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Optimization of biodiesel production from castor seed oil as an alternative fuel in sub-Saharan African countries

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2024

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UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

Optimization of biodiesel production from castor seed oil as an alternative fuel in sub-Saharan African countries

Ph.D. THESIS

Prepared by

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Submitted to

School of Chemical and Metallurgical Engineering

Faculty of Engineering and the Built Environment

University of the Witwatersrand, Johannesburg, South Africa

Supervisor: Professor Diakanua Nkazi

2022

Declaration

I affirm that " **Optimization of biodiesel production from castor seed oil as an alternative fuel in sub-Saharan African countries”** is unique research I completed under Professor Diakanua Nkazi.

Signature……

Abstract

Biodiesel-fuelled diesel motors offer a unique chance to address two general issues confronting our worldwide society: energy utilization and global warming. Biodiesel from utilized vegetable oil is simple and has numerous natural advantages. To generate a good fuel for use in diesel motors, these triglycerides are typically transformed into individual mono-alkyl esters by base-catalysed transesterification with short-chain alcohol, normally methanol.

Initially, the transesterification reactions of castor oil with methanol were studied by employing sulphuric acid as a catalyst in an ultrasound reactor. The castor oil and the methyl ester products were characterised by diverse analytical techniques such as gas chromatography (GC-MS).

The impacts of diverse reaction variables (reaction temperature, methanol to oil ratio, reaction time, catalyst amount) on FAME yield were studied. The optimum reaction conditions of the diverse process systems were established.

The optimum operating conditions for methyl esters production using ultrasound reaction, with the castor oil was established as follows: In the presence of sulphuric acid: reaction time of 40 min at 50 ºC with methanol to oil ratio of 6:1 as well as 0.5 H_2SO_4 wt. % of oil; in the presence of unsupported castor shell catalyst: reaction time of 40 min at 50 ºC with methanol to oil ratio of 9:1 and 1 unsupported castor shell (UCS) wt.% of oil; in the presence of Co/TiO_2: reaction time 40 min at 50 ºC with methanol to oil ratio of 9:1 plus 1 Co/TiO_2 wt.% of oil.

The transesterification reaction in the presence of sulphuric acid led to higher yields of methyl esters (90%) compared to methyl ester yields (85 and 83 %) for Co/TiO_2 and UCS, respectively.

The utilization of homogeneous catalysts presents several inconveniences; nevertheless, heterogeneous catalysts are exciting because their use could lead to biodiesel production in a low-cost manner.

Therefore, a solid base catalyst (UCS) was prepared from a castor shell (supplied by the Mpumalanga caster plant) and Co/TiO_2 was prepared by the incipient wetness impregnation method. Numerous analytical techniques were applied for characterization purposes.

EDS results showed that the UCS predominantly contained some elements such as calcium, oxygen, and potassium, and Co/TiO_2 contained titanium, followed by cobalt.

The high amount of calcium (Ca), carbon (C), and oxygen (O) in the UCS was beneficial because their combination probably leads to the formation of CaO or $CaCO_3$, which could increase the activity of the UCS catalyst. The presence of CaO and $CaCO_3$ was confirmed by Fourier- transform infrared. The XRD characterization of the castor shell reveal the presence of $CaCO_3$ peaks only, while XRD characterization of Co/TiO_2 indicated that the diffraction peaks at ca. $2\theta = 31, 59$, and 65° were observed only in the 10% Co/TiO_2 catalyst data (pattern

a) and can be ascribed to Co_3O_4 resulting from the decomposition of Co $(NO_3)_2.6H_2O$ during catalyst calcination in air. The BET described the specific surface area and pore volume distribution for 10% Co/TiO_2 catalyst, blank support TiO_2, and UCS catalyst. The assessment indicated that the specific surface and volume distribution for the Co/TiO_2 catalyst where the used blank supporter TiO_2 acting as a catalyst. The volume distribution and surface area for Co/TiO_2 were greater due to the heating treatment of the catalyst system, which removed all the volatile materials. This increased the activity of the catalyst.

Dedication

I would like to dedicate this Thesis to:

- My God Almighty My “ALL IN ALL”
- My wife July Samba Lumu
- My four children (Plamedi Lumu, Tegra Lumu, Jenovic Lumu, and Jehniss Lumu)
- To my late (Father, mother, and grandparents), would have loved to see this day
- To all children of Lumu Katumba and Debora Kasongo, my late parents

Acknowledgement

In the Name of Jesus Christ, the Rescuer and Lord of all.

Before everything, I would like to thank my God, the everlasting God, the father of our Lord Jesus Christ, the omnipotent, the Omni power, and the Omnipresent for helping me to accomplish my Ph.D. effectively.

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Abbreviations

ASTMD	American Standards Testing and Methods.
BET	Brunauer-Emmett-Teller
CFPP	Cold Filter Plugging Point.
COP	Conference of Particles
DDRBO	Dewaxed Degummed Rice Bran Oil
DG	Diglyceride
EU	European Union
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty acid methyl ester
FFA	Free Fatty Acid
FID	Flame Ionization detector
GC	Gas Chromatography
GHG	Greenhouse gases
JCPDS	Joint Committee of Powder Diffraction Standards
JIC	Joint Implementation Committee
MG	Monoglyceride
RBDPO	Refined Bleached Deodorized Palm Oil
RSM	Response Surface Method
SANS	South African National Standard
SAPIA	South Africa Petroleum Industrial Association
SCE	Super Critical Ethanol
SCM	Super Critical Methanol
SEM-EDS	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TG	Triglyceride
UCS	Unsupported catalyst shell
USA	United States of America
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Chapter one Introduction

1.1 Background

A significant part of all energy consumed in the entire world comes from petroleum, charcoal, and natural gas except for hydroelectricity and nuclear power. The sources are restricted and could be depleted before the end of the next century (Schuchardt et al., 1998); subsequently, searching for an alternative energy source is crucial.

Securing the supply of fossil fuel has seen war, human rights abuses, and environmental destruction to control this fuel source. Vegetable oils are known to be a renewable energy source, and their energy balance is still disputable (Zhou et al., 2008).

Historically, it was believed that Rudolf Diesel started research concerning using vegetable oils as fuel for diesel engines (Lang et al., 2001). In the following decades, the studies became more systematic, and, nowadays, much is known about its use as fuel. Despite being energetically favourable, using vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. In Rudolph Diesel's 1893 paper "The Theory and Construction of a Rational Heat Engine," the German inventor described a revolutionary engine in which air would be compressed by a piston to a very high pressure causing a sufficiently high temperature to ignite non-volatile oils. His first working engine could run on various vegetable oils, leading him to envision in 1911 that "the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it" (Balat and Balat, 2008). Since then, nearly all research has focused on improving the engine's performance when using biologically based diesel fuel.

The word biofuel includes liquid or gaseous fuels for the transport sector that are transcendently delivered from biomass. Liquid biofuels are principally applied to fuel vehicles. However, they can likewise fuel engines or fuel cells for electricity generation. As a substitute fuel, biodiesel is the main elective fuel presently accessible and has a general positive life cycle energy balance. In any case, it is generally acknowledged that biofuels are neither a remedy nor without their weaknesses and dangers. A significant disadvantage is that changing consumable vegetable oils like sunflower, soybean, and canola to fuel will, likely, bargain nourishment security.

The vegetable-oil subsidiary 'biodiesel' offers numerous benefits as a substitute fuel for diesel motors. These incorporate enhanced fuel execution and lubricity, a higher cetane rating than petrol-diesel, a higher flashpoint that generates it safe to deal with, lower poisonous quality to

plants and animals, decreased fume emanations, and the way that it is easy to phase in and out of utilization (Ma and Hanna, 1999; Zhang et al., 2003; Encinar et al., 2002; Sivaprakasam and Saravanan, 2007). It is a local renewable source of energy and profoundly biodegradable (Meng et al., 2008; Ahn et al., 1995).

Financially, it lessens imports and affords improved security of energy supply. Biodiesel can be mixed at any level with oil diesel to make a biodiesel blend that can be utilized in compression ignition (diesel) motors with next to zero alteration as the prevalent lubricating properties of biodiesel increment practical motor effectiveness. Biodiesel does not just have low viscosity and lower carbon monoxide discharges (Ryan et al., 1984), yet additionally is easy to utilize, nontoxic free sulphur (Alcantara et al., 2000) and aromatics (Srivastava and Prasad, 2000). Its higher flash point makes it more secure to store, and the presence of a higher measure of oxygen (up to 10%) guarantees the progressive and complete burning of hydrocarbons.

Historically, energy continues to be the pivot of all countries' economic and social development worldwide, and Africa is supplied with significant quantities of fossil and renewable energy (RE) resources. As per (Davidson et al., 2007), although energy has brought considerable economic prosperity, the way it is produced and used is inefficient and has adversely affected local, regional, and global environments, hence the ongoing debate about making the energy systems more environmentally friendly. Strategies to develop energy resources must be highly mindful of both the environmental pollution problems (through carbon monoxide, ozone-forming hydrocarbons, hazardous particulates, acid rain causing sulphur dioxide, etc.) and the threat of "climatic change" associated with the use of fossil fuels, the latter as a result of the accumulation of certain greenhouse gases (GHGs) in the atmosphere (mainly carbon dioxide, methane, and nitrous oxide that trap heat in the lower atmosphere and leads to global warming).

As embraced by the third conference of parties (COP3) in Kyoto, Japan in 1997, endeavours have been made to consent to lawfully restrict commitments by the most advanced nations to diminish their GHG discharges by about 5.2% below 1990 levels by 2012 (Amigun, et al., 2008a). In South Africa, the vehicle segment contributes 16% of its greenhouse gas emissions, the best in Africa (Nolte, 2007). Diesel fuel donates around 17% or 11,705,000 tons of CO_2 identical. An extra 1,622,000 tons were discharged from diesel fuel utilized for power generation (VonWedel, 1999). Accordingly, South Africa has decided to set a boundary on its greenhouse emanations and increment its utilization of renewable energy sources.

In December 2006, the South African cabinet approved the draft biofuel strategy to be implemented in consultation with industries. The draft strategy proposes a 4.5% biofuels industry development in South Africa and will achieve 75% of the country's renewable energy target of over a billion litres of biofuels by 2013. However, it has not made good progress in developing its biofuel policy. Recent progress in the Brazilian and other developed country's biofuels program has highlighted the enormous opportunities that are open to African countries to reduce their dependency on imported oil and make meaningful contributions towards minimizing GHG emissions (Al- Zuhair, 2007).

The review of the financial matters of climate change has likewise exposed the monetary need to limit global warming (Stern, 2006). An accelerated release of fossil-buried CO_2 because of human activity is commonly acknowledged as a central point that adds to the greenhouse impact (Houghton et al., 2001). The poor distribution of fossil fuel resources makes over 70% of countries on the African continent dependent on imported energy resources, which again supports the development of abundant renewable energy resources. The theme of this presentation centres around various catalyst system materials during the time spent making biodiesel. A comparative and process optimization study of the transesterification catalytic processes is a fundamental goal in reducing production costs in biodiesel production.

1.2 Research motivation

There are many reasons why biofuel production should be considered a pertinent technology by both emerging and industrialized nations. These include energy security, environmental concerns, foreign exchange, and socioeconomic issues identified with the rural area. The sustainability, environmental and inflationary issues related to customary fuels have prompted a worldwide quest for renewable biofuels (Amigun et al., 2008b).

Government care for biofuels is picking up force, and plans are being proposed and developed to encourage the planting, harvesting, and processing of crops, for example, maize, sugar sticks, soybeans, cassava, and oilseeds from trees and sorghum into bioethanol and biodiesel feedstock for use in the fluid fuels industry (Babajide, 2011). To this end, the South African government has set up a joint implementation committee (JIC) for the biodiesel business. The JIC involves a range of invested parties, for example, the South African Petroleum Industry Association, ranchers or farmers, oil organizations, and associations. A biodiesel standard has been completed with the help of the South African Bureau of Standards, and the JIC is right now building up a valued model for the local biodiesel industry (Takavarasha et al., 2005).

1.3 Thesis structure

This thesis is divided into seven chapters which are shown in figure 1 as follows:

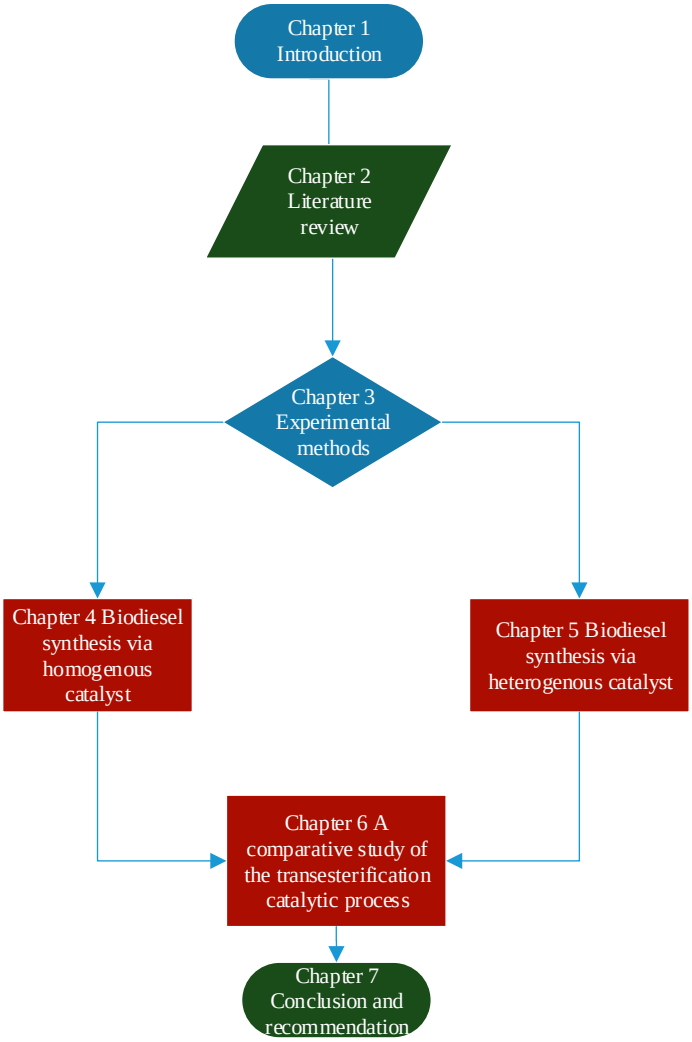


Figure 1 Thesis structure showing the relationship among chapters.

Outline of the following chapters

Chapter two: A literature review

The chapter addresses the review of the literature. It reviews the history, use, advantages, and difficulties of biodiesel, particularly, world biodiesel production, and the chemistry of biodiesel production.

Furthermore, the literature has insisted on using castor seeds as the feedstock in this study. In addition, the chapter examines the literature on cobalt oxide and shell catalysts.

Chapter three: Experimental and analytical methods

This chapter contains details of the research methodology used throughout this study. It provides the list of materials used, the research design, and the methods. A theoretical background to the analytical techniques applied in this study is also briefly presented. The experiment contains a general section that describes the laboratory procedures carried out in general.

Chapter four: Biodiesel synthesis via homogeneous catalysis

The fourth chapter describes the outcomes of optimizing the transesterification reactions of castor oil to its methyl esters in the presence of a homogeneous catalyst (H_2SO_4) although using an ultrasonic homogenizer. The influence of the appropriate procedure parameters and factors that affect the FAME yield obtained from castor oil is also reported.

Chapter five: Biodiesel synthesis via heterogeneous catalysis

The fifth chapter addresses and debates the consequences of the characterization of heterogeneous catalysts that have been prepared in the laboratory and utilized for transesterification reactions. The outcomes of the characterization and the ones for the catalytic activity of heterogeneous catalysts, Co/TiO_2, and UCS were investigated and debated in this chapter. The effect of the catalysts on the various reaction parameters concerning the heterogeneous catalytic transesterification reactions was likewise studied.

Chapter six: A comparative study of the catalytic processes

This chapter has presented the knowledge of the comparative study on transesterification catalytic processes via two scenarios, homogeneous catalysts (H_2SO_4) and heterogeneous catalysts (Co/TiO_2 and UCS).

Chapter seven: Conclusions and recommendations

Finally, the seventh chapter provides the overall conclusions, outlines the discoveries from this investigation, and recommendations for future studies are made.

1.4 Problem statement

Biodiesel presents a reasonable renewable replacement for petroleum-based diesel. Regardless of the successes experienced in the biodiesel industry as expressed beforehand, there remains significant difficulty in the biodiesel process, as production costs of biodiesel are still rather high contrasted with petroleum-based diesel fuel; the two principal factors influencing the cost of biodiesel to incorporate the cost of crude materials and the cost of processing (Demirbas, 2009).

The current and larger part of the process, the biodiesel production process is made by the transesterification of vegetable oils and animal fats with methanol or ethanol through a batch reactor (stirred tank reactor) in contact with the base or acid catalyst. There are some challenges associated with this procedure, which include: (i) the reaction rate can be limited by mass transfer between the oils and alcohol because they are immiscible, (ii) transesterification itself is a reversible reaction, and therefore there is an upper limit to conversion in the absence of product removal; (iii) most commercial processes are run in a batch mode and thus do not gain some of the advantages of continuous operation.

To overcome these problems, an obvious method to avoid or limit these challenges is to utilize a continuous production process. Therefore, in recent years, some intensification technologies have been developed and applied to improve mixing and mass heat transfer between the two liquid phases (Qiu et al., 2010). The continuous production process in this way allows the reaction conditions to be observed and optimized. Hence, the need for developing a new process intensification technology to improve mixing and mass/heat transfer between the two liquid phases to reduce production costs as current conventional techniques involves long reaction times, the high molar ratio of alcohol to oil, and catalyst concentration. Long residence times, high working costs, and energy utilization are required to purify biodiesel and recuperate

overabundance measures of alcohol and high catalyst during downstream processing amount of waste and cause low production effectiveness (Bournay et al., 2005).

Due to an increase in population which causes an increase in demand for diesel fuels, the mission for substitute powers is generally engaged. One potential option is utilizing feedstocks for biodiesel generation, which comprise methyl esters from vegetable oil or animal fats that can be delivered using acid or base catalysts. Biodiesel production is affected by the base catalyst, for example, NaOH, KOH, and CH_3COONa, however, separating homogeneous catalysts from the esters is troublesome (Ma and Hanna, 1999). This utilization of heterogeneous catalysts can solve this issue. Notwithstanding these, the advantages of the utilization of heterogeneous catalysts could likewise incorporate improvement of the separation and decontamination of the reaction product, exclusion of the water washing methodology as of now required for the neutralization of the biodiesel during the production process, simple reuse of the catalyst in the reactor and diminished corrosion issues.

1.5 Research aims.

Journals have indicated that there is an assortment of alternatives to produce biodiesel. The project aims to synthesise and optimize biofuel production using ultrasonic energy. The following are the set objectives to achieve the purpose:

a. The determination of the physical and chemical composition of the castor oil sample
b. The evaluation of the impacts of the diverse reaction parameters on the yield of the feedstock (castor oil) to its corresponding methyl ester
c. Maximization of process parameters and evaluation of the process optimization of the reaction systems used in producing the methyl esters.
d. Determining the characteristics of the methyl esters produced with castor oil were examined under various procedure conditions to meet industrial specifications.
e. Study of biodiesel production under a batch process employing ultrasound technology
f. Use South African castor shell seeds as a catalyst but unsupported as heterogeneous catalysts in biodiesel production.
g. Investigation of the effect of different reactions parameters with respect to FAME yields
h. Use cobalt oxide catalyst prepared from cobalt nitrate hexahydrate supported by titanium oxide as a heterogeneous catalyst in the production of biodiesel.

i. Compare the transesterification catalytic processes included in the diverse process intensification technique and biodiesel produced during these processes will be verified to determine if some standard parameters are met.

1.6 Research questions

The objective of this research is to address the following interrogations:

a. What are the optimum reaction parameters to process castor oil samples to yield biodiesel with high-quality yield?
b. What could be the optimum reaction parameters for biodiesel production using homogeneous or heterogeneous catalyst reaction systems?
c. Can an ultrasound reaction under the actual condition relating to this study (presence of UCS and Co/TiO_2 catalysts) improve FAME yield and fuel quality dependent on castor oil as feedstock, and can the utilization of this ultrasound reactor decrease the cost of production?
d. Can castor shells be used as a raw material to prepare heterogeneous catalysts that could lead to a potentially favourable yield of methyl esters?
e. Will the use of castor shell-based materials present a catalytic system that is environmentally benign processes?
f. Will the biodiesel produced from homogenous and heterogeneous transesterification catalytic reactions and process intensification meet standard quality specifications?

1.7 Research approach

The research approaches used in this study to achieve the aims and objectives of the study are hereby highlighted.

Homogeneous catalysis of castor oil to biodiesel

Gas-chromatography mass spectrometry (GC-MS) was used as an analytical tool to characterize castor oil as raw material and biodiesel products.

Transesterification reactions were run on the castor oil test sample in the presence of a homogeneous catalyst (H_2SO_4) to get methyl esters (biodiesel) through the ultrasound reactors.

Heterogeneous catalysis of castor oil to biodiesel

This part of the project includes a heterogeneous catalyst; two types of catalysts were used, such as (Co/TiO_2) and UCS prepared based on South African castor shell seeds. These catalysts

were utilized in the transesterification reaction of castor seed oil as feedstock with methanol to produce methyl esters.

Characterization of Co/TiO_2 catalysts was completed by XRD, BET, and SEM-EDS, while UCS, was characterized by SEM-EDS, XRD, FT-IR, and BET. These investigations were done with the aim of determination of the chemical and mineralogical composition of the individual catalyst (Co/TiO_2 and UCS).

1.8 Research hypothesis

a. Utilizing the ultrasound reactor under the actual condition will significantly improve the process strengthening and the working conditions for the transesterification reaction.
b. The utilization of Co/TiO_2 and UCS heterogeneous catalyst in transesterification reaction would show a procedure that is environmentally benign and prompts conceivably positive yield of methyl esters and simpler refining of the produced biodiesel, and improved recuperation of the catalyst.

1.9 Scope and limitation

Castor oil was utilized as a feedstock to synthesise methyl esters through transesterification run under homogeneous and heterogeneous catalytic procedures. The reaction process was additionally upgraded by using an ultrasonic homogenizer reactor. Optimum conditions under diverse processes were resolved. The product (FAME) characterizations from the various procedures were performed. To address the boundaries of the homogeneous catalytic process, heterogeneous catalysts Co/TiO_2 and UCS were characterized and utilized for the transesterification reaction essentially to produce methyl esters. This catalytic process was developed and optimised; a product characterisation was also performed and compared to standard specifications. At last, an examination study between the FAME dependent on the three diverse catalysts was conducted.

Limitation

This investigation did not cover the following:

a. Transesterification reaction using a supported shell castor as a base catalyst.
b. Determination of other causes of the deactivation of cobalt as well as an unsupported catalyst than water
c. Free fatty acid's impact on methyl yield is based on a cobalt oxide catalyst supported by titanium oxide and an unsupported castor shell catalyst.
d. Reusability test of unsupported castor shell
e. Characterization of catalysts after biodiesel production to determine mass balance.

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Chapter two Literature Review

2. Introduction

The principal focal point of chapter two is the evaluation of literature which is additionally founded on the principles, point of view, rationale, and inspiration as announced in the past chapter.

2.1 Biodiesel

All fossil fuels are non-renewable, but not all non-renewable energy sources are fossil fuels. Regardless of whether fossil powers generally contribute to the world energy supply, their production, and usage have raised natural caution and political dialogues. (Aransiola et al.,2012) have proven that 98% of carbon discharges are created from fossil burning. In view of the quick increment in the number of enterprises and vehicles, the requirement for energy has expanded. This energy is created from nuclear, natural gas, and petroleum. The inconveniences of utilizing petroleum are because of the catastrophe of the inadequacy of fossil fuels, just as the issue of ecological decay experienced by the planet. The investigation of an elective alternative to fossil fuel derivatives will probably diminish nations' reliance on oil imports and advance the decrease of ozone-depleting substance discharges.

Numerous alternative fuels are being investigated as potential choices for the present high toxin non-renewable energy source got from lessening business assets. (Gashaw et al., 2015) characterized biodiesel as mono-alkyl esters of long-chain fatty acids that began from natural oils and fats of plants and animals. This tends out amongst the most energy-efficient, environmentally friendly choices of late to fully fill future energy needs. (Saniet et al., 2013) have shown that biodiesel-fuelled diesel motors offer a noteworthy chance to address two prevailing issues confronting our worldwide society: energy utilization and global warming. Biodiesel has been produced in South Africa before World War II to control rock-solid vehicles. Biodiesel was initiated in South Africa in 1979 when sunflower oil was transesterified and refined to a standard equivalent to petroleum diesel fuel. Biodiesel from utilized vegetable oil is simple and has numerous natural advantages.

The transformation of pure glyceride to Fatty Acid Methyl Ester (FAME) is higher at the reaction time, a relatively short motivation behind why vegetable oil from plant sources the best beginning material for biodiesel generation, as is expressed by (Gashaw et al., 2015). It has been demonstrated by (Tan et al., 2011) that substitutes for biodiesel generation are edible vegetable oils, for example, olive oil, palm oil, soybean oil, canola oil, sunflower oil, and so

on. A large portion of these oils is of extreme interest in the nourishment business for human utilization. This, hence, presents significant trouble in commercialising biodiesel from food oils. (Murugesan et al., 2009) proposed the utilization of non-edible oils from neem, mahua, pongamia, karanji, babassu, jatropha, and so forth, which are open in numerous parts of the world and less expensive contrasted with edible oils. Because of the rainfall level of South Africa, the nonedible vegetable oils separated from the castor seed, known as the second-generation feedstock, can be considered a promising substitution for conventional edible nourishment crops for the generation of biodiesel. (Severino et al., 2012) announced that castor (Ricinus communis) is one of the most established developed yields; however, as of now represents just 0.15% of the vegetable oil delivered on the planet.

Castor oil has been in the chemical and pharmaceutical industries for hydroxylating, fatty acids, stimulants, and laxatives to discharge periodic constipation separately. It has a great future in the biofuel industry because of its higher oilseed content (more than 480 g/kg), exceptional fatty acid structure (900g/kg of ricinoleic acid), high oil yield production (1250-2500 L/ha), and capacity to be developed under dry season and saline conditions. Castor oil seed has sufficient potential to fuel compression ignition engines. Reducing the viscosity of vegetable oil, for example, castor oil is a striking test that can prompt operational fuel issues, such as engine deposits. This must be updated before using castor seed oil in the motor.

Biodiesel is a substitute diesel fuel that starts from vegetable oils or animal fats; the key sectors of vegetable oils and animal fats are triglycerides or otherwise called an ester of fatty acids joined to glycerol (Abdullah et al., 2013; Fadhil et al., 2012)

2.1.1 Biodiesel feedstock

Biodiesel is a biofuel acquired from vegetable or animal oil, changed by a chemical procedure called transesterification. Transesterification happens when oil reacts with an alcohol (methanol or ethanol) to get a methyl ester of vegetable oils or an ethyl ester (relying upon the alcohol utilized). The feedstock of this biodiesel has changed after some time and differs contingent on areas. This cutting-edge fuel can be produced from differing feedstock in which the oil can hold fatty acids like animal fats, non-edible oils (jatropha oil, karanji or Pongamia oil, neem oil, jojoba oil, cottonseed oil, linseed oil, mahua oil, deccan hemp oil, Kusum oil, orange oil, and rubber seed oil), and waste cooking oils and by-products of the refining vegetables oils and algae, (Gashaw et al., 2015). As of late, it has been presented (Kim et al., 2018) that the regional trends still proceed as the USA and the EU still dominantly use soybean

oil and rapeseed oil separately, and palm oil is the primary wellspring of biodiesel in Asia. It is normal that the food-crop-based biodiesel will continue prevailing for the following decade. However, it was discovered that habits for animal fats and utilized cooking oil are becoming most useful in both the USA and the EU. The writing from (Barnwal and Sharma, 2005) audited that biodiesel can be acquired likewise by super critical methanol (SCM) transesterification strategies, and the last technique has a more prominent extension for the generation of biodiesel than the previous, in light of the fact that the yield, greater product quality, and the time consumed in conversion is less.

The biodiesel feedstock is commonly made of four groups: edible oil, inedible oil, utilized oil, and seaweed, as shown in figure 2.1. A few researchers have considered biodiesel production from edible oil like palm oil; (Ooi et al., 2004; Sumathi et al., 2008), coconut (Kumar et al., 2010; Nakpong and Wootthikanokkhan, 2010), sunflower (Ghanei et al., 2011; Porte et al., 2010), canola (Dizge and Keskinler, 2008; Ilgen, 2011), shelled nut (Kaya et al., 2009; Nguyen et al., 2010), soybean (Liu et al., 2008; Yin et al., 2008), rapeseed (Georgogianni et al., 2009; Koda et al., 2010), and rice grain (Gunawan et al., 2011; Zullaikah et al., 2005). The production of biodiesel from inedible oil has also been explored in recent years. A portion of these inedible oil crops includes jatropha curcas (Ganapathy et al., 2009; Tiwari et al., 2007), castor (Ramezani et al., 2010; Sousa et al., 2010), linseed (Demirbas, 2009a), tobacco (Nicotiana tabacum) (Usta, 2005; Veljković et al., 2006), Karanja (Pongamia pinnata) (Agarwal and Rajamanoharan, 2009; Naik et al., 2008), (mahua Madhuca Indica) (Ghadge and Raheman, 2005; Puhan et al., 2005), elastic (Hevea rasiliensis) (Ikwuagwu et al., 2000; Ramadhas et al., 2005), neem (Azadirachta indica) (Rao et al., 2008). Because of the high cost of vegetable oil, less expensive waste oil is utilized, for example, cooking oil (Phan and Phan, 2008; Zhang et al., 2003) and animal fats (Canakci, 2007; Gürü et al., 2009) from households and restaurants are drawn into consideration as potential feedstocks. Another promising feedstock used for biodiesel production is microalgae (Amaro et al., 2011; Sánchez et al., 2011). A microalga, the third generation of biodiesel feedstock, ended up standing out amongst the most encouraging feedstocks for biodiesel production owing to its higher efficiency and becoming quicker than ordinary crops (Minowa et al., 1995).

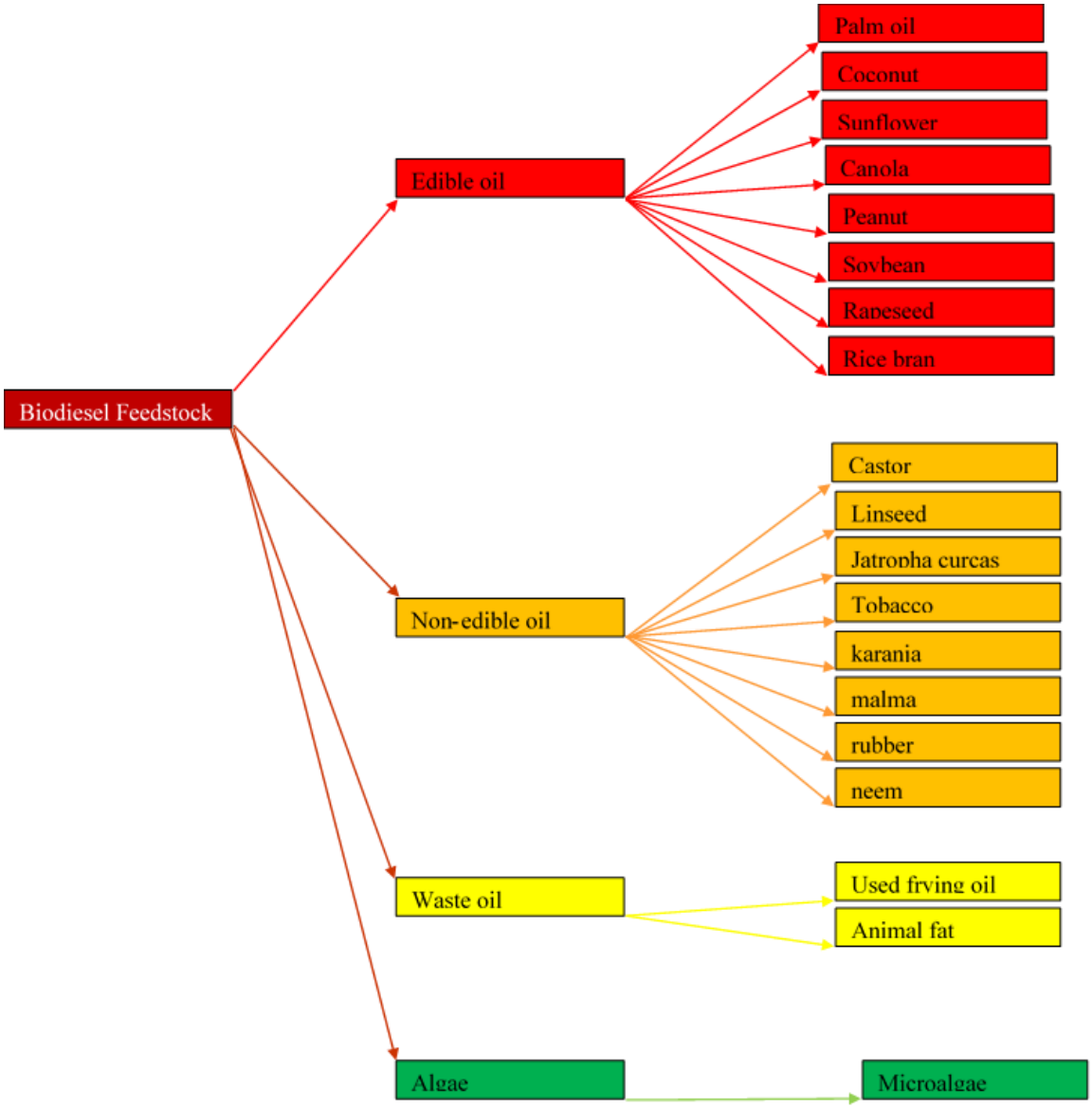


Figure 2.1 Types of biodiesel feedstocks

The primary source of biodiesel in the USA for this moment is soybean oil. Biodiesel from soybeans as feedstock is in enormous amounts; for example, over 55% of different sources utilized to produce the last mentioned, specifically animal fats, canola (rapeseed) oil (10%), corn oil (12%), white grease, i.e., lard (5%), poultry fat (2%) and tallow beef fat (3%) as appeared in figure 2.2b. Furthermore, reused vegetable oil, i.e., utilized cooking oil or yellow grease, has expanded many feedstock contributions to 13% in 2016 (Kim et al., 2018). It is noticed that, although soybean oil remains the most utilized feedstock with over 50% of the overall industry, the use of corn oil in 2013 expanded ten times more than in 2010, and yellow grease expanded six times in six years since 2010 as appeared in figure 2.2a. In both the USA

and EU, practically 80% of biodiesel is produced using vegetable oil. It is an outstanding discussion that soybean, canola (rapeseed), palm, and corn oils that make up most of the biodiesel feedstock are essentially foods, and the use of increasing vegetable oil for fuel may have negative effects on purchasers of these products with expanded nourishment and animal feed costs. Moreover, the EU around the world, representing 47 and 68% of absolute biodiesel production in 2016, separately. As appeared in Figure 2.2a, soybean oil is yet a significant source of biodiesel in the USA, speaking to 55% of absolute biodiesel feedstock contributions in 2016.

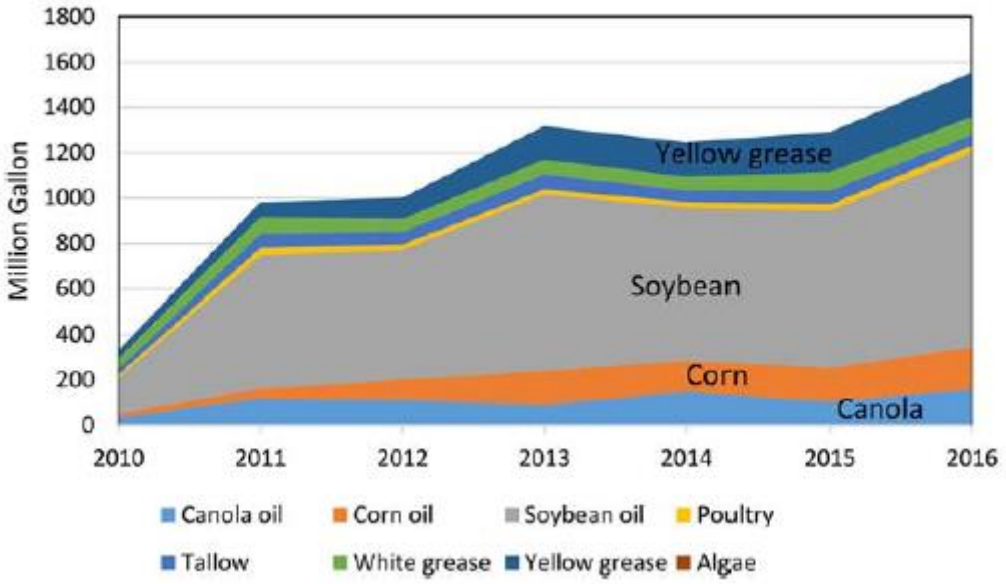


Figure 2.2a Feedstock inputs to US biodiesel production from 2010 through 2016 (Anikeev and Yakovleva, 2013)

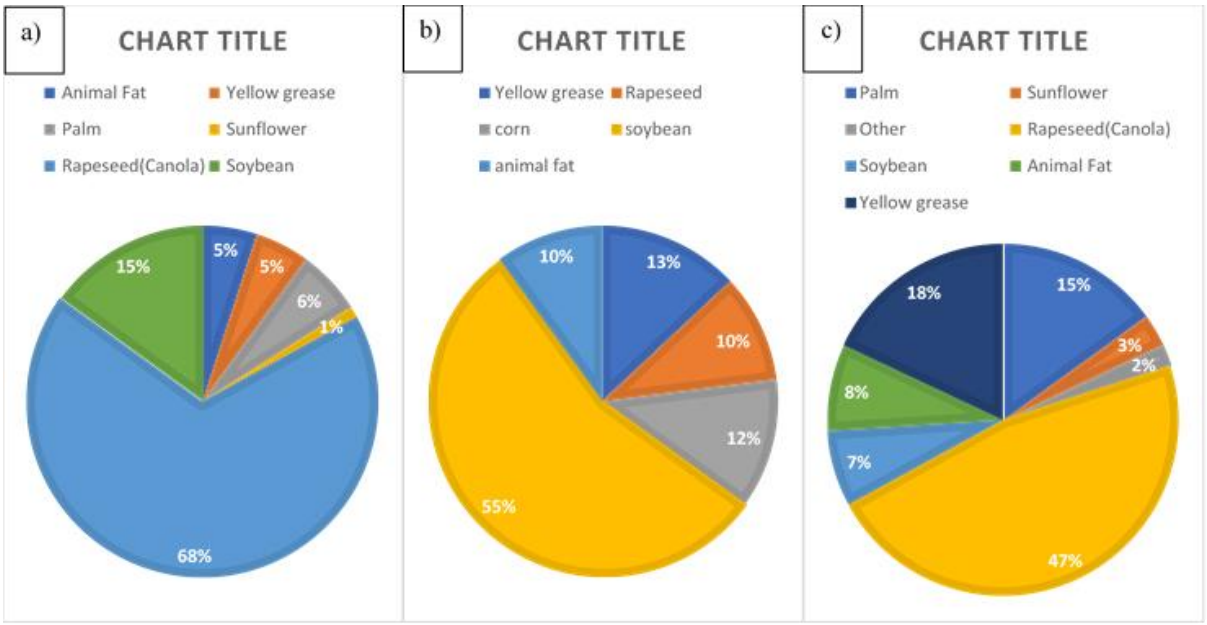


Figure 2.2b Feedstock inputs for biodiesel production. (a) USA (2016), (b) EU (2016), and (c) World (2013) (Kim et al., 2018).

