SYNTHESIS AND CHARACTERIZATION OF HETEROGENEOUS CATALYST FOR TRANSESTERIFICATION OF VEGETABLE OIL

By

BIRUK SOLOMON DEMISSIE

A Thesis Submitted to

The department of Chemical Engineering

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering Specialization in Process Engineering

Office of Graduate Studies

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As thesis research advisors, we hereby certify that we have read and evaluated this thesis prepared under our guidance by Biruk Solomon Demissie. We recommended the paper to be submitted as fulfilling the requirements for the Degree of Master in Chemical Engineering (Specialization in Process Engineering).

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We, the undersigned, members of the Board of Examiners of the final open defense by **Biruk Solomon Demissie** have read and evaluated his thesis entitled **"Synthesis And Characterization Of Heterogeneous Catalyst For Transesterification Of Vegetable Oil** " and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement for the Degree of Masters in Chemical Engineering (Specialization in Process Engineering) complies with the regulation of the University.

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Declaration

I hereby declare that this MSc Thesis entitled **"Synthesis And Characterization Of Heterogeneous Catalyst For Transesterification Of Vegetable Oil** " is my original work and has not been presented for a degree in any other university for the award of any degree, and all sources of material used for this thesis have been duly acknowledged.

Name: Biruk Solomon Demissie

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This MSc Thesis has been submitted for examination with my approval as thesis advisor/ dissertation Supervisor.

Advisor Name: Ali Shemsedin (PhD) Co-Advisor Name: Melaku Tesfaye (PhD)

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Abbreviations and Acronyms

FAME	Fatty acid methyl ester
SOME	Sunflower oil methyl ester
T G	Triglycerides
CCD	Central Composite Design
FTIR	Fourier Transform Infrared Spectroscopy
RSM	Response Surface Method
XRD	X-ray Diffraction
DOE	Design of Experiments
ME	Methyl Ester
ANOVA	Analysis of Variance

Abstract

In this work, calcium oxide (CaO) extracted from eggshell impregnated with Zinc nitrate (Zn $(NO_3)_2.6H_2O$) is prepared successfully and it had been applied on transesterification of sunflower oil. The effect of calcination temperature at (600ºC 700ºC, 800ºC, 900ºCand1000ºC for duration of time at 2h were studied. The catalytic performance of the prepared catalyst was examined by measuring basicity and confirmed by yield of Fatty acid methyl acid (FAME) through transesterification reaction. Response surface methodology (RSM) in combination with central composite design (CCD) was used to optimize the operating parameters. Methanol to oil molar ratio, catalyst loading and reaction temperature were chosen as the variables and the response selected was biodiesel yield. From the prepared catalyst the catalyst that was calcined at temperature of 600ºC for duration of 2h and 20:80 mixture ratio of zinc nitrate to chicken eggshell was the best catalyst selected for synthesis of fatty acid methyl ester (FAME) and this catalyst was further characterized by X-ray Diffraction (XRD), Fourier transfer infrared spectroscopy (FTIR) and Hammett indicator method with in comparisons of raw mixture of zinc nitrate and chicken eggshell sample. The prepared catalyst is tested for transesterification of Sunflower oil to produce biodiesel in which the optimal conditions of a methanol; oil molar ratio of 9:1, the catalyst weight of 3%, the reaction temperature of 65 ˚C, and the reaction time of 2 h. the transesterification product which showed the biodiesel yield of over 82% was obtained at the recalcined temperature of 600 ˚C and reaction time of 2h. The reusability of zinc nitrate and chicken eggshell mixture calcined at 600ºC for 2h catalyst has been reused successfully for five catalytic cycles. Heterogeneous base catalysts have advantages of being reusable, noncorrosive, show greater tolerance to water, improve biodiesel yield and purity, have a simpler purification process for glycerol and are easy to separate from the biodiesel product.

CHAPTER I

INTRODUCTION

Background;

Statement of Problem;

Objectives;

Significant of the Study;

Scope of the Study

1. INTRODUCTION

In this chapter, a brief discussion on alternative energy demands, biodiesel and suitable feedstock for production of biodiesel are provided. The target of this work is to synthesize and characterize the prepared catalyst for the production of biodiesel and characterize the different parameters that affect preparation of catalyst and that affect production of biodiesel. The chapter also elaborates challenges of current biodiesel production at large scale with regard to catalyst used for biodiesel production. Considering the environmental safety, an alternative way has been used to produce calcium source, namely it produced from some renewable resources which are available calcium based in nature, such as egg shell material wastes, because the egg shell well known as a natural material contained lots of calcium oxide. Finally, the chapter describes the significant and scope of a chosen research topic.

1.1. Background

Biodiesel, also called Fatty Acid Methyl Esters (FAME), is mainly produced by the transesterification reaction of vegetable oils and different alcohols (methanol, ethanol and propanol) as reactants in the presence of an appropriate catalyst. Due to reversible nature of the reaction, excess alcohol is used to shift the equilibrium to the product side(Ayhan Demirbas, 2008a). Glycerol, a by-product obtained from this reaction, can be refined and used in reforming reactions for the production of hydrogen(Dias, Araújo, Costa, Alvim-Ferraz, & Almeida, 2013). Homogeneous catalysts such as (NaOH and KOH) are used commercially due to their high activity and low cost. However, these catalysts pose some drawbacks including soap formation, waste water generation, as well as a high purification cost of the final product biodiesel. The use of heterogeneous catalysts is more favored for the synthesis of biodiesel due to their ability to overcome such problems. Heterogeneous catalysts are easily removed from the reaction mixture, recycled and regenerated which allows a continuous operation of the process. Moreover heterogeneous catalysts reduce the amount of disposed waste materials and prevent separation problems and soap formation. Such catalysts are environmentally friendly, non-corrosive and have longer lifetimes.

The most recognized problem with the heterogeneously catalyzed process is its slow reaction rate compared with the homogeneous process. For this reason, the reaction conditions of heterogeneous catalysis are intensified to enhance its sluggish reaction rates by increasing reaction temperature (100–250ºC), catalyst amount (3–10 wt %) and methanol/oil molar ratio (10:1–25:1)(Ulfah et al., 2018). Another problem of the

heterogeneous process is the dissolutions of active species into liquids, which makes the catalysis partly ‘homogeneous’ and then causes problems in biodiesel quality and limits the repeated utilization of catalyst.

Heterogeneous catalysts such as metal oxides, mixed oxides, supported alkali metals, zeolites, hydrotalcites, *etc.*, have been widely studied to replace homogeneous bases due to their less corrosion, easy separation, and low environmental pollution. Recently, the field of catalysis has a great attention to exploit and develop heterogeneous catalysts derived from high volume renewable resources to enhance the overall sustainability of catalytic processes because of the high production cost and metal losses of conventional catalysts. Apart from high catalytic activity and selection during reaction, renewable resources derived catalysts could be synthesized cheaply, which further reduces the cost of biodiesel production. Furthermore, the use of renewable materials in catalysts especially solid wastes can also partly solve the environmental problem and reduce the cost associated with disposal, which also means a value addition to these renewable materials(Shan, Lu, Shi, Yuan, & Shi, 2018).

Both chemical and biological catalyst is used to enhance the rate of transesterification reaction.Figure1:(Thangaraj, Raj Solomon, Muniyandi, Ranganathan, & Lin, 2018) Furthermore; homogeneous and heterogeneous catalysts are being used for the biodiesel production from vegetable oils and animal fat. In homogeneous catalysis, both strong acid and strong base can be used as catalysts for transesterification of triglycerides with short chain alcohols like methanol and ethanol. Due to low corrosive nature, liquid bases are generally preferred over liquid acid catalysts like sulfuric and sulfonic acids, etc. Hydroxides and methoxides of sodium and potassium are frequently used as homogenous base catalysts for transesterification reaction. Although, homogeneous catalysis provides fast reaction rate under mild reaction conditions, yet the catalysts have several drawbacks such as corrosive nature, non-recyclable, non-ecofriendly and formation of sodium or potassium ion contaminated biodiesel and glycerol. Homogeneous catalysts also produce large amount of waste water; which reduces their attractiveness. Therefore, the use of homogeneous catalyst requires more refined feedstocks for biodiesel production which makes the process uneconomical. However, heterogeneous catalysts have the potential to overcome the problems associated with the homogeneous catalysts, specially used for transesterification of triglycerides of vegetable oil produce biodiesel. Heterogeneous catalyzed transesterification process provide easier separation, catalyst free product

formation and no requirement of product neutralization and purification steps. Moreover, less consumption, and reusability of heterogeneous catalysts makes the biodiesel production much economical in comparison to homogeneous catalyzed processes(Joshi et al., 2015). A large number of heterogeneous solid acid and base catalysts have been investigated for transesterification of vegetable oils.

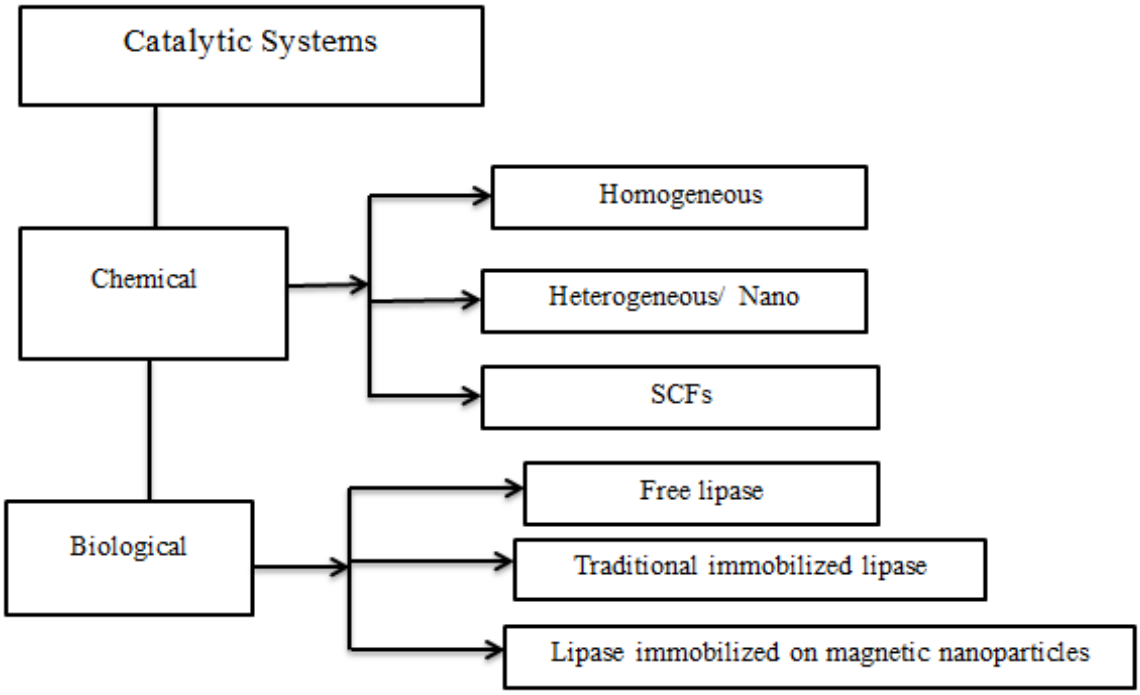


Figure 1: Various catalytic systems for transesterification reaction for biodiesel production

Solid base can leads to the heterogeneous catalytic process, which promises the cost reasonable for biodiesel production. Since the solid base catalyst is easy to separate from the transesterified product, there is some expectation that fixed-bed reactor system is advantageous to process operation is applied to biodiesel production. Furthermore, the solid base catalyst is active in the transesterification reaction at a temperature around boiling point of the reactant methanol. From the economical point of view, this research focuses chicken eggshell base calcium oxide (CaO) as a solid base catalyst due to availability and cheap cost of chicken eggshell. A solid base catalyst is a promising alternative to a homogeneous base catalyst for biodiesel production. Use of solid base catalyst for biodiesel production offers several process advantages including elimination of a quenching step to isolate products, thus reducing the risk of contaminated water, and the opportunity to operate a continuous process(D'Cruz, G. Kulkarni, Meher, & Dalai, 2007).

Calcium oxide (CaO) becomes the most attractive base catalyst in alkaline earth metal oxides group as it has high basic strength, causes less harm to the environment and can be synthesized from cheap sources such as limestone, eggshell, waste shell and calcium hydroxide. As the transesterification catalyzed by CaO suffers low reaction rate, many researchers have attempted to increase the reaction rate of CaO. Inhalation of calcium oxide dust also leads to inflammation of the respiratory passages, ulceration and perforation of nasal septum, and pneumonia(Ayodeji, Modupe, Rasheed, & Ayodele, 2018). Besides, abdominal cramps, vomiting and diarrhea might also take effect. Thus, care must be taken to minimize the inhalation or ingestion of CaO(Ngadi et al., 2018).

More recently, research interest has been grown towards the production of biodiesel using economic and natural calcium carbonate sources such as waste shells of egg, golden apple snail and Meretrix Venus, oyster shell, and mud crab etc. However, the high moisture sensitivity and lesser reactivity towards transesterification reaction is the major problem associated with calcium oxide derived from natural sources. The catalytic property of pure CaO could be improved by preparation of its mixed oxides with active metal oxides. Chicken egg shell is a rich source of calcium carbonate. It is composed of 85–95% calcium carbonate, 1.4% magnesium carbonate, 0.76% phosphate, 4% organic matter and trace amount of sodium, potassium, zinc, manganese, iron and copper(Joshi et al., 2015). Calcination of chicken egg shell at 600–900ºC produces basic calcium oxide which can be used as basic catalyst for production of biodiesel(Marinković et al., 2016).

1.2. Statement of the problem

Biodiesel is produce by transesterification reaction, reacting triglycerides of vegetable oils or animal fats with monohydric alcohol in presence of catalyst. The transesterification reaction is affected by various parameters; catalyst type is one of the parameter. Generally, catalysts used in transesterification reaction can be divided into three categories: homogenous, heterogeneous and enzymes. Industrially biodiesel production is being carried out using homogeneous catalyst (acids and bases catalysts).However, using of homogenous catalyst not qualified by researchers because of issues with catalyst deactivation(Balat, 2008), catalyst recovery(Baskar & Soumiya, 2016), large wastewater production(C.G. Albuquerque et al., 2008), and corrosion to operation facilities(Dahdah et al., 2019), all of which increase the production cost of biodiesel(Dasari & Goud, 2017).Recently, several researchers conducted various investigations to synthesize heterogeneous catalyst with high catalytic activity and stability to overcome the problems encountered with homogeneous catalysts. Heterogeneous catalysts offer numerous advantages over homogeneous catalysts as it can easily be separated from reaction mixture and can be reused, possess high thermal stability, have limited corrosion effect, and easily applied in continuous processes. Preparation of heterogeneous base catalysts derived from commercial chemicals sometimes consists of multiple complicated steps(Hattori, 1995). As a result, those catalysts might become uneconomical, especially on a commercial scale. One possible way to address the problem is the synthesize of the catalysts from natural resources and by products through Lowering the production cost and reducing environmental pressure simultaneously. Among the different kinds of natural sources (such as mollusk shells, eggshells, calcined fish scale, sheep bone, etc.), eggshells tend to be a suitable choice due to their high abundancy and nontoxic features.

Biodiesel production process using homogeneous catalysts such as sodium and potassium hydroxides causes apparatus corrosion, not reusable and requires further process for catalyst separation this leads to extra cost expense, but using a heterogeneous catalyst such as CaO is low cost, easily separated, reusable and provides higher conversion efficiency than a homogeneous catalyst. Hence, the eggshell waste is used as source feedstock for heterogeneous catalyst to produce environmentally friendly and economically acceptable biodiesel.

1.3. Objectives of the Research

1.3.1. General Objective

The main objective of this research is to synthesize CaO-ZnO solid base catalyst for production of biodiesel, optimize the process parameters and to investigate the stability, leaching and basic strength ability of CaO-ZnO.

1.3.2. Specific objective

In line with the main objective the following specific objectives conducted to accomplish the main objective

- Synthesize and characterization of calcium oxide catalyst from chicken egg shell and Catalyst recycling efficiency improvement by Transition metal oxide doping.
- Study the effect of reaction temperature, reaction time, Catalyst loading and methanol to oil molar ratio on the yield of biodiesel product during transesterification process and to optimize FAME yield and operating parameters using response surface methodology (RSM).
- To investigate the stability, leaching and basic strength ability of CaO-ZnO

1.4. Significance of the Study

Currently in Ethiopia, the demand for energy sources such as petroleum fuels with limited availability is increasing with increase in population and economic growth. Environmental concerns also related to excessive usage of fossil derived fuels. This research produces biodiesel using wastes of eggshells as raw material for catalyst synthesis. This could eliminate the wastes and simultaneously produced the heterogeneous catalysts with high cost effectiveness. Production of biodiesel by using this cost effective heterogeneous catalyst develop cheap, efficient and environmentally friendly biodiesel technology for sustainable energy production.

1.5. Scope of the Study

The study was started from preparation of necessary equipment's, raw materials and reagents for the experiment. Then based on the procedures different experiments were conducted such as preparation of high active solid based heterogeneous catalyst from mixture of waste chicken eggshell and metal nitrate by calcination at different calcination temperature and duration of time, characterization of the prepared catalyst, determination of the effect of different parameters on the production of Fatty acid methyl ester (FAME) through transesterification reaction with different reaction conditions such as, molar ratio

of methanol to oil, reaction time and catalyst loading in presence of produced solid base heterogeneous catalyst.

CHAPTER II

LITERATURE REVIEW

Heterogeneous catalyst;

Current Biodiesel production and status;

Parameters affecting biodiesel production

2. LITERATURE REVIEW

In this chapter, reviews the literatures related to biodiesel production from waste materials catalyst by heterogeneous catalyst and possible raw materials for this solid waste derived catalyst; (1) detail description of catalyst, comparison of heterogeneous catalyst over homogeneous one from environmental perspectives and from production cost and easy of production process of biodiesel;(2) detail description of several methods for the preparation of solid catalysts for the transesterification process and parameters that influence the biodiesel production process.(3)The chemistry, production processes with compassion of each process, factors that affect the production processes are summarized.(4)The current status of biodiesel in Ethiopia and all over the world is clearly discussed. (5) the contribution of this study for large scale application for one county from different perspectives are sited and finally different studies related to heterogeneous catalyst from waste materials for biodiesel application is summarized and different methods of characterization for biodiesel are briefly discussed.

2.1. Heterogeneous Catalysis in Biodiesel Synthesis

Heterogeneous catalysis is a surface phenomenon that involves a sequence of elementary steps, including adsorption, surface diffusion, chemical rearrangement of the adsorbed intermediates (the actual reaction), and desorption of the products, Thus, detailed experimental and theoretical characterizations of the surface electronic/geometric structures during these steps are indispensable in order to understand the reaction mechanisms and to be able to enhance the activity and selectivity of the catalysts. In this case, there is a cycle of molecular adsorption, surface reaction, and desorption occurring at the catalyst surface.(Takigawa, Shimizu, Tsuda, & Takakusagi, 2018). Figure 2 due to the complexity of catalyst surface structures and the effects of a large number of parameters (such as temperature, pressure, metal particle size/ shape, and metal–support interactions). Unfortunately, the empirical development of catalytic materials is typically time-consuming and expensive with no guarantee of success. However, even though surface characterization techniques have improved dramatically in recent years; new catalytic materials are still primarily developed through trial-and-error experiments.

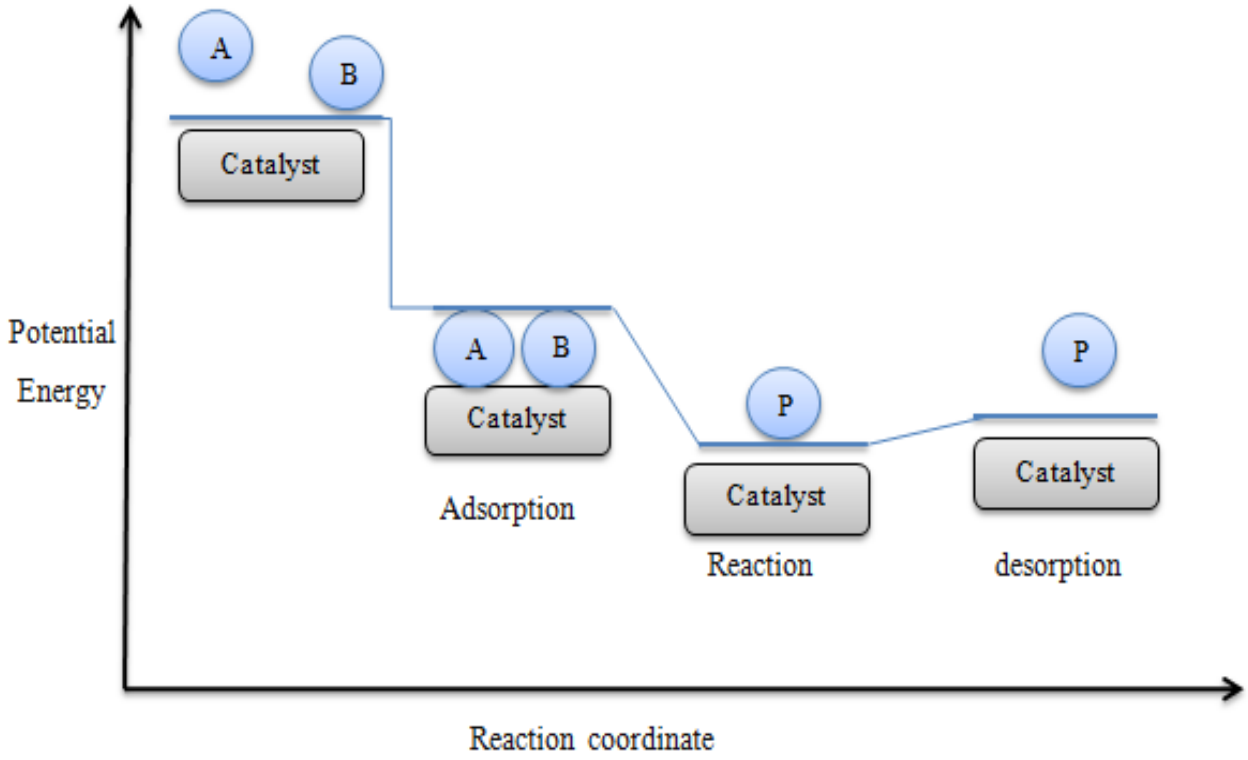


Figure 2: Potential energy diagram of a heterogeneous catalytic reaction (A + B → P) with gaseous reactants (A, B), product (P), and solid metal catalyst

The theory-based rational prediction of activity trends in catalysis is one of the ultimate goals in catalytic science. Such predictions would allow the design of surfaces with specific catalytic properties without extensive experimentation. To this end, it is important to elucidate the factors that control activity, also known as descriptors. To date, the bond energies derived from bulk oxide properties or the adsorption energies of reactants have been used as descriptors to predict the activity of metal/metal oxide surfaces. Activity–descriptor plots typically exhibit a so-called volcano shape due to several effects. First, the strong binding of an intermediate can result in surface poisoning, whereas weak binding leads to low coverage of the surface; in both cases, the catalytic rates are less than optimal. Consequently, moderate interactions produce the highest reactivity (representing Sabatier's principle). In addition, a linear relationship between activation energy and adsorbate–surface interaction energy, known as the Brønsted Evans–Polanyi relation, has been demonstrated by several groups based on theoretical calculations. The above effects allow a semi quantitative understanding of the activity trends in heterogeneous catalytic systems by simply considering the bond energies derived from bulk oxide properties and/or the adsorption energies of a reactant to a first approximation(Takigawa et al., 2018).

