



**SULPHONATED CARBON CATALYST FOR BIODIESEL SYNTHESIS**

**By**

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**BSc. Eng. (Chemical)**

**Submitted in Fulfilment of the Academic Requirements for**

**Master of Science in Engineering**

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**Durban, South Africa**

**September 2021**

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## **Preface**

The work presented in this dissertation was carried out in the analytical laboratory at the School of Chemical Engineering at the University of KwaZulu-Natal (Howard College Campus), Durban, from September 2020 to May 2021 under the supervision of Professor David. Lokhat. This dissertation is submitted as a full requirement for the degree of Master of Science in Engineering (Chemical). All the work presented in this dissertation is original, unless otherwise stated. It has not (in whole or in part) been previously submitted to any tertiary institute as part of a degree.

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Nomagugu Siwela

As the candidate's supervisor, I agree to the submission of this dissertation:

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Prof. D. Lokhat

## Declaration

I, Nomagugu Siwela, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other University.
3. This thesis does not contain other persons' data, pictures, graphs, or other information, unless specifically acknowledged as being sourced from other persons.
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Signed

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## **Acknowledgements**

I would like to express my gratitude to the following individuals:

My supervisor, Prof. D. Lokhat, for providing me with an interesting and important topic. His support, encouragement, guidance, consistency, and expertise offered during this project have been invaluable.

Miss N. Hadebe (especially Miss N. Hadebe) & Mrs. T. Mofokeng for their constant assistance and guidance in the laboratory and assistance in ordering the required chemicals and equipment.

My friends and colleagues who have been a great source of support and motivation during the project. In particular, I would like to express my gratitude to Kimaya Setty, Nosipho Yolanda Ngubane, Vulinhlanhla Mchunu, Thulani Bayeni, and Cameroon Peku.

My mentor Oladosu Teyibo for always being there for me, supporting me and motivating me.

My late mother Amukelani Ndlovu, for always believing in me. Her words keeps me going till this day.

Lastly, my father, Prof. M. Siwela and aunt Simangele Mafu, for always teaching me the importance of a good education and for their constant support throughout my career. I am where I am today thanks to them.

## Abstract

The uncertainty surrounding the sustainability of petroleum and petroleum derived products along with efficient waste management methods and the increasing energy demands are of great concern in modern society. As a result, the development of innovative industries capable of converting waste products into high value products has garnered interest from researchers and industrialists worldwide. Biodiesel is a promising candidate to replace or blend with petroleum-based diesel since it is synthesised using renewable sources and its application requires no modification to the existing engine. The fuel has many superior properties compared to petroleum-based diesel such as, increased lubricity, non-toxicity, biodegradability, ease of handling, transport, storage, and that production can be decentralized to improve rural economies. The Fatty Acid Methyl Esters (FAME) constituting biodiesel is manufactured commercially using two methods, which is the transesterification of triglycerides (TGs) and the esterification of free fatty acids (FFAs). Both these processes occur in the presence of a catalyst hence there is urgency for an efficient and cost-effective catalyst capable of promoting both reactions without the process challenges encountered when heterogeneous base or homogeneous acid and base catalysts are used. The main aim of the study was to synthesize a sulphonated catalyst based on tyre pyrolysis char, and to determine the performance of this catalyst for biodiesel production using the model esterification reaction between oleic acid and methanol. The sulphonation was carried out using concentrated sulphuric acid and under high temperature, and the final catalyst was subjected to Fourier transform infrared spectroscopy and surface area analysis. The characterization confirmed that the catalyst had been successfully prepared. The process was examined using a Box-Behnken experimental design. The process factors which were investigated were temperature, catalyst loading and alcohol to oil ratio. The experimental data were fitted to a quadratic response model with a satisfactory  $R^2$  value of 0.938. Temperature was found to have the most significant effect on product yield and that it may be possible to recover some of the energy used in heating the reaction mixture by condensing the exit vapour stream. The highest yield of methyl oleate obtained was 95.32% at a temperature of 65 °C, alcohol to oil ratio of 6:1, and catalyst loading of 1.5%. The lowest yield obtained was 75.44% at a temperature of 25°C, alcohol to oil molar ratio of 5.35 and catalyst ratio of 0.5%. The catalyst was recovered and reused and produced a methyl oleate yield of 75.58% which was 18.89% lower than the fresh catalyst so a regeneration may be required in the form of mild sulphonation. The sulphonated char catalyst was able to perform

as a solid acid catalyst for the esterification of oleic acid and methanol and hence is a viable catalyst for biodiesel production

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# CHAPTER 1: INTRODUCTION

## 1.1 Background

As the world-wide population continues to increase and industrialization evolves there is a growing need and demand for energy. To meet this demand fossil fuels are used. However, these have a limited supply because they are non-renewable sources of energy leading to higher fuel prices due to the increased demand of a non-renewable resource (Melero et al., 2008). Apart from this there are political challenges of legislation and policies associated with use of non-renewable sources of energy. Researchers and industrialists have since realised the need of a solution that can meet human needs while also being economically and environmentally sustainable. In South Africa, research in the field of renewable sources of energy such as vegetable oils have been considered as possible alternatives to fossil fuels (Brent, 2014). A key factor in sustainable development is energy sufficiency and security as it is a provider of vital inputs for socio-economic development. These will in turn enable the provision of essential services for a better quality of life at regional, national, and subnational levels (Amigun et al., 2008).

Fuels synthesized directly or indirectly from organic material consisting of plant materials and animal waste are called biofuels and are classified according to the source of their biomass. These classes include first-generation biofuels, which are obtained from biomass also used as food by humans, second-generation biofuel which is obtained from non-food biomass such as waste biomass and cellulosic biofuels which compete with food production for arable land and the third-generation are obtained from oil of algae and do not compete with food (Lee & Lavoie, 2013). Biofuels have environmental benefits and commercializing their production for use in the transport industry can provide people with a potential source of new employment thereby improving the economy. In fact, the amount of labour required to produce biofuels compares favourably with conventional fuels. According to a study by the World Bank biofuel production needs about 100 times more workers per joule of energy content produced than the fossil fuel industry (Lin, 2009). Thus, fostering the production and use of biofuels derived from renewable indigenous resources in developing countries where agriculture is the main economic sector and is highly labour intensive would be very strategic in both reducing poverty in rural areas as well as enhancing the country's energy security (Silalertruksa et al., 2012).

South Africa, like all the other developing countries is cognisant of the fact that first generation (crop-based) biofuels have the capacity to ameliorate the declining agricultural sector. The challenges that can come with that is the risk to food security if commercial farmers decide to grow biofuels feedstock product instead of food crops (Zhang et al., 2015) and (Tomei & Helliwell, 2016). Many African countries continue to experience the adverse impacts of climate change and the challenges of energy security. By employing biofuels such as biodiesel developing countries will be provided with an opportunity of a self-reliant energy supply with the potential to increase the economic, environmental, social, and security benefits (Babajide, 2013).

Vegetable oils and their derivatives (such as methyl esters), commonly known as biodiesel, have progressed from being experimental fuels to early stages of commercial production in several countries (Amigun et al., 2008). As early as 1900, Rudolf Diesel utilised peanut oil as a fuel for demonstration purposes in the first diesel engine (Shay, 1993). Ever since then diesel engines have remained an integral part of people's lives for over a century by supporting modern society through transport and construction. The term biodiesel was however first used in the year 1992 at the National Soy Diesel Development Board in the United States of America (Singh & Singh, 2010). Biodiesel is therefore an equivalent fuel to diesel and in some cases can be used as a blend to the conventional diesel. Although Rudolf Diesel was able to demonstrate using groundnut oil, there are challenges that arose from using straight oleaginous plants in a diesel engine. Some of the challenges which were reported included critical engine problems such as injector choking, deposition of combustion chamber, deterioration of lubricating oil and subsequently piston ring sticking, polymerisation and oxidation of vegetable oils were also observed when the engine was used for long (Schwab et al., 1987) and (Dermibas A, 2005). As already mentioned, the other challenge with using that type of feedstock on an industrial scale as with the other types of feedstock such as palm oil, rapeseed oil, sunflower oil and soy-oil is that they are costly and these are feedstocks also used by people for food. This can lead to competition with the food market posing a dilemma for nations that already face food shortages (HowStuffWorks Auto Efficiency and Biofuels, 2021)

Instead of using straight vegetable oils, the process of either transesterification of triglycerides (TG) or esterification of free fatty acids (FFAs) is an effective way to solve these technical challenges. This process converts vegetable oils to their methyl esters which are more compatible with the engine. Biodiesel is technically competitive to conventional fossil diesel;

however, it is not profitable compared to fossil fuel due to the types of raw materials used to produce it (Duncan, 2003). To make biodiesel production economical and hence profitable on an industrial scale, the production costs need to be reduced. This is done by using low cost raw materials such as waste cooking oil or use non-edible plants as raw material (Cardoso et al., 2008). Some of the non-edible raw materials that have been explored include *Jatropha* oil, *Euphorbia lathyris* oil (Zapata et al., 2021) and *Koelreuteria integrifoliola* oil. Waste cooking oils are also being recycled which can simultaneously reduce the cost of raw materials while also reducing the problem of environmental degradation (Cardoso et al., 2008). However, waste cooking oils and these non-edible oils are associated with high acid value, which is undesirable in the preparation of biodiesel. To deal with this problem, researchers are exploring different catalysts which will be more effective in converting raw materials with high acid values into biodiesel. Initially, biodiesel was prepared using homogeneous acids and bases such as  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ , and  $\text{KOH}$  (Xie & Zhao, 2014). These catalysts however, pose many process challenges such as the difficulty in separating the reaction products, corroding the reaction equipment and lastly, they cannot be recycled (Borges & Díaz, 2012). All these challenges lower the quality of the biodiesel produced and they also make the process more expensive. Furthermore, with high acid value raw materials, alkali catalysis cause saponification, therefore creating the need of a pre-esterification step before transesterification. It is possible to carry out esterification and transesterification simultaneously by acid catalysis in one pot and therefore this option could be a good choice (Wang et al., 2019). The challenge with this option is that solid acid catalysts require higher reaction temperature and longer reaction time to acquire high biodiesel yield using high acid value raw materials. To avoid these process challenges as well as to reduce the production cost of biodiesel it is essential to investigate more effective solid acid catalysts which can catalyse the pre-esterification of oils with high acid value under mild conditions. These should also simultaneously perform esterification and transesterification by one-pot method. As a result, the development of heterogenous and recyclable catalysts are more in line with concept of green chemistry and waste valorisation hence they have attracted the interest from researchers and industrialists (Wang et al., 2015).

A report by Amigun et al. (2008) states that in Africa although the biodiesel industry is marginal, there is still massive production potential. The need for the design of multifunctional catalysts containing carbon as a support from materials such as waste tyre is essential for turning waste into value which aligns with the concept of sustainable development towards the

future. To develop the catalysts the process of pyrolysis is one method used to convert carbon bearing materials into suitable catalysts. In this study tyre char was activated by means of sulphonation in a Monel Parr Reactor thereby forming a heterogenous sulphonated char catalyst. Tyre pyrolysis char already contains a high proportion of sulphur (due to the vulcanization process which is used to strengthen the rubber of a tyre), but sulphonation renders the carbon support active for the reaction thus making it effective for catalysis. The findings of this study will also then enhance the selective transformation of non-conventional sources into biodiesel as a sustainable source of energy. Heterogenous catalysts are desirable because they have high stability, efficient activity, and noticeable reusability (Dehkhoda et al., 2010). Furthermore, utilising waste tire (in the form of tyre char) material for catalyst production becomes an alternative to landfilling and other method of waste management.

## **1.2 Motivation & significance of the study**

The motivation for renewable fuel production in South Africa is driven by the increase in crude oil prices (fossil derived resource), imminent threat of the shortage of fossil fuels, the possibility of creating employment in the rural community, climate change concerns and the need for the growing economy to use its resources in a sustainable manner. These factors, have all contributed to the large research efforts aimed at achieving economical means of producing alternative fuels derived from renewable resources, such as biodiesel and bioethanol. The main environmental advantage of using biofuels is that they result in lower net-sum of CO<sub>2</sub> emissions, because plants use up carbon dioxide during photosynthesis when producing the fuel (Hara, 2010). Take for instance, biodiesel lessens net carbon dioxide emissions up to 78% when compared to conventional diesel fuel on a life cycle basis (Dehkhoda et al., 2010). Also, a biodiesel plant will promote employment and income generation through the formation of direct, indirect, and induced jobs varying between the plant itself, agricultural, processing sectors and spin-off industries.

Biodiesel is amongst the biofuels that are preferred since it is compatible with the existing diesel engine and transport infrastructures. Biodiesel is produced using the transesterification process mainly with the main purpose being to reduce the viscosity of the vegetable oil. The viscosity of vegetable oils is 10-20 times that of petrol diesel causing injector coking and engine deposits. Due to the continuous rapid growth of biodiesel markets it is evident that biodiesel production is technically feasible although the production costs are higher compared to

petroleum-based diesel fuel (Ma & Hanna, 1999). The two main factors that have a significant impact on the cost of biodiesel can be summarized as the cost of raw materials and the cost of processing. The cost of raw materials can be lowered by using cheaper raw materials as already mentioned. Using simplified operations and eliminating waste streams could reduce processing costs (Serio et al., 2008).

Apart from oil and alcohol, producing biodiesel requires the presence of a suitable catalyst to improve the reaction rate and yield. In industry homogeneous basic catalysts such as NaOH are employed as mentioned but they require many separation processes which result in high energy inputs (Serio et al., 2008). This makes the process more expensive leading to the search for alternative catalysts that are clean, affordable and can be recovered and reused in different catalytic cycle (Jamil et al., 2021). Heterogeneous catalysts obtained from carbon sources when immersed in acids such as sulphuric acid have several advantages over their counterparts thus proposing a more economical process for biodiesel production. It is the sulphonation that renders the carbon support active for the reaction. In this study, tyre char will be sulphonated to activate it and then used to produce biodiesel. Tyre pyrolysis char already contains a high proportion of sulphur (due to the vulcanization process which is used to strengthen the rubber of a tyre), and this could provide beneficial characteristics to the catalyst when exposed to thermal treatment which can also be further enhanced by the sulphonation.

Heterogeneous catalysts such as the sulphonated char catalysts have added advantages such as easily separated from the reaction mixture without the use of water, do not require neutralization and can therefore be potentially reused (Hara, 2010). Furthermore, they have the potential to catalyze both esterification and transesterification reactions concurrently, allowing cheaper feedstocks to be utilised. Sulphonated char catalyst is one such catalyst that has been explored due to the suggested advantages it has over acid catalysts and basic catalysts. These reasons have initiated the drive towards the improvement of new and operative solid catalysts necessary for inexhaustible and efficient fuel production (Borges and Díaz, 2012). Although other catalysts such as oxides, alkali oxides, mixed metal oxides, and zeolites have been studied, few studies have been done on carbon derived catalysts (Konwar et al., 2014).

### **1.3 Aim & objectives of the study**

This study aims to explore the efficiency and efficacy of a heterogeneous sulphonated catalyst based on tyre pyrolysis char in the production of biodiesel, using the model reaction of oleic acid and methanol.

#### **1.3.1 Objectives**

- Preparation of the sulphonated char catalyst by thermal treatment using concentrated sulphuric acid.
- Provide a characterisation of the catalyst using appropriate techniques.
- Conduct esterification reactions designed using the Box-Behnken method and obtain optimal conditions for biodiesel production.
- Analyse and characterize the biodiesel produced using gas chromatography mass spectrometry (GCMS).
- Recover and reuse the catalyst and compare the yield obtained between the fresh and recovered catalyst.

### **1.4 Outline of Dissertation Structure**

Chapter 1- Gives an introduction of the topic to the reader. The background introduces the topic to the reader. The background of the topic helps prove the relevance of the thesis being presented. The research aims and objectives are also outlined to set out the intention of the study and the steps taken to achieve it at the end of the project.

Chapter 2- is an in-depth review of relevant literature to ensure that the reader understands the existing literature and research around the topic. This also brings about the research gap which will bring further clarity as to why the research was conducted and the relevance to the topic. The sections covered include methods of biodiesel production, catalysts used in biodiesel production, optimisation studies conducted using the factors that affect the production of biodiesel as well as typical feedstocks to produce biodiesel. The main sources utilized for literature were journal articles and some books.

Chapter 3- provides an outline of the chemicals used together with the supplier and experimental equipment used in the project. The experimental apparatus used is described along with its purpose and how the experiments were designed to optimise the yield of biodiesel. The experimental method used in the study is also described step by step to enable the reader more understanding of how the objectives were achieved practically.



Chapter 4- presents the results and in-depth discussion of the esterification reaction of oleic acid with methanol using the heterogeneous sulphonated charred catalyst. The effects of the relevant process variables will be explored and the optimum process conditions that result in a maximum biodiesel yield are determined. Moreover, the yield obtained after catalyst recovery is investigated and the effects are explored. The catalyst is further characterised to gain more understanding of its properties.

Chapter 5- This will be the Conclusions and Recommendations Chapter and will outline the main findings from the project and some areas to improve for future work.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Introduction

The uncertainty concerning the sustainability of petroleum and petroleum derived products along with efficient waste management methods and the increasing energy demands are amongst the greatest concerns the current generation faces (Diamantopoulos, 2015). Presently and historically fossil fuels have catered for the global energy demands (Jayed et al., 2009). This was made possible by the invention of the diesel engine, named after its inventor Rudolf Diesel and patented in 1892 (Piriou et al., 2013). The diesel engine has met the energy demand considerably over the years and has been used substantially in many crucial economic sectors for heavy-duty and commercial transportation purposes. Its importance continues to grow consistently as the diesel engine is a highly efficient type of internal combustion engine, offering outstanding fuel economy and low carbon dioxide (CO<sub>2</sub>) emission (Fattah et al., 2020). When Rudolf Diesel tried the diesel engine for the first time, he used peanut oil, and hence encountered challenges that arise from using neat vegetable oil as fuel. The major problem being the high viscosity, normally in the range of 28–40 mm<sup>2</sup> /s, which causes operational problems in diesel engine that include formation of deposits and injector coking because of inefficient atomization upon injection into the combustion chamber. The high viscosity can be reduced by transesterification to 4–5 mm<sup>2</sup> /s which is closer to that of petro-diesel (Knothe, 2010). This is crucial as it alludes to the fact that petro-diesel can be replaced or blended since the global economy is heavily reliant on the transportation of goods and services (Sarkar et al., 2012) and (Jothiramalingam & Wang, 2009) in which case the transportation industry relies on energy from petroleum. As already mentioned, the fluctuating prices for petroleum are one area of concern but the more worrying issues include deterioration of health and environmental standards. In fact, the transportation industry is 96% reliant on fossil fuels with an annual global fuel consumption of 62% (Piriou et al., 2013). Undoubtedly diesel engines are significant in the transportation industry compared to any other power-producing device in terms of efficiency, torque, and overall drivability. The major drawback of the diesel engine is the inferior performance in terms of harmful emissions (Silitonga et al., 2013). As a result, the development of innovative industries based on renewable fuels has escalated exponentially. This is due to the necessity for the reduction in the disposal of hazardous process effluents and

products (Agarwal, 2021). It is for this reason that efficient deployment of biomass in addition to the conversion of waste products into high value products has emerged as an important area to investigate for both academia and industry. The concepts that were introduced above will be covered in more detail in the subsections that will follow.

### 2.1.1 The need for renewable sources of energy, biomass derived fuels and how they are produced

Biomass is the oldest fuel and has been providing energy for humans since prehistoric times. In modern society however, the traditional combustion of biomass is no longer used widely. This is due to its low combustion efficiency and its release of harmful gases to the atmosphere. Instead, biomass-derived fluids are better fuels more suited to present day society. Hence, biofuels production becomes a dynamic and important area of study. Figure 2 -1 shows the current conversion technologies used to transform biomass into various biofuels such as:

- biomass fermentation to produce bio-ethanol;
- esterification of vegetable oil or fat with alcohols to produce bio-diesel;
- biomass gasification to produce syngas and;
- fast pyrolysis of biomass to produce bio-oil.
- Anaerobic digestion to produce biogas

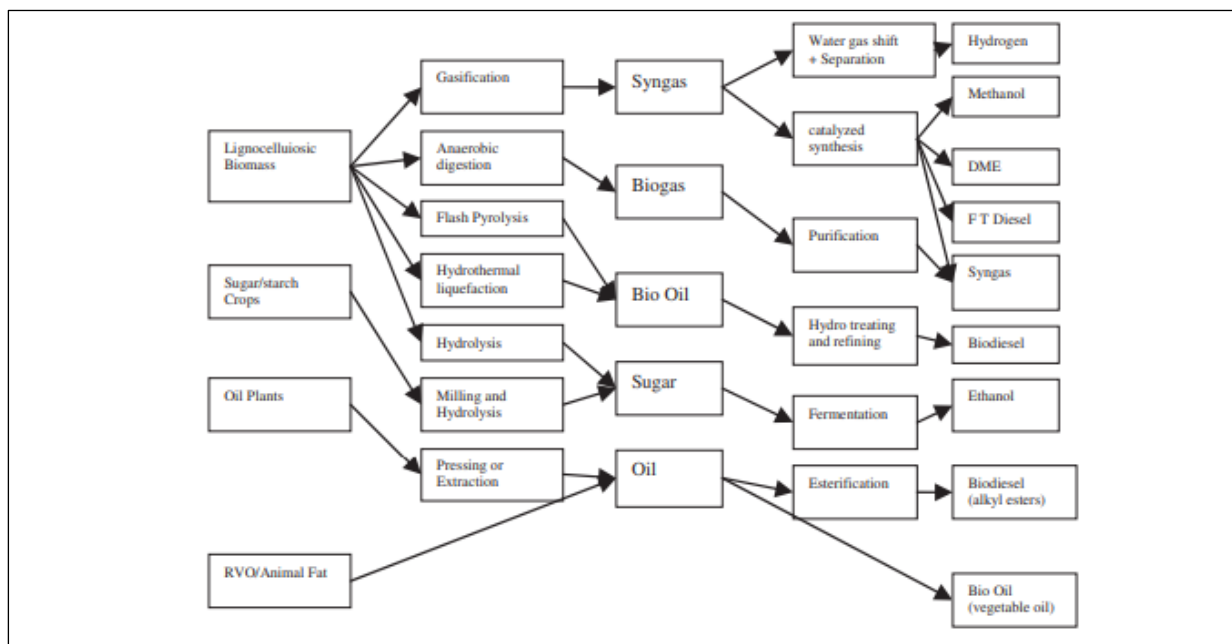


Figure 2-1: Overview of conversion pathways from biomass to biofuel (Hamelinck et al., 2004)

Biodiesel and ethanol are the most common biofuels in the world. Biodiesel gained immense interest following the global oil crisis of the 1970s, leading the United States, European Union, Brazil, China, India, and South Africa to establish a UN International Biodiesel Forum for biodiesel development. Presently the leading nations in the biodiesel market are the United States, European Union, Brazil, and Malaysia (Lee et al., 2014). Figure 2 - 2 displays the quantity of ethanol and biodiesel produced from 2008 to 2018 in the world. As can be observed in Figure 2 - 2, Europe is the highest producer of biodiesel because of the Environmental policy.