Sunflower oil only comprised 3% of the total biodiesel feedstock in the EU and 1% worldwide in 2016. It is essentially utilized in France and Greece which records 81% of EU sunflower oil-based biodiesel production. According to a market survey (Kim et al., 2018), the feedstock market for biodiesel is in change from the original feedstock, for example, soybean, rapeseed, and palm oil to non-sustenance, lower-cost feedstock, for example, jatropha, castor, used cooking oil, and animal fat. India has developed 60 million hectares of cultivatable land for jatropha generation and plans to supplant 20% of diesel with jatropha-based biodiesel. Another rising feedstock for biodiesel is a hydro-treated vegetable oil created through hydro-treating, a typical procedure in the petroleum industry.

Table 2.1 The principal potential feedstock of biodiesel in many nations

Country	Feedstock	Reference
Argentina	Soybean	(Jayed et al., 2011; Sharma and Singh, 2009)
Belgium	Rapeseed, animal fat	(Jayed et al., 2011; Sharma and Singh, 2009)
Brazil	Soybean, palm, sunflower, castor, cotton, Rapeseed, animal fat, yellow grease, tallow, mustard	(Atabani et al., 2012)
Canada	Jatropha, waste cooking oil, rapeseed	(Atabani et al., 2012)
China	Rapeseed, sunflower	(Atabani et al., 2012)
European Union	Rapeseed, sunflower	(Kim et al., 2018)
France	Rapeseed, animal fat	(Atabani et al., 2012; Sharma and Singh, 2009)
Germany	Rapeseed, sunflower	(Atabani et al., 2012)
Greece	Rapeseed, sunflower, cotton	(Atabani et al., 2012; Panoutsou et al., 2008)
Hungary	Rapeseed, sunflower	(Atabani et al., 2012; Kim et al., 2018; Sharma and Singh, 2009)
India	Jatropha, karanja, soybean, rapeseed, peanut	(Jayed et al., 2011; Sharma and Singh, 2009)
Indonesia	Palm oil, jatropha, coconut	(Atabani et al., 2012)
Ireland	Frying oil, animal fat	(Atabani et al., 2012)
Italy	Rapeseed, sunflower	(Atabani et al., 2012)
Japan	Waste cooking oil	(Atabani et al., 2012)
Latvia	Rapeseed, sunflower	(Kim et al., 2018)
Lithuania	Rapeseed, sunflower	(Kim et al., 2018)
Malaysia	Palm oil, jatropha	(Jayed et al., 2011; Sharma and Singh, 2009)

Mexico	Animal fat, waste cooking oil	(Atabani et al., 2012)
Netherlands	Soybean	(Jayed et al., 2011; Sharma and Singh, 2009)
New Zealand	Waste cooking oil	(Atabani et al., 2012)
Philippines	Coconut, jatropha	(Atabani et al., 2012)
Poland	Rapeseed, sunflower	(Kim et al., 2018)
Singapore	Palm oil	(Atabani et al., 2012)
Spain	Rapeseed	(Grau et al., 2010; Sharma and Singh, 2009)
Sweden	Rapeseed	(Atabani et al., 2012)
Taiwan	Waste vegetable oil, rapeseed	(Huang and Wu, 2008)
Thailand	Palm oil, coconut, waste cooking oil, animal fat	(Phalakornkule et al., 2009)
UK	Waste vegetable oil, rapeseed	(Atabani et al., 2012; Jayed et al., 2011; Sharma and Singh, 2009)
USA	Soybean, waste oil, peanut	(Atabani et al., 2012)
South Africa	Canola, sunflower seeds soybeans	(Pradhan and Mbohwa, 2017)

2.1.2 Basic facts about castor oil

Castor oil is a vegetable oil pressed (extracting strategy) from castor beans (Thomas et al., 2000). Castor oil is a pale yellow to exceptionally colourless fluid with a particular taste and smell. Its boiling point is 313 °C, and its density is 961 kg/m^3 (Sigma Aldrich Co, 2003). Castor oil, a nonedible oil, can assume a major significant role in the development of biorefineries; it is simple to cultivate and has low costs in production (Bart et al., 2010). The subsequent fuel is predominant in cold winters due to its uncommonly low cloud and pours points (Forero, 2005). The immediate utilization of vegetable oils in fuel motors is difficult because of their high viscosity (around 11–17 times higher than diesel fuel) and low volatility, and they do not ignite totally, and form deposits stored in the fuel injector of diesel motors (Demirbaş, 2003). Rapeseed oil, for example, is the dominating feedstock for biodiesel production in the EU, while soybean oil is overwhelming in the USA and Canada (Kinast, 2003). In any case, using oils from edible crops to produce biodiesel is discouraged as deficiencies may emerge over the long run. Developing nations like South Africa cannot bear to utilize edible oils to deliver biodiesel as it would prompt intense sustenance deficiencies. South Africa is honoured with a large group of non-edible oils like castor oils which ought to be exploited. The regular names are castor oil plants and palma christi. It is nonedible as it contains ricin, a toxic protein substance. Castor oil called Ricinus oil (Marter, 1981) contains around 90% of ricinoleic acid. While other vegetable oils have various syntheses of fatty acids and are normally insoluble in alcohol at room temperature, castor oil dissolves effectively in alcohol, ether, glacial acetic acid, chloroform, carbon sulphide, and benzene (Forero, 2005).

2.1.3 The castor oil properties

With respect to other vegetable oils, castor oil has diverse physical and chemical properties, which shift the technique for extracting the oil. The castor oil acquired from cold pressing has low acid and iodine values; also has a somewhat higher saponification value contrasted with the solvent-extracted oil (Ogunniyi, 2006). The typical characteristics and fatty acid composition of castor oil appear in Tables 2.2 and 2.3, respectively. Figure 2.3 represents the equation that displays the castor's oil constitution (Ogunniyi, 2006). The chemistry of castor oil is centred around its high substance of ricinoleic acid; furthermore, the other three points of function exist in the castor molecule. One of the molecule functions is the carboxyl group which can give a colossal and wide scope of esterification. The second is the single point of unsaturation which can be changed utilizing hydrogenation, epoxidation, or vulcanization

procedures. The last molecular function is the hydroxyl group in the castor oil which can be acetylated or alkoxylated possibly; it can be expelled from the oil molecule by utilizing the dehydration procedure to expand the unsaturation of the oil compound to give the semi-drying castor oil by high-temperature pyrolysis and caustic fusion, the hydroxyl position of oil which is so reactive that the molecule can be fragmented to yield a helpful product with shorter chain length. The presence of the hydroxyl group on the castor oil adds stability to the castor oil and anticipates the arrangement of hydroperoxides.

Table 2. 2 Typical characteristics of castor oil (Nangbes et al., 2013)

Properties	**Average result**
Moisture %	0.300 ± 0.01
Density	0.948 ± 0.02
Refractive index @ 28	01.792± 0.01
Fire point (^{o}C)	256.000 ± 1.20
Flashpoint (^{o}C)	225.000 ± 2.10
Smoke point (^{o}C)	215.000 ± 1.00
Viscosity (cps)	0.425 ± 0.12
Colour (TU)	14.000 ± 0.100
P^{H}	5.800 ± 0.100
Turbidity	5.000 ± 1.00
Free fatty acid (FFA) (as % oleic)	7.400 ± 0.07
Acid value (as % oleic)	14.800 ± 0.14
Saponification value (mgKOH/g oil)	180.770 ± 0.32
Peroxide value (Meq/kg)	158.640 ± 3.20
Iodine value (wijj' s value)	58.640 ± 0.71
Extraction yield (%)	48.320 ± 1.85

Table 2. 3 Typical fatty acid composition of castor oil (Nangbes et al., 2013)

Fatty acid	Carbon number	Result (%)
Ricinoleic	18:1	83.97
Palmitic	16:0	0.46
Oleic	18:1	2.28
Linoleic	18:2	0.61
Linolenic	18:3	0.33
Stearic	18:0	0.52
Dihydroxyl stearic	18:0	0.24
		88.41

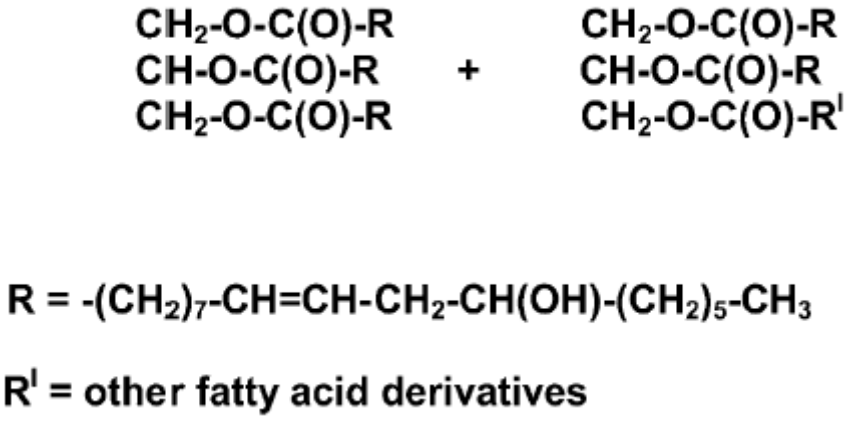


Figure 2.3 Equation showing the constitution of castor oil (Ogunniyi, 2006)

The castor oil comprises mostly of an ester of 12-hydroxy-9-octadecenoic acid (ricinoleic acid); the presence of hydroxyl groups and double bonds make the oil appropriate for some chemical reactions and adjustments. The different reactions of castor oil are given in Figure 2.3. Castor oil is an interesting naturally happening polyhydroxy compound that has restrictions which are hydroxyl and acid values that lessen the storage. The acid and hydroxyl values may change by about 10% if the oil is stored for around 90 days.

2.1.4 Features of castor seeds

The castor plant develops in the wild in enormous numbers in most tropical and subtropical nations. The plant is accessible at a low cost, and it is known to endure changing climate conditions. Typically, the castor plant needs a temperature somewhere between 20 and 26℃ and low humidity throughout the developing season to give the most yield. In addition, the climate conditions for its development limit its cultivation to tropical zones of the developing

world. There are various sorts of castor seeds all around the globe; however, on average, the castor seeds contain around 30 to 55% of oil by weight. The seeds are harmful to people and animals as the seeds contain ricin and certain allergens which are toxic. The impacts of the castor seed are unintentionally ingested, and the unfortunate casualties will confront stomach pain, spewing, and diarrhoea as little as one mg of ricin can carry a human to death. The dread of unintentional ingestion of the harmful castor seed by children does not support the utilization of the castor plant for medicinal reasons. Other than that, the seed cake is toxic and subsequently not reasonable for animal feed; a few people who worked with the meal built up a hypersensitive reaction, for example, asthma. The variety of great or poor seeds does not influence the nature of the seed oil. The oil from castor seed is an inedible oil that can be utilized and free up some edible oils-used in businesses for human utilization. Figures 2.4 a) and b) show castor plants and castor seeds separately.



Figure 2.4 (a) castor plant (b) castor seed

2.1.5 Extraction of castor seed oil

There are numerous approaches to acquiring oil from castor seeds. The extraction of oil from the castor seed is one combination of procedures, for example, mechanical pressing and solvent extraction. The instances of mechanical pressing are hydrated presses and nonstop screw presses. In any case, the best method to acquire the oil from the seed is hot pressing using a hydraulic press followed by solvent extraction (Akpan et al., 2006). In the mechanical pressing, the seeds are crushed to expel them from the shell, and the change in accordance to lower the moisture content by warming in a steam-jacketed vessel or oven. From that point forward, the crushed seeds are put into the hydraulic presses and pressed until they turn into the cake to free the oil. The properties of oil from the mechanical pressing are that the oil has a light colour and low Free Fatty Acid (FFA) (Ogunniyi, 2006). However, about 45% of the oil is obtained

through mechanical pressing, and the remaining oil in the castor cake can be recuperated uniquely using the solvent extraction technique. Throughout the extraction strategy utilizing solvents, for example, heptanes, hexane, and petroleum ether, the seed cakes are removed with the solvent in the soxhlet extractor.

2.1.6 Industrial castor oil

Castor oil has various uses in transportation, beautifying agents, pharmaceutical, and manufacturing industries. For instance, castor oil is utilized in adhesives (Yeadon et al., 1959), brakes, hydraulic fluids (Shough, 1942), caulks, dyes, electrical liquid dielectrics, lubricating greases, machining oils, paints (Razdi, 2012), pigments (Razdi, 2012), refrigeration lubricant, washing powder, sealants, textiles, waxes, leather treatment, etc. Vegetable oils are fascinating because of their great lubricity and biodegradability as they are alluring choices for petroleum-derived lubricants, but vegetable oils have the shortcomings of oxidative stability and low-temperature performance, which limits them across their well-known uses. Unlike other natural vegetable oils, castor oil has better low-temperature viscosity properties and high-temperature lubrication than most vegetable oils. Thus, castor oil is beneficial as the lubricant in jet, diesel, and race motors. Castor oil is likewise utilized in the industry as the feedstock for the generation of various chemical substances, for example, prominently dicarboxylic acid, which is utilized in plasticizers and the manufacture of dioctyl sebacate (a jet lubricant), undecylenic acid (perfume formulation) (Razdi, 2012) and nylon-11.

2.1.7 Castor oil as Biodiesel

The extricated castor oil, known as crude castor oil, is refined, and biodiesel is obtained through the procedure of esterification or transesterification (Canoira et al., 2010). The transesterification procedure hugely takes out the tendency of the castor oils and fats to experience the polymerization and auto-oxidation process. This procedure likewise lessens the consistency of the castor oil with the goal that the castor oil viscosity is about equivalent to the oil diesel viscosity (Valente et al., 2011).

2.2 Biodiesel production

Biodiesel can be produced from an assortment of sources, including vegetable oils, for example, oilseeds (rapeseed, soya bean, canola oil, sunflower oil), animal fats, waste oils, and greases (Van Gerpen, 2005), and most as of late possibly from algae which have higher yields and along these lines present to a lesser extent a risk to nourishment and water security. There are five essential ways for making biodiesel: (i) direct use and blending of vegetable oil (Ma et al., 2004); (ii) use of microemulsions with short-chain alcohols (Nimcevic, 2000); (iii) thermal cracking (pyrolysis) of vegetable oils (Babajide, 2011) and (iv) transesterification of triglycerides catalysed by bases or esterification of fatty acids with alcohols utilizing acid catalysts(H_2SO_4) or solid acid catalysts (Bournay et al., 2005; Kim et al., 2004; Ondrey, 2004) and utilization of enzymes (Hsu et al., 2004; Mittelbach,1990; Saka and Kusdiana, 2001; Shah et al., 2004) (v) catalyst-free processes.

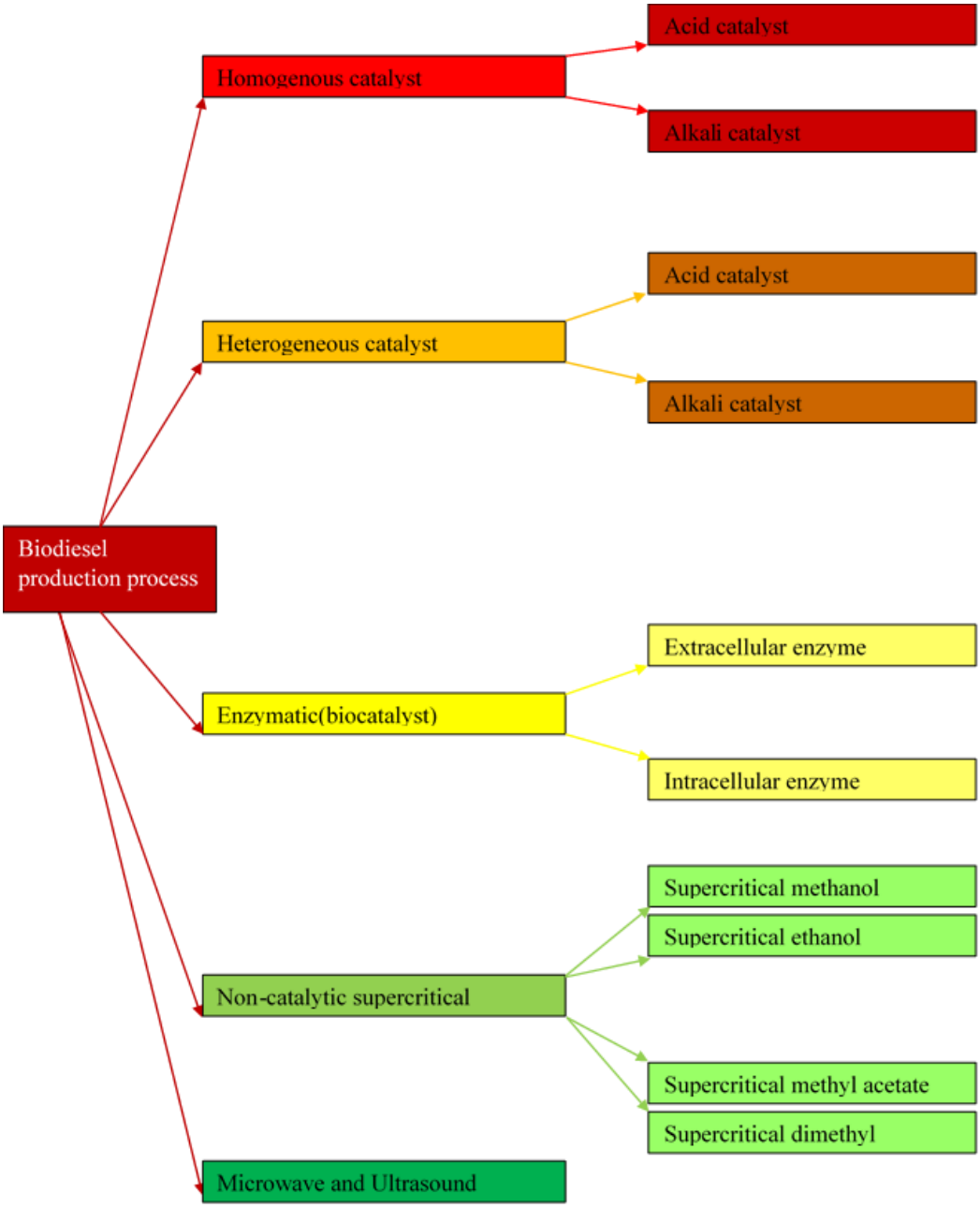


Figure 2.5 Biodiesel production process

2.2.1 Direct use and blending

Vegetable oils might be utilized as fuels or blended with fossil diesel for use in diesel motors. Be that as it may, a few deterrents should be survived, as these oils ordinarily show viscosities ten to twenty times higher than the viscosity of fossil fuel diesel. This quality prompts poor fuel atomization and results in inadequate ignition and the tendency for thermal and oxidative polymerization, prompting the preparation of deposits on the injector nozzles. This must be solved by adjusting the fuel to the motor and the other way around (Srivastava and Prasad, 2000).

Additionally, blending diesel fuel with vegetable oil would require vegetable oil from 0 to 34% if appropriate atomization is to be accomplished (Babajide, 2011). Biodiesel can be utilized in its pure form, otherwise called neat biodiesel or B100. This methodology shows the most decrease in fume particulates, unburned hydrocarbons, and carbon monoxide. It is likewise the ideal approach to utilize biodiesel when its non-poisonous quality and biodegradability are significant. Though neat biodiesel would not be required to cause any operational issues, its solvent properties are most intense. They may cause issues in releasing varnish deposits in fuel tanks and degradation of fuel since certain elastomers are not perfect with biodiesel, such as nitrile rubbers (Babajide, 2011).

2.2.2 Microemulsion

Various derivatives, for example, microemulsions or blends of different vegetable oils with ordinary fuel, have been proposed as alternative fuels for diesel motors. As the arrangement of microemulsions (co-solvency) is one of the four potential answers for tackling the issue of vegetable oil viscosity, and different researchers have considered micro emulsification of vegetable oils with various alcohols and landed at the end that microemulsions of vegetable oils and alcohols cannot be prescribed for long term uses in diesel motors for comparative reasons as connected to neat vegetable oils. The fuels are prone to deficient burning, the development of carbon deposits, and an expansion in the viscosity of the lubricating oil (Babajide, 2011).

2.2.3 Pyrolysis (thermal cracking)

Pyrolysis of fats has a past filled with over a century and has been utilized particularly in regions of the world where there was a non-renewable energy source (Ma and Hanna, 1999). Pyrolysis signifies a thermal decomposition reaction. This treatment results in a mixture of alkanes, alkenes, alka dienes, aromatics, and carboxylic acids; like hydrocarbon-based diesel fuel in numerous regards, however, the cetane number of oils utilized is expanded, and the concentrations of sulphur, water, and sediment for the subsequent products are adequate. Nevertheless, as indicated by present-day measures, the fuel's viscosity is considered excessively high, ash and carbon residues far surpass the qualities of fossil diesel, and the cold flow properties of the subsequent fuel are poor (Knothe and Steidley, 2005). It has likewise been contended that the evacuation of oxygen during this procedure disposes of one of the principal ecological advantages of oxygenated fuels.

2.2.4 Transesterification

Transesterification using a homogenous acid catalyst.

Up until now, hydrochloric acid and sulfuric acid (H_2SO_4) were the most utilized catalysts for the acid-catalysed transesterification process. Related to the alkali-catalysed system, the benefits of this technique are that the acid catalyst can continue esterification and transesterification simultaneously (Jacobson et al., 2008), not sensitive to the presence of FFA in the feedstock (Kulkarni and Dalai, 2006), and can be useful for low-cost lipid feedstocks, for example, waste cooking oil (Canakci and Van Gerpen, 1999). (Zhang et al., 2003) announced that acid catalyst gave better execution when the quantity of FFA in the feedstock is more noteworthy than one wt.%. Figure 2.6 demonstrates the mechanism of the homogeneous acid-catalysed transesterification process for biodiesel production utilizing methanol. This system incorporates the protonation of the carbonyl group by the acid catalyst, nucleophilic attack of methanol to deliver a tetrahedral intermediate compound, proton migration, and breakdown of the intermediate. This sequencing procedure is repeated twice to create biodiesel and glycerol.

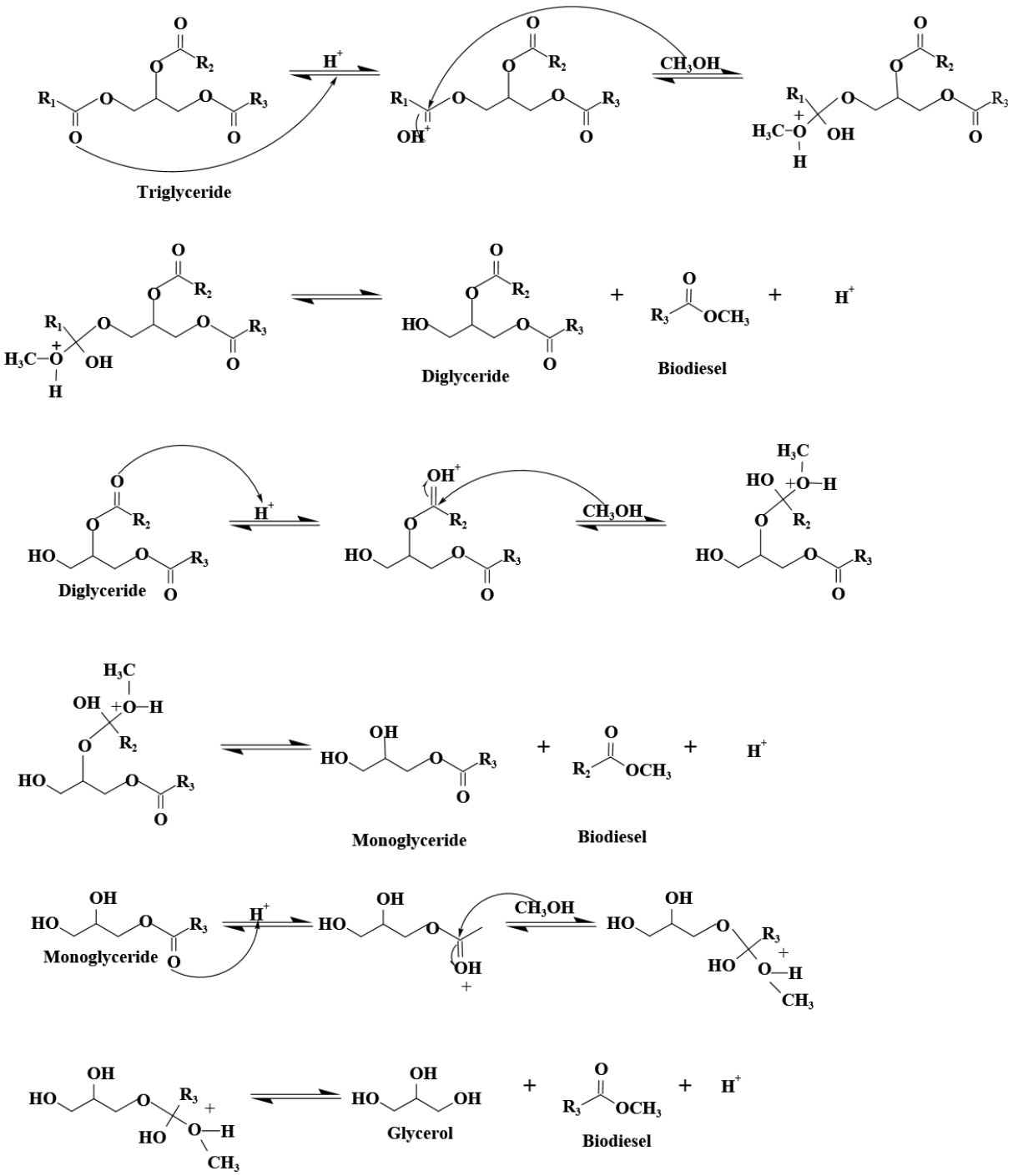


Figure 2.6 Mechanism of homogeneous acid-catalysed transesterification process for biodiesel production utilizing methanol (Farobie and Matsumura, 2015)

Although this catalyst is unresponsive toward the presence of FFAs, this procedure needs progressively extreme operation conditions over alkali-catalysed transesterification. In this way, it is not the potential to be applied for industrial applications. In addition, this procedure needs a high alcohol-to-oil molar ratio, and high temperatures, which takes more reaction time and causes an ecological issue due to corrosion (Goff et al., 2004 and Jacobson et al., 2008). It

was clarified in some past investigations that the transformation of waste cooking oil was accomplished over 90% after 10 hours of reaction time, the expansion of 4 wt.% H_2SO_4, and the methanol-to-oil molar ratio of 1:20 (Wang et al., 2006). (Freedman et al., 1984) additionally examined biodiesel production utilizing H_2SO_4-catalysed transesterification. They saw that 99% oil transformation was acquired inside 69 h reaction time by utilizing one wt.% catalyst and the oil-to-methanol molar ratio of 1:30. These past investigations demonstrated that acid-catalysed transesterification requires extreme reaction conditions for industrial processes.

Transesterification using a homogenous alkali catalyst.

These days, biodiesel is produced utilizing homogeneous alkali-catalysed transesterification because of the way that this procedure guarantees a few points of interest, for example, the catalyst is broadly accessible, the transesterification procedure is performed under a low reaction temperature, high transformation can be accomplished in a shorter time than acid-catalysed transesterification (Fukuda et al., 2001 and Lotero et al., 2005). The most regularly utilized catalysts in this procedure are sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Felizardo et al., 2006; Meher et al., 2006). (Fukuda et al., 2001) distinguished that the homogeneous alkali-catalysed transesterification reaction rate performs 4000 times quicker than the acid-catalysed transesterification process. Nonetheless, this procedure has confinement, for example, delicate to the presence of FFA in the feedstock. (Ma and Hanna, 1999) reasoned that vegetable oil's FFA content should be under one wt.% for the alkali-catalysed transesterification process. When the feedstock contains a huge measure of FFA, saponification will happen because of a reaction between FFA and alkali catalysts, as shown in Figure 2.7. This saponification reaction is unquestionably unwanted since it will deactivate the catalyst to enhance the transesterification process, and the tremendous quantity of soap can hinder the purification of biodiesel and diminish the biodiesel yield (Kulkarni and Dalai, 2006 and Yan et al., 2009).

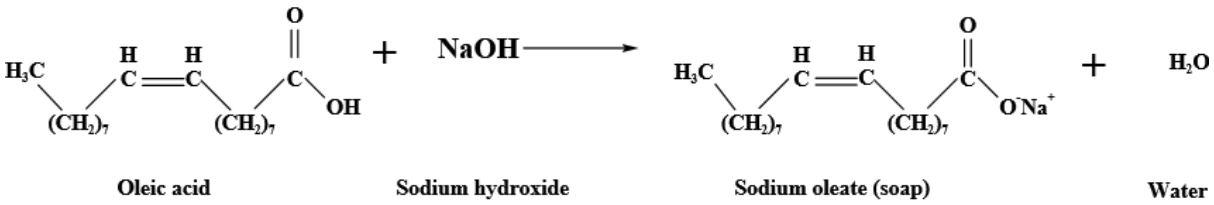


Figure 2.7 Saponification as a result of the reaction between oleic acid and sodium hydroxide (Farobie and Matsumura, 2015)

Another deficiency of the alkali-catalysed transesterification procedure is that this reaction is sensitive to the presence of water since it can hydrolyse triglycerides to shape diglycerides and FFA, as appeared in Figure 2.8. Along these lines, in industrial application, the FFA and water content of the feedstock must be carefully kept up to get high-quality biodiesel.

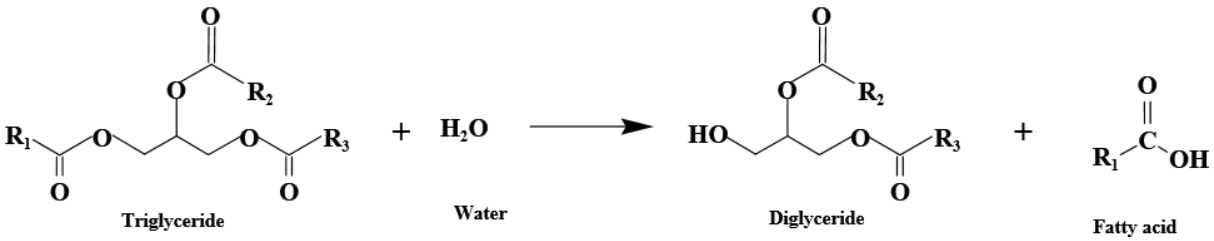


Figure 2.8 Hydrolysis of triglyceride to produce diglyceride and fatty acid (Farobie and Matsumura, 2015)

Figure 2.9 demonstrates the mechanism of a homogeneous alkali-catalysed transesterification process for biodiesel production utilizing methanol. This mechanism involves the formation of methoxide, nucleophilic attack of methoxide to a carbonyl group on triglycerides, framing a tetrahedral intermediate of the compound, breakdown of the intermediate, and recovery of the catalyst. This sequencing procedure is rehashed twice in which in the first reiteration, biodiesel and monoglyceride are developed, and biodiesel and glycerol are in the second reiteration.

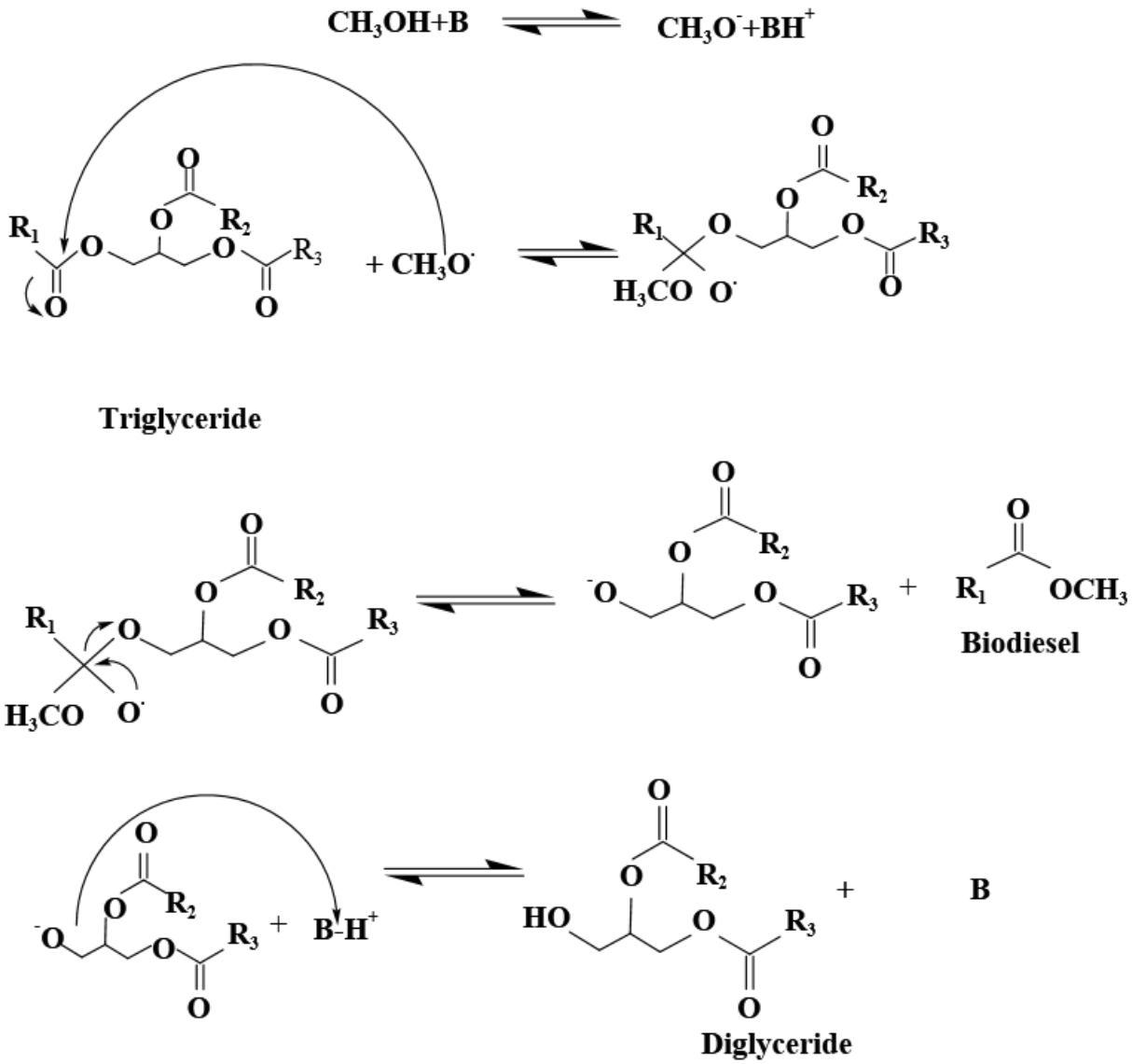


Figure 2.9 Reaction mechanism for homogeneous alkali-catalysed transesterification of triglyceride (Farobie and Matsumura, 2015).

Heterogeneous acid-catalysed transesterification

Despite the fact that heterogeneous acid-catalysed transesterification has lower action, this technique has been applied for industrial procedures because of certain reasons, for example, the capacity to catalyse both esterification and transesterification process at the same time, the catalyst is less lethal and destructive than a homogeneous acid catalyst, insensitive toward FFA content, dispose of the washing stage of biodiesel, contain a group of acid locales with various quality of Bronsted or Lewis acidity, the simple partition of the catalyst from the reaction medium, resulting in lower product contaminant, simple recovery and reusing of catalyst (Jitputti et al., 2006; Kulkarni and Dalai, 2006; Patil and Deng, 2009). Be that as it may, the heterogeneous acid-catalysed transesterification additionally has the downside of more

reaction time and possible undesirable side reactions. Some heterogeneous acid catalysts that have been used to produce biodiesel are zirconium oxide (ZrO_2), tin oxide (SnO_2), titanium oxide (TiO_2), zeolite, and sulfonic ion exchange resin plus Amberlyst-15, Amberlyst-35, and Nafion-NR50. Among these solid catalysts, Nafion-NR50 gave higher selectivity to deliver biodiesel and glycerol considering its acid quality (Antunes et al., 2008). In time, it has a restriction because of its costly and lower activity than a liquid acid catalyst (Farobie and Matsumura, 2015). A few analysts have utilized zirconium oxide (ZrO_2) as a heterogeneous acid catalyst for biodiesel production because of its strong surface acidity. This catalyst is regularly utilized by impregnating with an acidic solution, for example, H_2SO_4 to form sulphated zirconia, SO_4^{2-}–ZrO_2 (Miao and Gao, 1997) or by consolidating with alumina, Al_2O_3 to move toward becoming ZrO_2–Al_2O_3 or even with tungsten oxide (WO_3). There is an alternate activity while this catalyst was applied with or without impregnation. It was accounted for in the past investigation that when this catalyst impregnated with H_2SO_4 (SO_4^{2-}–ZrO_2), the yield of biodiesel after transesterification of palm kernel oil and crude coconut oil could be accomplished as high as 90.3 and 86.3%, distinctly. In the interim, when this catalyst was not impregnated, 64.5 and 49.3% of biodiesel were accomplished for the transesterification of palm kernel oil and unrefined coconut oil respectively (Jitputti et al., 2006). Accordingly, it could be affirmed that altering metal oxide surface activity is the key point to acquiring a high biodiesel yield. Other than that, (Jacobson et al., 2008) found that the blend of this catalyst with alumina and tungsten oxide (ZrO_2–Al_2O_3–WO_3) could upgrade the mechanical strength and acidity of the catalyst.

