OPTIMIZATION OF BIODIESEL PRODUCTION FROM CRUDE COTTONSEED OIL USING WOOD ASH AS A CATALYST

BY

TOO SIMON KIPKEMBOI

A Thesis Submitted to the Department of Manufacturing, Industrial and Textile Engineering, School of Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Science in Textile Engineering

Moi University

2025

DECLARATION

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the prior written permission of the author and/or Moi University.

Too Simon Kipkemboi. *Signature*: Date: 14/02/2025

Registration Number: TEC/PGMT/01/08

Declaration by Supervisors

This thesis has been submitted with our approval as University Supervisors.

Prof. Dr. Charles Nzila *Signature*: Date: 25/02/2025

Department of Manufacturing, Industrial & Textile Engineering

Prof. Eng Kirimi H. Kiriamiti *Signature*: Date: 27/02/2025

Department of Chemical & Process Engineering

DEDICATION

I dedicate this work to my late grandmother Martina Chepkurgat who despite her not having formal education struggled to ensure that I became the best I could. To my son Solace and daughter Shanimarvel Chemutai may you go even beyond the skies.

AKNWOLEDGEMENT

I acknowledge all those institutions and individuals who enabled me undertake this research. VLIR-UOS your immeasurable support in in funding this research and many thanks. To Moi University specifically, School of Engineering supervisors lead by my supervisors including Prof. Eng. H. Kiriamiti, Prof. Charles Nzila and Dr. Jerry Rawlings for coming through to ensure I completed this work. To Rivatex East Africa Limited management and staff, you won’t go unmentioned. You enabled me to get the reagents and apparatus for laboratory work. Lastly, to Moi University where wisdom oozed from its past and present studies within and beyond helped me great in undertaking this study.

ABSTRACT

World major sources of fuel are non-renewable fossils expected to be depleted. Availability of sustainable energy is a complex socially, technologically, economically and politically. Researchers have concentrated on the use of methanol and mineral catalysts although ethanol and wood ash have potential but available, affordable, environmentally friendly and reliable. The main objective was to optimize production of biodiesel using crude cottonseed Oil and wood ash. The Specific objectives were to; undertake pre-processing and produce biodiesel; determine optimum conditions for the yields; design suitable process and; model the reaction. Cottonseed was characterized, oil extracted, filtered, analyzed and transesterified, chemical and physical properties tested. Characterization results were lint, seed and waste averaged 35%, 60% and 5% respectively while; oil 20%. Mole ratios of alcohol to oil were varied from 9:1-12:1 with temperature at 60˚C and wood ash load ranges between 2.4- 6.05 g/l of oil and time ranged of 2-3 hours. Separation was undertaken, phases noted and esters washed using warm acidic water (30◦C and Ph.5). Refined soya bean oil was used as a control experiment and yields recorded. Eight experiments were performed according to the fractional factorial design and results analyzed to develop a Linear Regression equation. The variables were varied to get the optimum conditions to which a model was developed. The optimal conditions for obtaining maximum yield of 96.5% and meeting acceptable quality of biodiesel is: alcohol to oil mole ratio of 12:1, catalyst load of 6.05 g/l and time of 3 hours. The model result was linear equation with coefficient of Mole ratio being 1.8 while that of time being least at 0.0125.Physical and chemical properties per results compared against Standard for bio-fuel proved positive. The research proved the viability to optimize biodiesel production using wood ash catalyst while varying: temperature; mole ratios and wood ash load. The general objective was met with results showing similarity n properties with those of soya bean and mineral catalysts. Wood ash and ethanol proved to be substitutes including Other recommendations as follows: characterization of various wood ash sources; policy interventions to increase the production of feedstock to sustain supply; undertake the process at lower temperatures to save on energy; open batch system the suitable this process; more studies to establish various characteristics of wood ash.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

ASTM-American Society for Testing and Materials

ATM-Atmospheric Pressure

AEVO-Alcohol Esters of Vegetable Oils

Ca (OH)$_2$–Calcium Hydroxide

CaCl- Calcium Chloride

CGB-Cotton Gin By-product

CIGs-Cotton Investment Groups,

CO -Carbon Monoxide

CODA- Cotton Development Authority

CSLMB- Cotton Seed and Lint Marketing Board

CSTRs- Continuous Stirred Tank Reactors

EEWR- Ethyl Ester of Winter Rape

EU- European Union

FFAs-Free Fatty Acids

HPLC -High Performance Liquid Chromatography

HCl- Hydrochloric Acid

MEWR Methyl Ester of Winter Rape

NOx- Nitrogen Oxides

PM -Particulate matter

PSI-Pascal per Square Inch

PFRs-Plug Flow Reactors

RAC -Raw Agricultural Commodities

SNI- Shipp Nonionic

SOx- Sulphur Oxides

TOE- Tons of Oil Equivalent

ULSD -Ultra-Low Sulfur Diesel

US -United States

VOCs -Volatile Organic Compounds

VLIR-UOS- Flemish Interuniversity Council - University Development Cooperation

WVO -Waste Vegetable Oil

CHAPTER ONE: BACKGROUND

This chapter gives the background, statement of the problem, objectives of the study, justification, significance as well as scope of the study.

1.1 Background

The interest in vegetable oils which includes cottonseed as a viable renewable resource for producing an alternative to diesel fuel derived from petroleum has increased Ziolkowska JR (2019).Various alternative fuels for diesel engines have been recommended by experts, such as pure vegetable oil, mixtures of vegetable oil and petroleum diesel fuel, and alcohol esters sourced as vegetable oils. Biodiesel is produced from biological sources using a technique that is similar to the one used for diesel. The transesterification is a process which vegetable oil and alcohol reacts to produce biodiesel, specifically fatty acid methyl esters. Methanol has been the most commonly utilized. Biodiesel is an alternative to petro fuel. The process of vegetable oil transesterification is facilitated by the presence of a catalyst such as sodium or potassium hydroxide dissolved in alcohol Thangaraj B et al (2019).

Fossil are the main global source of fuel. A significant proportion of the Kenyan population lacks access to this fuel. On other hand, alcohol esters found in vegetable oils seem to be the most promising alternative. Vegetable oils consist of triglycerides, which are esters formed by fatty acids and glycerin. Alcohol esters of fatty acids are produced under transesterification. This process entails chemical reaction of linear, monohydroxy alcohols with vegetable oils in the presence of a catalyst. The product is Alcohol Esters of Vegetable Oils (AEVO) otherwise referred to as “biodiesel." Glycerin is also generated as a by-product.

Extensive research has been undertaken study on the production and application of AEVO information Malabadi, Ravindra et al (2023). This study reviewed various feedstock candidates of biodiesel production. demonstrated the conversion of rape oil, sunflower oil, cottonseed oil, peanut oil, soybean oil, and palm oil into methyl, ethyl, and butyl esters using methyl, ethyl, and butyl alcohols was further demonstrated. Catalysts that included potassium hydroxide, sodium hydroxide, sodium methoxide, or sodium ethoxide helped the transesterification process. The key variables that affect transesterification are the ratio of alcohol to vegetable oil, temperature, agitation rate, and water content in the reaction mixture. Major gaps in study included High Free Fatty Acid (FFAs) content in feedstock as well as costs of reagents including mineral catalyst Abeniece Z, Laipniece L, Kampars V (2020).

Alcohol Esters of Vegetable Oil exhibits a viscosity approximately twice as high as that of diesel fuel. Viscosity has a critical role in determining spray patterns and the formation of deposits, making it an essential component to take into account. AEVO demonstrates similar performance to diesel unlike unprocessed vegetable oil that causes injector blockage Kamiab et al (2024).

The emission characteristics of alcohol esters of fatty acids are highly advantageous. Winter rape methyl esters emitted significantly fewer total particles and polynuclear aromatic hydrocarbons in comparison to diesel fuel. However, the combustion of MEWR led to increased levels of NO and aldehyde emissions in comparison to diesel fuel. To facilitate the commercialization of biodiesel fuels, additional testing on their emissions may be necessary as recommended by Kamiab et al (2024).

Homogeneous catalysis yields high reaction efficiency under mild reaction conditions. The process produces biodiesel, glycerin, and a surplus of methanol mixed with water and salts. The mole ratios of alcohol to oil can range from 2:1 to 6:1. The temperature can vary between 25 °C and 85°C, the catalyst load can range from 0.3% to 1.5%, depending on the weight of the oil, Kamiab et al (2024) .Duration of reaction varies from 20 minutes to 1 hour, and it is essential to agitate the mixture during this period. The process of separation occurs in a settling tank, where esters neutralization and gently rinsing with warm water of Ph. of about 5.5 to eliminate any remaining alcohol and salts.

Purifying the crude biodiesel obtained after the process is expensive when done at a temperature of 40-60°C under atmospheric pressure Kamiab et al (2024). One reason is to remove a large amount of trash while washing the homogeneous catalyst from the crude biodiesel. Furthermore, the formation of a stable emulsion during the washing process hampers the operation of the process Oloyede et al (2022) and Rahman (2021).

From all these, issues of green and sustainable sources of catalyst was not studied even though were implied in the conclusion. Then begs the big research question: Is optimization of biodiesel production using crude cottonseed oil and wood ash a catalyst viable? What are process designs and optimal conditions model of the process. What are take home lessons? These are the research questions the study sought to answer.

1.2 Statement of the Problem

Fossil fuels are the primary global source of fuel. A significant proportion of the Kenyan population lacks access to commercial energy derived from hydrocarbons. Kenya’s petroleum industry has been experiencing economic challenges owing to international production dynamics of ‘artificially induced’ supply, conflicts in the crude oil producing nations among other factors. It is worth noting that the country no longer imports crude oil for processing owing to obsolete technology at its refineries that have been converted to oil reserve ‘banks’. In 2023, the imports amounted to 606 billion Kenyan shillings (approximately 4.7 billion U.S. dollars). This import value increased greatly in compared to the previous year, and this was majorly attributed to the rising costs of crude oil compounded by Russian-Ukraine war. There have been effort geared towards stabilizing prices and key in 2023 was the government of Kenya rolled out price stabilization trough purchase of oil from international oil exporting firms using Kenya shillings, a breakaway from initial subsidization of consumer prices. This effort has not yielded so much fruits as factors of geopolitics of dollar and Middle East conflict are at play Lamarque, Hugh. (2019), Fondo (2023) and Mutisya (2024).

These fossils are anticipated to be exhausted gradually over a specific duration. The objective is to guarantee the accessibility of renewable energy. The economy is experiencing significant levels of consumption across all sectors, along by ongoing population increase and growing industrialization. As a result, the existing energy infrastructure is under considerable strain. The emergence of increasing environmental and energy security threats has unavoidably led to a shift towards renewable energy sources. Fossil fuels, including coal, petroleum, and natural gas, currently account for

80% of the worldwide energy demand, making them the primary sources of the world's energy supply.

The remaining part consists mostly of conventional biomass, nuclear energy, and large-scale hydropower. To attain sustainable energy, it is important to shift the existing energy resource mix towards a greater dependence on low-carbon technology and renewable energy sources, such as biofuel. The need for ecologically friendly energy sources has arisen due to environmental concerns, in order to mitigate the greenhouse effect caused by air pollution.

Currently, crude oil derived from fossils is the only commercially available source of diesel fuel. This oil is classified as non-renewable, meaning that it cannot be replenished naturally within a reasonable timeframe. The ongoing and unsustainable extraction of this oil is driven by the ever-increasing global demand for diesel fuel. Therefore, urgent intervention is required to address this issue without compromising food security. The primary challenges in bio-diesel generation are the exorbitant expenses associated with methanol and the presence of water in ethanol. To resolve this issue, a reagent capable of reacting with the water present in the ethanol is necessary. Ethanol is both cost-effective and readily accessible within the country, unlike methanol.

To achieve cost-effective production of bio-diesel in Kenya, it is crucial to focus on researching sustainable, inexpensive, and readily available raw materials, economically beneficial and easily accessible alcohol reagents such as ethanol, and the potential utilization of locally sourced heterogeneous catalysts. Exploring these areas presents significant opportunities for advancement.

1.3 Objectives of the Research

1.3.1General Objective

The optimization of production process for crude cottonseed Oil biodiesel by using wood ash Catalyst.

1.3.2 Specific objectives

1. To undertake pre-processing of feedstock and produce biodiesel using heterogeneous wood ash catalyst in the transesterification of cottonseed oil.
2. To determine Optimum conditions that yields a maximum conversion for the transesterification of cotton seed oil.
3. To design transesterification process utilizing wood ash in the transesterification of vegetable oil produce biodiesel
4. To model production of biodiesel using wood ash catalyst, cotton seed oil and ethanol

1.4 Justification

There is a demand for cost-effective, renewable, ecological, and eco-friendly alternative energy sources. The manufacture of biodiesel encounters several obstacles. The success of the process is contingent upon the quality of the feedstock. The majority of researchers have focused their efforts on the utilization of methanol, despite the fact that ethanol, which is easily accessible in Kenya, possesses similar potential, with the exception of its impurity. Ethanol has a water content ranging from 2 - 5%, which results in the creation of soap during the process of transesterification. It is necessary to address the gap in utilizing ethanol as a replacement for methanol and calcinated limestone as a catalyst.

Research on the utilization of cottonseed oil as a bio-diesel source is currently restricted and primarily focused in industrialized countries. In 2023/24 crop season, the lint production annually stood at 2000 MT from 12,152 ha an increase from 1,253 MT harvested from 8,558 ha the previous year (Republic of Kenya 2024). From this cottonseed alone was 4000 MT, which majorly found its way as animal feed. Kenya possesses a significant human resource capability in this particular field, making it an excellent opportunity to capitalize on.

Relying on fossil fuels poses dangers to industrial and economic wellbeing of a country not forgetting the climate change effects of hydrocarbons on the planet. Pollution resulting from the processing and utilization of the petro fuel would persist. Hence, it is imperative to address this predicament by utilizing alternative energy sources that are not only cost-effective but also renewable, sustainable, and ecologically sound. Exotic trees, such as jatropha will be utilized for the production of eco-friendly green fuel. Jatropha appears to be an excellent choice due to its non-food nature and its ability to thrive in infertile land with few cultivation requirements.

Mineral catalysts are also non-renewable. Wood ash on other hand is readily available as a waste in many in agro processing industries and domestic thermal processes as well. Ash from wood sources has no major economic use and its disposal as refill in quarries is akin to burying money. The major composition being calcium carbonate and through calcination can be converted to calcium oxide and finally dissolved in water to get calcium hydroxide Van Ryssen, J.B.J. & Ndlovu, Hloniphile (2018). Undertaking this study and apart from saving close to KES 600 billion annually, there will be economic spur arising from value addition to the cottonseed which is typically regarded as waste in textile backward (ginning) process.

1.5 Significance of the Study/Motivation

This study was motivate by the need to add value to cotton industry chain at the same time mitigating effects of climate change by substituting mineral catalyst use with renewable and sustainable products i.e. wood ash and in so doing waste menace of ash will be cured. These motivations will ignite, spur and augment the climate change efforts by the government and its partners in Committee of Parties (COP)

1.6 Structure of the Thesis

This thesis structured in ten major themes outlined as:

1. Project Background
2. Problem Statement
3. Project Justification
4. Objectives
5. Literature Review
6. Methodology
7. Results and Discussions
8. Conclusions and Recommendations
9. References
10. Annexes

CHAPTER TWO: LITERATURE REVIEW

This chapter entails literature review on the biodiesel study. It includes history, production options, uses, advantages, and disadvantages of biodiesel. Quality issues and production systems are also explored

2.1 Baseline Review

Biodiesel is a type of fuel that is similar to diesel and is made from biological sources through a specific procedure. It is easily applicable in diesel-powered automobiles. The substance is a yellow liquid that ranges in color from light to dark. It does not mix easily with water, has a high boiling point, and a low vapor pressure Kumar D et al (2019). Average methyl ester biodiesel exhibits a flash point of approximately 150°C, rendering it significantly non-flammable. The density of the substance is 0.86 g/l. Biodiesel exhibits a viscosity of 1.9-6.0 $\text{mm}^{2/s}$ which comparable to that of conventional petroleum diesel. It can be utilized as an addition in diesel compositions to enhance the lubricating properties of pure Ultra-Low Sulfur Diesel (ULSD) fuel. The majority of countries worldwide utilize the "B" factor to indicate the quantity of biodiesel present in a gasoline blend, as opposed to the "BA" or "E" method employed for ethanol blends Karmarkar, Neha. (2023).

The global use of biodiesel has experienced a revival due to the growing awareness of environmental and economic issues, particularly in relation to the Kyoto Protocol. Currently, more than 29 countries across the world engage in the commercial production of biodiesel.

Plant oil is highly valued for its application as a biofuel sometimes referred to as "diesel" and can be transformed into biodiesel. Cottonseeds, which are domestically cultivated in

Kenya, possess significant potential as a feedstock for the manufacturing of bio-diesel. Extensive research has been conducted over a prolonged period, yielding a favorable outcome. The research has focused on two areas: transesterification and algal culture. The increasing demand for fuel in Kenya, along with the numerous advantages of biodiesel and the abundant and affordable availability of cottonseeds, all contribute to the necessity of producing biodiesel Mandari et al (2022).

2.1.1Historical Background

Transesterification of vegetable oil was conducted by E. Duffy and J. Patrick in 1853, predating the functionality of the first diesel engine by many years. The initial prototype of Rudolf Diesel, consisting of a solitary 10 ft. (3 m) iron cylinder equipped with a flywheel at its base, successfully operated using its own power for the first time in Augsburg, Germany, on August 10, 1893. In 1900, Diesel showcased his engine and was awarded the prestigious "Grand Prix" at the World Fair in Paris, France. The propulsion system of this engine utilized peanut oil, which is a type of biofuel.

In the 1920s, makers of diesel engines modified their engines to take advantage of the lower thickness of fossil fuel (petro diesel) instead of vegetable oil, which is a type of fuel derived from biomass. The cost of the fuel produced was significantly lower compared to the available biomass alternatives. The outcome was a significant reduction in the infrastructure for producing biomass fuel, but worries about the environmental impact and a decreasing difference in cost have led to the increasing popularity of biomass fuels like biodiesel as an alternative.

A study on the utilization of trans-esterified crude and refined oil of from sunflower to meet the specifications of petro-diesel fuel was started in republic of South Africa in 1979. By 1980s, the procedure to create biodiesel of engine-tested quality suitable for use as fuel was successfully finalized. Kenya has shown interest in two specific plants: jatropha caucus and the castor plant as well as other oil food crops (Republic of Kenya 2024).

2.1.2 Kenya's Energy Demand

The demand for diesel in Kenya has been increasing in recent years, leading to higher costs. Ensuring a sufficient and balanced energy supply is crucial and important for the fast expansion of all sectors of the economy. It is worth noting that the country no longer imports crude oil for processing owing to obsolete technology at its refineries that has so far been converted to oil reserve ‘banks’. In 2023, the imports amounted to roughly 606 billion Kenyan shillings (approximately 4.7 billion U.S. dollars). This import value increased greatly in compared to the previous year, and this was majorly attributed to the rising costs of crude oil compounded by Russian-Ukraine war. There have been effort geared towards stabilizing prices and key in 2023 was the government of Kenya rolled out price stabilization trough purchase of oil from international oil exporting firms using Kenya shillings, a breakaway from initial subsidization of consumer prices. With increase in industrial startups and coupled with demand for industrial goods the demand for energy is expected to rise.

