from each feedstock through GC-MS analysis. Furthermore, a total acid number was also measured.

4.2.1. Free Fatty Acid Content

Neem oil had the highest FFA content (3.25%) (Table 4-4). This would make neem FAME production highly susceptible to saponification if a homogenous basic catalyst (Table 4-4). This would result in high production costs and a low yield of biodiesel. However, due to the presence of acidic sites in the bi-functional catalyst, these free fatty acids would be esterified. Inedible oils such as jatropha and neem have higher FFA content compared to edible oils (Chuah *et al.*, 2016), which is confirmed by the tabulated results. Waste palm oil had the second highest FFA content (2.47%). Waste canola and waste sunflower oil had values of 0.78 and 0.72% respectively. The elevated FFA content in these waste oils is explained by exposure to high heat while cooking which breaks down the mono, di and triglycerides resulting in free fatty acids (Sajjadi *et al.*, 2016). Furthermore, the presence of animal fats acquired in waste oils during the cooking/ frying process exacerbates the increase of FFA, as animal fats are observed to have high FFA contents (Ramadhas, *et al.*, 2015).

Table 4-4: FFA content of feedstocks

Feedstock oil	FFA %
Virgin palm	0.67
Virgin sunflower	0.22
Virgin canola	0.33
Waste palm	2.47
Waste sunflower	0.72
Waste canola	0.78
Neem	3.25

4.2.2. Fatty Acid Profile

The six most predominant fatty acids were observed to be myristic acid (14:0), palmitic acid (16:0), palmitoleic (16:1), stearic (18:0), oleic (18:1) and linoleic (18:2) (Table 4-5). Waste palm oil and virgin palm oil had the highest myristic acid content with 0.87% and 0.86% respectively. The two feedstocks also contained the highest amount of palmitic acid. The presence of palmitic and myristic acid in a feedstock increases the cetane number of respective biodiesel produced. This is attributable to saturated long carbon chains found in these fatty acids (Hansen *et.al* 2015). Neem oil had a palmitic acid content of 35.29%. Waste canola,

however, exhibited the highest palmitoleic acid content at 0.29%. The highest stearic acid content was found in waste sunflower oil (7.51%) whereas virgin sunflower oil contained the highest linoleic acid content at 67.75%. A high linoleic acid content proves advantageous as the corresponding biodiesel produced is observed to have high lubricity (Mehrabadi *et al.*, 2017). Canola oil had the highest oleic acid content (71.07%), which contributes to the increase in the biodiesel cetane number (Hansen *et.al* 2015).

Table 4-5: Fatty acid composition of feedstocks (GC-MS)

Fatty Acid	Feedstock						
	Sunflower	Waste Sunflower	Waste Palm	Palm	Waste Canola	Canola	Neem
C6:0	-	0.0061	0.0155	0.0023	0.0437	-	0.0044
C8:0	0.0047	0.0370	0.1374	0.0200	0.0352	-	0.0331
C10:0	0.0002	0.0074	0.0731	0.0211	0.0643	0.0046	0.0280
C11:0	0.0005	0.0005	0.0020	0.0008	0.0020	0.0011	0.0004
C12:0	0.0012	0.0225	0.7120	0.2210	0.0733	0.0062	0.2682
C13:0	0.0003	0.0006	0.0019	0.0009	0.0026	0.0005	0.0008
C14:0	0.0332	0.0903	0.8632	0.8711	0.2597	0.0332	0.6232
C15:0	0.0957	0.0117	0.0336	0.0314	0.0342	0.0103	0.0287
C16:0	6.3424	7.9916	40.0830	34.4431	9.5102	6.3237	35.2904
C18:0	6.1691	7.5121	4.4508	3.7891	3.3263	2.5917	6.9891
C20:0	0.2007	0.2193	0.2683	0.2713	0.3596	0.3250	0.4563
C21:0	0.0027	0.0071	0.0049	0.0017	0.0087	0.0099	0.0052
C22:0	0.4627	0.4876	0.0618	0.0568	0.1669	0.1629	0.1914
C23:0	0.0173	0.0172	0.0197	0.0435	0.0436	0.0491	0.0306
C24:0	0.0888	0.0832	0.0670	0.0725	0.0912	0.0859	0.1099
C14:1	0.0006	0.0024	0.0037	0.0011	0.0255	0.0008	0.0007
C16:1	0.0287	0.1234	0.0816	0.1220	0.2973	0.0888	0.0340
C17:1	0.0033	0.0020	0.0135	0.0088	0.0065	0.0017	0.0012
C18:1	18.6984	19.3156	42.8035	47.2008	66.1820	71.0728	44.5430
C20:1	0.0034	0.0042	0.0050	0.0055	0.0093	0.0068	0.0062
C22:1	0.0029	0.0043	0.0040	0.0036	0.0049	0.0040	0.0056
C24:1	0.0119	0.0151	0.0104	0.0085	0.0821	0.0568	0.0111
C18:2	67.7463	63.9430	10.1425	12.6466	18.8510	18.5982	11.1922
C18:3	0.0056	0.0060	0.0792	0.1028	0.4584	0.5210	0.0938
C20:2	0.0072	0.0165	0.0035	0.0054	0.0091	0.0045	0.0073
C20:3	0.0022	0.0080	0.0035	0.0025	0.0045	0.0048	0.0025
C20:4	0.0140	0.0262	0.0213	0.0192	0.0148	0.0076	0.0180
C20:5	0.0071	0.0083	0.0102	0.0079	0.0108	0.0093	0.0091
C22:2	0.0490	0.0310	0.0236	0.0187	0.0222	0.0188	0.0155

The degree of unsaturation in feedstocks and the corresponding FAME synthesised has an antagonistic effect between cold flow properties and oxidation stability, where a high level of unsaturation enhances cold flow properties but consequently decreases oxidation stability.

Therefore, feedstocks with high monounsaturated fatty acids (MUFA) are favoured as they increase cold flow properties significantly, do not worsen oxidation stability and decrease NO_x emissions (Guirrerro-Fajaro *et al.*, 2018).

Table 4-6 shows the different groupings in fatty acids, namely, saturated (no double bonds present), monounsaturated (one double bond present) and polyunsaturated (two or more double bonds present). Waste palm oil had the highest saturated fatty acid (SFA) content. This would result in biodiesel with elevated oxidation stability as well as a higher heat of combustion but consequently poor cold flow properties. Both waste and virgin sunflower oil had the highest levels of polyunsaturated fatty acids (PUFA). This proves to be detrimental to the oxidation stability of biodiesel produced, however, cold flow properties would be improved (Guirrerro-Fajaro *et al.*, 2018). Canola and waste canola consisted of the highest monounsaturated fatty acids at 66.61 and 71.23% respectively. It is observed that the waste feedstock oils have higher saturated fatty acid contents than their virgin counterparts. This is explained by the heating and cooking procedures the feedstocks underwent which ultimately broke down existing double bonds. Moreover, the presence of impurities acquired during these processes contribute to these results (Daniali *et al.*, 2016).

Table 4-6: Saturation and unsaturation composition of feedstocks

Feedstock	SFA	MUFA	PUFA
Sunflower	13.42	18.75	67.83
Waste Sunflower	16.49	19.47	64.04
Waste Palm	46.79	42.92	10.28
Palm	39.85	47.35	12.80
Waste Canola	14.02	66.61	19.37
Canola	9.60	71.23	19.16
Neem	44.06	44.60	11.34

4.3. Biodiesel Characterisation

Biodiesel was synthesised from the seven feedstock oils namely virgin (palm, sunflower, and canola); Waste (palm, sunflower, and canola) and neem oil with methanol as the alcohol reagent of choice. Analysis done on the FAME include yield and transportation fuel characteristics such as viscosity, density, flash point, sulphur content, total acid number and oxidation stability.