Figure 2.10 demonstrates the proposed reaction mechanism of SiO_2/ZrO_2-catalysed transesterification for biodiesel production utilizing methanol. At first, carbonyl oxygen from triglyceride attacks zirconium to produce an intermediate compound. The intermediate compound is then attacked by methanol, forming another C-O bond. In conclusion, rearranging the intermediate compound outcomes in biodiesel and catalyst. As referenced already, this catalyst is reusable.

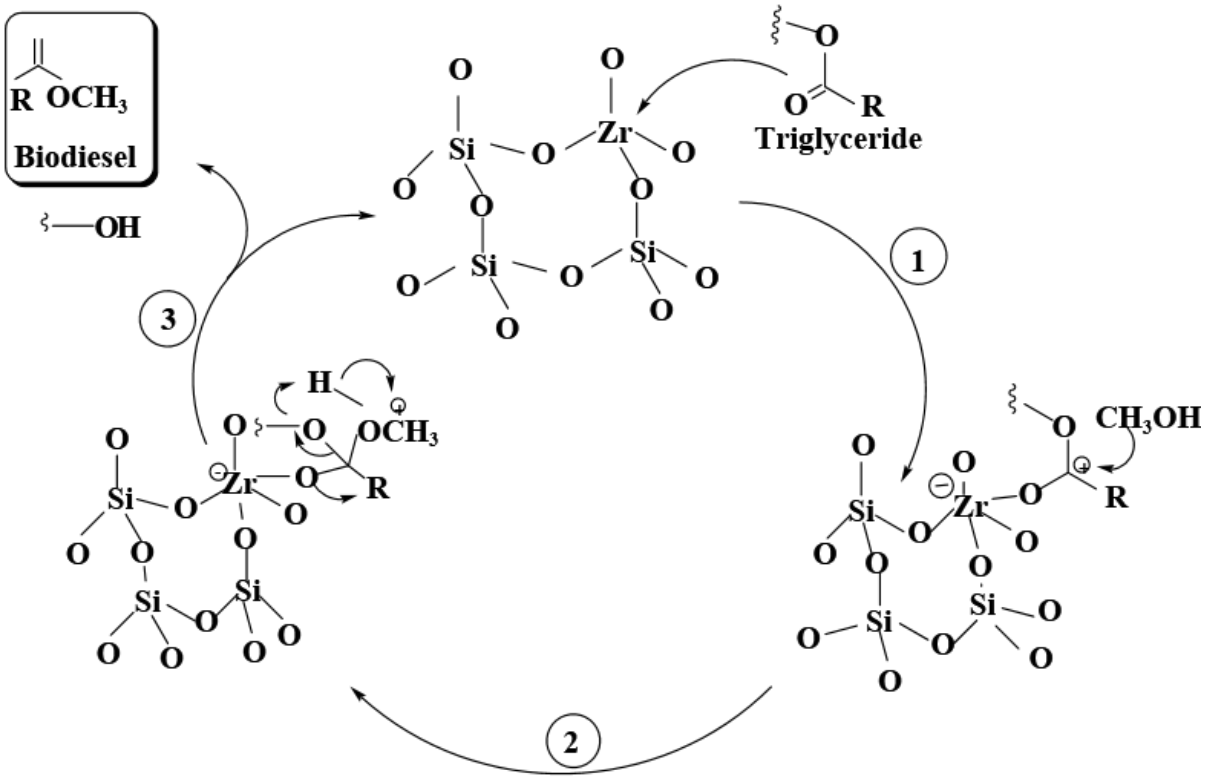


Figure 2.10 Proposed reaction mechanism of SiO_2/ZrO_2-catalysed transesterification adapted from (Farobie and Matsumura, 2015)

Tin oxide (SnO_2) also has been used as a heterogeneous acid catalyst for biodiesel production, but the study about this is still limited since the preparation method of this catalyst is complicated. The usage of this catalyst is almost the same as ZrO_2 in which this catalyst must be impregnated with a strong acid such as H_2SO_4 to form SO_4^2-SnO_2. (Furuta et al., 2004) deduced that the acid strength of SO_4^2-SnO_2 is higher than that of SO_4^2-ZrO_2. Thus, for the esterification of n-octanoic acid with methanol at a temperature below 150°C, the catalytic activity of SO_4^2-SnO_2 was observed more superior than that of SO_4^2-ZrO_2. However, since the pre-treatment of this catalyst is complicated due to the difficulty in obtaining oxide gels from its salt, this catalyst is rarely used for biodiesel production (khder et al.,2008 and Matsuhashi, 2001).

Another heterogeneous acid catalyst at any point utilized for biodiesel production is titanium oxide (TiO_2). Even though the investigation about the usage of this catalyst for biodiesel production is yet constrained, this metal oxide catalyst has great acidic properties. (Chen et al.,2007) announced that the transesterification of cotton oil by utilizing SO_4^2-/TiO_2 and SO_4^2-/ZrO_2 is relative to the surface area. It was discovered that biodiesel yields of 90 and 85% were produced for the transesterification of cotton oil utilizing SO_4^2-/TiO_2 with a surface area of

99.5 m^2/g and utilizing SO_4^{2-}/ZrO_2 with a surface area of 91.5 m^2/g, separately. Although this catalyst still has a deficiency, for example, this catalyst requires progressively serious reaction conditions (high reaction temperature of 230 °C) over homogeneous ones. (De Almeida et al., 2008) observed that a FAME yield of 40% was obtained after transesterification for one hour at 120 °C. It was observed that the surface area of the catalyst expanded to 258 m^2/g by adding SiO_2 to SO_4^{2-}/TiO_2. The ideal yield of biodiesel (90%) was accomplished at 200 °C, with catalyst loading of 3 wt.%, and the oil-to-methanol molar ratio of 1:9, after a three-hour reaction time.

Zeolite has likewise been utilized as a heterogeneous acid catalyst for biodiesel production in past research since it contains silicon (Si), aluminium (Al), and oxygen (O) in its structure. The profitability of biodiesel production utilizing zeolite is that this catalyst can be acquired naturally, and cheaply, and the acid quality can be constrained by modifying the aluminosilicate structure. Be that as it may, as per (Kiss et al., 2006), this catalyst has low action in the transesterification process because of the diffusion constraint of massive reactants; for this situation, triglyceride into the microporous structure of the zeolite. It was found by (Brito et al., 2007) that the biodiesel yield was obtained at about 26.6% for transesterification of waste cooking oil at a high reaction temperature of 460 °C, after 22 min reaction time, and the oil-to-methanol ratio of 1:6. In an ongoing report, (Kusuma et al., 2013) informed that to improve the action of zeolite, the KOH ought to be included. It was observed in their investigation that the most astounding yield of biodiesel (95.09%) was obtained at 60 °C, impregnation of zeolite with 100 g/100 mL KOH, palm oil-to-methanol molar ratio of 1:7, the addition of catalyst of 3wt%, after two hours reaction time. They likewise proposed a reaction mechanism for transesterifying triglycerides utilizing KOH-impregnated zeolite catalysts, as shown in Figure 2.11. The reaction mechanism is nearly equivalent to homogeneous alkali-catalysed transesterification. At first, the reaction between an active site of the catalyst (K_2O) with methanol results in methoxide ion (CH_3O^-). This methoxide ion attacks the carbonyl carbon of triglycerides, framing the tetrahedral intermediate compound. This intermediate compound, at that point, modifies to produce diglyceride anion and biodiesel. The diglyceride ion is formed from the reaction between H^+ and diglyceride anion. Other than that, there is a probability of a reaction between diglyceride anion with methanol to produce diglyceride and methoxide anion. This procedure will again happen twice.

Aside from that, sulfonic ion exchange and sulfonic-adjusted mesostructured silica have likewise been used as heterogeneous acid catalysts for biodiesel production. Amberlist-15,

Amberlist-35, Amberlist-15 DRY, and Nafion SAC-13 are the normal kinds of sulfonic ion exchange and have been utilized by certain scientists (Chang and Bae, 2011; de Rezende et al., 2008; Mo et al., 2008). The benefits of utilizing such sort of catalyst for biodiesel production are that this catalyst gives brilliant catalytic action in the esterification reaction. Nevertheless, the inadequacies of the biodiesel production procedure utilizing this catalyst, as revealed by (Lotero et al., 2005), are: Catalyst gives a low performance in the transesterification process; this type of catalyst requires a very high oil-to-alcohol molar ratio; it has low thermal stability and becomes unstable at a temperature above 140 °C; it needs a high reaction temperature (150-200 °C) to achieve a fast reaction rate.

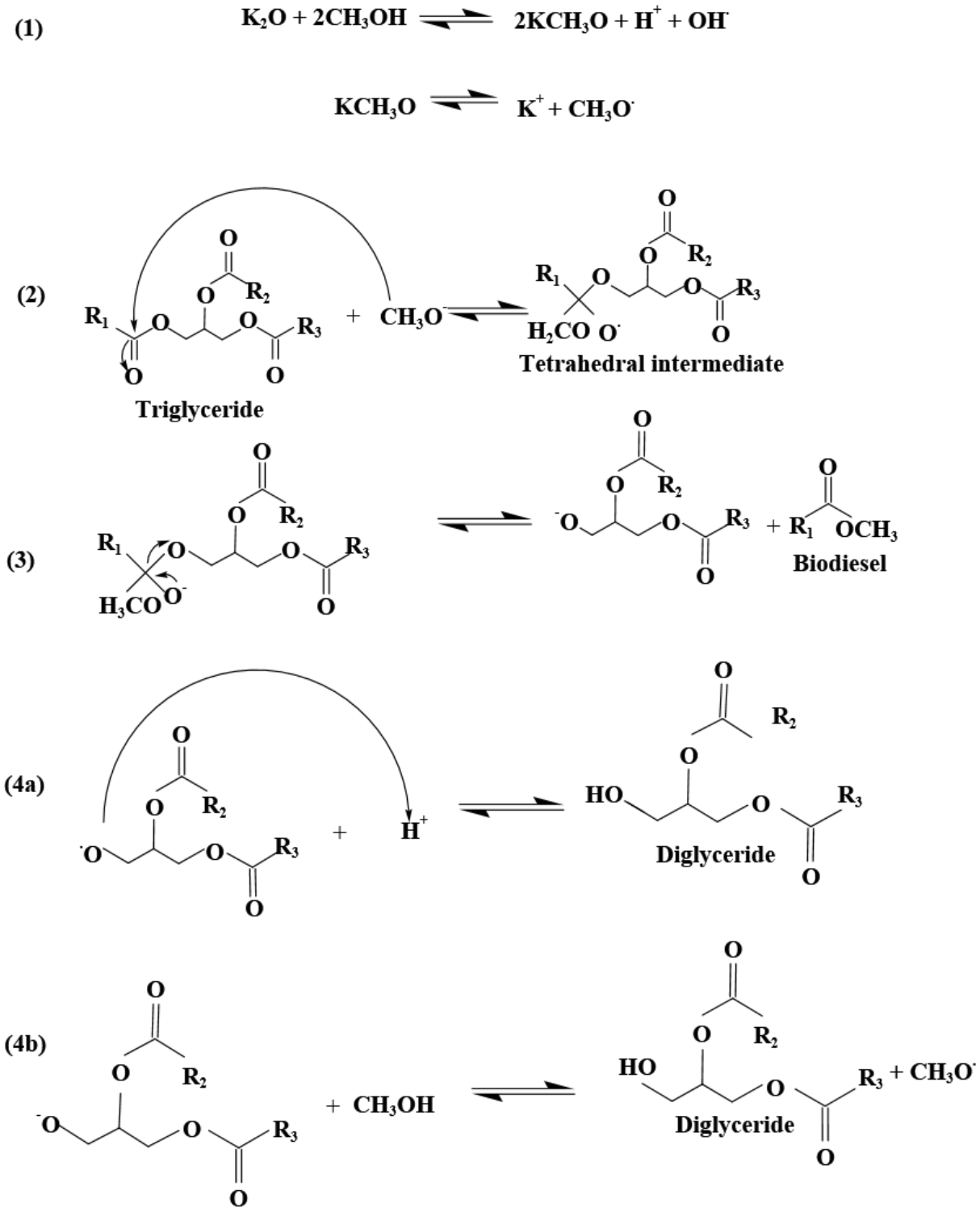


Figure 2.11 Proposed reaction mechanism for transesterification of triglycerides using KOH-impregnated zeolite catalyst adapted from (Kusuma et al., 2013)

Furthermore, (dos Reis et al., 2005) advised that to increase the biodiesel yield, the oil-to-methanol molar ratio ought to be expanded. The biodiesel yield of 80% was accomplished at 60℃ and the oil-to-methanol molar ratio of 1:100 after 8 hours of reaction time. In any case, the utilization of the catalyst for biodiesel production is yet constrained since there is a

probability of accumulation of the organic compound on the catalyst surface that can repress the active site. A recent study (Gutiérrez-Ortega, et al., 2019) reported that the use of catalyst-type mixed metal oxides with different compositions and Co/Fe ratios were obtained from layered double hydroxides to be used as heterogeneous catalysts in the production of biodiesel. Their conditions for obtaining biodiesel were optimized by selecting the catalyst and varying the percentage of catalyst, the methanol/oil ratio, and the reaction time. The catalysts reached yields of conversion to biodiesel of up to 96% in 20 min of reaction using only a 2% catalyst. The catalyst that showed the best catalytic activity contains a mixture of predominant crystalline and amorphous phases of $CoFe_2O_4$ and $NaxCoO_2$. The results suggest that cobalt is a determinant in the activity of the catalyst when forming active sites in the crystalline network of mixed oxides for the transesterification of triglycerides, with high conversion capacity and selectivity to biodiesel.

Heterogeneous alkali-catalysed transesterification

Heterogeneous alkali-catalysed transesterification was historically expected to have the option to defeat the issue faced in homogeneous alkali-catalysed transesterification. There were numerous points of interest when heterogeneous alkali-catalyst was utilized for biodiesel production. Some of them are (i) the catalyst is reusable, (ii) more environmentally considerate than homogeneous alkali-catalyst, (iii) the catalyst can be synthesized from cheap sources, for example, limestone or calcium hydroxide, (iv) the quantity of alkali wastewater is only a few, and (v) the activity of this catalyst is nearly equivalent with a homogeneous one, at the equivalent working condition (Kim et al., 2004). Nevertheless, this strategy is yet confronting a few constraints, for example, (i) catalysts should be activated through the calcination procedure utilizing high temperature, (ii) the reaction rate is more than the homogeneous alkali catalyst technique, and (iii) side the reaction is plausible because of reaction among catalyst and glycerol to produce calcium di-glyceroxide (Kouzu et al., 2008a) as appeared in Figure 2.12.

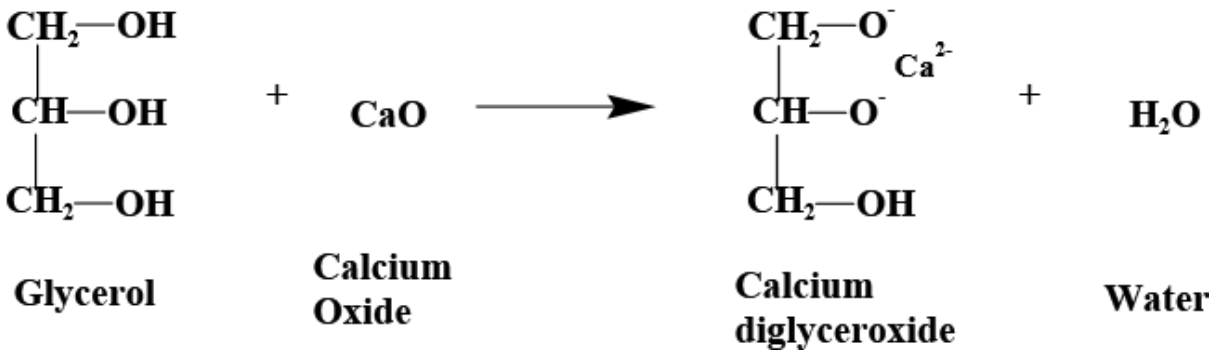


Figure 2.12 The reaction between glycerol and calcium oxide-forming calcium di-glyceroxide and water (Kouzu et al., 2008a)

Some heterogeneous alkali catalysts that were formerly utilized for biodiesel production are calcium oxide (CaO), magnesium oxide (MgO), strontium oxide (SrO), and hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$). As indicated by (Zabeti et al., 2009), calcium oxide is the most appealing heterogeneous alkali-catalyst attributable to low solubility in methanol and the strongest basic activity over alkaline earth metal oxide. In the past examination by (Kouzu et al., 2008b), it was seen that a biodiesel yield of 93% was found after a one-hour transesterification process at methanol reflux temperature with the oil-to-methanol ratio of 1:12 utilizing CaO catalyst, which was earlier acquired from calcination of pummelled limestone ($CaCO_3$) at 900 °C for 1.5 h. Furthermore, (Kazembe-Phiri et al., 2010) likewise saw that a biodiesel yield of 88.81% was acquired for the transesterification of groundnut after two hour transesterification reaction time with an oil-to-ethanol molar ratio of 1:9 utilizing one wt.% CaO catalyst calcined at 900 °C for 1.5 h. Then, (Di Serio et al., 2006) found that a FAME yield of just 20% was obtained after the transesterification of soybean oil at 100 °C. The previous examination approved that the activity of MgO is much lower than that of CaO. To upgrade the activity of MgO, (Xie et al., 2006) informed that the blended magnesium-alumina (Mg-Al) oxide calcined at high temperature and utilizing hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$) as a precursor could play out the helpful activity. It was discovered that a FAME yield of over 90% was obtained by utilizing magnesium-alumina oxide as a catalyst despite utilizing high reaction temperature (Di Serio et al., 2006). Figure 2.13 indicates the reaction system for CaO-catalysed transesterification of triglycerides utilizing methanol as a reactant. This reaction system is following a few stages: (i) the development of methoxide ion because of the idea of taking a proton from methanol by the essential site of CaO, (ii) methoxide anion at that point attacks the carbon atom of carbonyl functional group in a triglyceride compound to produce alkoxy carbonyl intermediate compound, (iii) modification

of alkoxy carbonyl intermediate outcomes in the more steady compound comprised of biodiesel and diglyceride anion, and (iv) calcium hydroxide cation is then attacked by diglyceride anion shaping diglyceride and CaO. As appeared in this figure, the catalyst is gotten again after the procedure. Also, this reaction mechanism is ceaselessly rehashed twice until biodiesel and glycerol are produced.

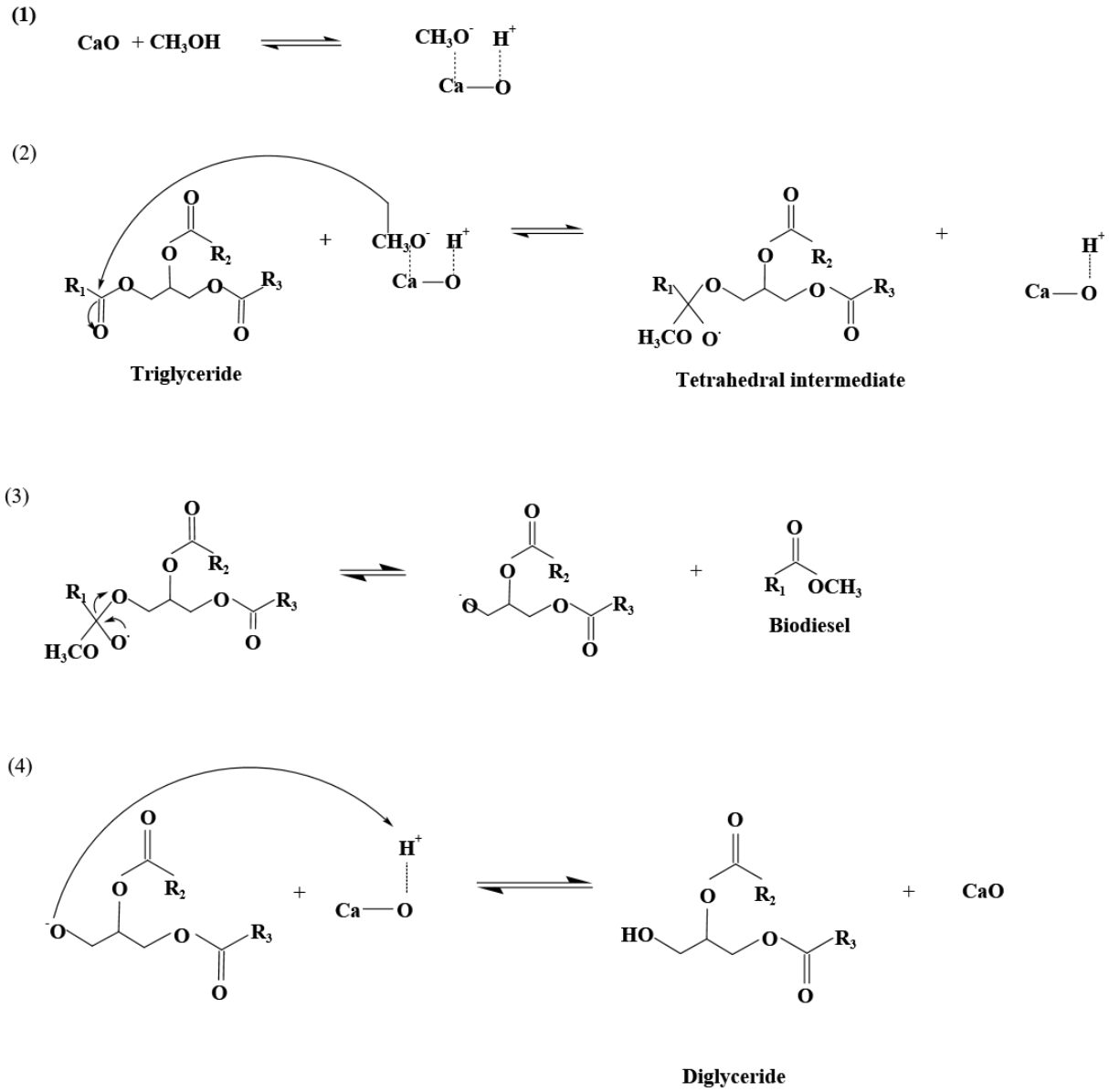


Figure 2.13 Reaction mechanism for heterogeneous alkali-catalysed transesterification of triglyceride (Farobie and Matsumura, 2015)

Enzymatic-catalysed biodiesel production

Because of the downsides related to wastewater treatment, environmentally unpleasant procedures, and troubles to recuperate glycerol from the catalyst faced by chemicals-catalysed

transesterification, a few analysts have proposed a green technique to produce biodiesel by utilizing the compound as a catalyst, also known as biocatalyst.

Production of biodiesel based on catalyst obtained from industrial waste.

Waste resulting from industrial processes and the surrounding environment can assist in the development of a low-cost solid base catalyst. These catalysts can promote a sustainable and environment-friendly approach toward biodiesel production (Majhi and Ray, 2016; Pandit and Fulekar, 2017). Calcium-enriched waste products, namely, shells of mussels, eggs, cockles, snail, and oyster; fish scales; animal bones; and ash resulting from plant species, etc. are easily accessible at low cost (Marwaha et al., 2018). Calcium found from these waste materials could be transformed into CaO, which is the most useful heterogeneous base catalyst. (Yasar 2019) worked on the catalytic activity of waste-eggshell-based CaO and compared it to pure CaO. Transesterification of rapeseed oil was carried out at 9:1 M methanol/oil ratio, 4 wt.% catalyst, and 60◦C reaction temperature for one hour. The maximum yield for these conditions was 96.81 and 95.12% for CaO and waste-eggshell-based CaO, respectively. (Sirisomboonchai et al. 2015) worked on the catalytic activity of calcined scallop shell in the transesterification of waste cooking oil utilizing methanol, a yield of 86% was observed in the presence of a small quantity of water with 5 wt.% catalyst loading, 6:1 M methanol/oil ratio, and 65◦C reaction temperature for two hours. Also, (Yusuff et al., 2019) investigated that anthill-eggshell-Ni-Co mixed oxide composite catalyst for biodiesel production from waste frying oil. They prepared the anthill-eggshell-Ni-Co catalyst by harvesting anthill in lump form and manually pulverized by mortar and pestle. They crushed and sieved the anthill through a mesh of 0.3 mm to obtain particles with a size of less than 0.3 mm. They dried the fine anthill powder in an oven at 105 °C for four hours to remove moisture content. Then, they washed the chicken eggshell thoroughly to remove the white membrane and impurities and then heated it up at 110 °C in an oven overnight to remove the water. After that, they mixed cobalt nitrate hexahydrate Co $(NO_3)_2.6H_2O$, nickel nitrate hexahydrate Ni $(NO_3)_2 \cdot 6H_2O$ together with anthill as well as chicken eggshell to obtain the anthill-eggshell-Ni-Co. They found that the maximum FAME yield of 90.23% was obtained under the optimal reaction conditions of 3 wt.% catalyst loading, 12:1 methanol/WFO molar ratio, the reaction time of two hours, and 70 °C reaction temperature. Also, (Niju et al., 2014) obtained CaO with high activity by using eggshell which was subject to calcination-hydration-dehydration treatment. They have compared the performance catalyst activity between the CaO generated from calcination-hydration-dehydration treatment and CaO commercial via transesterification of waste frying oil. Their

results showed that the methyl ester conversion was 67.57% for commercial CaO and it was 94.52% for CaO obtained from the calcination-hydration-dehydration treatment of eggshell at a 5 wt.% catalyst (based on oil weight), methanol to oil ratio of 12:1, a reaction temperature of 65 ℃ and a reaction time of one hour. (Hu et al., 2011) observed that calcination of mussel shell at 900 °C followed by impregnation in deionized water and calcination at 600 °C for three hours activates the catalyst with porous honeycomb structure. As per the results, the variables, catalyst concentration, and molar ratio (methanol/oil) positively affected the yield, with the former having a larger impact. A yield of over 90% was obtainable with a molar ratio of 12:1, catalyst amount of 5 wt.%, and reaction temperature of 70 °C in 1.5 h time.

2.3 Transesterification via ultrasound-assisted and microwave processes

The microwave-helped procedure can also be used to produce biodiesel. The benefits of this strategy incorporate short reaction time and are more ecologically friendly than the traditional heating procedure. In any case, this technique likewise has numerous imperatives involving high energy consumption, chemical catalysts required, challenges in scale-up due to unsafe tasks, the high temperature needed, and sensitivity to FFA and water of the feedstock because of reaction with a catalyst. Up to this point, this innovation cannot be utilized for commercial applications.

In recent years, several researchers have experimented on biodiesel production in laboratories using a microwave-helped transesterification process. (Leadbeater and Stencel, 2006) noted that a 98% biodiesel yield is at the maximum when produced at 323 K in the presence of 5% NaOH or KaOH under 25 W microwave release power and the oil-to-methanol molar ratio of 1:6 for 1 min. Likewise, (Azcan and Danisman, 2008), considering KOH as a catalyst, found that the optimum conversion to biodiesel, which was 93.7%, was accomplished in the presence of 1% KOH at 313 K, for a reaction time of 1 min. Further in the year, (Refaat et al., 2008) studied transesterification, considering KOH as a catalyst as well. They demonstrated that biodiesel production progressed faster, in a time of 2 min in microwave irradiation relative to the traditional method of 60 min. After a year, (Zu et al., 2009) witnessed that the highest yield of biodiesel which was 96% from yellow horn (*Xanthoceras sorbifolia Bunge*) oil, was attained at 60℃, 500 W power microwave irradiation, the oil-to-methanol molar ratio of 1:6, and one wt.% catalyst for 6 min. Lately, this method has been necessary to obtain biodiesel from microalgae (*Nannochloropsis*) by direct conversion. (Koberg et al., 2011) discussed that direct transesterification via microwave irradiation delivered a higher biodiesel yield of 37.5% relative to that of the sonication method of 20.9% within a reaction of 5 min for both methods.

Aside from that, for more than twenty years, sonochemistry has been produced as a growing research area. The ultrasonic field is known to produce chemical and physical impacts that emerge from the breakdown of cavitation bubbles. Low-frequency sonication can be used to deliver emulsions from immiscible liquids. This effect could be utilized for biodiesel production as the mixing intensity or disturbance is an important parameter that must be well thought out during the formation of biodiesel because of the way that oil and alcohol are immiscible. The utilization of ultrasonication additionally gives a promising option in contrast to the utilization of ordinary transesterification (Babajide et al., 2010).

Past studies have shown that the utilization of ultrasound gives the mechanical energy to mix, and the appropriate energy needed for starting the transesterification process. One noteworthy issue in the transesterification of oils utilizing methanol is the point that the alcohol is a poor solvent for fatty materials, in this way, the requirement for homogenization of the reaction mixture (Babajide et al., 2010). Since this reaction can just happen in the interfacial region between the liquids and because of the way that fats and alcohols are not miscible, transesterification is a moderately slow procedure.

Subsequently, complete mixing is needed to expand the area of contact between the two immiscible phases, and in this manner, to produce an emulsion. The forceful mixing of the components is one strategy for homogenization which has been discovered rewarding for both batch and continuous processes. The use of low-frequency ultrasonication to mount emulsions of oils and alcohols has been accounted for widely in writing (Babajide et al., 2010; Gogate and Pandit, 2005; Ji et al., 2006; Stavarache et al., 2007).

Research reports demonstrate that low-frequency ultrasound is effective, efficient, and financially useful, offering a lot of favourable outcomes over ordinary procedures. Reaction time is decreased significantly; the static separation time is diminished surprisingly, and yields are commonly higher (Refaat et al., 2008; Stavarache et al., 2007); (Lifka et al., 2004; Ji et al., 2006) both concentrated the impact of mechanical stirring, ultrasonication, and hydrodynamic cavitation on methyl ester yields in the alkali KOH transesterification of soybean oil utilizing methanol with oil to alcohol molar ratio of 6:1 at a temperature of 45 °C and revealed that ultrasonication gave the briefest reaction time and most astounding yield, while mechanical stirring gave the shortest reaction time and the least yield.

(Okitsu et al., 2010) likewise contemplated the alkaline transesterification utilizing KOH for a sequence of vegetable oils by means of mechanical stirring and ultrasonication processes and

reasoned those yields in the two cases were the same. Production of biodiesel under ultrasonic processing has the accompanying points of interest, decrease in preparing time, the measure of alcohol, catalyst amount, separation time, and reaction temperature as uncovered in the studies led in this examination work.

2.4 Biodiesel production in supercritical methanol (SCM)

As referenced beforehand, biodiesel production in SCM was initially examined by (Saka and Kusdiana, 2001) utilizing a batch-type reactor. They presumed that the discoveries could answer the issue faced by chemical-catalysed and enzymatic-catalysed transesterification where biodiesel could be produced in a faster reaction time without the adding of any catalysts and less complex separation and purification in the downstream procedure.

After a year, (Demirbas, 2002) affirmed what Saka and associates found. He linked biodiesel production between conventional and noncatalytic supercritical methods utilizing six vegetable oils, i.e., cottonseed, hazelnut portion, poppy seed, rapeseed, safflower seed, and sunflower seed. He likewise has seen that non-catalytic biodiesel production in SCM is better than the traditional method regarding the reaction time required to produce biodiesel. (Kusdiana and Saka, 2001) at that point clarified the reaction conduct of FFA under SCM conditions with no catalysts. They observed that FFA was effectively changed to biodiesel at a temperature of 350 °C, and complete conversion to biodiesel was found to be above 95%. This recent discovery demonstrated that noncatalytic biodiesel production via supercritical conditions could be used for a wide range of feedstocks and waste cooking oil and fats, which have high FFA.

In 2004, the impact of water on biodiesel production in SCM was likewise found by the equivalent researchers (Kusdiana and Saka 2004). They noticed that the water did not influence such a great amount of biodiesel yield. Then, a specific amount of water in the system could improve the production of biodiesel. They proposed that this water will hydrolyse triglyceride into FFA and glycerol, yet FFA then reacts with methanol to produce biodiesel. In addition, biodiesel under supercritical conditions has additionally been synthesized utilizing bio-methanol produced from wood gasification (Isayama and Saka, 2008). This bio-methanol consists of a few impure substances, for example, ethanol, 1-butanol, methyl formate, water, and di-isopropyl ether. They affirmed that the transformation to biodiesel was obtained with ethanol, 1-butanol, and methyl formate, while no change was made with di-isopropyl ether. Due to the recent discovery of biodiesel production-based SCM conditions that were effective. This methodology has attracted numerous researchers to direct a trial using it by means of

different feedstocks. (Song et al., 2008) researched biodiesel production in SCM utilizing a batch reactor and RBDPO (Refined Bleached Deodorized Palm Oil) as a feedstock. They found that the biodiesel production rate escalated significantly under supercritical conditions; however, the FAME yield diminished over a temperature of 350 °C because of the thermal decomposition of RBDPO or biodiesel. A similar derivative of palm oil was likewise utilized as a feedstock for biodiesel production in SCM by (Tan et al., 2009). They analysed that over 70% biodiesel yield was obtained by utilizing noncatalytic SCM technology within a reaction time of 20 min. Furthermore, (Kasim et al., 2009) found biodiesel formation from low-cost materials, for example, rice, wheat, and dewaxed degummed rice bran and oil (DDRBO), oil utilizing carbon dioxide as a co-solvent. They announced that in *situ* transesterifications of rice bran with SCM via an experimental state of 30 MPa, at a temperature of 300 ℃ and reaction time of 5 min was not a promising path because of the low biodiesel yield of 51.28%. Jatropha curcas and linseed have likewise been utilized as feedstock for noncatalytic biodiesel production utilizing supercritical fluid reactive extraction. They observed that an ideal oil extraction effectiveness of 105.3 and FAME yield of 103.5wt% were seen at a reaction temperature of 300 °C, 240 MPa, 2.5 ml/g of n-hexane to seed, and ten ml/g methanol-to-solid proportion. Besides, (Patil et al., 2011) optimised single-step conversion of wet algal biomass (*Inoculum Nannochloropsis*., CCMP1776) containing about 90% water in SCM. They distinguished that the ideal conditions for this procedure were met at a reaction temperature of 255 °C, a reaction time of 25 min, and the wet algae-to-methanol ratio of 1:9 dependent on the trial information and response surface method (RSM) research. Production of biodiesel via vegetable oil comprising sunflower, rapeseed, cottonseed, and camelina oils was likewise completed in SCM by (Anikeev and Yakovleva 2013). They inferred that the kind of oil utilized did not essentially influence the product yield and oil conversion value. Late, (Samniang et al., 2014) examined the comparison of biodiesel production from two diverse oils Jatropha *and Krating* oil, utilizing this method. Biodiesel yields of 90.4 and 84.6 % were produced from the transesterification of *Krating* and *Jatropha* oil, separately at a reaction temperature of 320 °C, 15 MPa, and the oil-to-methanol molar ratio of 1:40 because of the higher FFA of *Krating* oil (Farobie and Matsumura 2015).

Poor-quality feedstocks, such as waste cooking oil and waste fat, have likewise been utilized for biodiesel production in SCM. (Demirbas, 2009a) contemplated the correlation of biodiesel production by means of base catalytic and SCM transesterification utilizing waste cooking oil. He observed that the SCM technique was better than base catalytic transesterification giving critical preferences; for example, FFA in the waste cooking oil was transesterified simultaneously and not responsive within sight of water and FFA. Furthermore, (Shin et al., 2012) analysed the transesterification of waste fat in SCM utilizing a batch-type reactor. They noticed that the greatest yield of biodiesel (89.91 %) was produced at a reaction temperature of 335 °C, 20 MPa, the oil-to-methanol molar ratio of 1:45 inside a reaction time of 15 min and a disturbance speed of 500 rpm. (Lee et al., 2012) likewise explored biodiesel production from waste canola oil in SCM through generally moderate conditions (240-270°C reaction temperature/10 MPa). They revealed that the ideal yield of biodiesel produced using this examination was 102% which was acquired at a reaction temperature of 270 °C, 10 MPa, with the oil-to-methanol weight ratio of 2:1 for a reaction time of 45 min. As of late, (Ghoreishi and Moein 2013) run the advancement of biodiesel production from waste vegetable oil in SCM utilizing RSM. They assessed that the ideal biodiesel yield of 95.27% was produced at a reaction temperature of 271.1 °C, 23.1 MPa, and the oil-to-methanol molar ratio of 1:33.8 inside a reaction time of 20.4 min utilizing RSM.

Other than a batch mode reactor, a few specialists likewise utilized a continuous stream reactor to produce biodiesel under supercritical conditions. (He et al., 2007a) examined a continuous transesterification of soybean oil through SCM conditions. They observed that the maximum yield of biodiesel was 77% produced at a reaction temperature of 310 °C, 35 MPa, the oil-to-methanol molar ratio of 1:40 after a reaction time of 25 min residence time. Additionally, (Cheng et al., 2010) likewise inspected continuous biodiesel production from soybean oil utilizing a vertical tubular reactor. They noticed that biodiesel yields which were at their most at 92% were produced at a reaction temperature of 375 °C after about 23 min reaction time at 15 MPa and a constant oil-to-methanol molar ratio of 1:40. Furthermore, (Macaira et al., 2011) likewise found transesterification of sunflower oil utilizing a continuous reactor by mean of the SCM with the increasing of the dioxide mixture as a co-solvent. They concluded that the reaction rate of biodiesel production using noncatalytic SCM is 20 times quicker than that of the traditional ones, and the addition of cosolvent could upgrade the supercritical methanol transesterification rate. They additionally settled that the ideal yield of biodiesel which was 88%, could be accomplished at a reaction temperature of 200 °C after 2 min reaction time.