2.1.3. The Advantages of Bio-diesel.

Biodiesel can serve as an alternative to rapidly depleting fossil fuels, contributing to the reduction and stabilization of automobile fuel prices. Biodiesel possesses several advantages, such as being a sustainable energy source that can be utilized without any modifications to current diesel engines. Additionally, it may be derived from underutilized and untapped vegetable oils.

The product is ecologically sustainable and capable of decomposing naturally. It generates 80% fewer carbon dioxide emissions and eliminates sulfur dioxide emissions when compared to traditional diesel fuel. It offers a 90% decrease in the likelihood of developing cancer. It can be utilized independently or blended in any proportion with mineral oil or diesel fuel. The optimal blend ratio falls between the ranges of 5 to 20% (B5-B20). Biodiesel possesses a superior cetane rating compared to petro-diesel, resulting in a faster ignition upon injection into the engine. The ignition (flash point) of this substance is over 150°C, which is significantly higher than that of petrol at 64°C or gasoline, which is at -45°C Kumar D et al (2019).

2.1.4 Potential Drawbacks to Bio-diesel

Biodiesel exhibits corrosive properties towards rubber and concrete materials, rendering it unsuitable for storage in tanks walled with concrete. It may be necessary to decrease the size of the fuel intake orifices in order to generate greater cylinder pressures. At present petroleum prices, production costs of biodiesel are higher compared to petro-diesel. In addition, biodiesel exhibits a higher gel and cloud point compared to petroleum diesel Avhad MR, Marchetti JM (2015)

2.1.5 Biodiesel Feedstock Currently Being Used

The main constituents are derived from vegetable oils, animal fat, and recycled grease. The substances present in them include triglycerides, free fatty acids, and other impurities. Soybeans serve as a primary source of biodiesel, while various oils, such as cottonseed oil, can also be utilized for biodiesel production. Waste vegetable oil, animal fats like beef tallow and grease are used as well as a byproduct of producing omega-3 fatty acids from fish oil. Oil is available for purchase in three forms: crude degummed and refined. The choice of oil type influences the necessary manufacturing process.

The primary feedstock utilized in the methyl ester process in Kenya consists of com oil, cottonseed oil, castor oil, and animal fats. Methanol is the predominant main alcohol utilized in the manufacturing of biodiesel; however, alternative alcohols including ethanol and butyl can also be employed. The water content is a crucial determinant for the primary alcohol's quality. Transesterification processes are negatively affected by the presence of water, leading to low yields and elevated quantities of FFAs, soaps and triglycerides in the product. There is no chemical distinction between the alcohols utilized in the procedure. Factors such as the price of alcohol, the quantity required for the reaction, the convenience of recovering and reusing the alcohol, fuel tax credits, and concerns about global warming impact the selection of alcohol. Certain alcohols may necessitate minor technical adjustments to the production process, such as elevated operating temperatures, reduced mixing velocities and extended or slower mixing duration.

The ester formation process occurs on a mole-to-mole basis, while the buying of alcohol is on volume. As a result, the qualities of these substances have a considerable effect on the cost of feedstock. The stoichiometric ratio between alcohol and triglyceride is 3:1. Recovering methanol is more straightforward compared to recovering ethanol. Ethanol and water form an azeotrope, making it costly to purify ethanol throughout the recovery process. In contrast, azeotrope formation in methanol is unheard of in addition to its lower flash point of 10°C compared to that of ethanol at 60°C. The alcohol must meet the criteria of being un-denatured and anhydrous. Ethanol is commonly rendered unfit for consumption by adding toxic substances, so deterring its misuse. To reduce high operating costs and negative environmental apprehensions, it is necessary to recover and/or recycle the leftover alcohol back into the process Jambulingam R et al (2020).

A catalyst is necessary because of the limited solubility of alcohol in the oil/glycerol phase. The catalyst enhances the solubility apart from facilitating the reaction to occur at a faster and forward rate. Typically, the prevailing catalysts employed are potent mineral bases, such as potassium or sodium hydroxide.it is necessary to neutralize the base catalyst with a powerful mineral acid at the end of the process. Un-processed vegetable oil usually contains free fatty acid content of less than 2% on weight. These substances will undergo a chemical reaction to produce soap, which will ultimately be present in the crude glycerin. Base catalysts can also be utilized with refined feedstock, such as refined cotton oil, if the initial free fatty acid content and water content are minimal. Base-catalyzed reactions have a relatively high rate of reaction, which is affected by aspects among them temperature level, concentration of reagents, mixing, and the mole ratios of alcohol to oil. The majority of processes for economic reasons utilize NaOH or KOH catalysts. It is notably more expensive to use Potassium hydroxide (KOH) although the resulting products when neutralized with phosphoric acid, potassium can be precipitated as K3P04, which is a type of fertilizer that has economic value. Sodium methoxide, often in the form of a 25% solution in methanol, is a catalyst that exhibits more effectiveness per unit weight compared to the combination of sodium hydroxide and alcohol Jambulingam R et al (2020)

Enzymes catalyze the conversion of triglycerides into methyl esters, while others also act on the fatty acids. Nevertheless, the utilization of these substances is restricted due to their exorbitant expenses, sluggish reaction rates, and the fact that the production of methyl esters usually falls short of the 99.7% threshold necessary for biodiesel of fuel-grade quality. Neutralizers are incorporated in the processes to neutralize acidic or alkali catalysts in the biodiesel and its main by-product i.e. glycerol substances biodiesel and glycerol. Phosphoric acid is the preferred option for neutralizing base catalysts over hydrochloric acid due to the valuable chemical fertilizer that is produced as a result Ziolkowska JR (2019).

2.1.6. Crude cottonseed oil as feedstock.

Chemical Properties of cottonseed oil are not different from that of other vegetable oil that include soya bean that has been exploited for biodiesel production. These properties include free fatty acid content of less than 1% that are key in esterification process.in terms of yield cottonseed contains up to 25% of crude oil while soya bean and sunflower that have same uses have 18 % and 25% respectively Malabadi et al (2023).. Cottonseed oil therefore has substantive yield with equal qualities and comes at low cost effective since it is a by-product and majorly used as animal feed. After extracting the oil the seed cake will still serve same nutritional supply to animals as the protein content percentage will be enhanced.

2.1.7 Optimization of Experimental Designs

Experimental design methodology main aim is to provide statistical tools to analyse and understand problems and how best to optimise issues. This procedure is unique; not a routine, especially when the cost, time and environmental impact of the processes are significant aspects. Secondly, the performance indexes (outputs) should be determined and measured appropriately and accurately.

Researchers by great extension have utilised full-factorial or fractional factorial design in engineering problems. The application of experimental design techniques for process optimisation is suitable for numerous industrial applications Kacem, Prof. Dr. Imed (2017). Full Factorial and Fractional Factorials are common but Fractional Factorial having better advantage, For example, a 2^{5-2}design is 1/4 of a two-level, five-factor factorial design. For full factorial 32 runs would be required (i.e. 2^5) but for fractional factorial this experiment requires only eight runs.

Fractional factorial designs present an opportunity for reduced testing while potentially providing all necessary information, and options to learn about the system in a sequential manner Errore, et al 2017, Montgomery et al (2017). Applicable examples of optimization in biodiesel production factors include temperature, mole ratios, time, rate of flow, viscosity of oil among other factors. Taguchi and response surface methodology are used in process and system optimization. While Taguchi Method is an experimental design method that employs statistical techniques to reduce issues of variation and improve the quality of output, Response Surface Methodology on other hand is used to develop models that are predictive hence simulating how systems behave at different conditions Montgomery et al (2017). The most influential variables and interactions in the system are used in Taguchi method leading to determination of optimal values of process parameters.in surface response methodology the predictive models are used and thus simulates behaviour of process and factors that are of high influence in a process are identified Montgomery et al (2017).

2.1.8 Catalysts Being Used

Catalysts used in transesterification reactions are classified into two main categories i.e. as chemical (acid or alkali) and biological catalysts. These can further be classified as:

i. Homogeneous Alkali Catalyst,
ii. Homogeneous Acid Catalyst,
iii. Enzyme Catalyst and
iv. Traditional Immobilized Lipases.

Chemical catalysts have better yields and have ability to catalyze high free fatty acid feedstock. However, they pose significant challenges like difficulty in recovery and catalyst not reusable. Heterogeneous and enzyme catalytic processes solve these problems and come at an economic lower cost Mandari (2022).

Heterogeneous catalytic biodiesel productions with acid, acid–based bi-functional base, nano catalyst, and catalysts derived from biomass waste have been researched on Karmarkar, Neha. (2023). Enzymatic catalysts that include liquid lipase compounds, immobilized lipase on different carrier matrices, various lipase immobilization techniques in practice have offered reprieve although costs and sustainability supply are main problems Kumar D, Das T, Giri BS et al (2019, Jegannathan KR, Abang S, Poncelet D et al (2008).

With minimization of wastes produced during the process, the enzymatic reaction process complies with requirements of green chemistry; reduce environmental impacts Aghababaie M, Beheshti M, Razmjou A, Bordbar AK (2019).

Alternative processes include use of supercritical fluids with and without catalyst in spite being not recommended in open batch processes as well as its effects on environment Mandari (2022)

To cure above challenges, wood ash could offer alternative. The characteristics of wood ash as include:

i. Between 25 and 45% calcium oxide (CaO),
ii. Trace amounts of magnesium oxide (MgO), aluminium oxide, and iron oxide
iii. Up to 10% phosphorus pentoxide ,
iv. Potassium oxide (K2O) of 5-20% and

v. Trace amounts of micro-nutrients such as iron, manganese, boron, copper, and zinc, Van Ryssen, J.B.J. & Ndlovu, Hloniphile (2018).

2.1.9 Cottonseed Production in Kenya

The primary feedstock utilized in the methyl ester process in Kenya consists of com oil, cotton seed oil, castor oil, and animal fats. In 2023/24, crop season lint production annually stood at 2000 MT from 12,152 ha an increase from 1,253 MT harvested from 8,558 ha the previous year. From this cottonseed alone was 4000 MT, which majorly found its way as animal feed. The primary counties that produce cotton are Tharaka Nithi, Kirinyaga, Taita Taveta, Baringo, Elegeiyo/Marakwet, West Pokot, Kitui, Busia, Homa Bay, Kilifi, and Lamu (Republic of Kenya 2024).

2.1.10 Feedstock Costs

Supply and demand forces determine the cost of any commodity in any market. This law applies to vegetable oil and animal fat (tallow and lard).Generally; vegetable oils have a higher unit value compared to animal fats. There has been a fluctuation in global and local prices during the past five years. During the same period, the price of a kilogram of lint in Kenya has seen fluctuations, reaching a peak of Kes 500 in 2021-2022 and a low of Kes 170 in 2019. The cost factors include fluctuations in weather patterns, seasonal variations, the global impact of the COVID-19 pandemic, and conflicts in certain regions of Eastern Europe (Republic of Kenya 2024).

Despite the high prices of lint, farmers only earned between Kes 50 and Kes 90 per kilogram of cottonseed. This led to demoralization and a decrease in the area of land used for cotton cultivation. The cost of making bio-diesel is mostly dependent on feedstock expenses, which typically account for 50-75% of the total cost. Therefore, having a dependable and affordable source of feedstock, such as cottonseed, is crucial for achieving success in this industry.

2.1.11 Cotton for Fibre, Food and Energy

It is necessary to address the aforementioned issue in order to protect the economy of the country, which relies on agriculture. In order to preserve employment opportunities in the manufacturing and retail sectors, it is crucial to protect Kenyan farmers from unfair competition. The research will focus on enhancing the value of the seed, in accordance with the objectives of the textile project within the VLIR-UOS program. As depicted in Figure 2.1 there are other pathways of value chain.

The decline in Kenya's cotton production can be attributed to the implementation of structural adjustment programs. This is apparent from the ongoing decrease for land being used for cultivation, as well as the decrease for crops produced per unit of land. The attempted measures have included the implementation of tax exemptions to encourage domestic use of the lint, as well as providing subsidies to farmers. However, these efforts will prove ineffective unless there is an assurance of sustainable production.

Kenya possesses extensive expanses of promising agricultural land, primarily in regions characterized by unfavorable agro-climatic conditions, where it is possible to cultivate plant species that produce vegetable oil. Minimal investment is required to replenish the existing supply in the cotton business. Diversifying the utilization of the crop would subsequently result in increased profits. Consequently, the integration of industries will occur horizontally. Furthermore, enhancing the output of the agricultural yield will result in more efficient utilization of the ginneries and a plentiful provision of lint to the textile spinning mills and cottage industries. This initiative will provide employment for a larger number of individuals and provide prospects for training. Research on the utilization of cottonseed oil as a bio-diesel source is currently restricted and primarily focused in industrialized countries. Kenya possesses a significant amount of human resources in this particular industry, making it an excellent potential to capitalize on.

Without the development of alternative methods to raise farmers' morale and considering the global competition, Kenyan products will be gradually eliminated from the market. This will result in job losses and a rise in poverty levels. Similarly, relying on fossil fuels will subject the country to a state of dependence in terms of energy supply and consumption. Moreover, pollution resulting from the processing and utilization of the identical fuel would persist.

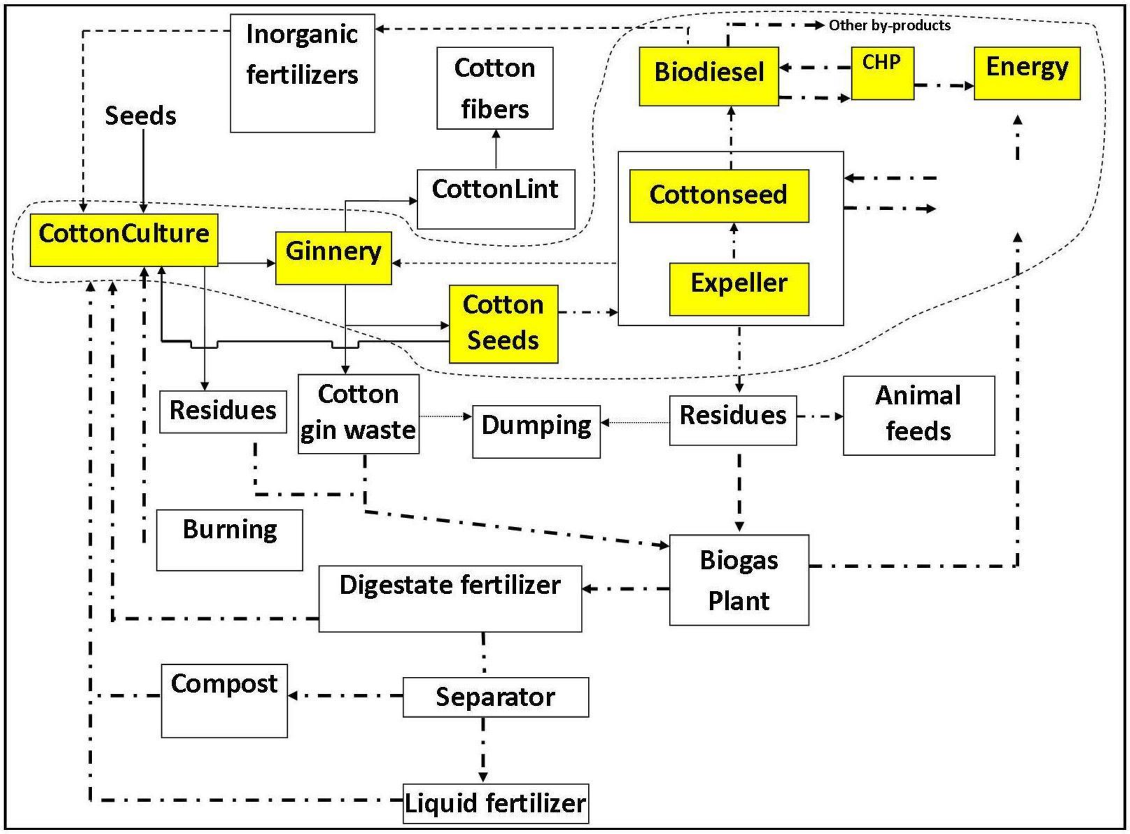


Figure 2.1: Cotton for Fiber, Food and Energy

Source MU-VLIR-UOS Report (2021)

Legend:

——▶ Existing material flows (classified as essential)

·········▶ Existing material flows (classified as non-essential)

▬ · ▬▶ Materials & energy flows yet to be exploited

-------▶ Materials & energy flows to be proposed for further consideration

CHP-Combined Heat Power

The looped area highlighted in yellow depicts the path to which this research concentrated.

2.2 Viability and Biodiesel Production Technologies

There are four main methods for producing biodiesel: direct usage and mixing, micro emulsions, thermal cracking (pyrolysis), and trans-esterification. The predominant technique employed is the transesterification of vegetable oils and animal fats.

2.2.1 Direct Use and Blending/Mixing

Utilization of food as a substitute for fuel has been examined extensively Mandari et al (2022). Africa has made significant progress in this field. In 1980, Caterpillar Brazil utilized engines with pre-combustion chambers that incorporated a blend of 10% vegetable oil. This allowed for the engine to keep its full power output without requiring any modifications or adjustments. The inaugural global conference on plant and vegetable oil took place in Fargo, North Dakota, during August of 1982. Filtered, used frying oil was utilized to make diesel fuel. Initially, a mixture consisting of 95% recycled cooking oil and 5% diesel fuel was utilized. Pre-heating was required to sustain the surrounding temperatures. There were no issues related to coking or carbon accumulation. The cited issue was lubricating oil contamination caused by an increase in viscosity due to the polymerization of polyunsaturated vegetable oils.

Subsequently, combinations of degummed soybeans and diesel were examined in ratios of 1:2 and 1:1. The primary issues identified during this test were the degradation of the oil and the inadequate combustion. Polysaturated fatty acids are highly prone to polymerization and the development of gum due to oxidation during storage, as well as complex oxidative and thermal polymerization at elevated temperatures and pressures during combustion. The gum formation rate on rapeseed oil (45%) was five times lower than that of high-linoleic oil (78–85%). It was found that there were no negative impacts on lubricating oil or power when the blend ratio of diesel to winter rapeseed reached

70/30 (B 30). Subsequent testing revealed significant coke in the injector, leading to a reduction in power output and thermal efficiency.

Therefore, the direct utilization of vegetable oil and mixtures of these oils can often be deemed undesirable and unworkable for any direct or indirect engines, owing reasons: High value viscosity, acidic content, gum production as a result of oxidation, polymerization under storage and carbon deposits and increase of viscosity of lubrication oil.

2.2.2 Micro emulsion

Researchers have investigated micro-emulsions that contain organic solvents such as ethanol as a potential solution to the issue of excessive viscosity in vegetable oils. A micro emulsion is unchanging mixture of very minute fluid structures that range in size from 1 to 150 nanometers, which are generated naturally when two liquids that do not normally mix are combined with one or more substances that have both hydrophilic and hydrophobic properties. Despite having a lower energy and cetane number, micro emulsions ethanol in unrefined soybean oil demonstrated comparable performance to high-sulfur diesel although this was only in a short term.

The issues that persisted were regular sticking of the injector needle, significant carbon deposits, poor combustion, and an elevation in the viscosity of the lubricating oil. The 200-EMA screening test revealed that the Later Ship Nonionic (SNI) fuel, which consisted of 50% No. 2 (high sulfur) diesel fuel, 25% degummed and alkali-refined soybean oil, 5% 190-proof ethanol, and 20% I-butanol, was successfully removed. However, significant issues arose due to the presence of carbon and lacquer deposits on the injector tips, intake valves, and cylinder tops. All micro emulsions including butanol, hexanol, and octanol satisfied the specified viscosity limits for NO.2 diesel. Nevertheless, methanol offers a cost benefit compared to ethanol Mandari et al (2022).