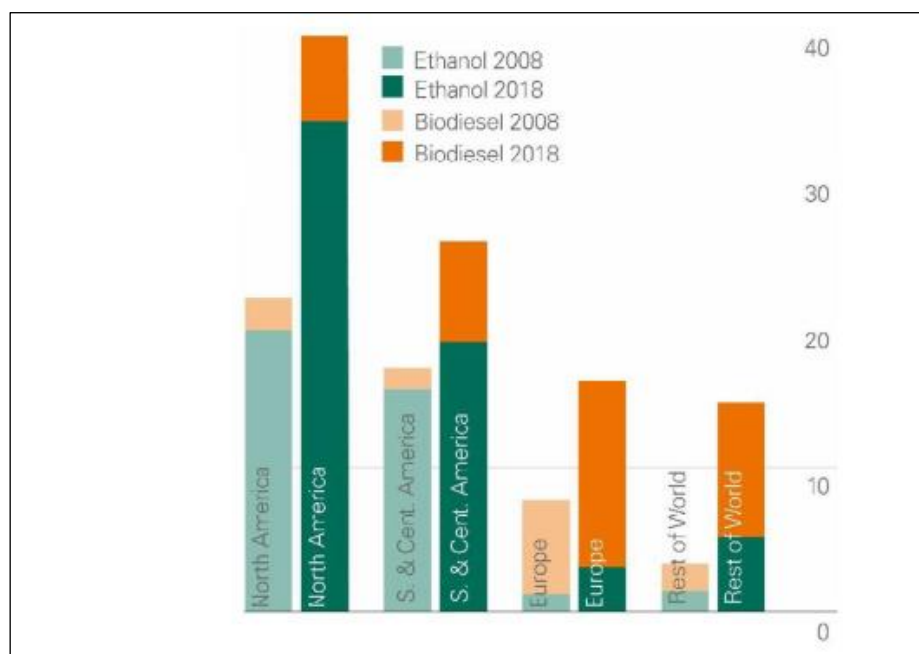


Figure 2-2: World ethanol and biodiesel production from 2008 to 2018 (vertical axis in million tonnes oil equivalent) (Lee et al., 2014)

### 2.1.2 Details on the production of FAMEs from triglycerides.

According to the renewable energy directive, it is mandatory that European Union member states use at least 10 % renewable energy in transport such as biodiesel by 2020 and to invigorate research into alternate feedstock for biodiesel production. The European Union member states have been assigned to reduce the use of food-based feedstock for fuel production from 20% to 5.5% by 2020 (Baroi & Dalai, 2013). In addition, a new European derivative under the Paris agreement was established, which requires a target 32% in the use of renewable

energy by 2030. In the same way, South Africa is part of the International Renewable Energy Agency (IRENA) which is a global organization promulgating the use of renewable energy policies. The main aim of IRENA is to equip member countries with tools to formulate policies and to also provide the transition of technology essential for renewable energy (Irena, 2016). The challenge faced by industries currently in commercialising biodiesel at a larger scale is the high costs associated with the production of biodiesel compared to traditional diesel (Kulkarni & Dalai, 2006). Although the renewable energy directive promotes the demand for biodiesel as a fuel additive it is still an unprofitable initiative. This is because 60-80 % of the cost in producing biodiesel is incurred from the raw materials required. As a matter of fact, 95% of biodiesel production worldwide uses edible food crops as feedstock since there is easy access to it from developed agriculture industry. Some of the edible feedstock being used include soybean (7.08 million), palm (6.34 million), rapeseed (6.01 million), castor, coconut, and *Jatropha curcas* oil. This large-scale utilisation of edible oils for biodiesel production, is risky because the slightest error in planning can lead to food insecurity (especially in underdeveloped countries) and consequently economic imbalance. Conversion of edible sources into fuels will compromise the supply balance in the food market (Gui et al., 2008). This is the major obstacle in making biodiesel commercially competitive with respect to petro-diesel.

Apart from the vegetable oil, some of the major cost comes from the lack of an appropriate low-cost catalyst to synthesize biodiesel (Kulkarni et al., 2006) and (Canakci, 2007). For industrial purpose the catalysts widely employed for the process are homogeneous bases such as sodium and potassium hydroxide and homogeneous acid catalysts such as sulfuric or hydrochloric acid. Carbon derived heterogeneous catalyst are a possible replacement for these homogeneous catalysts (Sangar et al., 2019). Using these catalysts will aid with the ongoing attempts to advance biodiesel production processes (McNeff et al., 2008). Also, the prospect of having these carbon heterogeneous catalysts capable of simultaneously catalysing both the esterification and transesterification of feedstocks particularly those containing high amounts of free fatty acids (FFAs) is appealing. The reason for seeking an alternative route to biodiesel production is that the conventional homogeneous catalysis pathway is associated with high separation and purification costs as well as large amounts of wastewater and waste generation because of the use of irrecoverable catalysts (Rathore et al., 2016). The wastewater produced is also hazardous to marine life and humans as it contains chemical elements that are harmful to life (Letcher & Vallero, 2019). Although heterogeneous acid catalysts are a promising

alternative type of catalysts to use for biodiesel production they also encounter challenges in the early stages of development namely high initial synthesis cost and high operating costs (Clark, 2002). The heterogeneous solid acids catalysts which include Lewis-type such as the mixed and sulfated oxides and Bronsted-type such as sulfonic acid-containing materials have been termed benign alternatives to the heterogeneous alkaline catalysts and the unrecyclable-homogeneous acid and alkali catalysts. Their strength mainly lies in being able to combine the advantages of both heterogeneous base catalysts and mineral acids. They also have additional desirable characteristics such as;

- Insensitivity to FFA contents implying that they can be used to catalyse cheaper and readily available feedstocks without undergoing any pre-treatment stage.
- They can simultaneously catalyse both esterification and transesterification reactions.
- There is no need of a biodiesel washing step.
- A purer and more high-quality product is obtained because of the ease of separation from the reaction medium with less contamination.
- The catalyst is easily modified, selective, easily regenerated and recycled (Guo et al., 2012).
- There is less corrosion even when acidic elements are present.
- Can be applied in continuous flow process.
- Their ability to sterically deter solvation of the catalytic active sites from water action diminishes catalyst deactivation. This is because the hydrophobic surface of the solid acid catalyst will hinder the water and glycerol by-products (which are polar) from deactivating the catalyst's active sites. Thus, the selective adsorption of oily hydrophobic species to the catalyst surface is enhanced (Clark, 2002).

The alkaline reaction has a higher reaction rate compared to the acid reaction. However, the reaction is affected by moisture content and FFA which have a strong effect on the process performance and economics. Water and FFAs usually react with the catalyst leading to formation of soap. Figure 2-3 shows the reaction taking place to form the soap. The soap has tenside properties which result in separation challenges of the pure glycerol in the final step of the process (Tesser et al., 2005). For oils with a free fatty acids (FFAs) content more than 1%, which is more common with waste materials a pre-treatment esterification is required to eliminate the free acidity. This becomes a major disadvantage with this type of catalyst since

low quality feedstock and waste materials cannot be used as feedstock which would have represented an opportunity to reduce production costs and thus making biodiesel more competitive with traditional diesel (Tesser et al., 2005).

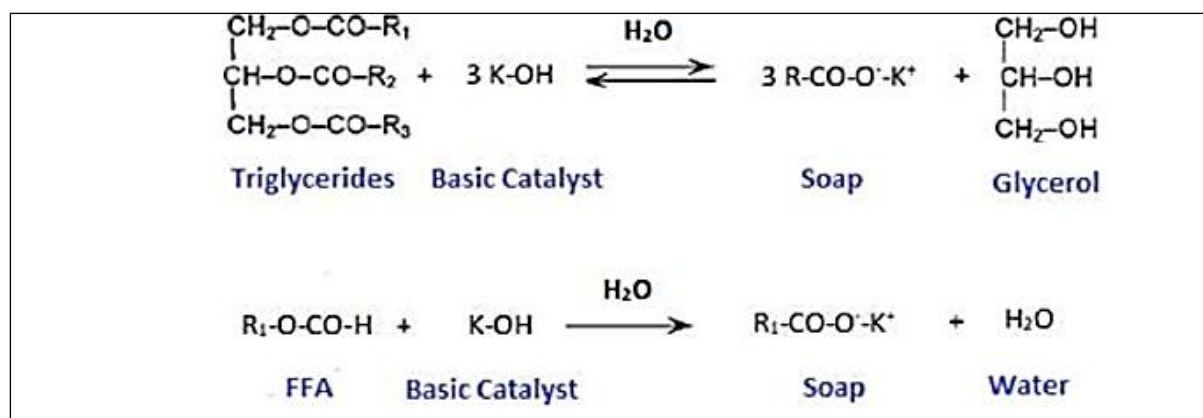


Figure 2-3: Saponification reaction of triglycerides and neutralization reaction of FFA (Borges and Díaz, 2012)

## 2.2 Biodiesel

Biodiesel is a complex mixture of C<sub>12</sub>–C<sub>14</sub> fatty acid monoalkyl esters (FAMES). Biodiesel has desirable properties such as being renewable, biodegradable, and eco-friendly (Ghadge & Raheman, 2005) making it worth the extensive study. Furthermore, biodiesel is classified as the fastest growing industry worldwide (Lam et al., 2010) and (Luque et al., 2010). It is essentially derived from non-edible plants, animal fats, waste oils and algal biomass and can potentially be used as an alternative or additive to the conventional diesel (Tran et al., 2017) and (Abedin et al., 2014). The first-generation biodiesel received criticism as it was produced from edible oils which could lead to food insecurity and competition between uses of agricultural lands for the cultivation of crops for food or fuel. The blends of biodiesel are commonly referred to as Bxx, in which xx represents the amount of blend. Thus, B100 would refer to pure biodiesel whereas B20 indicates a blend with 20% biodiesel and 80% petroleum diesel by volume (Manivannan & Kumar, 2019). As a matter of fact, the B20 blend is the most widely implemented blend worldwide. This is due to it being operational in almost all diesel-fuelled equipment as well as being stable during distribution and storage situations (Mardhiah et al., 2017). Biodiesel can be described as mono-alkyl esters of long-chain fatty acids with an ester functional group (–COOR) while diesel is made up of a mixture of pure hydrocarbon molecules (no oxygen molecule) that range in size from 8 to 21 carbon atoms resulting from

the fractional distillation of crude petroleum oil (Hoekman & Robbins, 2012). Biodiesel is produced using numerous techniques such as dilution, pyrolysis (thermal cracking), micro emulsification, supercritical process, microwave techniques, ultra-sonic reactor and lipase assisted enzymatic method (Tan et al., 2015) and Ma, F and hanna M., 1999. The Fatty Acid Methyl Esters (FAME) constituting biodiesel is manufactured commercially using two methods, which is the transesterification of triglycerides (TGs) and the esterification of free fatty acids (FFAs) (Diamantopoulos, 2015). Both transesterification and esterification occur in the presence of a catalyst and short-chain alcohol in a process known as alcoholysis, which is schematically presented in Figure 2-4. Transesterification of TGs to FAMES is a process with a sequence of three consecutive steps. The first step involves forming diglycerides from triglycerides followed by monoglycerides then the product is the FAMES. Glycerol is produced as a by-product of the reaction (Manivannan & Kumar, 2019) with 1 kg being produced for every 10 kg biodiesel synthesized. It has various use in many industries which include pharmaceuticals, cosmetics, tobacco, and textiles. Due to its extensive uses, it is crucial to attain high purity glycerol after transesterification. Methanol is a preferred alcohol of choice for the process because of its price and conversion rates though plant-based ethanol can be used too (Meneghetti et al., 2006).

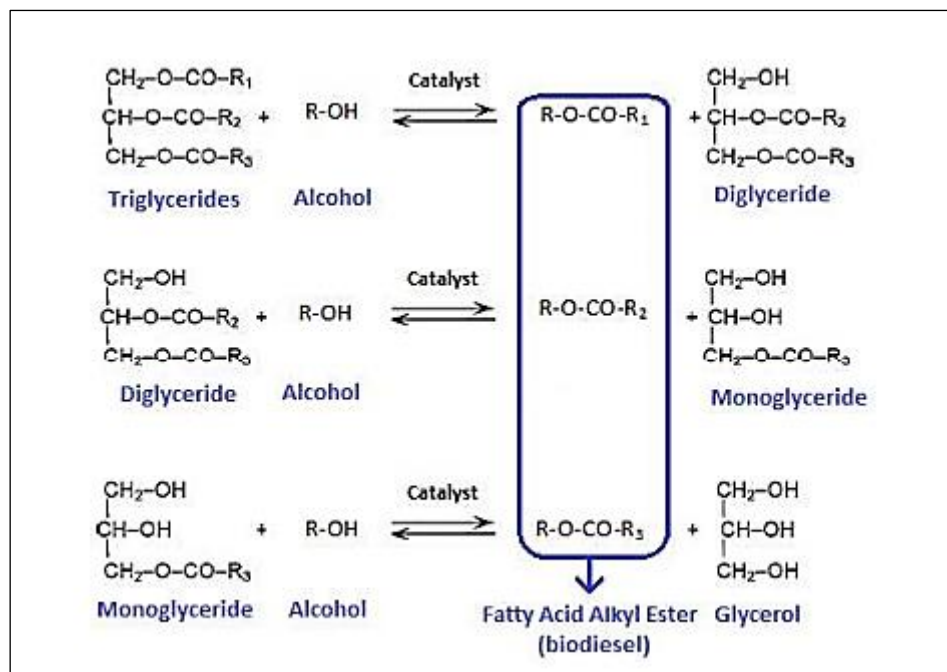


Figure 2-4: Transesterification reactions (Avhad & Marchetti, 2016)



Biodiesel has the potential to do well as an alternative fuel substitute as its production is technically feasible. In addition to that it is economically feasible, can be produced locally and is environmentally benign. The property of being environmentally acceptable stems from its property of emitting fewer carcinogenic particulate matter and being biodegradable. Moreover, the biodegradability and lubricity are important as they are essential properties in making biodiesel a sustainable resource for future diesel fuels (Gebremariam & Marchetti, 2018). Its emission property during combustion is almost sulphur free, has less smoke, and has reduced sulphur dioxide, hydrocarbons (HC), carbon monoxide (CO), CO<sub>2</sub> and particulate matter (PM) (Dorado, 2003). In addition to all this, it has higher cetane number and flashpoint than conventional petro-diesel diesel (Hasan & Rahman, 2017). Biodiesel emits less harmful chemicals because it possesses 10-11% by weight of free oxygen which is higher than petro-diesel enabling it to have a complete combustion reaction which then helps reduce harmful emissions (Hong et al., 2016). All this is possible without any modification of the initial design of the engine all the while improving engine efficiency. Moreover, feedstock to produce biodiesel can incorporate waste biomass such as waste animal fat, waste cooking oil (WCO) and factory effluents containing high oily sludge. This helps address both the issue of waste disposal worldwide while also helping in the reduction of the overall cost of biodiesel production.

This makes it a promising field for research due to its potential to reduce the production of greenhouse gases. The other superior properties that makes biodiesel more desirable compared to petroleum-based diesel is increased lubricity, non-toxicity, ease of handling, transport, and storage. To conclude this, replacing petroleum-based diesel with biodiesel will allow a balance to be found between agriculture, economic development and the ecosystem including sensitivity to water and FFA (Toda, 2005).

### **2.2.1 Factors affecting the production of biodiesel**

Production of biodiesel is affected by various factors. The main factors to consider include (Atabani et al., 2012);

- Free fatty Acid (FFA) moisture and water content
- Type of alcohol used and the molar ratio
- Concentration and type of catalyst used

- Reaction time and temperature
- Rate of stirring
- Purification of the final product
- Mixing intensity
- Specific gravity
- Effect of using organic co-solvents
- Feedstock

### **2.2.1.1 Type of Alcohol and Alcohol to Oil Molar ratio**

Different types of alcohols such as methanol, ethanol, propanol, and butanol can be used to produce biodiesel as already stated. Methanol and ethanol are the most popular and when methanol is utilised the product is called fatty acid methyl ester (FAME) while the product is called fatty acid ethyl ester (FAEE) when ethanol is used. Methanol is preferable because it uses simpler technology, allows for a faster reaction time, ease of phase separation, is cheaper and more industrially available making it the most utilised alcohol for biodiesel production (Borges & Díaz, 2012) and (Avramović et al., 2015). Although, it is the most commonly used in industry, (Lam et al., 2010) there are some disadvantages of using methanol such as that it is more toxic compared to ethanol, more volatile and dissolves oils at a lower capacity than ethanol. Moreover, most of the methanol is obtained from fossil sources and natural gas. Though some can be obtained from biomass gasification which would be more desirable if this was done at a larger scale to make the process fully renewable. Ethanol is regarded as renewable since it is completely bio-based, hence it has certain advantages such as being carbon neutral, less toxic, and environmentally friendly (Hameed et al., 2009). However, ethanol requires complex technology to use and is also used by humans for food consumption (Luque et al., 2008).

The molar ratio also has a major effect on the conversion efficiency and production cost of biodiesel. According to stoichiometry 3 moles of alcohol per mole of vegetable oil is required to synthesize 3 moles of biodiesel (fatty acid esters) and 1 mole of glycerol. This is shown in Figure 2 - 5.

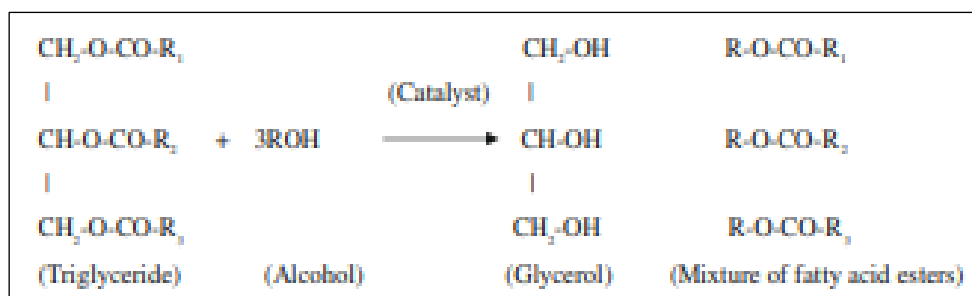


Figure 2-5: Stoichiometric transesterification reaction for biodiesel production (Leung, et al., 2010)

The reaction requires excess alcohol to ensure that the oils are completely converted to esters and higher ratios will result in higher ester yields being obtained in shorter reaction times. This is because higher concentrations of alcohol break the glycerin-fatty acid bonds during transesterification to form biodiesel (Miao & Wu, 2006), thus resulting in more biodiesel yields with higher purity in shorter reaction times (Fukuda et al., 2001). Another added advantage of using higher molar ratios is that they promote solubility (Noureddini et al., 1998). They also increase the contact between the alcohol and oil molecules thus improving interactions between molecules (Kevin & Liang, 2020) and (Mishra & Goswami, 2017). Although the yield increases when the alcohol triglyceride ratio is above 3, it eventually reaches a maximum where further increase will be undesirable as it will increase cost for alcohol recovery (Leung & Guo, 2006). Also, excess volumes of alcohol may inhibit the reaction by adsorbing onto the catalyst active sites thereby deterring catalysis (Zhang et al., 2012). Infact, a study conducted by Buasri et al. (2013) established a methanol to oil ratio of 9:1 as the optimal ratio for biodiesel yield at 96% and further addition of methanol above that led to a lower overall biodiesel yield. This is because excess methanol will hinder the separation of glycerine thereby inhibiting the reaction (Boey et al., 2009).

For alkali-catalyzed transesterification a molar ratio of 6:1 attains a yield of approximately 98% biodiesel (Fukuda et al., 2001). Acid-catalysed transesterification reactions are used mostly for oils with high free fatty acid content and require high alcohol-to-oil molar ratios to obtain high product yields in practical reaction times. The molar ratios can go as high as 15:1 for oils such as waste cooking oil (Leung & Guo, 2006). According to Balat and Balat (2008) the normal standard for the alcohol to oil molar ratios ranges from 6:1 to 30:1. However, the optimum molar ratio for any transesterification reaction is influenced by many process factors such as the type of catalyst used, type of alcohol, etc.

### **2.2.1.2 Effect of free fatty acid and moisture**

One of the major parameters used to determine the quality and hence the viability of a feedstock for the transesterification process is the amount of FFA and moisture content present. Their presence causes soap formation which is undesirable. Soap formation results in low biodiesel conversion as it consumes catalyst and decreases the effectiveness of the catalyst (Kusdiana & Saka, 2004). Soap formation can lead to an increase in viscosity, formation of gels and foams, thereby making the separation of glycerol, biodiesel, and wash water difficult (Ghadge & Raheman, 2005). Also, the presence of water decreases methyl ester yields for transesterification reactions.

Base catalysed reactions require an FFA value lower than 3% to avoid soap formation. The presence of water is said to have more negative impact compared to that of free fatty acids as water hydrolyses the alkyl esters to FFAs thus causing soaps to form (Demirbas, 2009) and (Kusdiana & Saka, 2004).