Although the basis of the chemical and petrochemical industry is catalysis, few biorefning processes use a heterogeneous catalyst. In principle, catalysts can be recycled and reused for prolonged periods of time and no catalyst losses occur. A solid catalyst can be separated by physical methods such as a hydro cyclone in the case where a multi-phase (e.g. slurry) reactor is used. Alternatively, a fixed bed reactor would eliminate the catalyst removal step entirely(Thangaraj, Raj Solomon, et al., 2018). Moreover, products of higher purity are obtained. There are also fewer restrictions on raw material specifications. In the transesterification(alcoholysis) reaction, free fatty acids eventually present in the feed are also esterified during the process, which is not the case with the commercially used $NaOCH_3$ catalyst and no, or less, foaming occurs(Gryglewicz, 1999).

Processes using heterogeneous catalysts need higher temperatures than homogeneous catalysts to be effective in a reasonable time. For efficiency reasons, solid catalysts should ideally work at temperatures below 423 K(Di Serio et al., 2010). Because of the presence of heterogeneous catalysts, the reaction mixture constitutes a three phase system, oil-alcohol-catalyst, which affects the reaction rate for diffusion reasons. The reaction rate can be enhanced by ultrasound as well as by introducing a co-solvent(Gryglewicz, 1999).

Heterogeneous catalysts are commercially viable in the 318–338 K range. Some may be operative at 373–423 K; however, reactor residence times are often in excess of 4 h, requiring large amounts of catalysts(Katabathini, Lee, & Wilson, 2007). Above 373–423 K, the high pressures needed to keep the methanol in the liquid phase significantly increase equipment costs. Although heterogeneous catalysts are typically preferred over homogeneous catalysts operating at the same temperatures and pressures, a homogeneous catalyst may be preferred if it is equally effective at lower loadings(Dahdah et al., 2019).

It is possible to distinguish three main groups of heterogeneous catalysts: metal, base and acid catalysts. Among the various heterogeneous alkaline alcoholysis catalyst classes proposed(Hattori, 1995). alkali/alkaline earth metal carbonates and inorganic oxides are most frequently used, such as CaO, MgO, Al_2O_3, silicates, $SiO_2 \cdot Al_2O_3$, boria, oxides of P, Ti, Zr, Sn, Cr, Zn and Fe, as well as salts. Table 1**(**Di Serio et al., 2010**).** Silicates such as $Na_2O \cdot SiO_2$ and $KO \cdot SiO_2$ show poor transesterification catalysis (2% yield for 1 wt% catalyst at 338 K(Boey, Maniam, & Hamid, 2011). Group IV B silicates, i.e. titanium and zirconium compounds, possess very good catalytic properties in transesterification reactions(Shan et al., 2018).

Table 1: Types of heterogeneous basic catalyst based on heterogeneities

Types of catalyst based on heterogeneity	**Common examples**
Single component metal oxides	Alkali metal oxides, Alkaline earth oxides Rare earth oxides, ThO_2, ZrO_2, ZnO, TiO_2
Zeolites	Alkali ion-exchanged zeolite Alkali ion-supported zeolite
Supported alkali metal (or alkaline earth metal)	Alkali metal ions on alumina, Alkali metal ions on silica, Alkali metal on alkaline earth oxides, Alkali metals and alkali metal hydroxides on alumina
Clay minerals	Hydrotalcites, Crysotile, Sepiolite
Non-oxides	Alkaline alkoxide, Alkaline carbonate Guanidine-containing catalysts

2.2 Acid and Base Catalysis for Biodiesel Synthesis

In laboratory, the production of biodiesel (fatty acid methyl ester) is mainly affected by the type and amount of catalyst (acid/base), oil to methanol molar ratio, reaction temperature, impurity contents (usually free fatty acids and water) and fatty acid composition (Table 2). Among these issues, the determination of type of catalyst is the first step for designing a transesterification system.

For acid catalysis, the transesterification process is usually progressed by a Brønsted acid. If the oil source has high free fatty acid (FFA) content, such as waste vegetable oil and most non-edible vegetable oils, acid-catalyzed transesterification is generally favored

because the FFA is also converted to biodiesel. Acid-catalyzed transesterification affords high yields in alkyl ester but suffers from a slow reaction rate when compared with base-catalyzed transesterification, resulting in a long process (and sometimes, high temperature) to reach complete conversion. The most common acid catalysis using H_2SO_4 requires more than 5 h to reach 100% conversion of soybean oil with a methanol/oil molar ratio of 30:1 at a reaction temperature of 65°C(Ayhan Demirbas, 2008b).Due to this sluggish reaction rate, acid catalysis is usually studied with a high catalyst content (low pH) and large methanol/oil ratio (20–300:1) at a high reaction temperature of 150–250°C and the reaction is very sensitive to water content in the reaction system(Lee, Park, & Lee, 2009).

Table 2: Fatty acid compositions in various sources vegetable oil

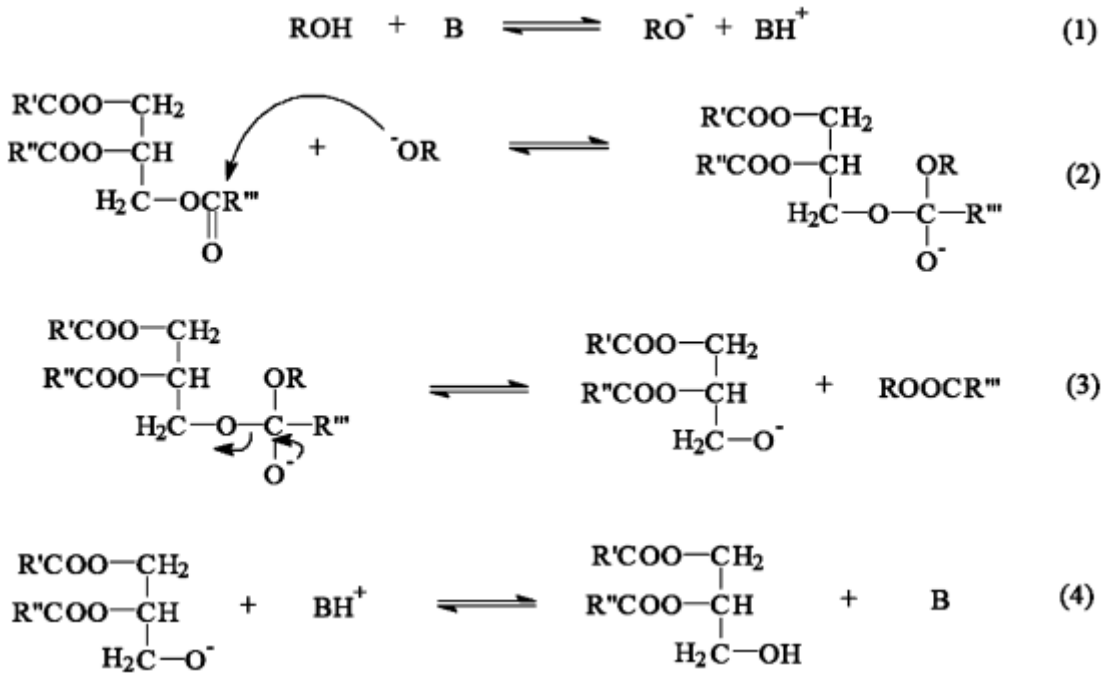
Type of fatty acid	Soybean Oil	palm Oil	Sunflower Oil
Palmitic (C16:0)	11.0%	42.8%	5.0%
Stearic (C18:0)	4.0%	4.5%	6.0%
Lauric (C12:0)	=	0.1%	=
Myristic (C14:0)	=	1.0%	=
Oleic (C18:1)	23.0	40.5%	30.0%
Linoleic(C18:2)	54.0	10.1%	59.0%
Linolenic(C18:3)	8.0	0.2%	=
Others	=	0.8%	=

Source:(Lee et al., 2009)

The mechanism of acid-catalyzed transesterification starts from protonation of the carbonyl group of triglyceride and generates a carbocation intermediate, which is readily converted to carboxylic acids in the presence of water. Since this depresses the biodiesel (fatty acid alkyl ester) yield, the acid-catalyzed transesterification should be operated in the absence of water, in order to slow down the competitive parallel reaction to carboxylic acids. On the other hand, base catalysis transesterification reaction,(Lee et al., 2009) in homogeneous state is fast and needs less methanol (5–15:1 methanol/oil ratio) and a lower reaction temperature (60–75°C, around the reflux temperature of methanol). Near complete conversion (>90%) is usually achieved within 2–6 h depending on the catalyst(Reyero, Arzamendi, & Gandía, 2014).

The first step is the generation of an alkoxide ion (RO^-) through proton abstraction from alcohol by base catalyst (B) for the production of active species RO^-.Then the alkoxide ion

attacks a carbonyl carbon of triglyceride molecule and forms a tetrahedral intermediate ion (step 2), which is rearranged to generate a diglyceride ion and the first alkyl ester molecule (step 3). Finally, the diglyceride ion reacts with the protonated base catalyst, which generates a diglyceride molecule and turns the base catalyst into the initial form (step 4). The resulting diglyceride is ready to react with another alcohol molecule, thereby starting the next catalytic cycle (Figure .3).



Where: B-base catalyst, R-alkyl group of alcohol; R', R", R'''Carbon chain of the fatty acids.

Figure 3: Reaction mechanism of base-catalyzed transesterification(Thangaraj, Raj Solomon, et al., 2018)

Homogeneous base catalysis also follows a similar mechanism. The alkoxide anion attaches to the basic site of the catalyst (for instance, the metallic elements of alkaline oxides) and reacts with triglycerides from the liquid phase. The most common base catalysts are alkaline metal hydroxides (NaOH, KOH). Their use, even at small amounts of 1–2 mol%, completes the reaction within a few hours. However, the homogeneous catalysis of alkaline metal hydroxide can be disturbed by water arising as either a reagent impurity or via the formation by in situ reaction between hydroxide and methanol. Water reacts with alkyl esters to produce carboxylic acids, which rapidly react with alkaline

metals to form ‘soaps’ such as $RCOO^-Na^+$. This soap formation makes the process inefficient by reducing alkyl ester yield and interrupting glycerol recovery.

2.3 Requirements of Heterogeneous Catalysis for Biodiesel Synthesis

In addition to this saponification issue, homogenously catalyzed transesterification, whether an acid or base catalyst is used, suffers some drawbacks in terms of process integrity. The first drawback is corrosion of the reactor and pipelines by dissolved acid/base species, which inevitably raises the material cost for process construction. The second is the impossibility of catalyst recovery from the reactant-product mixture. Catalyst separation can only be achieved by neutralizing the remaining catalysts and disposing of them at the end of the reaction, which raises problems with environmental pollution.

A third drawback of homogenously catalyzed transesterification is the limitation in establishing a continuous process. For these reasons, the heterogeneously catalyzed process, especially using solid base catalysts, has been studied continuously for the last decade. Many studies about the use of heterogeneous catalysts for transesterification treated anti-leaching performance as issue of equal importance to catalytic activities. The deactivation mechanism of heterogeneous catalysts towards transesterification can be classified into the leaching of active species and the adsorption of acidic hydrocarbons onto basic sites. The deactivation tests usually take the form of repeating the reaction cycle several times and measuring the catalytic activity in the interval between each cycle. If the deactivation of the catalyst is unavoidable, a method for regenerating its initial activity was suggested in most cases.

2.4. Chicken Eggshell Derived Solid Catalysts for Biodiesel Production

Due to the huge consumption of bird eggs and meat from mollusks, a large amount of waste shells are produced which pose a solid waste disposal problem. Because those shell consist mainly $CaCO_3$, the CaO can be obtained under the high temperature of 873 - 1273K(Rashid, Atiya, & H Hameed, 2017). Therefore, these waste shells could be simply calcined and used as catalysts for biodiesel production. The most common bird eggshell is chicken eggshell. Calcined chicken eggshell has also been used for the transesterification of nonedible vegetable oils. Before the shell derived CaO contacted with the reactants, an acid catalyzed esterification reaction should be conducted to reduce the free fatty acid (FFA) in nonedible oils. To further improve the catalytic performance of eggshell derived CaO catalysts, a series mixed oxides composites have been utilized for the modification of

freshly prepared CaO. Bird eggshells have been proven to be the reliable sources of CaO(Rashid et al., 2017). Subsequently, shells derived CaO was mixed with ZnO, MnO_2, Fe_2O_3 or Al_2O_3 to test the catalytic activities(Verma & Sharma, 2016). Moreover, among the synthesized mixed oxides composites, ZnO-CaO catalyst was found to exhibit higher catalytic performance than that of others which was attributed to its larger surface area and basicity(Shan et al., 2018).

The use of a catalyst in a reaction is still being developed. Catalysts are known as acid catalyst and base catalyst. The base catalysts are known to work faster than acid catalysts. Therefore, the uses of alkaline catalysts are preferred. Based on the nature of the catalyst there were homogeneous and heterogeneous catalyst. The heterogeneous catalysis is more profitable than the homogeneous catalyst because the heterogeneous catalyst can be reused after the first reaction is complete. This is because of heterogeneous catalysts have different phases of the substrate so it is easy to be separated and the rate of reaction although high. One of the base catalysts which often used in the reaction are metal oxide catalysts such as CaO, MgO or other alkaline metal oxide. However, the metal oxide catalysts are more expensive than metal hydroxides such as NaOH. Reviewing the efficiency of the catalyst and the economic aspects, it is necessary to get the base heterogeneous catalysts derived from nature material with a relatively low price. Chicken eggshell is household waste and it utilization is still relatively small, such as used as art or handcraft. Eggshell contains calcium carbonate (94%), calcium phosphate (1%), organic compounds (4%), and magnesium carbonate (1%)(Mohadi, Anggraini, Riyanti, & Lesbani, 2016).The high contents of calcium in eggshells can be converted as a CaO catalyst by calcinations process at temperature around 900ºC for 2 h where the reaction takes place as exothermic reaction.

2.4.1. Properties of Basic Sites on Surface of Calcium Oxide

Calcium Oxide (CaO) is one of alkaline earth metal oxides which are formed out of ionic crystal and Lewis acidity of the metal cation is very weak due to its small electronegativity. Therefore, the conjugated oxygen anion displays the strong basic property. Catalytic role of the basic sites generated on surface of CaO is to deprotonating from organic matter, which initiates the base catalyzed reaction. For transesterification of vegetable oil with methanol, which is a reaction to produce biodiesel, the catalytically basic sites allow methanol to be transformed into nucleophile that attacks carbonyl carbon in a molecule of glycerides. When CaO, MgO and SrO were employed for the transesterification of soybean

oil, the catalytic activity was in the order of MgO < CaO < SrO(Yusuf, Kamarudin, & Yaakub, 2011). Therefore, it seemed that the strong basic sites were required for catalyzing the vegetable oil transesterification. However, SrO causing the fastest transesterification was inferior in the reusability, because the greater part of SrO was dissolved into the products mixture after the transesterification (Kouzu & Hidaka, 2011; Masato Kouzu 2012).

Here, it should be noted that the vegetable oil transesterification is catalyzed by not only the basic sites generated on surface of CaO catalyst but also the soluble substance leached away from CaO catalyst. The leaching behavior and the following homogeneous contribution toward the vegetable oil transesterification appear independent of type of the active phase. In conclusion, due to a combination of the variable active phase and the homogeneous contribution, the CaO-catalyzed transesterification is too complicated to be understood sufficiently without the further study. Also, the kinetic study is important for understand of mechanism on the CaO-catalyzed transesterification(Zhu et al., 2006). A key point for the kinetic study is to express a shift in the rate determining step. The reaction rate that is observed at the beginning of the transesterification depends on a rate on mass transfer of the reactants, because vegetable oil and methanol do not merge together under the transesterifying condition. Then, an increase in the conversion ratio causes the shift in the rate determining step toward the chemical reaction controlled regime, since FAME produced by the transesterification serves as a co-solvent for dissolving methanol into vegetable oil. Furthermore, it was considered that the mass transfer became faster with an increase in the available active surface of CaO catalyst.

2.5. Mechanism of CaO Catalyzed Reaction

Many different studies reported the reaction mechanism of CaO-catalyzed transesterification; the proposed mechanism is shown in Figure 4;

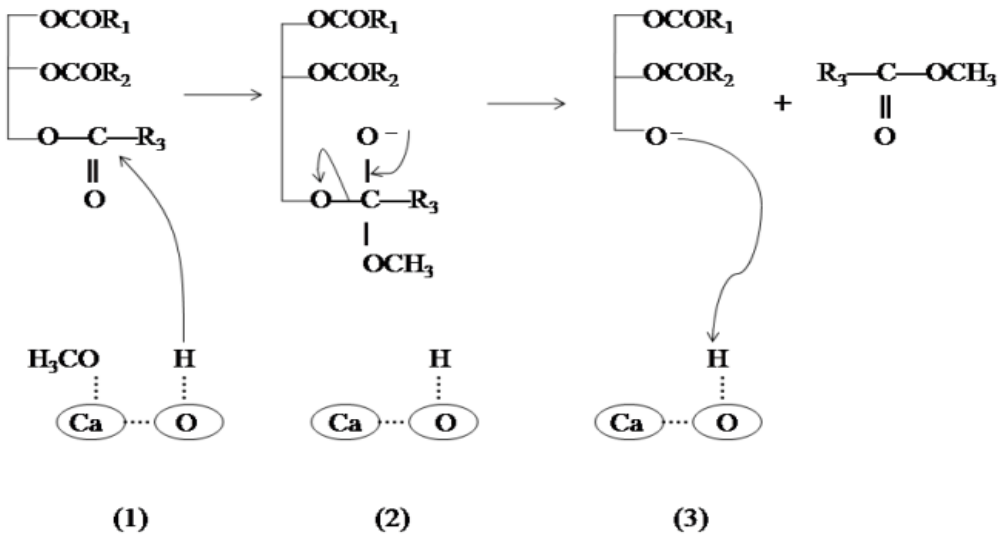


Figure 4: Mechanism of CaO catalyzed reaction of triglycerides of vegetable oil(Boey et al., 2011)

As shown in Figure 4: the reaction begins with attack of methoxide ion, attached to the catalyst surface, to carbonyl carbon of the triglyceride molecule to form a tetrahedral intermediate. In the second step, the unstable tetrahedral intermediate is rearranged and broken down to diglyceride anion and the first fatty acid methyl ester. The diglyceride anion is then stabilized by a proton from the catalyst surface to form diglyceride and at the same time the active site at catalyst surface is regenerated. Then, the methoxide anion attacks on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. These three steps are repeated until all three carbonyl centers of the triglyceride have been attacked by the methoxide ions to give one mole of glycerol and three moles of methyl esters(Marinković et al., 2016).

According to results of different investigations reported in literature the first and second step of complex process (reaction of triglyceride and methanol and formation of diglycerides and FAME, as well as, reaction of diglycerides with methanol in which monoglycerides and FAMEs are formed) are always much faster than reaction of monoglycerides and methanol producing the final amount of FAME and glycerol due high reaction rate and the fastest transfer of mass between them. (Yaşar, 2019).

2.6. Catalyst selection

Heterogeneous catalyzed methanolysis reaction is very complex because it occurs in a three phase system consisting of a solid (heterogeneous catalyst) and two immiscible liquid

phases (oil and methanol). Also, concurrently with methanolysis, there are some side reactions such as saponification of glycerides and methyl esters and neutralization of free fatty acids by catalyst(Yusuf et al., 2011).

The catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume, active site concentration, acidity and basicity. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acidity, i.e. they behave as electron acceptors, and negative oxygen ions (anions) which behave as proton acceptors and are thus Brønsted bases (Figure 5).This has consequences for adsorption. In methanolysis of oils, it provides sufficient adsorptive sites for methanol, in which the (O-H) bonds readily break into methoxide anions and hydrogen cations(Refaat, 2011).

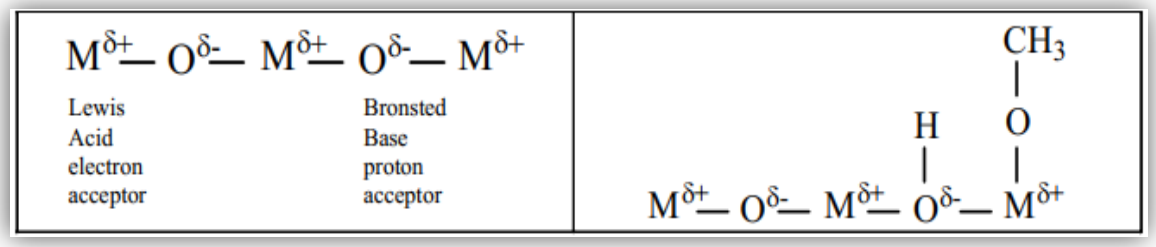


Figure 5: Surface structure of metal oxides(Refaat, 2011)

The methoxide anions then react with triglyceride molecules to yield methyl esters found that small amounts of water can improve the catalytic activity of CaO and biodiesel yields because in the presence of water, O^{-2} on the surface of the catalyst extracts H^{+} from water molecules to form OH^{-} which subsequently extracts H^{+} of methanol to form methoxide anions, which are the real catalyst of the transesterification reaction. However, if too much water (more than 2.8 % by weight of oil) is added to methanol, the fatty acid methyl ester will hydrolyze under basic conditions to generate fatty acids, which can react with CaO to form soap. Calcium oxide is the metal oxide catalyst most frequently applied for biodiesel synthesis, probably due to its cheap price, minor toxicity and high availability. It can be synthesized from cheap sources like waste chicken eggshell, limestone and calcium hydroxide. Calcium oxide possesses relatively high basic strength and less environmental impacts due to its low solubility in methanol and its easier handling as compared to KOH(Zhang & Meng, 2014).

Other alkali earth oxides, like for instance SRO, present high activity but they are fully dissolved in the reaction medium that means the catalysis is considered to be

homogeneous. Magnesium oxide which is produced by direct heating of magnesium carbonate or magnesium hydroxide has the weakest basic strength and solubility in methanol among group II oxides. The reaction rate was lowest when CaO powder was used as catalyst due to have lowest basic strength while magnesium oxide and calcium hydroxide showed no catalytic activity. The high activity of barium hydroxide was attributed to its higher solubility in methanol with respect to other compounds(Pinna, 1998).

The activities of three modified-zirconias (Titania zirconia, sulfated zirconia, and tungstated zirconia) were evaluated for both esterification and transesterification reaction. The study provided a quantitative comparison of the rate of transesterification and conversion of TGs versus the rate of esterification of FFAs under simultaneous reaction conditions, which is of great importance when using less pure biodiesel feedstock (such as waste cooking oil). As expected, esterification occurred at a much faster rate than transesterification. However, under simultaneous reaction conditions, by virtue of the water being produced in esterification and hydrolysis of the TG taking place, the conversion of the triglycerides to ester products was greatly increased. Although the fresh sulfated zirconia (SZ) catalyst was found to be the most active for these reactions, its activity was not easily regenerated. Titania zirconia (TiZ) was found to have a greater activity for transesterification than tungstated zirconia (WZ). However, the opposite result was found for esterification. The higher activity of TiZ towards transesterification is suggested to be due to its base sites, which are likely poisoned in the presence of the carboxylic acid during esterification. WZ was found to be the most suitable of these catalysts for carrying out these reactions as it is more active than TiZ for esterification and can be more easily regenerated than SZ by simple re-calcination in air(Refaat, 2011).

2.7. Catalyst Preparation

Several methods for the preparation of solid catalysts for the transesterification process were described in the literature. These methods include: (Calcination) thermal pretreatment, hydrothermal synthesis, physical mixing, impregnation, and precipitation.