2.2.3. Pyrolysis

Pyrolysis is a long-standing technology that has recently regained popularity. The process entails subjecting the substance to high temperatures without the presence of oxygen, resulting in the breaking of chemical bonds and the production of tiny molecules. When biomass is heated to remove the volatile stuff, it results in the production of charcoal that has double the energy density of the original material. Initial pyrolysis of vegetable oils was carried out with the aim of producing petroleum from vegetable oil. The process involved saturating Tung oil with lime and subsequently subjecting it to thermal cracking, resulting in the production of crude oil, which is further refined to produce diesel, gasoline and kerosene. The saponification of tung oil was reported to have yielded 68 kg of soap, which in turn resulted in the production of 50 liters of crude oil. Various researches have utilized catalysts, primarily metallic salts, to acquire paraffin and olefins.

The thermal decomposition and distillation of soybean oil were conducted using an ASTM distillation apparatus under both air and nitrogen sparing conditions. The combined amount of hydrocarbons recovered from distilling soybean and high-oleic sunflower oils was found to be between 73% and 77% for soybean oil, and between 80% and 88% for high-oleic sunflower oil. The primary constituents consisted of alkanes, comprising roughly 60% of the overall mass.

2.2.4 Transesterification

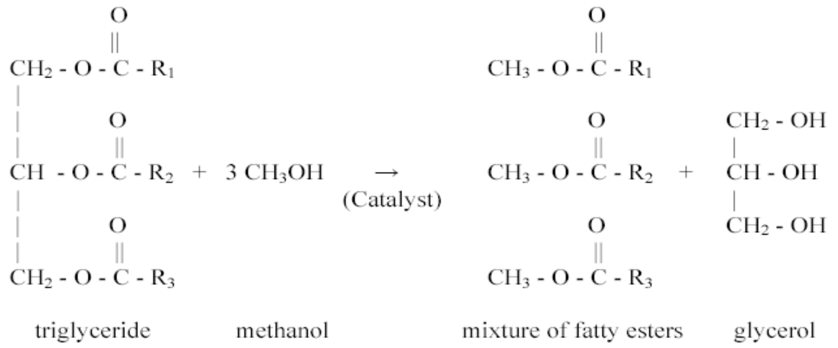
Transesterified biodiesel is chemically composed of a mixture of single-alkyl esters and those of long-chain fatty acids in various proportions. The predominant method involves utilizing methanol to generate methyl esters due to its affordability, while ethanol and higher alcohols like propanol and butanol can also be employed to create an ethyl ester biodiesel. Utilizing alcohols with greater molecular weights enhances the cold flow characteristics of the resultant ester, but at the expense of a less efficient transesterification reaction Duane J. (2003). Glycerol is a byproduct of the transesterification process.

Lipid transesterification is a production technique that converts the base oil into the required esters. All free fatty acids (FFAs) present in the base oil undergo one of three processes: conversion into soap, removal from the process, or esterification with an acidity catalyst to produce further biodiesel.

Animal and plant fats and oils consist primarily of triglycerides, which are esters formed by combining free fatty acids with the trihydric alcohol glycerol. During the process of transesterification, a base is used to deprotonate the alcohol, hence increasing its nucleophilicity. Typically, ethanol or methanol is utilized. The reaction exclusively takes in the triglyceride and the alcohol as inputs.

Typically, this reaction will either happen very slowly or not happen at all. Therefore, heat, together with an acid or base, is employed to expedite the reaction. The base-catalyzed technique is the predominant method for manufacturing biodiesel because to its cost-effectiveness. This process operates at low temperatures and pressures and has a conversion yield of over 98%.

Triglyceride + Methanol=Glycerol+ Esters ……………………*Equation 2.1*



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R_1 \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-R_2 \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array} + 3\,CH_3OH \xrightarrow[\text{(Catalyst)}]{} \begin{array}{l} CH_3-O-\overset{\overset{O}{\|}}{C}-R_1 \\ \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_2 \\ \\ CH_3-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array} + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Equation 2.2

In the esterification process, the triglyceride undergoes a reaction with alcohol in the presence of a catalyst, typically a potent alkaline substance such as NaOH, KOH, or sodium silicate. Based on empirical evidence, the concentration is 6.25 g/l. The alcohol undergoes a chemical reaction with the fatty acids, resulting in the formation of a compound called mono-alkyl ester, also known as biodiesel, as well as crude glycerol. The interaction between the bio-lipid (fat or oil) and the alcohol is a reversible reaction. To ensure complete conversion, it is necessary to supply an excess amount of alcohol, which will force the reaction towards the right.

2.3 The Biodiesel Production Processes

The predominant and cost-effective method is known as the base-catalyzed esterification of the fat with methanol, generally referred to as "the methyl ester process." The procedure entails the chemical reaction between the fat or oil and methanol catalyzed by either sodium or potassium hydroxide. In this reaction, the four primary yields are methyl ester (biodiesel), glycerin, feed-quality fat, and methanol. These products are subsequently reintroduced into the system for recycling. Biodiesel is the more commonly recognized name for the main product, methyl ester. To augment your earnings from the process, you have the option to vend the glycerin and fats.

The methyl ester procedure necessitates the elimination of unbound fatty acids and gums from raw or unprocessed vegetable oils. The pre-processing might involve several techniques such as refining, degumming, and filtration to eliminate contaminants. Degumming is the process of combining a small quantity of water (about 3-5%) with the feedstock. This causes the gums to form a solid and separate from the mixture using centrifugation. Refining entails the addition of sodium hydroxide to the feedstock, resulting in the formation of a soap that can be separated from the oil using centrifugation.

2.3.1 Batch Processing

The system undergoes agitation during the reaction period, which is then halted. During certain operations, the reaction mixture is permitted to undergo sedimentation within the reactor, resulting in an initial separation of the esters and glycerol. In alternative procedures, the mixture of reactants is transferred into a tank designed for the purpose of separating the components, and the alcohol is extracted from both the glycerol and ester streams. The biodiesel esters are neutralized then rinsed with warm slightly acidic water of Ph. 5.5 to eliminate any remaining alcohol and salts, and subsequently dehydrated. Subsequently, the completed biodiesel is moved to a storage facility while glycerol stream is neutralized, subsequently rinsed with soft water before refining it in a separate plant off the biodiesel production facility.

A batch, stirred tank reactor is the most straightforward approach for synthesizing alcohol esters. Reported alcohol to triglyceride ratios range from 4:1 to 20:1 (mole: mole), with a 6:1 ratio being the most frequently observed. The reactor can be hermetically sealed or fitted with a reflux condenser. The typical temperature is approximately 65 °C, although temperatures can vary between 25°C and 85°C.

Sodium hydroxide or potassium hydroxide are the catalysts most frequently employed, with a catalyst loading range typically ranging from 0.3% to approximately 1.5%. Certain groups employ a two-step reaction process, whereby glycerol is extracted between the phases, in order to enhance the overall reaction extent to more than 95%. Increased temperatures and higher mole ratios improve the rate of conversion as well as reduce reaction times from say one hour to twenty minutes, which is significant. In this process, oil is introduced into the system slowly followed by the catalyst and finally the alcohol methanol.

.

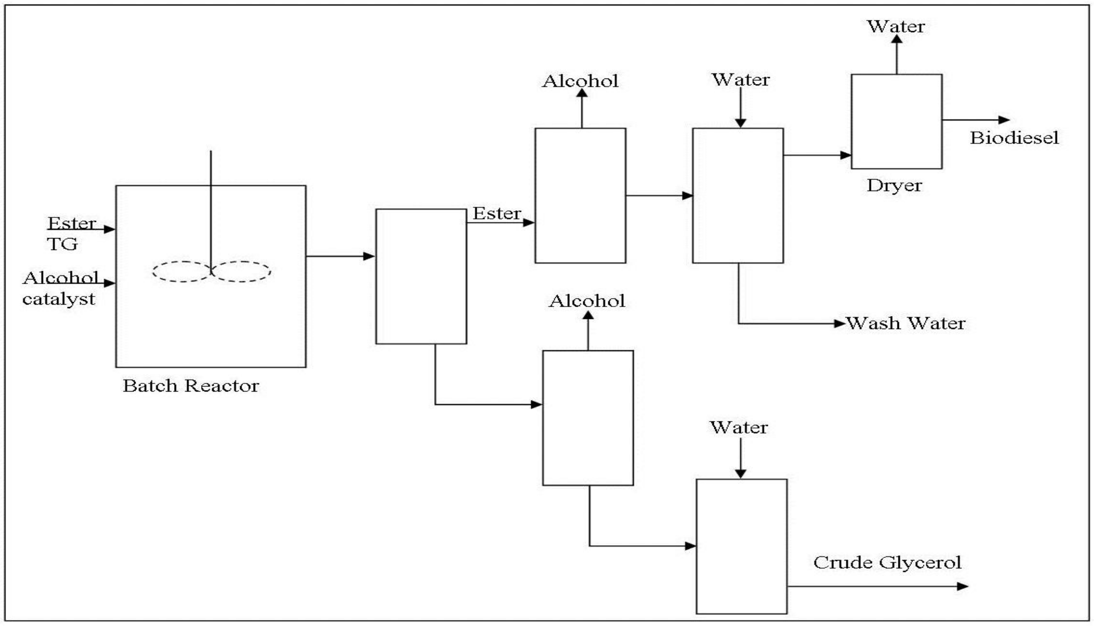


Figure 2.2: Batch reaction process

2.3.2 Continuous Process Systems

An often-utilized modification of the batch process involves employing a succession of continuous stirred tank reactors (CSTRs). By adjusting the volume of the Continuous Stirred Tank Reactors (CSTRs), you can increase the residence period in CSTR 1, resulting in a higher degree of reaction. Once the initial product, glycerol, is separated by decantation, the reaction in CSTR 2 proceeds swiftly. A crucial factor in the design of a Continuous Stirred Tank Reactor (CSTR) is the provision of adequate mixing input to maintain a uniform composition throughout the reactor. This results in an augmented dispersion of the glycerol product within the ester phase. Consequently, the duration for phase separation has been prolonged.

Instead of providing a sufficient duration for the reaction to occur in a reactor that is in a state of agitation, the reactor is designed in a tubular shape. The reaction mixture flows through this type of reactor in a continuous plug, with minimal axial mixing. The outcome is an uninterrupted system that necessitates relatively brief periods of stay, as little as 6-10 minutes, for the nearly full accomplishment of the reaction.

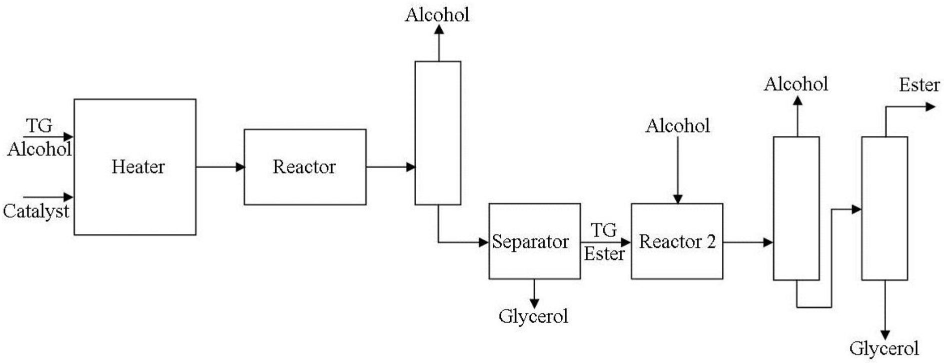


Figure 2. 3: Plug Flow Reaction System

2.3.3 High Free Fatty Acid Systems

If high levels of free fatty acid feedstock are introduced into a base-catalyzed system, they will undergo a reaction with the catalyst and result in the formation of soaps. In a base-catalyzed system, the highest permissible level of free fatty acids is below 2%, and ideally below 1%. Certain methods for utilizing high-free fatty acid feedstock employ this principle to extract and eliminate the free fatty acids from the feed for either disposal or independent treatment in an acid esterification unit.

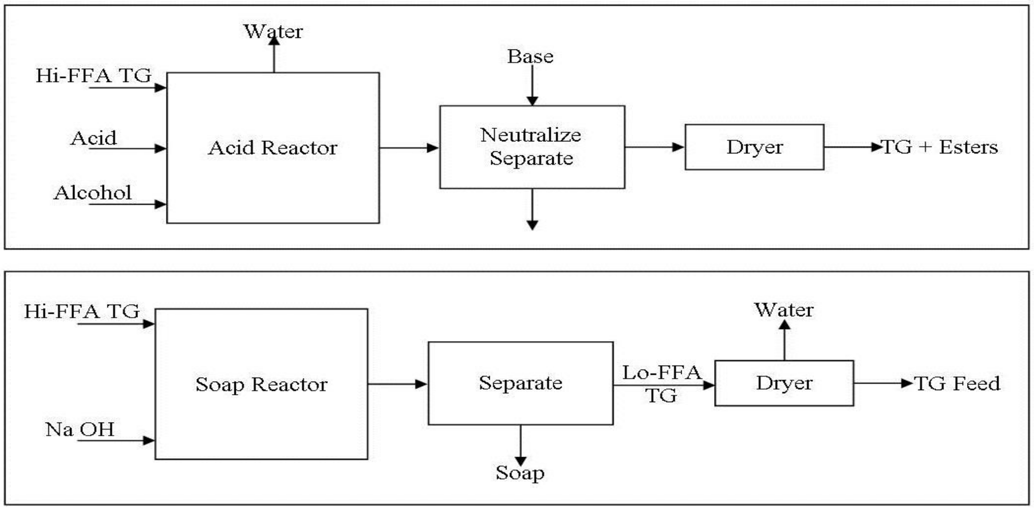


Figure 2. 4: Acid Catalyzed Direct Esterification Process

Caustic solution is introduced into the raw material, and the ensuing solidified substances are separated by means of a centrifugal force. Triglycerides are lost from the soaps during the process of caustic stripping. The soap mixture might be acidified in order to eliminate the fatty acids and extracted oils in a distinct reaction vessel. The purified oils are dehydrated and sent to the transesterification facility for additional treatment. Instead of squandering the free fatty acids in this manner, they can be converted into methyl esters by the acid esterification process. A technique that is catalyzed by acid can be utilized to directly convert free fatty acids in high-FFA feedstock into esters. Feedstock that is less costly, such as beef tallow or yellow grease, typically has a high concentration of fatty acid. The allowed level of free fatty acids (FFA) in tallow and yellow grease is 15%. There is a possibility that certain lots may surpass this particular standard. In order to carry out the direct acid esterification of high free fatty acids (FFA), it is necessary to remove water during the reaction. Failure to do so would result in the premature termination of the reaction. Additionally, a substantial alcohol-to-FFA ratio is necessary, often ranging from 20:1 to 40:1.

The esterification reaction also generates water as a byproduct that must be eliminated otherwise the process may proceed in a reverse direction resulting to water formation. However, the resulting combination of esters and triglycerides can be directly utilized in a traditional base-catalyzed system. The water in the methanol-water combination can be eliminated using processes such as vaporization, settling, or centrifugation. Incorporated in this system is a counter-current continuous-flow to remove the water through by washing it out with a stream of acidified methanol.

Based on the individual procedures and product requirements, we have the option to eliminate or retain certain impurities in the FFA. The pristine free fatty acid is subsequently subjected to acid esterification in a separate reactor operating in a countercurrent manner, resulting in its conversion into methyl esters. Subsequently, the process entails neutralizing and conducting tests on the methyl esters. Yields can surpass 99%. The equipment must possess acid-resistant properties, whereas the expenses associated with feedstock are often very low.

A different method for treating high-FFA feeds involves breaking down the feedstock into separate components of pure FFA and glycerin using hydrolysis. Usually, this process is carried out in a countercurrent reactor utilizing sulfuric acid and steam. The result is a combination of unadulterated free fatty acids and glycerin. The majority of pollutants in the feedstock are primarily found in the glycerin, although a portion may be carried away with the steam or water effluent.

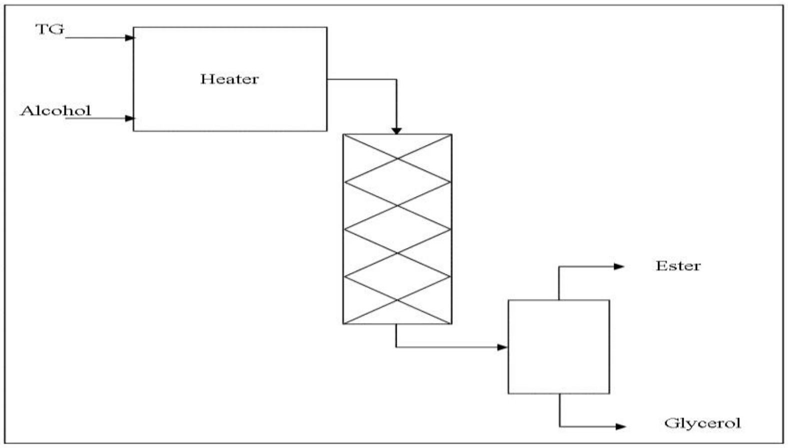


Figure 2. 5: Fixed beds, base catalyzed reactor systems

2.3.4 Non-Catalyzed Systems - Biox Process

2.3.4.1 Non-Catalyzed Systems - Biox Process

Tetrahydrofuran is employed as a co-solvent in this procedure to dissolve the methanol. The outcome is a rapid response, often taking 5 to 10 minutes, without any remnants of a catalyst present in methyl ester or its by-product phases. One reason for selecting the tetrahydrofuran co-solvent is its similar boiling point to methanol. Once the reaction has finished, the surplus methanol and the tetrahydrofuran co-solvent are both retrieved simultaneously.

In order to overcome the issue of high free fatty acid (FFA) content an alternative method is to use a fixed-bed, non-soluble base utilizing calcium carbonate as a catalyst.

This technology necessitates a relatively low operational temperature of 30°C. The separation of the ester-glycerol phases is thorough, resulting in products that are free from catalysts and water. The equipment volume must be increased to accommodate the additional volume of the co-solvent, resulting in a bigger quantity of the finished product. A solvent that contains hazardous and/or toxic air pollutants necessitates the use of specialized equipment that is designed to prevent leaks and tightly regulate any emissions that may escape. Both the glycerin and the biodiesel must be thoroughly purged of the co-solvent.

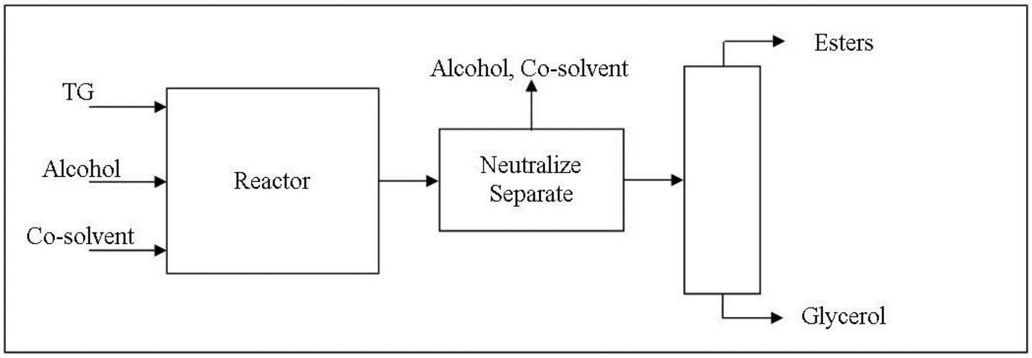


Figure 2. 6: Biox co-solvent process

2.3.4.2 Non-Catalyzed Systems - Supercritical Process

When a fluid or gas is exposed to temperatures and pressures that surpass its critical point, it displays certain exceptional features. There is now a unified fluid phase instead of separate liquid and vapor phases. Solvents that include a hydroxyl group, such as water or primary alcohols, exhibit the characteristics of super-acids.