### **2.2.1.3 The effect of temperature and time**

Temperature is regarded as one of the key parameters in biodiesel production. Depending on the type of feedstock used, transesterification and esterification reactions will take place at different temperatures (Chozhavendhan et al., 2020). Temperature has a considerable effect on the reaction rate and yield of esters (Ma & Hanna, 1999). Wendi et al. (2014) studied the effect of temperature on methanolysis of beef tallow and it was discovered that temperature had a positive effect. It was also deduced that reactions were slower initially due to lower reaction rate diffusion resistance as the heterogeneous CaO catalyst formed a three-phase system, that is, oil-methanol-catalyst. Wan Omar and Saidina Amin (2011) also deduced that higher reaction temperature reduces mass transfer limitation resulting in higher methyl ester yield and FFA conversion. Another study by Bouaid et al. (2009) where biodiesel was produced from *Brassica carinata*, also reached the same conclusion that temperature had a positive effect on the biodiesel yield demonstrating that heating was necessary for enhancing the alcohol solubility in the reacting system and increasing the rate of the reaction. Kusdiana and Saka (2004) also reported that high temperature conditions enhanced the yield of the esters from the reaction and it was faster and the reaction time was shorter, this is due to the reduction of viscosity in the vegetable oil. It is suggested that the transesterification reaction temperature should be kept below the boiling point of the alcohol used to prevent vaporization which can

then result in a lower biodiesel yield (Bo et al., 2007) and (Sharma et al., 2011). Due to the endothermic nature of the transesterification reaction, increasing temperature promotes the forward reaction thereby favouring the production of esters (Samart et al., 2009). From the work by Iso, et al. (2001) where they produced ethyl oleate using *P. fluorescens* lipase, they also found that the rate of transesterification also increased with temperature. This is because with higher temperatures there is more active movement of particle and more collisions between them thus increasing the reaction rate. In the same way, Buasri et al. (2013) established that for their biodiesel system, a temperature of 65 °C was optimal and resulted in a biodiesel yield of 96%. They also observed that lower temperatures resulted in a substantial decrease in the yield and temperatures higher than 65 °C also decreased the biodiesel yield. This was because the boiling point of methanol is 64.7°C and approaching 70 °C led to the rapid evaporation of methanol thus interfering with the mass transfer properties. Yet, maintaining high temperature becomes expensive as it comes with high heat duty and thus increasing operating cost. Undoubtedly, high temperatures are mostly desirable; however, they can also have a negative effect by also favouring side reactions as well as saponification thereby decreasing the biodiesel yield (Ramadhas et al., 2005) and (Sharma et al., 2011). Most literature report that although the transesterification temperature ranges in accordance with various factors such as the type of oil or alcohol used etc, the ideal temperature is between 50 °C and 70 °C (Meng et al., 2008).

Reaction time is an important factor to consider when producing biodiesel. A low reaction time will result in an incomplete reaction while excess time lead to reduced product yields. This is because the backward hydrolysis reaction of esters is being promoted, resulting in product loss as well as leading to the conversion of fatty acids to form soaps (Eevera, et al., 2009). The work done by Buasri et al. (2013), confirms this as they established that a reaction time of 4h was optimal for biodiesel yield at 96% in their experiments. They found that longer reaction time also had a negative effect on overall yield as with shorter reaction time (insufficient time to complete the conversion) and that overall yield displayed a decrease in the yield for reaction times longer than 4h. They concluded that the reaction becomes reversible when product output is high thus promoting the back-ward reaction. In most cases, at the beginning the transesterification reaction is slower because of the dispersion and mixing of alcohol into triglycerides and then picks up after some time, proceeding rather quickly from then (Freedman

et al., 1986). Thus, the fatty acid ester conversion rate increases with reaction time up until the optimal value is reached.

### **2.3 Details on the catalyst used for transesterification and esterification reactions**

As already outlined, an important aspect in the production of biofuels is the availability of an effective and low-cost catalyst. Biodiesel, which is produced through the transesterification and or esterification of oils with methanol requires such a catalyst for the reaction to take place. Biodiesel production through transesterification or alcoholysis can be catalysed by either a homogenous or heterogenous catalyst. Catalysts play a major role by increasing the reaction rate (Mittelbach, 2012). A homogenous catalyst is one that remains in the same phase (typically liquid) as the reactants while a heterogenous catalyst is in a different phase (typically non-liquid) to the reactants (Ruhul et al., 2015) and (Zabeti et al., 2009). The amount of free fatty acids (FFAs) in the oil, water content is some of the factors that need to be considered when selecting a suitable catalyst for biodiesel production. Reactions are usually faster when homogenous catalysis is employed and require lower catalyst loading than for heterogenous catalysis. However, homogenous catalysis is still uneconomical as the separation of the catalyst from the medium is intricate and it is difficult to reuse the catalyst (Gebremariam & Marchetti, 2018). To remove the catalyst, several washing stages are required in which some use deionised water thus consuming large amounts of water while also producing significant amount of wastewater (De Lima et al., 2016) and (Sharma Y. et.al.,2010). In contrast, the heterogeneous catalyst can be separated from the medium at different stages since it is in a different phase than the reaction medium. This eliminates the intensive purification steps as the catalyst can be reused subsequently without the need for rigorous washing steps.

Heterogeneous catalysts also offer high activity, selectivity, and water adaptability because there are many active acid or basic sites present (Goli & Sahu, 2018). Also, the glycerine attained through heterogenous catalysis is of higher purity compared with the one from homogenous catalysis because there will be fewer dissolved ions in the reaction system permitting more use for industrial processes. Although heterogenous catalysis is more desirable from an economic and process point of view, it also has its demerits. Some of these include, partial leaching of catalyst active sites, destruction of the catalyst microstructure, and organic

deposition from the reaction system pose a problem for the applicability of these catalysts. The leaching of the active phase starts to contribute to the homogeneity of the system which in turn affects the life expectancy of the catalyst and subsequently the quality of the diesel produced (Kouzu & Hidaka, 2012). Thusly, the heterogenous catalyst should not leach and must be recycled. Mass transfer resistance is a challenge when heterogenous catalysts are used due to the presence of three different phases, that is oil, catalyst, and alcohol phase (Ramos et al., 2019). Despite the challenges mentioned above, heterogenous catalysis has more advantages and hence there has been increased attention over the years (Romero et al., 1998), (Lam et al., 2010) and (Ling et al., 2019).

The main methods of biodiesel production can be classified as either chemical catalytic (base or acid catalysis), biocatalytic (enzyme catalysis) and non-catalytic processes. Catalysts fall into four main categories which are homogeneous catalysts, heterogeneous catalysts, biocatalysts, and nanocatalysts which can also be further classified into different subgroups. (Shan et al., 2018) and (Akubude et al., 2019). Figure 2 - 6 shows the different types of catalysts used during biodiesel production.

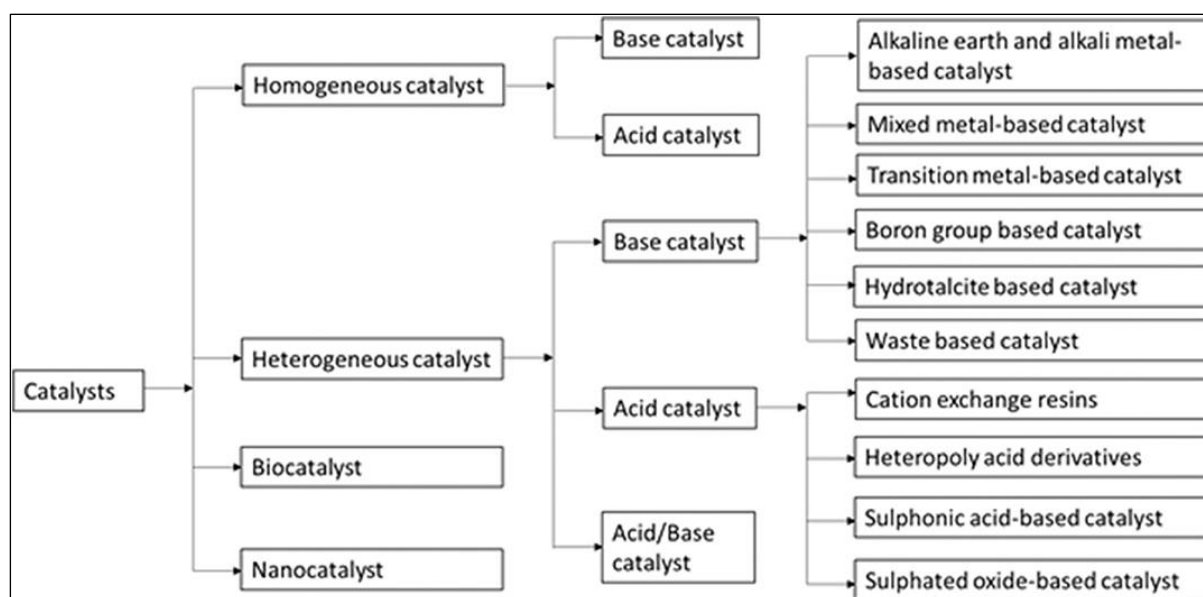


Figure 2-6: Different types of catalysts used to produce biodiesel (Fattah et al., 2020)

By employing a heterogeneous catalyst based on a solid carbon from waste tire pyrolysis, for example, the yield of bio-diesel can be enhanced using vegetable oil. In addition, a heterogeneous catalyst such as sulphonated char is easily recovered and reused lowering the

production cost of the biodiesel (López et al., 2005). The product contains less or no water and the subsequent by-product of glycerol from biodiesel is easier to separate. Sanchez-Olmos et al. (2017) prepared the catalyst from solid carbon and functionalized it using sulfuric acid as source of  $-\text{SO}_3\text{H}$  acid groups prior to using it for biodiesel production. From their work, it was discovered that the catalyst displayed a high catalytic performance which resulted in reduced temperature, shorter reaction time and reduced amounts of methanol compared to similar studies for biodiesel production (Kawashima, 2008).

## **2.4 Solid acid catalysts for biomass transformations, including transesterification**

When producing biodiesel, it was found that solid base catalyst shows higher catalytic activities than solid acids (Clohessy & Kwapinski, 2020) and (Kim et al., 2004). Although that is the case, the solid base has been found to get poisoned by FFA which leads to the formation of soap with the resulting separation difficulties. However, these catalysts ideally need refined oils to be more effective. For virgin plant oils like soybean oil, rapeseed oil or palm oil with FFA content less than 0.5%, an anhydrous alkali catalyst and anhydrous alcohol are essential for commercially viable alkali-catalysed production systems. This is a further limitation to the use of low-cost feedstocks and another reason why biodiesel is still not competitive with petrol diesel. Different solid acid catalysts can be used for the esterification process as they are preferred for operational reasons. Table 2 – 1 shows the different types of solid acid catalysts used and the yield produced.

In a study by Zhai et al. (2011) the esterification of oleic acid with methanol at 333 K was catalyzed by sulfated tin oxide with and without doping with Fe. In the study the conversion of oleic acid was 73.4% over tin oxide non-doped and 88.9% doped with Fe. This reaction took 6 h. The catalyst was then recovered through separation from the reaction mixture by centrifugation, washing with methanol and calcinating in air at 773 K for 1 hour for removal of adsorbed organic species. The catalyst's reusability was tested and it was found that after three cycles with the doped catalyst the conversion was reduced from 88.9% to 74.3%.



Table 2 - 1: Solid Acid Catalysts for Esterification (Hattori & Ono,2015)

Catalyst	Fatty Acid	Alcohol	Temperature /Time	Yield (Conversion)
Sulfated TiO <sub>2</sub>	Oleic	Ethanol	353K/6 h	86 %
Sulfated TiO <sub>2</sub>	Linoleic	Ethanol	353K/6 h	86 %
Sulfated SnO <sub>2</sub>	Lauric	Methanol	333 K/6 h	73.4%
Sulfated SnO <sub>2</sub> doped with Fe <sub>2</sub> O <sub>3</sub>	Lauric	Methanol	333 K/6 h	88.9 %
ZrO <sub>2</sub> /SBA-15	Lauric	Methanol	341K/24 h	87.4%
ZrO <sub>2</sub> /SBA-15	Palmitic	Methanol	341K/24 h	89.2%
WO <sub>3</sub> /Zr-promoted MCM-41	Oleic	Methanol	338K/24 h	~100%
WO <sub>3</sub> /Zr-promoted MCM-41	Oleic	Methanol	473 K/4 h	~100%
WO <sub>3</sub> -ZrO <sub>2</sub>	Palmitic	Methanol	Reflux/6 h	95%
WO <sub>3</sub> /Zr-phosphate	Palmitic	Methanol	333K/24 h	100 %
HPW/Nb <sub>2</sub> O <sub>5</sub>	Palmitic	Methanol	338K/4h	99.1%
HPW/Nb <sub>2</sub> O <sub>5</sub>	FAAs in sunflower oil	Methanol	338K/4h	97.3%
HPW/ZrO <sub>2</sub>	Oleic	Ethanol	373K/4h	88%
HPW/MCM-41	Palmitic	Methanol	333 K/6 h	100%
HPW/SBA-15	Oleic	Methanol	313 K/4 h	90%
HPW/SBA-15	Palmitic	Methanol	333K/5h	96%
HPW/SBA-15	Oleic	Methanol	333K/5h	85%
HPW/SBA-15	Oleic	Methanol	333K/5h	78%
HPW/Ta <sub>2</sub> O <sub>5</sub> composite	Lauric	Ethanol	351K/3h	100%
HPW/ Ta <sub>2</sub> O <sub>5</sub> composite	Myristic acid in soybean oil	Ethanol	338K/6h	100%
Carbon with SO <sub>3</sub> H	Oleic	Methanol	368K/4h	99.9%
Carbon with SO <sub>3</sub> H	Oleic	Methanol	338K/5h	>90%
SBA-15 with SO <sub>3</sub> H	Lauric	Methanol	323K/30h	~100%
SBA-15 with SO <sub>3</sub> H	Palmitic	Methanol	333K/35h	~100%
Nafion/SiO <sub>2</sub> Sulfated ZrO <sub>2</sub>	10 wt% Palmitic in sunflower oil	Methanol	333K/24h	~90%
Sulfated ZrO <sub>2</sub>	Myristic	Methanol	333K/7h	98%
Sulfated ZrO <sub>2</sub>	Myristic	Ethanol	333K/7h	98%
Sulfated ZrO <sub>2</sub>	Myristic	1-Propanol	363K/7h	98%
Sulfated ZrO <sub>2</sub>	Myristic	1-Butanol	363K/7h	98%
Polyvinylbenzene with SO <sub>3</sub> H	Lauric	Ethanol	343K/5h	99%
Zirconium sulfate/ SiO <sub>2</sub>	Oleic	Butanol	393K/4h	94%
Polyvinylbenzene with SO <sub>3</sub> H	Lauric	Ethanol	343K/5h	99%
Zirconium sulfate/ SiO <sub>2</sub>	Oleic	Butanol	393K/4h	94%
Zirconium sulfate/ Carbon	Oleic	Butanol	393K/4h	91.3%
Cs <sub>2</sub> .3H <sub>0</sub> .7PW12O <sub>40</sub>	Palmitic	Methanol	333K/6h	100%
Mesoporous ZrTiO <sub>3</sub>	Lauric	Methanol	333K/16h	92.3%
Mesoporous ZrTiO <sub>3</sub>	Palmitic	Methanol	333K/13h	78.1%
Mesoporous ZrTiO <sub>3</sub>	Oleic	Methanol	333K/18h	73.2%

The other solid catalyst which was studied for the esterification of oleic acid with methanol was tungsten trioxide ( $\text{WO}_3$ ) supported on Zr-doped MCM-41 (Hattori & Ono, 2015). The materials used had a catalyst loading of 15-20%  $\text{WO}_3$  loading and led to the most active catalysts after activation at 973 K. At a reaction temperature of 338 K in 24 h and at 473 K in 4 h a conversion close to 100% was observed. Moreover, when the catalyst was tested for reusability at 15% catalyst loading it was found to be reusable during at least 4 cycles with no leaching of tungsten species found. Hara (2010) prepared a new amorphous carbon from cellulose powder and then immersed it with sulphuric acid. The catalyst was found to be most active for the esterification of oleic acid with methanol at 368 K with a yield reaching 99.9% in 4 h. To regenerate the catalyst, it was washed with water and dried at 403 K and it was found that the catalyst remained active even after 10 times reuses. This would remain so if it was washed with water. The same material was tested for the transesterification of triolein with methanol and was found to be effective. When compared to other catalysts such as Nafion/silica, Nafion-H, and Amberlyst-15 at 403 K, the activity was found to be much higher. The high catalytic activity was maintained even in the presence of water.

Another catalyst mesoporous carbon was prepared using carbon-coated alumina joined with benzenesulfo groups by the reaction with 4-benzene-diazoniumsulfonate by researchers Geng et al. (2011). When the material was used for the esterification of oleic acid with methanol it was found to be effective as a high conversion of 90 % oleic acid was attained in 4 h at 338 K. The study done by Masakazu Toda (2005) agrees with the study also done by Hattori and Ono (2015) that recyclable solid acids, such as Nafion, make better catalysts than liquid acid catalysts. In this study Nafion-H and Amberlyst 15 at 403 K maintain high catalytic activity and conversion of up to 90 %. Although these solid acid catalysts are efficient, however although they are also expensive and their activity is less than that of liquid acids (Toda, 2005).

To counteract the challenges associated with high FFAs a pre-esterification step with the acid is done to eliminate FFAs before the oil contacts the soluble base catalyst. Various solid base catalysts for example base zeolites, alkali earth metal oxides, hydrotalcites, alumina loaded with different compounds and mixed oxides have been effective and have resulted in high conversions and yield of biodiesel obtained (Saifuddin et al., 2015). The challenge encountered is that basic sites can be poisoned by strong adsorption of FFA and water on the surface sites. Moreover, surplus soap formed with the products can hinder successive purification process of

biodiesel which include glycerol separation and water washing (Canakci & Van Gerpen, 2001). In some feedstocks where there is a high-water content, FAMES are hydrolyzed to form FFAs thus also neutralizing the basic active sites in the catalyst and preventing the biodiesel production by transesterification. After weighing all this homogenous acid catalysts seem to be a better option as they are simpler and promote both esterification and transesterification without forming any soap. The acid catalyst gives an added advantage in the sense that they directly produce biodiesel from low-grade, highly-acidic and water-containing oils. However, homogeneous catalytic transesterification has separation issues and the resulting glycerol produced is of low-quality necessitating complex and lengthy separation processes and distillation for purification (Canakci & Van Gerpen, 2007). Such separation processes eventually lead to an increased cost of the biodiesel and glycerine. With heterogeneous catalysis, such challenges are overcome since the alcohol (methanol or ethanol) remains insoluble within the reaction system. Homogenous acids however lead to faster reactions.. Although that is the case the homogenous acids in the form of strong Bronsted mineral acids (e.g. sulfuric acid or hydrofluoric acid) and p-toluene sulfonic acid lead to severe contamination and corrosion process challenges that need, additional separation and purification steps. Thus, these acids are not a good option for commercial use and the alternative heterogenous acids are explored as a better alternative.

Carbon-based solid acid (CBAS) catalysts derived from pyrolysis products offer advantages such as high surface area, elevated acid site density, enhanced catalyst activity, good operation stability, and relevant economic affordability in an environmentally friendly frame (Clohessy & Kwapinski, 2020). The most used feedstocks in the production of the pyrolysis char for the preparation of the catalyst are biomass (Clohessy & Kwapinski, 2020). Depending on the application, sulphonation of the pyrolysis char is mainly used in the preparation for biodiesel production (Clohessy & Kwapinski, 2020). However, there is a variety of feedstocks for pyrolysis char production that are readily available compared to biomass. Waste tires are categorized as hazardous waste in most countries. The environmental impacts associated with these wastes are severe since waste tires are non-biodegradable.

In response to the environmental challenges associated with waste pollution re-treading or the use of the waste crumb in sports fields, playgrounds, pavements, and roads have been investigated. However, this was unable to make a dent in reducing/elimination of high volumes

of discarded tires (Martínez et al., 2013; Williams & Brindle, 2003). There have been significant efforts on the study of the thermal treatments of waste tires such as incineration, combustion, and pyrolysis (Galvagno et al., 2002). Thermal treatment processes have both advantages and disadvantages.

The combustion of the feedstock with the objective of the complete burning of the material without the entire recovery of value, such as energy or valuable chemicals is referred to as incineration (Fullana et al., 2000). Incineration is relatively a simple process and the main disadvantage is enormous emission of toxic and mutagenic compounds, such as dioxins, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and particulate matter (PM) (Fullana et al., 2000). Since energy, materials and chemical products cannot be recovered from the incineration of waste tires, the incineration process is not a favoured process. Therefore, this is not an adequate solution in times when depletion of fossil fuels and environmental emissions are of critical concern.

When the waste tires are thermally treated under a controlled atmosphere in terms of the amount of oxygen to maximize energy recovery the process is referred to as combustion. Waste combustion has been attractive for various application in power plants, manufacturing facilities, cement kilns, and pulp and paper industry boilers (Barlaz et al., 1993). The main drawback from waste combustion is the costs of cleaning the hazardous flue gases, which are relatively high. Moreover, materials and valuable chemicals recovered from waste combustion are not viable with this process. Though the steel can be recovered after combustion, the polymeric matter is not recovered.

A pyrolysis process is defined as the thermal decomposition of organic volatile matter, in the absence of oxygen, to yield lower molecular chemical products, (solids, liquids and gases) (Aylón et al., 2010; Banar et al., 2012; Betancur et al., 2009; Darmstadt et al., 1995; Murugan et al., 2008). Some of the pyrolysis products, such as the liquid fraction, have the advantage that they are easy to handle, stored and transported (Banar et al., 2012). The solid product (char) can be used as an energy source (solid fuel), or upgraded to carbon black (CB) or activated carbon (AC) (Betancur et al., 2009; Darmstadt et al., 1995; De Marco Rodriguez et al., 2001). Pyrolysis gas as a fuel can supply enough energy for the pyrolysis process due to its high calorific value (Betancur et al., 2009; MoneyHarrison, 1999). Also, Fabiana et al. (2008)

reported that pyrolysis of waste tires is one of the most reasonable alternatives in terms of environmental protection, due to relatively low greenhouse gases emissions (Fabiana et al., 2008).

Among the techniques of waste processing, pyrolysis is one of the most promising, since it results in products that have a variety of industrial and domestic applications (Quek & Balasubramanian, 2013; Williams, 2013). With the growing interest in sulphonated catalysts, the waste pyro-char seems to be an attractive feedstock. Waste pyro-char is more suitable compared to the biomass char since it consists of sulphurous compounds and its shelf life is longer.

## **2.5 Different types of catalyst for biodiesel production**

### **2.5.1 Base Catalyst**

Homogenous catalyst are catalysts whose active sites are in the same phase as the reactants and thus making them interact effectively with reaction substrates (Helwani et al., 2009). This in turn results in higher turnover frequency rates in comparison with the heterogenous catalysts. These mainly consist of the base and acid catalyst.

Homogeneous base catalysts consist of alkaline liquid such as alkali metal-based hydroxides, alkali metal-based oxides and carbonates (Endalew et al., 2011). Alkali metal-based hydroxides include sodium or potassium hydroxide and alkali metal-based oxides include sodium and potassium methoxides. In fact, sodium methoxide ( $\text{CH}_3\text{ONa}$ ) and potassium methoxide ( $\text{CH}_3\text{OK}$ ) produce higher biodiesel yields compared to NaOH and KOH but they are expensive thus limiting their use (Atabani, et al., 2012). These catalysts are the most commonly used industrially, (Narowska et al., 2019) because of their high activity in transesterification, low cost and they are less corrosive compared to acid catalysts (Endalew et al., 2011) and (Rashid & Anwar, 2008). Moreover, the alkali-catalyzed transesterification process is favourable as it can be conducted under low temperature and pressure environment with high conversion rate and no intermediate steps (Leung, et al., 2010) and (Sharma et al., 2011).