4.3.1. Biodiesel Yield

Different catalysts consisting of different CaO/Al₂O₃ ratios (Table 4-7) were utilised in the production of biodiesel. The ratios are distinguished as follows:

Table 4-7: Catalyst labelling

Catalyst	CaO:Al ₂ O ₃ ratio
80% CaO	80:20
70% CaO	70:30
60% CaO	60:40
50% CaO	50:50

4.3.1.1. Effect of FFA and Catalyst Composition on Sunflower Oil FAME

The highest virgin sunflower FAME yield was recorded to be 95.6% (Figure 4-3a) with the use of 80% CaO which consisted of the highest CaO content. There was a steady decline in yield as the CaO catalyst content decreased with the lowest value of 83.5% yield produced by 50% CaO. Virgin sunflower oil (VSO) feedstock had the lowest FFA content of 0.22% and due to this, the transesterification reaction was dominant. The lack of free fatty acids required less acidic sites (Al₂O₃) for esterification to take place (Sánchez-Bayo *et al.*, 2019). Therefore, the catalyst with the lowest acidic (Al₂O₃) ratio would be the most efficient in producing a higher yield. This is evident in Figure 4-3 as 80% CaO has the lowest Al₂O₃ content. The second and third highest values in yield were 88.7% and 83.6% catalysed by CaO:Al₂O₃ ratios of 70:30 and 60:40 respectively (Figure 4-3). VSO had the highest PUFA content (67.8%) (Table 4-6).

80% CaO produced the 2nd highest yield of 95.5% in waste sunflower oil (WSO) FAME (Figure 4-3). This feedstock had an FFA content of 0.72% (Table 4-4). This is not considered high FFA feedstock as the content was below 1% (Mansir *et al.*, 2018). However, being a waste oil, it is a low-cost feedstock and its use will thus alleviate the food versus fuel dilemma. The FAME yield obtained was comparable to that of the virgin oil counterpart (VSO) (95.6%). The presence of a solid acid catalyst is shown to esterify >94% of FFA present in the feedstock (Mat *et al.*, 2012). However, a significant amount of basic catalyst needs to be present for adequate transesterification to take place (Mat *et al.*, 2012). This is seen by the decline in biodiesel yield catalysed by 60% CaO and 50% CaO (92.5% and 89.9% respectively). Although WSO had a low FFA content (0.72%) it was observed that the feedstock required a slightly higher alumina ratio in order to esterify most if not all FFA present. Resultantly 70% CaO produced the highest yield of biodiesel at 98.3%. Overall, waste sunflower oil obtained

averagely higher yields in comparison to virgin sunflower oil. Therefore, the significance of the use of a bi-functional catalyst on waste oil is evident.

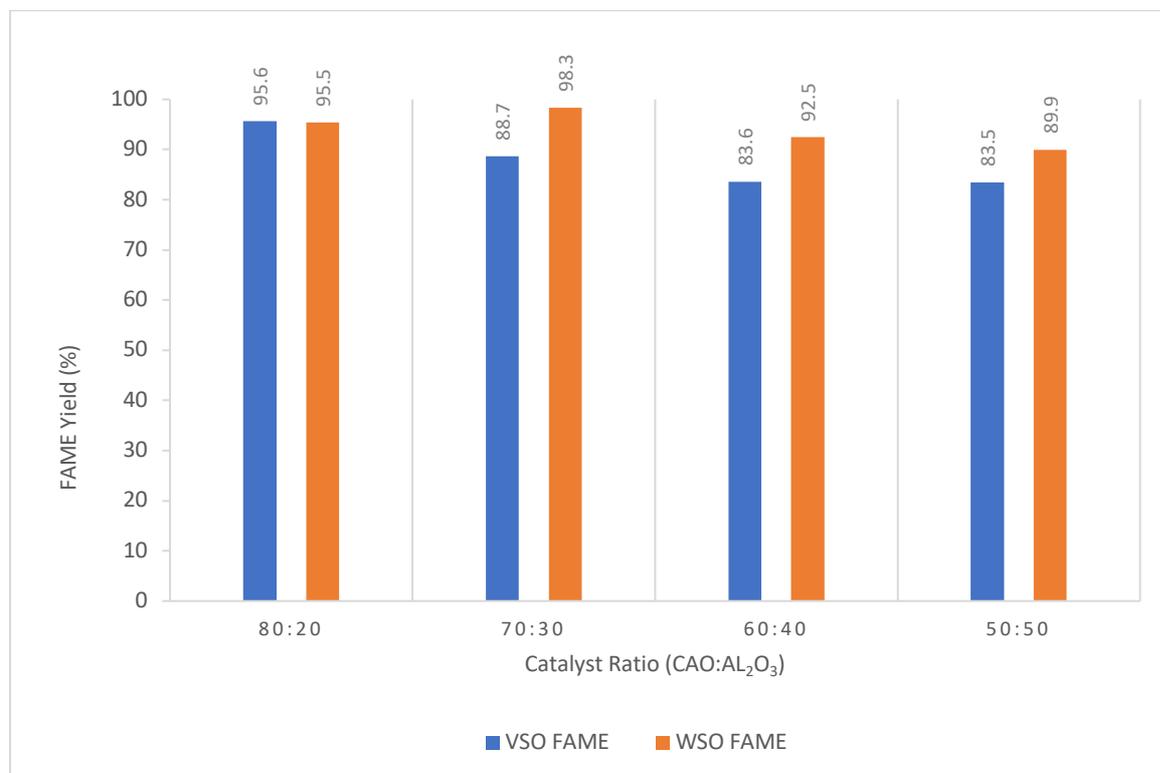


Figure 4-3: Effect of catalyst on virgin sunflower (VSO) and waste sunflower (WSO) oil FAME yield

4.3.1.2. Effect of FFA and Catalyst Composition on Palm Oil FAME

Virgin palm oil (VPO) had a low FFA content of 0.67% (Figure 4-4). The highest VPO FAME yield was 97.9% with the use of 80% CaO. This was similarly observed with virgin sunflower oil biodiesel with a yield of 95.6%. There was a steady decline in yield value as the CaO catalyst content decreased. This was attributed to the decrease of basicity in the catalyst as more of the acid sites (Al₂O₃) were added. Transesterification of triglycerides (TG) is aided by basic catalysts (Hanif, *et al.*, 2017). Virgin oils consist of very low FFA contents and consequently, very high TG contents. Therefore, a catalyst with a higher basic component/ basic sites (CaO) is favourable to such feedstocks (Figure 4-4). 50% CaO had the highest alumina content and consequently produced the lowest yield with a value of 79.2%.

Waste palm oil (WPO) had an FFA content of 2.47% which is considered high as it is greater than 1% (Mansir *et al.*, 2018). 80% CaO produced the lowest yield of 80%. This was attributed

to a high amount of basicity facilitated by CaO that in turn produced glycerol in the presence of FFA hence lowering the yield (Bhoi, Singh and Mahajani, 2017). Moreover, the lack of sufficient acidic component in 80% CaO did not facilitate optimal esterification of FFA present in WPO. 70% CaO produced the highest yield at 99.5%. The presence of FFA in conjunction with an acid catalyst accelerates the formation of biodiesel, as an increase in acid ratio facilitated the esterification of FFA (Sánchez-Bayo *et al.*, 2019). Moreover, FFA facilitates enhanced solubility in the oil phase under acid catalysed conditions (Bhoi *et. al.*, 2017). 60% CaO and 50% CaO produced yields of 94.1% and 89.9 % respectively. The presence of too much of the alumina, which consequently decreased the amount of basic sites in the catalyst, resulted in the hinderance of the main reaction (transesterification) and consequently decreased the yield (Sánchez-Bayo *et al.*, 2019). This is seen in the decline in yield values after the use of 60% CaO and 50% CaO (Figure 4-4).