An alternative method involves using a high alcohol-to-oil ratio of 42:1, without the need for a catalyst. At temperatures ranging from 350 to 400 °C and pressures above 80 atm or 1200 psi, the reaction reaches full completion within approximately 4 minutes. The capital and operational expenses can be comparatively higher, and the energy usage can be elevated. The outcome is an exceedingly rapid (3 to 5 minute) chemical response that produces esters and glycerol. In order to prevent the decomposition of the products, it is imperative to swiftly extinguish the reaction. In this scenario, a 5 ml cylinder reactor is immersed in a bath of molten metal and subsequently rapidly cooled in water.

Table 2. 1: Ester properties of Cottonseed Oil

S/ No	Product Specification	Cotton-Seed Oil
1.	Oil purity	90%
2.	Refractive index at 60°C	1.4572
3.	Moisture	12%

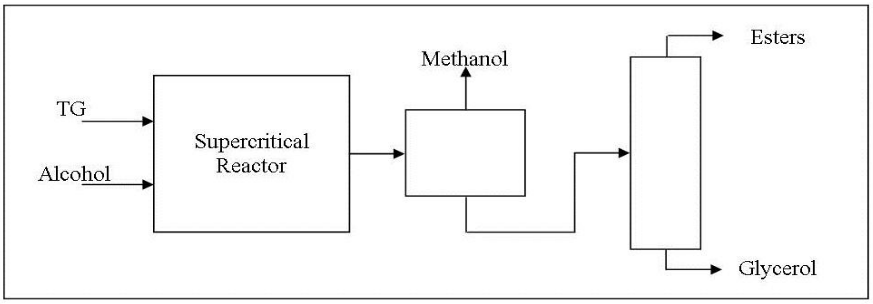


Figure 2. 7: Non-Catalyzed Systems - Supercritical Process

The overall quality of the glycerol produced and its worth as a co-product are significant economic factors. The glycerol typically produced by a biodiesel plant has a glycerol content of 50% or less. It also contains water, salts, methanol, methyl esters, unreacted glycerides, color and flavor compounds, impurities, and other minor substances. This is generally known as "biodiesel crude." By eliminating the water and methanol and increasing the glycerol concentration to 88%, it is possible to produce a financial benefit based on the market value of crude glycerol. The presence of salts, namely sulfur salts or potassium salts diminishes the quality of the crude glycerol generated.

2.4. Biodiesel Feedstock

2.4.1 Introduction

Biodiesel feedstock plants employ photosynthesis to transform solar energy into chemical energy. The majority of carbon dioxide released during the combustion of biodiesel is derived from the carbon dioxide that was first absorbed during the growing of plants. As a result, the overall emission of greenhouse gasses is minimal, and the net creation of carbon dioxide is effectively zero. Cottonseed oil can be extracted by employing methods that are not only suitable but also economical and efficient.

2.4.2 Cotton Seed By-Products and Their Uses

While cotton lint is commonly associated with the term "cotton," it is important to note that the agricultural product, seed cotton, also includes cottonseed as a by-product. Cottonseed, which is of lower worth compared to lint, is commonly processed to extract oil from meal. Cottonseed oil, which is in competition with other vegetable oils, is mostly utilized for human consumption and occasionally for soap production and various industrial applications, including plastics and pharmaceuticals. Cotton meal, which is in competition with other types of meals, is primarily utilized as animal feed. Meanwhile, the hulls or husks, which refer to the outer part of the seed, are either employed to create energy for the processing facility or mixed with the meal for animal feed. Occasionally, the hulls and husks are also utilized as fertilizer. Linters, which are residual fibers of inferior quality remaining after the ginning process, find application in diverse manufacturing sectors such as yarn production, plastics manufacturing, and filler materials production. Occasionally, cottonseed is utilized in its raw form, without undergoing any processing, specifically for animal feed, particularly in the dairy sector.

2.4.2.1 Edible Oil

The recent surge in commodity prices, particularly for edible oils, along with the lack of significant price changes for cotton, has renewed interest in the possibility of utilizing cotton byproducts as an additional source of income for cotton farmers. Cotton oil, along with other edible oils, has garnered significant interest due to its potential as a feedstock for biofuels. The increasing global demand for bio-fuels, specifically biodiesel made from edible oils, has sparked optimism over the potential transformation of the African edible oil industry and the opportunities for African cotton producers.

The weight composition of seed cotton is influenced by various factors. On average, one metric ton of seed cotton produces approximately 35-40% lint, around 10% cotton oil, and over 30% cotton meal. The distribution of proportions is influenced by the ginning outturn ratio, which varies from 30% to 40% of the weight of seed cotton, and the cotton oil extraction ratio, which ranges from 10% to 16% of the weight of cottonseed, depending on the crushing process.

2.4.2.2 Animal Feed

The process of separating lint from the seed in cotton production is known as ginning. This process produces a mixture called "cotton gin by-product" (CGB), which consists of various plant parts such as leaves, petioles, carpels, small seeds (motes), and lint. CGB offers beneficial dietary fiber and essential nutrients for ruminant cattle. Formerly referred to as gin trash, this by-product is a voluminous, nutrient-poor substance that accumulates after harvest and requires clearance from the gin yard.

Undoubtedly, CGB provides significant nutritional benefits to livestock producers, and its extraction from the gin has substantial economic consequences for the cotton business. However, it is important to acknowledge that CGB is a course that consists of a wide range of different, low quality, low-nutrient roughage with varying nutrient content. The crude protein content varies between 4% and 8%, depending on the quantity of cottonseed and motes (immature seed) present. The product has high crude fiber content because of its cellulose and hemicellulose components. We allocate a fraction of the overall corn grain biomass (CGB) to provide sustenance for beef cattle, as these herbivorous animals necessitate fibrous plant material throughout crucial periods throughout the year. CGB provides a diet consisting of beef cows, stocker cattle grazing on winter pasture, and steers and heifers in beef finishing lots.

2.4.2.3 Used as bio-fuel

Due to the increasing global demand for biofuel, which now accounts for approximately 9 percent of worldwide vegetable oil output, vegetable oils such as cotton oil have been suggested as a potential source of income for commodities producers in sub-Saharan Africa. Certain consumers of food commodities, who are willing to pay elevated prices, perceive this approach as a predicament, but others, such as commodity producers and the biofuel business, regard it as a chance for advancement. Sugarcane-based ethanol, primarily produced in Brazil, is the most lucrative among the three primary sources of biofuel. Maize-based ethanol, primarily manufactured in the United States, holds the second position. Edible oil-derived biodiesel, primarily manufactured in the European Union, holds the third position. The general agreement is that, other from ethanol derived from sugar cane, the profitability of biofuel production would have been unlikely without the implementation of different laws and requirements.

The need for biofuel can affect the cotton oil market through three avenues. Initially, it has the potential to immediately boost the demand for cotton oil as a feedstock for biofuel production. Furthermore, it has the potential to stimulate the demand for alternative oils, thereby indirectly increasing the need for cotton oil. Furthermore, it has the potential to stimulate the demand for other commodities, leading to a redistribution of resources that can affect the cotton oil market. In order to examine the impact of biofuel on the cotton oil market, it is necessary to consider each of these three channels individually.

2.4.2.4 Soil Dressing and Fertilizer

An aesthetically pleasing and practical landscape relies on careful consideration and strategic design, the use of well-suited plants, thorough soil preparation, appropriate fertilization, sufficient moisture, effective management of insects, diseases, and weeds, and consistent maintenance. While all of these criteria are crucial for good landscaping, none surpasses the significance of having a sufficient supply of plant nutrients.

Cottonseed meal is a highly beneficial organic source of nutrients for plants. The nitrogen, phosphorus, potash, and various trace elements in this product are gradually released, eliminating any wastage or runoff. This ensures that turf grasses, landscape plants, and vegetable gardens can experience sustained growth, attractiveness, and productivity over a long period. The high concentration of organic matter in the soil improves the structure of compact and heavy soils, while also benefiting light soils by enhancing their ability to retain moisture and nutrients. Cottonseed meal, being a slow-release organic fertilizer, can be applied in generous quantities without the risk of causing plant burn.

The Cotton Gin By-Product (CGB) is a raw agricultural commodity (RAC) that offers both economic and nutritional benefits to commercial animal businesses. It is possible to utilize more than 50% of all CGB (composted green biomass) as either a raw or a composted substance in soil. The product is typically applied on farmland adjacent to a gin as a soil amendment, usually at a rate of 3 tons or more per acre. An extra 4 to 6% is allocated for absorbent material, while a small quantity is processed, mixed, and packaged for consumer sale.

Cottonseed meal is a highly effective method of supplying plants with both the necessary organic matter and nutrients. The fertilizer is an organic, premium-grade product that releases nutrients slowly. It contains nitrogen, phosphorus, potassium, and many minor elements. When cottonseed meal is added to the garden soil, it undergoes decomposition over time, gradually releasing its nutrients and creating humus that improves the soil. Cottonseed meal with high nitrogen content and has traditionally been used as an organic fertilizer. It effectively reduces soil pH, does not represent a significant risk of plant burn, and supplies nitrogen, phosphorous, potassium, and various other essential plant nutrients. It is inexpensive and easily accessible.

2.4.2.5 The future of cottonseed oil

Although the majority of cottonseed oil is utilized for food purposes, very small amounts are used in the creation of non-edible items. Typically, these substances are comprised of low-quality oil or soap stock, which is a by-product of the refining process. Both crude oil and soap stock are utilized in the production of fatty acids, which are then incorporated into livestock feed and a diverse array of industrial products, including soaps, emulsifiers, medicines, insecticides, fungicides, cosmetics, rubber, plastics, and finishes for leather, paper, and textiles.

As science and technology progress, it is anticipated that these applications will grow. Cottonseed oil is being used in agricultural pesticide applications as an alternative to water- or petroleum-based oils, which has led to the development of a small but growing market for cottonseed oil. These innovations in spray nozzle design have contributed to this outcome to some extent. Low-volume and ultra-low-volume spray technique entails the even distribution of a little quantity of pesticide, typically just a few quarts, across an entire acre of land. The oil facilitates the adherence of the chemical to the target. These results in a decreased overall utilization of chemicals, thus mitigating environmental apprehensions associated with pesticide treatments.

Crude oil can also be utilized as an insect attractant, particularly in the form of insect baits like mole cricket bait. Due to its suitability for consumption, cottonseed oil is an excellent choice for dust management purposes in the food, feed, and bedding sectors. Chemical and physical properties of cottonseed oil are as shown in Table 2.2 while its FFAs composition by weight is as in Table 2.3.

Table 2. 2: Cottonseed Chemical and Physical Properties

Type oil	**Melting Range Degree Celsius**			**Cetane**	**Iodine value**
	Oil/Fat	Methyl Ester	Ethyl Ester		
Cotton seed oil	0	-5	-8	55	105

Table 2. 3: Fatty acids composition of cottonseed oil

S/ No	**Type of fatty acid**	**% By Weight**
1.	Linoleic	51
2.	Palmitic	21
3.	Stearic	2
4.	Arachid	1
5.	Oleic	25
	Total	100

2.4.3 Cottonseed oil extraction

Oil is extracted from cottonseed using two methods: mechanical crushing and solvent extraction. Smaller enterprises tend to use mechanical crushing due to its lower investment requirement. Prior to the extraction of oil, it is necessary to prepare the seeds.

This process entails the extraction of stems, leaves, metric tons, sand, dirt, and weed seeds. Seeds are often smaller than stems and metric tons, so they can be separated by screening. Typically, weed seeds, sand, and dirt are of smaller size and can be eliminated by using screens with finer mesh. Magnets have the ability to extract iron particles. After the delivery of cottonseed, the next step is to dehull the oilseeds before proceeding with further processing. We thoroughly remove the hull from cottonseed while retaining the lint on the seed.

The kernels and hulls are divided and allocated to separate operations. A lesser proportion of the extracted hulls are reintroduced into the cotton kernel to aid the operation of the mechanical screw press or expeller. The remaining hulls are packaged according to their weight as catch weights, then kept and marketed as exceptionally high-quality roughage. The cottonseed kernels are stored in a huge container to be processed further. The method is the same for all oil seed varieties used, starting from the kernel holding bin. The cookers convey the kernels, subjecting them to heat and moisture, resulting in a decrease in the oil's thickness and the softening of the kernels, so making it easier to press the oil. The desiccating action that accompanies the process of heating causes an augmentation in the level of friction in screw presses, resulting in elevated pressure and greater yields.

The conditional kernels are fed directly into a mechanical press, where a rotating screw gear operates within a horizontal steel barrel. The pressing process subjects the corn kernels to exceedingly high pressure, resulting in the extraction of 50% of the oil. The cake generated because of pressing, known as the extractor cake, is transported to the extractor. In the extractor, the cake is subjected to an organic solvent that dissolves the oil from the cake. The combination of solvent and oil is referred to as miscella. It is extracted from the extractor and subjected to distillation, where the miscella is heated and the solvent is evaporated from the mixture. The vaporized solvent is subsequently condensed using chilled water and recycled within this enclosed system. The de-oiled expeller cakes undergo steam treatment in a toaster to eliminate any remaining solvent and dry the finished cottonseed kernel. After the kernel is cooled, it is subsequently moved to the material handling section for either bagging or transfer to bulk.

Typically, the act of flaking oilseeds enhances their contact with the solvent in the process of solvent extraction. Currently, the prevailing technology for extraction is the use of hexane in a percolation extractor. Following the extraction process, raw cottonseed oil contains contaminants that can be categorized into two groups: insoluble in oil and soluble in oil. The oil-insoluble contaminants are comprised of pieces of seeds and tiny particles of meal, as well as unbound water and long-chain hydrocarbons or waxes that result in the oil being cloudy when it is cooled. The process of filtration can eliminate the majority of this substance.

2.4.4 Crude Oil Preparation for transesterification

Biodiesel processor machines need the crude vegetable oil to have some specific properties: Suspended particles lower than 1% (mass/mass) and less than 5 micrometers. Because of this, the following are necessary:

i. Filtration to 5 micrometers
ii. Washing with hot water
iii. Decantation
iv. Heating of the Oil
v. Second decantation
vi. Drying.

The further refinement of crude oil involves the following procedures: Degumming and refining/neutralizing processes. Bleaching, deodorization, and winterization are three processes used in many industries to remove impurities and improve the quality of a substance.

Degumming is achieved by adding hot water and acid. The chemical process that occurs causes the phospholipids (gums) in the oil to become hydrated. Degumming eliminates valuable emulsifying agents like lecithin. The process of degumming and neutralization of oil is typically conducted concurrently.

The process of refining or neutralizing degummed oil involves the controlled addition and mixing of caustic soda. Caustic soda chemically neutralizes the fatty acids and effectively eliminates certain color pigments present in the oil. The alkali reacts with a part of the oil to produce a substance called soap stock or foots. The soap stock, together with any accompanying contaminants, is subsequently isolated from the oil using a high-speed centrifuge. Excess soap residue in oil is eliminated through additional washes with hot water. The process of refining the oil yields a final product that is transparent, yellow-colored oil.

The process of color removal, known as bleaching, is typically accomplished with neutral clay or bentonite, specifically acid-activated earth. This clay binds with the coloring substances and oxidation byproducts that remain in the oil following the refining process. The clay is subsequently extracted and isolated from the liquid oil via filtration. The extent of bleaching varies, contingent upon the implementation of the final product.

Deodorization is the process of steam stripping the oil while operating under a vacuum, thereby eliminating volatile chemicals from the oil. This technique might be either batch or continuous. The final product is a blend of oil with a minimal amount of unbound fatty acids and a low level of peroxide value.

Winterization involves a procedure where the oil is cooled to temperatures below 38 °C while being gently stirred, causing the wax in the oil to crystallize. The oily crystals are subsequently separated from the oil by the process of filtration. If oil is not winterized, it might become turbid and experience wax precipitation during storage.

2.5 Feedstock Quality Issues

The proximity of a feedstock to pure triglycerides directly correlates with its ease of conversion to biodiesel and its corresponding cost. Converting feedstock to biodiesel becomes more challenging and costly as the cost of the feedstock decreases. The biodiesel feedstock may contain many potential impurities, including water, free fatty acids, particles, phospholipids, and sulphonated iodine. These impurities affect final product quality and thus need to be eliminated or minimized in preparatory processes. .

2.5.1Water

Water exclusion is crucial in the biodiesel synthesis process. Although most procedures can withstand water levels of up to 1%, even this minimal amount will enhance soap production and noticeably affect the thoroughness of the transesterification reaction. Water can be extracted using many methods. Key among the methods is following: Heating to high temperatures to break any emulsions between the water and oil followed by sedimentation of the water the bottom. Separation using centrifuges can also be used to allow separation of oil and water; and heating the oil under pressure and then spraying into vacuum chamber to bring the water content to a very law level.

2.5.2 Solids

It is imperative to filter the feedstock used for biodiesel. This prevents any impurities or particles from entering the processing system thus impeding the process. A 100-micrometer filter is used for this process.it is able to sufficiently eliminate particles from the majority of raw materials. The size of filter of 5 micrometers is good enough for oil to pass through.

2.5.3 Free Fatty Acids (FFAs)

FFAs can greatly influence the production process by deactivating the catalyst making it unable to function, producing soap through saponification process proceeding to left side, and generating water when they are converted into esters. Biodiesel produced using a traditional alkali-catalyzed method, which follows the American Standard for total glycerol, generally has a free fatty acid (FFA) content of less than 0.3%, regardless of the original acid level in the raw material. The catalyst used also acts as an agent that converts excess fatty acids to soap which is easily removed through washing process.

2.5.4 Phosphorus

The presence of phosphorus in biodiesel should be less than ten parts per million or lower. When crude oil is degummed, it eliminates phosphorus and the remaining can be eliminated in the process of esterification resulting to negligible quantities that will be in glycerol phase.

2.5.5Sulfur

One of the advantages of biodiesel is usually the low content. In Kenya the National Environmental Management Authority (NEMA) had set a requirement for sulfur levels in petroleum-based diesel fuel to decrease from 500 p.p.m. to 15 p.p.m. It is worth to note that biodiesel is already below this level.

2.5.6 Iodine Value

The iodine value is a basic yet widely used indicator of the oil's saturation level. Although the transesterification process is not significantly influenced by saturation and fatty acid profile, these factors do play a role in determining the properties of the biodiesel. Saturated fats result in biodiesel that has excellent oxidative stability as well as a higher cetane number but results to poor performance at lower temperatures. Biodiesel made from saturated fats solidify at lower temperatures and results to economic loss unlike those processed from vegetable oil.

2.6 Pretreatment of High Free Fatty Acid Feedstock

There is quite a number of oil from plants that can be used to produce biodiesel. Unfortunately, a substantial proportion of this feedstock is not suitable for the process due to high number of FFAs that are susceptible to saponification during transesterification. The free fatty acids will undergo a chemical reaction with alkali catalysts to form soaps that hinder the synthesis. The biodiesel feedstock usually exhibits the following ranges of Free Fatty Acid (FFA) content ranging to as low as 0.3 % for crude vegetable oil, 0.05 % for refined vegetable oil and as high as 50 to 90 % for trap grease.