Also, according to (De Lima et al., 2016) the rate of base catalysed reaction is 4,000 times faster than that of the acid-catalysed reactions during biodiesel production. The one drawback being that for oils with significant amounts of FFA the conversion is incomplete with a majority

of remaining as soap in vast quantities (Helwani et al., 2009). Also, base catalysts will react with water and this hydrolysis of triglycerides will result in diglycerides and new fatty acids, thus anhydrous alcohol and high-quality feedstocks are required (Gerpen, 2005) consisting of FFAs as low as 0.5% w/w (Graboski & McCormick, 1998). During storage the alkali homogeneous catalysts will absorb water from the air because it is highly hygroscopic. These should be handled well as they also produce water when dissolved with the alcohol reactant and affect the yield (Leung & Guo, 2006). Furthermore, homogeneous base catalyzed transesterification process is unable to handle multiple feed stocks effectively (Canakci & Van Gerpen, 2001). Oils with FFAs close to 5% can still be catalyzed with an alkali catalyst, though an additional amount of catalyst will be required to make up for the catalyst lost to soap (Gerpen, 2005). The accepted range for FFA content in literature should be <2wt.% for biodiesel production using the homogeneous base catalyst.

### **2.5.2 Acid Catalyst**

Bronsted acids such as sulfonic, sulfuric acids, as well as hydrochloric acid are used to catalyse the esterification process (Schuchardt et al., 1998). The alkyl ester yields produced from these catalysts are very high. However, this comes at a huge cost since acid catalysed biodiesel process requires extreme reaction conditions such as high reaction temperatures, high pressure, and high methanol to oil ratio and which can lead to environmental issues because the catalyst is highly corrosive (Farobie & Matsumura, 2017). In most instances the acid catalyzed biodiesel process is normally as a pre-esterification step where it is used to reduce the FFA content (to usually less than 1%) in low quality oil feedstock with high FFA to prevent the formation of soap. In most cases sulfuric acid and methanol (at 400 kPa and 70 °C) are used for this. Upon their formation, soaps usually solidify and form an unwanted semi-solid mass and gel (Sani et al., 2014). After the pre-esterification process, postproduction process for removal of water, methanol recovery and sulfuric acid neutralization requiring special units are employed. These make the end products expensive as their requirements make up to 75% of the final production costs (Sani et al., 2014), (Demirbas, 2007) and (Lotero et al., 2005). The base-catalysed transesterification process is then employed thereafter (Bart et al., 2010). Despite this, the reaction is still slower compared to the alkali catalysed reaction and is energy intensive (higher temperatures and pressures are required to speed up the process) making the process expensive (Silitonga et al., 2020) and (Pinto, et al., 2005). One major difference

between homogeneous acid catalysis and homogeneous basic catalysis is that it is insensitive to FFA content which enables it to catalyze both esterification and transesterification reactions. Though there are benefits of using homogenous catalysts, however both homogeneous acid and base catalysts are difficult to separate from the reaction medium containing biodiesel leading to significant expenditure of energy through many separation stages. The separation involves quenching and neutralisation steps which also form emulsions and soaps further exacerbating the separation challenges. the same separation issues as homogeneous base catalysts are experienced. Furthermore, both homogeneous acid and base catalysts are capable of corroding process equipment such as reactors and engine manifolds (Gerpen, 2005). This creates an urgency for much more effective catalysts capable of promoting both reactions without the process challenges outlined. Table 2 - 2 summarises the advantages and disadvantages of the different catalysts.

*Table 2 - 2: Advantages and disadvantages of homogenous and heterogenous catalysts*

	<b>Advantages</b>	<b>Disadvantages</b>
<b>Homogeneous</b>	<ul style="list-style-type: none"> <li>• Requires less time but produces higher yield</li> <li>• Base catalysts are more active than acid</li> <li>• Acid catalysts are not affected by the amount of FFA or water</li> <li>• Can simultaneously catalyse both esterification and transesterification</li> </ul>	<ul style="list-style-type: none"> <li>• Difficult to separate from the reaction mixture</li> <li>• Large amounts of water are needed to neutralize and purify the biodiesel</li> <li>• Base catalysts are affected by high FFA and water content</li> </ul>
<b>Heterogeneous</b>	<ul style="list-style-type: none"> <li>• Easily recovered, regenerated, and reused.</li> <li>• Available to batch or continuous fixed bed reactors</li> <li>• Requires fewer process units with a simple separation and purification process</li> <li>• The amount of water produced is reduced</li> <li>• Base catalysts are more active than acid catalysts</li> <li>• Acid catalysts are not affected by both FFA and water amount</li> <li>• Has the capacity to catalyse both transesterification and esterification</li> </ul>	<ul style="list-style-type: none"> <li>• Lower conversions achieved resulting in the need of more severe process conditions to achieve the same amount as homogeneous catalysts</li> <li>• Mass transfer resistance due to presence of three phases i.e oil, alcohol, and catalyst in the reaction mixture</li> <li>• Base catalysts are affected by high FFA and water content</li> </ul>

### 2.5.3 Enzymatic Catalysts

Both the transesterification of triglycerides and esterification of FFA process can also be effectively catalysed by enzymes such as lipase in both aqueous and non-aqueous environments. Lipase is a type of enzyme comprising a highly complex chain of amino acids

that possesses both acidic and basic properties due to its unique composition of amino acids which contain, both the carboxylic group ( $-\text{COOH}$ ) and amino ( $-\text{NH}_2$ ) groups simultaneously. The enzyme is water-soluble, part of hydrolases (enzyme which only catalyses hydrolysis reaction) and is present in living organisms (particularly for the hydrolysis of fats). In the production of biodiesel lipase permits the breaking down of ester bonds in triglycerides when water content in media is low and therefore, enhance the formation of ester in environments with low water content (Bart et al., 2010). As with the nature of enzymes, specific operating conditions of temperature and pH are essential in upholding the performance of lipase catalyst as it will denature if it is to operate outside the optimum range. Moreover, methanol, the most commonly used alcohol for biodiesel production is poisonous towards most of the different kinds of lipases (Bart et al., 2010). Also, the enzyme is sensitive to impurities such as phospholipids that might be in the oil feedstock used. This can poison the enzymatic catalyst thus reducing its performance (Zong M. et al., 2007). Therefore, the use of enzymes in commercial biodiesel production is still under development to overcome critical problems stated above.

The main benefit of using enzymatic catalyst is that the process can occur under mild reaction conditions at atmospheric pressure, neutral pH and ambient temperature (Dizge et al., 2009). Lastly, enzymes are tolerant of free fatty acid and water contents, simplifying the purification of biodiesel and glycerol (Dizge et al., 2009). An added advantage in using lipase is that the by-product glycerol can be removed easily without the need for complex separation processes and the FFA in the oils can be converted to alkyl esters (Marchetti et al., 2007). Also, the catalytic activity of lipase is insusceptible to the presence of water as opposed to homogeneous acid catalyzed process (Martin et al., 2019). Lipases are also non-polluting, produce purer biodiesel and glycerine without formation of any soap (Selmi & Thomas, 1998). However, the production cost using this material is high and the process is slower (long resident times) than that of an alkali or acid catalyst, hence it will be difficult to commercialize production of biodiesel using this route (Nelson et al., 1996). Furthermore, the enzymes can be denatured to some degree when they are used in the presence of FFAs and short chain alcohols such as methanol and ethanol. This makes the process economically unviable. To overcome the problems associated with homogeneous catalysts researchers and industrialists have started using various heterogeneous catalysts for the making of biodiesel. These catalysts exist in



different phase, usually solid phase, while the reactants are in different phases.. The catalysts have a potential to be applied in various energy- and environmental-related applications which include biomass upgrading. The main advantage of solid heterogeneous catalysts lies in the fact that they can be recovered from reaction mixtures and can be recycled in multiple catalytic cycles. This results in the sustainability of the process and its cost-effectiveness.

#### **2.5.4 Carbon based catalysts for biodiesel production**

Carbon based solid acids are very acidic and thermally stable and are suitable candidates for replacing homogeneous acids (Toda et al., 2005). Take for instance, Kevin and Liang (2020) synthesized a porous carbon-based solid acid by sulfonation of the  $\text{NaHCO}_3$  and used it to catalyze the biodiesel production from waste oil. The catalyst displayed high activity with a yield of 99% at a temperature of 70 °C and time of 9 hrs. The catalyst only decomposed at temperatures above 210 °C indicating high thermal stability (Kevin, M., & Liang, X. 2020). This study confirms the effectiveness of carbon-based catalysts though reaction time can be shortened by probably adjusting other operating parameters. Another study by Rocha et al. (2019) prepared a sulphonated carbon solid acid catalyst by utilising activated carbon obtained from corncobs as precursor material. This carbon catalyst was used in microwave-assisted transesterification reactions comprising soybean oil with ethanol. A biodiesel yield of 88.7% obtained after 20 mins under the following process conditions; microwave variable power of 0-600 W, alcohol-to-oil molar ratio of 6, and catalyst-to-oil mass ratio of 20%. The catalyst was regenerated after being used in five subsequent reaction cycles without any loss of catalytic activity (Rocha et al., 2019).

Waste disposal in the agricultural sector is persisting thus utilizing such waste for synthesizing catalysts would be especially beneficial to the environment by reducing agricultural waste land discarded in landfills. In fact, in Malaysia, it is estimated that 1.2 million tons of agricultural waste is disposed of at landfills every year (Periathamby et al., 2009). The same waste could be used to synthesize carbon-based catalysts. Carbon derived heterogeneous catalysts still considered significantly replace homogeneous catalysts in commercial biodiesel production as they have displayed good reusability and thermal stability, equivalent catalytic activity, and high surface area (Konwar et al., 2014). These catalysts are prepared by functionalising carbon with different components such as sulfonic acids, alkoxides, alkali metals, transition metals

and enzymes. This leads to an improved heterogeneous catalyst with high catalytic activity capable of synthesising biodiesel from oil feedstock.

Due to the beneficial properties that heterogenous catalysts have, there is this new carbon-based catalyst that can be used for biodiesel production. As already mentioned above, carbon-based catalysts have desirable properties such as being cost effective, having a high thermal stability and surface area all the while being greener at the same time since they are generated from biomass. The other numerous advantages associated with heterogeneous catalysts in general include low production costs, robustness, high resistance to unfavourable reaction conditions and durable lifetime. Under optimal conditions the yield of biodiesel can go up to 98.3 % while employing various carbon-based catalysts. A sulphonated carbon-based catalyst has also been used in the production of hydroxymethylfurfural (HMF) and furfural from cassava waste. HMF is used as a building block for many applications in different industries like packaging, construction, textile, cosmetics, food, and health. The work done by West et al. (2008) displayed that solid acid-catalyzed process for biodiesel production is more cost-effective compared to homogeneous acid and alkali catalysis as well as supercritical processes. Some of the main highlights in the study included that the process is technically simpler and requires less capital investment while having high return on investment compared to its counterparts. Thus, several solid acid catalysts have been established to overcome the adverse effects of utilising heterogeneous alkaline catalysts currently employed in industries (Sani et al., 2014).

## **2.6 Preparation of Acid Functionalized Carbon-based catalysts**

The two main types of carbon based catalysed are functionalized carbon catalysts and supported catalysts. The functionalized carbon catalysts essentially incorporate the various forms of activated carbon with the active part covalently joined to the support of active carbon material. The supported catalyst however, covers all the catalysts which contain a porous carbon material or activated carbon which is used as a support for active catalysts such as CaO and KOH. Carbon based catalysts are therefore prepared in several ways, using different carbon material as raw materials such as agricultural waste and waste tyres.

### **2.6.1 The problem of waste tyres and the methods used to degrade them**

It should be noted that burning waste tires discharges toxic gases such as CO<sub>2</sub> and CO, and harmful volatile organic compounds such as benzene, butadiene, and phenol substances and thus the environmental risks are immeasurable. In South Africa it is estimated that of the 10% overall waste produced, only 2% is processed in waste-to-energy programmes (Mpyane, 2019). Clearly, this is inadequate exploitation and management of waste. Thus, one of the most effective emerging methods for reducing waste tires is by using a pyrolysis process. The process involves chemically decomposing organic materials at elevated temperatures in the absence of oxygen. The process, which typically operates at temperatures above 430 °C and under pressure does not only provide a means for waste disposal, but also produces alternative fuel for internal combustion engines. Moreover, the pyrolysis is non-toxic unlike incineration which results in the emission of harmful gas (De Marco Rodriguez et al., 2001). Pyrolysis of waste tires produces pyro-char which is a valuable material that can be applied in various chemical industries. This further combats the challenge of waste disposal to the environment through making valuable material from waste.

### **2.6.2 Pyrolysis of tyres and the production of tyre pyrolysis char**

Pyro-chars are inexpensive materials, and can be easily activated through chemical treatment with acid such as sulphuric acid. Immersing the pyro-char in sulphuric acid results in the production of pyro-chars with increased specific surface area pore volume, enlarged pore diameter and enhanced porosity (Vakros, 2018). Recent years have seen an increased effort to work with 'green' catalysts as they have been found to be more environmentally friendly, cheap, and reusable. Moreover, producing biodiesel through pyro-char consists of a carbon which has a hydrophobic phase which permits the interaction of the organic chains with the surface and eliminate water. This waste water is an undesirable by-product which lowers the catalytic activity. The hydrophilic surface of –SO<sub>3</sub>H in the case of sulfonated pyro-chars can speed up the transesterification reaction while also enhancing the conversion efficiency to biodiesel. Chemical absorption of the pyro-char with sulphuric acid increases surface area and higher amount of surface groups (Vakros, 2018). The use of the pyro-char as the suitable catalyst in the production of biodiesel will substantially impact the environment (minimise or eliminate pyro-char disposal in the landfill) and eliminate process challenges associated with

conventional catalysts. The high sulphur content of the pyro-char is anticipated to aid the functionalization of the pyro-char during sulphonation, resulting in improvement of catalyst activity. Moreover, the use of sulphonated pyro-char in the biodiesel production will renew waste pyrolysis interests as well as improve pyrolysis process (Chaichana et al., 2019) to favour higher pyro-char fraction yield and quality. Facilitation of the biodiesel production from the use of materials that are categorised as having little or no value such as pyro-char is attractive.

In a study by Michikazu Hara (2010), a solid Bronsted acid of amorphous carbon containing  $\text{SO}_3\text{H}$ ,  $\text{COOH}$  and phenolic  $\text{OH}$  groups were used to catalyse the production of biodiesel. The catalyst formed biodiesel using oleic acid and methanol at 353 K was found to be stable and efficient and the catalytic performance was 70–80% that of sulfuric acid. The catalyst was also tested for triolein at 403 K and it displayed outstanding performance. Even in the presence of water the catalyst maintained high catalytic activity. The study confirmed that this catalyst can convert crude vegetable oils made up of triglycerides, free higher fatty acids and water into biodiesel while consuming minimal energy (Hara, 2010).

The acid functionalized carbon catalysts described in literature for biodiesel production are the sulphonated activated carbons (ACs). These catalyse the production of biodiesel through the esterification of free fatty acids (FFAs) which are present in oil and by also catalysing esterification and transesterification reactions like concentrated  $\text{H}_2\text{SO}_4$ . According to the studies done by Toda et al. (2005) sulphonated-AC was used as a catalyst for biodiesel production through the esterification of vegetable-oils. In this study, D-glucose was partially carbonized and a rigid graphite like framework was attained. This was then sulphonated with concentrated  $\text{H}_2\text{SO}_4$  thus introducing a  $-\text{SO}_3\text{H}$  group and forming  $\text{SO}_3\text{H}$ -sugar catalyst. This work became a basis for other researchers to prepare similar sulphonated carbon catalysts from various carbon precursors and then use them as acid catalysts in biodiesel synthesis. Sulphonated-carbon catalysts are synthesized in two main ways. These are direct sulfonation which is based on the studies conducted by Toda et al. (2005) and sulfonation through reductive alkylation/arylation.

The catalysts prepared in this way are the most common, widely studied, and are produced from a variety of carbon sources. These carbon sources include but are not limited to sugars, polycyclic aromatic compounds, polysne resins, activated carbon, biochar, and lignin and they

are prepared using the general scheme developed by Hara group. Different parameters such as sulfonating agent, sulfonation time and carbon precursor influence have been studied on the effect on the activity of such catalysts. In one typical process 10–15 g powder of sucrose was heated for 15 h at 400 °C under N<sub>2</sub> flow resulting in the production of a brown–black solid. This resulting brown-black solid was powdered and then heated in 200 ml of concentrated H<sub>2</sub>SO<sub>4</sub> or 150 cm<sup>3</sup> of fuming sulfuric acid. This was done at 150 °C under N<sub>2</sub>. The mixture was then heated for 15 hrs and then cooled to room temperature. Immediately afterwards, 1000 ml of distilled water was added and a black precipitate was formed. The precipitate was washed several times in hot distilled water to remove impurities such as sulphate in wash water. The catalytic ability of the sulphonated activated carbon (ACs) were inspected in esterification of higher fatty acids at 80 °C in a model ethanol-oleic acid mixture. After careful examination, it was found that the sulphonated-AC prepared with fuming sulfuric acid had higher acid site density (2.5 mmol/g total and 1.2 mmol/g SO<sub>3</sub>H density). When compared to other typical solid acids such as protonated nafion, H-MOR and niobic acid sulphonated-ACs display higher catalytic activity. Different catalysts from different carbon sources such as carbon from cellulose and carbon from glucose and biochar give different yield of biodiesel when methanol is used as a reagent. For instance, catalysts functionalize carbon for use as a solid catalyst for simultaneous esterification and trans-esterification of vegetable oils. This can give different yields that depend on reaction conditions when methanol is used as reagent. Take for instance, carbon (4 wt. %) from cellulose in the triolin oil esterification at 130°C for 5 hrs, gave a yield of 98%, while, carbon (3 wt. %) from glucose in the esterification of vegetable oils at moderate temperatures and a reaction time of 1 hr, gave a yield of 72.4%. Biochar, which is a charcoal-like substance made by burning organic material from agricultural and forestry waste (Cheng & Li, 2018) by pyrolysis was also tested. A biochar with (5 wt. %) was used to convert canola oil for 3 h of reaction time, exhibiting an efficiency of 18.9%. Asphalt carbonized (0.2 wt. %) was used to convert cottonseed oil and the reaction was completed in 3 h and obtaining 89 vol.% of biodiesels.

According to a study by Olmos (2016) sulphonated char catalyst was prepared by employing pyrolysis of rubber fibres at 520 °C for 2 h using a N<sub>2</sub> flow of 30 ml/min. The design methodology used was called Box-Behnken design, which deals with three levels in each specific factor which also can generate response surface plot after being fed with independent quadratic models. In this study, 1.0 g of tire rubber was placed inside a tubular micro-reactor

made of stainless steel. At the end of the reaction the solid carbon material was collected and washed repeatedly with distilled water until all contaminants were removed. Then a 10 g sample of the carbonaceous material was placed in a 500 ml flask. Afterwards, 100 ml of 98.3 % concentrated sulfuric was slowly added to the flask. The suspended mixture was heated from ambient temperature to 120 °C and the suspension was kept under reflux and stirred for 5 h. Afterwards, the suspension was then washed with deionized water at 80 °C where physically adsorbed species were removed. When treated, the suspension reached a pH of 7. The solid material was filtered and dried at 120°C for a period of 8 hrs to obtain a sulphonated carbon. This char was then used for the esterification and transesterification of vegetable oil (which was collected from a restaurant in Mexico) with methanol and gave a fatty acid methyl ester (FAME) or biodiesel of 80 % volume after 20 minutes. Anhydrous methanol was used for the process and 0.54 g of the carbon-based catalyst in a batch reactor (Olmos, 2016). 33 different combinations of experimental conditions were analysed via the design of experiments and the variables which were explored were temperature, reaction time and amount of catalyst used.

Upon completion of the reaction, the remainder was placed in a decantation flask to remove the catalyst from glycerine in the resultant solution. The unreacted methanol was recovered by evaporation and a liquid mixture of methyl-esters and a small portion of oil. Although a good yield of biodiesel in the study was obtained, there were no attempts to recover the catalyst in consecutive cycles. Moreover, the biodiesel obtained was not compared to the commercial biodiesel in terms of quality therefore the study is incomplete and can be explored further. Table 2 - 3 shows the comparison of transesterification of vegetable oil or organic acid in the presence of sulfuric acid, carbon and sulphonated carbonaceous materials.