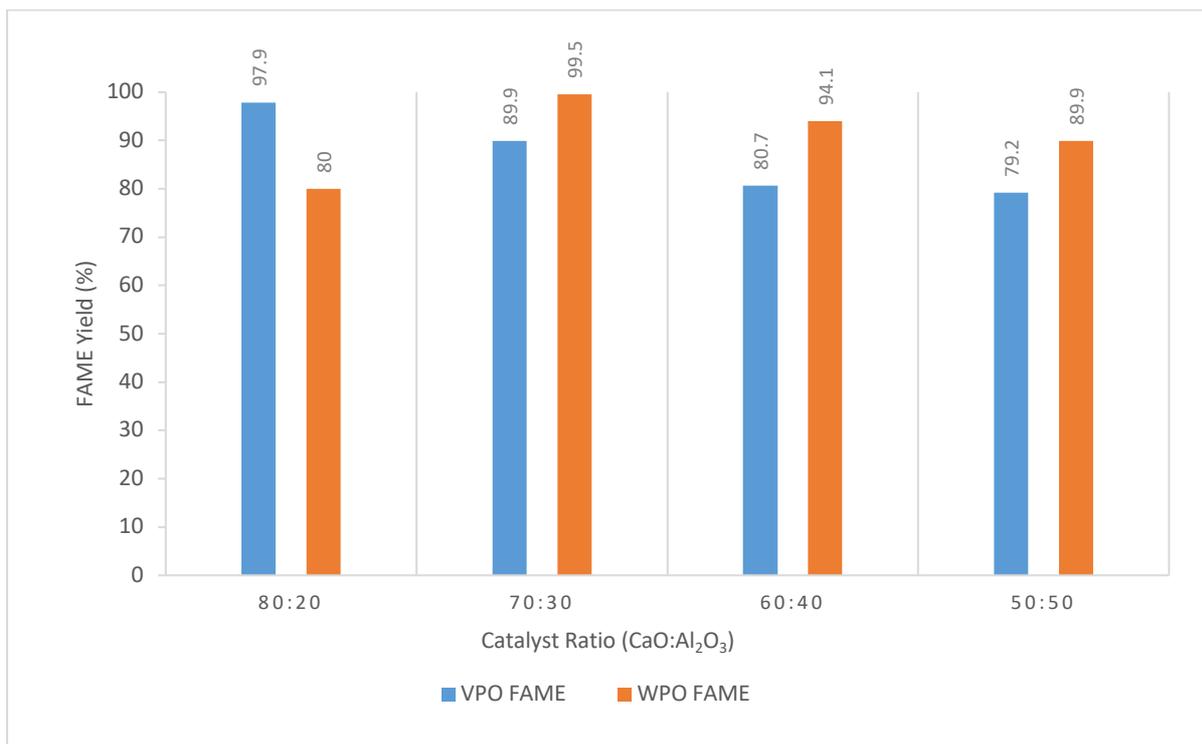


Figure 4-4: Effect of catalyst on virgin palm (VPO) and waste palm (WPO) oil FAME yield

4.3.1.3. Effect of FFA and Catalyst Composition on Canola Oil FAME

Virgin canola oil (VCO) and waste canola oil (WCO) had FFA contents of 0.33% and 0.78% respectively (Figure 4-5). A similar trend was observed in VCO FAME as the rest of FAME

synthesised from the other virgin oils as discussed above, where the highest yield, with the value of 98.9%, was achieved with 80% CaO. This is explained by the presence of negligible free fatty acids and the demand for more basic rather than acidic sites on the catalyst. However, the remaining catalysts achieved high yields (98.9, 96.5 and 95.4%) with the lowest being 94.8%. Therefore, virgin canola oil was the best performing feedstock with regards to yield.

WCO FAME yield peak was achieved by 70% CaO at 96.9% closely followed by 60% CaO at a 96.5% yield (Figure 4-5). The lowest performing catalyst was 50% CaO with an average yield of 84.45%. Due to the relatively low FFA content of WCO (0.78%), a CaO to alumina ratio above 70:30 proved to be less optimal. A similar trait was observed with waste sunflower oil where the FFA content was slightly lower at 0.68%.

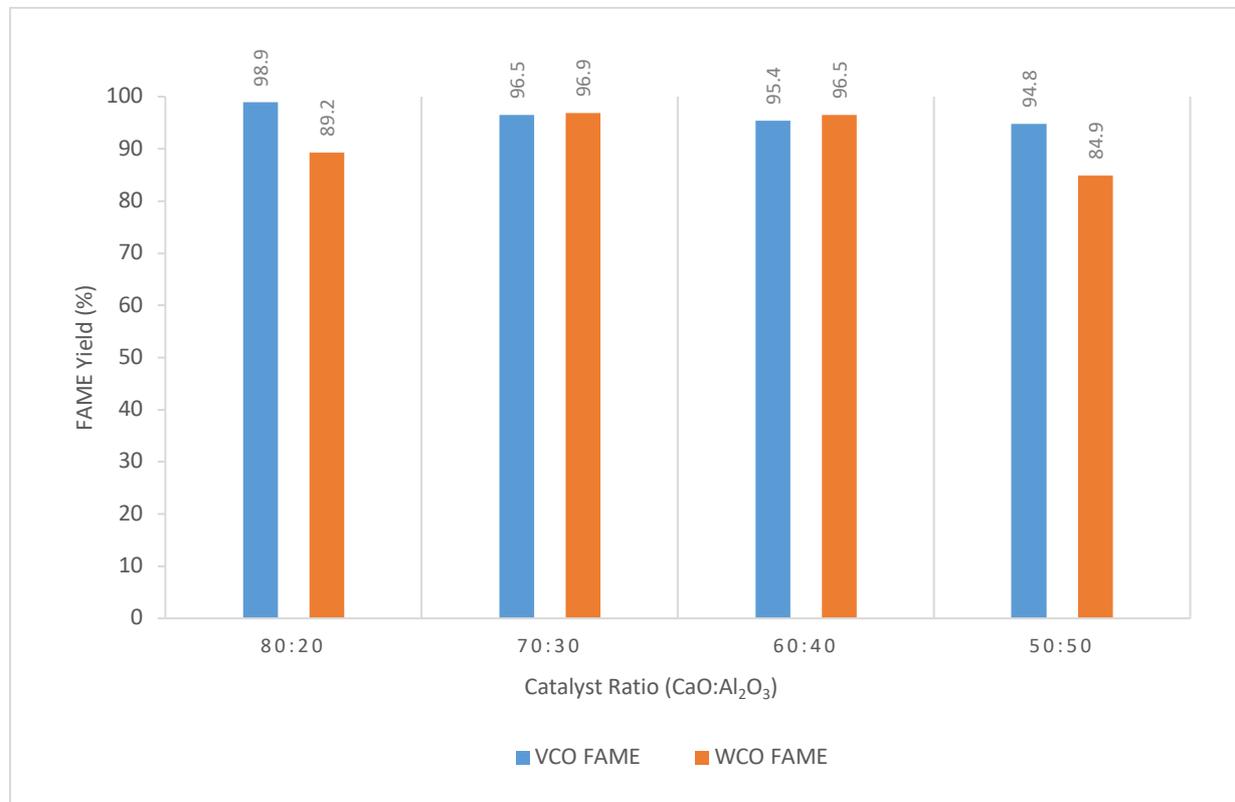


Figure 4-5: Effect of catalyst on virgin canola (VCO) and waste canola (WCO) oil FAME yield