The rule of thumb is, if the FFA level is below 1%, and especially if it is below 0.5%, the FFAs can be disregarded. Typical catalysts used include sodium hydroxide or potassium hydroxide, which are used in a quantity equal to 1% of the weight of the triglyceride. Soaps have the ability to facilitate emulsification, resulting in a less distinct distinction between the glycerol and ester phases. The process of soap synthesis also generates water, which can undergo hydrolysis of the triglycerides and so aid in the production of further soap.

With FFA exceeding 1%, it is required to use excess catalyst to allow neutralization of these FFAs. The quantities of additional catalyst can be determined using a formula that factors in the type of catalyst and percentage of free fatty acids. The following formulae are based on the fact reaction ratios is one to one mole to neutralize FFA:

For, sodium hydroxide (NaOH) catalyst

Amount of catalyst required is: [% FFA] (0.1440) + 1 %,

While for potassium hydroxide (KOH),

Amount of catalyst required: [% FFA] (0.197) / 0.86 +1%

Note: For the potassium hydroxide calculation, a factor of 0.86 denotes the purity level of it reagent grade. If a different grade or grades are used then, this factor is modified accordingly.

This method of neutralizing the FFAs is effective for FFAs with concentrations of up to 5-6%. However, the specific limitations may vary depending on the presence of other emulsifiers. Ensuring that the feedstock is completely devoid of any moisture is of utmost significance. If there are traces of water, the maximum allowable level for free fatty acids (FFA) maximum of 3%. Thus when using feedstock with greater levels of free fatty acids (FFA), adding additional catalyst can potentially exacerbate issues rather than resolving them.

The substantial quantity of soap produced may coagulate and it can inhibit separation process. In addition, this process transforms the FFAs into a byproduct instead of utilizing them for the production of biodiesel. When dealing with feedstock that has an FFA content of 5-30% or greater, it is a must to convert the FFAs as this are the reagents that yield biodiesel. There are other methods of converting FFAs. methods available for turning free fatty acids (FFAs) into biodiesel include: Enzymatic methods, conversion of

FFAs into glycerol and glycerolysis, It has been noted that the transesterification of the triglycerides is quite slow, requiring several days to fully finish Mandari et al (2022).

2.7 Basic Plant Equipment and Operation

This section outlines the primary plant equipment that would be used in a biodiesel production facility. These include reactors, pumps, centrifuges and distillery equipment.

2.7.1 Reactors

This is the location where chemical transformation takes place. Hence, it establishes the specific kind of response that must occur after the reactor. Reactors are categorized as either batch reactors or continuous reactors. There can be variation of each depending on the sizes and numbers of reaction sites. The two classes of reactors can also be re-classified as either plug-flow reactors (PFRs) or continuous stirred tank reactors (CSTRs). The reactants are introduced into the batch reactor in a predetermined quantity. Afterwards, the reactor is sealed and adjusted to the desired reaction conditions, including temperature, pressure, and stir rates. The chemical composition of the reactor varies over time. After the designated reaction period has elapsed, the chemical components inside the reactor are extracted and then forwarded for further processing. The primary factors to be taken into account in a reactor are the degree of reaction of the reactants, referred to as conversion, and the specificity of the reaction towards the intended products, referred to as selectivity. The conversion and selectivity of a reactor are determined by key variables such as temperature, pressure, reaction duration (residence time), and degree of mixing.

Batch reactors possess advantageous attributes such as effective mixing properties and the convenient management of homogenous catalysts employed in the biodiesel transesterification reaction. The concentrations of the reactants and products in the reactor vary throughout time. Thus, the impact of reaction inhibition caused by the reaction products, such as glycerol, can be reduced to a minimum. Nevertheless, batch reactors are typically not employed for the manufacture of substantial quantities of chemicals due to the fact that it is more effective to carry out the subsequent separation and purification processes in a continuous manner. To overcome the batch-to-continuous mode, one can utilize numerous reaction vessels that are sequenced in order to achieve effectively continuous operation. C.S.T.Rs, which eliminates the main issue with batch reactors, also offers excellent mixing properties. Nevertheless, the consistent concentration within the reactor results in a reduced reaction driving power and can also optimize the effects of reaction inhibition. P.F.R.s, sometimes known as tubular reactors, is widely used in the chemical industry. In this reactor, the concentration of the reactant varies throughout the bed to increase the driving force for the reaction, similar to a batch reactor, despite the continuous flow. Obtaining effective mixing can pose greater challenges in the case of Plug Flow Reactors (P.F.Rs), which commonly employ solid catalysts.

Batch reactors possess advantageous attributes such as efficient mixing properties and convenient management of homogenous catalysts utilized in the biodiesel transesterification process. The concentrations of the reactants and products in the reactor vary throughout time. Thus, the impact of reaction inhibition caused by the reaction products, as shown with glycerol, can be reduced to a minimum. Nevertheless, batch reactors are typically not employed in the manufacturing of high-volume chemicals because it is more effective to carry out the subsequent separation and purification processes in a continuous manner. The transition from batch mode to continuous mode can be resolved by employing multiple reaction containers arranged in series to provide a practically continuous operation. C.S.T.Rs, which eliminates the main issue with batch reactors, also offers excellent mixing properties. Nevertheless, the consistent concentration within the reactor results in a reduced driving force for the reaction and can also optimize the effects of reaction inhibition. Packed bed reactors (PBRs) or tubular reactors are widely used in the chemical industry. Although the reactant concentration in this reactor remains continuous, it varies as we move down the bed in order to optimize the driving force for the reaction. This behavior is similar to that of a batch reactor. Obtaining effective mixing can be more challenging when using Plug Flow Reactors (P.F.Rs), especially since these reactors commonly employ solid catalysts.

2.7.2 Pumps

They are responsible for facilitating the transportation of chemicals throughout the manufacturing plant. A centrifugal pump is the predominant type of pump used in the chemical industry. Positive displacement pumps encompass several types such as gear pumps (external and internal) and lobe pumps.

2.7.3 Centrifuges

Centrifuges are mostly employed for segregating solids and liquids, although they can also be utilized to segregate immiscible liquids with varying densities. A settling tank can also be used to produce this type of separation. Although a settling tank may have a lower cost, a centrifuge can be employed to enhance the separation rate compared to a settling tank. The separation in a centrifuge is achieved by subjecting the mixture to a centrifugal force. The more concentrated phase will be selectively segregated to the external surface of the centrifuge. The effectiveness of the centrifuge relies on both the specifications of the centrifuge itself and the properties of the mixture that needs to be separated. Although centrifuges are typically evaluated based on their ability to handle mixtures, the primary factor to examine is the specification for product quality. The selection of the suitable centrifuge type and size is determined by the required level of separation in a particular system.

The viscosity of a liquid has significant consequences for selecting the size of a centrifuge, as fluids with higher viscosity are more challenging to manage. Centrifugation is a more efficient method of separating immiscible fluids than settling when there is a significant difference in density between them.

2.7.4 Distillation

One such method of separating compounds in a fluid combination is by taking use of the disparities in boiling points among the components. If the boiling points of the chemicals, such as water and biodiesel, differ significantly, an evaporator or flash vaporizer can be employed to separate them. During the process of evaporation, the liquid is subjected to heating until it reaches a specific temperature at which only the chemical species with higher volatility will transform into vapor. Consequently, the vapor stream exiting the evaporator will have a higher concentration of the substances that are more easily vaporized, while the liquid stream from the evaporator will contain a higher concentration of the substances that are less easily vaporized.

The process of separation in an evaporator involves the application of heat to a mixture that is maintained at a constant pressure. On the other hand, a flash vaporizer initially raises the temperature of the liquid while maintaining a higher pressure. Subsequently, the heated liquid is directed via a flash valve, which effectively reduces the pressure. The reduction in pressure induces the vaporization of the more volatile component of the liquid combination. The distillation column is a crucial apparatus used to separate miscible fluids that have similar boiling points, such as methanol and water. Distillation columns have the option to utilize either trays or packing.

2.8 Post Reaction Processing

Post-reaction processing involves the sequential processes used to process the ester phase that is obtained from the transesterification process. The processing involves extracting the esters from the reaction mixture, purifying them to satisfy the standards of established procedures, separating the esters from glycerol, washing and drying the esters, applying additional treatments to the esters, and adding additization.

2.8.1 Esters and Glycerol Separation

The first stage in biodiesel post reaction process is separation of main product that includes biodiesel and glycerol. This process works on the chemistry principle of solubility and immiscibility of products .the densities also play a role in separation of ester and glycerol in the intermediate phases. The second stage is washing phase which aids to neutralize any remaining amount of catalyst, eliminate any soaps that may have been generated during the transesterification process, and eliminate any remaining free glycerol and excess alcohol. Drying of ester is necessary to comply with standard on water content, which should be less than 0.05 % weight in the ultimate product. Furthermore, there are alternative methods that can be employed to diminish chromatic particles in the gasoline, eliminate phosphorous, sulfur phosphorus content and or eradicate unreacted glycerides. Additization is done to fuel and this involves adding certain elements or compounds to fuel to alter or modify its properties functioning or otherwise purpose. Key instances encompass cloud point modification additives, smell additives, antioxidants, or other chemicals that enhance stability at various conditions.

The density of fatty acid alcohol esters is approximately 0.88kg per meter cube whereas that of glycerol phase is around 1.05 kg. /meter cube or higher. Variation in density is adequate to employ basic gravity separation methods for two distinct phases. Nevertheless, the rate of separation is influenced by other factors. The majority of biodiesel processes employ vigorous mixing at the start of the reaction to blend the poorly soluble alcohol into the oil phase. If the mixing process persists during the whole reaction, the glycerol can be uniformly distributed in extremely small droplets throughout the fluid. The dispersion process range between an hour to a day for the droplets to merge and form distinct phase of glycerol. To expedite phase separation, the mixing process is typically decelerated as the reaction advances. The speed at which the glycerol phase coalesces increases as the pH approaches neutrality. One rationale for reducing the overall utilization of catalysts is to decrease their usage. A blend of glycerol and alcohol layer may be formed at the boundary between aster and glycerol due to the existence of substantial amounts of glycerides that may be mono, di or tri. At its most favorable, this layer signifies a negative overall outcome in terms of products, unless it is retrieved and divided. In the most unfavorable scenario, the ester phase will not to the standard of biofuel and need to be reprocessed.

The esterification procedure is conducted with a surplus of alcohol in order to guarantee a thorough reaction and achieve enhanced reaction speeds. The excess alcohol will mix with both ester and glycerol. The alcohol can be used as a liquid soap, facilitating the dispersion of the ester into the glycerol phase vice versa. Additional processing is necessitated by specific product requirements and legal or environmental regulations for the specific countries or region of use.

2.8.2 Process Equipment for the Ester/glycerol Separation

2.8.2.1 Decanter Systems

There are three distinct sorts of equipment utilized to separate ester and glycerol phases. Decanter systems rely on difference in densities and durations of residency to settle. The desired residence time is the main factor to consider when building a decanter for biodiesel production. The size of the unit is determined by the combination of the product mixture flow rate and this factor. Decanter units should have a considerable height and a slender shape to facilitate the physical separation of the products at the miscible point where both products demarcation point may not be clear.

Temperature inside decanter has an impact on how alcohol is dissolved in the two phases, as well as the viscosity of the solutions in question. If the temperature in the decanter is excessively high, it can cause the remaining alcohol to evaporate suddenly, which may impede the movement of the ester phase out of the tank. Conversely, a temperature that is too low will cause an increase in viscosity in both phases. A high viscosity of the reagents reduces the rate and frequency at which various particles in the system combine or separate. Where an emulsion occurs, it means there is di or mono glycerides and this develop between the stages. For continuous operation, it is necessary to have a mechanism in place to remove the emulsion, preventing it from filling the decanter.

2.8.2.2 Centrifuge System

A centrifuge is commonly employed in several continuous factories for separating different phases. The centrifuge generates an artificial, intense gravitational field through rapid rotation at exceedingly high velocities. The separation can be swiftly and efficiently accomplished. The main drawbacks of centrifuges are its high initial cost and regular maintenance, which are extensive and need of long downtimes during maintenance.

2.8.3. Washing of Biodiesel (Ester)

The objective of this process is to eliminate soap if any that is produced during reverse process. Furthermore, the water, which is as a medium for the acid addition so as to convert any residual catalyst and as a method of removing alkali salt, produced. Excel alcohol is usually removed before washing stage.

This inhibits the introduction of methanol into the wastewater discharge. Using warm water at temperatures between 50 and 60 °C helps to avoid the separation of free fatty acid esters and slows down emulsion formation. Acidic soft water with Ph. 5.5 effectively neutralizes magnesium in the product.

Delicate washing inhibits the creation of emulsions and leads to a swift and thorough separation of phases.

The separation process for biodiesel and water is very efficient even though, the equilibrium solubility of water in esters must surpass designated concentration for pure bio-diesel, which is less than 0.05 %wt. Consequently, following the washing process, there will be an excess of water compared to the equilibrium amount. There are different types of washing including mist washing, and bubble washing.

2.8.3.1 Mist Washing

This method of washing employs a refined spray mechanism usually above the washing tank to disperse a very fine haze of water droplets on to the surface, resulting in a complete absence of agitation. Although this method involves the purification of biodiesel through washing, it is characterized by slow pace and excessive water consumption, with little to no water recycling.

2.8.3.2 Bubble Washing

The device utilizes a compact air pump, typically an aquarium aerator pump equipped with a bubble-stone. In the wash tank, a specific amount of water, typically ranging from a quarter to a half of the volume of biodiesel, is introduced. The water settles at the bottom of the tank, and a stone is submerged as well. The pump is then activated as air bubbles ascend passing through water and into the esters (bio-diesel); they transport a thin layer of water that envelops them, effectively dispersing the bio-diesel. Upon reaching the surface, the bubble ruptures, causing the water to descend once more to cleanse the fuel once again.

Typically, three or four cycles of washing, lasting six to eight hours each, are employed. The initial wash may be shorter in duration. It is important to allow for a settling period of at least one hour between each wash. Once the water has settled, it is drained from the bottom and replenished with fresh water. The washing process is considered complete when the water becomes transparent after settling, with a neutral pH of 7 for ease of use. Additionally, a timer is set to automatically turn off the air pump after eight hours. Benefits of bubble-washing: The process is simple, effective, and requires minimal exertion.

Drawbacks of bubble washing: While bubble washing may appear effortless, it actually requires a significant amount of effort. This method is mild and has the ability to conceal an incomplete reaction, but any agitation will quickly expose this.

2.8.4 Other Ester Treatments

There is no any exact color requirements for biodiesel. However, activated carbon can be utilized thus eliminating any unwanted excessive color. There are further bleaching technologies in the literature of the fats and oil sector that biodiesel producers should also consider exploring.

Vacuum distillation offers the advantage of deodorization and the elimination of other minor impurities, which might be beneficial for companies using heavily damaged raw materials. Filtering is a crucial component of the biodiesel manufacturing process. Feedstock entering the plant must undergo filtration with a minimum size of 100 um, whereas biodiesel leaving the plant must be filtered to a minimum size of 5 um. This is necessary to prevent any pollutants from being transported with the fuel, which might potentially harm the engine. One proposal is to cool the gasoline prior to filtering in order to catch crystallized saturated esters, which would lower its cloud point. Solidified esters can then be liquefied with the application of heat and utilized as fuel for the plant's boiler.

2.8.5 Additization of Esters

Additization is a process in petroleum products are enhanced by adding array of elements for various reasons. These additives serve to enhance lubrication, deterrence to oral consumption, resistance to oxidation, protection against corrosion, conductivity, and various other qualities. The level of advancement in additive technology for biodiesel is rather low, resulting in a limited availability of additions to improve performance. Biodiesel producers must prioritize the assessment of oxidative stability due to its high concentration of molecules containing double bonds. Biodiesel exhibits worse oxidative stability compared to petroleum-based gasoline. Fortunately, the food sector has made significant advancements in the technologies used to enhance stability. These advancements have resulted in the development of additives that may effectively stabilize biofuel for longer periods.

2.9 Post Reaction Treatment of Side Streams

2.9.1 The Side Streams

The three non-ester side streams that require treatment as part of the biodiesel process are the surplus alcohol that is reused in the process, the by-product of glycerol and effluent produced by the process.

Alcohol recycling is essential due to the need for an abundant supply of it to ensure the efficiency of the reaction system. Recovering the unused alcohol not only reduces input costs for the operation but also eliminates environmental pollution. Emissions reduction is necessary due to the high hazards it possess especially flammability and toxicity to aquatic ecology. Glycerol is extracted and partially purified to be used in subsequent process in synthesizing biofuel or for beauty product processing. About 10% by weight of the input reactants is converted to glycerol during process of transesterification.

2.9.2 Management of Alcohol in the Products

Physical properties of alcohol used play a crucial role in its recovery and recycling for instance, Methanol, which compared to others has as boiling point of 64.7°C making it very volatile and easier to remove from oil, ester, and aqueous streams through flash evaporation and later re-condensation. Due to its low boiling point and flush point of 8°C, methanol is classified as highly flammable. Methanol exhibits complete miscibility with both water and glycerol. Nevertheless, its solubility in fats and oils is minimal. Methanol has greater solubility in esters; however, it does not achieve complete miscibility. Methanol exhibits a higher affinity for glycerol and water, making it more likely to be found in more than one phase. Methanol limited solubility in oils and fats cause lower yield in the solubility-limited phase during the reaction. Distillation, using either traditional or vacuum methods can aid in methanol reclamation. The remaining methanol may be reclaimed by washing as post reaction processing of biodiesel. Esters are rinsed with warm (60°C), softened acidic water to eliminate surfactants and any remaining methanol. In order to save expenses, its recovery is crucial. There are two primary techniques for accomplishing including extraction of heat and/or vacuum extraction.

2.9.2.1 Heat Extraction Method

The mixture is heated to a temperature of 70°C inside a sealed chamber or a boiler and the resulting fumes directed into a condenser. The capture of the concentrated methanol in a liquid vessel trap is impacted. Due to the severe flammability of methanol and the explosive nature of its vapors, great caution is exercised. As the concentration of unreacted methanol drops, it will be necessary to raise the temperature.

2.9.2.2 Vacuum Extraction Method

This method is essentially equivalent to heat extraction with exception it necessitates a lower amount of energy. This method however needs investment in specialized vessels and equipment and the recovery quantities are approximately a quarter (25 %) of the methanol.

2.9.3 Refining of Glycerol

The glycerol obtained from the process comprises traces of alcohol, catalysts remnants, residual fat or oil, and other impurities. There are double methods available for purifying glycerol recovered in a process. Chemical refinement of glycerol involves numerous crucial processes. Initially, the catalyst has a tendency to accumulate in the glycerol phase, requiring neutralization.

The neutralization process results in the formation of alkali complex salt and the soaps generated during the esterification process. These by-products need to be eliminated through coagulation and precipitation with ferric chloride or aluminum sulfate. Centrifuge is also used to enhance the removal process. Controlling the pH is crucial as a low pH causes glycerol to form but polymerization of glycerol results at elevated ph.

Physical refining involves the initial removal of insoluble, fatty or precipitated particles by the process of filtering or centrifugation as well as combination of both methods. A pH modification in some instances is necessary for this elimination process. Subsequently, the process of evaporation eliminates the water. This physical procedure is carried out at temperatures ranging from 60 to 85^{o} C, as glycerol becomes less viscous but remains stable at these temperatures.