2.7.1. Calcination (Thermal Treatment)

The surfaces of metal oxides are covered with carbon dioxide, water, and in some cases, oxygen as they are handled in air. To have basic sites exposed on the surfaces, pre-treatment at high temperatures is required. The nature of the surface basic sites varies with severity of pretreatment conditions. Beside removal of water and carbon dioxide,

rearrangement of surface and bulk atoms occurs during pre-treatment, which changes the number and nature of the basic sites with increasing the pre-treatment temperature. Therefore, the optimum pre-treatment temperature varies with the type of reaction(Zhu et al., 2006). As the pre-treatment temperature increases, the molecules covering the surfaces are successively desorbed according to the strength of the interaction with the surface sites. The molecules weakly interact with the surfaces are desorbed at lower pre-treatment temperatures, and those strongly interacting are desorbed at higher temperatures. The sites that appear on the surfaces by pre-treatment at low temperatures are suggested to be different from those appearing at high temperatures. If simple desorption of molecules occurs during pretreatment, the basic sites that appear at high temperatures should be strong. However, rearrangement of surface and bulk atoms also occurs during pre-treatment, which may change the number and nature of the surface basic sites with increasing the pretreatment temperature.

The active surface sites of CaO are unavoidably poisoned by the atmospheric H_2O and CO_2. The catalytic activity of CaO can be improved if before the reaction the CaO is subjected to an activation treatment to remove and to clean the surface of the main poisoning species (the carbonate groups) and if after this treatment the contact with room air is prevented(Granados et al., 2007).Used the activated calcium oxide as a solid base catalyst in the methanolysis of sunflower oil to investigate the role of water and carbon dioxide on the deterioration of the catalytic performance by contact with air for different periods of time. In order to investigate the influence of temperature of the catalyst activation on biodiesel yield the authors prepared two batches of catalysts differing only in the calcination temperature: 500 and 900 °C. It was shown that the catalyst activation in static air conditions at 900 °C preceding the reaction is necessary for the sake of strong basic sites formation(Vujicic, Comic, Zarubica, Micic, & Boskovic, 2010). The results showed that the base strength of calcium oxide was more than 26.5 after dipping in an ammonium carbonate solution followed by calcination. After calcination at 850°C, the catalyst showed high activity for the transesterification process. When the calcination temperature was over 900 °C, the catalytic activity gradually decreased(Vujicic et al., 2010).

2.7.2. Impregnation

Impregnation is a procedure whereby a certain volume of solution with predetermined concentration is contacted with the solid support, which, in a subsequent step, is dried to

remove the imbibed solvent. Two methods of impregnation may be distinguished, depending on the volume and concentration of solution used: incipient wetness or dry impregnation and wet or soaking impregnation. In incipient wetness impregnation method, the volume of the solution is equal or slightly less than the pore volume of the support(Bourikas, Kordulis, & Lycourghiotis, 2006). The volume should be just sufficient to fill the pores and wet the outside of the particles. Although this volume may be determined from measured pore volumes, this is sometimes more reliably determined with preliminary test on aliquot samples.

In its essential features, this procedure requires that the support is contacted with a certain amount of solution of the metal precursor, usually a salt, and then it is aged, usually for a short time, dried and calcined. According to the amount and concentration of solution used, two types of impregnation can be distinguished: one called ‘‘incipient wetness’’ or ‘‘dry’’ impregnation because the volume of the solution containing the precursor does not exceed the pore volume of the support. In the simplest way, the impregnating solution is sprayed on the support which is maintained under stirring and has been previously evacuated. By removing the air trapped in the inner pores, a deeper penetration of the solution is allowed and a consequent more uniform distribution of the metal precursor should be attained. In principle this method appears to be simple, economic (especially when using solutions of costly active components) and able to give a reproducible metal loading which is however limited by the solubility of the metal precursor. However, when higher concentration of the metal are required, this limitation can be overcome by carrying out consecutive impregnation steps(Pinna, 1998).

The second type of impregnation, called ‘‘wet’’ or ‘‘soaking’’, involves the use of an excess of solution with respect to the pore volume of the support(Bourikas et al., 2006). The system is left to age for 4 h under stirring, filtered and dried: This procedure is applied especially when a precursor support interaction can be envisaged. Therefore, the concentration of the metal precursors on the support will depend not only on the concentration of the solution and on the pore volume of the support, but also on the type and/or concentration of adsorbing sites existing at the surface(Pinna, 1998).

There are some factors affects the prepared catalysts by impregnation method such as temperature and the concentration of precursor. The operating variable is the temperature, which influences both the precursor solubility and the solution viscosity and as a

consequence the wetting time. However, the maximum loading is limited by the solubility of the precursor in the solution. In addition, the concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying(Kašpar, Fornasiero, & Graziani, 1999). This method is faster, inexpensive, and allows the final property and configuration to be controllable in advance. It is, however, harder to prepare high concentration catalyst and to obtain even dispersion of catalyst components on the surface. But, wet impregnation method gains a great advantage when compared to other methods used in the preparation of catalysts, namely that it is easy to prepare a layer of active matter on the catalyst's surface. This could be attributed to change the solution transport from a capillary action process to a diffusion process, which is much slower. There are two mechanisms according to type of the impregnation method. In the Incipient wetness impregnation method capillary action draws the solution into the pores. But, the solution transport changes from a capillary action process to a diffusion process in the wet impregnation method.

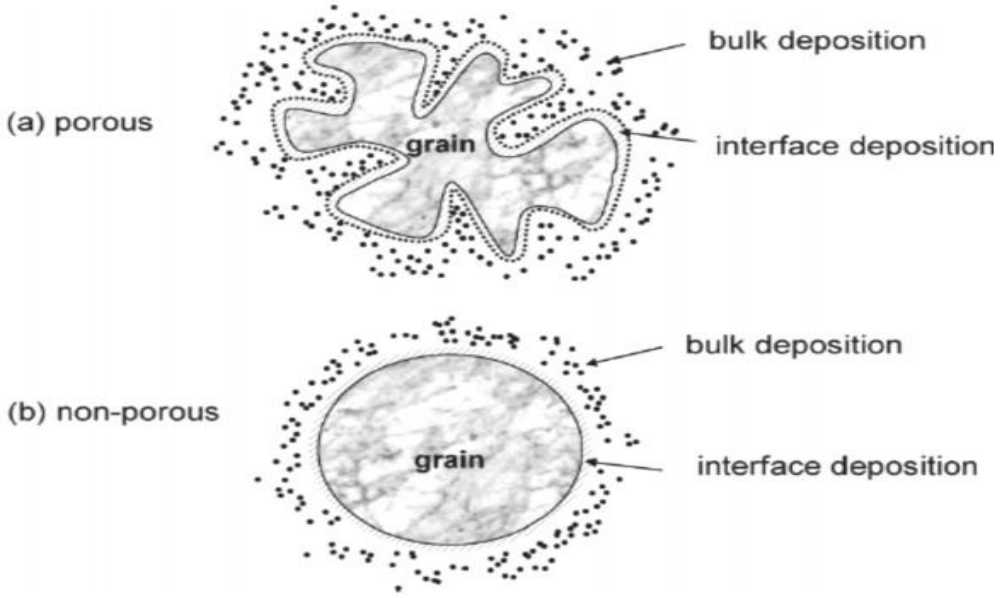


Figure 6: Schematic representation of the bulk deposition and interfacial deposition(Pinna, 1998)

The maximum loading is limited by the solubility of the precursor in the solution(Pinna, 1998). When higher loadings are required, this limitation is overcome by carrying out consecutive impregnation steps. In wet impregnation, an excess of solution with respect to the pore volume of the support is used(Campanati, Fornasari, & Vaccari, 2003). In general,

wet impregnation is used for the preparation of low-loaded catalysts and, in particular, expensive precious metal catalysts, where the active metal phases should be highly dispersed in order to obtain high activity. The distribution of the metal precursor will be based on the density of the exchanging sites in the support. With low metal loading and high density of adsorbing sites on supports in granules, pellets, extrudates (where diffusion effects are encountered), the distribution of the precursor will be inhomogeneous(Pinna, 1998). Deposition will mainly take place at the external layers of the particles.

Impregnation as a means of supported catalyst preparation is achieved by filling the pores of a support with a solution of the metal salt. The catalyst is prepared either by spraying the support with a solution of the metal compound or by adding the support material to a solution of a suitable metal salt; this is then followed by drying and subsequent decomposition of the salt at an elevated temperature, either by thermal decomposition or reduction. Prepared a series of CaO catalysts supported on mesoporous silica using an impregnation method, and prepared KF/CaO nanocatalyst by using impregnation method. prepared zinc oxide nanostructures with zinc acetate and activated carbon by impregnation using a matrix-assisted method(Wen, Wang, Lu, Hu, & Han, 2010). ZnO nanostructures have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity. Zinc oxide, obtained by thermal decomposition of zinc oxalate, has been impregnated with different amounts of calcium oxide, and used as solid catalyst for transesterification processes(C.G. Albuquerque et al., 2008). Calcium oxide is stabilized by filling the mesoporous network of ZnO, as revealed by the corresponding pore size distributions, thus avoiding the lixiviation of the active phase in the reaction medium. These supported CaO catalysts, thermally activated at 1073 K, can give rise to FAME (fatty acid methyl esters) yield higher than 90%, after 2 hr of reaction, when a methanol: oil molar ratio of 12:1 and 1.3 wt % of the catalyst with a 16 wt % CaO were employed(Lee et al., 2009).

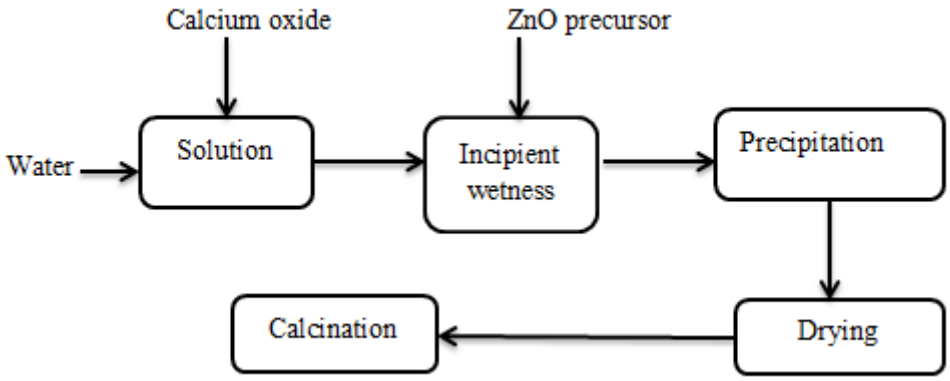


Figure 7: Impregnation catalyst preparation(Lee et al., 2009)

Calcination is the most common method utilized for the preparation of biomass-derived solid base catalyst. Calcination involved thermal treatment in the absence of air and oxygen in order to break down or decompose a compound into a smaller component in order to provide active catalyst. Generally, calcination can be carried out at a wide range of temperature ranging from 573K to 1273K depending on the type of feedstock. Upon combustion, $CaCO_3$ in the organic compound will break down into CaO and releases CO_2 gas. Figure 8 :(a) illustrates the general procedure for preparation of CaO-derived catalyst from waste shells. The calcination temperature plays a significant role in the formation of CaO as well as development of the surface morphology of the catalyst. Since most waste shells are most likely non-porous material, size of developed particles on the catalyst surface reflect the total surface area of a prepared catalyst. Hence, the catalytic activity of a prepared catalyst is highly dependent on the calcination temperature that determined the intensity of active sites(Abdullah et al., 2017).

The preparation of supported solid base catalyst can be carried out through a tri-step procedure of calcination-wet impregnation-activation as shown in Figure 8: (b).Calcination can be conducted at a specific temperature depending on the type of feedstock. Wet impregnation is a chemical treatment in which various types of active metal precursor mix with the calcined sample in an aqueous or organic solution in order to produce supported catalyst. High basic strength metal salts and oxides, including NaOH, KOH and CaO are being commonly used in wet impregnation. Upon impregnation, the metal salt will tend to diffuse in the porous structure of the catalyst support. Consequently, the impregnated calcined sample will be subjected to thermal activation to remove moisture and volatile matter as well as aid in depositing the metal salt on the catalyst surface. The catalytic

activity of supported catalyst is higher than that of unsupported one due to enhancement in their basic strength(Abdullah et al., 2017).

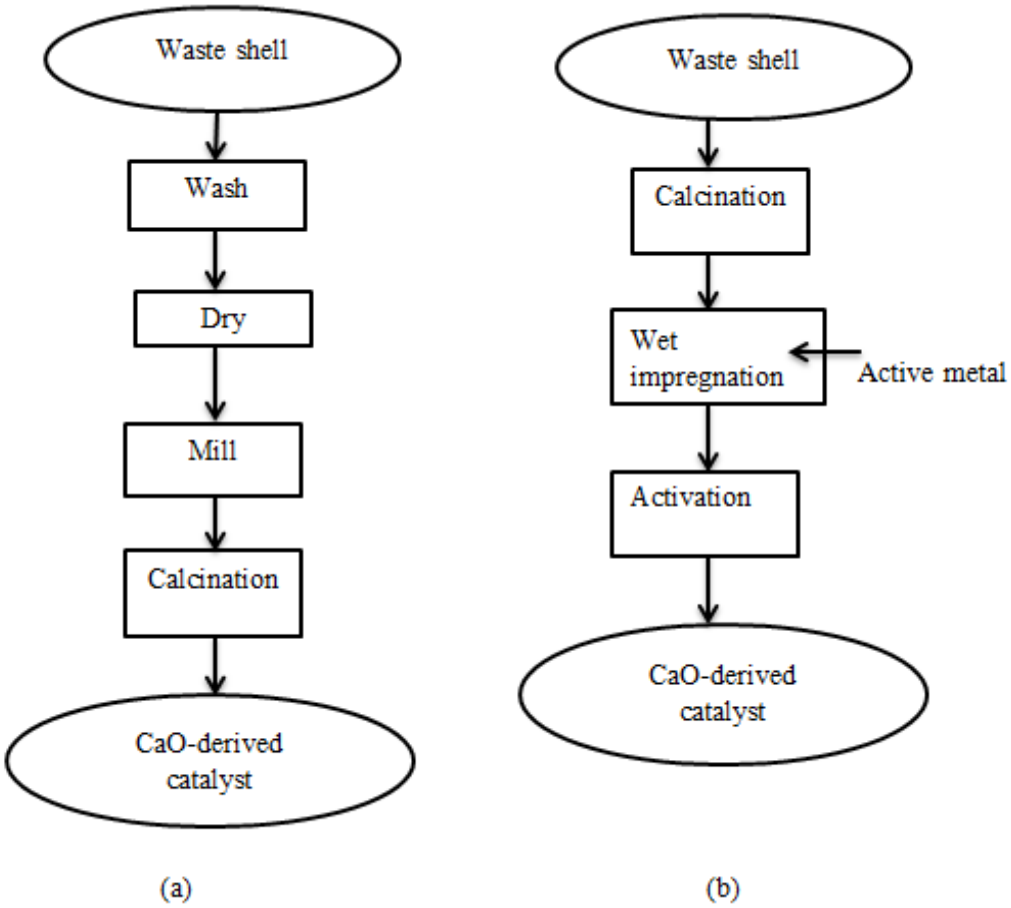


Figure 8: General flowchart for the catalyst preparation of (A) CaO-derived catalyst (B) Supported catalyst(Abdullah et al., 2017)

Catalyst synthesis is an important and vital segment of catalysis research. It is widely accepted that the catalytic activity of alkaline earth oxide catalysts is very sensitive to their preparation and activation procedure. Different methods of catalyst synthesis have been reported in literature including thermal pretreatment, precipitation (co-precipitation), impregnation, sol-gel, mechanochemistry. Several reported papers were focused to find the optimal temperature for CaO calcination and activation. There is disagreement in the literature regarding the optimal pretreatment temperature of CaO. As already mentioned, the surfaces of calcium oxide can be covered with carbon dioxide and water as it is handled in air. In order to have maximum basic sites on the surface of CaO catalyst, pretreatment at high temperatures is required. Thermal treatment at 1073k resulted in the best CaO crystallinity and preferable pore structure, which were beneficial for catalytic activity.

Solid super base of CaO was obtained by dipping CaO in ammonium carbonate solution, followed by calcinations at 1173K. The effect of the calcination temperature ranging from 393K to 1273K on the catalytic activity of the Ca/Al composite oxide which contained $Ca_{12}Al_{14}O_{33}$ and CaO was also investigated(Leung, Wu, & Leung, 2010).

2.7.3. Precipitation

Precipitation is another procedure where the solutions containing the metal salt and a salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxide and or/carbonates (Pinna, 1998). After washing, these can be transformed to oxides by heating. Figure 9: It has also been discovered that metal oxides can be deposited on the surface of supports by physically mixing and heating the resulting mixture to spread the active component. However, this method applies only to active metal oxides that are volatile or have a low-melting temperature, such as rhenium oxide, molybdenum oxide, tungsten oxide, and vanadium oxide. The disadvantage of this method is the long calcination times required to achieve complete spreading of the active metal oxide over the support surface(Campanati et al., 2003).

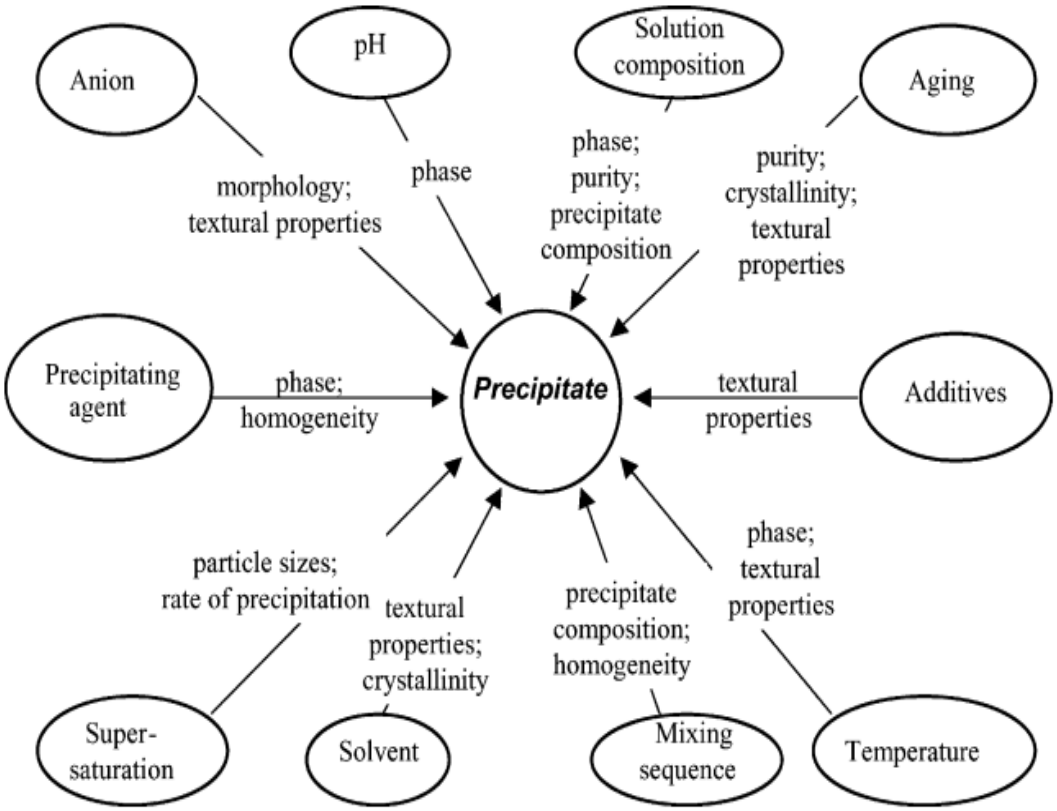


Figure 9: Factors affecting the main properties of precipitated catalysts(Campanati et al., 2003).

2.8. Calcium Oxide (CaO) based Catalysts

Alkaline earth oxides, as solid bases, have potential for transesterification processes. The basic sites in alkaline earth oxides are generated by the presence of M^{2+} and O^{2-} ion pairs in different co-ordination environments. It is known that the basic strength of group II oxides and hydroxides increase in the order Mg<Ca<Sr<Ba, which is confirmed experimentally by the CO_2 TPD(Reyero et al., 2014). Among the oxides, the catalytic activity is in the sequence of CaO<SRO<BaO. However, leaching of barium from BaO-based catalysts in the ester phase is too high. SrO shows a high activity but is fully dissolved in the reaction mixture, so the catalysis is not considered heterogeneous(Sharma, Ojha, Bharadwaj, Pathak, & Sharma, 2015). Another alkaline earth oxide, MgO, shows less catalytic activity. Despite its lower catalytic activity than that of SrO and BaO, CaO is most frequently applied for transesterification processes because of its low price, low solubility in methanol, minor toxicity, and high availability from both natural and waste sources, easy preparation, mild reaction condition and high ester yield(Shan et al., 2018).

According to the form of their use in transesterification, CaO based catalysts can be classified into four groups: (a) neat, (b) doped, (c) loaded and (d) mixed CaO. Commercial pure CaO is most frequently used after thermal activation, though nano-sized CaO has become also very attractive in recent years. The catalytic activity of neat CaO can be improved not only by enlarging the surface area (i.e. by reducing the catalyst particle size) but also by increasing the number of the basic sites by doping CaO particles by alkaline compounds – the obtained catalyst is denoted here as the doped CaO(Boey et al., 2011). The catalytic activity is also increased by incorporation of CaO into various carriers like alumina, silica, MgO and others(Thangaraj, Solomon, Muniyandi, Ranganathan, & Lin, 2018). These catalysts are described as the supported CaO. In the case of mixed CaO, the catalytic ability of CaO is enhanced by mixing it with metal oxides like zinc, lanthanum and cerium oxides. Besides CaO-based catalysts, some other calcium-based catalysts like calcium methoxide, diglyceroxide and glycerolate have also been tested in transesterification reactions.

2.8.1. Pure CaO Catalyst

An overview of the use of neat CaO, with a short description of the preparation procedures and the reaction conditions, CaO shows high catalytic activity at temperatures close to the boiling point of methanol at atmospheric pressure. Its catalytic activity is mainly due to strong basic sites(Ulfah et al., 2018). Unlike many other solid catalysts, catalytically active

CaO is prepared without much preparation effort. Moreover, its catalytic activity can be improved by employing thermal activation treatment (calcination), methanol washing and dipping in ammonium carbonate, followed by calcination.

The catalytic ability of CaO depends not only on the calcination temperature but also on the precursor salt used for obtaining CaO. In testing catalysts prepared from different salts, the lowest ester yield was obtained using the catalyst prepared from calcium nitrate tetrahydrate, which was almost inactive, while catalysts obtained from other salts like calcium acetate monohydrate, Calcium carbonate, calcium hydroxide and calcium oxalate monohydrate, showed significantly higher and quite uniform yields. The use of CaO should be thoughtful because its surface active sites can be poisoned by the adsorption of CO_2 and H_2O from the air(Verma & Sharma, 2016). CaO is rapidly hydrated and carbonated in the contact with room air, even a few minutes are sufficient to chemisorb significant amounts of H_2O and CO_2. It is worth mentioning that CO_2 is the main poisoning agent, whereas the negative effect of water is less important. In addition, it is possible to revert the CO_2 poisoning and reactivate the catalyst by outgassing at temperatures above 973 K(Semwal, Arora, Badoni, & Tuli, 2011).

Nano-crystallized CaO is also an efficient catalyst for the transesterification reaction due to its large surface area associated with small crystallite sizes and low number of defects. Nanocrystalline CaO was active in methanolysis of soybean oil at room temperature within 12 hr while the activity of amorphous CaO used without any pretreatment before the reaction was ignorable(Ramadhas, Jayaraj, & Muraleedharan, 2005). In another study, the nano-CaO produced by the thermal decomposition method showed a slightly better ester yield (94%) in methanolysis of palm oil than the bulk CaO prepared by calcination of $CaCO_3$ (90%). the shape-controlled growth of CaO nanoparticles appears to be an important factor to enhance its catalytic properties(Vujicic et al., 2010). Also, a simple and flexible method involving hydration–dehydration of calcined natural calcites resulted in CaO with less crystallinity, larger surface area and larger amount of basic sites compared to CaO generated by the decomposition of calcite. With these characteristics, CaO exhibited higher catalytic activity than the decomposed calcite as observed from the palm oil methanolysis in which a FAME content of 93.9% was obtained, while only 75.5% ester content was achieved by the calcined calcite(Alamsyah, Tambunan, Purwanto, & Kusdiana, 2007).