4.3.1.4. Effect of FFA and Catalyst Composition on Neem Oil FAME

Neem oil is the only non-edible oil used to synthesise FAME in this study and had an FFA content of 3.25% which is considered high according to (Mansir *et al.*, 2018). Due to this, a catalyst with more acidic sites would be more suited compared to the waste oils in order to optimise the esterification of FFA. This is shown in Figure 4-6 where the best performing

catalyst was 60% CaO, with a yield of 97.6%. However, the poorest performing catalyst was 50% CaO which had the largest amount of alumina and resultantly the highest number of acidic sites. This decline in yield can be attributed to inadequate mass transfer beyond the 60% CaO:40%Al₂O₃ ratio. The initial calcium to alumina ratio plays a major role in the microstructure as well as the physical properties of the catalyst where the more the calcium particles are dispersed in the alumina matrix, the more porous the structure (Salomão *et al.*, 2017). Therefore, a decrease in CaO leads to a decline in catalyst porosity and surface area. This hinders liquid-solid heterogenous phase reaction and the conversion of large triglyceride molecules into esters (Ljupkovi *et al.*, 2014). Consequently, this causes a lower yield due to the decrease in transesterification. This coincides with the results seen in Figure 4-6.

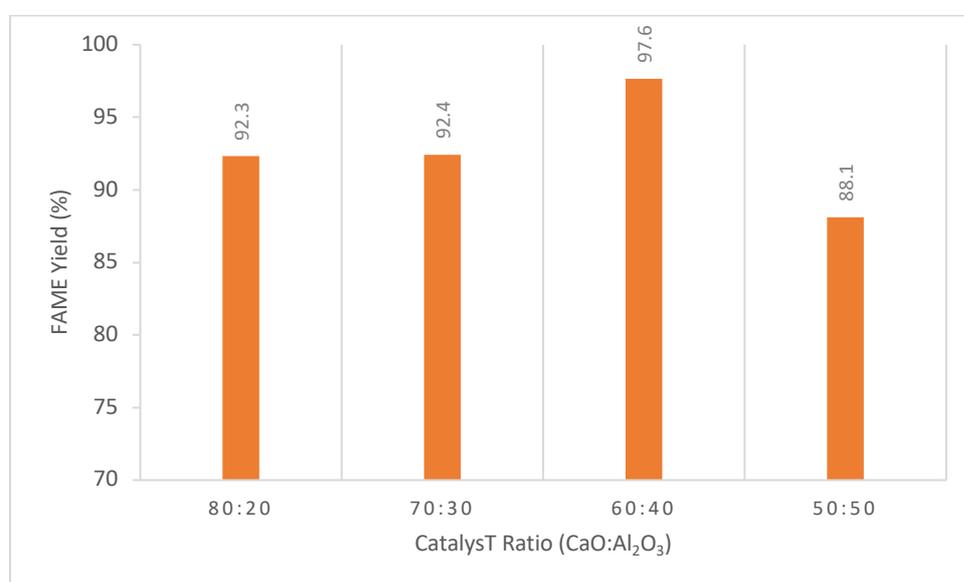


Figure 4-6: Effect of catalyst on neem oil FAME yield

4.3.1.5. Overall Biodiesel Yields of Feedstock

From the experiments done, it was evident that virgin oils with negligible FFA content favoured the use of the highest basic catalyst (80% CaO) (Table 4-8). The lack of FFA eliminated the need for esterification and therefore the need for acidic sites facilitated by alumina. Though alumina acts as an excellent support due to its large surface area, its addition decreases the overall CaO loading in the bi-functional catalyst and, consequently, the amount of basic sites needed for optimal transesterification to take place. Therefore, the presence of alumina might have hindered virgin oil feedstock reaction performance and it is possible that higher yields would have been achieved with the use of a 100% CaO content catalyst. It can therefore be concluded that these virgin oil feedstocks do not require a bi-functional catalyst in order to achieve optimal yields.

The waste oils in this study favoured the use of 70% CaO. Waste palm oil, in particular, had an FFA content >1 wt% (2.47 wt%) which is considered high. Therefore, there was a need for a bi-functional catalyst to facilitate an adequate amount of acidic sites, (alumina), needed for esterification of these free fatty acids. This is evident as the most basic catalyst (80% CaO) was the worst performing catalyst in the conversion of waste palm oil to FAME.

Similarly with neem oil the highest FFA content of 3.25 wt% performed best with the use of a more acidic catalyst (60% CaO) but there was a drastic decline in yield beyond this ratio as 50% CaO produced a neem FAME yield of 88.1%. Though a trend was established where increased FFA required increased catalytic acidity, an excess amount of acidic catalyst will hinder the main transesterification reaction. Therefore, to achieve maximum efficiency and conversion, a sufficient amount of acidic catalyst is required for optimal esterification of FFA without promoting inadequate mass transfer in the main transesterification reaction. The use of a bi-functional catalyst has been observed to be imperative in the conversion of low-grade feedstocks. This proves to be highly advantageous as the production costs of biodiesel production are decreased significantly as both feedstock and catalyst sources can be obtained from waste materials.

Table 4-8: Overall Biodiesel Yields of Feedstocks

	FAME Yield (%)			
	80% CaO	70% CaO	60% CaO	50% CaO
SB100	95.6	88.7	83.6	83.5
PB100	97.9	89.9	80.7	79.2
CB100	98.9	96.5	95.4	94.8
WSB100	95.5	98.3	92.5	89.9
WCB100	89.2	96.9	96.5	84.9
WPB100	80.0	99.5	94.1	89.9
NB100	92.3	92.4	97.6	88.1

4.3.1.6. Catalyst Reusability

Catalyst reusability is crucial as it contributes to the sustainability and cost of the overall process in the synthesis of biodiesel. Waste palm oil was used because of its a high FFA content (2.47%) therefore it was employed in testing the bi-functional catalyst robustness. Figure 4-7 shows that the four different catalysts underwent eight consecutive runs with no significant decrease in activity as the biodiesel yields remained constant (~ 79, 99, 94.5 and 89.5% for 80% CaO, 70% CaO, 60% CaO and 50% CaO respectively). However, there was a decrease in activity on all catalysts from run 10 to 12 as a decrease in yield was observed. CaO based

catalysts have been shown to maintain optimal activity for up to 14 runs (Tshizanga, 2015). The deactivation of these catalysts can be attributed to moisture exposure as well as CO₂ and impurities absorbed on the catalyst surface. This exposure causes agglomeration which enlarges the catalyst particle size and consequently causes decreased exposed surface area per unit mass (Tan *et al.*, 2019). Moreover, the accumulation of glycerol on the catalyst over consecutive runs further hinders its performance (Dai, Hsieh and Chen, 2014). Resultantly, the feedstock oil is exposed to less active sites during E and TE (Tan *et al.*, 2019).