*Table 2 - 3: Comparison of vegetable oil or organic acid in the presence of sulphuric acid, carbon, and carbonaceous materials (Medina-Valtierra, et al., 2017)*

<b>Catalyst Characteristics</b>	<b>Type of vegetable oil</b>	<b>Reaction Conditions</b>	<b>Reaction time</b>	<b>Biodiesel yield (%)</b>	<b>Reference</b>
H <sub>2</sub> SO <sub>4</sub>	10.68% FFA	EtOH/acids=6.12 T=55° C	4h	96	(Marchetti & Errazu, 2008)
98% Sulphonated carbon from carbohydrates	89.32% TGs Waste	Cat=2.26 wt% MeOH/oil=30 M T=80° C ,500 rpm	8h	>95%	(Lou et al., 2008)

Table 2 – 3 continued: Comparison of vegetable oil or organic acid in the presence of sulphuric acid, carbon, and carbonaceous materials (Medina-Valtierra, et al., 2017)

Catalyst Characteristics	Type of vegetable oil	Reaction Conditions	Reaction time	Biodiesel yield (%)	Reference
Sulphonated carbon from cellulose	Trioline	MeOH/Trioline= 3.8/1.7(g) T=130° C P=700 kPa Cat 0.4 g	5h	98%	(Hara, 2010)
Sulphonated carbon from vegetable oil asphalt	Cottonseed oil 50% Acetic acid 50%	MeOH/acid=16.8M T=220° C 240 rpm Cat=0.2 wt%	4.5h	94.8%	(Shu et al., 2010)
Sulphonated carbon from woody biomass	Canola oil	MeOH/OIL=15M T=150° C Cat=5wt%	3h	44.2%	(Dehkhoda et al.,2010)
Sulphonated carbon from lignin	Jathropha oil	MeOH/acid=6,9,12 M	5h	96.3%	(Pua et al., 2011)
Carbon from corncob residues	Waste vegetable oil	T=120° C Cat=5 wt% MeOH/acid=32 M T=80° C Cat=3 wt%	6h	>95 %	(Arancon et al., 2011)
Sulphonated carbon from glycerol	Oleic acid	MeOH/acid=25 ml/2.5 g T=65° C Cat=0.25g	4h	>95%	(Song et al., 2012)
Sulphonated carbon from lignosulphate	Acid cyclohexane	MeOH/acid=4.6/1.2 8g T=76° C	23h	92%	(Lee, 2013)
Sulphonated carbon material	Carboxylic non-edible seed oil	Cat=0.3g MeOH/acid=12-45M T=130-200° C Cat=1.5-7.5 wt%	5h	99%	(Dawodu et al., 2014)
Sulphonated carbon from waste tire rubber	Waste vegetable oil	MeOH/oil=142/60v /v T=180° C P=845 psi Cat=0.05 wt%	10 min	84.25%	(Medina-Valtierra et al., 2017)
Sulphonated carbon from waste tire rubber	Waste vegetable oil	MeOH/oil=142/60v /v T=210° C P=870 psi Cat=0.03 wt%	30 min	96.51%	(Medina-Valtierra., et al., 2017)
Sulphonated carbon from waste tire rubber	Waste vegetable oil	MeOH/oil=142/60v /v. Cat=0.03 wt% T=240° C P=900 psi	20 min	91.22%	(Medina-Valtierra,et al., 2017)

## 2.7 Optimization studies.

In a study done by Jorge Medina-Valtierral et al. (2017) a sulphonated char catalyst was used to produce biodiesel. In his work, he used waste frying oil and methanol for the transesterification reaction. After he optimized biodiesel production, and reused the catalyst, he found that the catalyst displayed a high stability in several cycles of the reaction. The parameters under investigation were temperature, reaction time (t) and the amount of carbonaceous material (W). Box-Behnken method was used for the optimization study. In another separate study done by Sanchez-Olmos (2016) the catalytic activity of sulphonated carbonaceous material prepared from the pyrolysis of tire rubber was investigated. The parameters of interest were the influence of the temperature-pressure in the process as well as reaction time and catalyst loading in the production of biodiesel. Similar to the study done by Medina-Valtierra et al. (2017) the Box-Behnken optimization method was used to determine the optimal reaction parameters and a response surface methodology was used to display the optimization. This statistical technique models analyses a process by involving multiple regression analysis and reducing the number of experimental runs for the design of experiments (Geiger, 2014). The optimal conditions for the trans-esterification of waste frying oil with methanol were temperature of 210 °C, reaction time of 20 min and a catalyst amount of 0.03 g. Under these conditions a 96.5 % conversion of triglycerides was obtained .

Tyre pyrolysis char without a doubt opens the possibility of an alternative pathway for biodiesel production. Moreover, the catalyst displays good operational stability in catalytic cycles. This is concurred by studies done by Medina-Valtierral et al. (2017) where he used sulphonated char catalyst to produce biodiesel and found the catalyst to exhibit high stability in several cycles of chemical reaction. The same conclusion is reached by Dehkoda et al. (2010) who found that sulphonated char catalysts have great potential to be used in the conversion of a high FFA feedstock to biodiesel. Methods for production of the catalyst using pyrolysis have already been outlined. Not only is the sulphonated char catalyst useful as a catalyst and catalyst support for the biodiesel production but it can also be applied in both domestic and industrial applications. The advantages of working with this catalyst have been outlined and more of its use implores for further and deeper research.



## 2.8 Summary

The most common method used to produce biodiesel commercially is by employing a homogenous acid or base catalyst using transesterification of triglycerides with alcohol with glycerol as a by-product. Both the homogenous acid and base catalysts experience several process limitations such as reactor corrosion, engine manifolds, is energy demanding due to the separation processes needed to purify the product and the neutralisation steps required lead to process challenges such as saponification. Also, high toxicity and inadequate reusability are some of the challenges met with these catalysts. Since the catalysts cannot be reused there is a considerable loss of energy and large amounts of chemical waste thus reducing their applicability in industry. The development of a cost effective, efficient, and green heterogenous catalyst using waste tyres in an economical manner will lead to great strides in the production of biodiesel. This catalyst has been found to be thermally stable, economical, recyclable and a promising candidate to be employed in the biofuels industry, specifically in biodiesel production. Biodiesel (a renewable fuel) consisting of fatty acid alkyl esters, has been found to be a possible replacement and or additive to petro-diesel. The present study will prove the validity of employing a sulphonated char catalyst for biodiesel production using pyrolysis of waste tires. It will also explore the opportunity of catalyst recovery after one cycle. The fluctuating oil prices, environmental pressure, political climate, and depleting oil reserves have become a great motivational factor to explore waste tyres as a possible raw material for catalyst synthesis and thus use it to produce biodiesel.

## CHAPTER 3: EXPERIMENTAL PROCEDURE

### 3.1 Materials and Equipment

The main aim of this study is to evaluate the effectiveness of the heterogenous sulphonated char catalyst by testing it on an oleic/methanol system. The experiments are undertaken in a batch type of process under a fume hood. The catalyst from tyre-char is sulphonated in a Monel Parr high pressure reactor to activate it and is then analysed using FTIR. This new catalyst is then tested by using it to facilitate the esterification reaction of oleic acid and methanol after which the product is analysed using gas chromatography mass spectrometer (GCMS). The chapter will give a description of the chemicals used, equipment used, the methods and design process utilised to evaluate the biodiesel (in the form of methyl esters) qualitatively and quantitatively and thus determine the efficacy of the catalyst in the model reaction outlined. Table 3 - 1 gives a description of the reagents used for the study.

*Table 3 - 1: Description of chemicals used in the study*

Chemical Name	Chemical Formula	Purity (mass %)	Supplier
Methanol	CH <sub>3</sub> OH	99.5	Sigma Aldrich
Oleic Acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	90	Sigma Aldrich
Sulphuric Acid	H <sub>2</sub> SO <sub>4</sub>	99	Sigma Aldrich

The following equipment shown in Figure 3 - 1 and Figure 3 - 2 was used for the esterification process. Each equipment is described as well as its purpose in carrying out the esterification reaction of oleic acid with methanol.

Table 3 - 2: Description of equipment used in the project

Equipment	Purpose	Key
3-Necked, round bottom flask (500 ml)	Contains the reaction mixture	1
Heating block-base	Holds the 3-Necked round bottom flask in place	2
Heating mantle	Provides heat to the reaction mixture	3
Reflux condenser	Condenses the vapours during the reaction	4
Water-tubing	Feeds cold water to the reflux condenser	5
Low temperature cooling bath	Supplies cold water to the reflux condenser	6
Thermocouple	Measures temperature of the reaction components and allows for effective temperature control	
15 ml glass sampling vials	Keep the reaction mixture before transferring to GC MS machine	
8 x 100 ml glass bottles	Contains the chemicals	
100 ml measuring cylinder	To measure the volume of the reaction components	
100 ml measuring beaker	Contains reaction mixture to be heated	
Laboratory mass balance	To measure the mass of the components	
Sulphonated char catalyst	To facilitate the production of biodiesel	
MONEL Parr high pressure reactor	To facilitate the sulphonation of the pyro-char using the pyrolysis process	
Centrifuge tubes	To store the products during centrifugation	
Centrifuge	To separate the solid catalyst from the liquid biodiesel product	
Rotary Evaporator	To remove water, a by-product of the reaction	
GCMS	To analyse and identify the products of esterification	
FTIR	To characterize the original char, wet sulphonated char and the sulphonated char after washing and drying.	

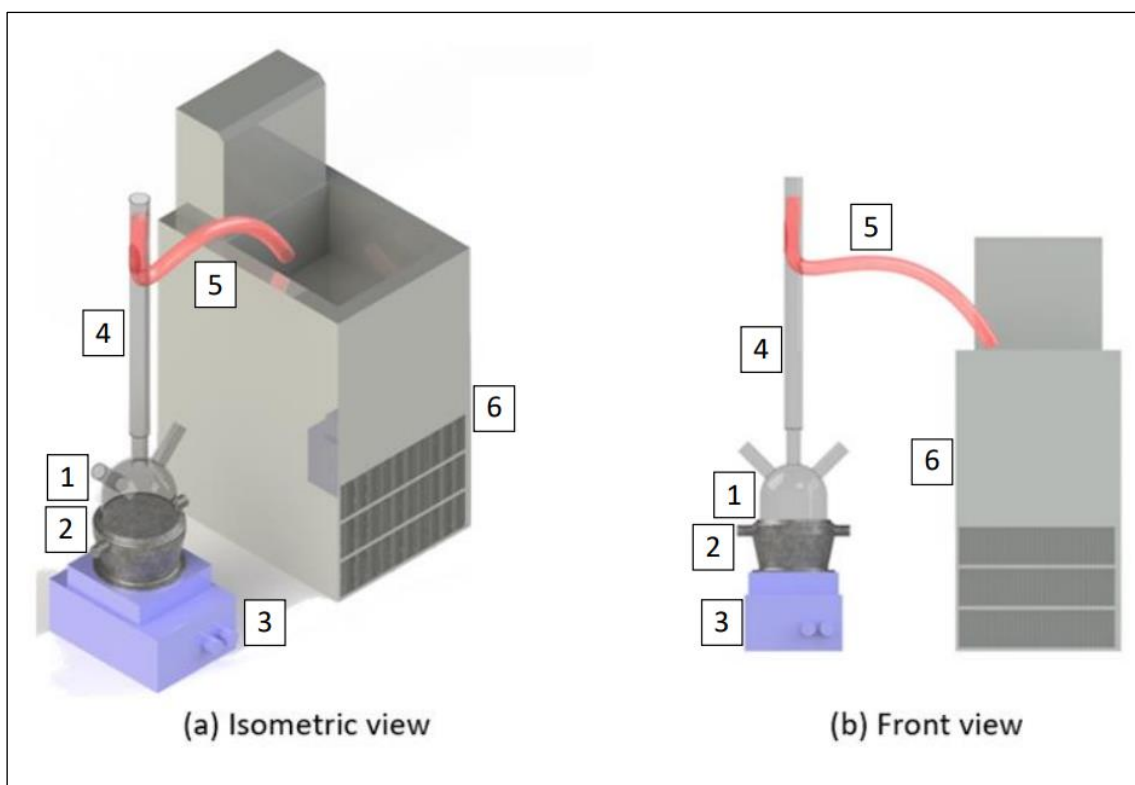


Figure 3-1: Experimental set-up drawing for the esterification reaction



Figure 3-2: MONEL Parr high pressure batch reactor

## 3.2 Methods

### 3.2.1 Synthesis and Characterization of the sulphonated char catalyst

A sulphonated char catalyst was made by mixing concentrated sulphuric acid with waste tyre char using a Monel Parr high pressure batch reactor using the method by Masakazu Toda et al. (2010). The catalyst is heterogenous in nature. Acid catalysts such as sulphuric acid have long been used for the esterification process however they cause separation challenges which results in high consumption of energy and at mild conditions, the process is extremely slow, and requires up to 48 hr to achieve conversions greater than 95% (Chouhan & Sarma, 2011). Although, homogeneous acid catalysis can accommodate lower quality (and therefore less expensive) feedstocks with FFA amounts up to 5 wt.%, the process still requires an excess of methanol. To overcome these process challenges a hybrid heterogenous sulphonated char catalysed was synthesised. The method for the process is described below;

At first, the MONEL Par high pressure reactor was sealed and leak tested with water and nitrogen. Then opened and emptied. Then the concentrated sulphuric acid and char were added. The unit was then sealed again and padded with nitrogen at a pressure of 6 bar. The main reason to increase pressure was to keep any water that is present in the concentrated acid solution in solution and prevent it from vaporizing. Therefore, the loss of water from the liquid into the headspace would further concentrate the acid and could lead to aggressive attack of the acid on the carbon substrate. The reactor was also pressurized incase the intimate contacting of the carbon substrate with the liquid could be compromised, and the acid functions would not be properly integrated into the surface structure. The components inside the reactor were then heated for 15 hours and then left to cool back to room temperature. The reactor was then opened and distilled water was added to the mixture. The solution was then filtered and washed several times using hot distilled water ( $>80\text{ }^{\circ}\text{C}$ ) to remove impurities such as sulphate ions. The wash water became clear after 3 washes and characterization did confirmed that no sulphur impurities remained after washing. Thereafter, a small amount of the wet sulphonated char catalyst was collected and analysed using FTIR spectrometer. The remaining wet sulphonated char was then placed in the oven to allow it to dry at  $80\text{ }^{\circ}\text{C}$ .

### 3.2.2 Analysis of char using FTIR spectroscopy

Fourier transform infrared (FTIR) analysis was used to characterize the original char and the sulphonated char from the reactor. When using FTIR, infrared (IR) radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The basic principle of operation is that each substance contains different bonds which will absorb light at different frequencies. Thus, to establish the composition and structure of the char the sample's absorbance of the infrared light's energy at various wavelengths is measured. FTIR can also be used to identify unknown materials such as additives within polymers and surface contamination on a material by searching the spectrum against a database of reference spectra (Mathias, 2015). Furthermore, the FTIR materials characterization technique can be used to quantify materials if a standard curve of known concentrations of the component of interest is created. Table 3 - 3 shows the specifications used for the analysis and characterisation of the sulphonated char using FTIR for this study.

Table 3 - 3: FTIR spectrometer specifications

Item	Specification
Manufacturer	SHIMADZU
Instrument model	IR Spirit
Measurement mode	(%) Transmittance
Apodization	Happ-Genzel
Number of scans	64
Resolution	16
Range (cm <sup>-1</sup> )	4000-400

### 3.2.3 BET surface area analysis of the pyrolytic char.

The surface properties of the pyrolytic char (BET surface area and pore volume) were determined using a Micrometrics ASAP 2020 gas adsorption analyser. Measurements were performed with nitrogen as the adsorbate at -196 °C. The samples were degassed under nitrogen at 200 °C for 18 hours prior to analysis. The BET surface area of the pyrolytic char was found to be 81 m<sup>2</sup>/g. The average pore volume was found to be 0.06 cm<sup>3</sup>/g.

### 3.2.4 Synthesis of biodiesel

Firstly, 100 ml of oleic acid was weighed using an electronic mass scale and this mass was then converted to moles. Then the appropriate molar ratio of oleic acid to alcohol was used to obtain

the required mass of methanol. The required amount of catalyst was then weighed (as per weight percentage of the oil being used) and dissolved into the methanol being used. All the contents were then placed inside a 500 cm<sup>3</sup> three-necked reaction flask, equipped with a reflux condenser, a mechanical stirrer, and a stopper to remove samples. The reaction took place inside the flask and the stirrer speed was set at 600 rpm to avoid mass transfer limitations on the process. The reactor was connected via a pipe to a constant-temperature bath set at 10 °C. The temperature controller was then set to the desired temperature. Then the heating mantle was turned to heat the contents in the reaction flask to the reaction temperature. The cooling water circulated inside the condenser to allow for total reflux to take place. The reaction was then allowed to proceed for further 4 hours. The reaction product was collected and centrifuged to remove the catalyst. This was done by spinning the reaction products in a centrifuge at 6000 rpm for 60 minutes. Two distinct layers were observed in the centrifuge tubes, one being biodiesel (mixed with water and other components) at the top and the bottom layer being the sulphonated char catalyst. The top biodiesel layer was then removed and placed inside a rotary evaporator at a vacuum pressure of 1000 mbar and temperature of 95 °C to remove water and any unreacted methanol. After this was done, the final biodiesel product and residual oleic acid was weighed and transferred to glass vials for characterisation and analysis using a GCMS. The residual catalyst (of used catalyst) was tested for reusability by using it to produce biodiesel again. The catalyst was filtered and washed several times with hot distilled water, then acetone (to remove impurities) and then dried and reused under optimal conditions which were determined statistically.

### **3.2.5 Analysis of reaction product samples by GCMS**

After centrifugation the product was placed inside the Gas Chromatography Mass Spectrometry (GCMS) instrument to accurately analyse it and attain the composition of free fatty methyl esters present and identify unknown peaks. The GCMS identifies the product by separating the chemical mixtures (the GC component) and then identifying the components at a molecular level (the MS component). The basic principle behind a GC instrument is that when a mixture is heated it will separate into individual components. The heated gas molecules are then carried through a column containing helium or any other inert gas. Thereafter, the separated substances will flow from the column opening into the MS. By measuring the mass of the analyte molecule, mass spectrometry (MS) can identify the compounds and is regarded

as the only definitive analytical detector. This is possible because the computer stores a library of known mass spectra, consisting of several thousand compounds to help identify substances.

### 3.2.6 Quantification of the methyl esters (biodiesel) yield

After separating the catalyst, methanol, and water the mass of the remaining product, i.e. the methyl oleate or biodiesel and residual oleic acid, was measured and recorded. The component peaks on the GCMS chromatogram were integrated and the area ratio method was used to determine the weight fraction of unreacted oleic acid. Equation 3.1 was used for this calculation;

$$wt\% = \frac{A_i}{\sum A_i} \quad (3.1)$$

Using the estimated weight fraction, the amount of residual oleic acid in the product sample was calculated and deducted from the total sample mass to determine the final methyl oleate or biodiesel mass. This was used to calculate the yield using equation 3.6. The yield and fractional conversion obtained from the esterification reaction were obtained in the following way;

#### 3.2.6.1 Amount of alcohol required

100 ml of oleic acid weighed 94.5 g. The number of moles of oleic acid was then calculated as follows;

Molar mass of oleic acid = 282.47 g/mol

$$n_{oil} = \frac{mass}{molar\ mass} = \frac{94.5}{282.47} = 0.335\ moles \quad (3.2)$$

For an alcohol to oil molar ratio of 6, the amount of alcohol required is;

$$n_{alcohol} = 6 \times 0.335 = 2.007\ moles \quad (3.3)$$

Methanol has a molar mass of 32.04  $\frac{g}{mol}$ . To compute the mass of methanol required, the following equation will be used:

$$m_{alcohol} = 32.04 \times 2.007 = 64.253\ g \quad (3.4)$$



### 3.2.6.2 Amount of catalyst required

For a catalyst of 1.5%, the amount of catalyst required is:

$$m_{\text{catalyst}} = \frac{1.5}{100} \times (\text{mass of oleic acid measured}) = 1.418 \text{ g} \quad (3.5)$$

### 3.2.6.3 Yield

The yield of the esterification process can then be calculated as follows;

$$\text{Yield} = \frac{\text{mass of methyl ester produced}}{\text{starting mass of oleic acid}} = \frac{90.078}{94.5} = 0.9532 \quad (3.6)$$

### 3.2.6.4 Fractional conversion

$$\text{Fractional conversion} = \frac{\text{number of moles that were reacted}}{\text{number of moles that were fed}} \quad (3.7)$$

For the conversion after recycling the catalyst in one cycle.

The purity of oleic acid is 90 % and 25.45 % remains unreacted from the reaction with the recycled catalyst. The fractional conversion is as follows;

$$\text{Moles of oleic acid in} = \frac{94.5 \times 0.90}{282.47} = 0.301 \quad (3.8)$$

$$\text{Moles of oleic acid out} = \frac{90.078 \times 0.2545}{282.47} = 0.0244 \quad (3.9)$$

Then using equation 3.7;

$$\text{Fractional conversion} = \frac{0.301 - 0.0244}{0.301} = 0.9189$$

### 3.2.7 GC-MS set up

The biodiesel samples obtained at the optimum conditions and after recovery were subjected to gas chromatography. A Shimadzu GC-MS machine equipped with an ultra-alloy column was utilized for the biodiesel analysis. The column specifications are shown in Table 3 - 4 below.

Table 3 - 4: GC-MS Column specifications

Item	Specification
Name	Ultra-Alloy Capillary Column
Inner Diameter (mm)	0.25
Thickness (um df)	0.25
Length (m)	30

Table 3 - 5: Gas Chromatography conditions

Item	Specification
Injection Temperature	250 °C
Column Oven temperature	180 °C
Carrier Gas	Helium
Injection Mode	Split
Injection Volume	0.1 mL
Pressure	94.7 kPa
Flow Control Mode	Linear Velocity
Column Flow	0.91 mL/min
Total Flow	167.7 mL/min
Purge Flow	3.0 mL/min
Linear Velocity	36.57 cm/sec
Split Ratio	180

Table 3 - 6: GC column oven temperature program

Rate ((°C)/min)	Temperature (°C)	Hold time (min)
-	180	0.00
2	200	1.00
1.00	215	2.00

The settings depicted in Tables 3-4, 3-5, and 3-6 were employed in the GC-MS which resulted in a run-time of 28 minutes. The chromatographic method was adapted from literature (Restek Pro EZGC Chromatogram Modeler, 2021).

### 3.3 Experimental Design

The experimental design method used for this study was a Box-Behnken Design of Experiments (DOE) which is one of the response surface design techniques (Develve, 2021). These are a set of advanced design of experiments techniques that enable researchers to get a deeper understanding of optimization of a response. For this study a DOE was conducted to analyse the process of converting methanol and oleic acid to FAME (referred to as biodiesel for this project). To analyse this process effectively, target quality attributes that describe the output of the process and essentially factors that could be related to those attributes needed to be identified. The factors identified as having a significant effect on the yield of biodiesel using oleic acid and methanol were temperature, oil to alcohol ratio (oleic acid to methanol) and catalyst loading. Afterward, the strengths of the associations between those factors and the target attributes were quantified. This type of methodology is usually employed to refine models after impelling variables have been determined using factorial designs especially if there is a probability of curvature in the response surface. The most common method used usually in most studies to determine the effect of different variables to optimise the yield of biodiesel has been one variable at a time (OVAT). This method however does not take into consideration the interaction effects between the variables of interest and requires numerous trials than necessary.

A statistical approach which considers the interactions between different variables was considered appropriate for this study. The Box-Behnken design approach was chosen as it decreases the number of experimental trials necessary while also keeping the accuracy of the optimisation when compared to traditional factorial design methods (Qiu, et al., 2013). The Box-Behnken method requires three levels to run an experiment. Moreover, in running these experiments the Box-Behnken approach does not use a combination of the variables at their maximum at once and thus avoids experiments performed under extreme conditions which are expensive and may result in unsatisfactory results (Ferreira, et al., 2007). Thus, the three chosen variables will not be at their maximum possible values to determine the response variable. The optimum conditions were expected to lie within the range of the variables of interest hence this method is appropriate for this study. Figure 3 - 3 shows the geometric view of the Box-Behnken DOE.