2.8.2. Doped CaO Catalysts

Many attempts have been made to promote the activity of CaO by increasing the number of basic sites. A possible approach is to dope CaO that serves as both a catalyst and a carrier with an active ingredient. Both alkali and organic compounds can be used as doping materials. Where a systematic survey of studies using catalysts prepared by loading a compound onto CaO is given, a high FAME yield is obtained in transesterification of different oily feedstocks over doped CaO. A clear correlation between the base strength and the activity is found for alkali-doped CaO catalysts, such as $LiNO_3$/CaO, $NaNO_3$/CaO and KNO_3/CaO.(Vedrine, 2015) Catalysts with alkali metal loading of 5% were prepared by the incipient wetness method, followed by drying performance among alkali doped CaO catalysts in the methanolysis of canola oil whereby the FAME yield of 70.7% is achieved under mild reaction conditions(Saxena, Jawale, & Joshipura, 2013).

The transesterification reaction was also studied in the presence of Li/CaO catalyst prepared by the wet impregnation method with and without thermal activation. Among non-calcined catalysts, the most active catalyst contained 1.23% Li, but higher Li loadings reduced the catalytic activity dramatically. The optimal activation temperature for calcined catalysts is from 773 K to 973 K, but the catalytic activity does not increase significantly with increasing temperature above 773 K(Reyero et al., 2014). Among MgO/CaO catalysts with Mg/Ca molar ratio between 3 and 15, prepared by the coprecipitation method, the catalyst with Mg/Ca molar ratio of 3 is the most active one in transesterification of ethyl butyrate, achieving conversion close to 60% within 3 h, whereas pure MgO is inactive(Shan et al., 2018).

2.9. Production of Biodiesel

Vegetable oils are chemically complex esters of fatty acids. These are the fats naturally present in oil seeds, and known as tri-glycerides of fatty acids. The molecular weight of tri glycerides is high; Because of their high molecular weights these fats have high viscosity causing major problems in their use as fuels in CI engines. These molecules have to be split into simpler molecules so that they have viscosity and other properties comparable to standard diesel oils. Modifying the vegetable oils (to make them lighter) can be achieved in many ways, including; Pyrolysis, Micro emulsification, Dilution and Transesterification. Among these, transesterification is the most commonly used commercial process to produce clean and environmentally friendly light vegetable oil fuel i.e. biodiesel(Ali & Semwal, 2014).

2.9.1. Dilution of oils

Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity and mitigates some engine performance problems such as injector coking and carbon deposits, *etc*. To dilute vegetable oils the addition of 4% ethanol to the oils increases the brake thermal efficiency, brake torque, and brake power while decreasing brake specific fuel consumption. Since the boiling point of ethanol is less than that of vegetable oils, it could assist in the development of the combustion process through an unburned blend spray(Bilgin, Orhan, & Sahin, 2002).

2.9.2. Microemulsions of oils

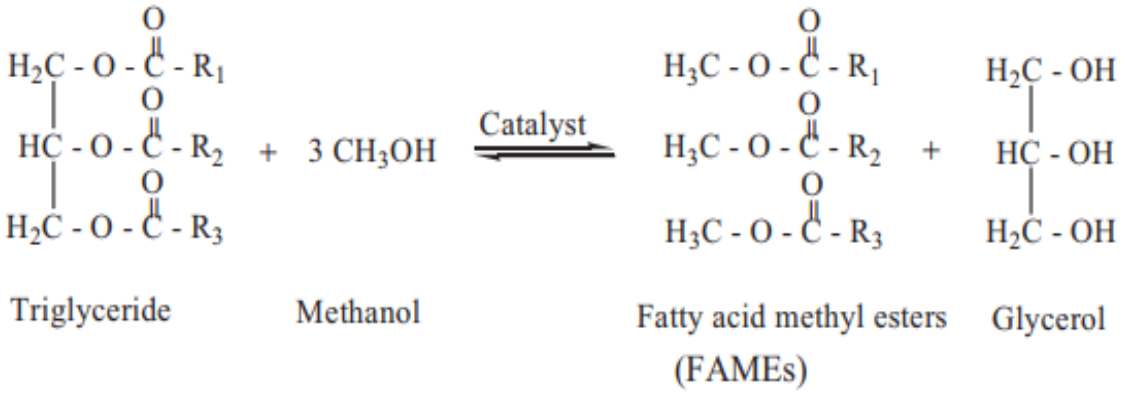
A micro emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphilic(Ma & Hanna, 1999).To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol and 1-butanol have been studied(Atabani et al., 2012).

2.9.3. Thermal cracking (pyrolysis)

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolysis material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum(Ma & Hanna, 1999).

2.9.4. Transesterification

The most common method is the transesterification of vegetable oils or animal fats. In this reaction, triglycerides react in the presence of a catalyst with an alcohol with short-chain to produce diglycerides, and then diglycerides react to produce monoglycerides. Then, monoglycerides react with alcohol to give ester and glycerol as a byproduct, as follows:(Keera, El Sabagh, & Taman, 2018).



Generalized schematic representation of transesterification reaction

The transesterification is usually carried out using primary and secondary alcohols. Methanol is the most used alcohol because it is the least expensive alcohol and it shows chemical advantages such as its shorter chain and its polar nature. Besides it does not form zoetrope, so it is the easier in recovery than ethanol. Transesterification can be carried out using acids (heterogeneous), alkalis (homogeneous), or enzymes as catalysts for the reaction(Keera et al., 2018).

The fatty acid triglycerides themselves are esters of fatty acids and the chemical splitting up of the heavy molecules, giving rise to simpler esters, is known as Transesterification. The triglycerides are reacted with a suitable alcohol (Methyl, Ethyl, or others) in the presence of a catalyst under a controlled temperature for a given length of time. The final products are Alkyl esters and Glycerin. The Alkyl esters, having favorable properties as fuels for use in CI engines, are the main product and the Glycerin, is a by-product. Without the use of a catalyst the reactions would be very slow and also incomplete. A temperature of 333K to 343K would be needed for the reactions to become effective. Also a vigorous agitation of the reactants would be needed and so a mechanized stirrer in the reaction vessel becomes necessary. Various catalysts can be used. The most common are the acid catalysts, like H_2SO_4 and the Alkalies, like NaOH or KOH. For trans-esterification any alcohol can be used (Ali & Semwal, 2014).

$$C_3H_5(OOCR)_3 + 3CH_3OH_3 \longrightarrow 3RCOOCH_3 + C_3H_5(OH)_3$$

Triglyceride Methanol Methyl ester Glycerine

Table 3: Comparison of common biodiesel production technologies

Technologies	Advantage	Disadvantage
Dilution(direct blending or micro-emulsion)	• simple process	• High viscosity • Bad volatility • Bad stability
Pyrolysis	• Simple process • No-polluting	• High temperature is required • Equipment is expensive • Low purity
Transesterification	• Fuel properties is closer to diesel • High conversion efficiency • Low cost • It is suitable for industrialized production	• Low free fatty acid and water content are required(for base catalyst) • Pollutants will be produced because products must be neutralized and washed • Difficult reaction products separation
Supercritical methanol	• No catalyst • Short reaction time • High conversion • Good adaptability	• High temperature and pressure are required • Equipment cost is high • High energy consumption

Source ((Atabani et al., 2012),(Campanati et al., 2003))

2.10. Transesterification methods

Catalysis of transesterification can be done by catalytic, non-catalytic and enzymatic. Non catalytic transesterification mechanism takes place at supercritical conditions. These conditions entail a greater temperature and higher pressure, which is not an economically viable choice, for this reason catalytic transesterification approaches for biodiesel production are more commonly used and more vastly preferred. At low temperature and pressure, basic catalysts have extraordinary activity rate in transesterification. Sulfuric, hydrochloric and sulfonic acids are the major acid catalysts; whereas homogeneous acids and bases have well defined chemical properties; heterogeneous acid and bases exhibit a variety of sites; while heterogeneous catalysts can be categorized by the Brønsted or Lewis nature of sites, acid or base strength of sites and the texture of support(Zhu et al., 2006).

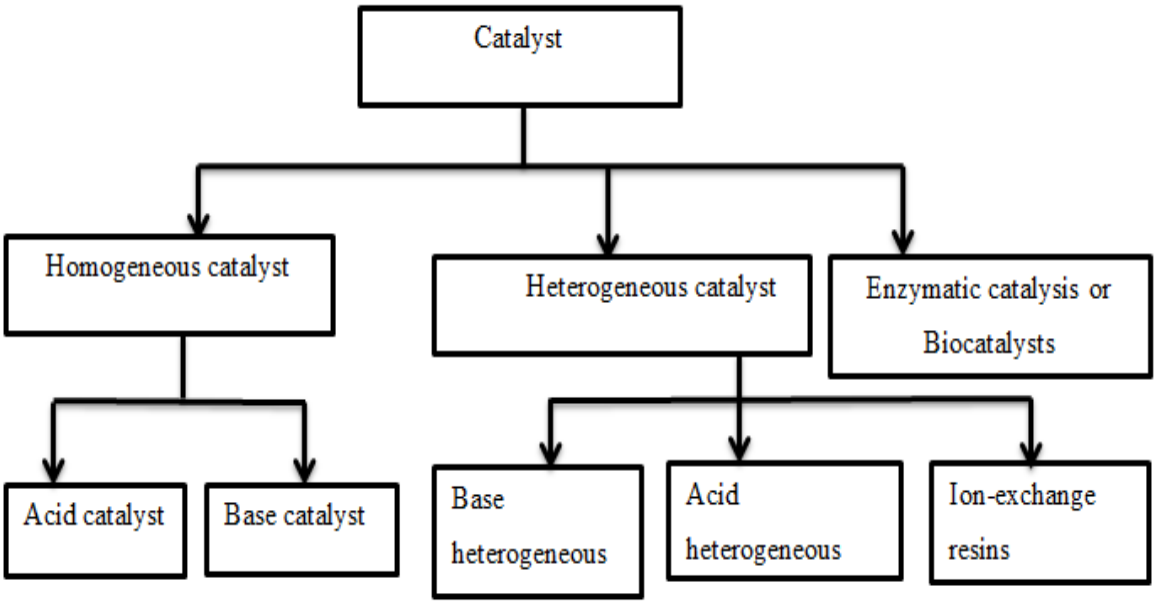


Figure 10: Catalytic Methods(A Demirbas, 2008).

The base catalyzed transesterification process is primary viable heterogeneous process practiced now a day. It has various mechanisms which convert the triglycerides (TG) to FAME with the liberation of glycerol as a byproduct. Specialists are seeking after new catalyst. Additionally, the limpidness of the required feedstock, reaction kinetics and postreaction processing is relying on the used catalyst.

2.10.1. Homogeneous catalysts

Generally, homogeneous chemical catalysts have several advantages, including high selectivity, turnover frequency, reaction rate and effortless optimization of activity. In earlier research acid or alkali was employed as a homogeneous catalyst. The common alkali catalysts being employed are sodium hydroxide (NaOH), sodium methoxide (CH_3ONa), potassium hydroxide (KOH) and potassium methoxide (KCH_3O).NaOH is preferred over KOH because it dissolves quickly in methanol. NaOH is considered in transesterification due to its high purity and low cost; in addition, a relatively low quantity is needed as compared to KOH. Strong alkali catalysts such as NaOH, KOH, CH_3ONa and CH_3OK (potassium methoxide) are used for biodiesel production(Aramendía, Borau, Jiménez, Marinas, & Romero, 1999). However, alkali metal alkoxides are found to be more active than hydroxides. In alkali catalyzed transesterification, even if water-free vegetable oils and alcohol are used, a certain amount of water is formed by the CH_3ONa solution because of the interaction between NaOH and methanol. The presence of water and FFA leads to soap formation by hydrolysis of the triglycerides, which reduces the

biodiesel yield and affects the quality of the product. Product recovery becomes complicated in an alkali-catalyzed transesterification reaction if the oil has >1% FFA; in such an event, part of the process may take the saponification route, thereby forming soap(Balat, 2008). The soap thus formed inhibits the separation of biodiesel and glycerine. Because of this, two-step transesterification—acid first and alkali next—is recommended. The initial acid based esterification effectively reduces the FFA content of the oil and presents the amended oil ready for alkali catalysis. In the esterification of candlenut oil, as a first step, sulfuric acid and acetonitrile were used as catalyst and co-solvent, respectively. The FFA level was reduced to 0.8 wt% and the esterification process continued subsequently as alkaline transesterification using acetone as the co-solvent and KOH as the alkali catalyst. The two-step processes achieved 99.3% biodiesel yield under optimum conditions(Thangaraj, Solomon, et al., 2018).Sulphuric, phosphoric, hydrochloric and sulphuric acids are used in such esterification as well as transesterification reactions; however, sulphuric acid is preferred.

The effect of the type of alcohol being used on the transesterification process indicated that methanol is best suited, with a faster reaction and good ester isolation. The reaction speed is relatively low in ethanol use, and the ester recovery also is low(Boey et al., 2011). The effect of different alcohols on biodiesel production from different vegetable oils has also been investigated. Methanol is a better reactant with vegetable oils than other alcohols (ethanol, 2-propanol and 1-butanol)(Bourikas et al., 2006). Biodiesel production using methanol as compared with ethanol is recommended because the ethanol purity is less than that of methanol. Ethanol procurement is relatively difficult and expensive. Long-chain alcohols such as 2-propanol and 1-butanol are also recommended for biodiesel production, especially when a high oil/alcohol (1:70) ratio is employed. 2-Propanol may not give a high yield of biodiesel in a shorter reaction time because of its branched chain and it also needs a high temperature to dissolve the alkaline catalyst. 1-Butanol also requires heat energy to dissolve the alkaline catalyst(Thangaraj, Raj Solomon, et al., 2018). The reactivity of 1-butanol is lower than that of 2propanol. Long-chain alcohols need a higher reaction temperature than methanol. In addition, 2-propanol and 1-butanol tend to retain the wash water. This phenomenon may increase the production cost and time. An increased stirring speed enhances the yield of biodiesel because uniform mixing of oil and alcohol is ensured. In the mixing process, a turbine impeller performs better than paddles.

2.10.2. Heterogeneous catalysts

Heterogeneous catalysis is the type of catalysis where the phase of the catalyst differs from the phase of the reactants. This contrasts with homogeneous catalysis where the reactants and catalyst exist in the same phase. Phase distinguishes between not only solid, liquid, and gas components, but also immiscible mixtures (e.g. oil and water), or anywhere an interface is present. Catalysts are useful because they increase the rate of a reaction without themselves being consumed and are therefore reusable. Heterogeneous catalysis typically involves solid phase catalysts and gas phase reactants. In this case, there is a cycle of molecular adsorption, reaction, and desorption occurring at the catalyst surface. Thermodynamics, mass transfer, and heat transfer influence the rate (kinetics) of reaction(Thangaraj, Raj Solomon, et al., 2018).

Heterogeneous catalysts are known to improve the transesterification process by eliminating the extra processing costs involved in homogeneous catalysis, as well as reducing the generation of pollutants. Heterogeneous catalysts promote easy recovery, reusability and a cost effective green process. These catalysts tolerate high FFA and moisture content. Efficient and inexpensive heterogeneous catalysts help to minimize the overall cost of biodiesel production. Heterogeneous catalysts are considered integral in certain harsh conditions such as high temperature and pressure(Dahdah et al., 2020). These catalysts are easy to recover from the reaction mixture, are capable of withstanding aqueous treatment steps and are amenable to modification to obtain high activity, selectivity and longer catalyst lifetimes.

Heterogeneous catalysts can be designed to bring out grafting and entrapment of the active molecules on the surface of or inside the pores of a solid support such as silica, alumina or ceria. Alkali earth metal oxides, transition metal oxides, mixed metal oxides, ion exchange resins and alkali metal compounds supported on alumina or zeolite are used in various chemical reactions such as isomerization, aldol condensation, Knoevenagel condensation, Michael condensation, oxidation and transesterification. Alkaline earth metal oxides are successfully used as catalysts which include BeO, MgO, CaO, SRO, BaO and RaO.MgO and SrO. SRO (strontium oxide) has high basicity and is not lost in methanol due to solubility. It maintains its efficiency for up to 10 cycles(Yusuf et al., 2011).

2.11. Global Situation of Biodiesel Production

Nowadays, the demand for fuels continues to increase due to the rapid growth of the global economy and population, leading to the imminent exhaustion of fossil fuel resources and environmental pollution. Given such a global energy situation, large-scale production of renewable, clean energy has become an urgent agenda in all over the world. Currently, the global productivity of biodiesel is on a rising trend, reaching more than 30 million tons/year worldwide because of the positive government policies and incentives (e.g., fiscal subsidies, tax preference, etc.)(Alamsyah et al., 2007). However, it still has an insignificant share in the present global diesel market. Currently, biodiesel has been considered as a main complement of fuels in transportation, and the worldwide demand for biodiesel has been increasing dramatically(Aransiola, Ojumu, Oyekola, Madzimbamuto, & Ikhu-Omoregbe, 2014). In 2014, global biodiesel production was about 25.2 million tons, 37.1% of which was produced in European Union (EU), 16.7% in the United States, 11.9% in Brazil, and 10.7% in Argentina(Aransiola et al., 2014). The (European Union) EU has the most technologically developed biodiesel industry, which benefits from many encouraging policies successfully implemented in the EU countries. According to the renewable energy directive (RED), greenhouse gas emissions should be reduced by 20% compared with 1990, while renewable energy must contribute to 20% of the EU total energy by 2020(Berhane, 2007). On the other hand, fuel quality directive (FQD) also required that the greenhouse gas emissions by transport industry should be reduced by 10%, of which 6% has been projected to be achievable by using biofuels by 2020(Atabani et al., 2012). However, the subsidies have been frozen for the first-generation biofuels derived from food in the EU since 2014, while the green light has been turned on for the development of the second and third generations of biofuels in the EU(Ayhan Demirbas, 2008b).

The United States is the world's second largest producer of biodiesel mainly derived from soybean oil(Yang & Xie, 2007). About 4.13 million tons of biodiesel was produced in 2014, and the demand had been projected to be 10% of total fuel consumption in the United States by 2020(Ali & Semwal, 2014). Currently, B10 biodiesel (i.e., 10% of biodiesel+90% of petroleum diesel) and B20 biodiesel (i.e., 20% of biodiesel 20%+80% of petroleum diesel) have been widely accepted with a market share of about 8% of the total transportation fuels(Aransiola et al., 2014). Brazil is the largest producer of biodiesel in South America, and also the world's fourth largest producer. Naturally Brazil is very rich

in feedstock for biodiesel production, for example, soybean oil, castor oil, cottonseed oil, etc.(Yang & Xie, 2007). Currently, there is a strong demand for biodiesel with the annual consumption of about 30 million tons diesel in Brazil, of which 8%–10% still needs to be imported. In South America, the biodiesel market is also developing very fast in Argentina, Colombia, Peru, and Ecuador(Mardhiah, Ong, Masjuki, Lim, & Lee, 2017).

The biodiesel industry in Southeast Asia is expanding due to its extremely rich resource of palm oil(Verma & Sharma, 2016), more than 85% of the world palm oil is produced in Malaysia and Indonesia. In 2014, Malaysia had over 35 biodiesel plants, with the annual production capacity of 2.5 million tons. To accelerate the biodiesel industrialization, many tax-reducing policies and subsidies are being formulated in Malaysia(Yusuf et al., 2011). Similarly, the biodiesel industry is also growing in Indonesia, with the total production capacity of more than 2.8 million tons yearly(Frías, Villar, & Savastano, 2011). Although African countries (e.g., Ghana, Mozambique, Kenya, etc.) have abundant natural resources of Jatropha and palm which are suitable for biodiesel production, there is a lack of infrastructure and investment, which seriously hinder the business development of biodiesel(Bernhardt & Notcutt, 1993).

Rising world fuel prices, the growing demand for energy, and concerns about global warming are the key factors driving the increasing interest in renewable energy sources and in biofuels in particular. This is more relevant for countries like Ethiopia that spend a considerable share of foreign currency reserves on fuel imports and consumes considerable biomass for domestic energy consumption(Adem, 2009). In 2005/06 fiscal year, Ethiopia used 86% of total export earnings on fuel imports(Rosegrant Mark W, 2006). Biomass accounted for about 92% of the country's total energy demand. Under the current scenario, the share of diesel energy requirement is about 58% of the total energy requirement in Ethiopia(Adem, 2009). In this regard, it seems that the priority for ethanol based biofuel development is highly associated with the sugar industry. The government promotes this strategy through the establishment of the public Ethiopian Sugar Corporation (ESC), which is given the mandate of expanding and developing huge sugar estates along with processing capacity. Under the current scenario, the share of diesel energy requirement is about 58%of the total energy requirement in Ethiopia. In this regard, it seems that the priority for ethanol based biofuel development is highly associated with the sugar industry. The government promotes this strategy through the establishment of the public Ethiopian Sugar Corporation (ESC), which is given the mandate of expanding and developing huge

sugar estates along with processing capacity. The main product of these will be sugar, and molasses for ethanol will be produced as a by-product(Adem, 2009).

2.13. Effect of the Different Parameters on Biodiesel Production

There are important parameters that influence the biodiesel production process. In order to obtain the maximum yield of biodiesel, these parameters must be optimized.

2.13.1. Reaction Temperature

A higher reaction temperature can decrease the viscosities of oils and result in an increase in reaction rate as more energy is being supplied for the reaction to occur. Thus the yield of the biodiesel product is improved. The rate of reaction is dependent upon the reaction temperature. In the alkali transesterification reaction, the temperature maintained by researchers during different steps ranges between 318 and 338K(Aramendía et al., 1999). The boiling point of methanol is 337.9 K. Temperatures higher than this will burn the alcohol and will result in much lower yield. It has been observed that temperatures higher than 323 K have a negative impact on the product yield for neat oil, but a positive effect for waste oil with higher viscosities. Therefore, the reaction temperature must be less than the boiling point of alcohol (the boiling point of methanol is 333–343K at atmospheric pressure) to ensure the alcohol will not be lost through vaporization(Aransiola et al., 2014). Also, the yield of biodiesel decreases if the reaction temperature goes beyond its optimum level because a higher reaction temperature will accelerate the saponification reaction which results in a lower yield. Depending on the type of oil, the maximum yield is obtained at temperatures ranging from 333 to 353K(Verma & Sharma, 2016).

2.13.2 .Reaction Time

The conversion rate increases with reaction time. For base-catalyzed transesterification, the yield of biodiesel reaches a maximum at a reaction time of 120 min or less. Acid catalyzed transesterification requires an even longer reaction time than the base-catalyzed reaction because base catalysts usually exhibit a higher reactivity than acid catalysts. The reaction time needed during the conversion of TGs to biodiesel may range from 18 to 24 h(D'Cruz et al., 2007) .However; an excessive reaction time will lead to a reduction in the product yield due to the back reaction of transesterification, causing more fatty acids to form soaps(Kafui Ayetor, Sunnu, & Parbey, 2015).

2.13.3. Catalyst Concentration

Catalysts are classified as alkali, acid, or enzyme(Dahdah et al., 2020). Alkali-catalyzed transesterification is much faster than acid-catalyzed. However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid(Di Serio et al., 2010). Alkalis include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, and potassium amide and potassium hydride. Sodium methoxide was more effective than sodium hydroxide because of the assumption that a small amount of water was produced upon mixing NaOH and MeOH. The presence of a catalyst such as calcium oxide (CaO) accelerated the methyl ester conversion from sunflower oil at 525 K and 24 MPa even if only a small amount of catalyst (0.3% of the oil) was added(Demirbaş, 2008). The transesterification step accelerates with the increase in CaO content from 0.3 to 3%. However, further enhancement of CaO content to 5% little increase in the yield of methyl ester.