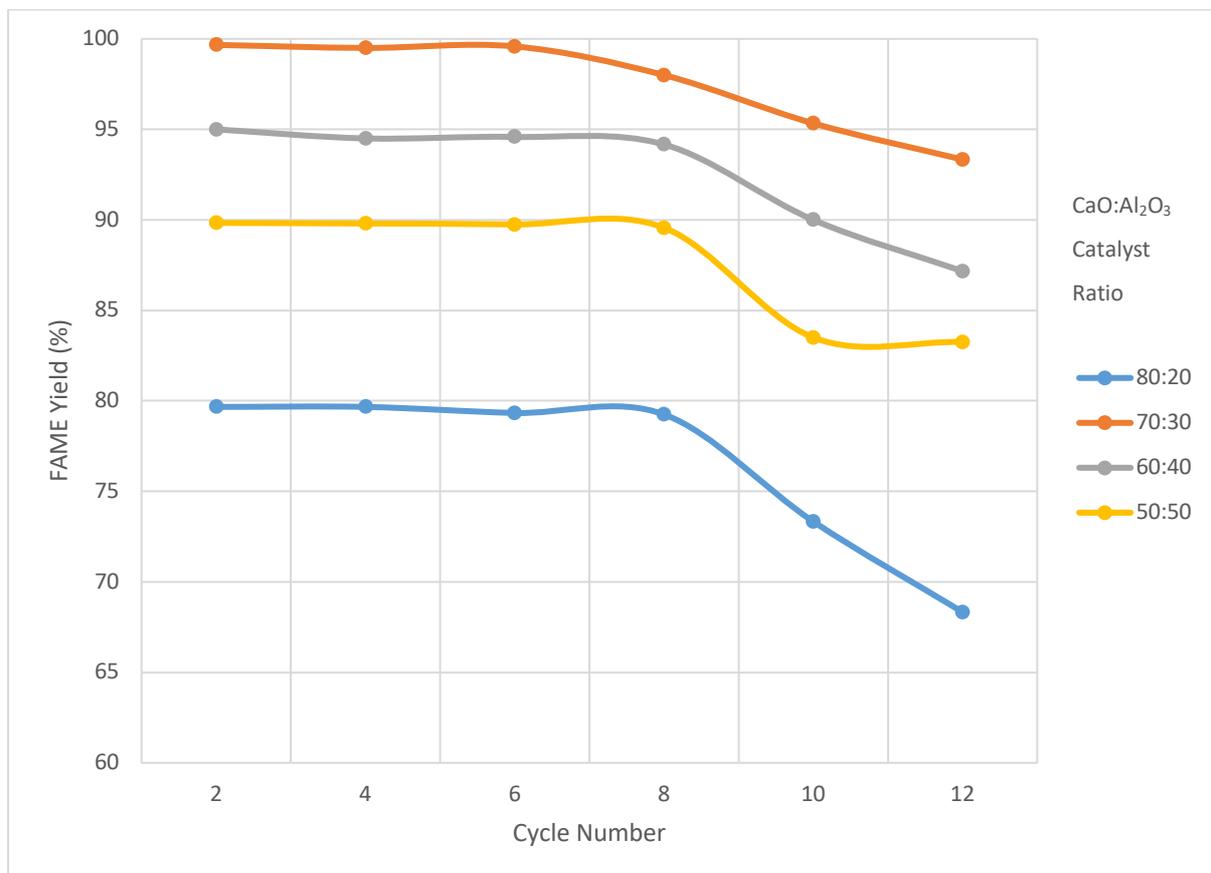


Figure 4-74: Catalyst Reusability

4.3.2. Biodiesel Transportation Fuel Characteristics

The transportation fuel characteristics were measured and analysed in accordance with the ASTM reference test methods (D 664, D 445, D 93, D 5453 and D 2709). The Rancimat procedure was also utilised for the measurement of induction time/ oxidation stability.

Synthesised FAME was also classified according to the number of transportation fuel characteristics satisfied on an average of the four fuels produced by each feedstock (Table 4-8). FAME highlighted in green (SB100, WSB100, WCB100 and PB100) satisfied all of the fuel characteristic restrictions. Whereas fuels highlighted in orange (CB100 and WPB100) satisfied a minimum 67% of (4 out of the 6) fuel characteristics measured. Neem oil biodiesel, highlighted in red, satisfied 33% of (2 out of 6) the measured fuel characteristics. This elaborates the need for pre-treatment of feedstocks such as waste palm and neem oil, or their respective products, in order to produce good quality biodiesel. In contrast, WSB100 and WCB100 were the only fuels synthesised from waste oils that satisfied all the measured transportation characteristics with TAN (0.25 - 0.51 mgKOH/g), density (0.887- 0.888 g/m³), viscosity (4.6 - 6.6 cSt), FP (155 - 165 °C), sulphur content (0 - 8 ppm) and water content (0.03 - 0.08 %vol), therefore, no feedstock pre-treatment was required.

Table 4-8: Transportation fuel characteristics of FAME produced

FAME	Catalyst (CaO:Al ₂ O ₃)	Total Acid Number mgKOH/g	Density (g/m ³)	Viscosity at 40°C (cSt)	Flash point (°C)	Sulphur Content (ppm)	Water content (%vol)
SB100	1 (80:20)	0.32	0.887	6.2	165	2	0.05
	2 (70:30)	0.33	0.887	5.5	160	2	0.07
	3 (60:40)	0.46	0.887	5.5	165	8	0.04
	4 (50:50)	0.51	0.888	5.3	155	3	0.05
WSB100	1 (80:20)	0.65	0.888	5.1	165	4	0.04
	2 (70:30)	0.25	0.887	4.6	165	2	0.03
	3 (60:40)	0.61	0.887	5.2	165	2	0.08
	4 (50:50)	0.32	0.887	6.6	160	0	0.08
PB100	1 (80:20)	0.40	0.887	6.8	160	3	0.03
	2 (70:30)	0.52	0.879	7.2	165	12	0.04
	3 (60:40)	0.17	0.876	5.1	165	1	0.03
	4 (50:50)	0.51	0.877	5.0	165	4	0.02
WCB100	1 (80:20)	0.37	0.886	4.8	170	13	0.03
	2 (70:30)	0.27	0.885	5.7	170	11	0.02
	3 (60:40)	0.39	0.884	5.1	170	9	0.02
	4 (50:50)	0.56	0.889	0.4	165	10	0.03
CB100	1 (80:20)	0.22	0.849	5.1	130	6	0.05
	2 (70:30)	0.88	0.883	5.1	160	4	0.02
	3 (60:40)	0.28	0.883	5.1	165	5	0.02
	4 (50:50)	0.25	0.884	18.6	165	1	0.02
WPB100	1 (80:20)	0.48	0.887	8.1	160	8	0.07
	2 (70:30)	0.45	0.88	7.6	160	5	0.03
	3 (60:40)	0.67	0.882	9.7	160	5	0.09
	4 (50:50)	0.38	0.879	16.9	155	11	0.19
NB100	1 (80:20)	0.64	0.889	9.5	165	137	0.11
	2 (70:30)	0.73	0.889	10.7	165	142	0.08
	3 (60:40)	0.70	0.887	11.1	165	334	0.04

4.3.2.1. Total Acid Number

The current allowable acid number according to the ASTM standard is 0.5 mgKOH/g which was lowered from 0.8 mgKOH/g a decade ago in order correlate to with the EN (standard European) restrictions (Altaie, 2020). This acid number setting which is equivalent to 0.25 wt% is set due to concerns about the possibility that fatty acids may cause engine deposits in fuel injectors. This is caused by the catalysing polymerisation in hot recycling fuel loops (Mahajan *et. al.*,2006).