•**Glycerol Purification**: The glycerol is purified using a process of vacuum distillation with steam injection, and then further bleached with activated carbon. A substitute process is by use of Ion exchange technique for small scale and pilot plants. This system employs anions, cation, anion, and mixed ions bed exchangers in order to eliminate catalysts and other contaminants. The glycerol is initially mixed with soft water to creating a solution containing about 30 % glycerol solution. After this process, vacuum distillation is then carried out to remove water, often resulting in 85 percent partially refined glycerol.

2.9.4 Wastewater Considerations

Each wash of ester yields approximately 1 liter of water for every liter of ester used. It is necessary to soften all process water in order to eliminate magnesium and calcium complex salts and then to treat to the removal copper and iron ions. The water used in washing the ester will have a higher biological oxygen demand (BOD) owing to the presence of residual oil or fat, traces of ester, and glycerol. Complete recovery of methanol in the plant is a component that must be complied as per disposal criteria of the local municipal waste treatment facility. By undertaking internal treatment and recycling of process, wastewater leads to substantial cost savings and is determined by existing facilities within the plant.

Alcohol has high impact on all operations related to the recovery of goods. Complete recycling of methanol is necessary for optimal cost-effectiveness and environmental protection. Glycerol is a valuable byproduct that should be purified to the greatest extent possible from an economic standpoint. When wastewaters are managed well, they can be treated via a municipal sewer system. However, it is important to also examine the option of treating and reusing the wastewater internally.

The overall procedure is that the cottonseed oil undergoes a reaction with an alcohol, such as ethanol or methanol, catalyzed by a base catalyst to yield glycerin and methyl esters, often known as 'biodiesel'. An excess amount of alcohol added to facilitates rapid conversion in a forward direction and may then recovered and re-used in subsequent batches of reactions. The catalyst typically consists of pre-mixed sodium or potassium hydroxide with methanol.

2.10 Using Of Biodiesel in Diesel Engines

The conversion process of crude cottonseed oil must be carried out by transesterification. The performance characteristics of this treated oil are superior to those when utilized in direct engine injectors. The issues encountered with utilizing oil as a pure vegetable oil are as follows;

I. injector coking
ii. Accumulation of carbon
iii. Oil ring adhesion and
iv. Thickening and gelling of lubricating oil.

To achieve optimal outcomes in base-catalyzed transesterification, it is crucial to ensure that both the alcohol and glycerides are free from water molecules. If water is present in the reaction, it may be able to cause process to shift towards saponification, reducing the desired results. The soap reduces the production of esters and makes it challenging to separate the ester from glycerol and water during the washing process. The alkali-catalyzed transesterification process necessitates a low concentration of free fatty acids in triglycerides. The transesterification of triglycerides results in a mixture of ester, glycerol, alcohol, catalysts, and Tri-, Di-, and monoglyceride products.

The following parameters must be carefully considered when executing the transesterification process. Analysis of the moisture and free fatty acid levels in raw cottonseed oil, the acid value of the cottonseed oil should be below one, and all materials should be mostly free of water. The stoichiometric ratio of alcohol to glycerides must be over 3: 1 to necessitate a quantity of three moles of alcohol and one mole of glycerol and the catalyst utilized, whether it is an acid or a base in the reaction.

CHAPTER THREE: MATERIALS AND CHEMICALS

This chapter provides an overview of the materials, apparatus, methods, and procedures used to accomplish the main and specific objectives of the study.

3.1 Overview of Research Procedures

The research methodology employed a practical approach, which encompassed several key steps. These steps included extraction of cottonseed oil from cottonseed, conducting tests on the cottonseed to characterized including determination of its free fatty acid content. This is followed by processing the oil into ethyl esters (biodiesel) using the open batch base catalyzed reaction method, purifying the fuel, modeling the reaction and yields, and finally analyzing the results and drawing conclusions and giving recommendations based on the findings. Refined soybean oil commercially being used as cooking oil was used for reaction comparison.

3.2 Cottonseed Oil Extraction and Characterization

3.2.1 Oil Extraction from Seeds

The cottonseeds were acquired from Kibos ginnery (Kisumu county) and Salawa Ginneries (Baringo county), where the plant is cultivated specifically for its cotton fiber content. This was then followed by conducting quantitative analysis to determine the oil content by weight of the seeds.

3.2.2. Mechanical Extraction

The manual expeller machine was used to employ batch pressing. The mechanical press operates by exerting increasing pressure on the cottonseed kernel, causing it to be squeezed through a narrowing outlet and resulting in the extraction of oil. The process was replicated three times and the resulting output was averaged.

3.2.3. Solvent Extraction

The solvent extraction method used is known as Soxhlet extraction. Three quantitative tests were conducted on both whole cottonseed and de-husked seeds, the results were recorded and averaged.

Chemical and Apparatus Requirements:

Each experiment requires 200 milliliters of Ethanol, 20 grams of powdered seed, a thimble to pack the powder, cotton wool to cover it, and a heating element.

Procedure

The seed was pulverized into a fine powder. The pulverized seeds were tightly filled into the small cylindrical container and coated with a layer of cotton wool before being inserted into the extraction chamber. After positioning the condenser above the extraction vessel, the heater was activated. After completing four iterations, the procedure was halted, partially cooled (to prevent solvent loss), and subsequently substituted with fresh samples. The process was iterated until a 100-gram sample of seed was obtained. Subsequently, the ethanol was retrieved and the oil was quantified in terms of both volume and weight. The process was replicated using de-husked seeds for the purpose and results compared.

In order to achieve optimal extraction values while taking into account the efficiency and complexity of the operation, the two methods were integrated. This mode of production process was chosen due to the need of costs minimization, enhance oil extraction efficiency, and improve the quality and variety of products. These oil percentages are crucial as they provide an indicator of the projected yield from the Biodiesel conversion process based on the anticipated amount of cotton farming yield.

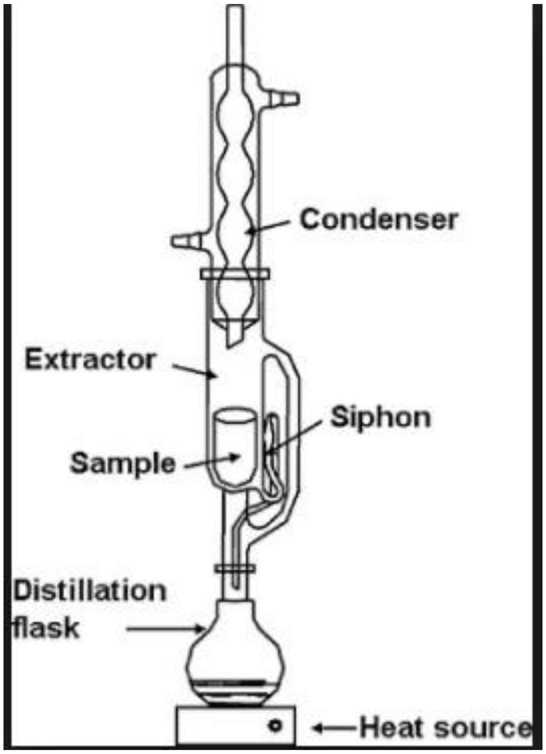


Figure 3. 1: A Diagram Chemical Extraction

3.2.4. Filtration of the Crude Cottonseed Oil

The cottonseed oil collected comprised heterogeneous solid particles of small and large but varying in sizes. The contaminants consisted of fragments of cake and solid waxes. The oil underwent filtering using an oil filtration system including a 50 cm square plain-woven double 100% cotton bag connected to a vertical loading pipe. The upper feeding point was equipped with a compact collection tank that stores oil, hence facilitating the efficient permeation of oil through the fabric acting as a filter. The oil dripped and was extracted from below the bag. Filtration rate of the oil was depending upon the thickness (viscosity) of the oil, the amount of particles present, and the height of the liquid column.

3.2.5 Analysis of Cottonseed Oil

For the oil to meet specification of a biodiesel feedstock, it was necessary to check three main parameters namely Free Fatty Acid (FFA) content, Water content and Solids

a) Free Fatty Acids (Determination of Acid Number by Titration :)

The sample was dissolved in a mixture of isopropanol and toluene that was 97% pure i.e. contains a small amount of water. The sample was titrated with a solution of an alcoholic potassium hydroxide. The FFA determination was by titration of the crude cottonseed oil with sodium hydroxide solution.

Titration

Materials

i. Phenolphthalein indicator
ii. Isopropyl alcohol.
iii. One liter of 0.1 % sodium hydroxide in distilled water

Equipment

i. Two glass 1 milliliter eyedroppers.
ii. 500ml, Half dozen Conical Cylinders.

The procedure

i. 10 milliliters of room – temperature isopropyl alcohol was transferred into one conical jar.
ii. About 3 drops of phenol red indicator was added to the alcohol.
iii. 0.1 % NaOH solution was introduced drop by drop as striring until the alcohol started changing color to red.
iv. 1 milliliter of the crude cottonseed oil to be titrated was added to the contents in iii above.
v. The eyedropper was then filled with exactly 1 milliliter of 0.1 % NaOH solution then solution dripped while stirring.

vi. The amount in milliliters of 0.1 % the solution needed the liquid to turn and stay red was tracked and noted down.

Free Fatty Acid Value Calculation

The calculated the acid value was done using the formula: AV = (A-B) *N*56.1/W (A.J. Dijkstra, 2016).Where A is the is the beaker with content oil and B the blank one, N is the normality of potassium hydroxide solution (KOH) solution 0.1 in my case, W= weight in grams of sample. It is theoretically known that the percentage FFA approximately equal to half the acid value, the constant of 56.10 is the molecular mass of the potassium hydroxide solution.

b) Water Removal

Water was removed by heating to break any emulsions between the water and the oil and then allowing the water to settle to the bottom can remove water. This sample was then heated to temperatures above 120°C to get rid of water content in the crude cottonseed oil. Mixing the oil and water was intermittently done to prevent violent boiling and possible cracking of the apparatus.

3.3 Transesterification Using Wood Ash as Catalyst

3.3.1 Reagents and Apparatus:

- 500 g of Catalysts: wood ash from *Rivatex* boiler furnace,
- Pump machine 30-60 times per minute,
- Digital Thermometer,
- A set of stirrers,
- 10 litres of crude mechanically extracted cottonseed Oil,
- 2.5 liters of refined soya bean oil,

- 2.5 liters of Alcohol: ethanol 99.7% purity level sourced from local chemical store
- 4 – 1000 mls separating funnels,
- 4 Conical Flasks,
- 4 Beakers.
- Pipettes,
- 100grammes of activated carbon,
- Digital Weighing scale that can weigh 0-50 g to the nearest 0.1 gram.
- Bunsen burner (Source of Heat).

3.4. Process Design of Transesterification and its optimization

3.4.1 Catalyst Preparation

Calcinated wood ash was collected from Rivatex furnace boiler. It was strained to remove bits of charcoal, foreign matter, etc. Wood ash was grounded and sieved to regulate its size distribution within the range of 1.0 to 1.7mm and strained for the second time. The grey/white ash is what is needed.

3.4.2 Design of the process of conversion

A volume of 40mls ash powder was measured and packed into a stainless steel column reactor (25mm in diameter and 300ml in length), and was located in its central part. The top and bottom spaces of the column reactor were filled with active carbon powder. Titration against 1 m hydrochloric acid was done to determine the amount of calcium oxide in the ash. Then, 4 g of the prepared catalyst was dissolve in 100 mls of distilled water and titrated against 1 m HCl from the reaction the amount of calcium oxide was calculated.

A schematic flow diagram of a laboratory-scale facility set up to use solid base catalysis of Calcium oxide (ash) for the transesterification of cottonseed oil with 99.7% pure ethanol was as drawn in figure 3.1. This was created using a column reactor filled with activated carbon as a carrier for calcium oxide and wood ash as a solid base catalyst. A 500ml glass vessel was included. The setup simulated a base catalyzed batch unit, where a circulating stream passed through the column reactor and reactants mixture were fed rapidly for a period of up to 50 times per minute as set in the pumping element. Activated carbon was positioned at the upper, central, and lower sections of the reactor.

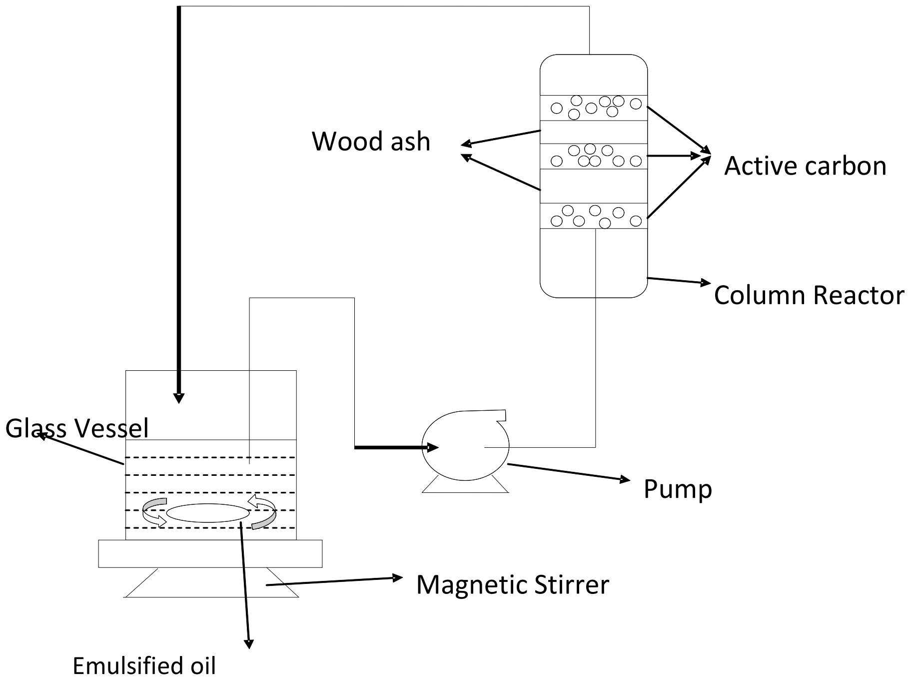


Figure 3. 2: A Schematic Flow Diagram of a Laboratory Set Up

The operational protocol was as follows: Initially, a quantity of 100ml of unrefined cottonseed oil was mixed with a measured amount of ethanol in a glass container. This process undertaken while maintaining a temperature of 60^0 C normal air pressures. The mixture was continuously stirred using a metal stirrer and heated using a flexible heater. The glass jar was sealed with a glass cover to prevent the release of ethanol vapor.

Due to the inability of vegetable oil and ethanol to mix even when subjected to reaction conditions, it was imperative to maintain the stability of the emulsification of vegetable oil in the column reactor. The pumping liquid to flow at rate of 50 times per minute was advantageous in creating a condensed batch unit. The emulsified reactants were introduced into the column reactor at a feeding rate of 50ml/min, and subsequently the effluent was returned to the glass vessel for circulation. The column reactor was maintained at a temperature of 60°C degrees using a tubular furnace, and the circulation continued until the maximum amount of cottonseed oil was transformed into biodiesel.

A sample of the liquid in the glass container was taken periodically to analyze the conversion rate of cottonseed oil using gas chromatography. Following the full conversion process, the operation of the heaters, stirring, and pumping was ceased. Subsequently, the entire mixture of products was extracted from the circulation loop in order to cleanse it using ethanol. After completing the washing process, the specified volume of reactants was reintroduced into the glass vessel to repeat the transesterification procedure. To ensure that the crude cottonseed oil included no more than 0.1% water, the sample was roasted to temperatures exceeding 120°C in order to remove any water content. The ethanol used was of ACS reagent grade, meaning it had a purity of 99.7%.

Following the completion of the reaction, the reaction was terminated and the mixture was left undisturbed overnight to allow for the separation of different phases. Measurements of ethyl ester, glycerol, and solid phases were documented. The ester phase was separated from the equilibrium mixture using decantation.

The biodiesel was carefully poured into a plastic beaker with a volume of 100 ml. Next, 20 milliliters of lukewarm water were carefully added to the beaker and gently swirled for 30 seconds before returning the beaker to an upright position. The beaker was inverted to facilitate decanting and the water was drained off.

The above process was repeated five times, with each subsequent repetition involving a slightly more vigorous shaking and a longer duration. During the fifth washing, there was a significant increase in shaking intensity, lasting approximately one minute. The ester was rinsed with water to remove any remaining alcohol and catalyst. The transesterification process was repeated using refined soy bean oil in place of crude cottonseed oil.

The biodiesel's quality, including its viscosity at 40°C, density, pH, minimum flash point, water content by weight, acid value, and copper strip corrosion, were examined at the Kenya Bureau of Standards according to the Kenya Bulk Liquefied Petroleum standard number Ks 2270-2010.

3.4.3 Design Optimization of the Reaction Process

Taguchi method was used in coming up with experimental design and its optimization. This was by use fractional factorial design of two level, three generators design thus experiment required eight runs with two generators, the number of experiments was halved twice.This was to ascertain the optimal values of mole ratios, catalyst quantity, and duration. A 2^n fractional factorial design was arrived at in considering the number of dependent variable i.e. 3 and two levels each i.e. low at -1 and high at +1. Thus, Central Composite Design (CCD) was employed to investigate three variables at two levels through the execution of eight experiments ($2^3 = 8$). The answer refers to the extent to which cottonseed oil is converted into ethyl ester, known as the degree of conversion in percentage. The design matrix, as presented in Table 3.2, displays the two levels of the variables together with the corresponding response whereby the levels are coded such that a value of -1 denotes the low level and a value of +1 represents the high level. The catalyst used for the lower level was 2.4 g/l of oil, whereas for the higher level it was 6.1 g/l.

The selection of levels for the several variables in this investigation was determined by prior tests conducted by Montgomery et al (2017), as well as practical factors. The time duration of 120 minutes was selected as the lower threshold, while the duration of 180 minutes was chosen as the higher threshold. The mole ratio of 1:12 (+l) indicates a high level, whereas the mole ratio of 1:9 indicates a low level (-1). The temperature was set at a constant 60°C, which aligns with the findings of prior studies conducted by Kianimanesh et al (2017). Additionally, this temperature is below the boiling point of ethanol. The selected ethanol had a purity of 99.7%, with a water content of 0.3% by weight. The agitation was moderately intense and forceful taking care not to splash.

Table 3. 1: Experimental Design Matrix Assignment

S/No	Dependent Parameters	Levels	
		High(+1)	Low (-1)
1.	Wood ash(catalyst) load	6.10 g/l	2.40 g/l
2.	Duration in minutes	180.00	120.00
3.	Oil to ethanol Mole ratio	1:12	1: 9

Table 3. 2: Experimental Design Optimization

	Number Of Parameters			
Experiment Number	1	2	3	% Conversion
1.	(-1)	(-1)	(-1)	S
2.	(+1)	(-1)	(-1)	T
3.	(-1)	(+1)	(-1)	U
4.	(+1)	(+1)	(-1)	V
5.	(-1)	(-1)	(+1)	W
6.	(+1)	(-1)	(+1)	X
7.	(-1)	(+1)	(+1)	Y
8.	(+1)	(+1)	(+1)	Z
9.	0	0	0	n/a
10.	0	0	0	n/a
11.	0	0	0	n/a
12.	0	0	0	n/a
13.	-α	0	0	n/a
14.	α	0	0	n/a
15.	0	-α	0	n/a
16.	0	α	0	n/a
17.	0	0	-α	n/a
18.	0	0	α	n/a
19.	0	0	0	n/a
20.	0	0	0	n/a
21.	0	0	0	n/a
22.	0	0	0	n/a
23.	0	0	0	n/a
24.	0	0	0	n/a

CHAPTER FOUR: RESULTS AND DISCUSSIONS

This chapter presents the laboratory test results (findings) for pre-experimental, extraction, and processing procedures conducted under optimum conditions as elaborated in central composite design. The interpretation of the findings is further elucidated by the utilization of charts, graphs and regression model equations.