2.13.4. The effect of molar ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. The practical range of molar ratio was from 3.3 to 5.25:1 methanol to vegetable oil. The ratio of 4.8:1 was used in some examples, with a yield of 97–98%, depending upon the quality of the oils(Joshi et al., 2015). If a three step transesterification process was used, the ratio was reduced to 3.3:1. Methanol present in amounts of above 1.75 equivalents tended to prevent the gravity separation of the glycerol, thus adding more cost to the process. Higher molar ratios result in greater ester conversion in a shorter time. One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol(Kouzu & Hidaka, 2011). The molar ratio is associated with the type of catalyst used.

2.13.5. The effects of moisture and free fatty acids

Water can cause soap formation and frothing. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and make the separation of glycerol difficult. Water has a more negative effect than the presence of FFA, and hence the feedstock should be

water-free. It was shown that even a small amount of water (0.1%) in the transesterification reaction will decrease the ester conversion from vegetable oil(Kumar & Ali, 2013). The presence of water and FFA in raw materials resulted in soap formation and a decrease in yield of the alkyl ester, consumed catalyst and reduced the effectiveness of the catalyst. The presence of water had a positive effect in the yield of methyl esters when methanol at room temperature was substituted by supercritical methanol(Lee et al., 2009).

The starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more CaO was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult. Also stressed the importance of oils being dry and free (<0.5%) of free fatty acids(Vedrine, 2015). ester yields were significantly reduced if the reactants did not meet these requirements. Calcium Oxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness. Transesterification does not require a nitrogen environment(Verma & Sharma, 2016). The reactor was open to the atmosphere via a condenser. Oxygen dissolved in the oil escaped to the atmosphere when the reactant was heated. In addition, alcohol vapour facilitated this process.

2.14. Catalyst leaching

Leaching affects the industrial application as extensive leaching may threaten the reusability and the environmental sustainability of catalyst (Granados et al., 2007). Ca concentration in the biodiesel is limited by strict regulations; moreover, the degree of leaching directly affects the number of runs that the catalyst can be reutilized when operating in batch-wise mode or the time of operation when working in a continuous process. Many studies about the use of heterogeneous catalysts for transesterification treated anti-leaching performance as issue of equal importance to catalytic activities. The deactivation mechanism of heterogeneous catalysts towards transesterification can be classified into the leaching of active species and the adsorption of acidic hydrocarbons onto basic sites. The deactivation tests usually take the form of repeating the reaction cycle several times and measuring the catalytic activity in the interval between each cycle. If the deactivation of the catalyst is unavoidable, a method for regenerating its initial activity was

suggested in most cases(Lee et al., 2009). Larger amount of leached species was observed when glycerol is present because Ca diglyceroxide is formed due to the reaction between CaO and glycerol and this is a more soluble compound than CaO(Granados et al., 2007).

some soluble substance was leached away from the CaO solid base catalyst during the transesterification reaction(Reyero et al., 2014). The amount of the soluble substance corresponded to 10.5 wt% of the employed catalyst. They also suggested that the reaction was catalyzed not only by basic sites on the surface but also by the soluble substance. This was due to moisture produced by transforming calcium oxide into calcium diglyceroxide at the beginning of the reaction. Although the leaching of solid base catalyst was inevitable even in this case, the soluble substance could be completely removed from the produced oil by cation-exchange resin. With the help of the purification technique, calcium oxide can be reused. On the other hand it means, showed that the catalytic activity was slightly reduced by turning calcium oxide into calcium glyceroxide, but the change in the chemical composition of the solid base catalyst provided a tolerance to air-exposure. This property offers an advantage for the practical use of the catalyst, because deterioration of the catalytic sites by CO_2 and H_2O contained in air is the established theory on solid base. Due to the tolerance to air-exposure, decrease in the catalytic activity was not obvious when the reaction was successively repeated with reusing the collected catalyst. The ultrasonic assisted transesterification of palm oil in the presence of alkaline earth metal oxide catalysts (CaO, SRO and BaO). It was found that BaO had the highest residual elements detected in biodiesel with nearly 14 wt. % of the catalyst leached into the biodiesel layer after the reaction(Mootabadi, Salamatinia, Bhatia, & Abdullah, 2010). Meanwhile, CaO had the minimum solubility with only 0.04 % weight loss. This result indicated that BaO had the highest solubility in biodiesel and appreciable leaching occurred.

Leaching of active species was observed in the reaction medium when the catalyst was activated at high temperature. However, the amount of leaching did not result in catalyst activity reduction and the catalyst was reusable for 8 cycles(Granados et al., 2007).The catalytic reaction is assumed to be the result of the heterogeneous and homogeneous contributions; part of the reaction takes place on basic sites at the surface of the catalyst and the rest is due to the dissolution of the activated CaO in methanol that creates homogeneous leached active species. The activity CaO catalyst used in transesterification was stable after 20 cycles of the reaction and the biodiesel yield at 1.5 h was not affected

much in the repeated experiments(Semwal et al., 2011).the stability of alkali-doped metal oxide catalysts for application to biodiesel production, concluding that metal leaching from the catalyst was detected, and this resulted in some homogeneous activity(Macleod, Harvey, Lee, & Wilson, 2008). The pointed out that this drawback would need to be resolved before scaling-up biodiesel production. the behavior of one of the more promising heterogeneous catalysts (TiO_2 supported on SiO_2) was investigated to verify its activity and the eventual leaching effect(Di Serio et al., 2010). The study was further deepened in batch and continuous reactors by using the catalysts in pellets, to evaluate the possibility of developing an industrial process based on this catalyst. The catalyst life-time run, in a continuous tubular reactor, was determinant for this evaluation. In such a case, the catalyst performances have been determined in both a batch and a tubular continuous reactor to evaluate the suitability of this catalyst for the development of an industrial process. It was shown in the study that only a slow leaching effect was present(Waidee, Unpaprom, & Ramaraj, 2018). This effect cannot easily be evidenced in batch conditions also by repeating many times the batch runs on the same catalyst, while, continuous runs in tubular reactor are determinant for evaluating deactivation effects and industrial suitability.

CHAPTER III

MATERIALS AND METHODS

Materials;

Methods;

Procedures;

3. MATERIALS AND METHODS

In this chapter, the details of experimental methods and procedure for the main processes;(1)pre-treatment for catalyst and biodiesel feed stocks,(2) solid catalyst synthesis through calcination of chicken eggshell and impregnation of CaO with metal oxide and(3) transesterification for sunflower oil. During transesterification process, response surface methodology (RSM) with CCD applied for parameter optimization. Further, the chapter elaborates about the solid samples characterization (solid catalyst) using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Basicity.

3.1. Materials

Raw materials which were required for this thesis work were Sunflower oil used as main reactant. Chicken eggshell were collected from different restaurants, and used as raw material for synthesis of heterogeneous base catalyst. Chemicals which were required for main reactant such as methanol and other property test chemicals such as, phenolphthalein, and Zn $(NO_3)_2.6H_2O$ (98.5%, Merck), KNO_3 (99%, Merck), were used as precursors for catalyst preparation were purchased from Supply PLC private chemical store Company in Addis Ababa, Ethiopia.

3.2. Equipment

Equipment used for different experimental works, characterization tests and different treatment processes in the present study are summarized in Table 4

Table 4: Major equipment used for the present study and their purpose

Items	**Purpose**
Equipment for sample characterization and pre-treatment	
Three neck round bottom flask	For Transesterification reaction
Hot plate with magnetic stirrer	To overcome homogeneity of reactants
Coffee grinder	To reduce the size of chicken eggshell
Analytical balance	Mass measurement
Glass beakers	Sample and product collection
Oven	Moisture removal
Muffle Furnace	For calcination
Titration instruments	For titration
Conical flask	For solution preparation

FTIR and XRD	For product characterization

3.3. Methodology

3.3.1 Calcium oxide (CaO) preparation

Sample preparation

The chicken eggshell was collected from local restaurant (Figure 11). The shell was washed several times with tap water to remove impurities adhering to the shells and rinsed with deionized water. Then egg shells soaked in hot water for 5-10 min. washed with tap water repeatedly to remove impurities. Further, the soaked shell was dried in oven at temperature of 105ºC for 24hr, then crushed with coffee grinder to a uniform size by sifting the powder using a sieve of 120mm meshes and ready for calcination.

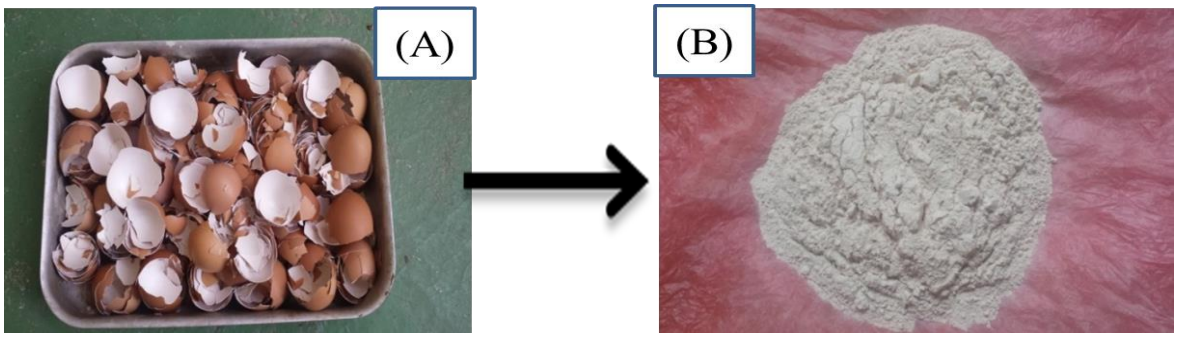


Figure 11: Waste chicken eggshells (A) Collected eggshells and (B) pre-treated and grinded eggshell

3.3.2. Calcination process

About 100 g of grinded chicken eggshell that pass 120mm mesh sieves was calcined in a furnace at atmospheric oxygen conditions at different temperatures 700°C 800°C 900°C and 1000°C for 2h, to convert the calcium species presents in the shells into CaO particle. After calcinations process completed a cold solid is obtained was measured and the structure of metal oxide was characterized using X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The structure of metal oxide was characterized using X-ray diffraction. The XRD pattern from the samples results were compared to the metal oxide CaO standard pattern and then further characterized using FT-IR spectroscopy to identify of functional groups of metal oxide.

3.3.3 Fabrication CaO Impregnation Catalyst

The incorporation of metals was carried out by impregnation of the Zinc nitrate (Zn $(NO_3)_2.6H_2O$ (98.5%, Merck)) on CaO support by using wet-incipient method with

aqueous solutions of their Zinc nitrate. Five gram of CaO was suspended in 30 mL of deionized water. To this 5 mL of aqueous solution of (3 wt%, 4wt%, 5wt %) of Zinc nitrate was added. The reaction mixture thus obtained was stirred for 4h at room temperature. The reaction mixture was filtered and the solid material was dried in air, then in oven at 120ºC for 4 hr and finally calcined in a muffle furnace at 600ºC. The catalysts thus prepared were characterized by powder XRD and FT-IR Techniques.

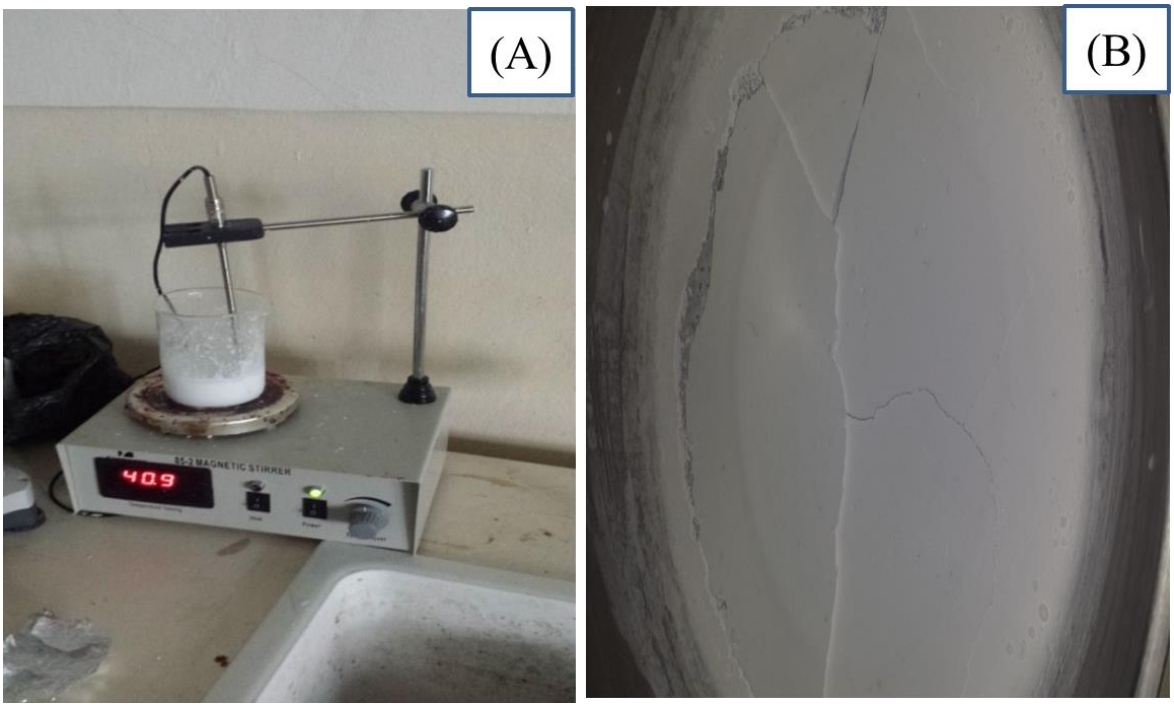


Figure 12: Impregnation process (A) Ca-Zn impregnation of catalyst and (B) Ca-Zn impregnation after drying in oven

3.4. Characterization of Catalyst

X-Ray Diffraction (XRD)

The purpose of X-ray diffraction analysis is to identify the structure, crystallinity and formation of a metal oxide in the material. The X-ray diffraction patterns of CaO and metal impregnated CaO based catalysts prepared were recorded on match Multi-Purpose X-ray diffractometer, PANalytica) with monochromated Cu Ka radiation (k-1.54 Å)**.**The structure of the calcium oxide calcined was characterized using X-Ray Diffraction (XRD). XRD is one of the most commonly used techniques for either crystalline or amorphous phase identification. In this technique, the catalyst sample is irradiated with X-ray of a known wavelength (λ). The samples were placed on a sample holder made up of silicon wafer and the measurements were taken continuously from 10^{o} to 70^{o} angles over the range

of 2θ. The resultant intensity data was processed by using origin 8 software to draw graph and analyze the peak position.

Fourier Transform Infrared Spectroscopy (FT-IR)

In order to verify the presence of characteristic absorption bands of CaO and ZnO, the FTIR spectra were collected by using a Nicolet Impact 410 spectrometer in transmission mode, from KBr pellets of solid samples; a total of 200 scans were averaged at a resolution of 4 cm^{-1}.Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared intensity versus wavelength (wavenumber) of light. The FT-IR spectra were recorded in KBr (0.3% w/w) disks in the wavelength region of 4000–400 $cm^{-1}$with a Perkin Elmer 1760 X FT-IR spectrometer.

Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. Hence, the correlation of the band wavenumber position with the chemical structure is used to identify a functional group in a sample. The wavenumber positions where functional groups adsorb are consistent, despite the effect of temperature, pressure, sampling, or change in the molecule structure in other parts of the molecules. Thus the presence of specific functional groups can be monitored by these types of infrared bands, which are called group wavenumbers.

3.5. Determination of Basicity of the Catalyst

Basic strength of the CaO (cesp) and other metal impregnated CaO (cesp) catalysts was determined by using Hammett indicators. The basicity (total basic sites) of the catalyst was measured by titration method following the procedure reported in the literature (Vedrine, 2015). For each catalyst, 20 mg of sample was put in a beaker containing 5 mL of 0.02 M aqueous HCL and the mixture was stirred for 1h at room temperature. The remaining acid was then titrated in the presence of three drop of phenolphthalein as indicator using 0.02 M aqueous NaOH as the titrant. The titration was continued until the end point (colorless to pink color) is recognized. Basicity in mmol/g was calculated as follows (Eq.3.1):

$$\text{Basicity} = \frac{\text{volume of HCL} * \text{Normality of HCL} - \text{volume of NaOH} * \text{Normality of NaOH}}{\text{Mass of Catalyst}} \quad \text{.....3.1}$$

The Basic strength of catalyst was determined by a Hammet indicator titration, catalyst was shaken with Hammet indicator and left to equilibrate for 1hr (Figure 13.). Colour changes were observed and phenolphthalein (H_9.3) was used as Hammet indicator.

Figure 13: Determination of Basicity of Catalyst

3.6. Testing Catalysts for Transesterification Reaction

Transesterification of sunflower oils with methanol were carried out in a transesterification reactor with 250 mL three-neck round bottom flask and water-cooled reflux condenser. The reactor was also equipped with an oil bath with digital temperature controller for heating purpose. Amount of catalyst was suspended in required volume of methanol and heated under a control temperature of 65ºC (±2ºC) for 5 min, and then the desired amount of oil was added to the reaction mixture. The reaction mixture was stirred at 500 rpm from literature for required time duration. After the completion of the reaction the catalyst was separated by filtration and the excess methanol was recovered by evaporation at reduced pressure. The mixture was then washed three to four times with lukewarm distilled water to remove the glycerol formed. The mass thus obtained was dried with anhydrous sodium sulphate. The transesterification of oil was carried out under different reaction conditions in order to optimize the best condition, such as catalysts loading from 1 to 5 wt%, reaction time from 0.5 to 3 h, reaction temperature from 30ºC to 70ºC and methanol to oil ratio from 6:1 to 18:1. After the reaction finished, the biodiesel product (FAME) was separated after aged for 24h forming 3 layers (residual methanol, FAME, and glycerol as well as used solid catalyst) and the yield of biodiesel calculated (Eq.3.2).

$$\text{Yield} = \frac{\text{FAME}}{\text{mass of oil used}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Screening of the catalytic activity of ZnO-impregnated calcined egg shells catalyst was carried out to obtain catalyst with better loading. In order to compare the performance of the prepared catalysts, the same reaction conditions(methanol to oil molar ratio of 9:1, catalyst loading of 3wt%, reaction temperature of 65^{o}C,for 2h.reaction time) and feedstock(sunflower oil) were used for each catalyst in all the transesterification processes. Catalyst with high basicity and FAME yield was selected for further investigation and its properties were studied.

3.7. Catalyst reusability and stability

One of the most important features for a heterogeneous catalyst is the ability to be recycled. Reusability of CaO catalyst obtained by the calcination at the optimum conditions concluded in this study was examined with 3 wt% catalyst loading (based on oil weight), a methanol to oil ratio of 9:1, a reaction temperature of 65 °C and a reaction time of 2 h. After each cycle, the solid catalyst was separated from the reaction mixture by filtration and washed with n-hexane to remove the adsorbed stains without further treatment.

After each reaction, the solid CaO catalyst was separated from the reaction mixture by filtration and washed with methanol and hexane to remove the adsorbent such as glycerol, triglyceride and biodiesel and it was reused again without any further treatment. After completion of the transesterification reaction employed at the optimal conditions, the catalyst was collected from the reactant mixture by filtration; the catalyst was washed with hexane several times to remove the adhered oil particles, and then dried at 110°C for 2 h. To evaluate catalyst stability, the optimum amount of CaO that was obtained by examining the operating condition was stirred with methanol at the optimum conditions obtained.

3.8. Design of Experiments

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to investigate the interaction effect of process variables and to optimize this response. It has been applied for optimization of several chemical and physical processes. RSM design features called central composite design (CCD) was applied to study the interaction and cross effect of transesterification reaction variables. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments,

as well as to analyze the interaction between the parameters. Generally, the CCD consists of a 2^n factorial runs with 2n axial runs and n_c center runs.

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA).The analysis of variance will be used as one of the primary tools for statistical data analysis. The Design Expert 6.0.8 program was used in the regression analysis and analysis of variance. The Statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent constant variables. The most extensive applications of RSM are in the industrial world, particularly in situations where several input variables potentially influence performance measures or quality characteristics of the product or process. These performance measures or quality characteristics are called the response. They are typically measured on a continuous scale, although attribute responses, ranks, and sensory responses are not unusual. Most real world applications of RSM will involve more than one response. The input variables are sometimes called independent variables, and they are subject to the control of the engineer or scientist, at least for purposes of a test or an experiment. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables).

The dependent variables selected for this study were (i) x_1, methanol/oil molar ratio; (ii) x_2, reaction time and (iii) x3catalyst amount.(iiii) Reaction temperature selected as dependent variable. A statistical optimization was conducted by using CCD. Methanol/ oil molar ratio, reaction time and catalyst amount were chosen as independent variables in the experiment, each considered at two levels namely; low (-1) and high (+1). For each categorical variable, a 2^3 full factorial CCD for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the center points were employed, indicating that altogether 20 experiments were required, as calculated from the following equation:

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 3 + 6 = 20 \quad \text{.....3.3}$$

Where N is the total number of experiments required and n is the number of factors. The center points are used to determine the experimental error and the reproducibility of the data. The independent variables are coded to the (-1, 1) interval where the low and high levels are coded as -1 and +1, respectively. The axial points are located at (±α, 0, 0),(0, ±α, 0) and (0, 0,±α) where α is the distance of the axial point from center and makes the design rotatable.

CHAPTER IV

RESULTS AND DISCUSSION

Synthesis and characterization of catalysts;

Heterogeneous Catalyst performance;

Synthesis and Parameter Optimization for Transesterification Process;

Catalyst reusability;

4. RESULTS AND DISCUSSION

In this chapter, the details of experimental results; (1) Calcination of chicken Eggshell at different temperature and best Calcination temperature are selected (2) best calcination temperature and calcination time of a mixture of chicken eggshell catalyst and zinc nitrate are selected by comparing the basicity and conversion of sunflower Oil to fatty acid methyl ester (3) different characterization results for efficient catalyst produced from mixture of chicken eggshell and zinc nitrate such as, Fourier Transform Infrared Spectroscopy (FT-IR) and X-Ray Diffraction (XRD) are discussed, (4) transesterification reaction results for different reaction conditions are presented and optimum condition are selected based on maximum Fatty acid methyl ester (FAME) yield, and finally the characterization result Fourier Transform Infrared Spectroscopy (FT-IR)of FAME taken from optimum condition are qualitatively presented,(5)reusability and leaching of selected catalyst are studied at different cycle.

4.1. Catalyst Screening

The reaction conditions were not optimized for the highest reaction yield for each catalyst; however, they provided a way to compare the activities of catalysts, when the basic catalyst was loaded on the supports and activated at a high temperature, the supported catalyst showed activities toward the sunflower oil transesterification. The activity of the prepared catalysts, having different basic strengths towards the transesterification of sunflower oil with methanol, was measured in terms of methyl esters yield. Calcined eggshells at 600ºC loaded with precursor had the superior catalytic activity giving the highest yield of 82% over 2h in a reflux of methanol, compared to the neat calcined eggshells 900ºC catalysts giving of 70% yield; Calcined eggshells loaded with mixed oxides have high basic strength, therefore it gives more yield than neat calcined eggshell.