The highest average acid number in the biodiesel produced was 0.635 from neem oil FAME and the lowest being 0.3975 from waste canola FAME (Table 4-8). Sunflower, canola and palm FAME had a similar average of ~0.4 whilst waste sunflower FAME had an average value of 0.4575. The acid number is a measure of acidic constituents in the fuel and is directly proportional to the feedstock free fatty acid content (Fernando *et.al.*, 2007). This correlates with the observations presented earlier as the highest acid number was produced by the feedstock with the highest FFA content (neem oil). Similarly, the feedstock with the second highest FFA content (waste palm oil) produced a fuel with the second highest acid number. Although feedstock FFA proves to be a major factor in the biodiesel's acid number, other elements such as inadequate catalyst separation from the biodiesel and incomplete conversions of (free) fatty acids to methyl esters. The latter phenomenon can be observed in CB100, SB100, WCB100 and WSB100 where the lowest acid number correlated with the highest yield achieved. However, the lowest acid number achieved by WPB100 and NB100 did not follow this trend and it is observed that their lowest acid number was produced by the catalyst with the highest amount of alumina. Although this catalyst did not produce the highest yield, the elevated acidic sites facilitated more in the conversion of free fatty acids (esterification) compared to the other catalysts used. This proved to be effective in lowering the fatty acid content and consequently, the acid number in NB100 and WPB100 as waste palm oil and neem oil had the highest FFA contents.

4.3.2.2. Density

The density of a fuel is a significant parameter as it directly affects the engine performance as it is found more efficient in the combustion process (Altaie, 2020). As stated in Table 4-8, the maximum allowable biodiesel density is 880 kg/m³ (ASTM) and a range of 860-900 kg/m³ (EN). The fuels produced in this study ranged between 880 and 889 kg/m³ which is within the European standards. Although denser feedstocks are commonly observed to produce denser

biodiesel, oxidation remains one of the main attributes that contribute to this as sludge and gunk is formed during storage.

4.3.2.3. Kinematic Viscosity

Similar to density, viscosity is critical in the combustion efficiency of an engine. High viscosity fuels prove to be problematic as they have an adverse effect on fuel dispersion and fuel-air mixing. Consequently, this causes excessive wear and tear in fuel injection equipment which results in inefficient combustion (Sundus *et. al.*, 2017).

According to ASTM standards, kinematic viscosity of B100 at 40 °C ranges between 1.9 and 6 cSt where the European specifications are stricter with a range of 3.5-5 cSt (Tiwari *et. al.*, 2018). 50% of the biodiesel produced adhered to the ASTM density range and 7.14% to the EN standards (Table 4-8). Viscous feedstock has a tendency to produce viscous biodiesel (Chuah *et al.*, 2016). After heat treatment, neem oil remained the feedstock with the highest viscosity upon observation. Consequently, NB100 had the highest average kinematic viscosity (15.425 cSt). It is also observed that four out of the seven synthesised biodiesel variants (NB100, CB100, WSB100 and WP100) had their highest viscosity when the catalyst with a ratio of 50:50 was used. This could be attributed to incomplete transesterification as this catalyst had the lowest quantity of CaO. Other factors include oxidation and the presence of glycerol (Tshizanga, 2015).

4.3.2.4. Flash Point

The flash point is a crucial measure of volatility as it consequently determines storage and transportation specifications to ensure safety. Both ASTM and EN specifications require a B100 flash point temperature range of 100 to 180 °C. This range was satisfied by all the biodiesel produced in this study as the minimum flash point value was measured as 130 °C and a maximum of 170 °C (Table 4-8). CB100 had the lowest average flash point temperature of 155°C where WCB100 had the highest average flash point temperature at a value of 168.75°C. Flash point temperature is increased as the degree of unsaturation of the parent oil, and its corresponding ester is higher (Ayoola *et al.*, 2016). A similar trend was observed as VCO and WCO had the highest quantities of unsaturates with monounsaturated fatty acids (MUFA) at 71.23% and 66.61% as well as polyunsaturated fatty acids (PUFA) at 19.16% and 19.37% respectively (Table 4-6).

4.3.2.5. Sulphur Content

A major advantage that biodiesel holds is the relatively low sulphur content compared to petroleum diesel which drastically decreases sulphur-based emissions. The maximum allowable sulphur content with regard to both American and European standards is 15ppm (Yadav *et al.*, 2019). The biodiesel synthesised adhered to these restrictions with the exception of neem oil where the average sulphur content value was 191.5 ppm (Table 4-8). This is attributed to the nature of the feedstock itself. Apart from triglycerides, neem oil consists of large amounts of triterpenoid compounds ($C_{30}H_{48}O_7S$). This consequently contributes to the increase in sulphur content in neem oil FAME.

4.3.2.6. Water Content

A water content of 0.05wt% max in B100 is the standard specification provided by both the EN and ASTM systems (Yadav *et al.*, 2019). The lowest average water contents were measured in CB100, WCB100 and PB100 with values of 0.0275 wt%, 0.03 wt% and 0.25 wt% respectively. SB100 and WSB100 had slightly higher than standard values of 0.0525 wt% and 0.0575 wt% respectively (Table 4-8). The highest average contents were 0.095 wt% in WPB100 and 0.07 wt% in NB100 (Table 4-8).

There are various factors that influence the presence and quantity of water in biodiesel which includes the amount of water in the oil feedstock itself. Waste oils generally tend to have a higher water content as they contain remnants of moisture from previous cooking processes. However, the existence of water (< 1 wt%) does not have a significant effect on biodiesel yield. Another factor includes the lack of proper drying after synthesis. This proves detrimental as a high water content in biodiesel might potentially affect fuel delivery materials degradation (Chandran *et al.*, 2017)

4.3.4.7. Oxidation Stability

Oxidation stability is one of the main fuel properties affecting the storage of a biodiesel fuel as it indicates the fuel's ability to resist auto-oxidation and degradation. The current restrictions surrounding oxidation stability of a B100 fuel is a maximum induction time of 3 h (ASTM) and 6 h (EN)

The highest induction times recorded in this study were 7.7 h and 7.67 h achieved by NB100 and PB100 respectively (Table 4-10). The least stable fuels with the lowest induction time were WSB100 and SB100. This demonstrates the relationship observed between the presence of unsaturated fatty acids in the feedstock and oxidation stability of the biodiesel product.

Oxidation is mainly caused by the presence of double bonds in the carbon chains, hence feedstocks with high levels of polyunsaturated fatty acids (PUFA) are likely to produce biodiesel that is more susceptible to oxidation. Sunflower oil and waste sunflower oil had the highest quantities of PUFAs with values of 67.83% and 64.04% (Table 4-6) and consequently produced biodiesel with the lowest oxidation stability. This correlation is further supported as the feedstocks with the highest amounts of saturated fatty acids and the lowest amount of PUFAs (palm, neem and waste palm oil) produced biodiesel with the highest oxidation stability. Moreover, it was observed that 50% CaO produced the least stable fuels in six out of the seven feedstocks used.

Table 4-10: Induction times of FAME produced.