In the late year, (Tsai et al., 2013) conducted a non-catalytic biodiesel production from waste cooking oil with or without carbon dioxide expansion utilizing a continuous reactor. Their finding is in opposition to the past investigation of (Macaira et al., 2011), in which they affirmed that the impact of carbon dioxide on biodiesel yield was irrelevant to biodiesel production. The most extreme yield of biodiesel, 90%, was acquired at 573.2 K inside a reaction time of 13 min, and the kinetics in SCM have likewise been accounted for in the past examinations. It is outstanding that the transesterification of triglyceride under SCM continues through three back to backreaction steps. To start with, the reaction between triglyceride and methanol results in FAME and diglyceride. This intermediate compound, diglyceride, then reacts with another methanol compound to produce FAME and monoglyceride. At long last, the reaction between monoglyceride and methanol gives FAME and glycerol. This reaction component is introduced in Figure 2.14.

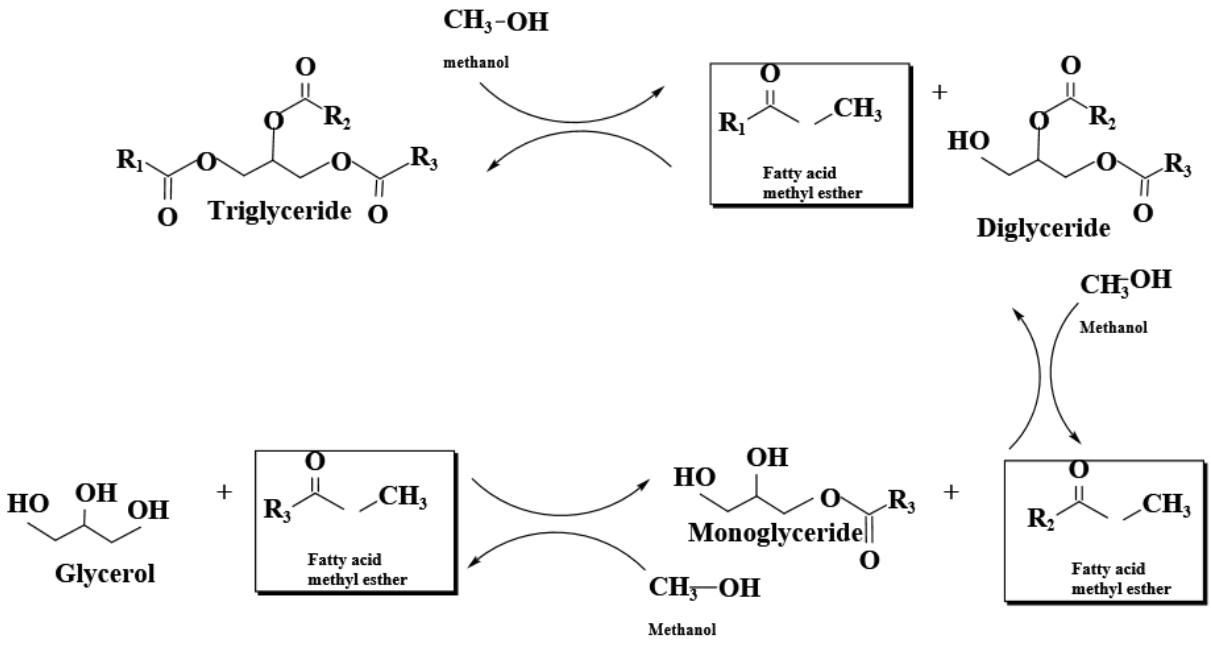


Figure 2.14 Reaction mechanism of biodiesel production under SCM conditions (Farobie and Matsumura 2015).

(He et al., 2007b) explained reaction kinetics of soybean oil conversion into biodiesel under SCM. The activation energy, as well as the volume of activation for transesterification of soybean oil under SCM, was acquired around 56 KJ/mol and 206 cm^3/mol, separately. Additionally, (Varma and Madras, 2007) likewise determined the activation energies for castor and linseed oil under states of 200-350°C and 20 MPa. They decided that individually, the

activation energies of 35 and 46.50 kj mol^{-1} for transesterification of castor and linseed oil in SCM. As of late, (Choi et al., 2011) additionally deduced the transesterification energy of palm olein oil at a reaction temperature of 350°C, 35 MPa, the oil-to-methanol molar ratio of 1:40, and a reaction time of 20 min. They determined activation energy, reaction activation volume, and entropy of activation of 81.37 kJ/mol, 175.35 J/mol K, and 233.29 cm^3/mol individually.

2.5 Biodiesel production in supercritical ethanol (SCE)

With the knowledge that ethanol can be obtained from biomass by means of the fermentative procedure, a few scientists are keen on investigating biodiesel generation under supercritical ethanol conditions. In 2007, (Silva et al., 2007) researched biodiesel generation from soybean oil under sub-and supercritical ethanol conditions utilizing a tubular reactor. Experiments were run at a temperature interim of 473-648K, a pressure of 7-20 MPa, and oil to-ethanol molar ratio of 1:10 to 1:100. They discovered that under subcritical conditions, Fatty Acid Ethyl Ester (FAEE) showed excessive low. So long, biodiesel yields as high as 80% were seen at 623K, 20 MPa, and the oil-to-ethanol molar ratio of 1:40 within 15 min. After a year, (Vieitez et al., 2008) additionally directed the analysis of the continuous formation of soybean oil under SCE conditions with the option of water. Investigations were utilized at 350°C, 20MPa, oil-to-ethanol molar ratio of 1:40. The outcomes indicated that biodiesel yields of 77.5 and 68.1% were gotten in a water-free framework and 10 wt.% of water additions, respectively. It showed that the water in the system gave the unconstructive procedure effectiveness. In 2009, (Gui et al., 2009) played out the optimization of the SCE process for production utilizing response surface methodology (RSM) by differing a few parameters, to be specific temperatures of 300-400 °C, ethanol-to-oil molar ratio 5:50, and reaction time of 2-30 min. It was accounted for in this examination that the ideal yield of biodiesel was obtained to be 79.2 wt.% which was acquired at 349 °C, the oil-to-ethanol molar ratio of 1:33, and a reaction time of 30 min. As of late, there is a fascinating investigation of biodiesel production utilizing this innovation from the third generation of feedstock, i.e., microalgae (*Nannochloropsis Salina),* in which the author's trans-esterified algae by a direct transformation without pre-treatment (Reddy et al., 2014). They affirmed that the best yield of biodiesel was 67% which could be made at 265 °C, an algae-to-ethanol ratio of 1:9 after 20 min.

One of the superiorities of biodiesel production under supercritical conditions over the compound as well as enzymatically catalysed transesterification is the effortlessness in delivering biodiesel utilizing the continuous process. There were a few reports with respect to continuous biodiesel generation using SCE conditions. (Da Silva, 2010) led the continuous

generation of biodiesel from soybean oil utilizing a microtube and tubular reactor. An experimental investigation was done in the temperature range of 523-598 K, the pressure of 10-20 MPa, and the oil-to-ethanol molar ratio of 1:10-1:40 with the expansion of carbon dioxide as cosolvent. They announced that the microtube reactor could produce a higher biodiesel yield relative to the tubular reactor. It may be because of the mass exchange phenomenon. Moreover, it was recognized that the expansion of the co-solvent did not have a huge impact on biodiesel yield. Along these lines, (Trentin et al., 2011) likewise examined continuous biodiesel generation under SCE utilizing a microtube reactor; however, there was no essential difference with the past examination led by (Da Silva., 2010). (Vieitez et al., 2011) performed a continuous generation of biodiesel from castor oil under SCE conditions. They affirmed that the most extreme yield of biodiesel was 74.2% at 573 K, 20 MPa with an expansion of 5 wt.% water, and feedstock flow rate of 0.8 $ml.min^{-1}$.

The impact of FFA, co-solvent and catalyst expansion on biodiesel generation in SCE was additionally inspected in the past examinations. (Vietiez et al., 2012) examined the impact of FFA formation on the procedure efficiency of biodiesel generation by nonstop SCE utilizing a few feedstocks, in particular soybean oil, rice grain oil, as well as high oleic sunflower oil. They noticed that the expansion of FFA on the structure could upgrade the proficiency of every single vegetable oil change demonstrated by higher biodiesel yield (Farobie and Matsumura 2015).

The impact of co-solvent, for example, n-hexane on biodiesel generation in SCE, was accounted for by Muppaneni and colleagues utilizing camelina oil (Muppaneni et al., 2012) and palm oil (Muppaneni et al., 2013) as feedstocks. They saw that the expansion of cosolvent could improve biodiesel yield and diminish the importance of basic operational parameters. What is more, the ideal conditions obtained by utilizing the RSM technique were at 295 °C, the oil-to-ethanol molar ratio of 1:45, and the n-hexane-to-oil proportion of 0.2% inside a reaction time of 20 min for camelina oil. Also, the ideal conditions for palm oil were set up at 300 °C, an oil-to-ethanol molar ratio of 1:33, and an n-hexane-to-oil proportion of 0.4% inside a reaction time of 30 min.

Barely any researchers explained a similar report among methanol and ethanol through supercritical conditions. The primary investigation was directed by (Warabi et al., 2004) utilizing rapeseed oil in the batch mode reactor. They built up that the most extreme yield of biodiesel, which was practically 100%, was within a reaction time of 15 min in SCM; however,

it required a reaction time of 45 min in SCE. Likewise, (Tan et al., 2010) optimised biodiesel produced under SCM and ethanol. They saw that the SCM could accomplish a total change of approximately 85% at a lower reaction time contrasted with SCE with a biodiesel yield of 79.2%. Essentially, (Vieitez et al., 2010) additionally distinguished a similar finding that oil conversion to biodiesel by methanolysis was higher than that by ethanolysis. A comparable finding was accounted for by (Santana et al., 2012), who analysed a similar report among methanol and ethanol in a continuous-mode reactor. They noticed that SCM provided a biodiesel yield of 90% contrasted with SCE of 80% with the residence time of about 2 and 6 min for SCM and SCE, individually. Also, (Kiss et al., 2014) likewise discovered a similar report that SCM is better than SCE as far as reaction rate.

Like biodiesel production in SCM, the reaction mechanism of triglyceride conversion to biodiesel via SCE conditions continues through the three steps reversible reactions displayed in Figure 2.15.

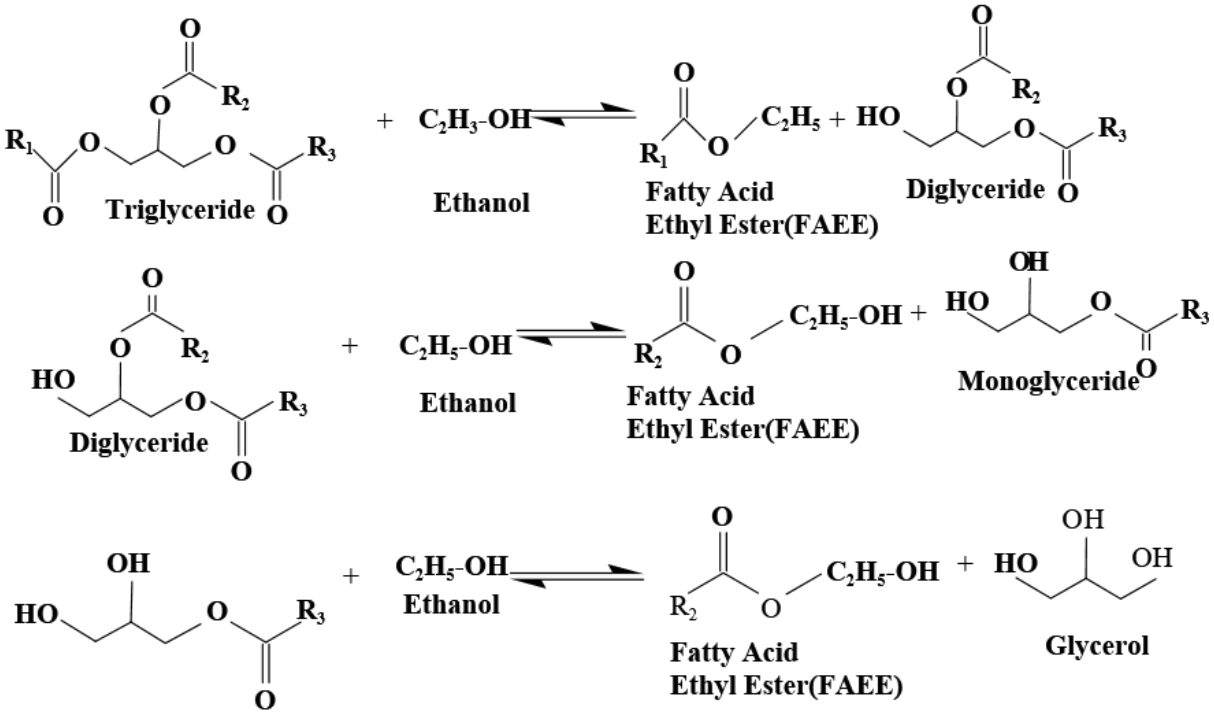


Figure 2.15 Reaction mechanism of biodiesel production under SCE conditions (Farobie and Matsumura 2015)

A few scientists clarified the reaction kinetics of oil conversion to biodiesel under SCE conditions. (Velez et al., 2012) decided reaction kinetics of sunflower oil conversion to FAEE utilizing SCE conditions in a continuous mode reactor. They suggested a first-order kinetic model as well as the calculated activation energy of 67.6 kJ/mol. Moreover, (Santana et al.,

2012) additionally determined the reaction kinetics of sunflower oil conversion to biodiesel in SCE. They observed that the activation energies ranging from 104.82-139.95 kJ mol^{-1} were acquired for reaction change of TG to DG, DG to TG, DG to MG, MG to DG, MG to GL, and GL to MG, separately. In another investigation by (Silva et al., 2007), they determined the reaction kinetics of transesterification of soybean oil in SCE utilizing a tubular reactor in a continuous mode, getting activation energy of 78.7 kJ mol^{-1}.

2.6 Biodiesel fuel properties and it's standards.

Fuels that are to be utilized in any type of motor should usually finish various tests and obey the indicated rules to regulate their value. Biodiesel and oil petroleum diesel vary in their chemical composition. Fossil diesel regularly comprises around 30-35 % aromatic carbons and 65-70 % paraffin, as well as traces of olefins, the greater part of which are in the C10-C16 interval (Chang et al., 1996) and almost without oxygen although biodiesel produced from rapeseed, soybean or sunflower seed oil essentially comprises C16-C18 FAME with one to three double bonds for each molecule and its oxygen comprises adds up to around 11% (Schäfer, 1998). These dissimilarities provide biodiesel with diverse physical and chemical properties. The biodiesel's composition and properties likewise depend greatly on the feedstock utilized in the production procedure. Therefore, a portion of the parameters based on current biodiesel standards is featured and examined. The fuel properties of biodiesel, for example, the heat of combustion, viscosity, melting point, and cetane number, have been seen to increment with increasing carbon number and unsaturation degree, accordingly, requiring improvement by enhancing parent oil plants with precise fatty acid through genetic engineering to progress the fuel properties of biodiesel (Lee et al., 2009).

Specific standards are fundamentals for the business utilization of various fuel products. They fill in as rules for the conception procedure, ensure clients of great fuel, and furnish specialists with endorsed devices for evaluating dangers and ecological contamination (Babajide, 2011). Along these lines, customary tests should be run on biodiesel to guarantee that it meets and keeps up a consistently high level of quality in line with industrial standards. Because of the generally recent appearance of biodiesel, there are no acknowledged worldwide standards. In the year 1997, the European Committee for standardization was required to build up a uniform standard for FAME fuels and think of measurement methods. The subsequent standard EN14214 (European Union quality standard for biodiesel fuels), which has come into power in 2004, is substantial for all part conditions of the European Union. This standard incorporates 26 parameters: some of these are controlled to regulate the production procedure and guarantee

the great conversion of the fatty acid into FAME. Different parameters rely upon the feedstock attributes, for example, the iodine value that relies on the oil's fatty acid profile. As EN14214 is extremely prohibitive in its restrictions, some oil crops that would have been appropriate for biodiesel production are dispensed by choice since they surpass these cut-off points of significance, for example, iodine value, stability, and cold filter plugging point (CFPP) for the winter period. Nonetheless, a portion of the EU standards, for example, CFPP, will not be significant in certain parts of the Southern region because of their diverse climatic conditions. The US standard, conversely, for FAME fuels follows the ASTMD 6571 (American standards testing and methods) (Table 2.4).

Most Southern African nations do not have any standard on biodiesel; in South Africa, the standard for automotive fuel for diesel motors is SANS 1935:2004. This standard indicates the necessities and test techniques to be utilized for advertised and conveyed biodiesel either as automotive fuel for diesel motors at 100 % concentration or as an extender for automotive fuel for diesel motors. At 100 % concentration, fuel for use in diesel motor vehicles is planned or thusly adjusted to keep running on 100 % biodiesel.

Table 2.4 Selection of international quality standards on neat biodiesel blends fuels

Country	Region/Standard	Date	Applicable to
Australia	Australian standard	2003	FAME
European Union	EN14214	2003	FAME
USA	ASTM 6751	2003	FAME

The tables displaying the standard requirements for automotive biodiesel in the USA, EU, South Africa, and other countries can be obtained in appendices 1, 2, and 3. The importance of this table will be viewed in Chapter 4.

2.6.1 Cetane number

The cetane number means that the fuel readiness to auto-ignite when it has been infused into the diesel motor. Diesel fuels require a cetane number higher than 40, and most refineries produce diesel with cetane numbers somewhere between 40 and 45. Biodiesel has a higher cetane number somewhere in the range of 46 and 60 (contingent upon the feedstock utilized),

which shortens the ignition delay in the motor and improves the combustion quality (Meher et al., 2006).

2.6.2 Flashpoint

The flashpoint of a fuel is the temperature at which the vapor over the fuel moves toward becoming combustible. Petroleum-based diesel has flashpoints of 50 to 80 ºC, which makes them intrinsically safe. Biodiesel has a flashpoint of more than 160 ºC, which implies that the fire risk related to transportation, storage, and use of biodiesel is significantly less than other usually utilized fuels (Biodiesel Education, 2009).

2.6.3 Viscosity

Plants and waste oils have higher viscosities contrasted with diesel fuel; transesterification of these oils lessens the viscosity to a huge degree in converting to biodiesel. Viscosity measurement is an essential parameter mirroring the degree of the reaction since it is straightforwardly identified with the FAME content of the transesterified product and is one of the details to conform to when delivering biodiesel (it is an indicator to measure the effectiveness and totality of the ester conversion process).

2.6.4 Sulphur content

The sulphur content of fossil diesel must be below 50 ppm since the start of 2005 (Sapia, 2006). The high sulphur content in fuels has been related to negative health impacts and an expanded service frequency on vehicles. Biodiesel is critically observed as sulphur-free when produced using new vegetable oil.

2.6.5 Cold filter plugging point (CFPP)

Cold temperature properties are proportions to the conduct of the fuel under low encompassing temperatures. The cold filter plugging point is particularly significant in nations where the temperatures drop under 50°C. The cloud point is the minimal temperature at which the sample might be cooled while holding its fluidity.

2.6.6 Heat of combustion

The heating value, otherwise called the heat of combustion, of biodiesel, relies upon the oil source. On a mass premise, fossil diesel has a higher heating value, about 13% higher than that of biodiesel, yet because of the higher density of biodiesel, the burden of biodiesel is just about 8% lower on a volumetric premise. This implies that motor-burning biodiesel has somewhat

lower power and torque for similar infusion volumes. Similar power and torque can be accomplished if the infusion volumes are changed for biodiesel.

Adding in the infusion volume prompts marginally higher specific fuel consumption when utilizing biodiesel. It is essential to remember that the above properties are those of unadulterated biodiesel. If biodiesel is mixed into a fossil at 5% or 10%, the properties of the fossil diesel would not be influenced to a detectable degree. The "lubricity" property of biodiesel has an impact, regardless of whether utilized in low blends. This property makes biodiesel a perfect added substance for fossil diesel.

2.7 Main factors affecting biodiesel production.

2.7.1 Reaction temperature

The reaction temperature is another significant parameter that influences the yield of biodiesel. For instance, a higher reaction temperature increases the rate of reaction and shortens the reaction time because of the decrease in the viscosity of oils. In any case, (Eevera et al., 2009; Leung and Guo, 2006) found that increments in reaction temperature past the ideal level led to a reduction of biodiesel yield in light of the fact that higher reaction temperature quickens the saponification of triglycerides. More often, the temperature of the transesterification reaction ought to be beneath the boiling point of alcohol to avoid alcohol from evaporating. The range of optimal reaction temperature may fluctuate from 50°C to 60°C depending on the oils or fats utilized (Freedman et al., 1984; Leung and Guo, 2006).

2.7.2 Reaction time

When there is an increase in the rate of reaction, the number of fatty acid esters will likewise increase, according to the observation done by (Freedman et al., 1986). The reaction takes time around the beginning considering the mixing and scattering of oil as well as alcohol. From then on, the reaction continues with incredible speed. In any case, the most obtained ester conversion was produced inside a reaction time of 90 min. Further augmentation in the rate of reaction does not elevate the amount of yield, for instance, biodiesel/mono-alkyl ester (Alamu et al., 2007; Leung and Guo, 2006). Furthermore, a longer rate of reaction prompts the diminishing of the biodiesel product in view of the reversible reaction of transesterification, achieving a setback of esters similar to soap formation improvement (Eevera et al., 2009; Ma et al., 1998).

2.7.3 Oil-to-methanol molar ratio

The molar ratio of alcohol expects an important part of biodiesel yield (Freedman et al., 1986; Leung and Guo, 2006). Ordinarily, the transesterification reaction requires 3 mol of alcohol for one mol of triglycerides with three mol of unsaturated fatty acid ester and one mol of glycerol. An additional amount of alcohol increases the conversion of triglycerides into esters inside a short reaction time. Therefore, the yield of biodiesel could be said to be directly proportional, for as the concentration of alcohol increases, the FAME yield increases although this is only up to a certain concentration. Anyway, a further increase in alcohol concentration does not increase the yield of biodiesel, but instead, in the same manner, it increases the cost of alcohol recovery (Leung and Guo, 2006). Additionally, the ratio of alcohol content may vary with the catalyst used. For instance, when we use a soluble base catalyst, the reaction requires a 6:1 ratio of alcohol to catalyse the transesterification of oils or fats (Freedman et al., 1986; Zhang et al., 2003). In case the samples of oil contain high FFA, such a reaction will not respond to the alkali catalyst. In that condition, the acid catalyst will be convincing to catalyse the reaction, and the reaction requires a higher ratio of alcohol than alkali catalysts. This is a result of how the acid catalyst allows the FFA and water content in the oil samples. For example, waste cooking oil requires a higher ratio of alcohol, such as 15:1 when presented with an acid catalyst reaction (Leung and Guo, 2006).

2.7.4 The amount and type of catalyst

The production of biodiesel is furthermore impacted by the catalyst concentration, the common catalyst for biodiesel production is sodium hydroxide (NaOH) or potassium hydroxide (KOH). In any case, (Freedman et al., 1984) found that the sodium methoxide would be progressively influential because the mixing of NaOH with methanol produces a small amount of water which prevents biodiesel production considering the hydrolysis reaction (Guo, 2005). This is one explanation behind firstly mixing with methanol and after that adding to the oil or fats. Therefore, when the catalyst concentration increases with the oil sample, triglycerides change into biodiesel is also increased. Of course, the lacking number of catalysts prompts the inadequate transformation of triglycerides into fatty acid esters (Guo, 2005; Leung and Guo, 2006). Regardless, the ideal biodiesel yield was obtained when the concentration of NaOH escalates to 1.5 wt.%; meanwhile, further increasing of the catalyst concentration showed a disadvantage in biodiesel production. Due to the addition of the alkali catalyst amount, the alkali catalyst will react with triglycerides to produce more soap (Gabelman and Hwang, 1999; Leung and Guo, 2006).

2.7.5 FFA and water content of oil

FFA and water contents are basic variables for the transesterification reaction. Base-catalysed transesterification reaction necessitates water-free and small acid value (< 1) crude materials (Demirbas, 2009b) for biodiesel generation. If the oil tests have high FFA content (over 1%) at that point, the reaction requires more alkali catalysts to neutralize the FFA. The nearness of water gives a more noteworthy negative impact than that of FFAs because water can cause soap development and foaming, which causes an increment in consistency. Furthermore, the presence of gels and froths ruins the detachment of glycerol from biodiesel (Demirbas, 2009b and 2005). Free fatty acids and water consistently produce negative outcomes during transesterification, cause soap development, and consume the catalyst, prompting a decrease in catalyst impact. Water and FFA likewise prompt a decrease of methyl esters. To defeat this issue, the supercritical methanol technique (623 K, 43 MPa, 4 min of treatment with methanol to oil molar ratio of 42:1) was proposed by (Kusdiana and Saka 2004), which was contrasted with alkaline and acid-catalysed strategy. It might be noticed that water has less impact on the supercritical methanol technique.

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Chapter three Experimental methods

3. Introduction

Chapter three of this project details the analytical methods, chemical and sample preparation. Section 3.1 is a general idea revealing a short description of what is happening in the chapter. Section 3.2 speaks of the materials utilized in this study to produce FAME. The three main parts of this chapter are sections 3.3, 3.4, and 3.5. Section 3.3 illustrates the experimental method, which consists of fatty acid composition and determination of the properties of the castor oil. Section 3.4 speaks about Unsupported Castor Shell (UCS) and cobalt supported by titanium Oxide ($Co/TiO_{2)}$. Section 3.5 is based on the sample preparation, the analytical and experimental method in investigating the transesterification of castor oil (FAME) using the prepared catalysts UCS and Co/TiO_2.

3.1 General idea

The General idea of this chapter is presented in this manner:

a. The preparation of the sample as well as pre-trial.
b. The reaction between the castor oil with the methanol in the presence of one of the precited catalysts to generate FAME.
c. Detailed examination of FAME: this was done by mean of gas chromatography (GC-MS) and was utilized at diverse phases to gain pertinent information with the aim of the determination of the yield and concentration of the methyl esters obtained from the transesterification reaction through the heterogeneous (Co/TiO_2 and UCS catalyst).
d. FAME standard testing: laboratory tests were conducted to approve and find the properties and qualities of the methyl ester (biodiesel) produced under the optimal condition given in this study. The result is then related to the biodiesel fuel standard prepared by SIGMA-ALDRICH (SUPELCO and TRACE CERT).
e. Catalyst preparation: the preparation of these two catalysts, particularly the heterogeneous (Co/TiO_2 and UCS), was set in this section. But the homogenous catalyst (sulphuric acid) was not required any preparation.
f. Catalyst characterization: the prepared heterogeneous catalyst (Co/TiO_2) was characterised by mean X-ray diffraction (XRD) analysis, Brunauer-Emmet Teller (BET) and Scanning Electron Microscopy-Energy Dispersion Spectroscopy (SEM-EDS), while UCS was characterised using Scanning- Electron Microscopy-Energy Dispersion Spectroscopy

(SEM-EDS), X-ray diffraction (XRD) analysis, Fourier transform infra-red (FT-IR) and Brunauer-Emmet Teller (BET)

3.2 Materials

The feedstock used in the study is castor oil extracted from the castor seeds. The castor seeds were collected from Selokong Sa Dimelana (Pty) (Limpopo- South Africa) plantation. And their shells were utilized as feedstock in the preparation of the UCS catalyst.

Table 3.1 List of chemicals used in this investigation.

Chemicals	**Source**	**Purity (%)**
Potassium hydroxide pellets	Rutland industry (Ltd)	99.9
Methanol	Rutland industry (Ltd)	99.9
Hexane	Rutland industry (Ltd)	99.9
Diethyl ether	Rutland industry (Ltd)	99.9
Phenolphthalein	Rutland industry (Ltd)	-
Ethanoic potassium hydroxide	Rutland industry (Ltd)	-
Carbon tetrachloride	Rutland industry (Ltd)	99.9
Potassium iodine	Rutland industry (Ltd)	99.9
Sodium-thiosulphate solution	Rutland industry (Ltd)	99.9
Sodium hydroxide pellets	Rutland industry (Ltd)	99.9
Concentrated sulphuric acid	Rutland industry (Ltd)	99.9
G.C Internal standards:	**Sigma Aldrich**	**Chromatography Purity (%)**
Methyl tetra decanoate		99.9
Methyl palmitate		99.9
Methyl octadecenoate		99.9
Trans-9-elaidic acid methyl ester		99.9
Cis-9-oleic acid methyl ester		99.9
Lionolelaidic acid methyl ester		99.9
Methyl arachidate		99.9
Methyl linoleate		99.9
Methyl docosanoate		99.7
Cobalt (II) nitrate hexahydrate		95

3.3 Experimental methods

3.3.1 Castor oil extraction

Castor seed oil was extracted from castor seed by means of the hexane solvent method. The extraction using the hexane solvent has been useful because it is the way that is permitted to extract at a high yield of about 100%. This was done using the Soxhlet apparatus. Figure 3.2 shows the flow chart of castor oil extraction.

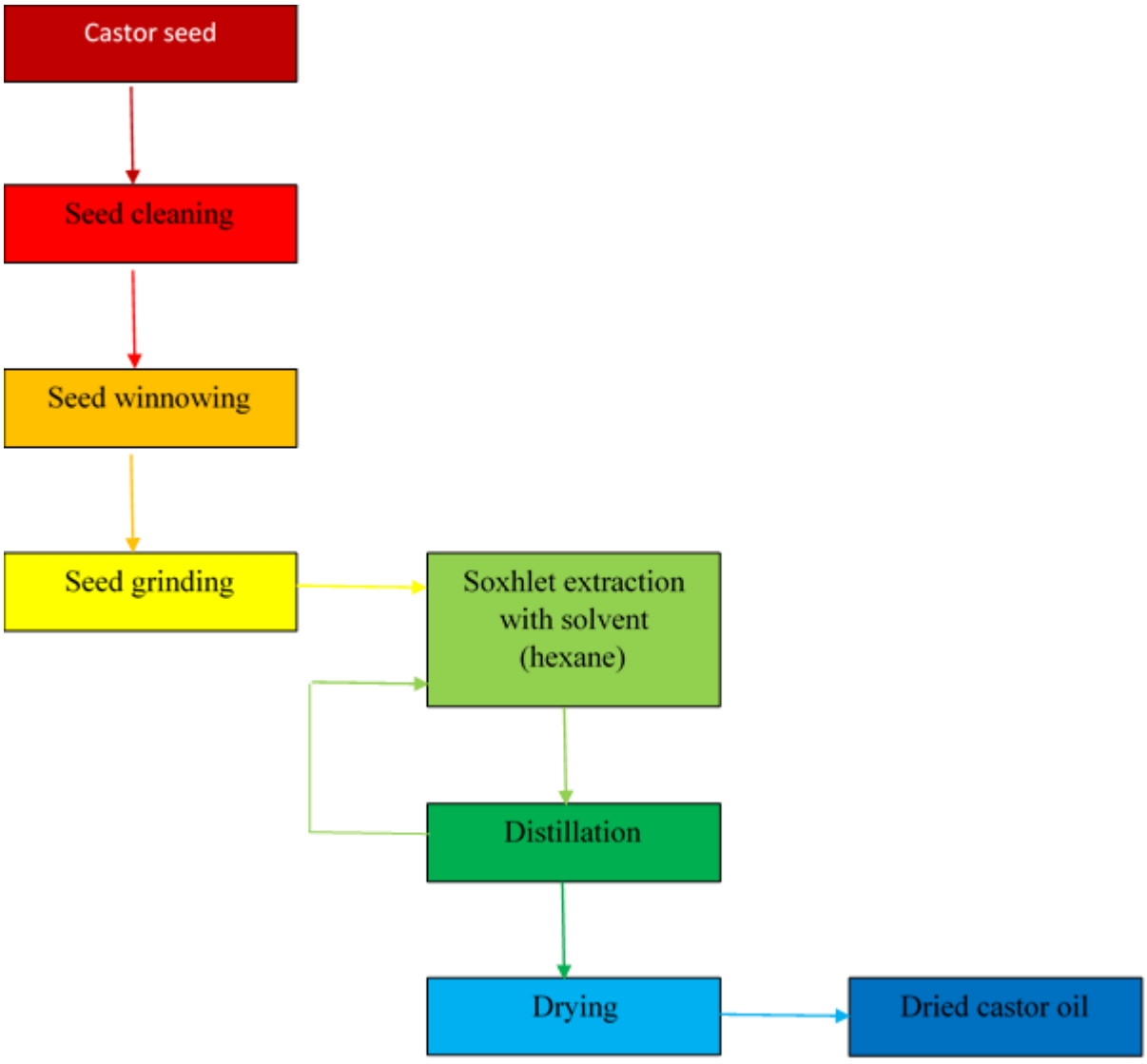


Figure 3.1 Flow chart of castor bean oil processing

Before the extraction of the castor oil by means of hexane and Soxhlet, the castor seed undergoes the following operations:

- Clearing: separating the castor bean from general waste materials surrounding the bean by hand sorting.

- Drying: The bean goes through a thermal process to expose the seeds inside it when the shell cracks. Thereafter the seeds are placed in an oven at 60℃ so that the moisture can be fully separated from the seed.
- Winnowing: The shell was removed by throwing the mixture into the air so that the wind blows the lighter particles (shell) away and the nibs remain.
- Mechanic pressing (size reduction): this process gives the best quality oil. Mortar and pestle were utilized to pulverize the beans into a glue (cake) to debilitate or break the cell wall to discharge castor oil for extraction. Once the seed is crushed correctly, it goes through pressing to force out the oil. The operation is generally done in two stages; most of the oil is extracted at a pressure of about 300 kg/cm^2 or 31% of first quality oil; the second pressing gives 5 to 10% of the oil of second quality 55% of the cake remains.
- Solvent extraction: When the oil yield is 20% after mechanical pressing, there is still 80% of the paste (cake). Due to that, we will need to use a Soxhlet extractor for solvent extraction. This technique is required for volatile organic solvents, mainly petroleum ether, trichloroethylene, and more recently hexanes which have many qualities. It is nontoxic, very effective, and inexpensive. Figure 3.2 represents the laboratory Soxhlet extractor.



Figure 3.2 represents the laboratory Soxhlet extractor

3.3.2 Fatty acid composition of castor oil and its properties

i. Density

Density is the mass per unit volume of any fluid at a given temperature. Specific gravity is the proportion of the density of a liquid to the density of water. This property is significant because it impacts the effectiveness of the atomization of the fuel and, is extremely important in the assurance of the cetane index of an oil sample (Srivastava and Prasad 2000). The density of the oil test at 15 °C was resolved, keeping the ASTMD 1298.

ii. Acid value

Acidity is the mass of KOH in milligrams (mg) that is needed to nullify a gram of a component. Acidity is a proportion of the measure of carboxylic acids in a component, for example, fatty acids. The acid number is utilized to measure the quantity of the current acid, for instance, in the biodiesel sample. It is equal to the amount of base in milligrams of the KOH that is compulsory to nullify the acidic contents in a gram of sample. The castor oil was examined to learn their acidity index needed to complete the transesterification reaction. The acidity index of the crude oils was broken down after an entrenched trial titration methodology as per ISO 1242:1999.

Procedure

In a usual method, a known measure of sample broken down in an organic solvent is titrated with a solution of KOH with the concentration that is already given and phenolphthalein as an indicator. Every titration was rehashed four times, and the standard deviation was determined. The value is given by equation 3.1:

$$Y = \frac{c*v*56.1}{m} \qquad 3.1$$

In the equation above, Y represents the acidity, the consumed volume of KOH in millilitres is given by v, the number of moles per volume of KOH is represented by c, and m shows the mass of the sample in grams and the sum of the atomic masses of KOH is equal to 56.1. It can likewise be determined by 1.99 x FFA %.

iii. Saponification value

The saponification value displays the number of milligrams of KOH or NaOH needed to saponify a gram of fat according to the determined conditions. It is a proportion of the normal molecular weight (chain length) of all the present fatty acids. As the greater part of the mass of

a fat/tri-ester is found in the three fatty acids, it considers the examination of the normal fatty acid chain length. The long-chain fatty acids present in fats have little saponification value since they have a moderately smaller number of carboxylic per unit mass of fat when contrasted with short-chain fatty acids. If more moles of the base are needed to saponify N-grams of fat, then there are more moles of the fat, and the chain lengths are comparatively little, given the accompanying equation 3.2:

$$number\ of\ moles = \frac{mass\ of\ oil}{relative\ atomic\ mass} \quad 3.2$$

The determined molar mass is not appropriate to fats and oils containing high measures of unsaponifiable material with FFA under 0.1 %.

Procedure

Saponification measurement value can be achieved by conferring the official test methods. A fatty acid sample is initially saponified by adding 0.5 mol/L potassium hydroxide ethanol, and afterward, the extra KOH is titrated with 0.5 mol/L HCl until the endpoint is come to. As shown in equation 3.3

$$saponification = \frac{(V1-V2)*56.1*C}{m} \quad 3.3$$

iv. Iodine value

The iodine value is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. An iodine solution is yellow/brown in colour, and any chemical group in the substance that reacts with iodine will make the colour disappear at a precise concentration. The amount of iodine solution thus required to keep the solution yellow/brown is a measure of the amount of iodine-sensitive, reactive groups. The iodine value gives a measure of the average degree of unsaturation contained in fatty acids. This unsaturation is in the form of double bonds which react with iodine compounds. The higher the iodine number, the more unsaturated fatty acid bonds (C=C double bonds) are present in a fat Mittelbach and Remschmidt, 2006, as reported by (Babajide,2011).