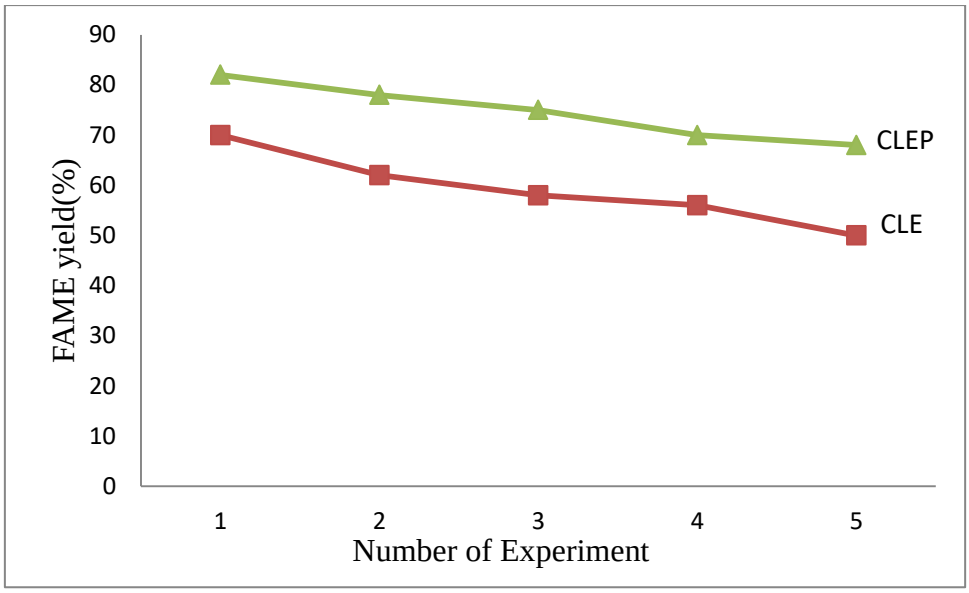


Figure 14: Catalyst Screening

Note; CLE; neat calcined Eggshells, CLEP, Calcined egg shells loaded with precursor

4.2. Synthesis of Catalyst

The amount of chicken egg shell used for calcination was 100g. This powder was calcined at different temperatures such as 600ºC, 700ºC, 800 ºC, 900ºC and 1000ºC with constant time of 2h. During calcination weight loss was observed.

4.2.1 Calcination of Eggshell

The Eggs shell was subjected to different temperature of calcination. The calcination time and temperature changed the catalyst structure; consequently, this affects catalyst activity and the concentration of FAMEs produced. The chicken eggshell powder that was decomposed in the furnace at different temperatures 600ºC, 700 °C, 800 °C, 900 °C, and 1000 °C were shown physically different in colour to the eggshell powder after calcined. Calcination at temperature of 600 °C produced powder in black colour, at 700 °C produced black powder mixed with gray, at 800 °C formed solid gray, at 900 °C calcination obtained white solid with little gray, and at 1000°C obtained white solid. The higher calcination temperature, the more metal oxide was formed indicated from the change of the colour of the chicken eggshell powder became white. Picture of chicken eggshell and eggshell after decomposed at various temperatures are presented in Figure 15.

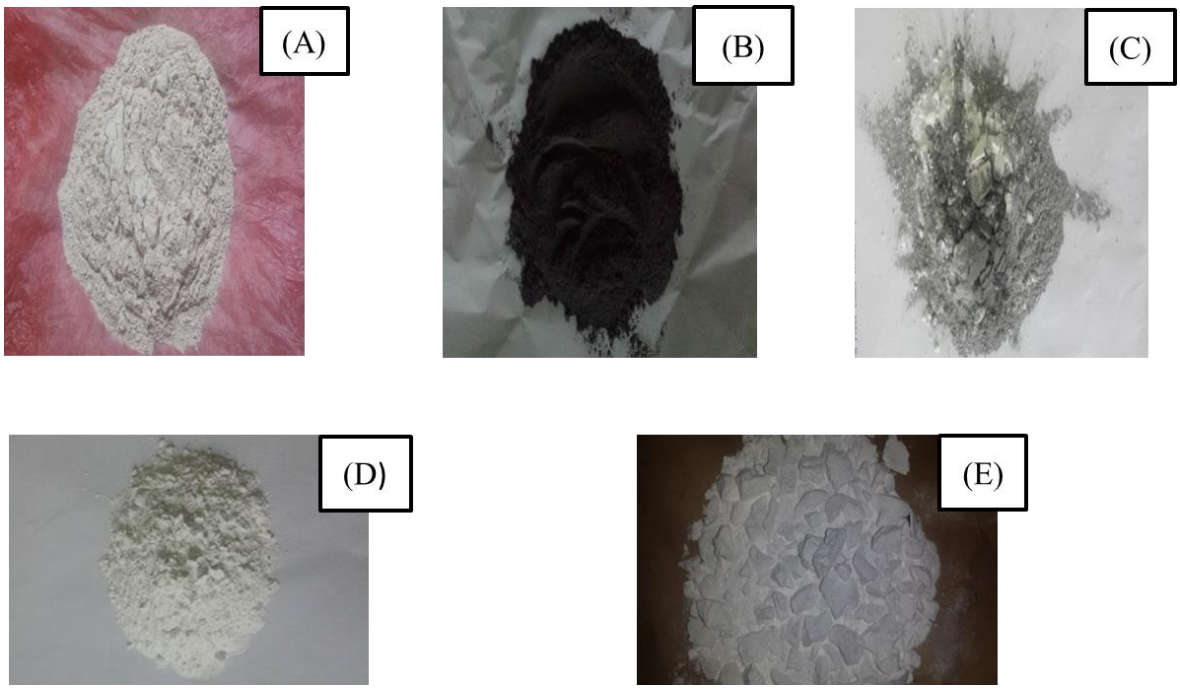


Figure 15: Chicken Eggshell powder (A) before Calcined and Eggshell powder after calcined at various temperatures (B) 700ºC, (C) 800ºC, (D) 900ºC, (E) 1000ºC

The results also have differences lost weight of the samples before and after calcination. The $CaCO_3$ which is the main component of eggshells are known to have a decomposition temperature at 900 ºC. At temperature of 600ºC and 700°C the samples reduction in weight ranged up to 5wt%, this is due to the loss of organic compounds contained of eggshell which known to have about 4wt% in the eggshell. Organic compounds are easily damaged and lost at temperatures above 100°C. In both calcination temperature above is not yet formed metal oxide CaO, while at 800 ºC the sample weight was reduced by 26%, perhaps at this temperature the $CaCO_3$ has been converted into CaO and CO_2, but only in slightly amounts. The calcination temperature at 900ºC reduced the sample weight by 46wt% indicated that the decomposition temperature of $CaCO_3$ to CaO and CO_2. At calcination temperature 1000ºC the sample weight reduced by 52.8wt%, the sample weight becomes lowest as it converted into CaO and gas-phase of CO_2. The results also have differences lost weight of the samples before and after calcination. The $CaCO_3$ which is the main component of eggshells are known to have a decomposition temperature at 900ºC. Organic compounds are easily damaged and lost at temperatures above 100°C.

Table 5: Effect of eggshell calcination temperature on weight loss and yield of Fatty acid methyl ester (FAME)

Calcination Temperature(ºC)	Weight loss (%)	Basicity(mmol HCL/g of catalyst	FAME yield (wt %)
Non-calcined	=	0.8	=
CLEG-600	4	9.02	49.8
CLEG-700	5	10.08	56.4
CLEG-800	26	11.21	62
CLEG-900	46	11.58	70
CLEG-1000	52.8	11.42	68

Note: CLEG: calcined eggshell at different temperature

4.2.2. Eggshell based CaO Impregnation

As it has been mentioned, the chicken eggshell has been modified via calcination followed impregnation process with zinc nitrate (Five gram of CaO was suspended in 30 mL of deionized water. To this 5 mL of aqueous solution of (3 wt%, 4wt%, 5wt %) of Zinc nitrate was added.) for 4h from different literature data through the wet impregnation method. Specifically, the catalysts (CaO/ZnO) were treated at temperature of 600ºC. The optimal yield of FAME obtained was around 82% using the catalyst CaO/ZnO. However in the case of the prepared catalyst modified with zinc nitrate precursor, the yield of biodiesel produced was high due to have high basic strength.

Table 6: Basicity for catalyst samples

Catalyst name	Basicity (mmol HCL/g catalyst)
CLEGZ-1	12.69
CLEGZ-2	12.81
CLEGZ-3	12.75

CLEGZ: Impregnated catalyst after calcination

4.3. Characterization of Synthesized catalyst: XRD, FTIR and Basicity analysis

4.3.1 XRD Analysis

The results of XRD determination of chicken eggshell powder and after calcination show differences XRD diffraction patterns, where each pattern indicates the different structure of

compounds. The differences in the diffraction patterns of the chicken eggshell after calcination process show in Figure 16.The X-ray diffraction measurements performed at 2θ of 0º to 90º. Diffraction pattern of eggshell samples at various calcination temperatures showed a characteristic variation in CaO at 900 ºC while Apart from CaO diffraction pattern, the XRD data also shows the characteristic pattern of $CaCO_3$ at 900 ºC the $CaCO_3$ diffraction intensity diffraction show five pattern with very high intensity which characteristic diffraction pattern of $CaCO_3$(Zhang & Meng, 2014). In addition, it means also observed diffraction pattern that can identify the presence of Ca $(OH)_2$, Ca $(OH)_2$ can be formed due to the interaction of CaO with water vapour on the air.

XRD analysis is useful to see the catalyst components produced. The results of XRD analysis showed that the dominating components were CaO and Ca $(OH)_2$. Calcination in this study aims to form CaO which is used as a heterogeneous base catalyst. However, if the CaO is in contact with air it will form Ca $(OH)_2$, Ca $(OH)_2$ compounds reduce the alkalinity and catalytic surface area so that catalytic activity decreases. As observed from (Figure 16) Based on the XRD analysis the powder calcined at 900^{o}C shows that a well crystallized structure. Diffraction pattern of eggshell samples at various calcination temperatures showed a slight characteristic variation in CaO at 900ºC. XRD spectra of calcined eggshell samples were obtained with Cu-ka1 (λ=0.154056 nm) at 37.5, a scan speed of 2˚/ minute, and a scan range of 10º to 80º. The sharp peaks resulted at 2θ was 32.24^o, 37.42^o, 53.92^o, 64.22^o, and 67.42^o. So the catalyst used for transesterification was selected by testing of their conversion efficiency. Therefore, the CaO calcined at 900^{o}C was used to produce FAME, since the catalyst that has small particle size gives higher yield.

Calcium oxide is a popular heterogeneous catalyst because of its availability. However, the activity of this catalyst will decline after multiple uses due to leachate into the reaction medium. An approach to overcome this problem is to bind the calcium oxide onto a catalyst support such as zinc oxide. It can be deduced from the results above that the formation of Ca–Zn mixed precipitate significantly reduced the decomposition temperature of $CaCO_3$ to form CaO.

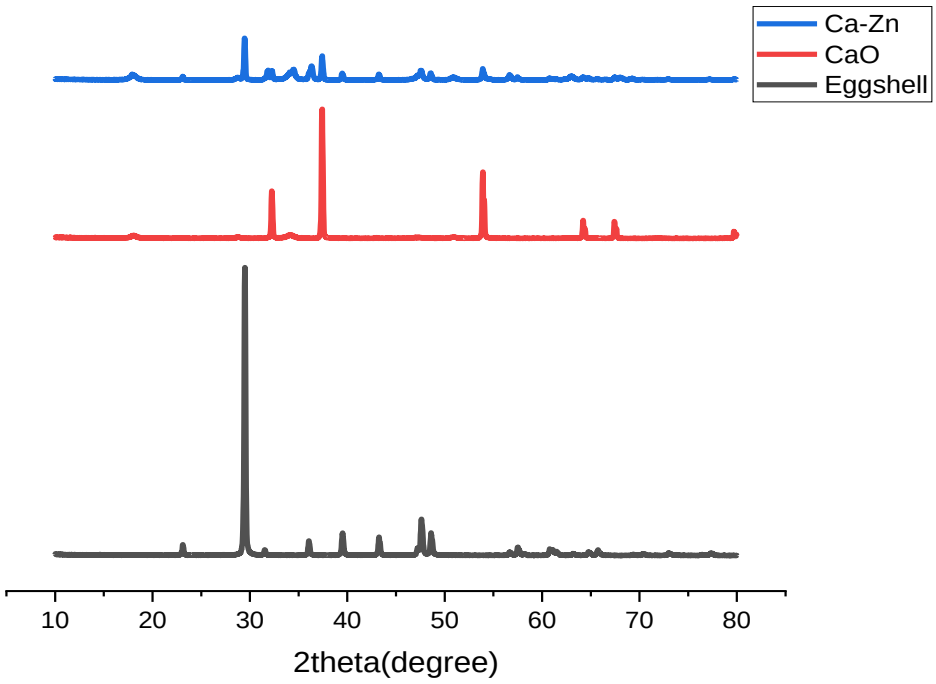


Figure 16: XRD analysis of Eggshell, Calcium Oxide and Zinc-calcium oxide

As can be seen, when the calcination temperature was 900ºC, the samples had similar XRD patterns, identical to that of the CaO carrier (2θ=32.24^{o}, 37.42^{o}, 53.92^{o}, 64.22^{o}, and 67.42^{o}) but in no case resembled that of elemental zinc phases. Considering the low zinc loading amounts, the absence of diffraction lines of ZnO and $ZnNO_3$ compounds may be attributed to their high degree of dispersion on the CaO surface (in the form of a monolayer, because of their interactions with the support surface), or to their amounts being smaller than those detectable via the XRD technique. An alternative reason for the absence of diffraction lines of Zinc compounds may be due to the higher scattering factor of the Zn^{2+} cations, which is comparable to that of the Ca^{+} cations in the catalysts. The scattering factor of an atom is affected by the atomic number; therefore, it is difficult to detect the lighter atoms (Zn) in the presence of heavier atoms (Zn), because of weak diffraction of the former(Joshi et al., 2015).

ZnO impregnated CaO has the maximum surface area and pore volume(Granados et al., 2007). Whereas the surface area and pore volume of other metal impregnated CaO catalysts were comparatively less than that of Zn impregnated CaO(Treacy & Higgins, 2007). This may because of the higher dispersion ability of Zn metal in comparison to rest of the metals used(Vedrine, 2015). The differences in surface areas of M-CaO and CaO

indicate that the metal impregnated catalysts should have greater activity than neat CaO(Di Serio et al., 2010).

4.3.2. FTIR Analysis

Infrared (IR) spectroscopy is a chemical analytical technique, which measures the infrared Intensity versus wavelength (wavenumber) of light. Based upon the wavenumber, infrared light can be categorized as far infrared (4 ~ 400cm^{-1}), mid infrared (400 ~ 4,000cm^{-1}) and near Infrared (4,000~14,000cm^{-1}).infrared spectroscopy detects the vibration characteristics of chemical functional groups in a Sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. Hence, the correlation of the band wavenumber position with the chemical structure is used to identify a functional group in a sample(Demİrbaş, 2003).

The wavenumber positions where functional groups adsorb are consistent, despite the effect of temperature, pressure, sampling, or change in the molecule structure in other parts of the molecules. Thus the presence of specific functional groups can be monitored by these types of infrared bands, which are called group Wavenumbers. Fourier Transform Infrared Spectroscopy Analysis of Eggshell This experiment examined the chemical composition of eggshell using Fourier transform infrared spectroscopy (FTIR) analysis. Figure 17 shows the absorption bands of unburnt eggshell and the pre-incineration absorption bands centered at 711, 875, 1799 and 2518 cm^{-1}, and this spectrum is due to the presence of carbonate, CO^2_3, species on the catalyst surface(Veriansyah et al., 2010).

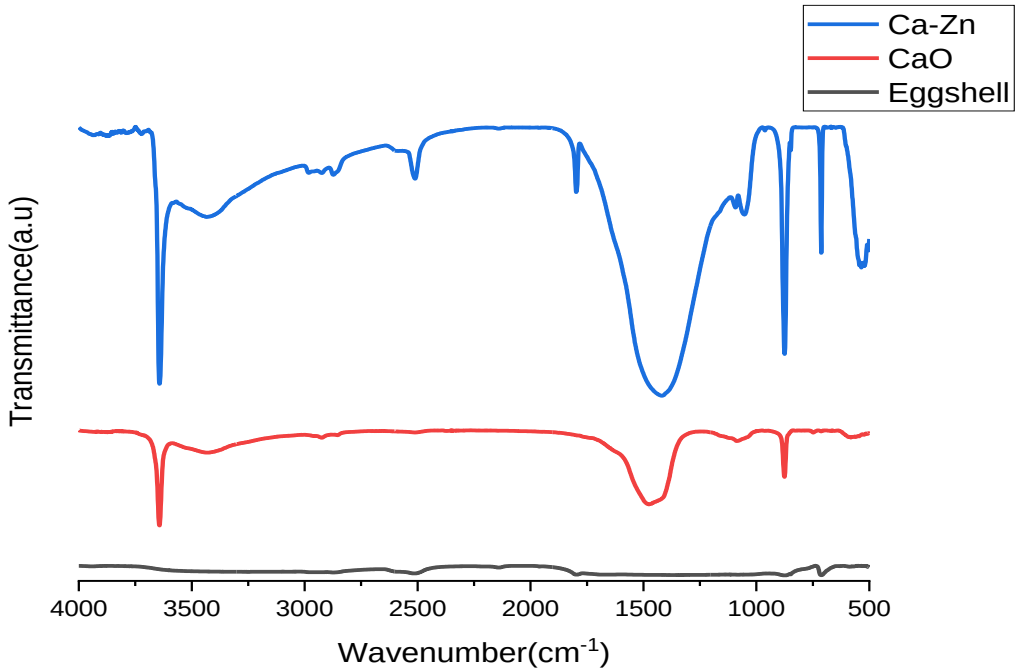


Figure 17: FTIR analysis of Eggshell, Calcium Oxide and Zinc-calcium oxide

The XRD findings of CaO samples are also supported by the FTIR results, as shown in figure. The separate figures are for clear identification of the stretching of bonds. The Infrared spectra of synthesized CaO are in the range of 400–4000 cm^{-1} wavenumber. The displayed bands of 1477 and 876 cm^{-1} shows asymmetric stretching of C=O for carbonaceous group. Another peak observed at 3644 cm^{-1} is assigned to OH- stretching this is due to the chemisorption of atmospheric CO_2 over the CaO surface(Abdullah et al., 2017). It is evident from the graph that the extra stretching of Ca-O bond appeared at about 580 cm^{-1}, which shows the formation of oxides of calcium during calcination of egg shells at various temperatures and cooling subsequently inside the furnace. This is explained from the Ca-O lattice vibrations of pure CaO. The present study findings are coherent to findings of other researchers(Joshi et al., 2015).

FTIR spectra of CaO and CaO-ZnO calcined (Figure 17) showed similar absorption mode, at 876cm^{-1}. These peaks represent the out-of-plane bending and in-plane bending from CO_3^{2-} group. Peaks were also observed at ~1477 cm^{-1} for both samples, which is assigned to asymmetric stretching from CO_3^{2-} group. Another peak observed at 3644 cm^{-1} is assigned to OH- stretching. However, two additional peaks at ~1797 cm^{-1} and ~2515 cm^{-1} are exhibited by the CaO-ZnO sample and another three additional peaks also observed at

417,452 and 535 cm^{-1}, but not CaO. Such peaks are probably originated from the CaO lattice structure. From Figure 17, it is suggested that the modified CaO with ZnO produce strong basic property at ~1797 cm^{-1} and ~2515 cm^{-1} which is caused by the absorption of gaseous CO_2 from atmosphere onto the catalysts, where the intensity still increased after modification. Therefore, the IR spectra result has proved that the CaO catalyst was successfully modified with ZnO and resulted in overall improvement of the product yield.

4.3.3 Basicity Analysis

Bromothymol blue, pKa = 7.2; phenolphthalein, pKa = 9.8; 2, 4, 6- Trinitrobenzene amine, pKa = 12.2; 2, 4-dinitroaniline, pKa = 15.0; 4-chloride-2–nitroaniline, pKa = 17.2 and nitroaniline pKa = 18.4 exhibits a color change, this indicates that the basic strength of the catalyst is stronger than the indicator used(Hargreaves*, 2005). However, when the solution produces no color change, the basic strength of the catalyst is weaker than that of the indicator used. The data reveals that the CaO-Zn catalyst has shown better basic strength in comparison to neat CaO and other metal impregnated catalysts(Joshi et al., 2015). The basicity of transition metal impregnated CaO is comparatively greater than that of neat CaO may be because of the synergistic relation between multi-metal ions which generally enhances the basicity on active site of the catalyst(C.G. Albuquerque et al., 2008). The synergistic effect of multi-metal ions may also be explained as the basicity of an metal oxide surface is closely related to the electron donating property of oxygen anion which increases with the increase in electropositive character of combined metal ion which will probably form more Lewis base sites (–O–) on CaO surface(C.G. Albuquerque et al., 2008).

Base strength of a species is its ability to accept H^+ from another species (see, Brønsted-Lowry theory). The greater the ability of a species to accept a H^+ from another species, the greater its base strength(Boey et al., 2011). Organic chemists customarily compare the strength of bases using the strengths of their conjugate acids, measured as pK_a(Colombo, Ender, & Barros, 2017). One way to increase the catalytic activity of catalysts is to increase the ability. The spirit can be enhanced by the impregnation method. Zn $(NO_3)_2.6H_2O$ is used as the precursor for the impregnation process of the CaO catalyst. The impregnation process causes the catalysts to increase. The greater the catalyst will increase the catalytic activity of the catalyst(Campanati et al., 2003).

4.4. Fatty Acid methyl ester (FAME) production from sunflower oil

In the present study the parameters such as, catalyst loading, molar ratio of methanol to Oil, Temperature and Reaction time were considered to investigate the effect on the yield of SOME.

4.4.1. Effect of catalyst loading on yield of FAME

Various impregnated catalyst amounts was investigated from 1 to 5 wt%, based on the amount of sunflower oil used, for the transesterification, as presented in Figure 18.The FAME content increased remarkably from about 60% to almost 82% when increasing the catalyst amount from 1 to 5 wt%. Apparently, this is because the number of basic sites from the catalyst increased(Kouzu & Hidaka, 2011). The maximum value of FAME content was 82% with using the catalyst amount at 3 wt%. However, with further increase of the catalyst amount, the FAME content was slightly decreased, which could be attributed to poor mixing between the solid (i.e. the catalyst) and the liquid (i.e. the MeOH and oil) phase, because the viscosity of the system became higher as increasing the catalyst amount. Furthermore, it was that the transesterification process was emulsified more easily and this resulted in difficult separation of products when an excessive catalyst amount was used.

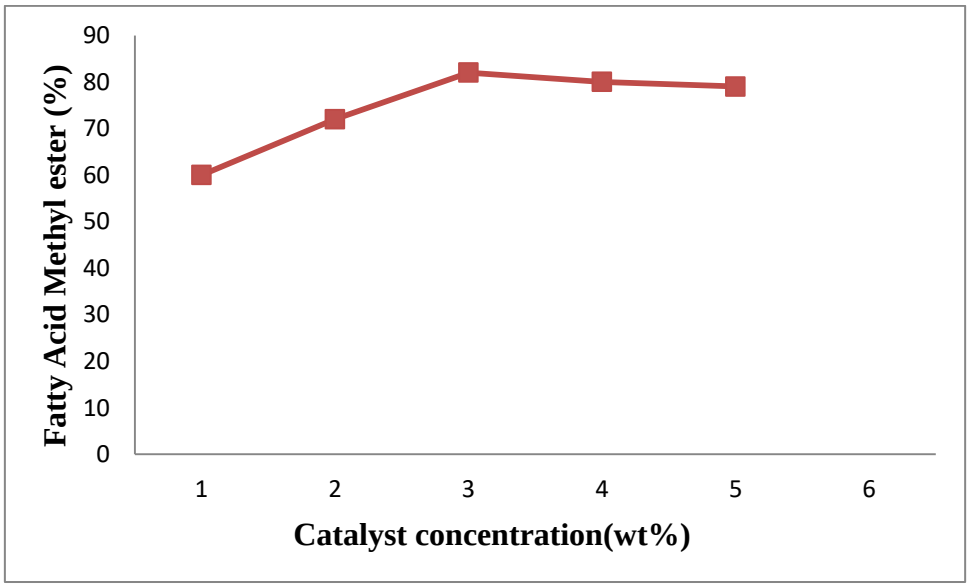


Figure 18: Effect CaO-ZnO catalyst amount on the ME content Reaction conditions: 65ºC, 2h and 9:1 MeOH-to-oil molar ratio.