4.1 Cottonseed Oil Extraction and Characterization

4.1.1 Mechanical Extraction

Mechanical method of extraction yield averaged .The values for the lint, seed and waste averaged 35%, 60% and 5% respectively. The proportions of this products are as recorded in figure 4.1.These average yield is approximately equivalent 20% which is equal to that recorded in books, indicating that the average oil content of cottonseed is between 20-25% based on seed quality and condition of extracting machine Eryılmaz, Tanzer et al (2014).

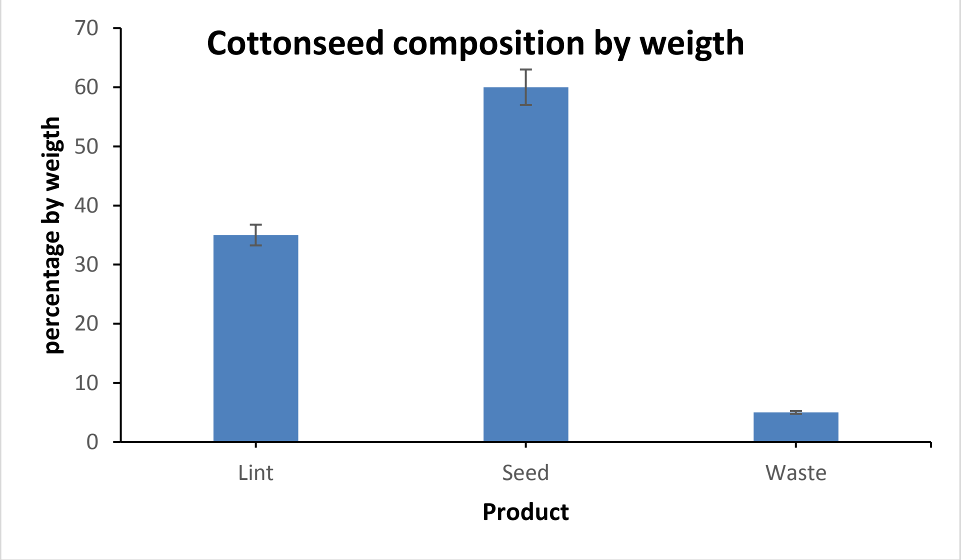


Figure 4. 1: Graph of cotton product by weight percentages

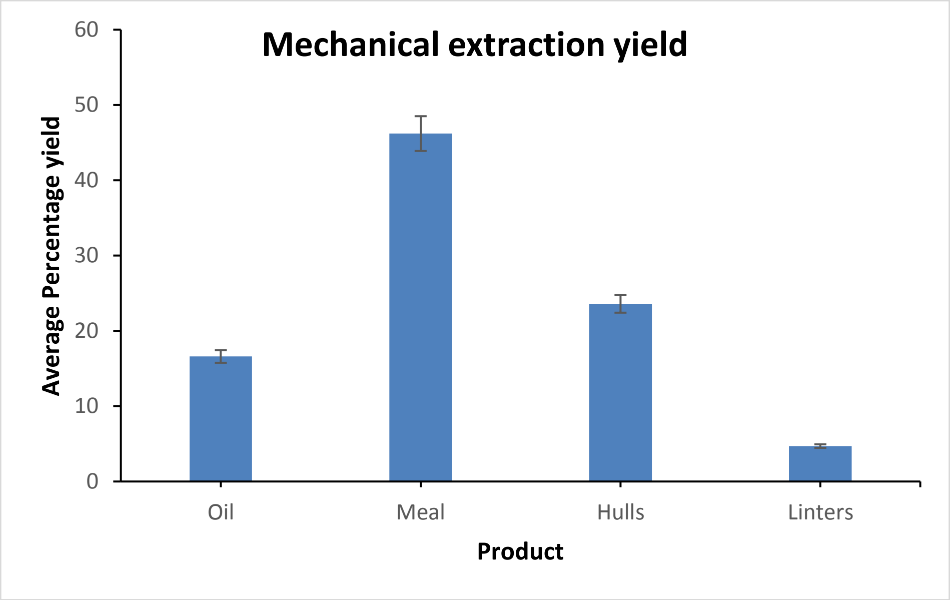


Figure 4. 2: Graph of Cottonseed Products (mechanical)

4.1.2 Soxhlet Extraction

This is a chemical method of extraction of oil using a liquid called a solvent that dissolves the oil then later separated to two distinct liquids. The average yield for the oil as recorded in figure 4.3 was 25%, which was higher than that from mechanical extraction.

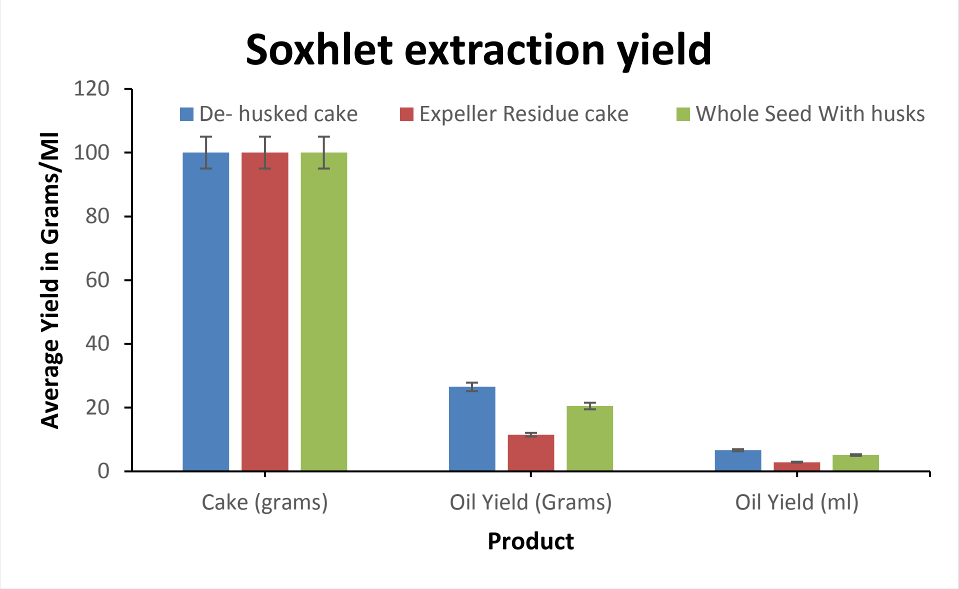


Figure 4.3: Graph of solvent extraction method yields

The solvent extraction technique yielded better amount of oil rates compared to the mechanical technique. The residues (obtained after this method of extraction) contained minimal amount of oil of less than 2% oil un-extracted. The whole seeds was cleaned and conditioned, then subjected to pre-pressing in expellers and the product, which is a cake, delivered directly to the solvent extraction without been undergoing flaked or granulated. These results are comparable to other studies which put the oil content by mechanical extraction and solvent at a maximum of 22% Eryılmaz et al (2014). It is worth nothing that the oil content is a factor of seed type, agronomical practices as well as weather conditions. The mode and condition of ginning machinery could also be having significance on oil quantity. Implication of the above has direct bearing on the efficiency and the cost of production process. When the two methods are use combined then better yield are realized. The mechanical extraction will also grind the cake to powder form hence easily proceeds in subsequent processes of animal feed blending and consumption.

4.1.3 Determination of Fatty Acid

The results for four experiments were averaged as recorded in table 4.1. The result is key in determining the quality of any biodiesel feedstock. It is significant in determining the process and amount of catalyst to be used.

Table 4. 1: Titration Volumes for Blank Test

Titration	**1st**	**2nd**	**3rd**	**4th**	**Average Value**
Volume of titer (ml)	1.60	1.40	1.50	1.50	1.50

Table 4. 2: Titration of Sample

Titration	1st	2nd	3rd	4th	Average Value
Volume of titer (ml)	2.90	3.00	2.80	3.00	3.00

4.1.4 Free Fatty Acid Value

The calculated the acid value was done using the formula: AV = (A-B) *N*56.1/W

(A.J.

Thus by using the formula and substituting with the figures the results from the process were,

Acid Value = ((3.00 – 1.50) (*0.10*56.10/50))

= 1.683

Via estimation method the above figure is halved and results to:

Acid value = 0.5 (1.683%)

Acid value = 0.8410 %

The above results are closely related those by (A.J. Dijkstra, 2016) which was less than 1%. It is suffice therefore to say that the amount of FFAs were within the limit.

4.1.5 Wood Ash Characterization

The process of characterizing wood ash is key as it projects the quantities needed in the process bearing in mind that each wood source has its variability in contents of calcium carbonates.

Table 4. 3: Titration of wood ash against 1M HCL

Order of Titration	**1st**	**2nd**	**3rd**	**4th**	**Average**
Volume of titer in mls	29.0	30.0	28.6	29.9	29.4
Vol. of ash soln.(mls)	25	25	25	25	25

The average amount of titer required to neutralize 25ml of wood ash solution was as recorded in table 4.3, which equated to 29.4 mls. As calculated and recorded in Appendix 1, the number of calcium carbonate moles present in the ash is approximately 82.24 % of calcium hydroxide moles. Since, from calculation the amount of free fatty acids (FFAs) was below 1% there was no necessity to use excess catalyst.

4.1.6 Removal of water

The heating process removes excess water in the samples. The results were as recorded in Table 4.4. From the three tests, the average value of water content was 1.5%.

Table 4. 4: Water Content Analysis

S/No	Set up	Test I	Test II	Test III
1.	Wt. of beaker	104.91	104.91	104.91
2.	Wt. of beaker + oil+ H2O	214.37	214.37	214.37
3.	Wt. of beaker + oil-H2O	212.73	212.65	212.825
4.	Wt. of H_2O	1.64	1.72	1.545
5.	Wt. of oil + H_2O	109.46	109.46	109.46
6.	Water as% of oil	1.498	1.569	1.4
	Average % of water in oil			**1.50%**

Heating was to ensure the water content reduces to acceptable value as water concentration affects the transesterification process thus adding the cost of the feedstock and final product. The water content of cottonseed on large scale can be determined conditioning the cottonseed before extracting the oil, and by ensuring that the extracted oil is stored under favorable conditions before being converted into biodiesel. From results in table 4.4, all the recordings for three tests fall within the allowable standard.

4.2 Transesterification Results and Optimum Parameters, Design and Model of the Process

4.2.1Transesterification process and optimum conditions

The yield results at various conditions were as recorded in figure 4.3.The temperature was constant at 60^0C. It worth to note that temperature does not have any discernible impact on the final conversion to ester. Nevertheless, elevated temperatures reduce the duration needed to achieve maximal yield or conversion. The hypothetical expense of energy required for heating would be better than that of longer reaction time. Hence, the temperature at which a room is typically maintained is regarded as the ideal temperature for conversion.

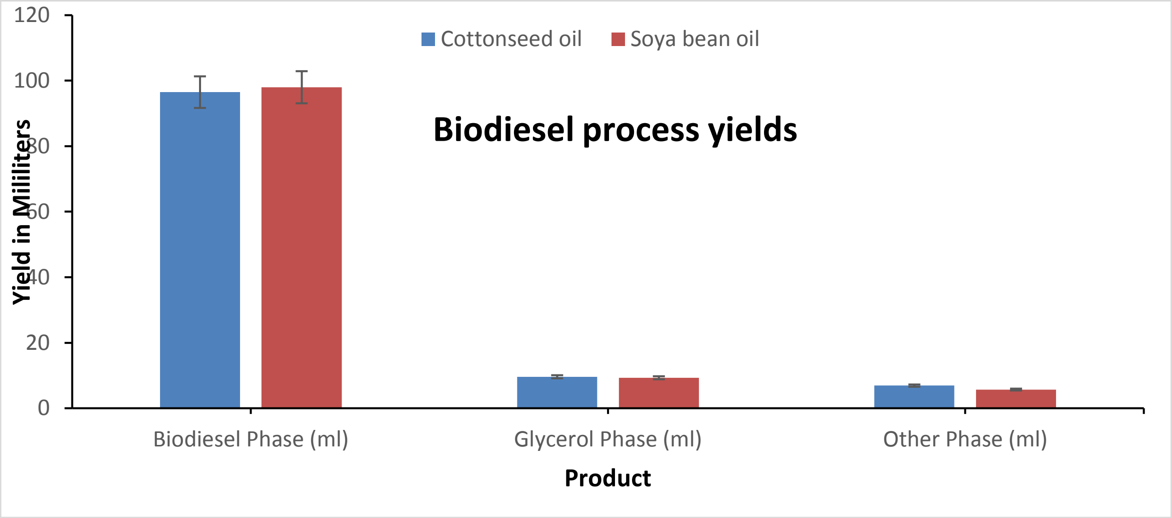


Figure 4.4: Graph of Biodiesel and By-Products Yields

As depicted in figure 4.3 yields from cottonseed oil does not deviate from that of refined soya bean oil. Soya bean oil had a great yield of bio-diesel by about 2 per cent. This can be attributed to the fact that the oil was refined hence lower salt phase (other phase) thus the reason for it lower amount of free fatty acids compared to that of cottonseed oil. The conversion neared full completion and thus reduction of glycerol and other by products from the process. To achieve a significant level of conversion, it is necessary to thoroughly mix the oil and alcohol phases until they form a single, uniform phase. This necessitates highly intense agitation accompanied by initial splashing during the onset of the reaction.

Higher amount of water in the reaction mixture significantly hampers the transformation of oil into ester. Thus to achieve a high degree of conversion, it is necessary to employ ethanol with a purity level that exceed 99.5% purity level. Studies involving varying levels of surplus alcohol in the reaction mixture have found that a 50% excess of the stoichiometric ratio resulted in a significant conversion rate.

In addition to water reacting with catalyst and FFAs to form soap, its presence in excess lowers the activity of catalyst F. Ferella et al (2010) This process of saponification results into lower biodiesel yield as well as causing difficulty in separation and purification post reaction processes of the biodiesel. It is therefore advisable for biodiesel and by-products i.e. glycerol to be subjected to refining process through washing with hot water of ph. 5-6 for about three times, implying increased cost due to longer time, increased energy and amount of water Mandari, Venkatesh & Devarai, Santhosh. (2022).

The catalyst quantity ranges up to three times in excess (84 g/l of oil) were used thus ensuring the process moves toward the right and avoid saponification. Incorporating the titration findings of the FFAs' percentage, a concentration of 0.25% was inserted to facilitate the conversion of the FFAs. In the set up excess of catalyst, amount function was also to shorten reaction times. Notably, the amount of catalyst has cost implication as well as quality of the final product. Higher quantity of ash catalysts could increase the cost apart from making phase separation bit difficult.

After optimizing all parameters, the of biodiesel was recorded as 96.50 milliliters, glycerol 9.60 milliliters and other phase containing slats and oil mixtures as 6.90 milliliters. The results were statistically comparable to those of those from refined soybean oil used as control experiment.

Decreasing of the alcohol to oil from 12:1 to 9.0:1 at the same time keeping catalyst and time in their respective optimal conditions gave conversion of 89.5 -96.5% implying less variation (equation 4.5). This would result in economic advantages and less complications especially in post processes including recycling of alcohol from the glycerol phase if it were to be undertaken. To increase the biodiesel yield by about 3% is financially beneficial but limitation could be the cost of alcohol. This is because the percentage-increased yield has a cost component thus it preferably better to have it as by product then recover in post reaction processes. Kamiab et al (2024) found that in order to accomplish equivalent conversion and phase separation from glycerin, a calcium oxide catalyst required an excess of alcohol that was 200% greater than the amount needed. The reaction time ranged from 2 to 3 hours.

The experimental results are significantly comparable to those by Karmarkar, Neha. (2023) that found the optimum condition as the follows: alcohol/oil mole ratio of 8:1; temperature of 55 °C; time at 45 minutes; catalyst (base) concentration of 1.00 %; and speed of agitation 268 rpm.

The limited availability of equipment prevented the complete conversion of biodiesel.

Upon completion of the reaction, the resulting products underwent phase separation, resulting in three distinct layers. The upper layer consisted of the ester, while the central middle layer contained glycerol. The bottom layer consisted of calcium ethanoate salts. The remaining catalyst and excess alcohol that did not react were evenly distributed amongst the different phases. Following the separation of the phases, the ester was rinsed with water to remove the catalyst and alcohol.

Phase separation variation depended on the quantity ethanol purity used. There is also possibility the amount and type of impurities in the raw materials could have an impact on the same however, these factors were beyond the scope of this research.

Water was added to the ester phase cautiously and gradually, using a fine misting technique. The purpose of agitation of the ester in the presence of warm water was to minimize loss of ester by preventing its emulsion. The washing was also to eliminate any remaining catalyst from the ester. The complete elimination of the catalyst from the ester was ensured by using an excessive amount of washing water.

The ash catalyst and other sediments (resulting from impurities of feedstock) were removed from the biodiesel using excess slight acidic water (PH. 4.5-5.5). The process also removed Free Fatty Acids which must be less than 0.8 mg of KOH for biofuels A. Demirbas (2009).The optimal conditions for obtaining maximum yield and quality of biodiesel was alcohol to oil mole ratio of 12: 1,catalyst load of 6.05 g/l and time of 3 hours. This yield as 96.5%.

4.2.2 Design and Model of the Process

The design of the process suitable for any transesterification is dependent on quality of feedstock and the type and amount of other reagents including catalyst. While washing, a portion of the ester created an emulsion with the water. It took 24 hours for the water phase, which contained alcohol, catalyst, and emulsified ester, to separate and for the ester phase to become transparent.

The findings of ester conversion rate at various levels of variables acquired from the eight experiments was as recorded in Table 4.5 and analyzed using Excel Regression method. The experiments were conducted based on a fractional factorial design. The research yielded an equation that demonstrates the correlations between conversion yields, catalyst load, and mole ratio and time duration.

$$y=\boldsymbol{a}+\boldsymbol{b}x_1+\boldsymbol{c}x_2+\boldsymbol{d}x_3. \qquad \text{Equation 4.1}$$

$$y=71.7250+0.1650x_1+0.0125x_2+1.8x_3 \qquad \text{Equation 4.2}$$

If we assume one variable as constant, then the two variables the interaction for either two of them will be given by:

For Catalyst and Time,

$y=71.725+0.165x_1+0.0125x_2$ *Equation 4.3*

For Catalyst and mole ratios,

$y=71.725+0.165x_1+1.8x_3$ *Equation 4.4*

For Time and Mole Ratios

$y=71.725+0.0125x_2+1.8x_3$ *Equation 4.5*

Given that **a** is a constant, **b, c,** and **d** represents the coefficients of catalyst concentration, time in minutes, and mole ratios correspondingly.

Let take x_1 represent the catalyst concentration,

x_2 represents the duration in minutes,

x_3 represents the mole ratio, and

y represents the yield conversion of oil to ester.

The equation has two possible values for x_1: -1 (2.420 Gram /Liter) or +1 (6.050 Gram /Liter). Similarly, x_2 can take on either -1 (120 min) or +1 (180 min) as values. Lastly, x_3 can be either mole ratios of -1 (1:9) or +1 (1:12).

From critical examination of equation (4.1), it evident that the mole ratio is the primary independent element, that significantly influences the degrees of conversion. Conversely, time has the least impact on the degree of conversion. Further, equations 4.3 to 4.5 reveals that the relationship between mole ratios and that of catalyst load concentration is highly significant. The unvaried factors were temperature, catalyst type, water content of alcohol, and oil type.