Procedure

In a typical procedure, the fatty acid is treated with an excess of Wijs solution, which is a solution of iodine monochloride (ICl) in glacial acetic acid. Unreacted iodine monobromide (or monochloride) is reacted with potassium iodide, converting it to iodine, whose concentration can be determined by titration with sodium thiosulfate. A scheme of the reactions, as shown in Equations 3.4. The concentration of C=C in the original sample can,

therefore, be calculated by measuring the amount of sodium thiosulfate needed to complete the titration. Therefore, the higher the degree of unsaturation, the more iodine absorbed and the higher the iodine value. As shown in equation 3.4

$$ICl_3 + I \longrightarrow 3\,ICl$$
$$IC + KI \longrightarrow I_2 + KCl$$
$$2(SO_3)\,S^{2-} + I_2 \longrightarrow 2I^- + (S_2O_6S_2)^{2-}$$
$$R\text{-}CH{=}CH\text{-}R' + ICl_{excess} \longrightarrow R - CHI - CHCl - R' + ICl_{remaining} \qquad 3.4$$

For a simple analysis, 0.2 grams of fat was mixed with 20 ml Wijs solution and 10 ml 1,1,1-trichloroethane. It was then left in the dark for 30 minutes. Next, 15 ml of 10% potassium iodide solution and 10 ml of deionized water were added. This is then titrated with 0.1 M sodium thiosulfate (VI) solution. 1 ml of 0.1 M sodium thiosulfate solution equal to 0.01269 g of iodine. The difference between a control titration and the titration with the fat present multiplied by this factor gives the mass of iodine absorbed by the oil. Standard methods for analysis are, for example, ASTM D5768-02 (2006).

v. Viscosity

Viscosity can also be considered as a measure of the friction of fluids, as it also describes the internal resistance of fluid flow. There are two ways to report or measure a fluid of viscosity. It can either be expressed as dynamic viscosity or kinematic viscosity. Dynamic viscosity (μ), also referred to as absolute viscosity, or just viscosity is the quantitative expression of fluid resistance to flow (shear). Its SI unit is in pascal seconds (Pa. s), which is mainly used in ASTM standards. On the other hand, kinematic viscosity is the ratio of the viscous force to the inertial force. Inertial force is characterized by fluid density (p). Kinematic viscosity (v) is shown in equation 3.5.

$$V = {}^{\mu}/_{p} \qquad 3.5$$

Viscosity is closely related to the fatty acid composition of a given oil sample; it increases with the increasing length of the fatty acid chain which also relates to the rate of transesterification reaction of a given oil sample. The major aim of these reactions is to reduce the viscosity values of the triglycerides (before transesterification) and FAME(s) produced (after reaction) since the major drawback of using neat vegetable oils as fuels is due to the high viscosity values they possess. This viscosity forms the basis of an analytical method (viscometry) applied to determine the conversion of vegetable oils to methyl esters. The viscosity difference between

the component triglycerides and their corresponding methyl esters resulting from transesterification is approximately one digit (Knothe, 2001).

Procedure

The dynamic viscosity of the oil sample (castor oil) was determined using the Anton Parr Physica Rheometer, Rheoplus /32 V 2.81 MCR 501 operating on a rolling ball principle at a temperature of 40 ºC. One replicate for each sample was done as the instrumentation gave consistent results.

vi. Water content

During the transesterification reaction, the presence of water causes the loss of yield of methyl ester due to the formation of soaps. In biodiesel products, water can promote biological growth and hydrolytic reactions, which are linked to automotive filter blockage. The water content in the castor oil was measured using a Thermo Orion AF7LC Coulometric Karl following EN ISO 12937 norm. The same method was used in the determination of the water content of the biodiesel obtained from the reactions.

vii. Chemical composition

GC identified the fatty acid composition and the average molecular mass of the oil sample. The fatty acid compositions of these fats and oils were determined by a well-established GC procedure (Alacantra et al., 2000). A standard mixture of these esters was injected into the GC for identification and quantification purposes. 0.50 g of standard and samples were dissolved in 10 ml of n-hexane and injected (1 ml) in a Varian CP-3380 GC, equipped with a carbowax capillary column (15 m x 0.53 mm x 1mm). The GC oven was kept at 100 °C for 2 min, heated at ten ºC/min up to 220 ºC, and kept at that temperature for 10 min. The detector was a flame ionization detector (FID) and the carrier gas helium (30 mL/min).

3.4 Ultrasound process with the different catalysts (H_2SO_4, Co/TiO_2, and UCS)

The present section describes the methodology used during transesterification in the homogeneous (H_2SO_4) and heterogeneous (Co/TiO_2 and UCS) catalysts.

Sonication experiments were done utilizing an Omni ultrasound with a 20 kHz frequency and a power output of 400 Watts. The experiments were performed in this manner:

a) Catalyst amount: FAME was produced at different amounts of catalyst, i.e., 0.5%, 1%, 1.5%, and 2%, while other parameters are unchanged.

b) Time: the FAME was gotten at diverse times such as 35 min; 40 min; 45min, and 50 min while other parameters were remaining the same.

c) Temperature: the biodiesel was obtained at different temperatures, i.e., 35; 40; 45, and 50, while other parameters were kept constant.

d) Methanol to oil ratio: the biodiesel product was collected at different methanol to oil ratios, i.e., 3:1; 6:1; 9:1, and 12:1, while others are kept constant.

The reaction vessel containing the catalyst and the oil was set under ultrasound with the ultrasound macro tip immersed into the oil and kept in place about 5 cm away from the bottom of the reaction vessel. After a complete reaction, the mixture was allowed to stand for at least ten hours for phase separation. The esters mixture formed the upper layer, and the glycerol, the lower layer after separation by gravity, the upper layer (methyl esters, methanol, and traces of the catalyst) was placed in a rotary evaporator to distill the excess methanol and then passed through a column packed with macro-porous polymer resins (GF 202) to eliminate traces of methanol and water.

3.5 Experimental setup

This experiment design involved the use of methanol and castor oil over sulphuric acid (homogeneous catalyst transesterification), Co/TiO_2, and UCS (heterogeneous catalyst transesterification) to investigate free FAME. Figure 3.3 below is a diagram of the transesterification system experiment setup used.

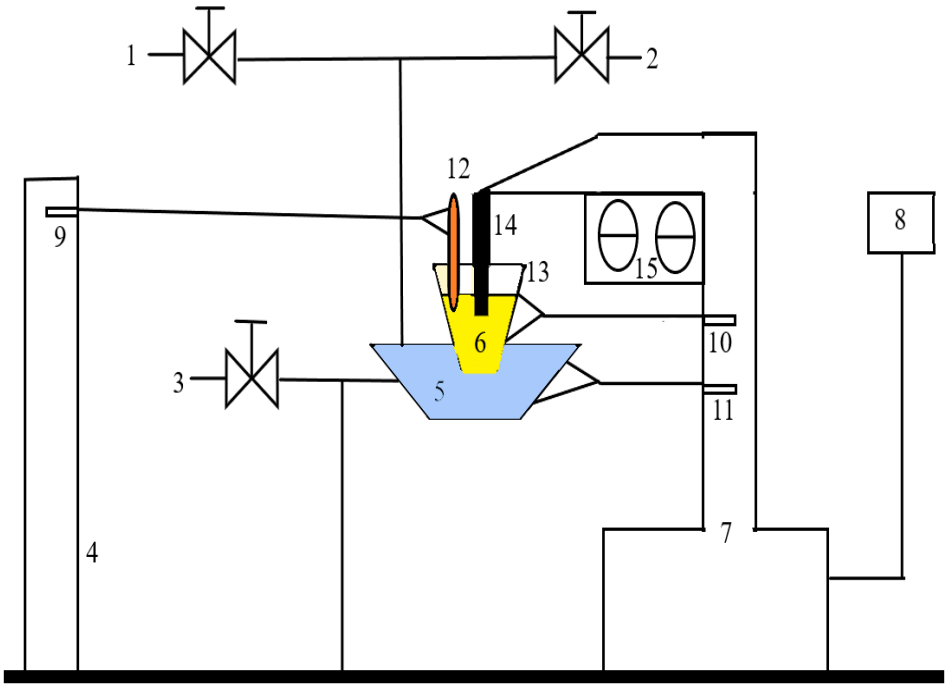


Figure 3.3 Transesterification system experiment set up used.

1 The Shut-off valve leads cold water to dissolve from the ice block to the water bath when the operating temperature increases above the operating condition temperature.

2 The Shut-off valve leads hot water (50 - 70ºC) to the water bath when the temperature decreases below the operation condition temperature.

3 Shut-off valve leading water to the sink.

4 Clamp stand

5 Water bath

6 Oil, methanol, and catalyst (heterogeneous or homogenous) in a reaction vessel

7 Ultrasound reactor

8 Electrical switch

9 Clamp

10 Clamp

11 Clamp

12 Thermometer

13 Reaction vessel

14 Macro probe

15 Cycle and amplitude controllers

3.6 Analysis of FAME

Observing the degree of the transesterification reaction and FAME analysis included a strategy that is utilized regularly to do fat analysis where non-volatile fatty acids are changed chemically to the relating methyl esters, which are volatile. The subsequent volatile blend was broken down by a progression of systematic stratagems that will be portrayed in the following section.

3.6.1 Composition of FAME

The synthesized biodiesel samples of the FAME composition obtained in the examination were resolved and then distinguished by Gas Chromatography (SHIMADZU GCMS-QP2010 SE utilizing Software: GCM solution workstation) with a column (SP-2560, 100m×0.25mm×0.2µm) as indicated by Sigma-Aldrich (TraceCERT, SUPELCO). The following strategies are appropriate to examine the samples containing methyl esters in the range of C14 and C22.

Gas chromatography investigations were done to quantitatively and qualitatively decide the methyl esters generated. The carrier gas used in this GC-MS was helium with the oven set at an initial temperature of 140 ºC, held for 4 min and increased in this way to 250 ºC (hold 12.5 min) at four ºC/min. The detector temperatures were set at 260 ºC with a solution of 10mg/mL. In the column, 1µL was injected for every run. The standard using during the transesterification reaction was Sigma-Aldrich (TraceCERT, SUPELCO).

The transesterification reaction yield after GC analysis using the Sigma-Aldrich (TraceCERT, SUPELCO) standards was calculated utilizing Equation 3.6. The chromatograms of the FAME obtained using different catalyst (H_2SO_4, Co/TiO_2 and UCS) are found in the Appendix (1;2 and 3) respectively.

$$FAME\ YIELD\ (\%) = \frac{Total\ weight\ of\ methyl\ esters}{total\ weight\ of\ oil\ in\ sample} * 100 \qquad 3.6$$

3.6.2 Viscosity measurements

The viscosity of the FAMEs generated from the castor oil sample was resolved utilizing the Anton Parr Physica Rheometer, Rheoplus/32 V 2.81 MCR 501 working on a moving ball guideline at the test temperature of 40°C. One reproduces for the castor oil sample was done as the instrumentation gave reliable outcomes. The conversion effectiveness of the oils obtained from the viscosity results was determined to utilize Equation 3.6.

$$C = \frac{V(tri)V(me)}{V(tri)}\% \quad 3.6$$

Where *C* is the oil change (%), *V (tri)* is the viscosity of triglyceride, and *V (me)* is the viscosity of the changeover methyl ester. The difference in viscosity of the pre-trans esterified oil and the FAME derivative can likewise be used to screen biodiesel generation and catalyst activity. This relationship has been accounted for in writing (Babajide et al., 2011) in this manner, permitting the total concentration of methyl esters to be obtained from just the viscosity measurement.

3.7 Catalyst preparation

3.7.1 Introduction

In this thesis, two types of catalysts (Co/TiO_2 and UCS catalyst) were prepared at the temperature of 400 ℃. Degussa Titania (TiO_2) P25, Surface area (SA) = 50 m^2g^{-1} and Co $(NO_3).6H_2O$ were mixed to make Co/TiO_2 catalyst.

3.7.2 Catalyst preparation procedure

Co/TiO_2 catalyst

The Co/TiO_2 catalyst was prepared by impregnating TiO_2 as a catalyst supporter with cobalt nitrate hexahydrate (Co $(NO_3)_2{\cdot}6H_2O$). TiO_2 was added with distilled water in a mass ratio of 1:1, and the paste was dried at 120 ℃ for 2 hours. After that, the support was calcined in a muffle oven at 400 ℃ for 16 hours. Then the calcined TiO_2 catalyst supporter was crushed and sieved. The particles with diameters between 0.5 and 1 mm were selected for use. Also, the cobalt nitrate hexahydrate was mixed with distilled water in a mass ratio of 1:1 to obtain a cobalt nitrate hexahydrate solution. The support was then impregnated with a sufficient cobalt nitrate hexahydrate solution to give a mass cobalt metal loading of 10%. After that, the mixture of the support and cobalt nitrate was dried in air at 120 ºC for 16 hours, and then calcined in the muffle oven at the following temperature program: the oven temperature was ramped at 5℃/min until it reached 400℃ and kept at these temperatures for 6 hours to allow it to decompose and transform from cobalt nitrate to cobalt oxide.

UCS catalyst preparation

Crush and grind the castor shell into powder using mortar and pestle. Dissolve castor shell powder in distilled water. Dry paste at 120℃ for 2 hours. Move this dried paste to a crucible and calcine it in a muffle oven at the following temperature program. The oven temperature

was ramped at 5℃/min until it reached 400 ℃ and kept at these temperatures for 6 hours. It was left to cool down overnight. Crush the dry paste after it cools down to room temperature and choose the particle size between 0.5mm and 1mm for catalyst preparation.

3.8 Catalyst characterization

3.8.1 Introduction

The physicochemical characteristics of these two catalysts were determined as follows: UCS was characterized utilizing SEM-EDS, XRD, FT-IR and BET, while the Co/TiO_2 was characterized using the BET, XRD strategies (Chorkendorff and Niemantsverdriet, 2017; Niemantsverdriet, 2007) and SEM-EDS. For a supported catalyst Co/TiO_2 and the blank catalyst support TiO_2, the BET technique provided the surface area and volume pore distribution of the catalyst support TiO_2 and the supported catalyst Co/TiO_2. The metal oxide is an integral asset to dissect the reduction kinetics of oxidized catalyst precursors, allowing the analyst to choose the most proficient reduction conditions. XRD is utilized to distinguish crystalline stages inside catalysts by methods of lattice structural parameters as an indication of particle size.

3.8.2 Pore size determination and surface area

The BET played the role of determining the pore size and surface area of the catalyst supported and supporter. However, a significant physical analysis of the heterogeneous catalyst prepared as indicated was conducted using gravimetric nitrogen N_2-BET surface analysis strategy. The catalyst samples (0.35-0.5g) were outgassed at 110 ºC using helium gas using the Micro metrics Flow Prep 060. The Micromeritics Tristar instrument was utilized with nitrogen as the analysis of gas and surface area dependent on a 5- point with 30 adsorption and 30 desorption points, together with a complete pore size measurement.

3.8.3 Qualitative XRD analysis

The qualitative analysis of the mineral and amorphous stages in the catalyst sample was completed by XRD. The samples (Co/TiO_2 and UCS) were set up respectively for XRD analysis utilizing a back-loading preparation technique. The sample in the wake of being ground to a fine powder was put in a sample holder, and the crystalline stages were characterized utilizing a Philips X-ray diffractometer with Cu-Kα radiation. The XRD instrument working conditions were as given in Table 3.2.

Table 3.2 XRD operating parameters

Radiation source	Cu-Kά
Radiation wavelength (λ)	1.542 Å
Range	104
Time constant	1 s
pre-set	1000 counts/s
Voltage	40 kV
Current	25 mA
2 θ range	$4^o < 2\theta < 60^o$
2 θ /step	0.1^o
Anti-scatter slit	1^o

The stage identification was performed via observing and coordinating obtained spectra with the powder diffraction record information base with the assistance of JCPDS (Joint Committee of Powder Diffraction Standards) documents for inorganic compounds.

3.8.4 Scanning Electron Microscopy (SEM)

SEM is to help to acquire fast qualitative elemental analysis of an unknown sample. The morphology of the catalysts used in this investigation was inspected utilizing a Carl Zeiss FE-SEM. The sample was placed in the microscope, and it was splutter coated with palladium and gold to increase the conductance of the sample.

3.8.5 Energy Dispersive Spectroscopy (EDS)

Likewise called Energy Dispersive X-ray Spectroscopy (EDS) is a method dependent on the assortment and energy dispersion of X-rays made when high-energy electrons shell a sample. This strategy distinguishes all elements from boron to uranium and is typically non-damaging. Two techniques are utilized to decide the x-rays that are formed: (1) energy dispersive investigation, which isolates and distinguishes x-rays of explicit energy and showcases them as histograms, while (2) wavelength-dispersive examination utilizes the reflection of x-rays of a crystal at a characteristic angle, to identify x-rays of explicit wavelengths (Babajide, 2011). The EDS is connected to the SEM, and the two systems are regularly utilized together. The X-rays have energies that are distinctive for the elements in the sample. The instrument electronically processes the signals to provide histograms of energy versus signal strength, the last being identified with relative elemental concentration. Detection restrictions extend from 0.05-2 % for high to low Z elements, individually. EDS is especially useful for relating elemental composition to topographical features. The Co/TiO_2 and UCS catalysts were oven-dried at 105 °C for 12 h in preparation for the SEM-EDS analyses. The dried samples were sprinkled on special glue, mixed with carbon graphite, and mounted on aluminium stubs. The morphology of the samples was built up by the secondary electron mode. The "photo" imaging was utilized to recognize the region of relative homogeneity, and from there on, an EDS investigation was done on certain spots for qualitative elemental composition.

3.8.6 Fourier Transform Infra-Red (FT-IR)

Fourier Transform Infrared spectroscopy (FT-IR) was utilised to monitor changes and provide information about the molecular structure of the UCS catalysts. 15 mg of the catalyst samples was placed on the Attenuated Total Reflectance (ATR) sample holder of a Perkin Elmer spectrum 100 FT-IR spectrometer. The sample was recorded in the range of 4000-250 cm-1, the baseline was corrected, and the spectra smoothened. The use of diamond cells with a beam condenser or microscope allowed adjustment of the thickness of a sample by squeezing which enables analysis of microgram samples to be performed.

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Chapter four Biodiesel Synthesis via Homogeneous Catalysis

4. Introduction

This chapter initially shows the major physical and chemical properties of the feedstock (castor oil) utilized in this investigation. The chapter likewise emphasizes the reaction parameter optimization results for producing the FAME employing low-frequency ultrasound technology.

The impact of related procedure factors, which include methanol to oil ratio, amount of catalyst, temperature, and reaction time on the FAME yield utilizing castor oil sample, is accounted for to improve the production of this FAME. The outcomes in this chapter come from the experimental procedures outlined in the experimental methods (section 3.3).

4.1 General idea

FAME referred to as biodiesel, has been seen as a potential source of renewable and environmentally friendly energy, replacing depletable petroleum-derived diesel. Much research has been done globally to produce FAME because of its advantages in contrast to traditional diesel. For example, biodiesel is better than diesel as far as aromatic content, biodegradability, sulphur content, and flash point (Murugesan et al.,2009; Demirbas et al., 2003). Aside from that, the feedstock for biodiesel production is obtained from renewable sources, for example, edible/non-edible oils and waste animal fats, which are plentiful and endless. Consequently, biodiesel production will guarantee the supportability of human improvement and energy sources later. Despite the brilliant prospect of biodiesel as a feasible wellspring of energy, its commercialization works have been constrained all through the globe. Moreover, it is evaluated that about 70% of the biodiesel production cost comes from the expense of crude materials (Bautista et al., 2009; Bušić et al., 2018; Chung et al., 2009; Meng et al., 2008 and Phan and Phan, 2008). Subsequently, to reduce the expense of biodiesel and not to bargain feedstock for humans, castor oil as nonedible can be used as feedstock. The characterization of the oil sample utilized, in this investigation, and the impact of the operating conditions, on the transesterification procedure, in deciding yields of triglycerides to FAME by means of various reaction procedures are relied, upon to give an understanding of the compositions of these triglycerides and ascertain their overall effects on the different process operations and impacts, on the optimization of the whole biodiesel production. The objectives of this chapter are: (i) to discuss the results of the physical and chemical compositions of the oil sample, (ii) to evaluate the impacts of the diverse reaction parameters on the yield of the FAME, (iii) to maximize and evaluate the process optimization of the reaction system utilized

in producing the FAME, (iv) to determine if the FAME produced with castor oil meets industrial specification through ultrasound technology, as the product is not classified as "Biodiesel" if industrial specifications are not met.

4.2 Materials and methods

The point-by-point characterizations of the oil sample's chemical properties and the sample preparation utilized in the section of the investigation are introduced in chapter 3. In this section, sulphuric acid was utilized as the homogenous catalyst, and the strategies and methodology utilized for the transesterification reactions led under this section are portrayed in section 3.3, while the experimental procedure of the homogeneous transesterification reactions and pictorial characterizations of the trial set-ups under ultrasound technique is displayed in sections 3.5. The analytical procedures involved in determining the physical and chemical properties of the oil are also presented under section 3.3.2.

4.3 Results and discussion

The outcomes and discussion presented in this project chapter are in the accompanying sequence; section 4.3.1 displays and debates the castor oil sample characterization outcomes. Section 4.3.2 presents the properties and fatty acid composition of castor oil. Section 4.4 talks about the aftereffects of the preliminary investigations to decide the impact of procedure parameters on FAME yield through ultrasound reaction while utilizing sulphuric acid. In section 4.5, the characterization results of FAME produced under the distinctive reaction system are given, and after that, think about the standard details.

4.3.1 Castor oil characterization

The characterization of the castor oil utilized for further experiments is introduced in this section. The principal justification for the characterization of the oil sample utilized in this investigation was to decide the fatty acid composition of the triglycerides present in the oil sample, as the chain length and number of double bonds decide to a large degree the physical characteristics of both fatty acids and triglycerides. The characterization is additionally important to quantify the accompanying standard values, such as density, viscosity, water content, saponification, and acid value. Viscosity is firmly identified with the fatty acid composition of a given oil sample. It increments with the expanding length of the fatty acid chain and identifies the rate of transesterification reaction of a given oil sample. The significant point of these reactions is to decrease the viscosity values of triglyceride before transesterification and FAME delivered since the real disadvantage of utilizing perfect

vegetable oils as fuels is their high viscosity values. The acid value of the oil sample is resolved to a huge degree by the feedstock and the level of refinement, although the water content as a quantity plays a significant role in the transesterification procedure as high-water content is related to hydrolytic reactions. The castor seed oil sample's characteristics decide the triglyceride yields to its equivalent FAME and are likewise expected to give knowledge of the degree to which the FAME produced met set down the quality particulars of biodiesel.

4.3.2 Castor oil fatty acid composition and its properties

Before running the transesterification reactions on any oil sample, it is appropriate to decide the physical and chemical properties to ascertain whether the oil sample would require pre-treatment.

I. Chemical and physical properties of castor oil

The chemical and physical properties of castor oil, for example, density, acid value (AV), iodine value (IV), viscosity, saponification value, and water content, were controlled by strategies depicted already in chapter 3 (section 3.3.2). The physical and chemical properties of the oil sample utilized in this examination are displayed in Table 4.1.

Table 4.1 Physical and chemical properties of the feedstock used in this study.

Property (Unit)	Castor oil	Literature
Iodine value (g/mg)	86.05 ± 0.81	82-86 (Zhang et al., 2020)
Density (g/cm^3)	0.89± 0.05	0.956 (Zhang et al., 2020)
Acid value (mg KOH/g)	0.65 ± 0.28	1 (Zhang et al., 2020)
Viscosity (pas at 25^{o}C)	5.9 ± 0.47	6-8 (Kaur and Bhaskar, 2020)
Water content	0.75±0.02	≤ 0,3
Extraction yield (%)	47.16 ± 1.98	42-60 (Dwesh and Ali, 2021)
Saponification value (mg KOH/g)	176.59 ± 0.27	179-185 (Zhang et al., 2020)

***N. D Not Detected**

Table 4. 1 exhibits the results of the yield and physicochemical parameters of castor seed oil. The density was resolved to be 0.89 ± 0.05. FAME density is extremely influenced by the level of unsaturation, with higher unsaturation leading to rising in the density. It has been accounted for that biodiesel density is likewise influenced by chain length. That is, the higher the chain length, the higher the density (Saxena, 2013; Makanju and Bello, 2011). Density is the mass per unit volume of any fluid at a given temperature. Specific gravity is the ratio of the density

of the fluid to the density of water. This parameter is significant in engine performance since fuel injection works with a volume metering system and density is likewise exceptionally applicable in the determination of the cetane index (Srivastava and Prasad, 2000). The acid value was 0.65 ± 0.28. This value is near to that prescribed by both EN 14214 and ASTMD 6751 standard fuel. The measured results of the oil sample parameters show positive repeatability with under 0.5% relative standard deviation considering three imitates. The iodine value of the oil sample (castor oil) was 86.05 ± 0.81. The iodine value could be a measure of the degree of unsaturation of oil, which gives an indication of the presence of double bonds; the higher the iodine value, the more reactive, the less steady, softer, and more vulnerable to oxidation and rancidification the oil would be. The viscosity was decided at 25℃ utilizing viscometers. The value got was 5.9 ± 0.47, appearing that the oil is light and so probably profoundly unsaturated; the high value can be a result of suspended particles still displayed within the crude oil sample. It increments with expanding the length of the fatty acid chain, in this way, clarifying the high viscosity value of the castor oil. The water content value of the castor oil was 0.75 wt.%. This revealed a higher moisture content making it essential to heat the oil sample to 60ºC to eliminate water before the main transesterification to prevent side reactions during the transesterification reactions. Once more, a moderately high saponification value of 176.59 shows that the oil can be utilized in cleanser and beauty care products enterprises.

II. Castor oil fatty acid profile

The oil sample utilized for producing the FAME in this work was examined to decide the fatty acid composition agreeing with the analytical methods examined within the previous chapter, particularly in section 3.3, and the discoveries are summarized in table 4.2. The values are measured in triplicate.

Table 4.2 Fatty acid composition of the castor oil feedstock sample used in this study.

Fatty acid	Carbon number	Result (%)
Ricin oleic	18:1	81.87
Palmitic	16:0	0.49
Oleic	18:1	2.15
Linoleic	18:2	0.59
Linolenic	18:3	0.31
Stearic	18:0	0.48
Dihydroxyl stearic	18:0	0.22
		86.11

Table 4.2 depicts the result of the fatty acid composition of castor seed oil. The histograms of table 4.2 can be seen in (Appendix 4). The saturated fatty acids identified within the sample were ricinoleic, palmitic, oleic, linoleic, linolenic, stearic, and dihydroxyl stearic acids. The values were 81.87%, 0.49%, 2.15%,0.59%, 0.31%, 0.48%, and 0.22%, respectively. The evaluation of the fatty acid composition of castor oil addresses several constraints that are not encountered with most other vegetable oils (Binder et al., 1962). The total fatty acids recognized was 86.11%. The reason may be because of impurities that are displayed within the crude castor seed oil undetected (Cooper and Johson), as cited by (Abitogun et al.,2008). Also, the fatty acid profile is imperative since of the reliance of biodiesel properties on the structure and sort of fatty acid alkyl esters (Knothe and Steidley, 2005; Cooper and Johnson, as cited by (Abitogun et al., 2008).

4.3.3 summary

The mains sections used in the present chapter which will lead to the transesterification reaction based on the homogeneous (section 4) and heterogeneous (Chapter 5) catalyst assisted by ultrasound process are **a**- Material and methods for castor oil characterization; **b**- result and discussions about the characterized castor oil.

The section concerning results and discussion is split into two subsections which are: castor oil characterisation and castor oil fatty acid composition and properties. The objective of the characterisation of the castor oil was to decide whether the oil contains triglyceride and quantify the standard values such as density, viscosity, etc.

The section related to castor oil fatty acid composition and its properties is also, divided into two subsections as chemical and physical properties of castor oil and castor oil fatty acid profile. The first subsection (chemical and physical properties of castor oil) gives the results and debates on the physical and chemical properties of the feedstock used in this study while the second subsection (castor oil fatty acid profile) produces the information and argument about the fatty acid composition of the castor oil feedstock sample used in this work.

4.4 Preliminary study on ultrasound process and its influence on FAME yield at different operating conditions

The preliminary ultrasound transesterification reaction on the castor oil sample was run to understand the impact of methyl ester by changing the amount of catalyst (sulphuric acid) whereas keeping others steady. Once getting the ideal optimum of methyl ester, the sulphuric acid as catalyst was kept constant, whereas other parameters were changed such as reaction temperature, reaction time, and methanol to oil ratio see (section 3.4 Ultrasound process with different catalysts (H_2SO_4, Co/TiO_2, and UCS). The findings of the preliminary samples were utilized as the premise for selecting the parameters to be applied within the ultrasound samples. The preparatory study was carried out by reacting measured volumes of the oil sample with methanol at diverse ratios (3:1-12:1), at varied times (35-50 min) with temperatures of (35-50ºC) at catalyst amounts (0.5-2wt%). This section conducted transesterification reactions at a 100% ultrasound amplitude and 0.5 ultrasound cycles.

4.4.1 The effect of the amount of sulphuric acid catalyst on methyl ester

The sulphuric acid transesterification reaction was examined for four diverse parameters (reaction temperature, reaction time, amount of catalyst, and molar ratio of alcohol to oil). The catalyst amount was shifted from 0.5 to 2 % within the extend of 0.5 these percentages are based on the volume of the castor oil utilized for the sulphuric acid catalyst transesterification reaction, whereas the other parameters were kept constant at 35 min reaction time, 35℃ reaction temperature, 6:1 alcohol to oil molar ratio as shown in table 4.3.

Table 4.3 Results of the effect of the catalyst on the transesterification reactions

Catalyst (wt.%)	Temperature (℃)	Time (min)	Methanol: oil ratio	Methyl ester (%)
0.5	**35**	**35**	**6:1**	**83**
1	35	35	6:1	67
1.5	35	35	6:1	54
2	35	35	6:1	30

The catalyst amount influences the yield process, as appeared in figure 4.1. The acid-catalyst process achieved a maximum yield for castor oil at 0.5% catalyst concentration. The methyl ester yield began to decline when the catalyst concentrations increased to over 0.5%. These results were affirmed as comparable trends were observed previously by (Gude et al., 2012)

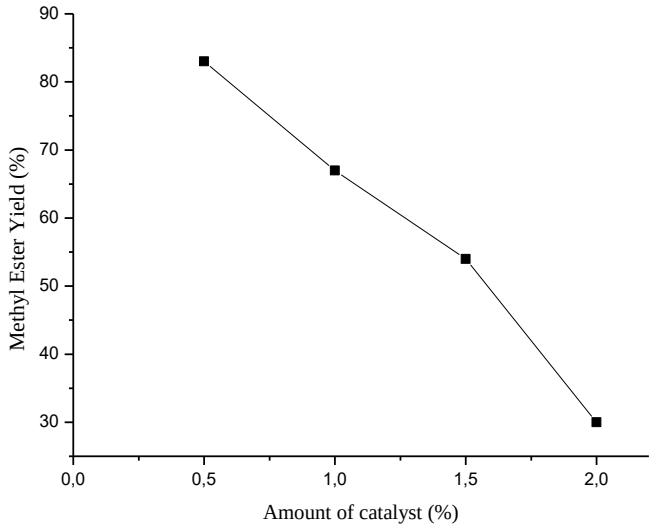


Figure 4.1 The influence of sulphuric acid catalyst on castor oil transesterification reaction, 35℃ reaction temperature, 6:1 methanol to oil ratio, 35 min reaction time, 100% amplitude, and 0.5 cycles.

The information detailed by (Gude et al., 2012) shown in Figure 4.2 also appears the influence of the sulphuric acid catalyst on biodiesel yield. These researchers have utilized (Jatropha curcas) as feedstock, and they found a high amount of methyl ester at 0.5% sulphuric acid for jatropha. In this way, 0.5 wt.% concentration of catalyst is known to be the ideal catalyst

concentration when the researchers are assessing the impact of other parameters such as temperature, alcohol to methanol molar ratio, and time for homogeneous catalyst section.

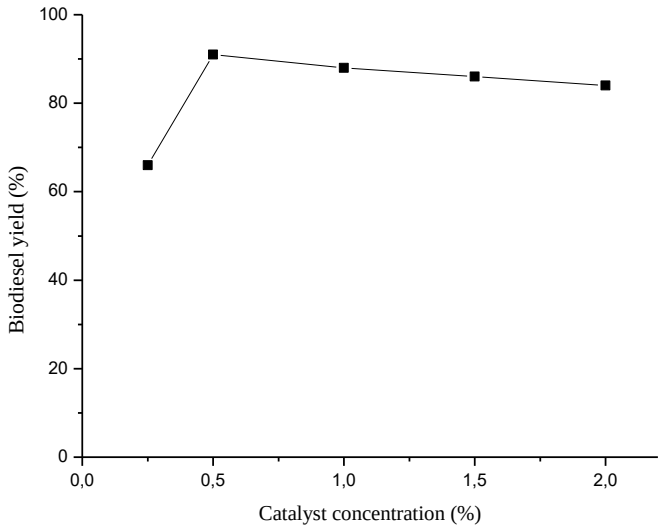


Figure 4.2 Process optimizations for jatropha (Gude et al., 2012)

4.4.2 The effect of reaction time on methyl ester yield

When the reaction time was changed from 35 to 50 min ranging within 5 min and maintaining 0.5% amount of catalyst, 35℃ reaction temperature, 6:1 molar ratio of methanol to oil as shown in table 4.4.

Table 4.4 Results of the effect of time on the transesterification reactions

Catalyst (wt.%)	Temperature (℃)	Time (min)	Methanol: oil ratio	Methyl ester (%)
0.5	35	35	6:1	83
0.5	**35**	**40**	**6:1**	**85**
0.5	35	45	6:1	75
0.5	35	50	6:1	69

The methyl ester reached its maximum of 85% at 40 min reaction time. This was because the experiment was done at a smaller scale which is an experimental process, but the experiment

occurred with correlating operating conditions as suggested by (Goff et al., 2004 and Jacobson et al., 2008), who stated that the homogenous transesterification procedure requires high reaction temperature, high oil-to-alcohol molar ratio, and takes more reaction time, although the statement was because the reaction occurred in an industrial or large scale process and not an experimental or small scale process such as in this study (see section 2.3.4). The decrease of methyl ester from 85 to 75% increased the reaction time from 40 to 45 min. Hence, the methyl ester decreased also from 75 to 69% when the reaction time increased from 45 to 50 min. Be that as it may, working beneath conditions, the equilibrium of esterification can be accomplished at 40 min, which is very more prominent than 69%, getting at 50 min with 0,5% as the amount of catalyst. At a reaction time of 50 min, apparently, the triglyceride in the product mixture had been used up. The ester content increased and reached a maximum of 85 % at 40 min reaction time, and then decreased with an increase in reaction time. This observation is contrary to the comment done by (Goff et al., 2004 and Jacobson et al., 2008), which explained that the hydrolysis of the ester is enhanced due to a longer reaction time reverse reaction of transesterification, therefore, loss of esters and foam formation. By the way (Goff et al., 2004 and Jacobson et al., 2008) worked at the industrial level relative to the case of this study which is based on the laboratory level. The results have been summarised in figure 4.3. The graph of fatty methyl esters in terms of time in figure 4.3 is like the graph reported by (Keera et al., 2018) in figure 4.4. Their graph represented the yield of methyl esters at different reaction times while maintaining the temperature, concentration, and methanol-to-oil ratio constant. When observing both graphs from this study and from (Keera et al., 2018), the fatty methyl ester decreases as time is increased. However, (Keera et al., 2018) showed a smooth straight line, while this investigation showed a decrease in concentration. The difference is due to the type of reactor used. The ultrasound energy had a dumping behaviour, which varies the amplitude of the wave, but the overall behaviour confirms the decrease in biodiesel yield.

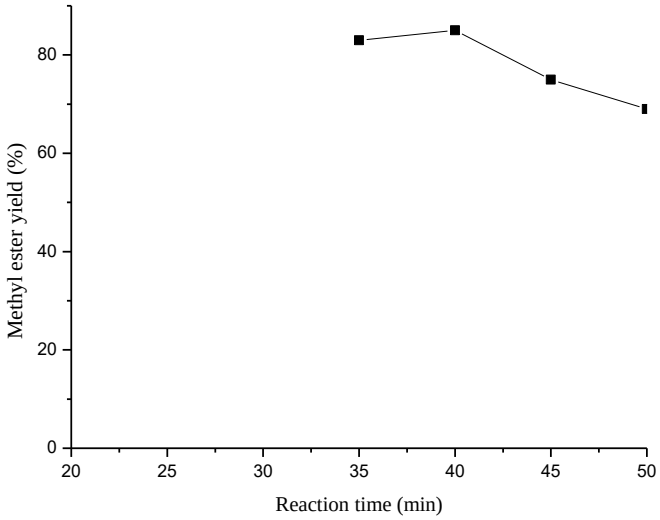


Figure 4.3 The influence of reaction time on castor oil transesterification reaction, 50 ℃ reaction temperature, 0.5 wt. % sulphuric acid catalyst, 6:1 oil to methanol ratio, 40 min reaction time, 100% ultrasound amplitude, and 0.5 ultrasound cycle

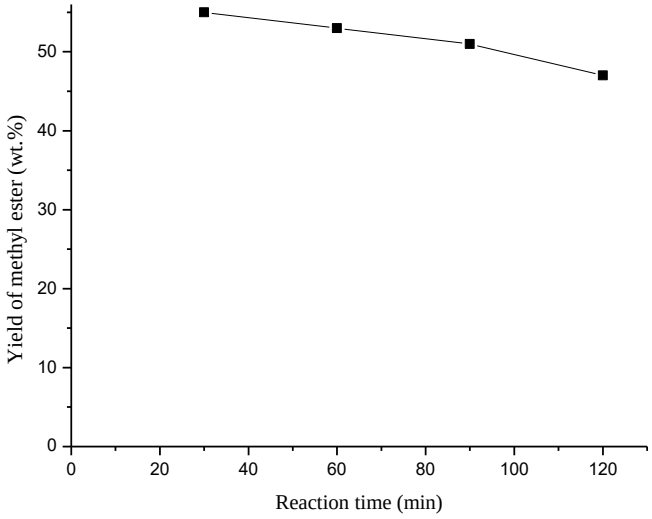


Figure 4.4 Yield of methyl ester at different catalyst concentrations 0.5 wt.% as a function of reaction time, 60 °C temperature, and 6:1 methanol: oil (Keera et al., 2018).