Figure 18: represents the yield of methyl esters at different catalytic concentrations (1–5 wt %), reaction time (30–120 min) while maintaining the temperature and methanol: oil molar ratio constant at 65ºC and 9:1, respectively. It is observed that the lower catalyst concentration of 1% CaO-ZnO is insufficient for completion of the reaction; the yield of sunflower oil methyl ester is 60%. By increasing the catalyst concentration to 3%, the yield of methyl ester increases to 82%. Further increase in the catalyst reduces resulted in reduction of a yield decrease. This behavior is due to the high concentration of an alkaline catalyst which prevail the saponification reaction which forms soaps in the presence of fatty acids resulting in emulsion formation between soaps and water molecules. Thus, 3 wt% catalyst concentrations considered to be the optimum catalyst concentration for our study.

4.4.2. Effect of methanol to oil molar ratio on yield of FAME

The effect of the methanol/oil molar ratio on the transesterification reaction is one of the important parameters that affect the methyl ester yield as well as the cost of the biodiesel production. To determine the optimum methanol/oil molar ratio for catalysts, the reactions were performed by varying the methanol/oil molar ratio from 3:1 to 18:1 for 120 min. The FAME yield increases from 60 to 82% upon an increasing methanol/oil molar ratio from 6:1 to 9:1, and a further increase in the latter were not found to influence the FAME yield significantly.

The stoichiometry ratio of the transesterification reaction requires 3 mol of methanol to yield 1 mol of glycerol and 3 mol of methyl ester. Being a reversible reaction, excess methanol is used to shift the reaction to the right(Xie & Zhao, 2013). The reaction was carried out by varying methanol: oil molar ratios from 6:1 to 18:1, reaction time (30–120 min) while maintaining the reaction at 65ºC and 3 wt% catalysts **(**Figure 19). It is clear that, 6:1 methanol: oil molar ratio led to 75 wt % methyl ester yield; however, this alcohol concentration did not lead to spontaneous phase separation. Through increasing methanol: oil molar ratio from 6:1 to 9:1 separation between the transesterification products became possible provides an increase of the methyl ester yield to 82%. Then, the yield decreases from 82% to 55% with increasing molar ratio to 18:1, this is due to excess amount of methanol as a result separation of FAME from methanol becomes impossible accumulation of methanol and viscous nature of the fluid.

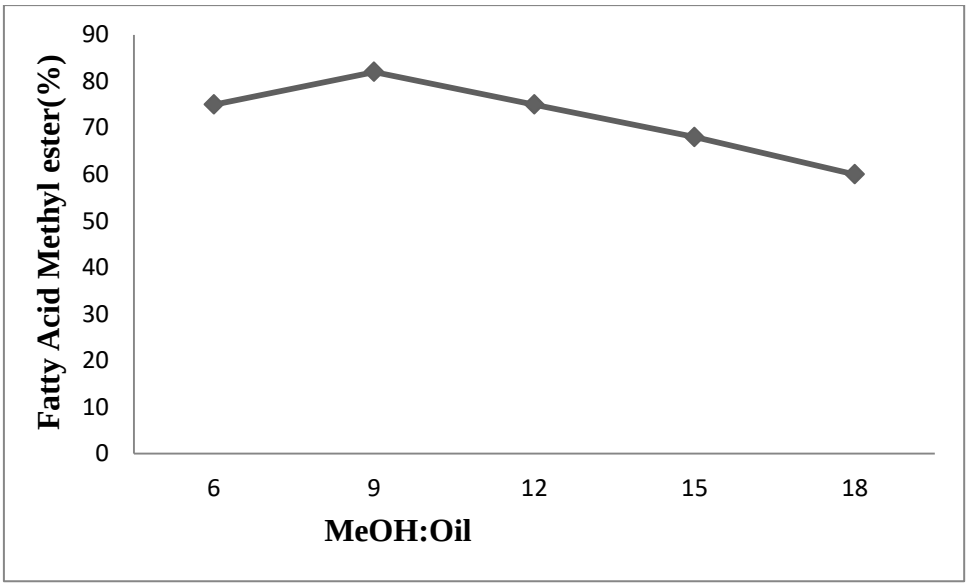


Figure 19: Effect of methanol to oil molar ratio on the ME content Reaction Conditions:65ºC,2h and 3wt% catalyst amount.

Figure 19 shows the effect of Methanol to oil molar ratio on the yield of biodiesel at constant temperature and catalyst concentration in the center point. In addition the figure shows that, the yield of biodiesel is highly affected by Methanol to oil ratio, as the Methanol to oil ratio increases from 6:1 to 9:1 the yield sharply increases. Therefore, the MeOH-to-oil molar ratio was chosen at 9:1, producing the highest FAME content at 82%, to further study for the other parameters. Whereas beyond 9:1 the yield of biodiesel slightly decreased, the decrease in biodiesel yield at a high molar ratio beyond 9:1 could be due to the dissolving of glycerol in the Methanol and this hinders the interaction of Methanol with catalyst.

4.4.3. Effect of Reaction Temperature on yield of FAME

In this work, the effects of reaction temperature on production and methyl ester yield decreases with increase in temperature. This can be as a result of higher solubility of reactants because higher temperature reduces the separation of methyl ester and glycerol phase. Also, a higher reaction temperature of 65^{o}C that was chosen is close to the boiling point of methanol which can lead to evaporation of some of the methanol during transesterification process. As a result, lower Fatty acid methyl ester yield was observed at 30^{o}C as compared to that obtained at 65^{o}C leaving all other variables constant under the same reaction conditions. I should observe that longer reaction time leads to the reduction of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation.

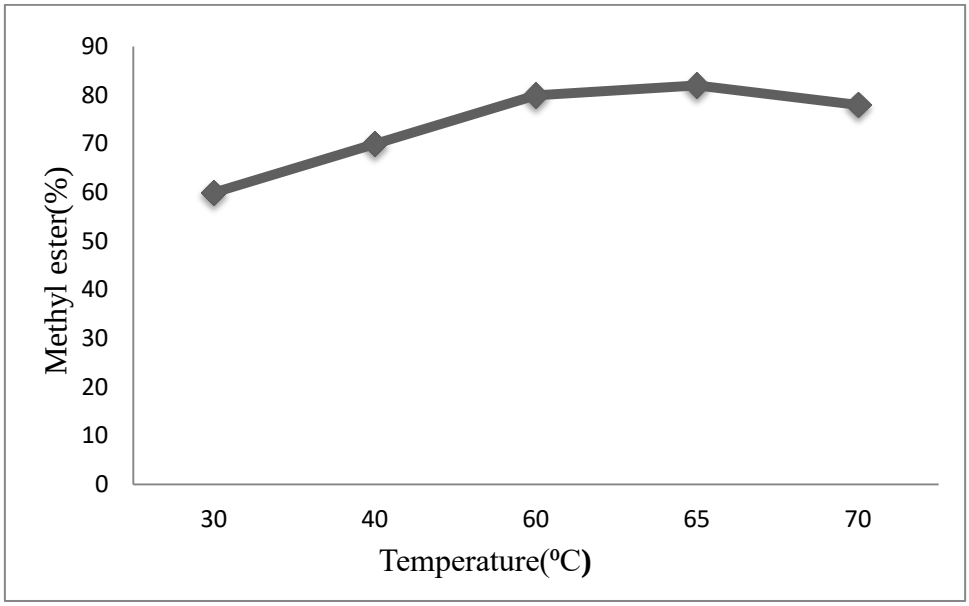


Figure 20: Effect of temperature on the ME content, Reaction Conditions: 65ºC, 2h, methanol to oil molar ratio amount and 3wt% catalyst amount.

Heterogeneous catalysts, because of the phase difference from reagents, usually required a high temperature and pressure and longer reaction period to yield the significant conversion(Ulfah et al., 2018). In the present study, the FAME yield was found to increase regularly as the reaction temperature was increased from 30°C to 65°C and a further increase in the reaction temperature was not found to influence the FAME yield significantly. Although the catalyst was found to be more effective at 65°C, however, even at room temperature (30°C), complete conversion of sunflower oil into corresponding FAMEs was achieved in 2h of reaction duration.

4.4.4. Effect of Reaction time on yield of SOME

Reaction time in this study was investigated between 0.5 and 3.0 h under the optimal reaction parameters as obtained in the previous sections, and the results are presented in Figure 21: It can be seen that the transesterification reaction started rapidly, giving the methyl content more than 60% in the first 30 min. After that the FAME content was further increased with the time for transesterification to the maximum value of almost 82% in 2 h where equilibrium was reached. Thus, the maximum FAME content was found at the reaction time of 2 h.

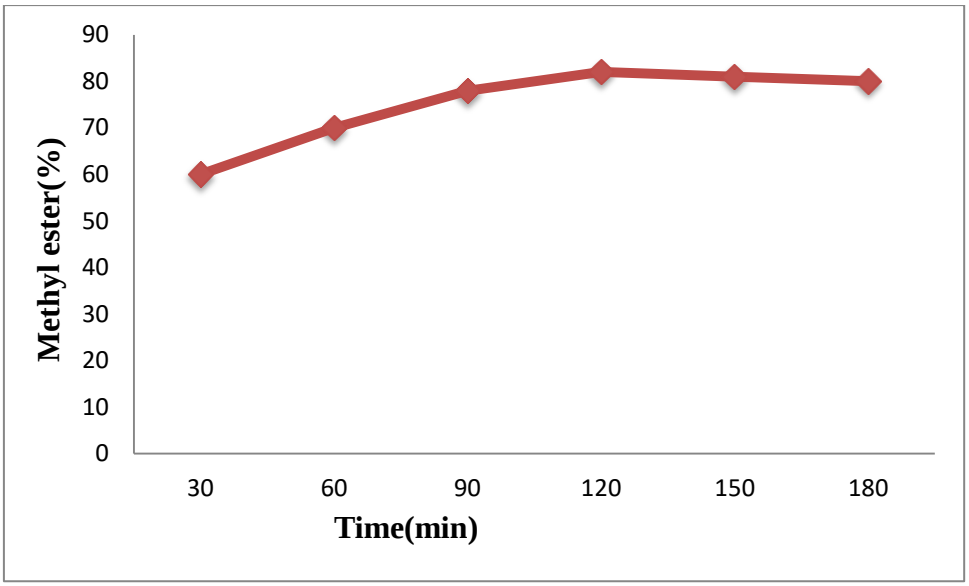


Figure 21: Effect of time on the ME content, reaction conditions: 65ºC, 2h, 3wt%catalyst amount and methanol to oil molar ratio (9:1).

On the basis of the above-mentioned experiments, a 9:1 methanol/oil molar ratio, 3 wt % catalyst concentration (with respect to oil), 65°C reaction temperature, and 120 min reaction duration have been established as optimum reaction conditions for the transesterification of Sunflower oil.

4.5. RSM for FAME synthesis

4.5.1. Analysis of variance (ANOVA)

Based on the ANOVA results obtained, catalyst amount was found to have the greatest significant effect on biodiesel yield, while methanol/oil molar ratio and reaction time were insignificant on the response. The high catalyst activity observed was due to its strong basic sites. Figures 21 and 22 show the three-dimensional response surfaces which were constructed to show the effects of the reaction condition variables on the biodiesel yield (Y).

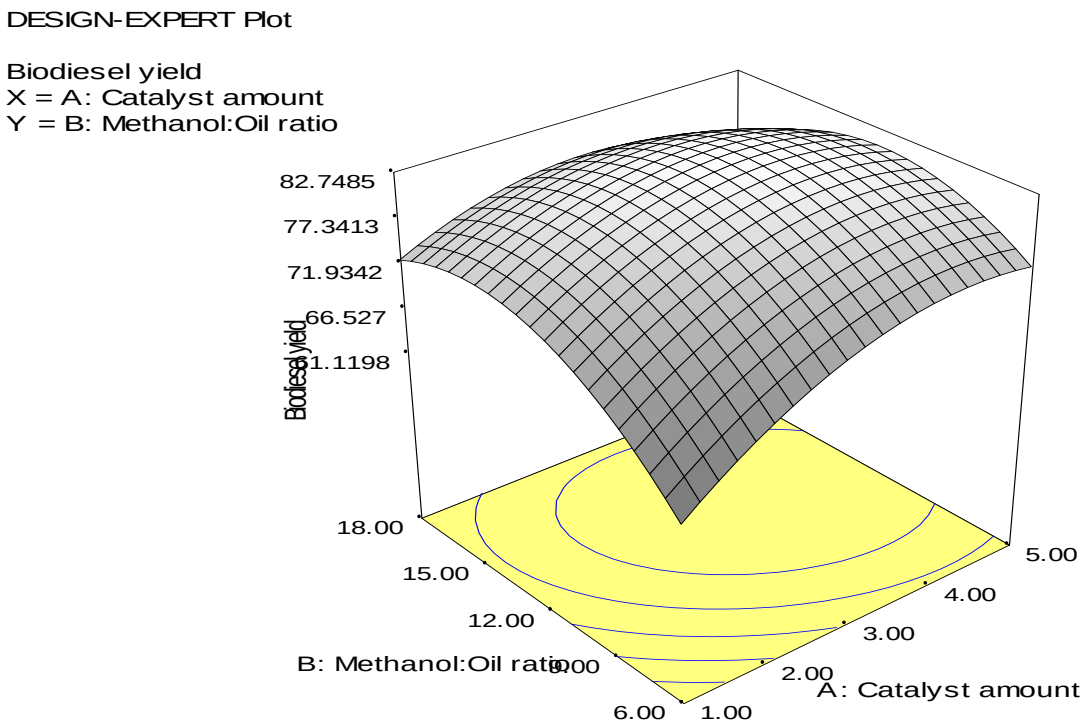


Figure 22:Three-dimensional response surface plot of biodiesel yield (effect of catalyst amount and methanol to oil ratio, reaction time (2h), reaction temperature (65ºC)

Figure 22: shows the effect of catalyst amount and methanol/oil molar ratio on yield (reaction time was fixed at zero level, reaction temperature was fixed at 65°C) whereas Figure 23: shows the effect of catalyst amount and reaction time on the biodiesel yield (methanol/oil molar ratio was fixed at zero level, reaction temperature was fixed at 65°C). The biodiesel yield was found to increase with increasing catalyst amount, methanol/oil molar ratio and reaction time. The highest yield was obtained when all the three variables were at the optimum point within the range studied.

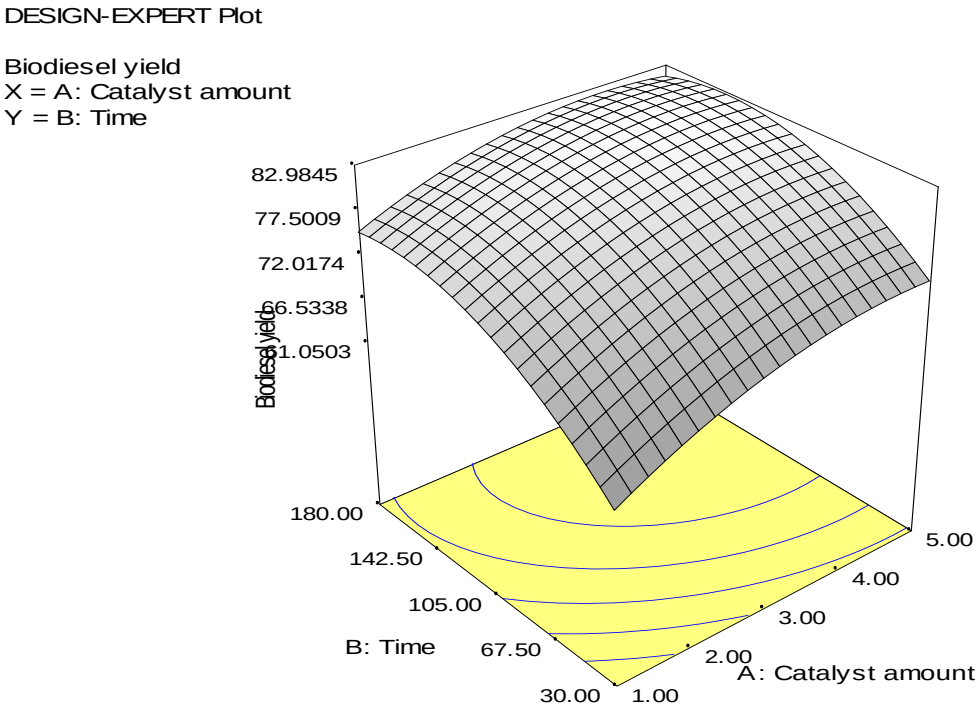


Figure 23:Three-dimensional response surface plot of biodiesel yield (effect of catalyst amount and reaction time (2h), methanol to oil ratio (9:1), reaction temperature (65ºC).

The transesterification of sunflower oil using CaO-ZnO catalyst is strongly dependent upon the catalyst applied. Without addition of the catalyst, the transesterification procedure did not occur, and the presence of the catalyst really increased the reaction rate. The conversion to methyl esters increased when the amount of loaded catalyst increased from 1% to 3%.

The graph of the predicted vs. actual values was obtained using the experimental data run correlation shown in Figure 24: below. The plot contains a line of unit slope (i.e. the line of perfect fit) with points corresponding to zero error between predicted values and actual. This plot therefore indicates the performance of the correlation in an evident way. Hence, the regression model equation granted a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This outcome indicates that it was successful in creating the correlation between the four process variables to the FAME.

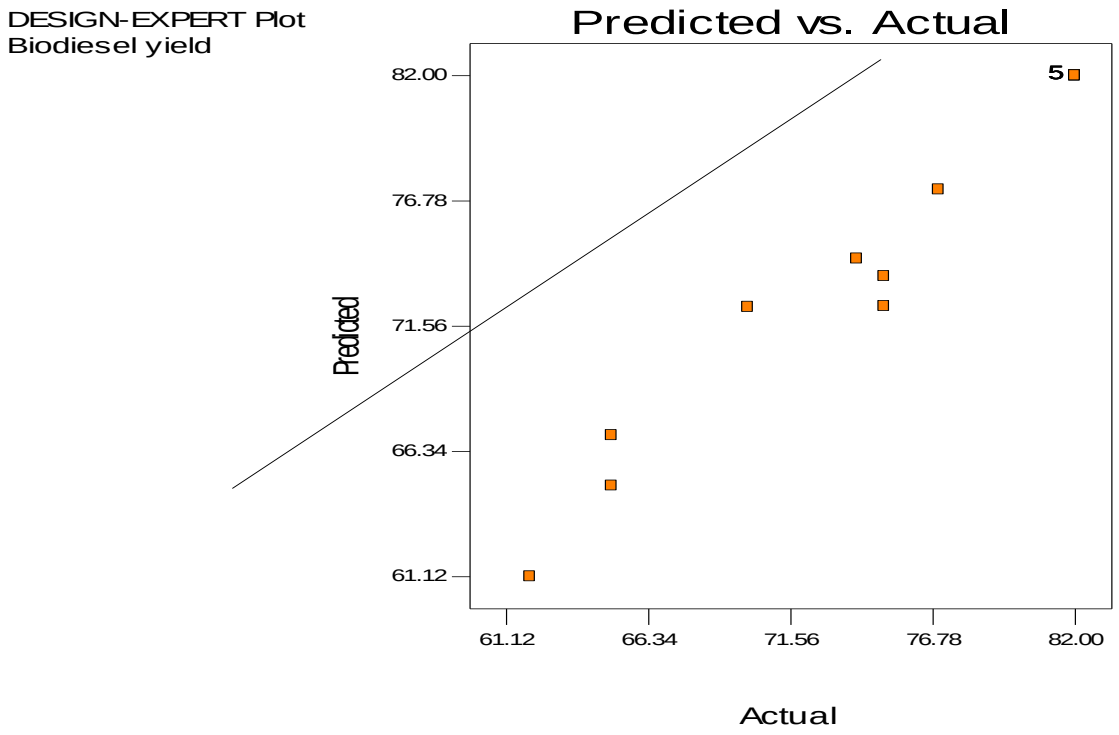


Figure 24: Yield plot for the actual vs predicted of FAME yield.

A graph of the predicted response values versus the actual response values helps us to detect a value, or group of values, that are not easily predicted by the model. The data points should be split evenly by the 45 degree line. If they are not, it is necessary to try a transformation to improve the fit. But in the case of my experimental result it is not necessary to try transformation since it is adequately checked by 45 degree line(y = x graph). The results in Figure 24 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit and splits evenly by the 45 degree line. This result indicates that it was successful in capturing the correlation between the three transesterification process variables to the yield of FAME.

The graph of the predicted vs. actual values was obtained using the experimental data run correlation shown in Figure 24 above. The plot contains a line of unit slope (i.e. the line of perfect fit) with points corresponding to zero error between predicted values and actual. This plot therefore indicates the performance of the correlation in an evident way. Hence, the regression model equation granted a very accurate description of the experimental data,

in which all the points are very close to the line of perfect fit. This outcome indicates that it was successful in creating the correlation between the four process variables to the FAME.