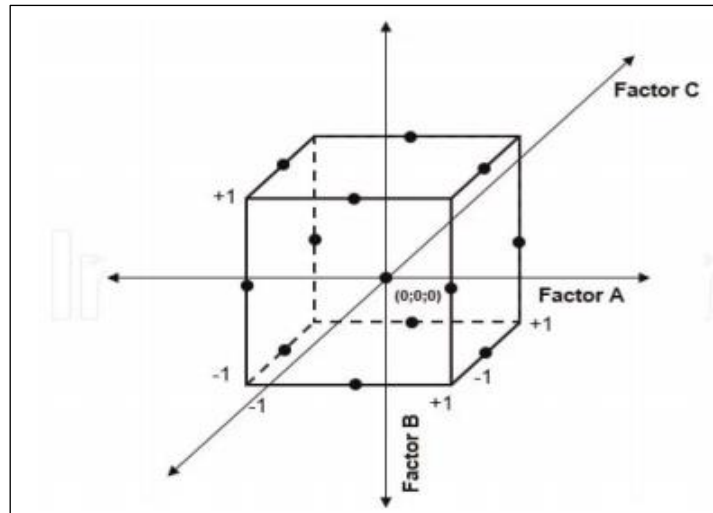


Figure 3-3: Geometric view of Box-Behnken design (Peixoto, et al., 2018)

The number of experiments ( $N$ ) using Box-Behnken design can be calculated in the following way (Ferreira, et al., 2007):

$$N = 2k(k - 1) + C_0 \quad (3.10)$$

Where  $N$  represents the number of experiments,  $k$  is the number of factors and  $C_0$  is the number of central points. In the case where there are 3 factors with 3 central points, the number of experiments to be conducted were 15. A total of 15 experimental runs were designed using the Box-Behnken design including 1 replicate. The data was fitted to this quadratic regression model using Minitab and the model was used to generate the response surfaces that were probed for optimal points using equation 3.9. Coded values were used in generating the quadratic regression equation. The coded variables are as follows:

$A$  = Reaction temperature ( $^{\circ}\text{C}$ )

$B$  = Alcohol/oil molar ratio

$D$  = Catalyst loading (g)

The following regression equation was used to generate the response surface plots;

$$\begin{aligned} \text{Yield} = & 120.0 + 0.451A - 16.24B - 10.65D - 0.0050A^2 + 1.30B^2 + 1.60D^2 + 0.0375AB \\ & + 0.0500AD + 1.40BD \end{aligned} \quad (3.11)$$

The upper and lower limits used for the process variables for the oleic acid/methanol model system are shown in Table 3 - 7.

Table 3 - 7: Factor Levels for Biodiesel production

Variables	Factor Levels	
	Low (-1)	High (+1)
A (Temperature °C)	25	65
B (Alcohol to oil molar ratio)	4.5 : 1	6 : 1
D (Catalyst Loading %)	0.5	1.5

The levels for each of the three factors with the highest effect on the yield were adopted from the study conducted by Vicente et al. (2004) as well as taking into consideration the operating limits of the experimental apparatus and the properties of the reactants. For temperature, the high level chosen was 65 °C based on the boiling point of methanol which is approximately 64.7 °C (Perry, 2008). Choosing to maintain the upper limit of temperature at 65 °C was deemed a good balance between preventing rapid evaporation of methanol while remaining high enough to provide a wide enough range for boiling. A temperature of 25 °C was chosen as the low level as temperatures below 25 °C (the ambient temperature in the laboratory) would require a cooling system for the reactor thereby also increasing the cost of the process. The chosen levels for the high and low levels for the catalyst concentrations were 1.5 wt. % and 0.5 wt. %. The range was chosen as it is a typical concentration range for transesterification and esterification reactions according to literature (Freedman et al., 1984). The basis for the choice of the upper and lower limits for the alcohol-to-oil molar ratio was stoichiometry and nature of the reaction. According to stoichiometry 3 moles of methanol will react with every 1 mole of triglyceride molecules. However, the reaction is also reversible, thus, by Le' Chatelier's principle, an excess amount of alcohol is required to shift the equilibrium to the right and promote the forward reaction. As a result, the lower and upper limit for the alcohol-to-oil molar ratio was chosen to be 4.5:1 and 6:1, corresponding to approximately 50% and 150% excess methanol respectively. This also agrees with a study by Freedman et al. (1984) where the largest conversions to methyl esters were obtained for a methanol to triglyceride molar ratio 6:1 corresponding to twice the stoichiometric ratio. Therefore, it was justified to choose a molar ratio of 6:1 as the upper limit for the process.

The stirrer speed was set at a constant value of 600 rpm. The stirrer speed that was used was the highest without coming into problems of vortexing and poor mixing and reaction performance, whilst also maintaining a uniform distribution of phases, components, and

temperature within the vessel. In this study the experiments were conducted at atmospheric pressure to make the process as economical as possible by avoiding production costs related with high pressures in terms of equipment and energy. Also, preliminary tests which were conducted by Vicente et al. (1998) in their study when comparing different catalysts to produce biodiesel showed that transesterification and esterification proceeded well even at low pressures. This was the case in this study. The reaction time chosen for the experiments was 4 hrs which was high enough to allow for the reactions to reach completion. Also, using longer reaction times is considered impractical from an industrial point of view as it would also take longer for the product to reach the market which would be uneconomical. A condenser was placed above the reaction vessel and was responsible for condensing the water and methanol vapor, returning water-free methanol to the reaction vessel. This is important as water is a by-product in the reaction and would otherwise become an inhibitor for more production of biodiesel. Table 3 - 8 shows the actual experimental runs undertaken and the conditions for each run.

*Table 3 - 8: Experimental runs for biodiesel production*

<b>Run Number</b>	<b>Temperature (°C)</b>	<b>Oil to Alcohol ratio</b>	<b>Catalyst Loading (g)</b>
8	65	5.25:1	1.50
11	45	4.50:1	1.50
2	65	4.50:1	1.00
15	45	5.25:1	1.00
13	45	4.50:1	1.00
4	65	6.00:1	1.00
10	45	5.25:1	1.00
5	25	5.25:1	1.00
9	45	5.25:1	1.00
1	65	5.25:1	1.50
14	45	5.25:1	0.50
13	25	6.00:1	1.00
7	25	6.00:1	1.50
12	45	4.50:1	1.50
6	65	5.25:1	0.50

## CHAPTER 4: RESULTS AND DISCUSSION

As already outlined in previous chapters of the study a hybrid heterogenous sulphonated char catalyst was synthesised to overcome the process challenges encountered when using other catalysts for biodiesel production. This section will discuss the results obtained from catalyst synthesis as well as from the production of methyl oleate (the biodiesel model for this study).

### 4.1 Catalyst preparation and characterization

During the synthesis, the main parameters which were temperature, pressure, concentration of acid, mass of char and time were fixed. However, a pressure of 6 bar was chosen for the process and the pressure was increased by padding the reactor headspace with nitrogen. The main reason to increase pressure was to keep any water that is present in the concentrated acid solution in solution and prevent it from vaporizing. The remaining parameters were adopted from the method outlined by Masakazu Toda et al. (2010) where they used similar methods and parameters to sulphonate char from carbon derived from sugars. Table 4 - 1 shows the exact amounts of each parameter used in the pyrolysis process:

*Table 4 - 1: Conditions used for sulphonation of tyre char*

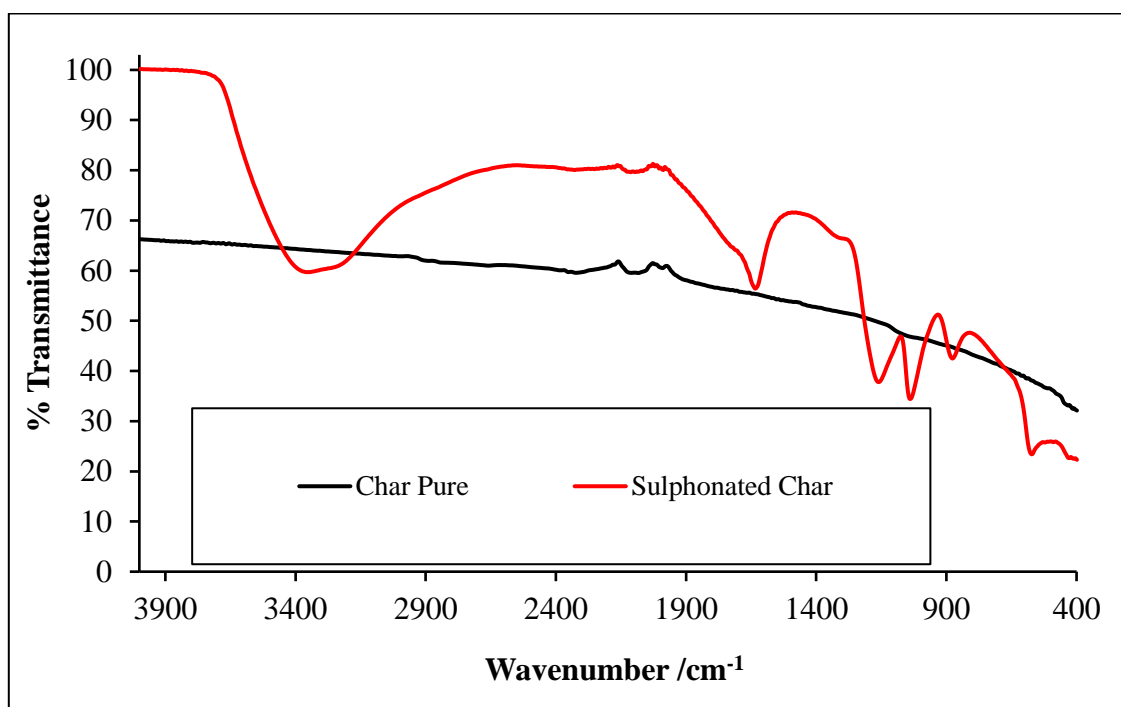
Temperature of Reactor (°C)	Pressure bars	Time (hours)	Mass of Char (g)	Volume of Sulphuric Acid (ml)
150	6	15	20	200

Figure 4 -1 shows the characterization of the untreated char and sulphonated char from the reactor. This was analysed using a Fourier-Transform Infrared (FTIR) spectrometer. It can be observed from the sulphonated char that the sulphonate groups ( $-\text{SO}_3\text{H}$ ) have attached to the char. The absorption bands at peaks at  $1167$  and  $1258\text{ cm}^{-1}$  are characteristic absorption bands of  $-\text{SO}_3\text{H}$  group (Thombal et al., 2015). This is consistent with Dawodu et al. (2014) and Wang et al. (2019) who reported that the absorption bands at  $1178$  and  $1026\text{ cm}^{-1}$  are attributed to  $\text{O}=\text{S}=\text{O}$  stretching vibrations. This indicates that  $-\text{SO}_3\text{H}$  functional group has been grafted onto  $-\text{OH}$  of char and the preparation of the catalyst is successful. Observation of the new functional groups confirmed that the catalyst has been successfully prepared. The peak at  $3381\text{ cm}^{-1}$  on



the sulphonated char signifies the O-H band which is absent in the original char indicating that sulphonation took place.

When the sulphonated char was washed with water to remove excess sulfonate ions, after being filtered a blue residue was observed in the bottom of the flask. This indicated the presence of Fe ions. These ions are present most likely due to the inherent nature of char as it contains metals ions such as Fe inferred by the blue residue. These ions are leached to the surface of the char by the thermal acid treatment. By washing the catalyst several times with water at 80 °C, there is guarantee that all ions which may be present are removed and a sufficiently pure product is obtained. Presence of unwanted ions would result in low quality products that would compromise the integrity of the biodiesel produced.



*Figure 4-1: FTIR spectrum for untreated char and sulphonated char*

## 4.2 Effect of process variables on the biodiesel yield

The reaction of oleic acid and methanol to give methyl oleate was used as a model reaction, to explore the effectiveness of the sulphonated char catalyst for biodiesel production. The Box-Behnken (which was implemented on Minitab (version 17)) was used to establish the impelling variables to produce biodiesel which were temperature, catalyst loading and the alcohol to oil ratio. Table 4 - 2 below shows the experimental runs undertaken, the experimental yield actual and predicted mass yield (obtained from using the quadratic model) of biodiesel in each of the runs. The experimental yield is mass based and was obtained using the method in Chapter 3, subsection 3.2.5 and the predicted yield is obtained using the quadratic model (equation 3.11, in Chapter 3). To avoid systematic errors the order in which the runs were made was randomized.

*Table 4 - 2: Results for Esterification of Oleic acid with Methanol*

Run Number	Temperature (°C)	Oil to Alcohol ratio	Catalyst Loading (%)	Experimental yield (mass based % yield)	Yield Produced % (Predicted)
<b>8</b>	65	5.25	1.5	93.80	95.08
<b>11</b>	45	4.50	1.5	88.50	91.45
2	65	4.50	1.0	92.20	92.90
15	45	5.25	1.0	90.10	90.10
13	45	4.50	1.0	89.50	91.50
4	65	6.00	1.0	94.47	94.77
<b>10</b>	45	5.25	1.0	93.70	90.05
5	25	5.25	1.0	75.44	76.01
9	45	5.25	1.0	77.39	78.11
1	65	5.25	1.5	91.60	90.36
14	45	5.25	0.5	89.50	90.15
13	25	6.00	1.0	80.90	81.74
7	25	6.00	1.5	79.44	80.17
12	45	4.50	1.5	84.50	85.26
6	65	5.25	0.5	86.30	88.93

The oleic acid/methanol reaction was used as a model reaction to quantitatively test how the catalyst performs. Oleic acid was chosen as a model feedstock for the esterification process as it constitutes about 35% in the *Jatropha* plant which is non-edible and does not compete with the food market (Jonas et al., 2020) and (Lee et al., 2014). Also, the non-edible *Jatropha* plant does not compete for arable land with food crops as it is able to be grown on waste land and infertile soil further solidifying the use of oleic acid for the model system. Reducing the cost of biodiesel by using non-edible sources of raw materials has been a focus for many researchers as the cost of raw material been an impediment towards commercialising it on a large industrial scale (Canakci and Van Gerpen, 2007). Methanol was chosen as it leads to a faster reaction and is the most commonly used as it is the least expensive alcohol (Dehkhoda et al., 2010).

Table 4 - 3 shows the optimum conditions to produce biodiesel are at temperature of 65 °C, alcohol to oil molar ratio of 6% and catalyst loading of 1.0 % as they resulted in the highest yield of 94.47%. The lowest yield is 75.44 % and is observed at a temperature of 25°C, alcohol to oil molar ratio of 5.35:1 and catalyst ratio of 0.5 %. The highest yield can be attributed to using the highest value for temperature which will increase the equilibrium constant. The same results are obtained by researchers Lucena et al. (2008) who confirm that increasing temperature increasing yield which is the characteristic trend of reactions with high activation energy which are favoured by higher temperatures. Higher reaction temperatures reduce mass transfer limitation as there is more active movement of particles and more collisions between them thus increasing the reaction rate.

In this study it was observed that temperature had the highest significant impact on the reaction with the lowest yields generally attained at low temperatures even if other process variables were at their peak levels. Moreover, the alcohol to oil molar ratio was also at its highest which resulted in a shift of equilibrium towards the right (formation of products). High alcohol concentrations increase solubility by increasing the contact between the alcohol and oil molecules thus improving interactions between molecules. High temperature also has the same enhancing effect on solubility hence the combination led to the highest yield obtained in this study. Though operating at high temperature can come with high heat duty thus increasing the operating cost which is undesirable but it is possible to recover some of the energy used in heating the reaction mixture by condensing the exit vapour stream. The lowest temperature resulted in the lowest yield because of the low equilibrium constant and the low catalyst

concentration. At low temperatures the reaction was slower (resulting in lower yields at the given reaction period) because molecules have decreased energy and the diffusion resistance is higher at low temperatures. Moreover, low catalyst concentration means that there are fewer active sites of the catalyst to promote the forward reaction. Also, according to Tesser et al. (2005) the reaction rate of the esterification reaction is directly proportional to catalyst concentration which would explain the low yield obtained.

*Table 4 - 3: Optimisation Results*

<b>Temperature (°C)</b>	<b>Catalyst Loading (%)</b>	<b>Alcohol to Oil Ratio</b>	<b>Time (mins)</b>	<b>Experimental Yield (%)</b>	<b>Predicted Yield (%)</b>
65	1	6	240	94.47	94.77

The optimum yield for biodiesel production experimentally was 94.47% while that predicted by the model was 94.77% leaving a difference of 0.003 further validating the goodness of fit of the model.

The reusability of the sulphonated char catalyst was tested for the esterification of oleic acid with methanol under the optimum conditions. The reusability of the catalyst is significant to its application in industry, as this will decrease production cost. A yield of 75.58% was obtained which is 18.89% lower than the original catalyst. The loss of catalytic activity emanated from a loss of sulphonate groups and probably the addition of some impurities left-over during the recovery process. The drop is quite significant which means a regeneration may be required in the form of mild sulphonation. The biodiesel yields were around 75–94% for both fresh and reused catalyst.

The presence of methyl esters was detected by GCMS and the chromatogram revealed that several types of ethyl and methyl esters had been produced such as dodecanoic acid, methyl ester (RT 3.318), hexadecanoic acid methyl ester (RT 8.913), linoleic acid ethyl ester (RT 13.525) 9-octadecenoic acid, methyl ester (RT 13.906) and 9-octadecenoic acid, methyl ester (RT 13.975) shown in Figure A - 3 in Appendix A.

### 4.3 Development of statistical model and optimization

In this study a total of 15 experimental runs were designed using the Box-Behnken design including 1 replicate. A regression analysis was implemented to fit a quadratic model to the 15 experimental runs with the goal being to find the optimal region for the biodiesel yield. After the model was fitted, it was then used to plot the response surfaces, and contour plots and main effect plots. The significance of the impelling process variables as well as their interactions was explored and is shown in Table 4 - 5 in the ANOVA table. Data from the experiments was collected and analysed using Minitab 17 and thereafter a model was developed. Statistical criteria consisting of F-value, p-value, coefficient of determination ( $R^2$ ),  $R^2$ -adj,  $R^2$ -pred were used to evaluate the performance of the developed quadratic model. Thus, to develop the quadratic model, perform the ANOVA test and optimise the process variable Minitab 17 was utilised. Also, by choosing the Box-Behnken design methodology, the effect of the process factors on the yield of biodiesel was analyzed through a lower number of experiments, which essentially reduced time, cost, laboratory work and reagent use. Coded values were used in generating the quadratic regression equation. The coded variables are as follows:

$A$  = Reaction temperature ( $^{\circ}\text{C}$ )

$B$  = Alcohol/oil molar ratio

$D$  = Catalyst loading (g)

A quadratic regression was developed to describe the relationship of biodiesel yield with the three process variables in the form of a second-order quadratic equation:

Regression equation for the quadratic model.

$$\begin{aligned} \text{Yield} = & 120.0 + 0.451A - 16.24B - 10.65D - 0.0050A^2 + 1.30B^2 + 1.60D^2 + 0.0375AB \\ & + 0.0500AD + 1.40BD \end{aligned} \quad (4.1)$$

Table 4 - 4 shows the model summary for the esterification of oleic acid with methanol. The R-squared (co-efficient of determination) is the percentage of the response variable variation that is explained by a linear model that is, how close the data are to the fitted regression (Hamilton et al., 2015).  $R^2$  adjusted is similar to  $R^2$  with the difference being that it considers and tests different independent variables against the model which makes it more accurate as it

can provide a more precise view of the correlation. The  $R^2$  predicted means how well a regression model will predict responses for new observation if it was systematically removed from the data set and a new estimated regression equation without the said observation was then used. These are all exceptional parameters to consider when establishing a mathematical model. According to Moore et al. (2013) an  $R^2 > 0.7$  value is generally considered to have a strong effect size. The R-squared value for this study was found to be 0.9376 which is satisfactory indicating the adequacy of the quadratic model established. The predicted yield of the biodiesel produced was analogous to the experimental result which validates goodness of fit indicated by the R-squared value. The R-squared values for all the models were above 0.8 hence they were all in the acceptable range however, the quadratic model had the highest R-squared and R-squared adjusted value. Having a higher adjusted R-squared value substantiates the goodness of fit as it means that a higher amount of variation in the data is accurately accounted for. In a study by Hasni et al. (2017) values of 0.91 for  $R^2$  and 0.80 for  $R^2$ -adjusted were found in a comparable optimization study where they produced biodiesel using *Brucea javanica* and employing response surface methodology (RSM), also based on the Box-Behnken design, hence demonstrating the aptness of the model within the context of this study (Hasni et al., 2017). Although the linear-squared model also could explain the data well, the quadratic model was slightly higher (especially when it came to the adjusted R-squared value) hence it was deemed the most suitable.

Also, the linear + squares model had a higher standard deviation of 1.19 compared to 0.6 of the quadratic model implying that data was more spread-out and the model may be imprecise. According to Halder et al. (2015) a reliable model has an R-squared value and adjusted R-squared valued less than 0.1. This was the case as the difference between the two was found to be 0.05. The adjusted R-squared and predicted R-squared values should be within 0.2 of each other as well. The difference was 0.177 for the quadratic model further validating its effectiveness in describing the process. The predicted R-squared value of 0.745 reveals that the model is only 74% accurate in predicting the biodiesel outside the parameter of this study. This is slightly lower than the one using the linear-square model however the overall R-squared values are higher which is why the quadratic model was selected. Therefore, the full quadratic response model with an R-squared value of 0.972 and an adjusted R-squared value of 0.922 at a confidence level of 95% can satisfactorily describe the esterification of oleic acid with methanol.

Table 4 - 4: Model Summary for esterification of oleic acid with methanol

Terms	S	R <sup>2</sup>	R <sup>2</sup> (adjusted)	R <sup>2</sup> (predicted)
Linear	1.779	84.45	80.21	66.73
Linear + squares	1.196	94.89	91.06	79.57
Linear + Interactions	1.924	86.78	76.86	29.73
Full quadratic	0.61	97.22	92.21	73.51

Figure 4 - 2 is a parity plot of the statistical analysis which shows the yield obtained experimentally against the yield obtained using the predicted model. Although some values do not lie very close to the 45-degree line, the model is still valid because of the high R-squared value of 0.9358 which shows that approximately 93% of the results are described by the model leaving only a few outliers. This also suggests that there is a high degree of correlation between the results obtained in the study in relation to the model. The runs that depicted a strong deviation between the predicted and experimental results were runs 8, 10 and 11 (refer to Table 4 - 2). Experimental run 10 displayed the highest deviation between the predicted and experimental yields. The errors obtained are in a reasonable range because the highest deviation amounts to 3.65%, demonstrating that the regression model is suitable to describe the process. The S-value indicates the distance between the experimental data values and the fitted values. Although the S-value of 0.6 is slightly higher, however the regression equation is still valid since the other R-values are within specification and the difference could be because of fewer experiments being done due to employing the Box-Behnken design of experiments.