4.4.3 The effect of reaction temperature on methyl ester

The upper-temperature level was decided by the most extreme temperature of ultrasound 50 ºC, which was appropriate due to the boiling point of methanol being 65 ºC. The reaction temperature is another imperative criterion` that will influence biodiesel yield. The effect that

the reaction temperature had on methyl ester production was determined based on optimal conditions obtained in the preceding sections, i.e., 0.5 wt.% of H_2SO_4, a reaction time of 40 min, and methanol to oil molar ratio of 6:1. The experiments were run at temperatures extending from 35 to 50 ºC with five ºC gaps shown in table 4.5.

Table 4.5 Results of the effect of the temperature on the transesterification reactions

Catalyst (wt.%)	**Temperature (℃)**	**Time (min)**	**Methanol: oil ratio**	**Methyl ester (%)**
0.5	35	40	6:1	85
0.5	40	40	6:1	87
0.5	45	40	6:1	88
0.5	**50**	**40**	**6:1**	**90**

It is illustrated that the steady state of the reaction is reached within a short period of time. This is because castor oil dissolves effectively in alcohol at room temperature (Forero, 2005), and the polarity of ricinoleic acid and methanol, castor oil's miscibility produces miscibility in the alcohol. This may likely be due to the high miscibility of castor oil in methanol at room temperature. But after 45℃ of the reaction, this variable is somewhat important. The ester yields after 45 to 50℃ changes by only two wt.%. Hence, for the reaction to occur at 50℃ is very suitable, also (Freedman et al., 1984; Leung and Guo, 2006) stated that the range of optimal reaction temperature might fluctuate from 50 to 60 ℃ depending on the oil and alcohols utilized. This is because higher temperature accelerates the side saponification reaction of glycerides (Eevera et al., 2009). Effect of temperature on methyl ester as shown in Figure 4.5.

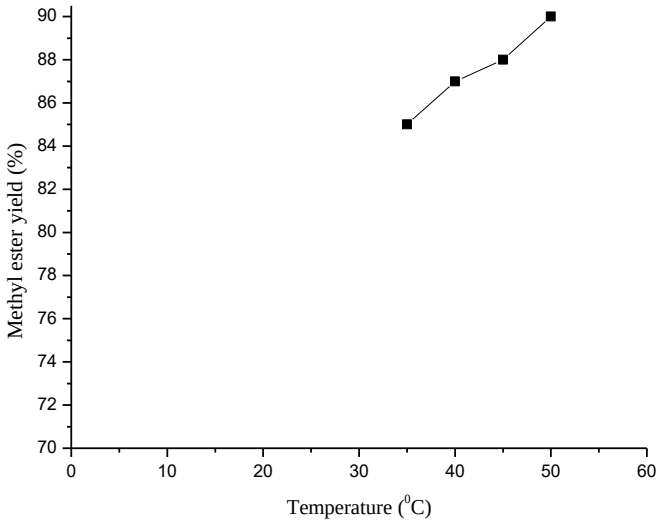


Figure 4.5 The influence of reaction temperature on castor oil transesterification reaction, 0.5 wt.% sulphuric acid catalyst, 6:1 oil to methanol ratio, 40 min reaction time, 100% ultrasound amplitude, and 0.5 ultrasound cycle.

4.4.4 The effect of methanol to oil ratio on methyl ester

The impact methanol to oil ratio on the castor oil sample was explored from a molar ratio of 3:1 to 12:1 at an interval of 3:1 under the ideal reaction parameters obtained from the past ultrasound reactions, which were 0.5% amount of catalyst, 50℃ reaction temperature, and 40 min reaction time as appeared in table 4.6.

Table 4.6 Results of the effect of methanol to oil molar ratio on the transesterification reactions

Catalyst (wt.%)	Temperature (℃)	Time (min)	Methanol: oil ratio	Methyl ester (%)
0.5	50	40	3:1	50
0.5	**50**	**40**	**6:1**	**90**
0.5	50	40	9:1	88
0.5	50	40	12:1	87

The transesterification reaction was run at a methanol-to-oil ratio of 3:1, where the methyl ester yield was 50%. However, a foam layer was seen during the phase separation, with the lower layer being coagulated and the upper layer being opaque. This was most likely because of the presence of unreacted triglycerides, demonstrating that the methanol at a 3:1 ratio was not enough to run a complete reaction because of the stoichiometric necessity of three mols of alcohol to produce one mole of glycerol and three mol of the separate methyl esters. Along these lines, considering that the excessive methanol should be evacuated through the utilization of a rotary evaporator, a methanol-to-oil ratio of 6:1 was regarded to be progressively appropriate in a viable procedure. It was in this manner clear that a high methanol-to-oil ratio would support an increase in biodiesel, and the excess unreacted methanol could be reused effectively by vaporization after the reaction. The alcohol/vegetable oil molar ratio is one of the primary factors that impact the transesterification reaction. An excess of alcohol supports the formation of product and salt waste streams brought about by the utilization of homogeneous catalysts that need neutralization (Meher et al., 2006). Typically, a high methanol-to-oil ratio improves the oil dispersion under agitation. Subsequently, transesterification can be performed effectively. Nevertheless, at a methanol oil ratio of 6:1, transesterification developed with a maximum methyl ester yield of 90%. A small decrease of methyl ester (88 to 87%) was observed from the respective molar ratio of 9:1 and 12:1. The results are shown in figure 4.6 below.

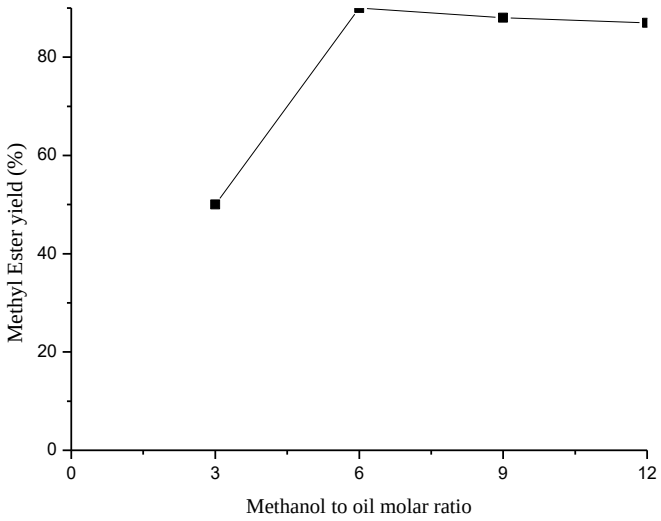


Figure 4.6 The influence of molar ratio (methanol: oil) on castor oil transesterification reaction, 0.5 wt. % sulphuric acid catalyst, 35 min reaction time, 50 ℃ reaction temperature, 100% ultrasound amplitude, and 0.5 ultrasound cycle.

4.4.5 Summary

The purpose of the preliminary investigation of the transesterification using castor oil as feedstock was to gain an insight into the impact of the catalyst and process factors, such as methanol to oil ratio, reaction time, and reaction temperature, would have on the methyl ester yield. Additionally, the methanol-to-oil ratio fundamentally influenced the yield of methyl esters processed from the castor oil. The significant impact of the measure of methanol utilized in the transesterification reaction demonstrated that a measure of methanol was required for the completion of the reaction, which was consistent with the outcomes. Accordingly, a methanol oil proportion of 6:1 was picked in the resulting primary ultrasound reaction tests. The impact of reaction temperature and time on the transesterification reaction was shown to assume an important role in accomplishing the high yield of methyl esters. This primary sample indicated the reaction times and temperature range in which the ultrasound reaction sample was to be run; reaction time (35 - 50 min) and reaction temperatures (35 - 50 °C).

4.5 Characterization of FAME

The quality of the FAME produced beneath ultrasound transesterification reaction was found by changing the following factors (reaction temperature, reaction time, methanol to oil ratio, and sulphuric acid catalyst amount), the quality of the ultimate FAME product gotten from the optimal conditions was further characterized utilizing the services of an authorized biodiesel investigation organization. The comparison of the characterization results of the biodiesel products gotten from the castor seed oil sample under the diverse process systems is given in table 4.7.

Table 4.7 Biodiesel properties of biodiesel produced from castor oil using ultrasound process.

Test parameter	**Unit**	**SANS 1935:2004**	**Test method**	**Ultrasound process** **Castor Oil**
Appearance				
Density (15^0C)	$Kg.m^{-3}$	860-900	ISO 3675	899
Viscosity	(mm^2/s at 40^0C)	1.9-6.0	ASTM D 445	13.465
Iodine value	I_2/100g	140 max	ASTM D 5768	82
Acid value	mg KOH/g	0.5 max	ASTM D 974	0.31
Water content	Ppm	0.05 max	EN ISO 12937	0.02
Cetane number	Nil	51 min	ASTM D 613	39
Total ester	mass %	96.5 min	EN 14103	90
Methanol content	mass %	0.2 max	EN 14110	0.1

4.5.1 Density at a temperature of 15 °C

In table 4.7, the density results which were found in this study with regards to the ultrasound process used for all conditions in producing biodiesel were obtained at 899 $kg.m^{-3}$, although the biodiesel standard gives the condition that the FAME must have a density in the range of 854-900 Kg/m^{-3}. (Sreenivas et al., 2011) indicated that this is one of the important factors of fuel emission control.

4.5.2 Kinematic viscosity at 40 °C

SANS biodiesel norms state that the biodiesel viscosity must be within the range of 1.9 to 6.0 mm^2/s. The castor oil biodiesel viscosity exceeded the SANS biodiesel norm (14.465). High viscosity prompts more unfortunate atomization of the fuel spray and less precise operation of the fuel injectors (Table 4.7). Viscosity is another fuel parameter that depends on its liquid flow. The higher viscosity may be a major issue of biodiesel in diesel engines (Akpan et al. 2006). The high value of the viscosity of fuel causes deposition on the engine, which affects its function. Hence, this biodiesel cannot be directly utilized in a diesel engine. To reduce the viscosity of the fuel, other blends can be utilized. This high value of 14.465 is most likely a result of a deficient transesterification reaction (Knothe and Steidley, 2005). The immediate utilization of vegetable oils in fuel motors is difficult because of their high viscosity (around 11-17 times higher than diesel fuel) and low volatility, and they do not ignite totally, and form deposits stored in the fuel injector of diesel motors (Demirbaş, 2003).

Indeed, more than density, kinematic viscosity is a necessary property for the atomization of fuel and fuel distribution. For biodiesel to be utilized in diesel engines, the kinematic viscosity must be within the range of 3.5 and 5.0 mm^2/s. (Dernotte et al., 2012) stated that fuel viscosity seems, by all accounts, to be the most significant physical property since it influences the flow characteristics. The availability of glycerides modifies the apparent viscosity of the methyl esters, showing the extend of the transesterification reaction and the methyl ester's phase purity (De Filippis et al., 1995). In this biodiesel production process, the experimental conditions utilized, and the extent of the reaction were incredibly affected by the fuel properties as well as its apparent viscosity.

4.5.3 Value of iodine

In Table 4.7, the iodine value of the FAME produced from castor oil uncovered values 82. This is a vital measure that permits assurance of the degree of unsaturation of fuel. This is a property of biodiesel that incredibly impacts fuel oxidation and aging deposits and products produced in diesel engine injectors. Coming to terms with EN 14214 (2003), diesel fuel should have an iodine value below 120 g I_2 per 100 g of the sample when utilizing methyl esters.

4.5.4 Acidity

The measure of acidity or the acid value was found to be 0.31 for the biodiesel produced in this study from castor oil using the ultrasound process, and this result was also found by (Patil and

Deng, 2009). The SANS specifications indicate that the acid value of the biodiesel obtained should not surpass an acid value of 0.5, which was obtained in this study.

4.5.5 Water content

One of the basic parameters of biodiesel is water content. The presence of water influences the spray and ignition qualities of diesel motors and assumes a noteworthy role in the destruction of diesel biodiesel mix brought about by microbial development. Furthermore, according to EN14214 (2003), not more than 0.05% should be obtained when determining the amount of water in biodiesel. The methyl esters found in the castor oil sample after the oil sample went through an ultrasound process were dried over anhydrous magnesium sulphate as per the normal procedure. Even though this method is used in laboratory practice, it is very effective due to its reduction of the water content in the biodiesel sample obtained, which was 0.02%, Table 4.7 distillation under vacuum is a usual way of drying with the vacuum being set at 0.05 bars at temperatures ranging from 30 - 40 ºC.

4.5.6. Total ester content

Ester content in biodiesel assumes a significant role in assessing biodiesel quality. The gas chromatography strategy has been demonstrated as the most unique technique for deciding the ester content (Thoai et al., 2017). The total methyl ester content of the produced biodiesel was 90%. It is significant to notice the influence the transesterification reaction and the feedstock had on the amount of ester produced from the resulting biodiesel produced in this study. After analysing the results, it is easy to say that the ester content met the desired specifications of EN 14214. Due to the specifications of the EN 14214 (2003), the SANS allows the researcher to obtain a purity of at least 96.5 % in methyl esters when producing biodiesel, be that as it may, the acceptable purity for biodiesel concurring with the ASTM D 6751 has no restrained (Appendix 5). The net result of an efficient depletion of glycerol and adequate reaction extent, especially using the ultrasound process, is the amount of purity of the biodiesel produced by the researcher (Freedman et al., 1984; Tomasevic and Siler-Marinkovic, 2003).

4.5.7 Methanol content

Another conceivable pollutant of the methyl ester stage that can cause the destruction of metal is methanol, which is especially harmful to aluminium, and it is responsible for lowering the fuel’s flashpoint. The exorbitant amount of methanol allowed in biodiesel production, according to EN 14214 (2003), is 0.2%. During the washing step, the methanol was without

difficulty expelled from the ester stage, which allowed the amount of methanol or methanol content to be reduced to 0.1% during the reaction processes. Therefore, as per the amount of methanol content prescribed by the SANS specifications, the methanol content of the biodiesel used in this study is appropriate.

4.5.8 Summary

The information obtained from the above figures (4.1;4.3;4.5 and 4.6) revealed that the increase in the amount of catalyst decreases the yield of the product methyl ester. O.5% catalyst showed a better yield of methyl ester. The time is inversely proportional to the yield of methyl ester like the amount of catalyst. 40 minutes was the optimum time to be reached. However, the temperature of 50℃ had a positive effect on the yield of methyl ester produced. The methanol-to-oil ratio of 6:1 was the optimum.

The formation of biodiesel from castor oil is feasible by acid-catalysed transesterification (H_2SO_4), and the biodiesel fuels to be supplied under the ultrasonic homogenization reactor have the requisite quality to be a diesel substitute. This happen after observing that the density amounts were similar to fuel for cars and heavy engines. The operating condition in which the maximum biodiesel was obtained is in Table 4.5. It is permissible to clarify that biodiesel's value can be a significant problem in commercial production. It is worth of mention that as the quality of biodiesel is a crucial issue in commercial production, biodiesel quality depends not only upon the reaction process which it goes through but also on the downstream processing like product separation, water washing, and methanol recovery; hence such improvements can then allow a feasible scaling and exploitation of the production of biodiesel.

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Chapter five Synthesis of biodiesel based on the heterogeneous catalyst.

5. Introduction

This chapter explores the transesterification reaction resulting from the heterogeneous catalyst. It also addresses and discusses the outcomes of the physical, and chemical characterization of the UCS and Co/TiO_2 catalyst. SEM-EDS, XRD, and BET were the analytical techniques employed for the characterization of the Co/TiO_2 catalyst, while SEM-EDS, XRD, FT-IR and BET were used for the characterization of the UCS catalyst. The listing of these methods and the results debated in this chapter come from the experimental procedures described in the materials, and methods of chapter 3. The enumerations of the procedure for the preparation of the catalyst and the sources are presented in chapter 3, section 3.8.2. The influence of different reaction parameters such as methanol to oil ratio, reaction time, temperature, and deactivation of the catalyst was studied. The catalytic activity results of these catalysts and the effect of the reaction parameters on the catalytic efficiency are presented. This chapter also gives a comparison between UCS and other catalysts.

5.1 General idea

The utilization of UCS as an adequate raw material to be applied as a heterogeneous catalyst for transesterification will permit beneficiation in making the transesterification process more economically viable. (Rizwanul et al., 2020) stated that homogeneous catalysts are generally effective in converting biodiesel with low free fatty acid (FFA) and water-containing single-origin feedstock. On the other hand, heterogeneous catalysts provide superior activity, range of selectivity, good FFA, and water adaptability.

However, the defy of a less expensive procedure still exists because there is a constant need to build up an improved cost-effective, and eco-friendly for producing biodiesel. Enhanced processing could lead us to easier refining of the produced biodiesel and glycerol, reusing the catalyst, and lowering the production cost (Bournay et al., 2005). As early expressed, a solid, strong base is highly desirable for developing environmentally benign processes to catalyse diverse reactions based on mild conditions and minimize pollutants' production (Son et al., 2010).

Many researchers (Niju et al., 2014; Boro et al.,2012; Piker et al., 2016) have reported about solid base catalysts derived from catalyst shells from different substances than castor shells seed for biodiesel production. Moreover, a few attempts, for example, (Yusuff et al., 2019; Gutiérrez-Ortega et al., 2019), have been made to elucidate the effect of cobalt oxide catalysts

on biodiesel production. To promote mass transfer, it was necessary to use an ultrasonic reactor that used sufficient energy to produce biodiesel using heterogeneous catalysts which provide more specific area and pore volume for the actives species to react.

Considering the importance of developing environmentally safe and biodiesel formation from low-cost materials, applications for the utilization of unsupported castor shell and the supported cobalt catalyst was made in this project to develop an efficient, inexpensive, and environmentally friendly unsupported castor shell-based catalyst as well as a cobalt-based catalyst to be used in the transesterification reactions for the production of biodiesel (FAME). The application of a new based solid catalyst prepared from the South African castor shell but not supported denoted as UCS for use as heterogeneous catalysts in the production of biodiesel is hence reported.

This chapter gives the outcome of (i) The physical and chemical composition of UCS and Co/TiO_2, (ii) the impact of the diverse reaction parameters on the yield of oil triglycerides to their related FAME(s) utilizing these heterogeneous catalysts, (iii) the enhancement of the reaction procedure utilizing the UCS and Co/TiO_2 catalysts. (iv) the quality and appropriateness of the FAME(s) formed under the above set of conditions using the UCS catalyst and Co/TiO_2 catalysts in evaluation with standard specifications.

5.2 Materials and method

The different analytical procedures, for example, BET, XRD, SEM-EDS, and FT-IR are exhibited under sections 3.8.2, 3.8.3, 3.8.4, 3.8.5, and 3.8.6, respectively, though the experimental setup of the transesterification reactions (conducted utilizing ultrasound technology) displayed in sections 3.5. The illustration of the source materials and procedure utilized for the preparation of the heterogeneous catalysts utilized in the investigation are displayed in Chapter 3, Section 3.7.2. The analysis of the methyl ester product obtained under the operating conditions of trials conducted in this chapter was finished by applying the GC-MS refer to the composition of FAME in section 3.6. Analytical tests to determine in accordance with the biodiesel sample produced based on its international standards are set out in Appendix 5.

5.2.1 Oil characterization

The characterization of the feedstock material (castor oil) utilized for all investigations is displayed in section 4.3.1, Table 4.1. As seen from those outcomes in the previous section, castor oil was utilized as a feedstock to perform the transesterification reactions and determine

the catalytic activity of UCS and Co/TiO_2 catalysts. All physical properties and chemical composition of the oil utilized in this section can be seen in the past chapter, section 4.3.2. Ongoing characterization was done on the feedstock utilized in the transesterification reactions.

5.3 Results and discussion

5.3.1 Catalyst characterization

The characterization of the UCS and Co/TiO2 catalyst used for additional tests is shown separately in sections 5.3.2; 5.3.3; 5.3.4; 5.3.5; and 5.3.6. The fundamental explanation behind the characterization of the UCS and Co/TiO_2 catalysts utilized in this investigation is to determine the morphology, composition, and structure of the prepared catalyst. The goal of this section is to comprehend the physical, chemical, and mineralogical composition of the UCS and the Co/TiO_2 catalyst, and from that point, to decide the activity of the catalyst and performance of the above-mentioned catalyst on the transesterification reactions and the conversion/yields of castor oil to its respective methyl esters. The characterization of the UCS and Co/TiO_2 catalysts and their utilization in the transesterification of castor oil is relied upon to give knowledge of its chemical composition and catalytic activity in such a manner.

5.3.2 Morphology and relative proportions composition of the calcined UCS (SEM-EDS)

The morphology of the UCS obtained by SEM is shown in Figure 5.1, and the elements presented including their relative proportion in the composition of UCS are given in figure 5.2.

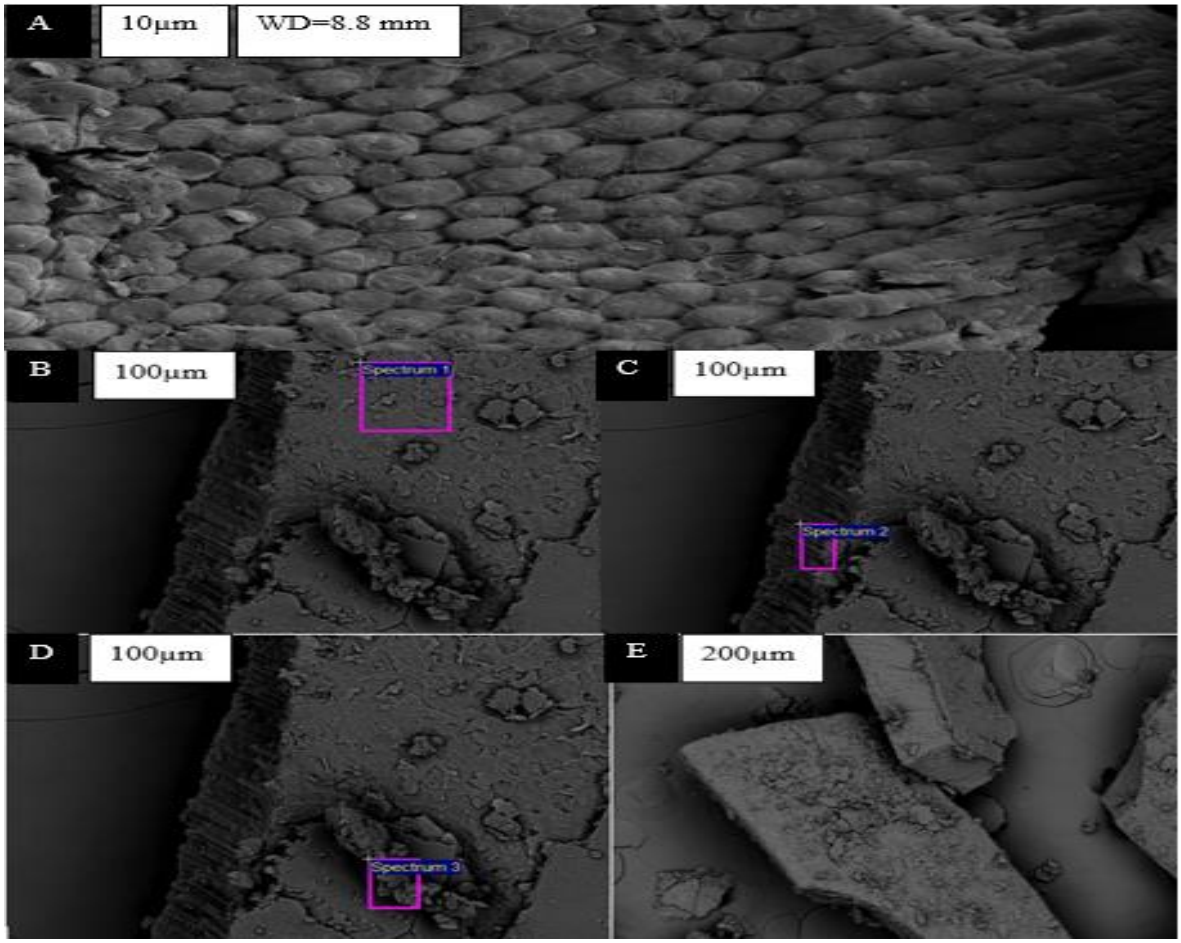


Figure 5.1 SEM micrograph of (E) the castor shells and (A, B, C, D) showing the area chosen for SEM analysis at different magnifications.

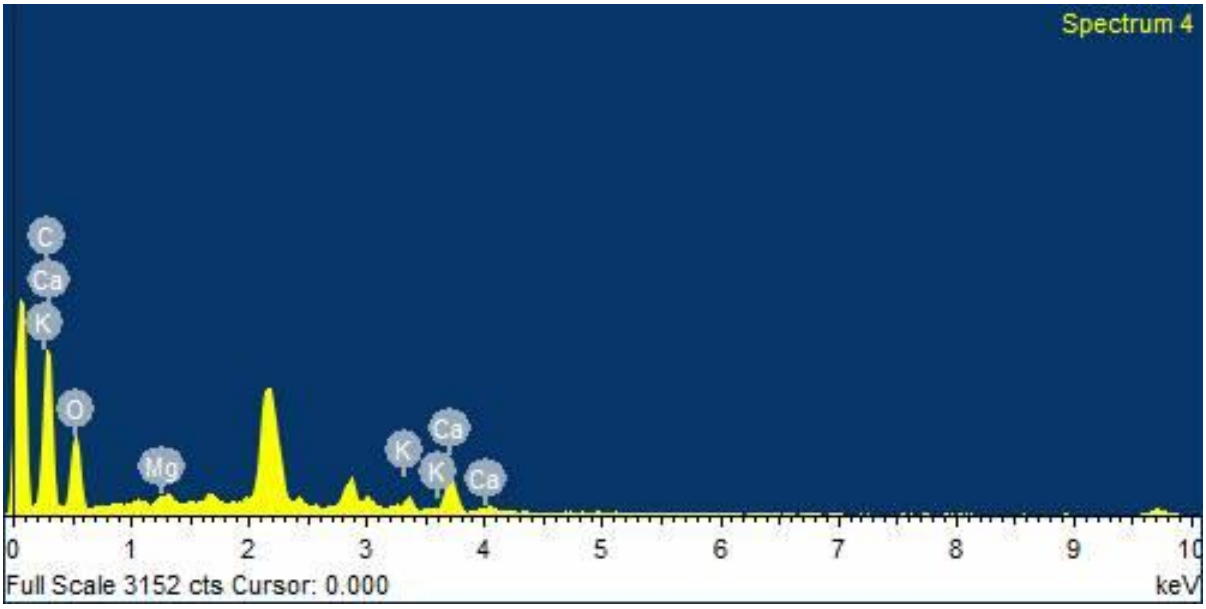


Figure 5.2 Energy Dispersive Spectroscopy (EDS) allows identifying what the elements are and their relative proportions in the composition of castor shells.

The morphology of the surface of the castor shell is displayed in Figure 5.1, although Figure 5.2 represents the EDS related to the qualitative compositional analysis of a selected area of the SEM micrographs. It indicates a honeycomb-like porous surface as observed by (Hu et al.,2011) and (Niju et al., 2014) for eggshells and treated mussel shells, respectively. However, according to (figure 5.1) the castor shell's case shows a regular micromorphology of honeycomb-like particles with sizes ranging from 100 to 200µm in width was also observed. The increase in pore volume and surface area; and the decrease in the mass of the catalyst system are an indication of the removal of the volatile materials, which leaves the system above its boiling points. This created more room to accommodate the reactants (methanol) and enhanced the transesterification process. The EDS confirms that the matrix of castor shells is composed mainly of K, Ca, O and C with minor Mg.

The calcium and oxygen obtained from the UCS materials could probably react to produce $CaCO_3$ or CaO which is the most adaptable heterogeneous base catalyst. As per (Zabeti et al., 2009 and Di Serio et al., 2008) many metal-based oxides, including alkali metal, alkaline earth metal, and transition metal oxides have been used as a catalyst for the transesterification process of oils. UCS powders in an aqueous environment had a basic p^H (P^H increases with the amount of the added powders), which had properties of a basic heterogeneous catalyst. This can be supported by the presence of metal oxides found in the UCS.

5.3.3 Fourier transformed infrared (FT-IR) spectroscopy of UCS

The FT-IR spectrum of calcined unsupported castor shell catalyst is shown in Figure 5.3

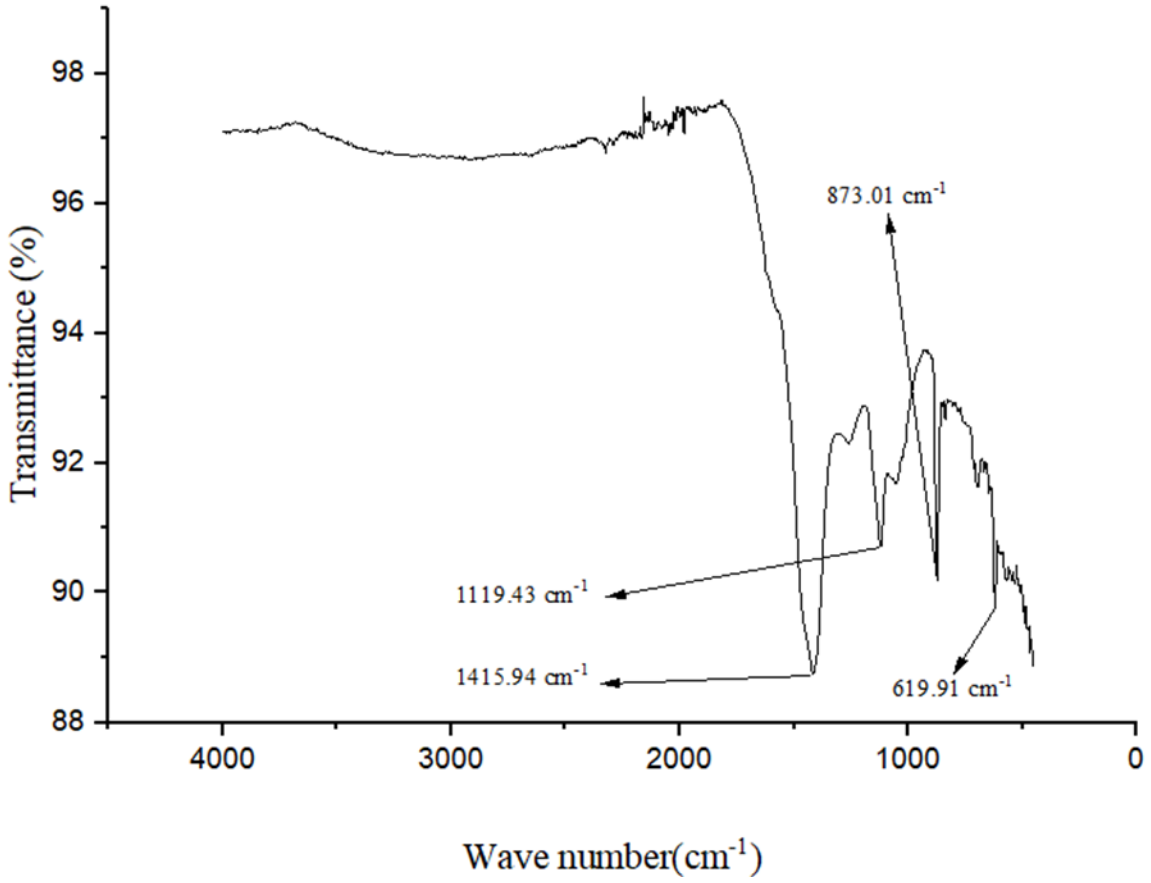


Figure 5.3 FT-IR spectrum of UCS catalyst

The FT-IR spectrum of unsupported castor shell catalysts is shown in Figure 5.3. In the spectrum, the existence of peaks at 1415,9 cm^{-1}, 1111,49 cm^{-1} and 873 cm^{-1} are revealing of C-O stretching vibrations due to the presence of metal carbonates (Ca CO_3) in the catalyst which is in conformity with the FT-IR study results of catalyst reported by (Betiku et al., 2017), (Gohain et al.,2017), (Pathak et al.,2018) and (Nath et al.,2020). The peak at 619,91 corresponds to Ca-O stretching vibrations which may be due to the presence of CaO in the catalyst. This is in the agreement with the FT-IR results obtained by (Nath et al.,2020).

5.3.4 Phase and crystallite size of the UCS catalysts using X-ray diffraction (XRD)

To characterize the crystallinity patterns of the unsupported castor shell catalyst XRD analysis was performed for the samples. The XRD pattern of UCS powder is shown in figure 5.4.

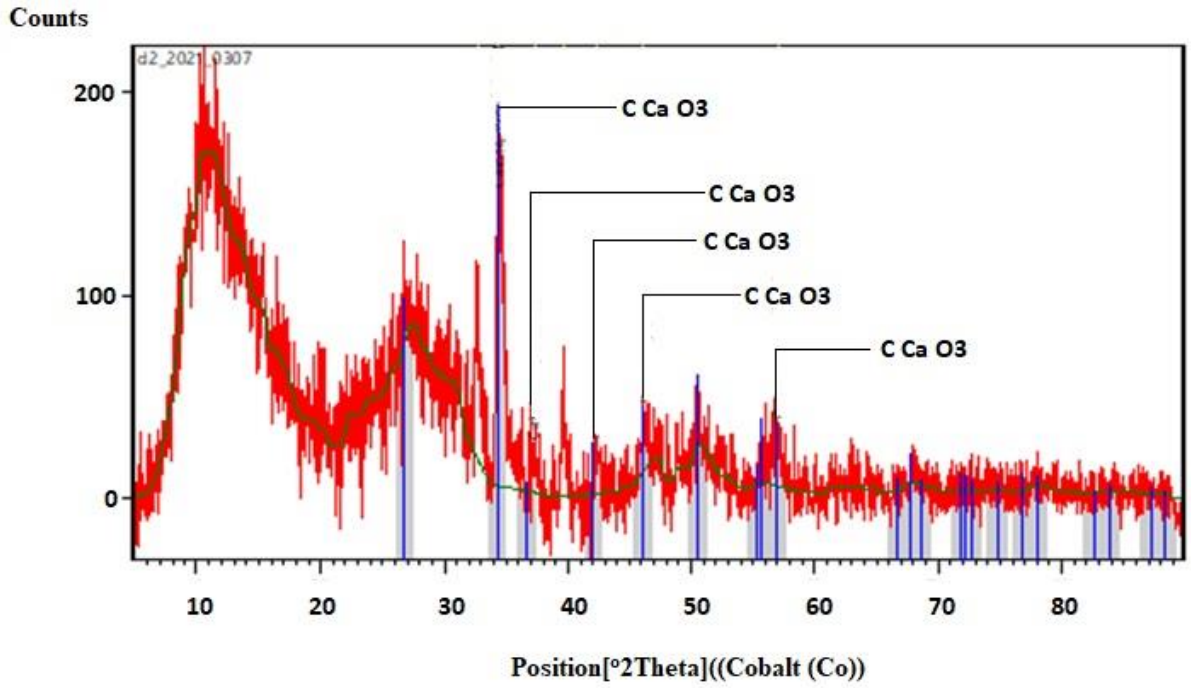


Figure 5.4 XRD pattern of UCS catalyst

The catalyst crystallite size was determined using Scherrer's expression, which is given by,

$$d = \frac{0.9\lambda}{\beta \cos\theta} \qquad 5.1$$

where d is the crystallite size of the active phase (nm), λ is the x-ray wavelength, θ is the angle of diffraction and β is the full width at half maximum of the peak.

The XRD pattern reflects the existence of calcite ($CaCO_3$) peaks. The XRD peaks at 2Θ values are 32.8, 34.4, 37.3, 39.6, 42.4, 46.2 and 57.1 revealing that $CaCO_3$ formed following the JCPDS card No 00-005-0586. All these values are reflected to the $CaCO_3$. The average $CaCO_3$ crystallite size determined from XRD data using the Scherrer equation was 20.16 nm.

5.3.5 Surface area, pore size and pore volume determination UCS

A surface area of 1.59 m^2/g was determined by the BET surface area analysis of the calcined UCS catalyst. The UCS catalyst's pore volume is revealed to be 0.010 cm^3/g. 1.84 nm represented the UCS pore size distribution. In contrast to the current study, a study by (Pathak et al. 2018) found that the surface area of Musa acuminata peel ash catalyst was lower (1.45 m^2/g). By calcining Acacia nilotica wood at various temperatures for three hours, (Sharma et al., 2012) also prepared a solid heterogeneous catalyst, reporting surface areas between 1.33 and 3.72 m^2/g. According to reports, the main factors that affect the surface area of the heterogeneous catalyst that is directly linked to the catalytic activity providing superior results of oil transesterification reaction with the higher surface area are calcination temperature and time (Mendonca et al., 2019 and Sharma et al.,2012).

5.3.6 Morphology and relative proportions composition of the prepared Co/TiO_2 using (SEM-EDS)

The SEM images of this catalyst are shown in Figure 5.5. The surface of the Co/TiO_2 catalysts appears more regular and porous. Approximate chemical compositions of the cobalt oxide catalyst supported by titanium oxide were obtained from the EDS data figure 5.6.