Catalyst	Induction Time (h)						
	Low saturation PUFA dominant		—————>			High saturation SFA dominant	
	SB100	WSB100	CB100	WCB100	PB100	NB100	WPB100
80% CaO	4.90	5.31	6.24	6.09	8.69	7.96	7.02
70% CaO	5.08	3.61	6.25	7.44	8.31	6.97	7.83
60% CaO	4.02	4.12	4.54	4.41	8.22	8.68	7.24
50% CaO	2.88	2.08	4.93	4.68	6.46	7.41	6.11
AVG	4.22	3.78	5.49	5.62	7.67	7.70	7.03

4.3.3. Effect of Feedstock Unsaturation on Catalyst Performance

Observations were done with regard to the relationship between unsaturation and FFA content and it was found that feedstocks with the lowest degree of unsaturation exhibited the highest FFA content (Table 4-11). Moreover, the more saturated feedstocks performed optimally with 70% CaO and 60% CaO which had higher acidic sites where more unsaturated feedstocks favoured a higher basic catalyst (80% CaO). Studies done indicate catalytic (basic) activities were observed to be higher when a parent oil with short-chain fatty acids or a high unsaturation degree were used (Abreu *et al.*, 2004). However, Neem and waste palm oil had the highest levels of palmitic acid which exhibits a relatively short chain compared to the remainder of the dominant fatty acids found in the feedstocks used in this study

Yang, Astatkie and He, (2016) stated that monoglycerides conversion of FAME was faster for oils exhibiting a higher degree of unsaturation. Pinzi *et al.*, (2011) further observed that saturated fatty acids were transesterified mostly at the beginning of the reaction while the unsaturated fatty acids conversion increased as the reaction progressed. This suggests that

unsaturated fatty acid dominant feedstocks would take longer to achieve optimal yield. However optimal yields achieved in this study show negligible differences between PUFA, MUFA and SFA dominant feedstocks (Table 4-11). Due to this, it was evident that the degree of unsaturation of the feedstock had no significant effect on catalyst performance.

Table 4-11: Effect of saturation on catalytic performance

	PUFA dominant		MUFA dominant		SFA dominant	
Feedstock	VS	WS	VC	WC	WP	N
FFA (wt%)	0.22	0.72	0.33	0.78	2.47	3.25
Highest Yield (%)	95.6	98.3	98.5	96.9	99.5	97.6
Catalyst	80% CaO	70% CaO	80% CaO	70% CaO	70% CaO	60% CaO

VS: Sunflower oil; WS: Waste sunflower oil; VC: Canola oil; WC: Waste canola oil; WP: Waste palm oil; N: Neem oil

4.4. Summary

The four catalysts synthesised (Table 4-7) contained negligible trace amounts of impurities such as $\text{Ca}(\text{OH})_2$ and CaCO_3 which was attributed to incomplete calcination (Table 4-1). However, they exhibited adequate morphological and catalytic characteristics where pore size was $>209 \text{ \AA}$, surface area $>11 \text{ m}^2/\text{g}$ and pore volume $>0.072 \text{ cm}^3/\text{g}$ (Table 4-3). Due to the method in which these catalysts were prepared (co-precipitation), they were bi-functional in nature with basic sites (CaO) and acidic sites (Al_2O_3).

The use of these catalysts to simultaneously esterify and transesterify with varying FFA content (0.33 - 3.25%) was done in order to determine the effectiveness and relationship between catalyst bi-functionality and FFA levels in a feedstock. It was found that there was a correlation between FFA concentration and the quantity of acidic sites on the catalyst used for biodiesel synthesis. This was seen in figure 4-7 where neem oil, which had the highest FFA content of 3.25%, achieved an optimal yield with the use of catalyst 3, which had the 2nd highest alumina loading (60% CaO 40% Al_2O_3). Furthermore, virgin oils which had low FFA contents (0.22 - 0.67%) achieved the highest yield with the use of 80% CaO which consisted of the lowest alumina loading (20% Al_2O_3). Therefore, it was determined that a higher yield was achieved as the increase of FFA was favoured by an increase in acidic sites which facilitated adequate esterification. In contrast, a lower FFA feedstock required more basic sites in order for sufficient transesterification to take place.

This study also analysed the effect of feedstock chemical and structural nature on fuel characteristics from their corresponding synthesised biodiesel. Such characteristics included total acid number (TAN), density, kinematic viscosity, flash point, sulphur content and oxidation stability. NB100 had the highest TAN at 0.635, which was attributed to the feedstock used (neem oil) which had the highest FFA content. NB100 was also found to be the most viscous at 15.45 cSt, this was again attributed to the nature of the parent oil used as neem oil was the most viscous feedstock. CB100 and WCB100 had the highest flashpoint temperatures 155 and 168.75 °C respectively. Flash point is directly correlated to the level of unsaturation where the higher the unsaturation, the higher the FP temperature. This was evident as both waste canola oil and virgin canola oil had a high amount of unsaturates with MUFA at 71.23% and 66.61% as well as PUFA at 19.16 and 19.37% respectively (Table 4-6). NB100 contained the highest amount of sulphur content. This was explained by the presence of triterpenoid compounds ($C_{30}H_{48}O_7S$) found in neem oil. Oxidation stability on the biodiesels was also measured. It was found that PB100 was the most stable with an induction time of 7.67 h. Oxidation stability is governed by the level of unsaturation where a more unsaturated feedstock would produce a less stable fuel. This is evident as palm oil had the highest level of saturation. Furthermore, it was concluded that the degree of unsaturation of a feedstock does not affect catalytic performance.

CHAPTER 5

CONCLUSION AND RECCOMENDATIONS

Chapter 5 Conclusion and Recommendations

5.1. Conclusion

The aim of this project was to assess the efficiency of bi-functional catalysts on the production of biodiesel with feedstocks with varying FFA contents. The factors investigated included basic to acidic site ratio and its effect on biodiesel yield, catalyst robustness/ reusability as well as the effect of feedstock composition and nature on transportation fuel characteristics. 7 feedstocks (palm oil, waste palm oil, sunflower oil, waste sunflower oil, canola oil, waste canola oil and neem oil) were used to produce biodiesel with the use of four catalysts with ratios of CaO:Al₂O₃ at 80:20, 70:30, 60:40 and 50:50. These experiments were conducted at a temperature of 65 °C, an agitation rate of 1200 rpm with a catalyst loading of 2.5 wt% and a methanol to oil molar ratio of 12:1. It was assumed that the catalyst amount used was sufficient to facilitate the formation of methyl esters.

It was observed that the catalysts synthesised performed well, facilitating the simultaneous esterification and transesterification of the feedstocks that contained up to 3.25% FFA. The catalysts were synthesised through co-precipitation to ensure bi-functionality and calcined at 600 °C. The four catalysts (Table 4-7) were characterised with large pore sizes (>209 Å), high surface areas (>11 m²/g) and pore volumes >0.072 cm³/g (Table 4-3). Furthermore, it was observed that all four catalysts could be reused for up to 8 cycles without significant loss of activity. This showed industrial catalytic potential compared to conventional homogenous as low-grade feedstock was successfully converted to methyl esters.

An investigation on the relationship between FFA content and acid site quantity was done. It was found that virgin oils which had low FFA contents (0.22-0.67 wt %) required minimal acidic sites to achieve optimal yield with the use of 80% CaO. Moreover, neem oil which had the highest FFA content (3.25%) achieved an optimal biodiesel yield of 97.63% with the use of 60% CaO,40%Al₂O₃ which had a higher alumina loading and resultantly more acidic sites. However, a significant drop in yield was observed beyond this ratio. This was attributed to poor mass transfer and the diffusion limitations observed in solid acid catalysts reported in literature. Waste oils with FFA contents ranging from 0.78% to 2.47% were observed to perform best with the use of catalyst 2 (70% CaO,30%Al₂O₃). The decline of CaO and ultimately basic sites beyond this ratio proved detrimental as it did not facilitate optimal

transesterification. Furthermore, it was evident that the degree of unsaturation of the feedstock did not affect catalyst performance.

Transportation fuel characteristics were also determined on the biodiesel samples produced in accordance with the ASTM (D 664, D 445, D 93, D 5453 and D 2709) and EU standards. These included density, kinematic viscosity, flash point, sulphur content, oxidation stability and water content. Overall, the various biodiesels satisfied these conditions with the exception of NB100. Sulphur content and viscosity was found to be higher than the stipulated restrictions. This was explained by the chemical and physical nature of neem oil as it was very viscous and contains triterpenoid compounds ($C_{30}H_{48}O_7S$) which consequently elevate sulphur content.