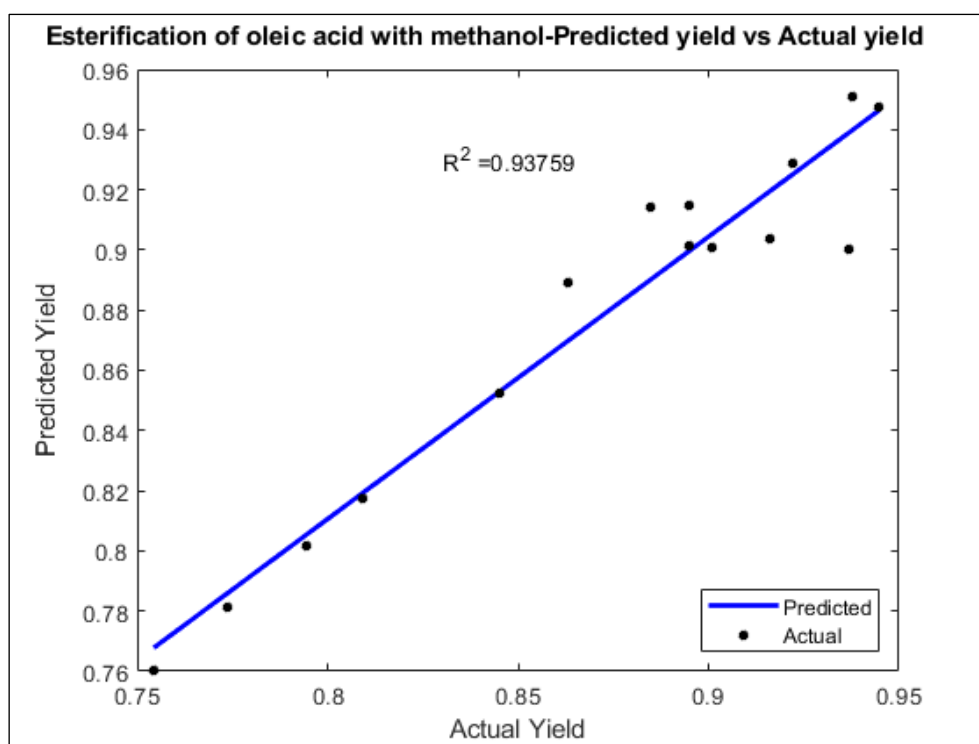


Figure 4-2: Parity plot comparing the predicted yield vs the experimental yield

#### 4.3.1 Analysis of Variance (ANOVA) for full quadratic model

Analysis of variance (ANOVA) is essential in determining the significance and adequacy of mathematical models proposed by response surface methodology. Therefore, significance of each process factor and their interactions were assessed by the ANOVA with a confidence level of 95%. The results on Table 4-5 displays a p-value of 0.002 and a high F-value of 19.42 which indicates that the quadratic model is significant at 95% confidence level. For a 95% confidence level, a p-value less than 0.05 indicates statistical significance, while a value higher than 0.1 indicates statistical insignificance (Brereton, 2018) and (Zhang & Zheng, 2009) implying that variables with lower p-values have a significant effect on the response variable whereas higher values are insignificant. Also, it can be deduced that higher values of significance are indicative of a better degree of correlation between the experimental and predicted value. From Table 4 - 5 the linear terms are positive and significant revealing a positive effect by both temperature (A), and alcohol to oil ratio (B) on the biodiesel yield. The p and F-value also imply that they are significant at 95% confidence interval. The co-efficient for catalyst loading (D) does not have a significant effect on the yield of biodiesel according to the linear model. Also, according to the linear model the temperature had the highest effect on biodiesel yield. For the square



model, the coefficient of catalyst loading (D-squared) also does not have a significant impact on the yield of biodiesel. The other two terms are significant hence the terms of this model do affect the yield of biodiesel at 95% confidence level. The 2-way interaction is slightly significant which is indicated by its high value of 0.0947, which is less than 0.1 but still quite large to have some effect on the yield. Hence, the term was added though a model without the two-way interaction would seem more accurate but when the model was regressed again, the R-squared value decreased hence it was deemed appropriate to leave it unchanged. The lack of fit is also insignificant indicating that the model could adequately describe the experimental data. In conclusion the ANOVA revealed that only 2 process factors, the quadratic model, linear model had a significant effect on the biodiesel yield while a 2-way interaction model had slight significance influence on the biodiesel yield within the specified experimental region at the 95% confidence level while the other factors were not significant.

Table 4 - 5: Analysis of Variance for Quadratic model

Source	Degrees of Freedom (DOF)	Sum of Squares	Mean Squares	F-Value	P-Value	Significance
<b>Model</b>	9	217.651	24.1834	19.42	0.002	Significant
<b>Linear</b>	3	20.603	6.8676	5.52	0.038	Significant
A	1	6.334	6.3339	5.09	0.024	Significant
B	1	8.945	8.9454	7.19	0.044	Significant
D	1	2.368	2.3681	1.90	0.086	Not significant
<b>Square</b>	3	23.376	7.7920	6.26	0.038	Significant
A <sup>2</sup>	1	14.769	14.7692	11.86	0.018	Significant
B <sup>2</sup>	1	6.240	6.2400	5.01	0.035	Significant
D <sup>2</sup>	1	0.591	0.5908	0.47	0.522	Not Significant
<b>2-Way Interaction</b>	3	5.210	1.7367	1.39	0.057	Slightly significant
AB	1	2.250	2.25	1.81	0.107	Not significant
AD	1	1	1	0.80	0.411	Not significant
BD	1	1.96	1.96	1.57	0.265	Not significant
<b>Error</b>	5	0.0225	0.02450			
<b>Lack of Fit</b>	3	0.0225	0.0750	1.2	0.45	Not significant
<b>Pure Error</b>	2	0.001	0.0023			
<b>Total</b>	14	223.876				

To select the optimal operating conditions using Minitab response optimiser the biodiesel yield was set to its maximum with the process variables constrained to the chosen experimental boundaries. The optimisation results are shown in Table 4 - 6 below. The optimum yield for biodiesel production suggested by Minitab was 95.50%. An experiment was replicated under

the optimum conditions suggested and the experimental yield obtained using the optimum conditions was 95.32 % leaving a difference of 0.177 further validating the goodness of fit of the model. It was then decided to select the new experimental yield using the optimum conditions suggested by Minitab (version 17) as the optimum yield for the study.

*Table 4-6: Optimised results using Minitab response optimiser for biodiesel production*

<b>Temperature (°C)</b>	<b>Catalyst loading (%)</b>	<b>Alcohol to oil molar ratio</b>	<b>Predicted Yield (%)</b>	<b>Experimental yield (%)</b>
65	1.5	6	95.50	95.32

#### **4.3.2 Effect of Alcohol to Oil Ratio and Catalyst Loading on Biodiesel Yield**

The surface plot shows the effect of the two response variables on the biodiesel yield. The response surface makes it easier to visualise the tendency of each factor to influence the biodiesel yield. Contour plots are shaped to display the nature and extent of the interactions between factors. If the contour plot is elliptical then the interaction is prominent while a circular contour plot means that the interaction is negligible. Equation 4 - 1 was used to acquire the response surface and contour plots that describe the relationship and interactions between the chosen variables and the biodiesel yield. A 3-D surface plot cannot represent all the 4 parameters hence one variable was held constant each time (at its average value) while the influence of the other two factors on the biodiesel yield was plotted. The third variable was the response variable (biodiesel yield in this case). The response surface and the contour plots are shown in Figure 4 - 3 to Figure 4 - 5. A three-dimensional response surface and contour plots showing the influence of catalyst loading (wt.%) and alcohol to oil ratio on biodiesel yield is presented in Figure 4 - 3 (a) and Figure 4 - 3 (b) respectively. The third factor (temperature) is not displayed in the plot and it is held at its median constant value of 45 (°C).

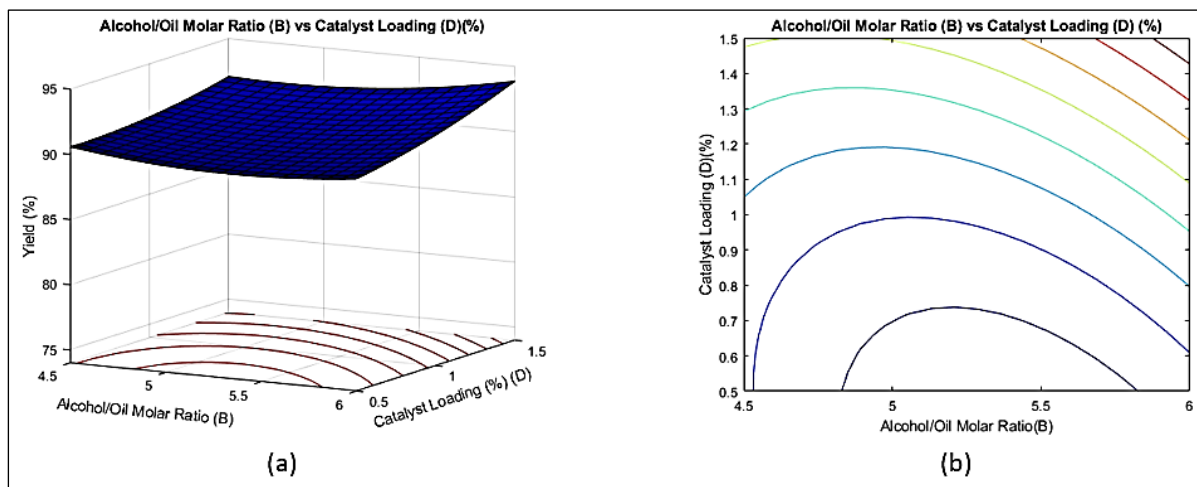


Figure 4-3: Response curve (a) and contour plot (b) of the effect of catalyst loading and alcohol to oil ratio on biodiesel yield

The highest values of biodiesel yield are in the upper right corner which corresponds with high values of both alcohol to oil ratio and catalyst loading. The lowest values of biodiesel yield are in the lower right corner which also correspond to high values of alcohol to oil ratio and low values of catalyst loading. The relationship between the catalyst loading and biodiesel yield can be described as directly proportional. The catalyst loading has a higher effect on the yield since when it is high, higher yields are obtained. However, even at higher alcohol to oil molar ratio, when catalyst loading is low the yield also decreased. This is because at high catalyst loading there are many active sites for the reaction to take place thereby increasing the rate of the forward reaction. In fact, having more of the catalyst is related to increased formation of  $H^+$  surface protons that catalyses the reaction thus increasing the reaction rate and yield. Adding more catalyst would also require addition of more alcohol to maintain higher biodiesel yields since esterification is an equilibrium reaction. This is also in line with La Chatelier's principle that higher catalyst concentration will favour the forward reaction until one of the factors becomes limiting. This is also supported by Tesser et al. (2005) who also observed that the reaction rate of the esterification reaction is directly proportional to the amount of catalyst. Figure 4 - 3 (b) is parabolic which indicates the interaction between alcohol to oil and catalyst loading is negligible in affecting the biodiesel yield. The surface is relatively flat within the design region, implying that a suitable compromise in process cost can be achieved by using

less alcohol and catalyst and still achieving yields more than 90%. This would impact on the separation step that has to be used post reaction.

### 4.3.3 Effect of Alcohol to Oil ratio and temperature on biodiesel yield

Figure 4 - 4 (a) and Figure 4 - 4 (b) represent a three-dimensional response surface and contour plots displaying the influence of alcohol to oil ratio and temperature ( $^{\circ}\text{C}$ ) on biodiesel yield. The third factor (catalyst loading) is not displayed in the plot and it is held at its median constant value of 1%. The model is curved because it contains quadratic terms that are statistically significant. The influence of the two variables showed a larger impact on the biodiesel yield. This is because esterification reaction is an equilibrium reaction and, as such, is subject to a maximum yield of methyl ester that depends largely on the reaction temperature and on the initial alcohol to oil ratio.

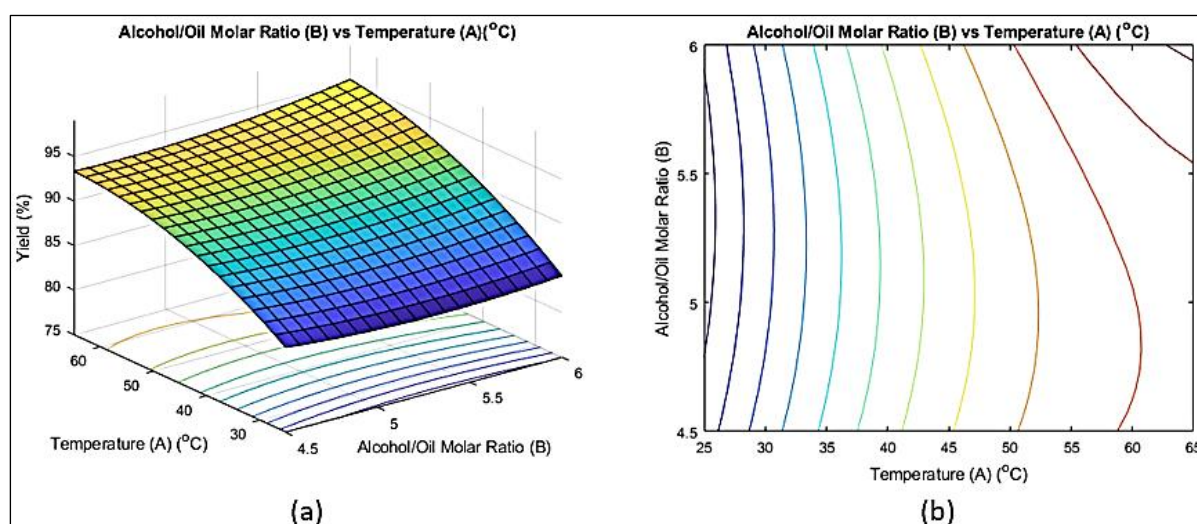


Figure 4-4: Surface plot (a) and contour plot (b) of the effect of temperature and alcohol to oil molar ratio on the biodiesel yield

The highest values of biodiesel yield are in the upper right corner which corresponds with high values of both temperature and alcohol to oil ratio. Increasing temperature also favours high yields at high alcohol to oil ratio. This is because high temperatures rapidly activate the carboxylic group in the oleic acid molecules making it more accessible for nucleophilic attack by the hydroxyl group of the methanol (Medina-Valtierra et al., 2017). Also, the increase in yield at higher temperatures is because of the temperature dependence of the rate constants and the shifts in equilibrium to favour the forward reaction. Furthermore, this is expected as the rate of esterification increases with increasing temperature for an endothermic reaction

(Freedman et al., 1984). Moreover, similar results were obtained by Marchetti and Avhad (2016), where the reaction of free fatty acids and ethanol was carried out using sulfuric acid, and it was observed that biodiesel yield increased with increasing reaction temperature (Mittelbach & Tritthart, 1988). Yield is also increasing gradually with an increase in alcohol to oil ratio. This is because concentrations of alcohol to oil ratio will promote the forward reaction in accordance with Le Chatelier's principle. The increase is thus explained by the shift in the equilibrium caused by the excess of methanol. The lowest values of biodiesel yield are in the lower left corner which also correspond to low values of temperature and alcohol to oil ratio. Figure 4 - 4(b) indicates the interaction between reaction temperature and alcohol to oil significantly influences the conversion of triglycerides to fatty acid ethyl esters. Reaction temperature not be compromised, as it has a significant effect on yield. It may also be possible to recover some of the energy used in heating the reaction mixture by condensing the exit vapour stream

#### **4.3.4 Effect of Temperature and Catalyst Loading on biodiesel Yield**

Figure 4 - 5 (a) and Figure 4 - 5 (b) represent a three-dimensional response surface and contour plots displaying the influence of temperature (°C) and catalyst loading (wt%) on biodiesel yield. The third factor (alcohol to oil ratio) is not displayed in the plot and it is held at its median constant value of 5.25.

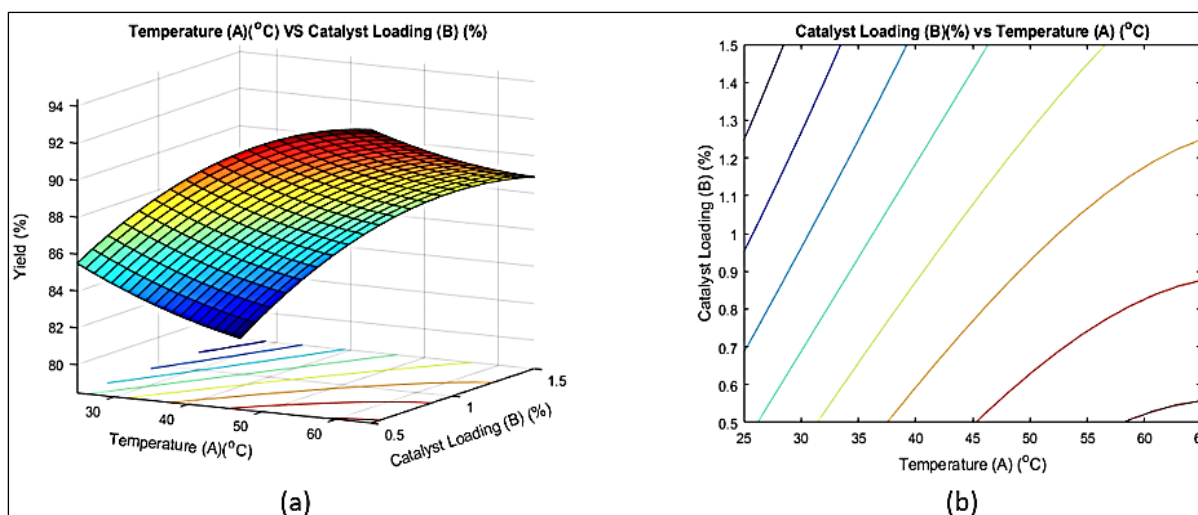


Figure 4-5: Surface plot (a) and contour plot (b) of the effect of temperature and catalyst loading on biodiesel yield

Yield increased with an increase in catalyst loading. However, increases in the catalyst loading and temperature beyond a certain value (40 °C and ~1.3% catalyst loading) did not lead to any further increase in yield but rather a decrease in yield with increasing catalyst loading. The same observation was seen by Freedman et al. (1984) where the yield of biodiesel also decreases when optimum temperature was reached and they suggested that is polarity of methanol reduces the concentration of methoxide ions in the reaction mixture leading to the reduction of catalytic activity. This can be also attributed to Le Chatelier's principle where increasing the concentration of products will drive the reaction to the left to maintain equilibrium. Also, a reversible reaction which resulted in the formation of water resulting in the decrease in biodiesel yield. As can be observed in the plot yield is increasing with increase temperature which resulted in the formation of water occurred resulting in the decrease in biodiesel yield. The yield is also observed to be increasing with increase in temperature because the diffusion rate is promoted when reactants are miscible which permits higher reaction rates in a broader temperature range thus assisting the preservation of catalytic activity (Alba-Rubio et al., 2010). This observation can also be explained by the collision theory, which states that as the temperature of a substance increases, the rate of the reaction increases as well due to faster moving particles in the reaction vessel. Thus, when there is an increased rate of successful collisions, more conversion of oil to biodiesel occurs, hence the increase in the biodiesel yield (Daramola et al., 2016). The highest values of biodiesel yield are in the upper right corner which corresponds with high values of both temperature and catalyst loading. The lowest values of biodiesel yield are in the lower right corner which also correspond to low

values of temperature and catalyst loading. This is an example of a positive temperature-concentration interaction and a positive quadratic catalyst concentration factor. Figure 4 - 5 (b) indicates the interaction between reaction temperature and catalyst loading significantly influences the conversion of triglycerides to fatty acid ethyl esters.

#### 4.3.5 Main effects of the optimization variables

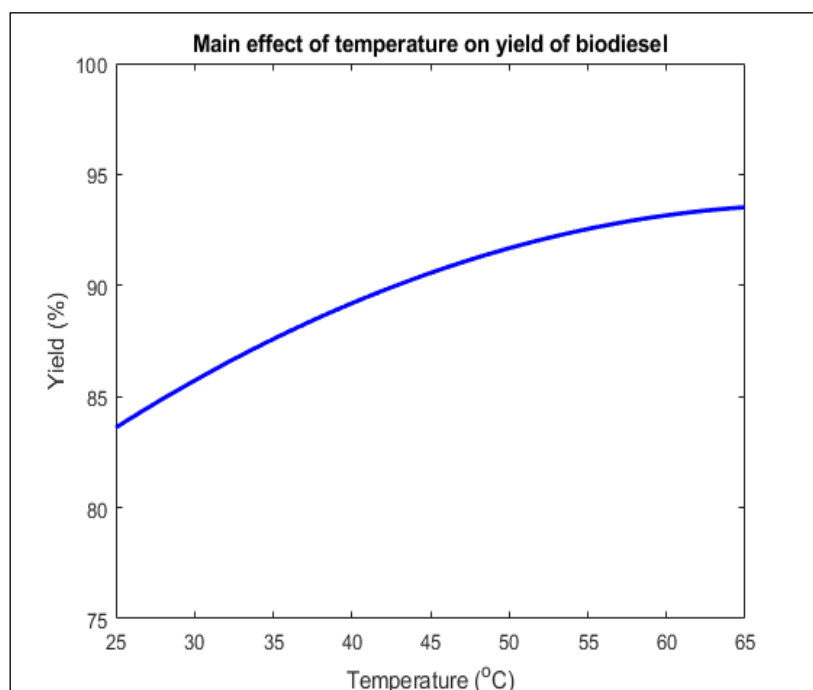
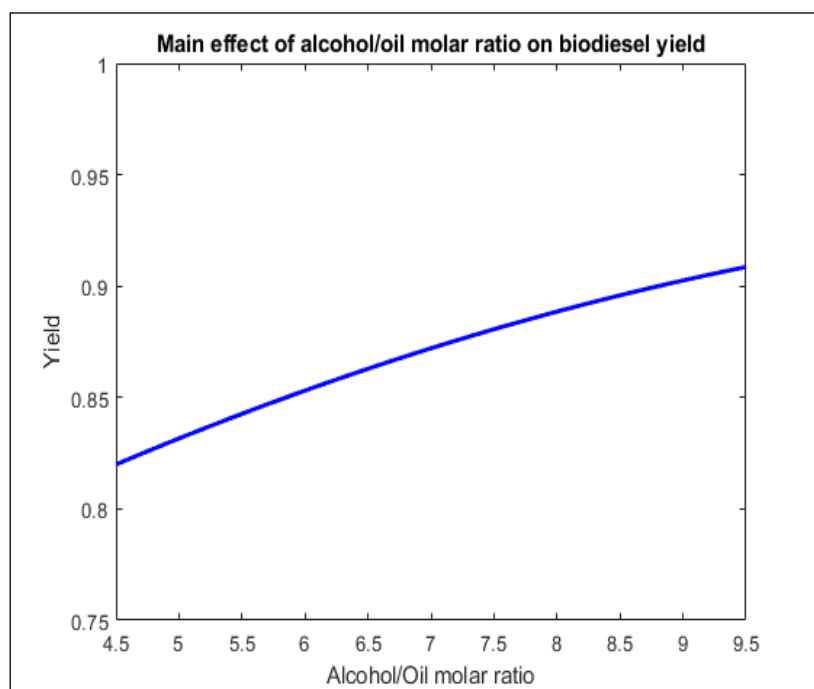


Figure 4-6: Effect of Temperature on biodiesel yield

The main effect plots shown above was obtained by varying one variable, while holding all the other variables at their median values. In this instance, catalyst loading was kept at 1% and alcohol to oil ratio was kept at 5.25. With these plots, the interaction effects are not accounted for. Figure 4 - 6 shows the main effect of temperature on biodiesel yield and it can be observed that the biodiesel yield has almost a positive linear relationship with temperature therefore increasing the temperature will cause the yield to increase, while all other variables are at their median values. This is because the rate of esterification increases with increasing temperature (Freedman et al., 1984). This is attributed to increased kinetic energy and hence more particle movement and collisions because of higher temperature. Furthermore, according to Le Chatelier's principle, an increase in reaction temperature will yield in an increase in the product. The same observation was reported by Daramola et al. (2016). This is attributed mainly to the fact that the transesterification reaction is endothermic (Antolin et al., 2002) and

an increase in temperature favours endothermic reactions. Operating at high reaction temperatures can result in an expensive process hence it is critical to recover some of the energy used in heating the reaction mixture by condensing the exit vapour stream.