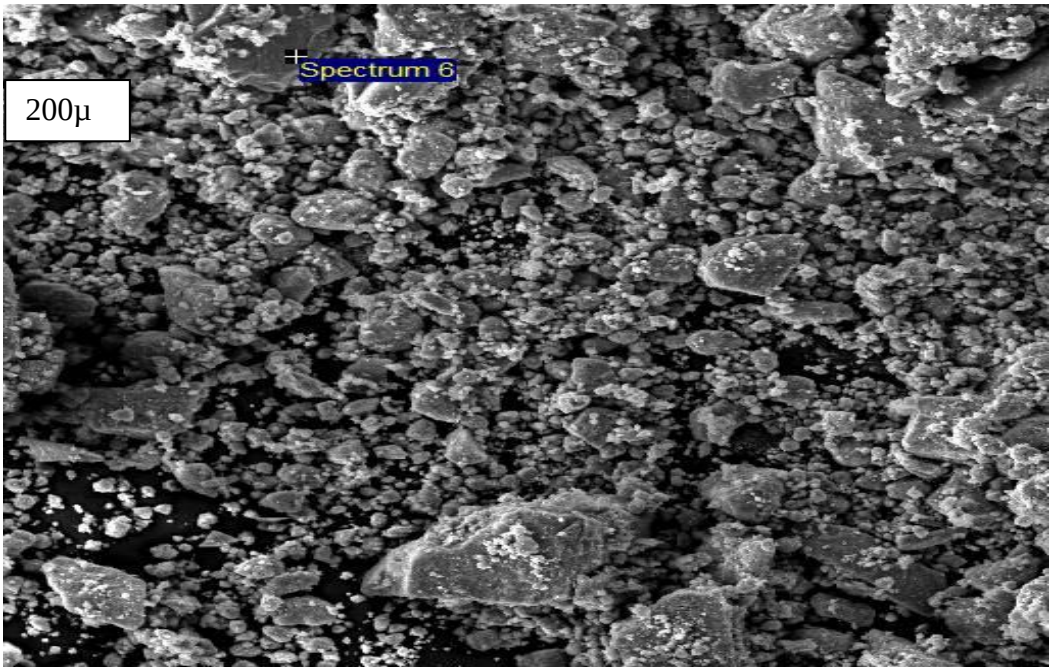


Figure 5.5 SEM is showing the physical composition of the prepared Co/TiO_2 catalysts.

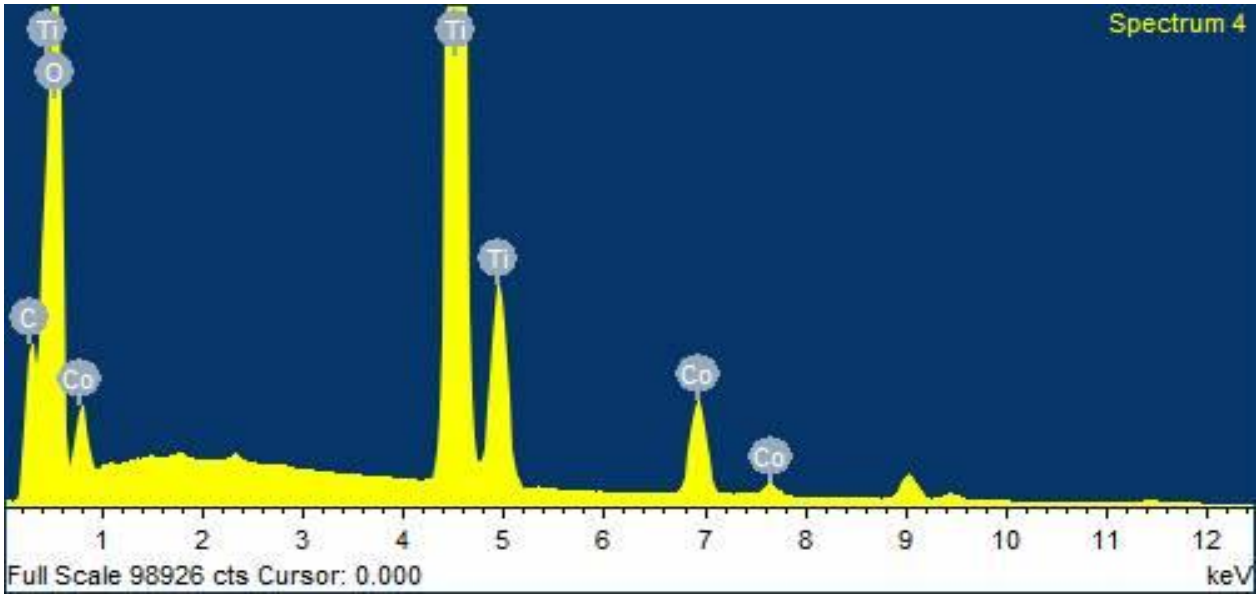


Figure 5.6 Energy Dispersive Spectroscopy (EDS) allows identifying what the elements are and their relative proportions in the composition of the Co/TiO_2 catalyst composition.

5.3.7 Phase and crystallite size of Co/TiO_2 catalysts using X-ray diffraction (XRD)

The XRD analysis data for the blank titanium support and the Co/TiO_2 catalyst are shown in Figure 5.6. X-ray diffraction analysis was carried out to evaluate the catalyst structure and to identify the phases that constitute the catalyst. However, Figure 5.7 displays the X-ray diffraction profile against the angle of diffraction (2θ) of the calcined 10% Co/TiO_2 catalyst and the blank TiO_2 as a catalyst supporter.

It is evident that Co_3O_4 is the main phase in the Co/TiO_2 catalyst's calcined in that most of the peaks were characteristic of Co_3O_4. The JCPDS card number for diffraction peaks observed in the 10% Co/TiO_2 was 44-145.

However, the diffraction peaks observed in both the 10% Co/TiO_2 catalyst and the blank TiO_2 support are for anatase at 2θ = 25.3, 36.8, 37.8, 38.3, 47.8, 53.8, 54.8, 62.6, 68.6, 70.0, 74.9 and 82.50°, and for rutile at 2θ = 27.4, 36.0, 41.1 and 56.5°. The diffraction peaks at ca. 2θ = 31, 59, and 65° were observed only in the 10% Co/TiO_2 catalyst data (pattern a) and can be ascribed to Co_3O_4 resulting from the decomposition of Co $(NO_3)_2.6H_2O$ during catalyst calcination in air. The average Co_3O_4 crystallite size determined from XRD data using the Scherrer equation was found to be 19.7 nm. According to (Zabeti et al., 2009 and Di Serio et al., 2008) many metal-based oxides, including alkali metal, alkaline earth metal, and transition metal oxides have been used as a catalyst for the transesterification process of oils. This cobalt

oxide (Co_3O_4) has properties of a basic heterogeneous catalyst because of the structure of metal oxides which consists of positive metal ions (cations) that possess Lewis acid characteristics and negative oxygen ions (anions) that possess Brønsted base characteristics.

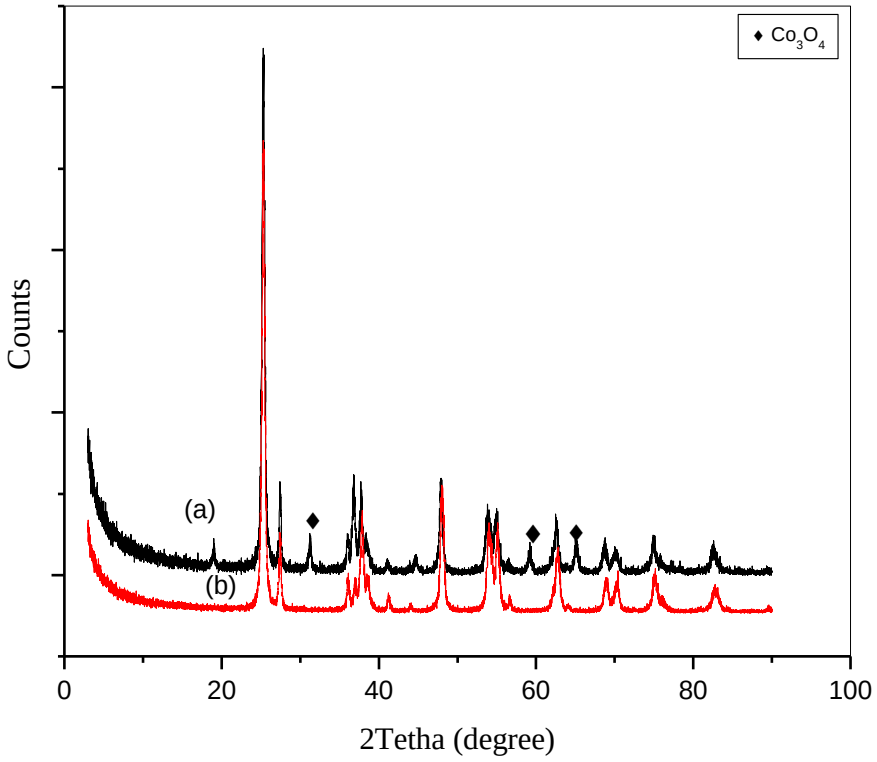


Figure 5.7 XRD results for a) 10%Co/TiO_2 catalyst and b) blank TiO_2 support calcined at 400° C in air.

5.3.8 Surface area, pore volume and pore size of Co/TiO_2 catalyst using (BET) analysis.

The BET analysis data for both the blank TiO_2 support and the 10% Co/TiO_2 catalyst are reported in table 5.1.

Table 5.1 Summary of BET results for 10% Co/TiO_2 and blank TiO_2

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
TiO_2	41.00	0.37	36.9
Co/TiO_2	49.05	0.46	38.6

The data show an increase in surface area from 41 to ca. 49.05 m^2/g; a pore volume from 0.37 to 0.46 cm^3/g; and pore size from ca. 36.9 to 38.6 nm subsequently from blank supporter TiO_2 to Co/TiO_2 catalyst. The increase in surface area was expected due to the heating treatment of the catalyst-support system. It was also expected that some of these cobalt oxide species would stabilize in the pores of the support, which would lead to a decrease in pore volume and size in contrast to the measured data in Table 5.1. Therefore, the measured data suggest that some pores collapsed during the process of stabilizing the cobalt oxide species in the titanium oxide supporter. This most probably happened during the second calcination process, which was done only for the Co/TiO_2 sample, to decompose the cobalt nitrate hexahydrate, that was used as a catalyst precursor. In addition, (Olutoye, and Hameed,2013) have postulated that the large BET surface area and expanded pore volume of calcined catalyst indicated that the catalyst's external surface is dominated by active molecular sites and, therefore, can promote the adsorption of methanol.

The calcination temperature had a great impact on the textural structures. At 400° C, anatase was the main peak, while the rutile effect was insignificant. However, the surface area is supposed to be less than 40-48 m^2/g which will be corresponded to the P25 calcined. The change with specific surface area decreasing could be observed after an increase in the temperature, which was not a concern for this research. A similar result was obtained (Wu et al., 2014).

5.4 Transesterification reactions based on Co/TiO_2 and UCS catalyst.

The prepared Co/TiO_2 catalyst was studied in heterogeneous transesterification using castor oil as a raw material. The effect of the cobalt catalyst was studied in comparison with a different catalyst nominal (UCS catalyst).

With the objective of enhancing the conversion of oil and yield of the product, an investigation was likewise issued to optimize the reaction parameters, for instance, methanol to oil molar ratio, the effect of either UCS or Co/TiO_2 catalyst, temperature, reaction time and reusability of catalyst on the production of methyl ester from castor oil.

5.4.1 Influence of Co/TiO_2 and UCS as catalysts

The influence of Co/TiO_2 and UCS as catalysts on the yield of methyl ester for the transesterification completed on castor oil was run under these operating conditions: reaction time of 50 min, methanol to oil ratio of 6:1, reaction temperature 50 °C, and the ultrasound was set up at amplitude 100%, 1cycle per second. Catalysts varied between 0.5 to 2 %. Results are presented in tables 5.2 and 5.3, which are graphically displayed in figure 5.8.

Table 5.2 Influence of catalyst amount of Co/TiO_2

Catalyst (wt.%)	**Temperature (°C)**	**Time (min)**	**Methanol: oil ratio**	**Methyl ester (%)**
0.5	50	35	6:1	44
1	**50**	**35**	**6:1**	**75**
1.5	50	35	6:1	50
2	50	35	6:1	49

Table 5.3 Influence of catalyst amount of UCS

Catalyst (wt.%)	Temperature (°C)	Time (min)	Methanol: oil ratio	Methyl ester (%)
0.5	50	35	1:6	35
1	**50**	**35**	**1:6**	**65**
1.5	50	35	1:6	40
2	50	35	1:6	30

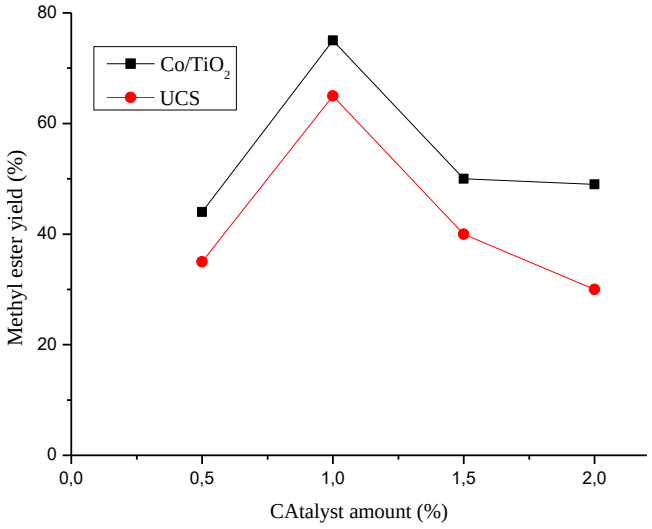


Figure 5.8 Methyl ester yield in terms of the amount of catalyst, at reaction conditions: reaction temperature of 50 °C, the reaction time of 35 min and methanol: oil ratio of 6:1 and an ultrasound set up at 100% amplitude and 0.5 cycles.

To decide the impact of the amount of catalyst utilized per unit volume on the methyl ester yield, the catalyst amount was shifted inside the range from 0.5 - 2 wt.%. The reaction was completed with Co/TiO_2 and UCS as catalysts at a methanol to oil ratio of 6:1, a temperature of 50 °C for 35 min, and ultrasound set up at an amplitude of 100% and 0.5 cycles. The outcomes indicated that the measure of catalyst per unit volume of methanol and oil mixture using UCS was increased (0.5 - 2 wt.%), the yield of methyl ester has attended the maximum of 65%, and as the quantity of the Co/TiO_2 (0.5-2%) catalyst increased there was a maximum of methyl yield of 75%. For the same amount of the catalyst (1%), the methyl yield of the Co/TiO_2 catalyst was 75% higher than the methyl yield of the UCS catalyst at 65 %. Regarding

the reaction kinetics, a small measure of catalyst prompts a better yield of methyl esters in a quicker reaction time (35 min). Nonetheless, with an increment in the measure of catalyst to over 1%, the mixture of reactants and catalysts became viscous, leading to an issue of mixing and a request for higher power utilization for satisfactory mixing. Then again, when the catalyst loading measure per unit volume was less than 1% for both heterogeneous catalysts (UCS and Co/ TiO_2), the most extreme production of yield could not become to. To stay away from this sort of issue, an ideal measure of catalyst loading per reaction volume must be examined. This is a direct result of the way that the solid-catalysed process is an immiscible liquid-liquid-solid 3-stage structure (corresponding to oil, methanol, and catalyst) that is exceptionally mass transfer constrained (Lee et al., 2009). In addition, when the catalyst loading was augmented to more than 1 wt.% for UCS and Co/TiO_2, the FAME content was reduced. This is because when the catalyst amount was in great abundance, the mass transfer between the catalyst and reactants diminished along these lines decreasing the interactions among them and, simultaneously, lessening the FAME content.

Also, the probability of accumulation of the organic compound on the catalyst surface can repress the active site and might be responsible for FAME decreasing yield.

It seems that the combination of calcium with oxygen, both present in the unsupported castor shell according to the results given by SEM-EDS, produces the CaO or $CaCO_3$, which is contributing to the elevation of the methyl yield.

In conclusion, an effective catalyst measure was set up to 1 wt.% as it was adequate in catalysing the transesterification. The most extreme methyl ester yield came to 75%, which was somewhat lower than the methyl ester yield acquired in the regular homogeneous H_2SO_4 catalyst system, 90 %, as exhibited in the past chapter (Table 4.6 in section 4.4.4).

5.4.2 Influence of the methanol-to-oil ratio

The impact of methanol: oil ratio on the methyl ester yield based on the transesterification reaction completed with the Co/TiO_2 and UCS as catalysts on the castor oil was run under these operating conditions: the amount of catalyst 1wt%, reaction temperature of 50 °C, reaction time 35 min as well as an ultrasound set up at 100% amplitude and 0.5 cycles. Results are shown in tables 5.4 and 5.5, Figure 5.9.

Table 5.4 Influence of methanol to oil ratio of Co/TiO_2

Catalyst (wt.%)	Temperature (°C)	Time (min)	Methanol: oil ratio	Methyl ester (%)
1	50	35	3:1	54
1	50	35	6:1	75
1	**50**	**35**	**9:1**	**80**
1	50	35	12:1	71

Table 5.5 Influence of methanol to oil ratio UCS

Catalyst (wt.%)	Temperature (°C)	Time (min)	Methanol: oil ratio	Methyl ester (%)
1	50	35	3:1	47
1	50	35	6:1	65
1	**50**	**35**	**9:1**	**72**
1	50	35	12:1	49

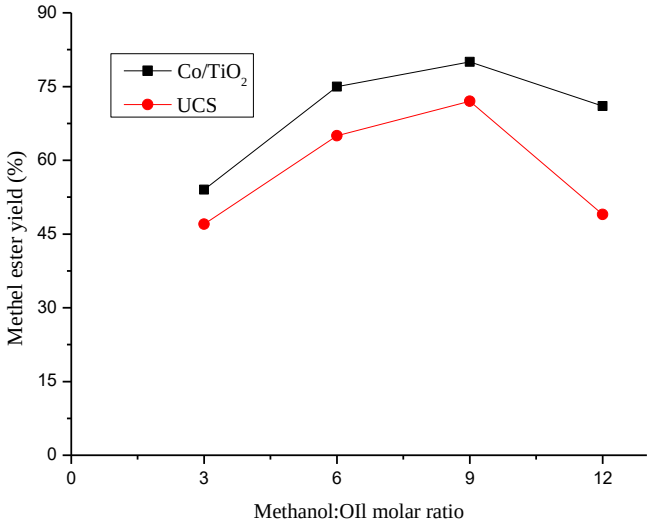


Figure 5.9 Influence of methanol to oil ratio on yield of methyl ester at a catalyst amount of 1wt%, reaction temperature of 50°C, a reaction time of 50 min, and an ultrasound set up at 100% amplitude and 0.5 cycles.

The impact of varying the methanol to oil ratio on the methyl ester yield was analysed by changing the measure of methanol while the amount of catalyst is kept constant at 1 wt.%. The primary amounts of methanol and oil were set comparing to the methanol: oil ratios of 3:1, 6:1, 9:1, and 12:1 was utilized as represented in Figure 5.9. The outcomes in figure 5.8 likewise show that a higher molar ratio of methanol to oil 9:1 gave a high methyl ester yield of 80 % and 72 % for both the Co/TiO_2 and UCS as catalysts, respectively. From that point, an important increment in the methyl yield was seen at the methanol-to-oil ratio of 9:1. In this way, a high ratio of methanol to oil is advantageous for this situation. It has been accounted for that a constraint exists to the utilization of a more noteworthy measure of methanol expected to move the reaction forward, which is an event of flooding of the active sites by the methanol molecules as opposed to triglyceride molecules. This flooding may obstruct the achievement of the triglyceride conversion to methyl esters, as conversions at methanol oil proportions higher than 15 seemed to decrease (Shu et al., 2009).

Additionally, feeding an excess of alcohol highly influences the transesterification procedure by making the product not simply separated as glycerol; the co-product of methyl ester is exceptionally dissolvable in methanol, which inverts the transesterification improvement as per the Le Chatelier principle (Lee et al., 2009). Furthermore, a significant variable influencing methyl ester yield is the kind of alcohol to triglyceride. Short-chain alcohols, for example, methanol, just as ethanol, propanol, and butanol, can be utilized in the transesterification

reaction for getting high methyl ester yields (Hanh et al., 2009). Different types of alcohol except methanol were not used in this project. In the case of the UCS catalyst, an increase in yield paralleled to an expansion in methanol content, the presence of calcium (Ca), potassium (K), carbon (C), magnesium (Mg), and oxygen (O) in the castor shell may contribute to the increase observed. Likewise, the expansion in biodiesel yield at 9:1 molar ratio of methanol to oil was because of the moving of the reaction equilibrium to the forward direction, as in the transesterification reaction is reversible (Tan et al.,2015). After the 9:1 methanol to oil ratio, the methyl ester yield decreased to 49 for UCS and 71% for Co/TiO_2. This phenomenon is suggested that methanol might prevent the separation of product, therefore influencing the final yield of methyl ester.

In conclusion, the methanol-to-oil ratio of 9:1 gave the highest FAME yield. Therefore, it was chosen as the optimum molar ratio.

5.4.3 Influence of reaction time

The effect of the reaction time (35-50 min) on the yield methyl ester from the transesterification run with the Co/TiO_2 and UCS as prepared catalysts on castor oil was achieved under these operating conditions: methanol to oil ratio 9:1, 50 ºC, and 1wt% as well as an ultrasound set up at 100% amplitude and 0.5 cycles. Results are shown in table 5.6 and 5.7 figure 5.10.

Table 5.6 Influence of reaction time of Co/TiO_2

Catalyst (wt.%)	Temperature (℃)	Time (min)	Methanol: oil ratio	Methyl ester (%)
1	50	35	9:1	80
1	**50**	**40**	**9:1**	**85**
1	50	45	9:1	71
1	50	50	9:1	69

Table 5.7 Influence of reaction time of UCS

Catalyst (wt.%)	Temperature (°C)	Time (min)	Methanol: oil ratio	Methyl ester (%)
1	50	35	9:1	72
1	**50**	**40**	**9:1**	**83**
1	50	45	9:1	70
1	50	50	9:1	64

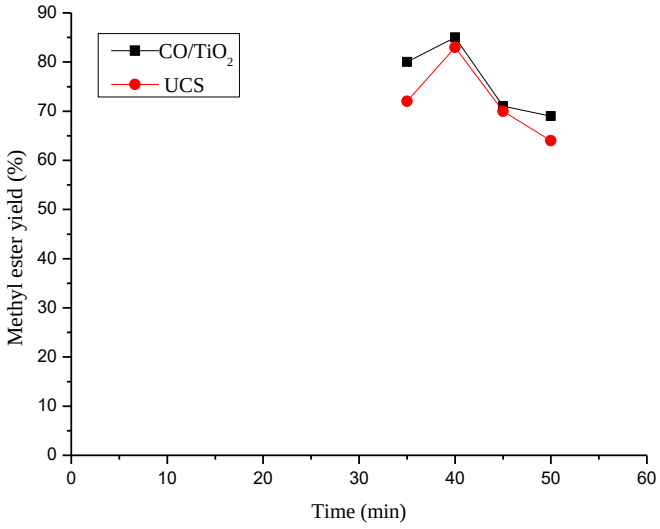


Figure 5.10 Effect of reaction time on methyl ester yield based on the following operating conditions: reaction temperature of 50 °C, catalyst amount 1wt% and methanol: oil ratio of 9:1 and an ultrasound set up at 100% amplitude and 0.5 cycles.

The influence of reaction time on the methyl ester yield was investigated using Co/TiO_2 and UCS as prepared catalysts. The experiments were run at diverse times from 35-50 min at intervals of 5 min. As from Figure 5.10, for the Co/TiO_2, the methyl ester yield reached 80 % at 40 min. After the addition of 5% of the biodiesel yield to 80% yields, when reaction times were 40 min, the total methyl ester increased to 85% but, from 45 to 50 min, the methyl yield decreased from 71 to 69, respectively. However, the UCS catalyst had a yield that enlarged from 40 to 45 min, collecting a maximum yield of 83 % at 40 min. Henceforth, a methyl ester yield of 70% was detected at 45 min and 64% at 50 min thereafter. The conceivable reason for biodiesel's high yield at a lower reaction time could be the high reaction temperature for this

investigation (40ºC), as the reaction rate increments with temperature. In the greater part of the heterogeneous transesterification reactions, high temperature or time is required to accomplish high methyl ester yield (Yee and Lee, 2008). To a great extent, the methyl ester yield relies upon the methanol-to-oil molar ratio. Conferring to (Musa, 2016 and Yin et al., 2012), the higher methanol to oil molar ratio, the shorter the reaction time for attaining the equilibrium. Since the transesterification reaction is reversible, extending the reaction time leads to diminishing the methyl yield (Tan et al., 2015; Lu et al.,2010).

In this investigation, the maximum methyl ester yield was attained for both catalysts at a reaction time of 40 min. Therefore, they were considered as the optimum values for the following reaction.

5.4.4 Influence of reaction temperature

Figure 5.11 along with Tables 5.8 and 5.9 display the effect of temperature reaction (between 35-50℃) on the yield of methyl ester based on transesterification completed with Co/TiO_2 and UCS as set catalysts on the castor oil at a reaction time of 40 min, an amount of catalyst which was 1wt% as well as methanol to oil ratio of 9:1 and an ultrasound set up at 100% amplitude and 0.5 cycles.

Table 5.8 Influence of reaction temperature of Co/TiO_2

Catalyst (wt.%)	Temperature (℃)	Time (min)	Methanol: oil ratio	Methyl ester (%)
1	35	40	9:1	74
1	40	40	9:1	76
1	45	40	9:1	79
1	**50**	**40**	**9:1**	**85**

Table 5.9 Influence of reaction temperature UCS

Catalyst (wt.%)	Temperature (°C)	Time (min)	Methanol: oil ratio	Methyl ester (%)
1	35	40	9:1	65
1	40	40	9:1	72
1	45	40	9:1	67
1	**50**	**40**	**9:1**	**83**

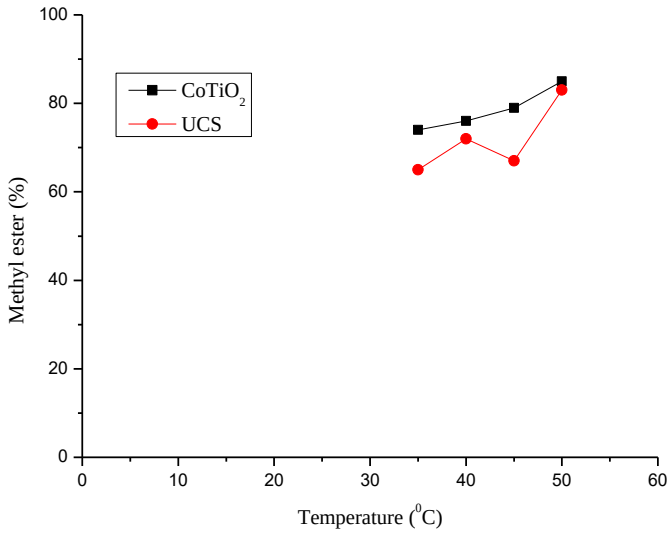


Figure 5.11 Effect of the reaction temperature on the yield of methyl ester at 40 min reaction time, catalyst amount 1wt%, and methanol to oil ratio 9:1 and an ultrasound set up at 100% amplitude and 0.5 cycles.

The effect of reaction temperature on the methyl ester yield was investigated with Co/TiO_2 and UCS as prepared catalysts. It was seen from the results displayed in Figure 5.11 that when the reaction temperature increased, there was a growth in the conversion of triglycerides to methyl esters. This is because castor oil is effectively dissolved in alcohol at room temperature (Forero, 2005), producing yields of methyl ester (85% and 83%) when a temperature of 50°C was reached for Co/TiO_2 and UCS, respectively. A stable and minor increase in the yield of methyl ester was achieved as the temperature was increased for a while. The conversion of triglycerides to methyl esters occurred since the maximum temperature of the ultrasound

technology used in this study was 50℃, and the methanol was not used up despite its boiling point of 64℃ (see section 4.4.3).

This discovery has shown that the methyl ester was reliant on the reaction temperature. Therefore, the raised reaction temperature improved the reactant's mass transfer, and catalyst particle dispersion, as informed by (Olutoye and Hameed, 2013).

5.4.5 Comparison of catalyst and operation condition of previous work and this investigation

(Aleman et al., 2021; Nath et al., 2020; 2019) have performed their experiments for methyl ester production using a batch reactor while the ultrasound-assisted batch reactor was used in this study. The two researchers (Aleman et al., 2021) and (Nath et al., 2020; 2019) have set the reaction temperature at 65^{o}C for methyl ester production, but this investigation used a reaction temperature lower than theirs (50 ℃). (Aleman et al., 2021) and (Nath et al., 2020, 2019) used different types of catalysts prepared from different waste, moringa waste leaves; waste sesamum plant; brassica Negra plant and castor shell waste from oil refining plant was used in this project. Both researchers used 6 and 7% of the catalyst load respectively, which was greater than the amount of the catalyst used in this work (1%). Also, the methanol to oil ratio was 12:1 for (Nath et al., 2021, 2019), and (Aleman et al., 2021), and the present study used respectively (6:1) and (9:1) as it can be seen in table 5.10. below. The three processes yield biodiesel as followed: (Aleman et al., 2021):86.7%; (Nath et al., 2020): 98.9%; (Nath et al., 2019):98, 79 and this work: 83%. Therefore, this study with the two other investigations proved that waste materials are suitable for the catalyst used in biodiesel production.

Table 5.10 Comparison of castor shell catalyst as waste and operation condition of previous work and this investigation

Catalyst name	Catalyst composition	Catalyst load (wt.%)	Methyl to oil ratio	Reaction time (Min)	Reaction temperature (^oC)	Methyl ester yield (%)	Type of reactor	Feedstock	Characterization tools	References
Moringa waste leaves	Inorganic carbonate minerals of dolomite, calcite, and $K_2Ca(CO_3)_2$	6	6:1	120 min	65	86.7	Batch reactor	Soybean oil	XRD; SEM and X-rays (EDS)	(Aleman et al., 2021)
Waste sesamum plant	Na, K, Ca, Mg, Fe, Si, Mn; Sr and Cl.	7	12:1	40	65	98,9	Batch reactor	Sunflower oil	XRD, FT-IR,BET,TGA,XRF,AAS,XPS,SED-EDX and TEM.	(Nath et al., 2020)
Brassica nigra plant	K, CaO, carbonate and chloride	7	12:1	25	65	98,79	Batch reactor	Soyabean oil	XRD,FT-IR,BET,XRF,AAS,XPS,SEM-EDX and TEM	(Nath et al., 2019)
Castor shell waste from oil refining plant	K, C, Ca, O, and Mg, $CaCO_3$	1	9:1	40	50	83	Ultrasound assisted batch reactor	Castor oil	SEM-EDS,XRD, FT-IR and BET	This study

5.4.6 Effect of water

The Co/TiO_2 and UCS catalysts were examined in the heterogeneous transesterification utilizing castor oil in this study by changing the measures of water so that its effect on the activity of the catalyst Co/TiO_2 and UCS could be examined for transesterification. Subsequently regarded as a poison to both homogeneous acid and base catalysts in customary forms of biodiesel production, the catalytic activities of the Co/TiO_2 and UCS catalysts were examined in these situations.

A few investigations were done with different percentages of water content from 0.5 % to 2 wt.% with respect to castor oil. The reaction mixtures were explored to decide the impact of water on the catalytic activity of the Co/TiO_2 and UCS catalysts. The outcome of these impacts on methyl ester yields was run under these operating conditions; reaction time of 50 min, catalyst amount of 1wt% methanol to oil ratio of 9:1, and reaction temperature of 50ºC and the results are appeared in Table 5.11 and plotted in figure 5.12.

Table 5.11 Effect of water

Methyl ester yield (%)		
Water content (%)	**UCS**	**Co/TiO_2**
0	83	85
0.5	61	72
1	49	63
1.5	38	51
2	25	35

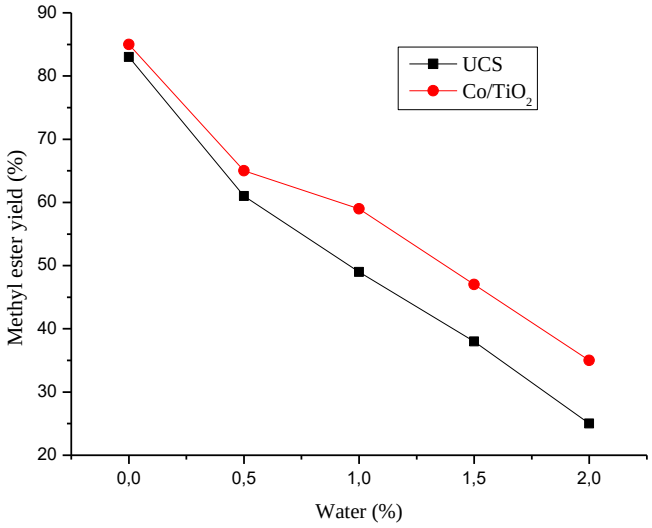


Figure 5.12 Influence of water with respect to oil on methyl ester yield under a reaction temperature of 50°C, the reaction time of 40 min, catalyst amount 1wt%, and methanol: oil ratio 9:1 and an ultrasound set up at 100% amplitude and 0.5 cycles.

From the outcomes that appeared in Table 5.12, with the utilization of both Co/TiO_2 and UCS catalyst, the addition of water deeply diminished the yield of methyl esters. For instance, without water, 83 % methyl ester yield was attained for the UCS at 0 % of the water contained, and 85 % of methyl ester yield was obtained for Co/TiO_2. This means the methyl ester yield was influenced by the presence of water in the castor oil feedstock as the yield diminished consistently with expanding measures of water content, demonstrating that the Co/TiO_2 and UCS catalysts had a low resilience to the water present in the castor oil feedstock. Water content in the oil is a significant concern that unfavourably influences the yield of biodiesel. This perception can be best clarified by two-stage forms; hydrolysis and esterification, which ruins the great yield of esters, section 2.8.5.

5.4.7 Impact of mixing

Oil and Methanol are identified to be immiscible, as the reactants, at first, structure a three-stage system: catalyst-methanol-oil. The distinction in properties between triglycerides and methanol at first makes a heterogeneous biphasic system rendering a mass transfer constraint. This causes methanolysis reaction diffusion-controlled, as meagre diffusion amongst the outcomes of the stage in a slow reaction rate, while a more rapid stirring speed causes better contact among the reactants and solid catalyst, bringing about an expansion of the reaction rate (Noureddini and Zhu, 1997).

The transesterification reactions were consequently done at an arbitrarily picked stirring speed (1 cycle per minute at 100% amplitude). This indicated that an effective mixing of the reactants was essential to arrive at the chosen conversion rate. To defeat this mass transfer constraint, great mixing is essential (Zhou and Boocock, 2006) as inadequate mixing would not enable the reactions to continue as required.

5.4.8 Catalyst stability and reusability test

To study the strength of 0.5% of Co/TiO_2 catalyst, the reutilization of the prepared catalyst was studied in the production of biodiesel from castor oil to its methyl ester through the transesterification reaction. The reactions were rehashed four times under the same operating condition depicted earlier in section 3.4. Subsequently, each cycle of utilization in the transesterification reactions, the catalysts were recuperated by filtration before using it again. The comparative activity of the catalyst utilized for the first ultrasound reaction was characterized as 100 %. Figure 5.13 shows the de-active profile of the catalytic runs for the 0.5 % Co/TiO_2.

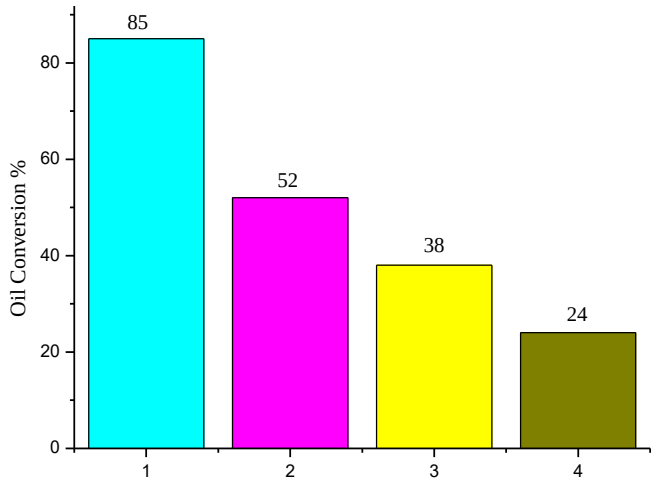


Figure 5.13 The de-activation profile of 0.5 % Co/TiO_2 catalyst after recycling

Figure 5.13 displays the deactivation profile of the catalyst on reuse, where 1, 2,3, and 4 mean the number of runs. Castor oil conversion values of 85, 52, 38, and 24% were observed separately. A decrease in oil conversion was seen after each catalyst reuse and could be ascribed to the draining and loss of active species from the composite catalyst to the product over the extent of the reaction. The product was expelled after each run; thus, any leached would have been lost.

5.4.9 Characterisation of biodiesel production based on castor oil

The biodiesel product was characterized after obtaining it under the best optimized operating conditions of transesterification reaction: methanol to oil proportion of 9:1, reaction temperature of 50 ºC, amount of catalyst 1wt%, the reaction time of 40 min and an ultrasound set up at 100% amplitude and one cycle per second, as obtained utilizing the heterogeneous Co/TiO_2 catalyst. The chemical composition and physical properties of the methyl ester samples obtained were examined and studied to determine their characteristics and then compared to the standard specifications. The outcomes are given in Table 5.10. A correlation can be obtained based on biodiesel fuel norms; SANS 1935:2003, ASTM D6751, and EN 14103 (Appendix 5). The analysis of the biodiesel product was completed by a certified laboratory using certified analytical techniques.

Table 5.12 Methyl esters properties-based castor oil using the Co/TiO_2 catalyst under the optimum operating conditions: 9:1 methanol to oil ratio of 50 ºC reaction temperature, 1wt% amount of catalyst, 40 min reaction and 100% ultrasound amplitude and 0.5 cycles.

Parameter	Unit	Value range	SANS 1935:2003 Test method	Product
Density (15 ^oC)	Kgm^{-3}	860-900	EN ISO 3675	837
Viscosity	(mPa at 40 ^oC)	1.6-6.0	ASTM D 445	3.840
Iodine value	I_2 g/100g	140 max	ASTM D 5768	135
Acid value	mg KOH	0.5 max	ASTM D 974	0.600
Water content	ppm	0.05 max	EN ISO 12937	0.031
Cetane number	nil	51 min	EN D 345	48
Total ester	Mass %	96.5min	EN 14103	85 and 83
Total glycerol	Mass %	0.25 max	AOCS ca 14-56	0.029
Free glycerol	Mass %	0.02 max	AOCS ca 14-56	0.150
Methanol content	Mass %	0.2 max	EN 14110	0.250

The critical properties of the testing results showing the properties of the methyl ester obtained in this project will be discussed (Table 5.12). The castor oil showed a primary high viscosity of 58 mPas (table 4.1) before and after transesterification; the dynamic viscosity of the methyl

ester product analysed recorded a dynamic viscosity of 3.840 mPas, which was in the domain of the standard ASTM D6751 for biodiesel.