The use of a bi-functional catalyst has proved to be highly effective in the simultaneous esterification and transesterification of low-grade high FFA feedstocks. The first major advantage is an economic one. The raw materials used (feedstock and catalyst synthesis) are low cost and easily attainable. CaO can be obtained from bones, eggshells and limestone where alumina is a waste biproduct of aluminium production. Moreover, due to the heterogeneous nature of the catalyst, separation and purification costs compared to the use of homogenous catalysts are significantly reduced. Due to the simultaneous nature of the reaction, a two-step process, where the feedstock is subjected to acid treatment (to lower FFA) and is thereafter transesterified, is not necessary and thus further cuts production costs. Another advantage pertains to environmental friendliness as there is no wastewater generated with the use of a heterogeneous catalyst. Cumulatively, these factors provide the production of biodiesel through bi-functional catalysis sufficient rationale and competitiveness against fossil diesel.

5.2. Recommendations

This study reported on the core objectives which included the use of a bi-functional catalyst for the production of biodiesel from feedstocks with varying FFA contents. This was done to potentially minimize the cost of production of biodiesel as well as catalyst synthesis costs. However, the following areas need to be investigated further:

- Exploration of feasible industrial use of bi-functional catalysts
- More studies should be done to combat catalyst deactivation and poisoning when exposed to air or moisture.

- Further work should be done to investigate ways to improve bi-functional catalyst activity.
- Further investigations should be done to reduce the excess methanol needed for optimal E and TE.
- A technoeconomic analysis can be conducted to assess the feasibility of the approach employed in this study.

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Appendices

Appendix A: Sample Calculations on Biodiesel Production

A.1 Acid Number and Free Fatty Acid Determination

Using waste Canola oil (WCO):

$$FFA = \frac{AN}{2} \quad \text{E-1}$$

Where

$$AN = \frac{56.1(N)(V)}{M}$$

$$AN = \frac{56.1(0.1)(0.5)}{1.8}$$

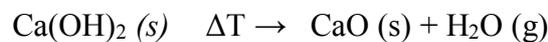
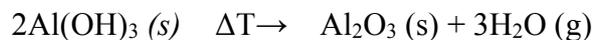
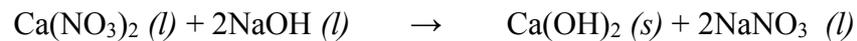
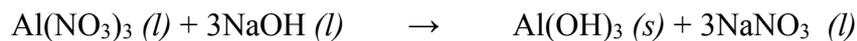
$$= 1.5583$$

$$FFA = \frac{1.56}{2} = 0.7792$$

$$\approx 0.78$$

A.2 Catalyst Preparation

Preparation of 80% CaO/Al₂O₃ catalyst by co-precipitation method



M_w of Al₂O₃ = 101.96 g/mol

M_w of CaO = 56.0774 g/mol

M_w of Ca(NO₃)₂ = 164.088 g/mol

M_w of Al(NO₃)₃ = 212.996 g/mol

M_w of Al(NO₃)₃.9H₂O = 374.996 g/mol

M_w of Ca(NO₃)₂.4H₂O = 236.172 g/mol

100 g of combined catalyst = 80 g CaO/20 g Al₂O₃

moles of $\text{Al}_2\text{O}_3 = m_{\text{Al}_2\text{O}_3} / M_{\text{WAl}_2\text{O}_3} = 20/101.96 = 0.2$ moles of Al_2O_3

Since 1 mol of $\text{Al}(\text{NO}_3)_3 = 1/2$ mole of $\text{Al}_2\text{O}_3 = 0.5$ moles

Then moles of aluminium nitrate = $0.2/0.5 = 0.4$ moles of $\text{Al}(\text{NO}_3)_3$

Mass of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 0.4 \times 375 = 150$ g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Moles of $\text{CaO} = 80/56.0774 = 1.4266$ moles

1 mol of $\text{Ca}(\text{NO}_3)_2 = 1$ mol of $\text{Ca}(\text{OH})_2 = 1$ mol CaO

Then moles of $\text{Ca}(\text{NO}_3)_2 = \sim 1.4266$ moles

Mass of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} = n_{\text{Ca}(\text{NO}_3)_2} \times M_{\text{WCa}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}} = 1.4266 \times 236.172 = 336.923$ g of

Calcium nitrate = 340 g of Calcium nitrate

Preparation of the precipitating agent (NaOH) solution:

$155/2 = 78$ g Aluminium nitrate

$340/2 = 170$ g of Calcium nitrate

New moles of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 78/375 = 0.21$ moles

1 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 3$ moles of NaOH

moles of $\text{NaOH} = 0.21 \times 3 = 0.63$ moles

New moles of $\text{Ca}(\text{NO}_3)_2 = 170/236.2 = 0.72$ moles

1 mol of $\text{Ca}(\text{NO}_3)_2 = 2$ mol of NaOH

moles of $\text{NaOH} = 0.72 \times 2 = 1.44$ moles

Total moles of $\text{NaOH} = 2.07$ moles

1L = 2 moles of NaOH

0.03 moles = x

- $0.03/2 = 0.015$ L which equals 150 mL of 2M solution
- 508 mL of 4M solution of NaOH
- 160 g in 1L of NaOH

A.3 Biodiesel Yield Calculations

The theoretical maximum yield for biodiesel was 60g. Actual biodiesel was yield was determined by:

$$\% Yield = \frac{Mass_{BD}}{Mass_{oil}} \times 100 \quad E-2$$

For virgin sunflower oil catalysed by 80% CaO,20%Al₂O₃:

$$\begin{aligned} \% Yield &= \frac{57.36}{60} \times 100 \\ &= 95.6\% \end{aligned}$$

Table A-1a: Sunflower Biodiesel Yields

Virgin sunflower oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	57.36	95.6
70/30	53.21	88.68333
60/40	50.16	83.6
50/50	50.08	83.46667

Table 2b: Waste Sunflower Biodiesel Yields

Waste Sunflower Oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	57.27	95.45
70/30	58.99	98.31667
60/40	55.5	92.5
50/50	53.93	89.88333

Table A-2a: Palm Oil Biodiesel Yields

Virgin Palm oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	58.71	97.85
70/30	53.96	89.93333
60/40	48.4	80.66667
50/50	47.53	79.21667

Table A-2b: Palm Oil Biodiesel Yields

Waste Palm Oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	48	80
70/30	59.71	99.51667
60/40	56.45	94.08333
50/50	53.93	89.88333

Table A-3a: Canola oil Biodiesel Yields

Virgin Canola Oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	59.37	98.95
70/30	57.87	96.45
60/40	57.21	95.35
50/50	56.88	94.8

Table A-3b: Canola oil Biodiesel Yields

Waste Canola Oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	53.54	89.23333
70/30	58.13	96.88333
60/40	57.9	96.5
50/50	50.91	84.85

Table A-4: Neem Biodiesel Yields

Neem Oil		
Catalyst ratio	Biodiesel produced (g)	Yield
80/20	55.39	92.31667
70/30	55.45	92.41667
60/40	58.58	97.63333
50/50	52.86	88.1

Table A-5: Waste palm oil yields (Catalyst reusability)

Cycle	Cat 1	Cat 2	Cat 3	Cat 4
2	47.8	59.8	57	53.9
4	47.8	59.7	56.7	53.88
6	47.6	59.75	56.75	53.85
8	47.55	58.8	56.5	53.74
10	44	57.2	54	50.1
12	41	56	52.3	49.95