*Figure 4-7: Effect of alcohol to oil molar ratio on biodiesel yield*

Figure 4 - 7 shows the effect of alcohol to oil ratio on the yield while the other variables were held constant at their median values. Temperature was held at 45°C while catalysts loading was held at 1%. As can be seen, when alcohol to oil ratio increases, the yield also increases. However, towards the end one can observe that the curve will eventually plateau because of another variable becoming a limiting factor despite adding more alcohol. This is expected and typical of equilibrium-based reactions



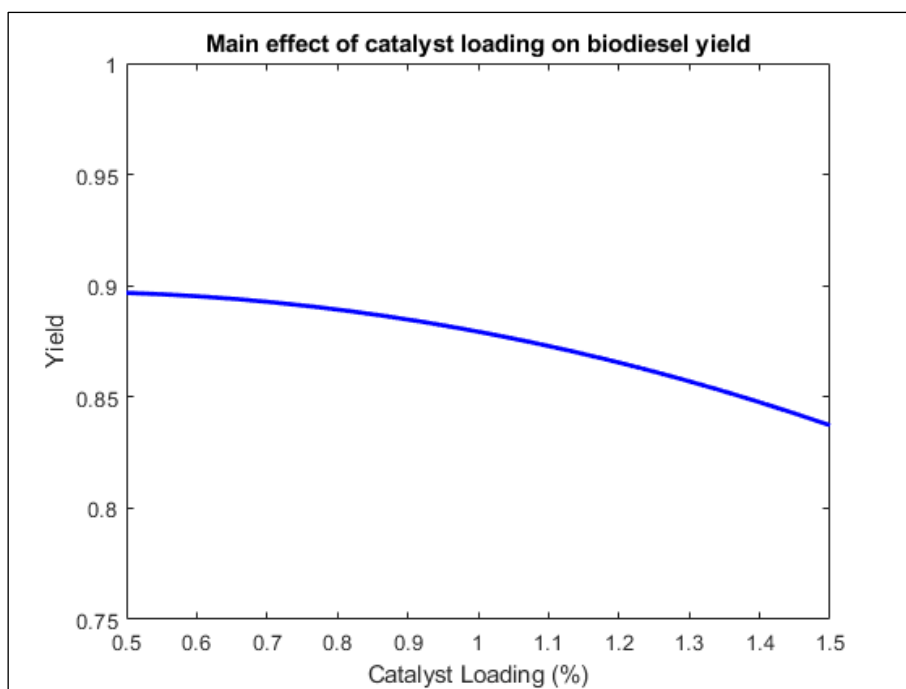


Figure 4-8: Effect of catalyst loading on biodiesel yield

Figure 4 - 8 shows the effect of catalyst loading on the biodiesel yield while the other factors remain constant at their median values. In this instance, temperature was held at 45 °C while alcohol to oil ratio was held at 5.25. According to the plot, yield decreases when catalyst loading is increased which is the opposite of what was expected. In most instances, an increase in catalyst loading would have a positive impact resulting in high yield over a shorter reaction period but when catalysts concentrations are in excess, the reaction mixture may become more viscous, increasing mass transfer resistance and reduce surface contact between the reactants and the catalyst active sites. the yield however that was not the case in this instance. It could also be a result of more water forming because of the reverse reaction thus decreasing the biodiesel yield Buasri et al. (2013) also confirms that lower catalyst loading generally result in low yields because there are fewer active sites for reactants to react but higher catalyst will inhibited the reaction because of the undesirable mass transfer limitation

It is important to understand that the main effect plots only explained the effect that a single variable has on the yield when all other variables are constant. These plots did not determine the optimum conditions as all factors need to be varied with the interaction considered. The Box-Behnken design, and the response optimiser was used on Minitab for this purpose. The yield was held between 0 and 1 or 0 or 100% as yields exceeding 100% are impractical. The

process variable was fixed between their maximum and minimum values hence the model will inaccurately describe the trends that may be observed outside the range used in the study.

#### **4.3.6 Comparison of the yield obtained from the model reaction to literature**

The performance of the sulphonated char catalyst can be compared with four carbohydrate-derived catalysts from D-glucose, sucrose, cellulose, and starch in the esterification of oleic acid with methanol which were prepared by Lou et al. (2008). These carbon-based catalysts were all prepared the same way as the sulphonated char catalyst. After 3 h, the starch, cellulose, sucrose and D-glucose catalysts had attained a conversion of 95%, 88%, 80% and 76%, respectively (Clohessy and Kwapinski, 2020). The starch catalyst resulted in a yield of 95% in comparison, which is slightly higher than the 94.47% obtained from this study. It can be concluded that the sulphonated char catalyst exhibited high catalytic performance compared to the starch derived catalyst. However, the process conditions for the starch catalyst were higher with an alcohol to oil ratio of 10:1 and temperature of 80 °C. The optimum conditions found for with this study were at a temperature of 65 °C, oil to alcohol molar ratio of 6:1 and catalyst loading of 1%. Thus, the esterification of oleic acid with methanol to biodiesel catalysed by a sulphonated char catalyst in this study displayed a higher biodiesel yield at a lower reaction temperature and lower alcohol/oil molar ratio using a similar reaction time. This is more favourable from a process and economic point of view.

The reusability of the sulphonated char catalyst was also good after one run though the other catalysts still showed good reusability after 5 runs. The reusability of the sulphonated char catalyst, however cannot be deemed better than the others since only one run was done while the others were recycled multiple times meaning more runs will have to be done to make further conclusions. However, it can be concluded that the preparation of the sulphonated char catalyst was successful and that it performs well when compared to similar carbon derived catalyst when producing biodiesel.

#### **4.4 Proposed process based on catalytic technology.**

The sulphonated char catalyst has potential to be applied in practical industrial process for biodiesel production. The catalyst could be used in a continuous stirred-tank reactor (CSTR) or semi-batch system. As already stated, recycling the catalyst was important in reducing the production cost of biodiesel. A simplified block flow diagram of the biodiesel process is shown

in Figure 4 - 9. In the proposed process, the vegetable oil undergoes pre-treatment and is then heated to 80 °C before the catalyst and alcohol mixture are added to the CSTR. This is all done at atmospheric pressure and the reactants are stirred by means of an in-built magnetic stirrer. After the reaction, the product is passed through centrifugation (or any gravity separator) to separate the liquid phase from the solid phase. The liquids that is, glycerol and biodiesel are passed through filters where the biodiesel layer will be at the top and the glycerol layer at the bottom. The biodiesel, will be washed at 50 °C, and dried for 15 hrs at a temperature of 180 °C before being transferred to the distillation column where leftover alcohol and other impurities are removed. In most cases a drying temperature above 110 °C is used to remove moisture content to below 500 ppm (Iglesias et al., 2012). Gaseous alcohol will be passed through condensers for a phase change to liquid to promote solubility. It is expected to come out at approximately 60 °C (close to the boiling point of methanol if it is the alcohol in use) and will be then sent for recovery where it will mix with fresh alcohol for a new reaction cycle. The glycerol product is further purified by removing left-over alcohol, catalyst, and other impurities, and then stored in tanks ready for transportation to other industries such as pharmaceutical companies where it is used as a sweetener for syrups and lozenges. The heterogenous catalyst, will be filtered and washed with water at 80°C to remove impurities. Afterwards, it will then be immersed in acetone to remove leftover ions and then dried at 150 °C for 24 hours. The dried catalyst will be reactivated by mild sulphonation (at 80 degrees) and sent back to the CSTR for another production cycle.

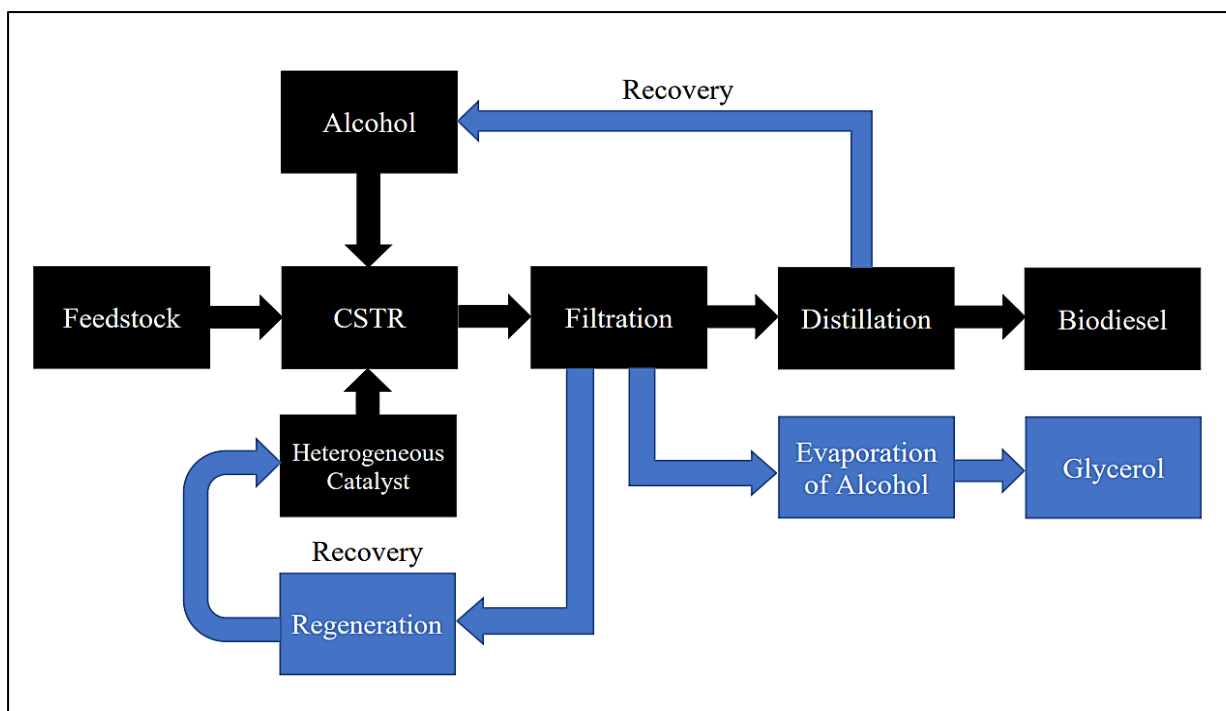


Figure 4-9: Box Flow diagram for potential industrial process

## CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

### 5.1 Conclusions

A tyre pyrolysis char was successfully sulphonated using concentrated sulphuric acid and under high temperature. The surface functionalization was confirmed through FTIR analysis, which showed absorbance bands of  $\text{-SO}_3\text{H}$  and  $\text{O=S=O}$ . The Micrometrics ASAP 2020 gas adsorption analyser was used to determine the BET surface area of the pyrolytic char and average pore volume which were found to be  $81 \text{ m}^2/\text{g}$  and  $0.06 \text{ cm}^3/\text{g}$  respectively. The maximum yield of biodiesel which was, determined through Box-Behnken experimental campaign and response surface methodology, was 94.47% and the optimum conditions were; a temperature of  $65^\circ\text{C}$ , alcohol to oil molar ratio of 6:1 and catalyst loading of 1 %. However, the optimum yield suggested using Minitab response optimiser was 95.50 % and the optimum conditions were; a temperature of  $65^\circ\text{C}$ , alcohol to oil molar ratio of 6% and catalyst loading of 1.5% and an experiment was replicated using those conditions which gave a biodiesel yield of 95.32% hence that was deemed the optimum yield. The lowest yield obtained was 75.44% at a temperature of  $25^\circ\text{C}$ , alcohol to oil molar ratio of 5.35 and catalyst ratio of 0.5%. A quadratic response model was used to fit the experimental data and the coefficient of determination ( $R^2$ ) for the regression model was 0.938 which means that only 6.24% of the total variation was unaccounted for by the model indicating a strong fit to the data obtained in the study in relation to the model. All the three factors considered in the esterification reaction, that is, the reaction temperature, alcohol to oil ratio and catalyst loading had an impact on the biodiesel yield. However, the reaction temperature has the most significant impact hence it cannot be compromised. It may be possible to recover some of the energy used in heating the reaction mixture by condensing the exit vapour stream. The results obtained using the GC-MS confirmed that methyl oleate (the model compound representing biodiesel) was produced hence the sulphonated char catalyst is effective thus its applicability should be explored in other biofuel processes. Lastly, the reusability of the catalyst was an important aspect to consider as it can decrease production cost hence the catalyst was recycled and produced a yield of 75.58 % after one cycle. This was 18.89% lower than the original catalyst so a regeneration may be required in the form of mild sulphonation.

## 5.2 Recommendations

The production of biodiesel from carbon-based catalysts has gained interest in recent years. For future work coupling the reactor system with an adsorption apparatus filled with zeolite or any other drying agent to remove the water produced during the esterification reaction should be considered. Employing this apparatus could possibly shift the equilibrium towards fatty acid methyl ester production hence higher yields could be attained. The conversion and yields attained in the study were satisfactorily and relatively high but this can be considered in future to reach close to full/complete conversion. Also, the sulphonated char catalyst should be tested on a range of actual complete vegetable oils, which was beyond the scope of this study. To improve catalytic activity when recycling the catalyst, mild sulphonation using the Monel Parr high pressure reactor should be considered but the sulphonation may be done for shorter reactions times and or with a weaker sulphonating agent such as dilute sulphuric acid.

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## APPENDIX

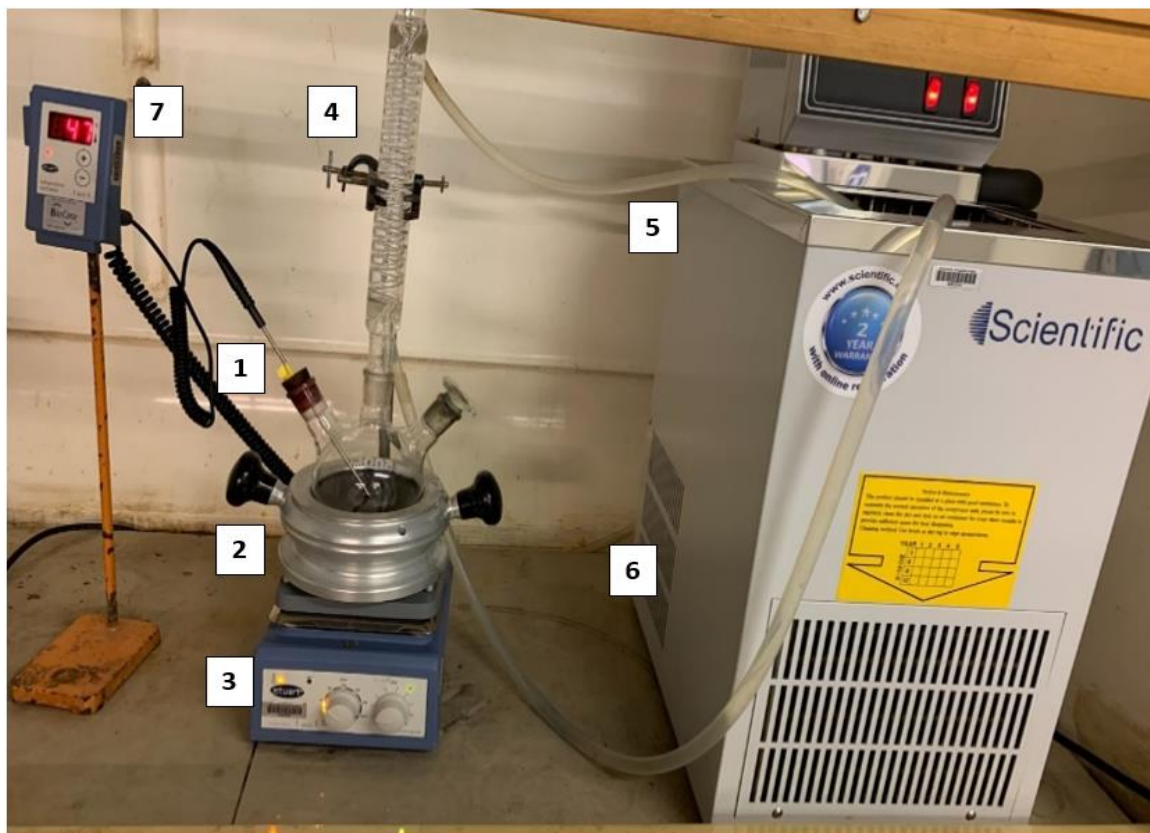


Figure A-1: Picture of the reaction set-up for the esterification reaction

Table A- 1: Components of the experimental set-up

Equipment	Key
3-Necked round bottom flask	1
Heating block base	2
Heating mantle	3
Reflux condenser	4
Water tubing	5
Low temperature cooling bath	6
Temperature probe	7

### GCMS of methyl esters produced after one catalytic cycle.

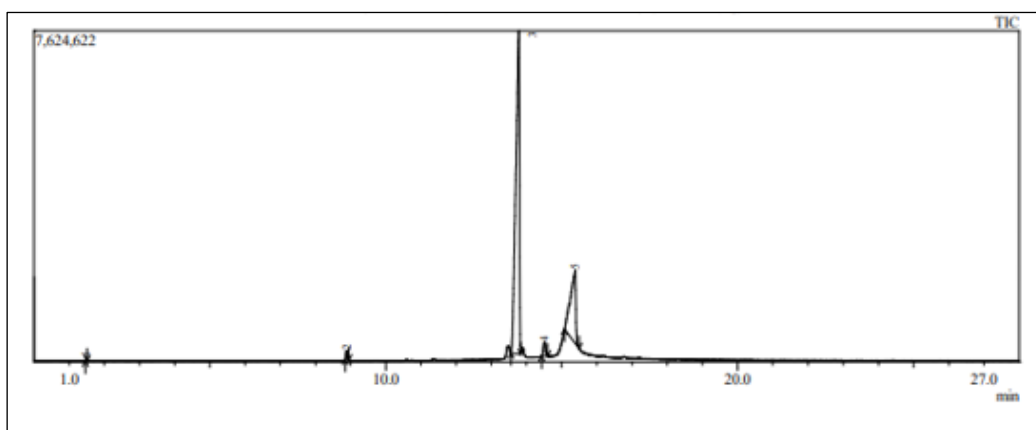


Figure A-2: Chromatogram for biodiesel produced after catalyst recovery

Table A-2: GCMS results for biodiesel obtained after catalyst recovery

Peak number	Retention Time	Area %	Similarity	Name
1	1.488	0.14	98	Methylene chloride
2	8.887	0.90	96	Hexadecanoic acid,methyl ester
3	13.783	72.45	95	9-Octadecenoic acid, methyl ester, (E)
4	14.513	2.09	96	Methyl stearate
5	15.385	24.42	95	Oleic acid

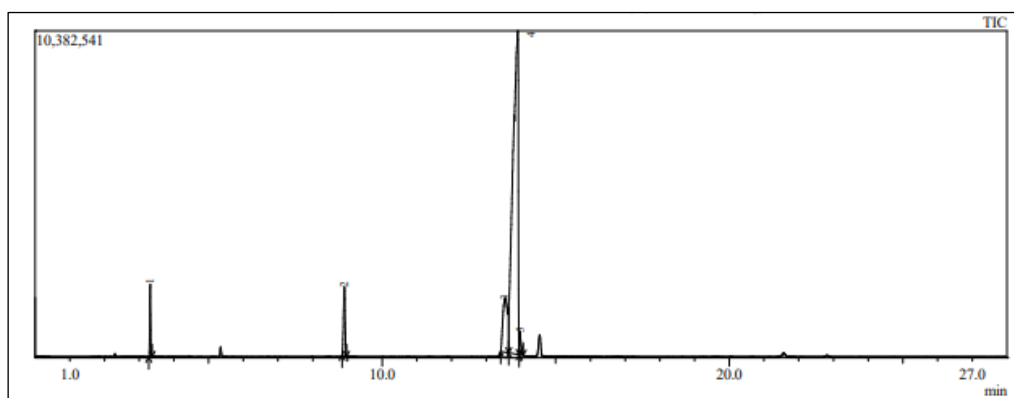


Figure A-3: Chromatogram for the optimised biodiesel

Table A-3: GCMS results for optimised biodiesel

Peak number	Retention Time	Area (%)	Similarity	Name
1	3.318	2.82	97	Dodecanoic acid, methyl ester
2	8.913	5.09	95	Hexadecanoic acid, methyl ester
3	13.525	12.25	90	Linoleic acid, ethyl ester
4	13.906	78.10	95	9-Octadecenoic acid, methyl ester (E)
5	13.975	1.74	94	9-Octadecenoic acid, methyl ester (E)

Table A-4: Raw experimental data

Run Number	Mass of oleic acid (g)	Mass of alcohol (g)	Mass of sulphonated char catalyst (g)
8	94.5	56.2	1.42
11	91.6	46.8	1.37
2	87.1	44.4	0.87
15	91.2	54.3	0.91
13	86.5	11.1	0.87
4	98.2	66.5	0.98
10	89.4	53.2	0.89
5	96.5	57.4	0.97
9	91.5	54.4	0.92
1	92.1	54.8	1.38
14	88.9	52.9	0.44
13	91.5	63.0	0.92
7	95.6	65.0	1.43
12	90.2	45.9	1.35
6	91.3	54.4	0.46