The iodine content analysis gives as a result 135 g/100 g, which was moreover within the necessity, although the maximum acidity accomplished was 0.600 mg KOH/g. The total amount of ester obtained was 85 % which was recorded and obtained to be simply underneath the specified value. The methanol content was 0.250 %, which is over the maximum specification of 0.2. The low methanol content achieved was perfect considering the measure of methanol expended in the transesterification reaction. The abundance of methanol was effectively expelled from the methyl ester stage after transesterification utilizing a rotary evaporator during the washing step. However, the rest of the values in table 5.12 are in the domain provided by EN standard.

5.5 Summary

This chapter gives the outcome of the physical and chemical composition of the FAME, and the physical and chemical composition of the UCS and Co/TiO_2 catalyst. The impact of the diverse reaction parameters on the yield and conversion rate of oil triglycerides to their related FAME utilizing these heterogeneous catalysts, the enhancement of the reaction procedure utilizing the UCS and Co/TiO_2 catalyst, and evaluation of the outcomes acquired when sulphuric acid was utilized as a homogenous catalyst. The quality and appropriateness of the FAME formed under the above set of conditions utilizing the UCS and Co/TiO_2 catalysts in evaluation with standard specifications. The goal of this chapter is to comprehend the physical, chemical, and mineralogical composition of the UCS catalyst and the Co/TiO_2 catalyst, and from that point to decide the activity of the catalyst and performance of the above-mentioned catalyst on the transesterification reactions and the conversion/yields of castor oil to its respective methyl esters.

The characterization of UCS and Co/TiO_2 and its utilization in the transesterification of castor oil are relied upon to give a piece of knowledge on its chemical composition and catalytic activity in such a manner. With the objective of enhancing the conversion of oil and yield of the product, an investigation was likewise issued to optimize the reaction parameters, for instance, methanol to oil molar ratio, the effect of UCS catalyst, temperature, reaction time, and reusability of catalyst on the production of methyl ester from castor oil.

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Chapter six Comparative study between catalyst H_2SO_4, Co/TiO_2, and UCS with respect to transesterification processes

6. Introduction

This chapter illustrates the correlation of the transesterification reaction reflected through the three catalytic processes (H_2SO_4; UCS, and Co/TiO_2) engaged in this investigation. It addressed two cases: one with the homogeneous catalyst (H_2SO_4) on the one hand and the heterogeneous catalyst (Co/TiO_2 and UCS) on the other hand. A relative report is completed for the distinctive catalytic processes associated with biodiesel production. Studies and technical investigations for every situation (homogeneous and heterogeneous catalyst) are exhibited. The fundamental contrasts between each procedure with the preferences and hindrances of every one of the procedures are likewise introduced. The goal is to research and analyse the various situations, to assess productivity, crude material utilization, and environmental effects of each procedure.

6.1 General idea

Biodiesel has become an interesting diesel fuel auxiliary because of its environmental advantages. Subsequently, it tends to be produced using renewable resources. Be that as it may, the high expenses encompassing biodiesel production are still a primary issue in making it focused on the fuel advertised either as a mix or as a flawless fuel. Over 80 % of the production cost is related to the raw material itself, and subsequently, work is centred around creating innovations fit for utilizing less expensive raw materials, for example, utilization of the castor shell as the catalyst for biodiesel production on one side and the opposite side utilizing the castor oil as a feedstock for biodiesel production, (chapter 4).

The traditional innovation utilizes sulphuric acid blended with methanol to give a homogeneous base catalyst for the transesterification reaction. The current investigation outlines the downsides of working with castor seed oil as a raw material. Then again, the investigator completed utilizing heterogeneous catalysts based on UCS and Co/TiO_2. These are stated in chapter 5. Other than Co/TiO_2, the UCS catalyst permits the utilization of vegetable oils that will allow biodiesel generation at lower investment costs.

6.2 Study cases

Two distinct procedures were considered: 1) homogeneous catalyst utilizing H_2SO_4 and 2) heterogeneous catalyst utilizing the UCS as well as Co/TiO_2.

Table 6. 1 Result of varying Co/TiO_2 and UCS catalysts for the preparation of FAME from castor seed oil and methanol.

Catalyst	Temperature (^{o} C)	Time (min)	Methanol to oil ratio	Methyl ester (%)
Co/TiO_2				
1	**50**	**40**	**9:1**	**85**
UCS				
1	**50**	**40**	**9:1**	**83**
H_2SO_4				
0.5	**50**	**40**	**6:1**	**90**

Table 6. 2 A comparative analysis between scenario one and scenario two and their detailed technical aspects.

	Scenario 1	Scenario 2	
	H_2SO_4	UCS	Co/TiO_2
Operating temperature ℃	50	50	50
Feeds Streams			
Feedstock (castor oil) (ml)	12.36	12.36	12.36
Methanol (ml)	74.16	111.24	111.24
Catalyst (wt.%)	0.5	1	1
Outcoming Streams(%)			
Biodiesel yield	90	83	85

The process parameters and yields achieved are compared in table 6.1 for the different catalysts Co/TiO_2, UCS, and H_2SO_4. The reactions for each scenario were carried out in an ultrasound reactor. The reaction temperature was set at 50 °C for the catalysts (heterogeneous and homogeneous). This was able to achieve an adequate change from castor oil to biodiesel. The

methanol quantity was not the same for both scenarios (Homogenous and Heterogenous catalysts), although the catalyst amount was different in both scenarios, with 0.5% for homogenous catalysts while 1% was used for heterogeneous catalysts. The heterogeneous, as well as the homogenous processes, proved to be appropriately conceivable intended for the production of biodiesel through the surplus alcohol (methanol) required to drive the Co/TiO_2 and UCS, catalysts reactions in scenario 2, leading the production process to be quite disagreeable. The final biodiesel product of the stream concentration was less than 96.5% but not too far.

6.3 Summary

This chapter has presented the knowledge of the comparative study on transesterification catalytic processes via two scenarios, homogeneous catalysts (H_2SO_4) and heterogeneous catalysts (Co/TiO_2 and UCS). The objective of the chapter is to illustrate the correlation between the transesterification reaction reflected through the diverse catalytic processes engaged in this investigation.

The discussion in this chapter begins with a general idea of the biodiesel production process considering how the traditional innovation utilizes H_2SO_4 blended in methanol to give a homogeneous acid catalyst for the transesterification reaction on the one hand and another the advantages of working with castor seed oil as raw material using H_2SO_4 as the catalyst. Then again, the chapter discusses how the investigator utilized heterogeneous catalysts based on UCS and Co/TiO_2, which is stated in detail in chapter 5.

The chapter goes on to present two flow diagrams explaining in the short two scenarios respective to the homogeneous and heterogeneous catalyst to optimize biodiesel production. The objective of these two scenarios is to illustrate how to apply these two flow diagrams at the industrial level. The discussion concludes with a table that displays a comparative analysis between scenario one and scenario two and their detailed technical aspects.

Chapter seven Conclusions and Recommendations

7. Introduction

This chapter takes as its beginning point a summary of the main questions addressed in the preceding chapters and to what degree the expressed goals were accomplished, and the research questions responded. It is at that point taken after by an outline of the most commitments made and main discoveries. Contemplations of conceivable bearings and suggestions for supplementary work are moreover given.

7.1 General idea

The goals and purposes of this research were to deliver comprehensive persistent knowledge in the optimization of biodiesel production by means of ultrasound-assisted utilizing H_2SO_4, Co/TiO_2, and UCS as catalysts. The optimization study decided on the impact of the distinctive reaction parameters on the yield of castor oil as a feedstock to its equivalent methyl ester. The methyl ester obtained from castor oil in terms of diverse operating conditions was characterized to decide the fuel properties of the definitive biodiesel product.

The study also addressed the investigation questions, and a summary of findings is initially presented.

- The high quality of biodiesel was completed by optimizing the operating condition using ultrasound.
- A new catalyst made up of castor shell seed but unsupported leads to the production of methyl ester.
- Castor shells could be used as a catalyst in the preparation of a heterogeneous catalyst in a favourable yield of methyl esters from castor oil with easier refining of the produced biodiesel. It was envisaged that the use of this cheap catalyst would present a process that is environmentally benign for the conversion of castor oil.
- The biodiesel produced from these heterogeneous transesterification catalytic reactions involving the Co/TiO_2 castor-based catalyst and ultrasound-assisted were shown to meet almost the standard quality specifications for FAME.

7.2 Findings Summary

The main result of this investigation is set out in this section.

7.2.1 Transesterification reactions based on homogeneous catalysis.

The operating conditions, especially reaction temperature, reaction time, catalyst, and methanol quantity are the main variables that are influencing the product and yield of methyl esters, these variables are presented in this investigation significantly. To achieve a high yield of oil with methyl ester, the optimum value of the parameters (reaction time, reaction temperature, catalyst, and methyl amount) is equally dependent on the physical and chemical properties of the oil feedstock.

Subsequent discoveries were likewise drawn from this study; (i) the addition of excess catalyst causes a reduction in the ester yield; (ii) The biodiesel production process is not complete in the domain whereby the methanol to oil ratio is less or greater than 6:1; (iii) Therefore, functioning beyond the ideal esteem of methanol to oil, the ester yield would not be expanded but would result in an additional cost for methanol recuperation; (iv) Higher reaction temperatures such as diminishing the viscosities of the oils and brought about in an expanded rate of transesterification and shortening of the response time. In any case, when the temperature expanded past the ideal level of 50 °C, (v) Adequate reaction time was vital to guarantee the total conversion of triglycerides into esters. Nonetheless, overabundance reaction time did not advance the transformation, however, supported the switch reaction of transesterification, causing a decrease in the ester yield.

This investigation moreover illustrated that the ultrasound-assisted transesterification reaction of castor oil and methanol with sulphuric acid was exceptionally productive in maximizing the FAME yield. At long last, the properties of the product of methyl esters got from the ultrasound-assisted transesterification reaction met the South African Standard (SANS 1935:2004), which is nearly the same as EN14214 and ASTM D6751 standards.

7.2.2 Transesterification reactions based on heterogeneous catalysis.

The castor shell seed without any support from South Africa was utilized within the transesterification of castor oil to methyl esters to generate a significant utilization of castor shells as a catalyst in biodiesel.

Throughout the transesterification reaction ran in this project, it was discovered that the Co/TiO_2 catalyst gave an outstanding and high activity. The further optimum operating condition of these studies was extended to reaction parameters, namely: catalyst amount, reaction time, the molar ratio of methanol to oil, and reaction temperature on methyl ester yield utilizing the Co/TiO_2 and UCS wt.% catalysts.

A Methyl ester yield of 85% was obtained as a result of 1% Co/TiO_2 catalyst, at the ideal operating condition, which was established as follows: methanol to the oil of 9:1, reaction temperature 50 ºC, reaction time 40 min at 100% ultrasound amplitude and 0.5 ultrasound cycle.

After testing the methyl ester product obtained from the transesterification reaction, it was found that this product fulfilled the requirements of the SANS 1935:2003 and EN144214 standards. The castor seed shell utilized in South Africa was considered used as a catalyst without any supporter in the transesterification reaction. Based on our information, no report on UCS as well as Co/TiO_2 has been used in different research as catalysts.

To advance the change from triglyceride into biodiesel throughout the transesterification reaction process, the UCS and Co/TiO_2 catalysts were necessary for this study in biodiesel synthesis, and this was because it was suggested to cope and boost the catalytic reaction of the large molecules of triglycerides.

General outcomes show that a FAME of yield 85 and 83 % may well be gotten from the transesterification reaction of vegetable oil by independently utilizing the UCS and Co/TiO_2 catalyst at a reaction temperature of 50 °C, catalyst amount one wt.% and methanol: oil ratio 9:1 and 40 min reaction time. The discoveries appeared noteworthy advancements in reports in writing as this catalyst can be delivered cheaply.

7.2.3 A comparative study of the transesterification reaction via homogeneous and heterogeneous catalyst

The transesterification reaction was evaluated via the different catalytic procedures (homogeneous and heterogeneous) included in this work.

Heterogeneous and homogeneous processes have been found to be suitable for biodiesel production, noting that castor oil has been studied with a negligible or relatively small amount of water.

The activity of the Co/TiO_2 catalyst gave a better marginally lower yield (85 %) when compared to the yield gotten from the homogeneous H_2SO_4 catalyst (90%) at comparative reaction conditions of methanol/oil molar ratio of 6:1, and a reaction temperature of 50 °C enhanced beneath the homogeneous system.

In the case of the UCS catalyst, the temperature of 50°C, a catalyst amount of (1 wt.% of oil), and volumes of methanol (methanol to oil ratio of 9:1) were required in comparison to its conventional homogeneous partner to obtain an ideal yield of 83 %.

A large number of catalysts and utilization of overabundance methanol was a fault within the utilisation of both UCS and the Co/TiO_2 catalyst; however, the methanol was, recovered and reused within the system.

It is worthy to noting that at this stage, considering cost and energy utilization, the homogeneous process utilizing the ultrasound-assisted reactor technologies would be a better option to follow. Still, possible developments on the heterogeneous system especially involving South African (castor shell) based catalysts have much potential.

7.3 Conclusion

Considering the high yield of the castor seed oil (47,16 %), cultivating a castor plant ought to be encouraged to boost the commercialization of castor seed. Subsequently, this crude castor seed oil can be satisfactorily used as crude material within the transesterification experiments.

Taking everything into account, the combination of the transesterification reaction trials, and FAME analysis tests employed in this project demonstrated the critical impact of various reaction parameters (catalyst amount, methanol to oil ratio, reaction temperature, reaction time) on methyl ester/FAME yield. The ultrasound-assisted transesterification reaction at ideal conditions and much-diminished processing time on the oil test prompted led to higher yields of methyl esters. This study has shown that the use of South African castor shells and Co/TiO_2 catalysts can be used as heterogeneous catalysts in biodiesel synthesis. Furthermore, the use of the solid base catalysts in this study possesses the potential for new developments in the production of biodiesel; allowing process simplification and offering a reduction in processing costs by improving the mass transfer limitation of the three-phase reaction and simplifying the

product purification processes compared to what is required in conventional homogeneous catalysis.

7.4 Recommendations for future examination

The vast extent of this project suggests that a lot of additional work should be possible even now because the innovation in heterogeneous catalysis structure and materials does not require subsequent other purification steps, less complex preparation techniques or refining steps, and economic considerations. Because additional materials are used as reaction conditions, it is not as critical as the traditional homogeneous reaction system.

After exploring the catalytic activity of solid base catalysts obtained from South African castor shells, more examinations are currently in progress to decide the ideal operating conditions for the castor shell catalyst. Tests were not done to deactivate the recuperated castor shell catalyst found in this investigation. The general properties of the methyl ester product obtained at optimum operating conditions would likewise be in this manner decided.

The utilization of ultrasound could also be explored in the heterogeneous framework utilizing the prepared UCS catalyst to decide the acceptability of finding a supporter for the castor shell required for the optimum transesterification reaction to occur. This will empower a decrease in the cost of biodiesel generation, mainly when the continuous procedure is industrialized.

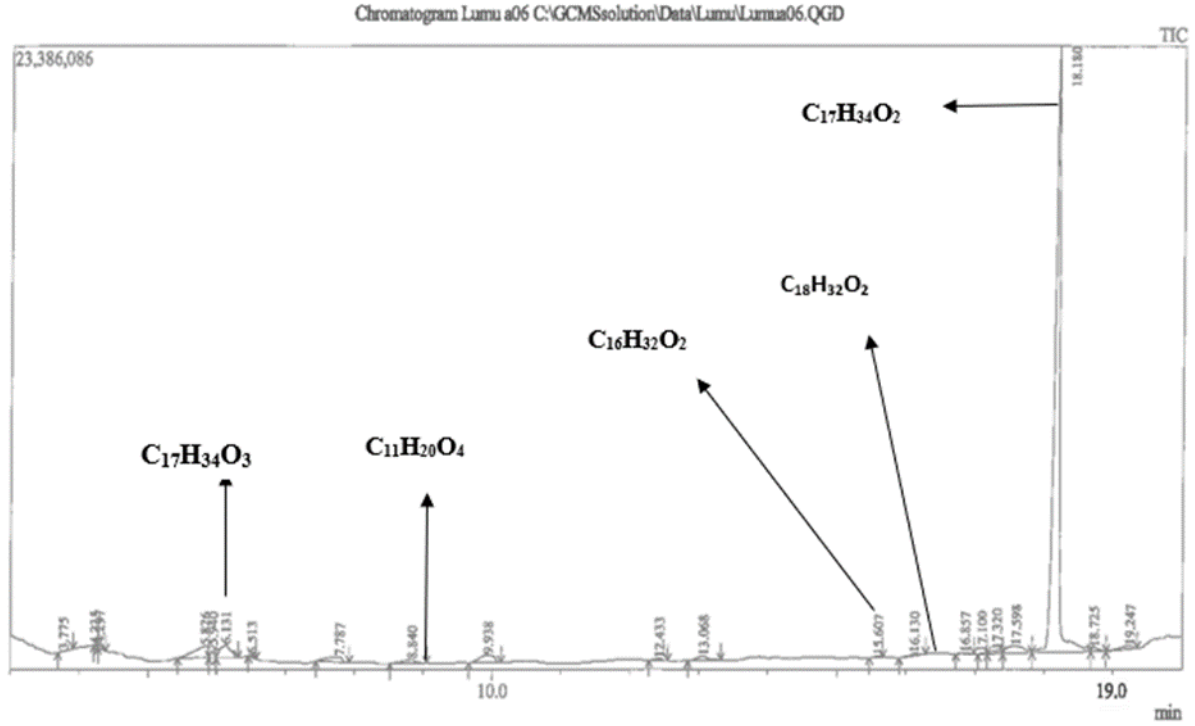
The investigation of monetarily valuable applications for crude glycerol is relied upon to increase significantly more considerably inside biodiesel investigation sooner rather than later, as increments in the overall FAME fuel production will essentially involve augmented production of unrefined glycerol too. Potential utilization of the crude glycerol stage is constrained, anyway, to keep the expense of biodiesel fuel production challenging; guaranteeing the evacuation and resale of high-quality product glycerol in its unadulterated structure is fundamental. This supposedly is a secondary product of the reaction and can be utilized for different applications as well as carbon sources, biological conversion, catalytic conversions, fuel oxygenates, bioreactors treating acid mine waste, and horticultural applications.

Significant work should be developed with respect to fuel ranges for biodiesel that will guarantee predictable value and execution but not tie the final fuel to any specific raw material, in view of significant variation in biodiesel properties based on the raw material and sometimes the process conditions.

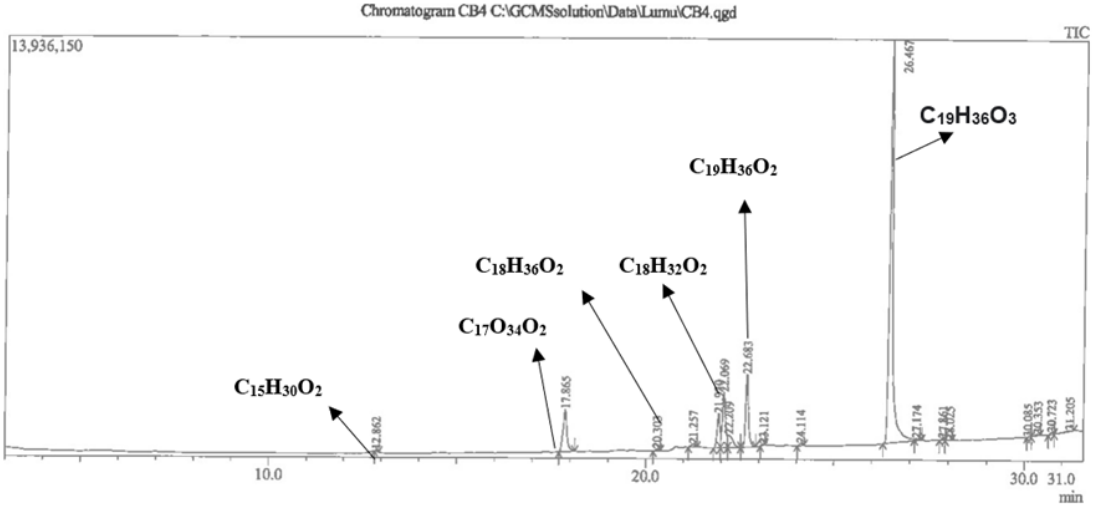
In light of emerging discussions on the environmental effects of biodiesel fuel, the negative impacts of biodiesel production, conversion, and transport must be considered as well, so life cycle assessment studies could be done to compare the fuel energy input and the emissions of certain ecologically relevant compounds throughout the whole fuel cycle.

Appendices

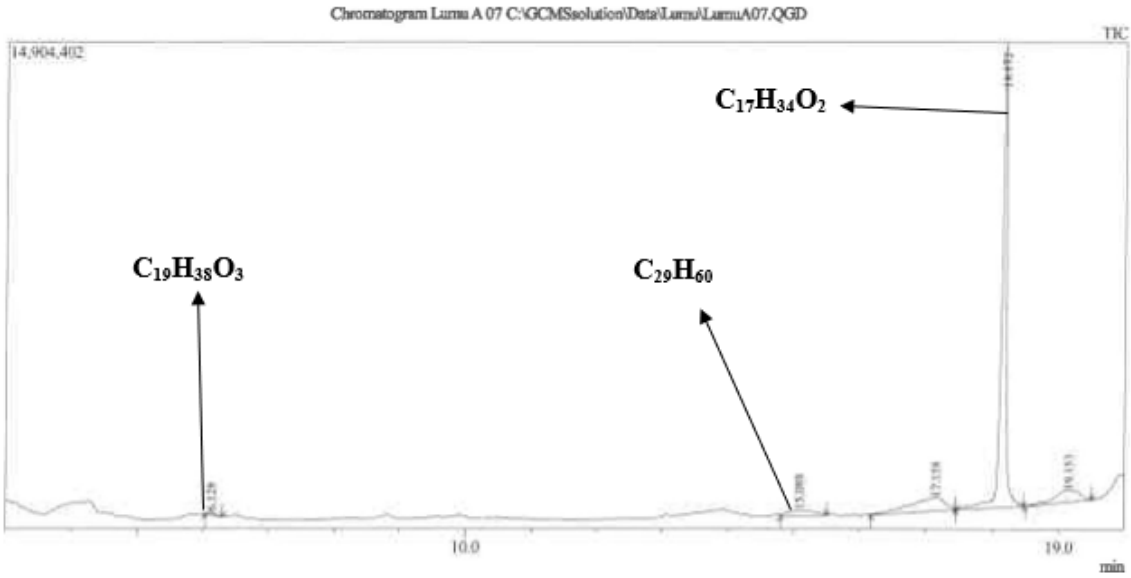
Appendix 1 Chromatograms of FAME-based castor oil using H_2SO_4 catalyst.



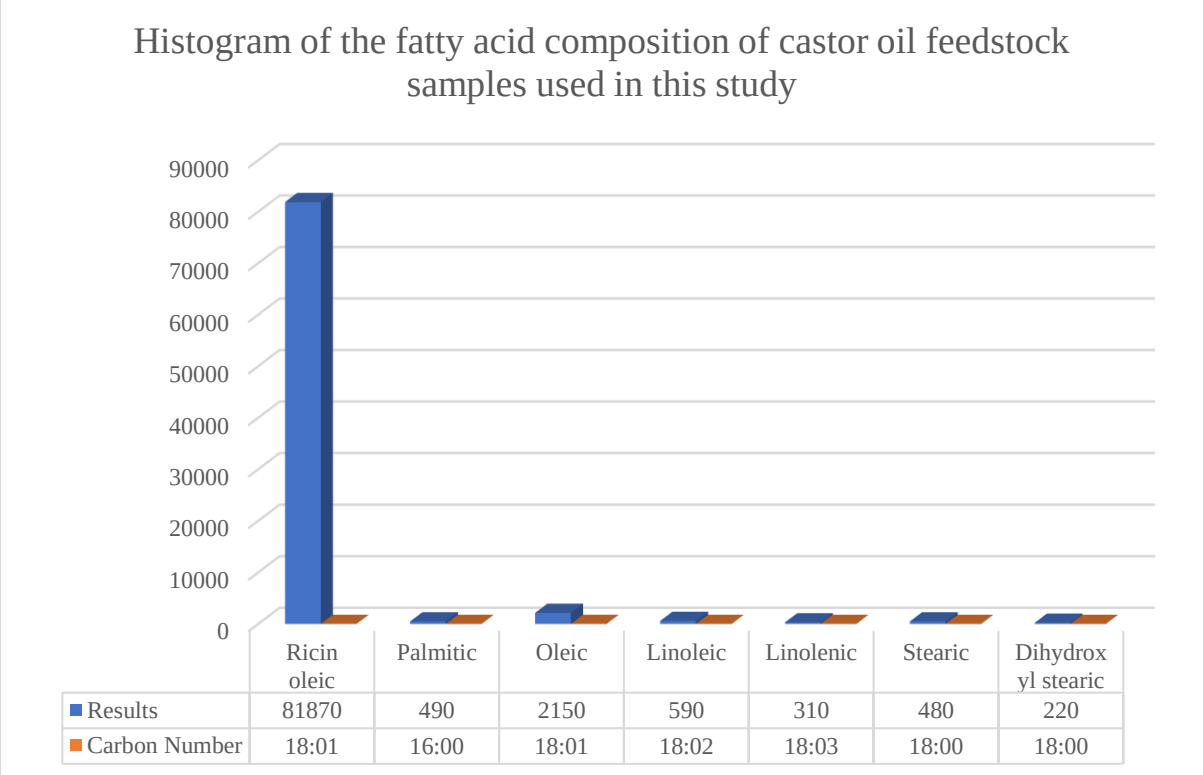
Appendix 2 Chromatograms of FAME-based castor oil using UCS catalyst.



Appendix 3 Chromatograms of FAME-based castor oil using Co/TiO_2 catalyst.



Appendix 4 Histogram of the fatty acid composition oil feedstock uses in this study.



	Ricin oleic	Palmitic	Oleic	Linoleic	Linolenic	Stearic	Dihydroxyl stearic
Results	81870	490	2150	590	310	480	220
Carbon Number	18:01	16:00	18:01	18:02	18:03	18:00	18:00

Appendix 5 Biodiesel standards from different international countries (Journey to Forever,2006)

	Europe	Austria	Czech Republic	France	Germany	Italy	Sweden	USA	Australia
Standard/Specifications	EN 14214	ON C1191	CSN 656507	Journal Official	DIN V 51606	UNI 10635	SS 155436	ASTMD 6751	Fuel Standard (Biodiesel) Determination
Date	2003	July1997	Sep 1998	Sep 1997	Sep 1997	April 1997	Nov 1996	Jan 2002	Sep 2003
Application	FAME	FAME	RME	VOME	FAME	VOME	VOME	FAME	-
Density 15℃ g/cm	0.86-0.90	0.85-.089	0.87-0.89	0.87-0.90	0.875-0.90	0.86-0.90	0.87-0.90	-	0.86-.89
Viscos. 40℃ mm^2/s	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0	3.5-5.0
Distillate. 95℃	-	-	-	<360	-	<360	-	90% at 360 ℃	<360
Flashpoint ℃	>120	>100	>110	>100	>110	>100	>100	>130 (150av.)	>120
CFPP ℃ (cold filter plugging point)	*Country specific	0/1.5	-5	-	0/10/-20	-	-	-	-

Pour point	-	-	-	<-10	-	<0/<-15	-	-	-
Sulphur mass %	<10mg/kg	<0.02	-	<0.01	<0.01	<0.01	<0.001	<0.05	50 mg/kg (max) 10 mg/kg (max) (from 1 Feb 2006)
CCR 100% % mass	-	<0.005	<0.005	-	<0.005	-	-	-	-
10% dist. resid. % mass	<0.3	-	-	<0.3	-	<0.5	-	-	-
Sulphated ash % mass	<0.02	<0.02	-	<0.3	-	<0.5	-	-	-
(Oxid) Ash% mass	-	-	-	-	-	<0.01	<0.01	--	--
	<500	-	<500	<200	<300	<700	<300	<0.05%	<0.05% vol
Water								Vol. (water & sediment)	(water & sediment)
Total contam. mg/kg	<24	-	<24	-	<20	-	<20	-	<24
Cu-Corros. 3h/50°C	1	-	1	-	1	-	-	<No.3	<10 mg/kg sulphur class 1 (max)> 10 mg/kg sulphur No. 3(max)
Oxidation stability	6h min	-	-	-	-	-	-	-	6 h min

Cetane No.	>51	>49	>48	>49	>49	-	>48	>47	>51
Neural No (Acid value) mg KOH/g	<0.5	<0.8	<0.5	<0.5	<0.5	<0.5	<0.6	<0.8	<0.8
Methanol mass %	<0.20	<0.20	-	<0.1	<0.3	<0.2	<0.2	-	0.2
Ester Content mass %	>95.5	-	-	>96.5	-	>98	>98	-	>96.5
Monoglyceride mass %	<0.8	-	-	<0.8	<0.8	<0.8	<0.8	-	-
Diglyceride mass %	<0.2	-	-	<0.2	<0.4	<0.2	<0.1	-	-
Triglyceride mass %	<0.2	-	-	<0.2	<0.4	<0.1	<0.1	-	-
Free glycerol mass %	<0.02	<0.02	<0.02	<.002	<0.02	<0.05	<0.02	<0.02	<0.02
Total glycerol mass %	<0.25	<0.24	<0.24	<0.25	<0.25	-	-	<0.24	<0.25
Iodine No.	<120	<120	-	<115	<115	-	<125	-	-
Linoleic acid ME % mass	<12	-	-	-	-	-	-	-	-
C18:3 and high unsaturated acids % mass	-	<15	-	-	-	-	-	-	-
Phosphorus mg/kg	-	<1.5	-	-	-	-	-	-	-
Ramsbottom carbon residue, mass %	<10	<20	<20	<10	<10	<10	<10	<0.001% mass	<10
Carbon residue	-	-	-	-	-	-	-	0.10	-

Gp 1 metals (Na, K) mg/kg	-	-	-	-	-	-	-	<0.050% by mass	<0.30% mass (10% distillation residue)
Gp 1 metals (Na, K) mg/kg	<5	-	-	-	-	-	-	-	<5
Alkalinity mg/kg	-	-	<10	<5	<5	-	<10	-	-

Appendix 6 Requirements for Automotive Biodiesel in South Africa (SANS 1935:2004)

Property		Requirements
Ester content	methyl ester, % mass fraction	min 96,5
Linolenic acid	methyl ester % mass fraction	max 12
Polyunsaturated (> = 4 double bonds)	methyl ester % mass fraction	max 1
Methanol content	% mass fraction	max 0,2
Monoglyceride content	% mass fraction	max 0,8
Diglyceride content	% mass fraction	max 0,2
Triglyceride content	% mass fraction	max 0,2
Free glycerol	% mass fraction	max 0,02
Total glycerol	% mass fraction	max 0,25
Density	15°C, Kg/ m^3	860-900
Kinematic viscosity	40°C, mm^2/s	3,5-5,0
Flashpoint	°C	min 120
Sulphur content	mg/kg	max 10,0
Sulphated ash content	% mass fraction	max 0,02
Water content	% mass fraction	max 0,05
Total contamination	mg/kg	max 24
Copper strip corrosion	(3 h at 50°C), rating	max class 1
Oxidation stability	at 110°C, h	min 6
Acid value	mg KOH/g	max 0,5
Iodine value g of iodine/100 of FAME		max 140
Carbon residue (on 10% distillation residue)	% mass fraction	max 0,3
Cetane number		min 51,0
Group II Metals (total of Ca and Mg)		max 5,0

Group I metal (total of Na and K)		max 5,0
Phosphorous content	mg/kg	max 10,0
Cold filter plugging point (CFPP)		
winter,	℃	max -4
summer	℃	Max 3

Appendix 7 European Standard for testing method EN 14103

Property		Requirements
Ester content	Methyl ester % mass fraction	**min 98.2**
Linolenic acid	Methyl ester % mass fraction	max 12
Methanol content	% mass fraction	max 0.2
Monoglyceride content	% mass fraction	max 0.8
Diglyceride content	% mass fraction	max 0.2
Triglyceride content	% mass fraction	max 0.2
Free glycerol	% mass fraction	max 0.02
Total glycerol	% mass fraction	max 0.25
Density	15℃ g/cm^{-1}	0.860-0.90
Kinematic viscosity	40℃, mm2/s	3.5-5.0
Flashpoint	℃	min 120
Sulphur content	mg/kg	max 10
Sulphated ash content	% mass fraction	max 0.02
Water content	mg/g	max 500
Particulate	mg/kg-1	max 24
Copper strip corrosion	(3 h at 50℃), rating	1
Oxidation stability	At 110℃, h	min 6
Acid value		max 0.5
Iodine value		max 120
Carbon residue (on 10% distillation residue)	% mass fraction	max0.3

Cetane number		min 51
Group II Metals (total of Ca and Mg)	mg/kg	max 5
Group I metal (total of Na and K)	mg/kg	max 5
Phosphorous content	mg/kg	max 10.0
Cold filter plugging point (CFPP) **winter,** **summer**	 °C °C	 max -4 max 3

Appendix 8 South African past and future diesel consumption (SAPIA, 2006)

Year	Fossil Diesel Million Litres	1% Biodiesel Million litres	5% Biodiesel Million litres	10% Biodiesel Million Litres
2000	6254			
2001	6488			
2002	6831			
2003	7263			
2004	7679			
2005	8115			
2006	8521			
2007	8947	89	447	895
2008	9394	94	470	939
2009	9864	99	493	986
2010	10357	104	518	1036
2011	10875	109	544	1087
2012	11419	114	571	1142
2013	11990	120	599	1199
2014	12589	126	629	1259
2015	13218	132	661	1322
2016	13879	139	694	1388
2017	14573	146	729	1457
2018	15302	153	765	1530
2019	16067	161	803	1607
2020	16871	169	844	1687

Crop	Country Group	Area harvested (ha)	Production (tons)
Cashew nuts	Angola	2800	
	Mozambique	60000	
Sesame seeds	Angola	2700	
	Mozambique	16000	
Castor oil	Angola	13500	
	Mozambique	150000	
	South Africa	8000	
Pumpkin	Mozambique	330	
	South Africa	11000	
Rapeseed	South Africa	35000	
Avocados	South Africa	17000	
	Swaziland	50	
	Zimbabwe	170	
Coconut	Mozambique	70000	
Soybean	Malawi	70000	
	South Africa	174400	
	Zambia	10000	
	Zimbabwe	65000	
Cottonseed	Angola	2700	
	Botswana	1100	
	Malawi	69826	
	Mozambique	360000	
	Namibia	3800	
	South Africa	14000	
	Swaziland	14800	
	Zambia	127000	
	Zimbabwe	400000	
Sunflower	Angola	15000	
	Botswana	6200	
	Malawi	7575	
	Mozambique	12000	
	Namibia	135	

	South Africa	564300	
	Zambia	15000	
	Zimbabwe	23000	
Maize	Angola	1115000	
	Botswana	56000	
	Lesotho	160000	
	Malawi	1596955	
	Mozambique	1284930	
	Namibia	18000	
	South Africa	2799000	
	Swaziland	47409	
	Zambia	663990	
	Zimbabwe	1730000	

Appendix 9 Potential oil crops/ seeds in Southern Africa (Amigun and Musango, 2011)

Plant	Latin name	Kg oil/hectare	Plant	Latin name	Kg oil/hectare
Corn	*Zea mays*	145	Tung oil tree	*Aleurites fordil*	790
Cashew nut	*Anacardium occidentale*	148	Sunflower	*Helianthus annuus*	800
Oat	*Avena Sativa*	183	Cocoa	*Theobroma cacoa*	863
Palm	*Erythea Salvadorensis*	189	Peanut	*Arachis Hypogea*	890
Lupine	*Lupinus albus*	195	Opium poppy	*Papaver Somniferm*	978
Rubber seed	*Hevea brasiliensis*	217	Rapeseed	*Brassica nappus*	1000
Kenaf	*Hibiscus cannabainus L.*	230	Olive tree	*Olea Europaea*	1019
Calendula	*Calendula Officinalis*	256	Piassava	*Attale Funifera*	1112
Cotton	*Gossypium Hirsutum*	273	Gopher plant	*Euphorbia lathyrism*	1119
Hemp	*Cannabis Sativa*	305	Castor bean	*Ricinus communis*	1188
Soybean	*Glycine max*	375	Bacuri	*Platonia insignis*	1197
Coffee	*Coffee Arabica*	386	Pecan	*Carya illinoensis*	1505
Linseed	*Linum Usitatissimum*	402	Jojoba	*Simmondsia chinensis*	1528
Hazelnut	*Corylus Avellana*	405	Babassu sam	*Orbignya martiana*	1541

Euphorbia	*Euphorbia lagascae*	440	Jatropha	*Jatropha carcus*	1590
Pumpkin seed	*Cucurbita Pepo*	449	Macadamia nut	*Macadamia Terniflora*	1887
Coriander	*Coriandrum sativum*	450	Brazil nut	*Bertholletia excelsa*	2010
Mustard	*Brassica Alba*	481	Avocado	*Persea americano*	2217
Camelina	*Camelina Sativa*	490	Coconut	*Cocos Nucifera*	2260
Sesame	*Sesamum Indicum*	585	Oiticia	*Licania Rigida*	2520
Crambe	*Crambe abyssinica*	589	Buriti palm	*Mauritia flexuosa*	2743
Safflower	*Carthamus tinctorius*	655	Pequi	*Caryocar Brasiliense*	3142
Buffalo goud	*Cucurbita Foetidissima*	665	Macaube palm	*Acrocomia Aculeata*	3775
Rice	*Oriza Sativa*	696	Oil palm	*Elaeis guineeansis*	5000