Table 4. 5: Ester Conversion Rate at Various Levels of Variables

	Number of parameter			
Experiment	1	2	3	% Conversion
1.	(-1)	(-1)	(-1)	89.5
2.	(+1)	(-1)	(-1)	90.6
3.	(-1)	(+1)	(-1)	90.7
4.	(+1)	(+1)	(-1)	91.2
5.	(-1)	(-1)	(+1)	95.5
6.	(+1)	(-1)	(+1)	95.7
7.	(-1)	(+1)	(+1)	95.9
8.	(+1)	(+1)	(+1)	96.5

4.3 Biodiesel Product versus Quality Standard

The properties of biodiesel have been grouped by multiple criteria. These are viscosity at specific temperature, Ph., flash point, acid value density, water value content and copper *strip corrosion. The biodiesel's produced under optimal conditions, was examined at the* Kenya Bureau of criteria according to the Kenyan Standard for Fuel (Ks 2270-2010) criteria. As recorded in Table 4.6 the product met the standard for use as fuel.

The physical and chemical observations recorded during the experiments are as recorded in Table 4.7.These properties are of importance in identifying the raw materials and final products of biodiesel. They are comparable with all parameters of base catalyzed reaction products of transesterification G. Antolın et al (2002).

Table 4. 6: Results Compared Against Kenya’s Standard for Biodiesel.

S/ No	Biodiesel Test Parameter	Results	Standard
1	Viscosity at 40°C	3.75(mm)$^{2/s}$	1.9-6.0(mm)$^{2/s}$
2	Ph.	8.3	Not specified
3	Density	0.88	0.86-0.90
4	Flash Point °C	130	120(minimum)
5	Acid Value	0.05 mg of KOH/g	0.8 mg KOH/g max.
6	Water Content % weight	0.005%wt	0.05 % wt. (maximum)
7	Copper Strip Corrosion	Not detected	Class 3 max.

Table 4. 7: Physical and Chemical Properties of Products

S/ No	Product	Physical observation	Chemical observation
1.	Crude Oil	Dark brown in color and has Density of 0.90 It is less viscous	FFA value of 0.841 and water Content of 1.5 %
2.	Unwashed Biodiesel	Light Yellow with More viscous liquid than the Oil	Has ph. value of 6.0
3.	Washed Biodiesel	More lighter in color than the Unwashed one	Has ph. level of 8.
4.	Glycerol	Very dark liquid & denser	Was not analyzed

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

This chapter represents the final section of the study. The report provides conclusions derived from the findings and analysis, as well as suggestions for areas of future study.

5.1 CONCLUSIONS

This study has led to four main conclusions as follows:

a) *To undertake pre-processing of feedstock and produce biodiesel using heterogeneous wood ash catalyst in the transesterification of cottonseed oil*

Firstly, based on the findings that Transesterification of crude cottonseed oil using ethanol and wood ash as catalyst is viable and that the biodiesel produced from wood ash and ethanol has similar physical and chemical properties as those produced using mineral catalysts

Wood ash characterization differs in content and thus amount required will depend on the source of wood ash as well as agronomic conditions. The other feedstock including cottonseed oil availability will be dependent on lint production. It is therefore feasible to produce biodiesel utilizing a heterogeneous catalyst in the transesterification process of cottonseed oil. It is therefore logical to conclude that Wood ash can substitute mineral catalysts in cottonseed transesterification.

b) *To determine Optimum conditions that yields a maximum conversion for the transesterification of cotton seed oil*

Secondly, the optimal conditions for obtaining maximum yield of 96.5% at temperatures of 60°C and meeting acceptable quality of biodiesel is: alcohol to oil mole ratio of 12: 1,catalyst load of 6.05 g/l and time of 3 hours. Since the conversion was at fixed temperature it is save to conclude that the rate of conversion is directly proportional to catalyst load, time and amount of ethanol. It can also be assumed that optimum conditions vary if the process is undertaken at different temperatures.

c) To determine Optimum conditions that yields a maximum conversion for the transesterification of cotton seed oil

Thirdly, Production of biodiesel using open batch process with the use of continuous stirred tank reactors (CSTRs) in series is suitable for cottonseed oil and wood ash catalyst. Wood ash load of 2.4 g/l of cottonseed oil and ethanol is effective to produce biodiesel that meets standards for bio-fuel. A series of continuous stirred tank reactors (CSTRs) in this batch operation may be varied

d) To model production of biodiesel using wood ash catalyst, cotton seed oil and ethanol

Finally, the model of the production process can be expressed mathematically by linear equation as: $y=\mathbf{a}+\mathbf{b}x_1+\mathbf{c}x_2+\mathbf{d}x_3.$ *Equation 4.1*

Where x1 = Catalyst Concentration, x2 = Time in minutes; x3 = Mole ratio; and y = yield conversion of oil to ester.

5.2 RECOMMENDATIONS

Having undertaken this study and in order to optimize production process of biodiesel using crude cottonseed and wood ash Catalyst there are a number of recommendations .These are categorized into policy, practice and further research related.

5.2.1Policy

Measures be put in place to increase the production of cotton to sustain supply of enough cottonseed oil. These measures could include legal frameworks on enforcing ‘buy Kenya, build Kenya’ slogan. Apart from saving the country on foreign exchange, it will result in better resilience to climate change, better utilization of all potential land to produce sufficient quantities of cottonseed oil thus spurring industrial growth.

5.2.2 Practice

Use wood ash as a substitute to organic catalyst. On the use of wood ash, the national and county governments need to co-operate in the issues of re-usability and recyclability of wood ash. Since the ash is usually waste in many hopes as well as wood-fired boilers, the solid waste disposals need to be relooked at dumpsites by introducing the issue of waste segregation. Once the wood ash is segregated at source, transported to a storage facility it can be harvested and calcinated, and packaged in quantities convenient for transportation.

Undertake the esterification process at lower temperatures to save on energy. The esterification process of cottonseed oil could be undertaken at lower temperatures. The number of batches and design be in volumes that are economically for both small and large-scale production. The customization of the design and process can lead to setting up of small-scale plants at local level that otherwise would have required large startup capital.

5.2.3 Further Research

Since ethanol, purity varies from batch to batch it therefore imperative to have standard measurement for any raw material to be used in biodiesel production. This helps in designing of a process of production. Feedstock poses greatest challenges in the process. There is need to do characterization of various wood ash sources, ethanol purity from various sources and regions in the country. Research into the exact quantities of wood ash been produced annually at industrial and domestic use be undertaken and repository established and be updated on regular basis. This will ease process of industrial set up and ensures investors in green energies make informed decisions accurately and timely. Research can be further undertaken to establish other environmental friendly feedstock that could complement ethanol, cottonseed oil and wood ash. Since there is not enough of everything, these complements and/or substitutes will help in the attainment of sustainability in the production and use of this feedstock. To drive the point home, there are times certain feedstock are out of season and since production is a business centered it has to ensure that its capacity is always at optimal performance. In having complementary feedstock that can be processed without equipment modification, it will ensure uninterrupted production due to fall in supply of certain feedstock.

REFERENCES

Abe niece Z, Laipniece L, Kampars V (2020) Biodiesel production by in the esterification of rapeseed oil with methyl formate in presence of potassium alkoxides. Biomass Convers Biorefinery 10:1–9.

Aghababaie M, Beheshti M, Razmjou A, Bordbar AK (2019) Two phase enzymatic membrane reactor for the production of biodiesel from crude Eruca sativa oil. Renew Energy.

Almadani, Enas & Abdalghani, Karema A. & Omar, Fatma. (2023). Calcium Oxide as an Efficient Heterogeneous Catalyst for Production of Biodiesel. The Scientific Journal of University of Benghazi.

Avhad MR, Marchetti JM (2015) A review on recent advancement in catalytic materials for biodiesel production. Renew Sustain Energy Rev 50:696–718.

Dias JM, Alvim-Ferraz MCM, Almeida MF (2008) Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. Fuel 87:3572–3578.

Dizge N, Aydiner C, Imer DY et al (2009) Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel micro porous polymer. Bioresour Techno 100:1983–1991.

Du L, Li Z, Ding S et al (2019) Synthesis and characterization of carbon-based MgO catalysts for biodiesel production from castor oil. Fuel 258:116122.
Efavi JK, Kanbogtah D, Apalangya V et al (2018). The effect of NaOH catalyst concentration and extraction time on the yield and properties of Citrullus vulgaris seed oil as a potential biodiesel feed stock. South African J Chem Eng 25:98–102.

Errore, A., Jones, B., Li, W., & Nachtsheim, C. J. "Benefits and Fast Construction of Efficient Two-Level Foldover Designs." Technometrics, vol. 59, no. 1, 2017, pp. 48-57.

Eryılmaz, Tanzer & Yesilyurt, Murat & Yumak, Hasan & Arslan, Mevlut & Şahin, Seda. (2014). Determination of the Fuel Properties of Cottonseed Oil Methyl Ester and Its Blends with Diesel Fuel. International Journal of Automotive Engineering and Technologies. 3. 79.

Farouk, Sabah & Tayeb, Aghareed & Osman, Randa & Abdel-Hamid, Shereen. (2024). Sustainable production of biodiesel from waste cooking oil using magnesium oxide nano catalyst: An optimization study. Scientific Reports. 14.

Fattah IM, Ong HC, Mahlia TMI et al (2020) State of the art of catalysts for biodiesel production. Front Energy Res 8:1–17.

F. Ferella (2010) Optimization of the transesterification reaction in biodiesel production Fuel.

Firdaus MY, Brask J, Nielsen PM et al (2016) Kinetic model of biodiesel production catalyzed by free liquid lipase from *Thermomyces lanuginosus*. J Mol Catal B Enzym 133:55–64.

Fondo, Kalama & Onago, A & Leonard, Kiti & Cyril, Otulo. (2023). Modeling of Petroleum Prices in Kenya Using Autoregressive Integrated Moving Average and Vector Autoregressive Models. 18-27.

Gu L, Huang W, Tang S et al (2015) A novel deep eutectic solvent for biodiesel preparation using a homogeneous base catalyst. Chem Eng J 259:647–652.

Jambulingam R, Srinivasan GR, Palani S et al (2020) Process optimization of biodiesel production from waste beef tallow using ethanol as co-solvent. SN Appl Sci 2:1–18.

Jamil F, Kumar PSM, Al-Haj L et al (2020) Heterogeneous carbon-based catalyst modified by alkaline earth metal oxides for biodiesel production: parametric and kinetic study. Energy Convers Manag X 10:100047.

Kacem, Prof. Dr. Imed. (2017). Applications of Optimization Methods to Industrial Engineering Problems. Computers & Industrial Engineering. 112. 467-468.

Karmarkar, Neha. (2023). Biodiesel Production: An Overview and Prospects for Sustainable Energy Generation. 1123-1131.

Karmee SK, Patria RD, Lin CSK (2015) Techno-economic evaluation of biodiesel production from waste cooking oil—a case study of Hong Kong. Int J Mol Sci 16:4362–4371.

Kamiab, Behzad & Beims, Ramon & Chambers, Darren & Bassi, Amarjeet & Xu, Chunbao. (2024). Sustainable production of high-performance bio-based hydraulic fluids from vegetable oils: Recent advances, current challenges, and future perspectives. Biomass and Bioenergy. 183.

Kianimanesh, Hamid & Abbaspour-Aghdam, Farzin & Valizadehderakhshan, Mehrab. (2017). Biodiesel production from vegetable oil: Process design, evaluation and optimization. Polish Journal of Chemical Technology.

Kumar D, Das T, Giri BS et al (2019) Biodiesel production from hybrid non-edible oil using bio-support beads immobilized with lipase from Pseudomonas cepacia. Fuel 255:115801.

Lamarque, Hugh. (2019). Profitable inefficiency: The politics of port infrastructure in Mombasa, Kenya. The Journal of Modern African Studies. 57. 85-109.

Malabadi, Ravindra & M R, Sadiya & Kolkar, Kiran & Chalannavar, Raju & Castaño Coronado, Karen. (2023). Biodiesel production: An updated review of evidence.

Malpartida I, Maireles-torres P, Vereda C, Lacoste F (2020) Semi-continuous mechanochemical process for biodiesel production under heterogeneous catalysis using calcium diglyceroxide. Renew Energy 159:117–126.

Matinja AI, Zain NAM, Suhaimi MS, Alhassan AJ (2019) Optimization of biodiesel production from palm oil mill effluent using lipase immobilized in PVA-alginate-sulfate beads. Renew Energy 135:1178–1185.

Mohamed RM, Kadry GA, Abdel-Samad HA, Awad ME (2020) High operative heterogeneous catalyst in biodiesel production from waste cooking oil. Egypt J Pet 29:59–65.

Montgomery, Douglas C. Design and Analysis of Experiments. 9th ed., John Wiley & Sons, Inc., 2017.

Mutisya, Charles & Gachanja, Isaac. (2024). Influence of Technology on Business Sustainability in Petroleum Firms in Nairobi, Kenya. International Journal of Management, Knowledge and Learning.

Oloyede, Christopher & Jekayinfa, Simeon & Alade, Abass & Ogunkunle, Oyetola & Otung, Nsikak-Abasi & Laseinde, Opeyeolu. (2022). Exploration of agricultural residue ash as a solid green heterogeneous base catalyst for biodiesel production. Engineering Reports.

Prates CD, Ballotin FC, Limborço H et al (2020) Heterogeneous acid catalyst based on sulfated iron ore tailings for oleic acid esterification. Appl Catal A Gen 600:117624.

Rahman, M. & Hassan, Tafsirul & Rabbi, Md & Shakil, Md & Khan, Md. (2021). Transesterification of vegetable oil with ethanol using different catalysts. AIP Conference Proceedings.

Republic Of Kenya, National Cotton Textile and Apparel Policy Ministry for Investments, Trade and Industry State Department for Industry*: Draft Cotton, Textile and Apparel Policy, 2024.*

Sahoo, A. K.; Sahoo, B. Mathematical Modelling and Multi-Response Optimization Using Response Surface Methodology and Grey Based Taguchi Method: An Experimental Investigation. International Journal of Experimental Design and Process Optimization 2011, 2 (3), 221.

Selvakumar P, Sivashanmugam P (2017) Optimization of lipase production from organic solid waste by anaerobic digestion and its application in biodiesel production. Fuel Process Technol 165:1–8.

Singh R, Bux F, Sharma YC (2020) Optimization of biodiesel synthesis from microalgal (*Spirulina platensis*) oil by using a novel heterogeneous catalyst, β-strontium silicate (β-Sr_2SiO_4). Fuel 280:118312.

Talha NS, Sulaiman S (2016) Overview of catalysts in biodiesel production. ARPN J Eng Appl Sci 11:439–442

Thangaraj B, Solomon PR, Muniyandi B et al (2019) Catalysis in biodiesel production - a review. Clean Energy 3:2–23.

Van Ryssen, J.B.J. & Ndlovu, Hloniphile. (2018). Wood ash in livestock nutrition: Factors affecting the mineral composition of wood ash. 11. 53-61.

Wang HG, Shi GL, Yu F, Li RF (2016) Mild synthesis of biofuel over a microcrystalline $S_2O_8^{2-}/ZrO_2$ catalyst. Fuel Process Technol 145:9–13.

Yu, Bing-Sheng & Liu, Yi-Yu. (2018). Improvement in phase purity and yield of hydrothermally synthesized smectite using Taguchi method. Applied Clay Science.

Ziolkowska JR (2019) Biofuels technologies: an overview of feedstocks, processes, and technologies. In: Ren J, Scipioni A, Manzardo A, Liang H (eds) Biofuels for a more sustainable future. Elsevier Inc., Amsterdam, pp 1–19

APPENDICES

Appendix 1: Determination of Amount of Sodium Oxide in Wood Ash

During the process of calcination, which is a type of breakdown, the chemical reaction that occurs can be represented as:

During calcination, a decomposition process occurs where a chemical reaction takes place: $CaCO_3$ (s) → CaO(s) + C O_2 (g)..Equation 6.1

The product obtained after calcination underwent a reaction with water, resulting in the formation of calcium hydroxide. The reaction is exothermic and releases heat to the environment.

In the reaction, calcium hydroxide combined with concentrated hydrochloric acid to produce calcium chloride and water, as shown by the equation 6.1.

The reaction between calcium hydroxide (Ca $(OH)_2$) in aqueous solution and hydrochloric acid (HCl) in aqueous solution produces calcium chloride.

From the reaction,

Ca $(OH)_2$ (aq) +2 HCl(aq) →$CaCl_2$ (aq) +2H_2 O(l)............................Equation 6.2

Using the given formula, the calculation was performed to determine the amount of calcium oxide. It was found that, one mole of calcium hydroxide reacts with two moles of hydrochloric acid.

Calculating the number of moles in a solution can be done by multiplying the volume in liters by the molarity. In this case, the volume of the solution is 29.5 mL, which is equivalent to 0.0295 liters. The molarity of the solution is 1 M. Therefore, the number of moles in the solution is 0.0294 moles.

There is an equal number of calcium hydroxide as there are in acid, based on the mole ratio.

So, the number of hydroxide moles is calculated by dividing 0.0294 by 2, resulting in 0.01470 moles in 30 mls.

Calculating the mass of calcium hydroxide involves using formulae,

Calculating the mass of the hydroxide involves multiplying the molecular mass by the number of moles. In this case, the result is 1.0878 grams of hydroxide.

There are an equal number of moles of calcium oxide based on empirical formulae.

Therefore, Mass equals the molecular mass multiplied by the number of moles, which in this case is 56.0774 multiplied by 0.01470, resulting in 0.8224 grams of calcium oxide, which is equivalent to 82.24% of CaO(s).

Appendix 2: Calculations and Formulae of Alcohol to Oil Volume

a. Average reading is equal to the sum of all the readings. ... (i) Total count of readings

b. The required amount of catalyst is equal to the volume of oil used in milliliters multiplied by the g/l, divided by 1.018 multiplied by 0.8271 multiplied by 1000 milliliters.

The number of moles of ethanol required can be calculated using the formula: moles of ethanol = (volume of oil in milliliters x density of the oil / molecular weight of the oil). …….. (iii) 1000 milliliters

the amount of ethanol required in moles is calculated by multiplying the volume of oil used in milliliters by 0.8988 and dividing the result by 885.46, then multiplying the whole expression by 3. Using the given formula, we can calculate that 1000 milliliters is equal to 0.00030455 moles.

The reaction necessitates a mole ratio of alcohol to glycerides of 3:1, which is equivalent to 18.28 milliliters of ethanol per 100 milliliters of oil.

b. Converting moles to volume

The volume of methanol necessary for a 6:1 molar ratio is calculated as follows: 1000 * (6 * 46.07.04) / 0.789) * 0.0001015 = 35.56 mls.

The volume of methanol required for a 9:1 molar ratio is calculated as follows: 35.56 multiplied by 1.5, which is 53.34 milliliters.

The volume of methanol necessary for a 12:1 molar ratio is 71.12 mL, calculated by multiplying 35.45 by 2.

The quantities of 71.12mls, 106.68 mls, and 142.24 mls correspond to an excess of 100% for mole ratios of 1:6, 1:9, and 1:12 correspondingly.

The densities of Biodiesel are measured in kg/l, while the molecular weights are measured in kilograms per mole. Input substances:

The density of triolein is 0.8988 g/cc and its molar mass is 885.46 g/mol. The density of ethanol is 0.789 g/cc and its molar mass is 46.07 g/mol.