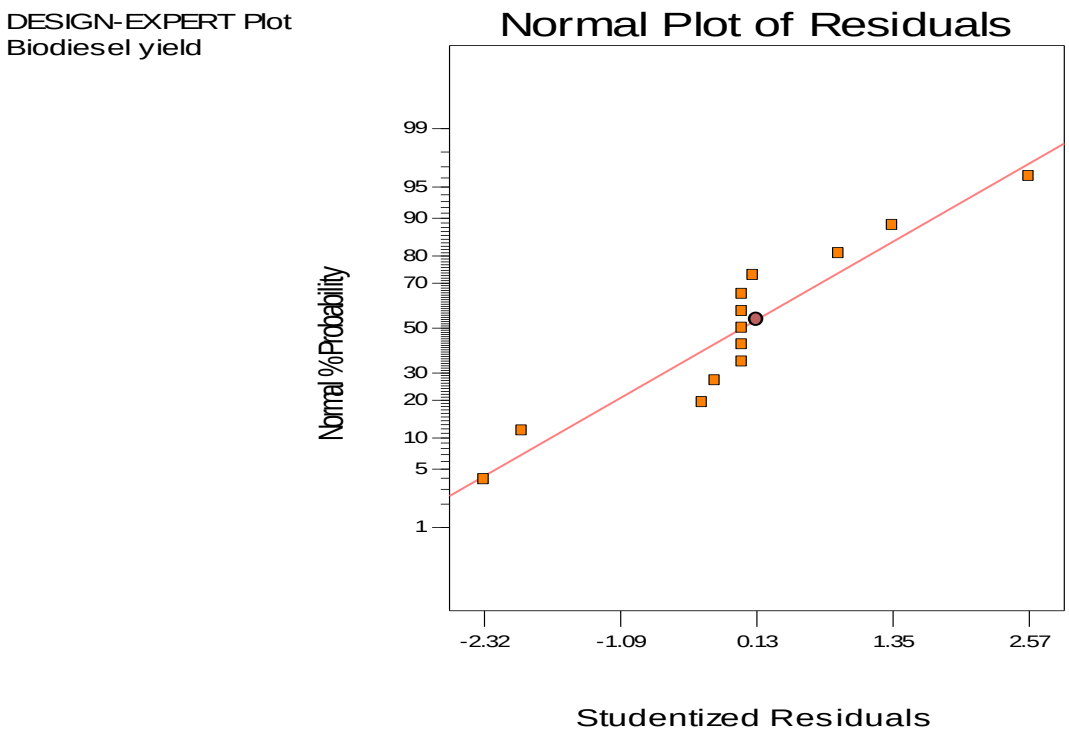


Figure 25: Normal plots of residuals

From the plot as shown above, the normal probability plot indicates the residuals following a normal distribution, in the case of this experiment the points in the plots shows fit to a straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately

normal

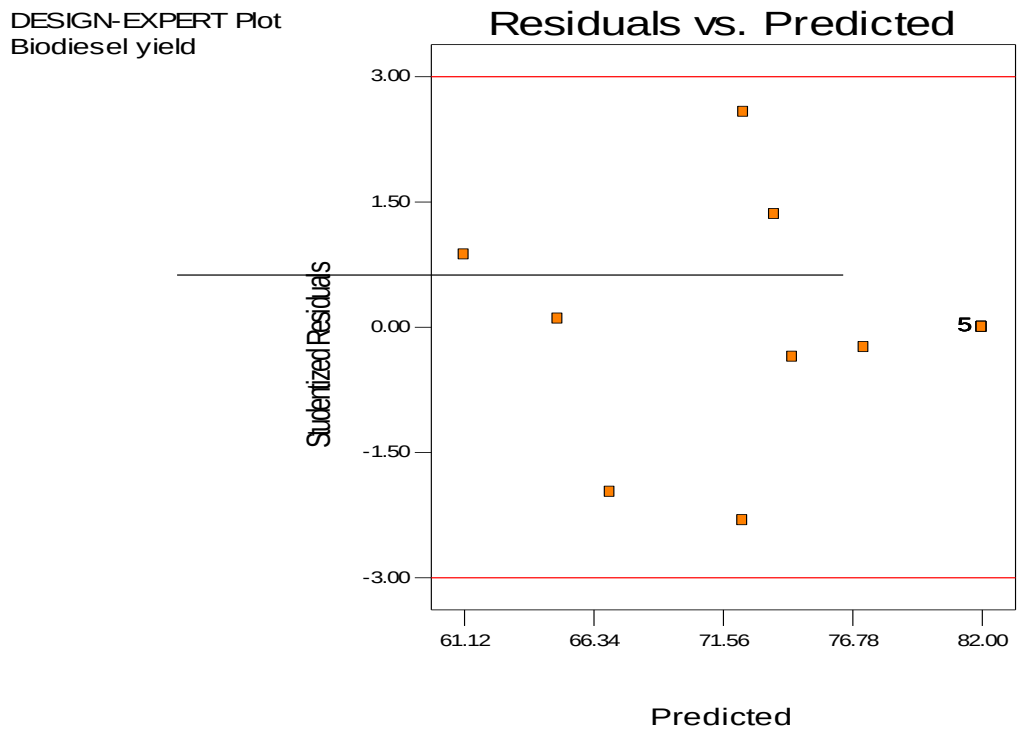


Figure 26: Residual vs Predicted Values

From the model, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

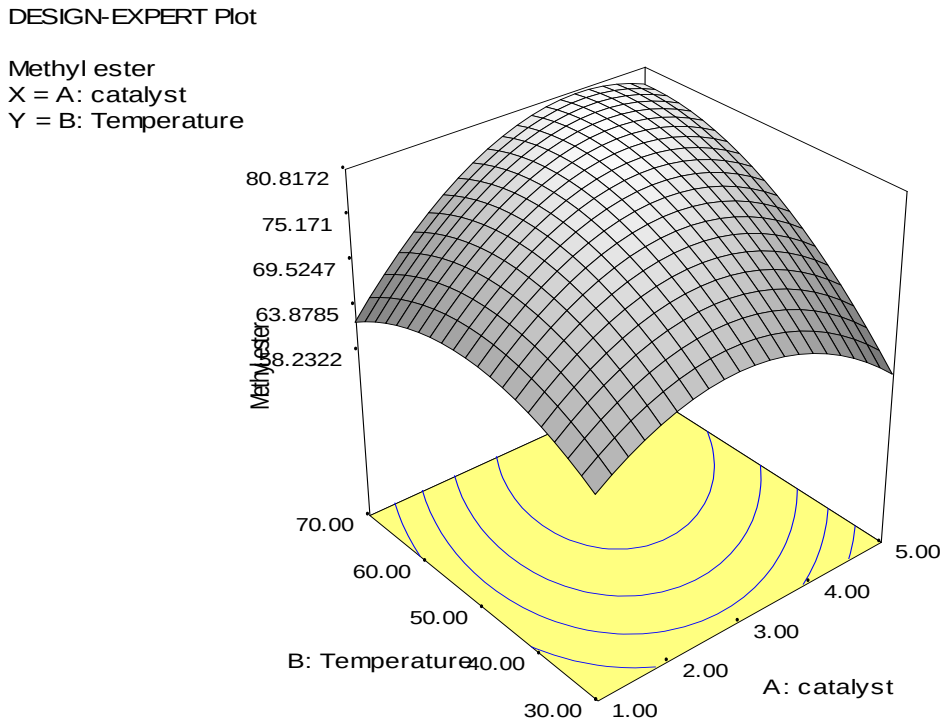


Figure 27:Three-dimensional response surface plot of biodiesel yield (effect of catalyst amount and reaction temperature) at reaction time (2h), methanol to oil ratio (9:1)

The process variables were found to have significant interaction effects. Figure 27 and 28 shows the interaction between catalyst amount and reaction temperature and reaction temperature to methanol to oil molar ratio, respectively, on the yield of biodiesel yield. Generally, an increase in reaction temperature is found to increase the yield of biodiesel up to some optimal value in all cases. Additionally it was observed that at lower range of reaction temperature, higher weight of catalyst and higher molar ratio of Methanol to oil, always resulted in higher yield than when using lower weight of catalyst and lower ratio of Methanol to oil. Reactions which were carried out using lower ratio of methanol to oil and lower weight of catalyst is found to have higher yield as compared to reactions using lower reaction temperature, higher molar ratio of Methanol to oil and higher weight of catalyst. However, at higher range of reaction temperature, the observations showed that using a combination of both, higher reaction temperature and higher molar ratio of Methanol to oil or higher weight of catalyst used is not beneficial in increasing the yield of biodiesel. This is probably because at these conditions, the higher reaction temperature is already sufficient to push the reaction forward. This phenomenon is further supported by the fact

that reaction temperature is the most significant process variable that affects the yield of the biodiesel as indicated by graphs.

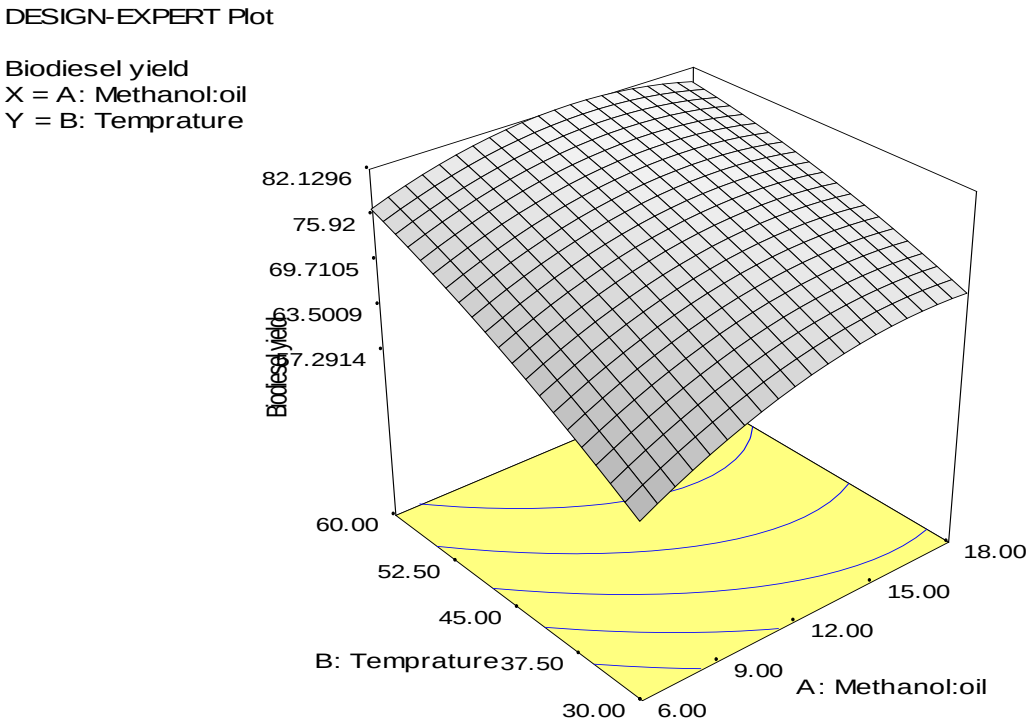


Figure 28:Three-dimensional response surface plot of biodiesel yield (methanol to oil ratio and reaction temperature) at reaction time (2h), catalyst amount3wt%

4.5.2 FAME Process optimization

The optimization of process variables within the selected ranges for maximum conversion of the oil to FAME was evaluated using Design Expert 6.0.8. In the production of biodiesel, relatively high product yields are expected for economic feasibility. The yield of biodiesel can be increased by manipulate the transesterification reaction condition such as catalyst amount, methanol/oil ratio and reaction time. In order to optimize the response, the function of desirability was applied using Design Expert software version 6.0.8 (STAT-EASE Inc., Minneapolis, USA). There are many methods available to optimize a process. In this work, numerical optimization was chosen. Numerical optimization presents a comprehensive and up-to-date description of the most effective methods in continuous optimization. It responds to the growing interest in optimization in engineering, science, and business by focusing on the methods that are best suited to practical problems. In the numerical optimization, biodiesel yield was set to a maximum range whereas methanol/oil

ratio, reaction time and catalyst amount are set in a range between low and high levels which coded as -1 and +1. The experimental conditions with the highest desirability were selected to be verified. The transesterification reaction was prepared under the experimental conditions, together with the predicted (85%) and experimental biodiesel yield (82%). The optimum transesterification reaction condition was prepared by using methanol/oil ratio of 9:1, reaction time of 2h and catalyst amount of 3 wt.%. The optimum biodiesel yield was 82%. It was observed that the experimental value obtained was in good agreement with the value predicted from the models, with relatively small errors because of different parameters effect between the predicted and the actual value, which were only 3% for biodiesel yield.

4.6. FTIR analysis for FAME

The infra-red spectrometry of the methyl esters was shown in Figure 29. It can be observed form the figure that the stretching at 3009 cm^{-1} shows the presence of C-H stretch, 2923 cm^{-1} also shows CH_2 presence in the sample. Similar presence is also seen at 2853 cm^{-1}. The ester presence, C=O is detected at 1744 cm^{-1}, while bending vibrations of CH_2 is present at 1464 cm^{-1}. (CO)-O-CH_3 is observed at 1378 cm^{-1} and C-O ester is detected at 1245 cm^{-1}, 1169 cm^{-1} and aliphatic is present at 3200cm^{-1} and OH^- acid also observed. The CH_2 rocking is observed at 723 cm^{-1}.

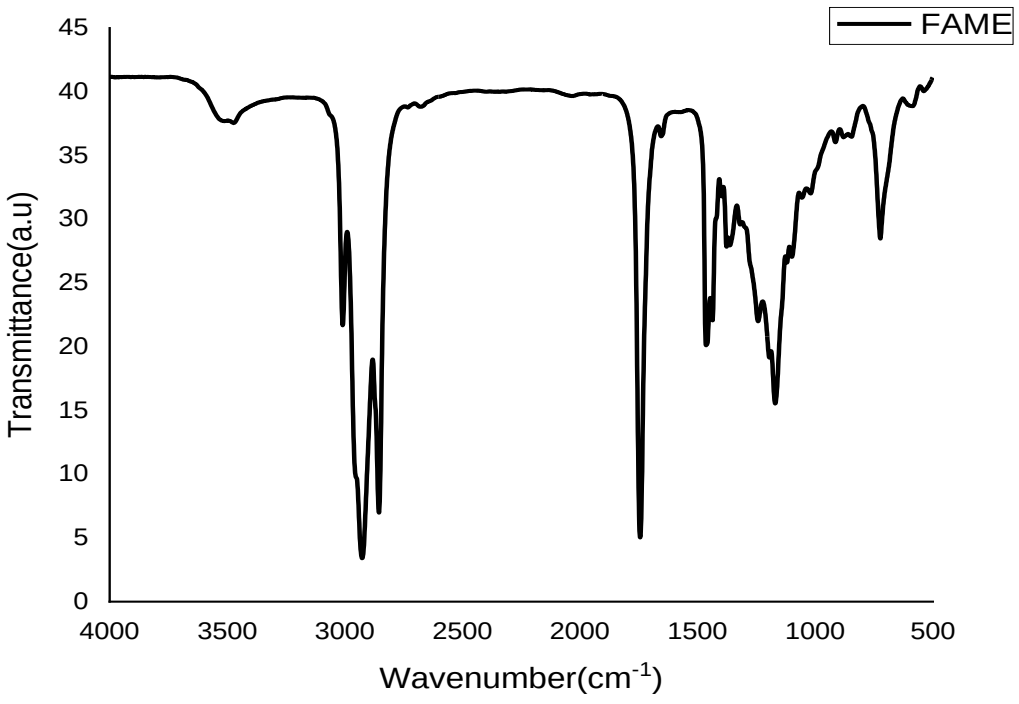


Figure 29: FT-IR spectra of Fatty acid methyl esters

4.7. Reusability and catalyst leaching analysis

One of the advantages of a heterogeneous catalyst over a homogeneous one is the ability to reuse it in multiple reaction cycles. Therefore, catalyst reusability is an important test in developing a new heterogeneous catalyst for transesterification, especially when losing active ingredients by leaching was a drawback of many solid catalysts reported previously.

The ability to be recycled is one of the most significant features for the heterogeneous catalyst. The reusability of eggshell waste derived CaO catalyst in the transesterification of sunflower oil has been examined for four cycles under an optimum condition is shown in Figure 30. After each cycle, the solid catalyst was separated from the reaction mixture by filtration and solid catalyst washed with methanol to remove adsorbed material and recalcined at 600ºC for 2 h for further use. The result indicates that a high biodiesel yield of 70% was achieved in the first cycle and biodiesel yield of 50% were achieved at fourth runs.

Leaching of the active site to the reaction media (mainly alcoholic phase) causes decay in catalytic activity due to bond breaking and formation of Ca^{+2} and CH_3O^-(Ayodeji et al., 2018).Beyond that, the catalytic activity dramatically reduced and completely deactivated after being reused more than 4 times. The loss in activity was attributed to the dissolution of active sites in the catalyst such as a result of catalyst poisoning, leaching of catalyst in methanol, change in catalyst surface structure or loss of catalyst during washing(Bourikas et al., 2006). Furthermore, indicated that CaO catalyst from eggshell could be repeatedly used for 4 times due to its surface area and chemical composition(Islam, Taufiq-Yap, Chu, Chan, & Ravindra, 2013).

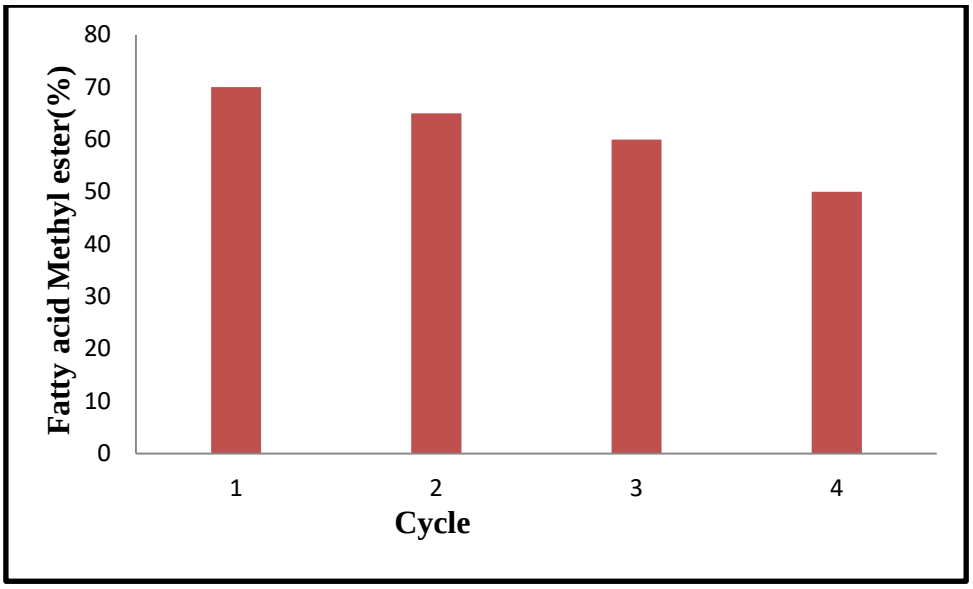


Figure 30: Effect of reusability of catalyst (CaO) on FAME yield

In this study, the regeneration via a hydrothermal treatment was performed by washing the used CaO-ZnO catalyst with methanol, followed by the calcination in a muffle furnace at 600ºC for 2 h. The reusability of the catalyst ZnO–CaO was also investigated by performing the transesterification of sunflower oils with methanol under optimized reaction conditions. The ZnO–CaO catalyst was recovered after the fresh reaction by filtration and was washed twice with distilled water followed by hexane and dried for overnight at 120ºC(Joshi et al., 2015).The results are shown in Figure 31. The reused catalyst gave >82% conversions of sunflower oil biodiesel and >65% conversions of biodiesel after four successive cycles. The gradual loss in catalytic activity of catalyst may be due to the adsorption of organic matters on the catalyst surface, and/or leaching of active sites during the reaction(Dasari & Goud, 2017).

To further investigate the cause of catalyst deactivation, we compared the thermal analysis results of spent mixed oxide catalyst before and after methanol washing. The recycled catalyst (after 4 cycles) has shown slight shifting of the peaks, this may be because of the separation of the CaO and ZnO upon repeated use and recalcination, this may also be the reason for significant decrease in basicity of recovered ZnO–CaO catalyst, consequently catalytic activity was decreased(Di Serio et al., 2010). It was observed that because of the separation of CaO and ZnO the surface area and basicity was also decreased significantly(Joshi et al., 2015). By using CaO based mixed oxides reduced the catalyst cost and made the process more economic and also more environmental benign.

The results indicated in Figure 31, consistent activity up to five runs with a marginal decrease in the FAME yield, which is 82, 76, 70, 65 and 63%. The degradation of catalytic activity throughout the five runs may cause by three main reasons: (i) leaching of metal ion from active sites into reaction medium(Yoosuk, Udomsap, Puttasawat, & Pitakjakpipop-Krasae, 2010); (ii) poisoning of the catalyst active sites by the reaction medium (oil, biodiesel and glycerol) which reduced contact between basic sites and reactants(Wen et al., 2010); (iii) catalyst structure collapsed(Zhang & Meng, 2014).

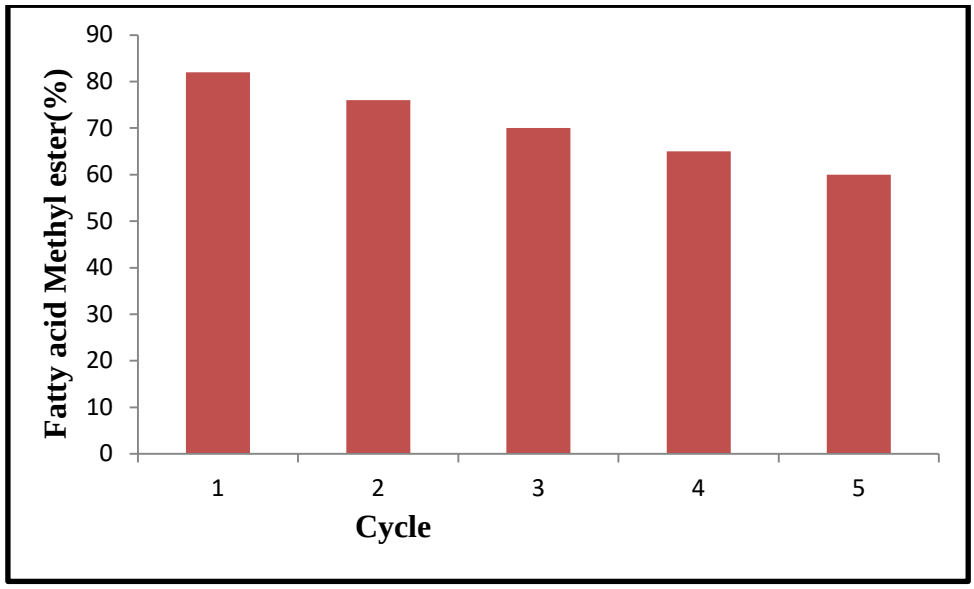


Figure 31: Shows the reusability of the synthesized catalyst (CaO-ZnO)

The study concluded that slight leaching occurred during transesterification reaction. Small amount of active component (Zn^{2+}) was leached into the reaction medium during every cycle and thus reduced catalytic activity for each reusability test. Besides, leached active ions in reaction mixture promote unfavorable side saponification reaction. This situation bring difficulties in the separation process as a layer of soap was formed between biodiesel and glycerol phase, thus more wastage is expected in separation process hence FAME yield throughout the five runs was reduced. In the range of these experiments, FAMEs yield decreased by increasing the number of cycles. It has also been observed that FAMEs yield decreases from 82% for the fresh catalyst to 60% for the fifth use catalyst. This can be attributed to the fact that oil molecules coverage the active site over the catalyst surface and/or proves that catalyst deactivation take place. However, the catalyst can be regenerated to recover the original pattern by routine calcination.

CHAPTER V

OVERALL CONCLUSIONS AND RECOMMENDATIONS

Conclusions;

Recommendation

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The present study reveals that the calcination-hydration-dehydration treatment is a sufficient method to increase the activity of a solid catalyst prepared from eggshells waste to produce biodiesel through transesterification reaction from Sunflower oil with methanol as reactant. The catalytic performance of the prepared catalyst was examined by measuring basicity and confirmed by yield of Fatty acid methyl acid (FAME) through transesterification reaction. The optimal conditions of the transesterification experiment were found to as a reaction time of 2 h, the reaction temperature of 65ºC, the methanol to oil molar ratio of 9:1, and the catalyst loading of 3% wt. The results showed that the methyl ester was the main compound in the obtained biodiesel, with the yield of 70% was obtained when using the CaO catalyst and a yield of 82% obtained when CaO/ZnO was applied as a catalyst instead of CaO. This experiment also found that the calcination temperature of the catalyst was an important parameter during the catalyst treatment; while high calcination temperature was required in order to gain mechanical strength to prevent the leaching process on their application.

The effects of process parametrs such as catalyst loading, methanol to oil molar ratio and temperature were investigated. Based on a detailed inspection using response surface methodology coupled with central composite design, the optimal operating parameters for transesterification of sunflower oil to biodiesel for a well agitated reaction over a period of 2h were determined to be methanol to oil molar ratio of 9:1, catalyst loading of 3wt% and temperature of 65^{o}C. At this optimal operating condition, the catalyst gave a maximum biodiesel yield of 82 %. The biodiesel yield was not much affected by the increase in optimized catalyst loading, reaction temperature and methanol: oil molar ratio. In the reusability study, the ZnO-CaO catalyzed reaction showed a slight decrease in FAME yield content in each cycle, which suggested that the catalyst degradation was due to the slight leaching of active ion during reaction. Thus, the utilization using mixture of Zinc nitrate and chicken eggshell heterogeneous base catalyst was a considerable potential especially in terms of simplification of separation process form biodiesel mixture, waste reduction from the environment, producing environment-friendly products and cheap catalyst.

5.2. Recommendations

Calcium Oxide (CaO)-impregnated calcined egg shells catalyst had proved to be effective in transesterifying with methanol for biodiesel production. Some of the most important future research works are listed below.

- By further studying the textural properties of the catalyst such as surface area, pore volume and pore diameter, and the surface morphology also needs to test
- The issue of catalyst leaching has been found to be the main problem in most of the heterogeneous catalysts studied so far. Therefore, studies on leaching of the catalyst still need to be carried out for its commercialization.
- The reusability of the catalyst was moderate and future studies need to be conducted to enhance the reusability of the catalyst after being treated with solvents.
- The performance of the synthesized biodiesel in compression ignition engines also needs to test.
- Further study on improvement of the transesterification process parameters reaction time, molar ratio of methanol to oil and speed of stirring on percentage of FAME yield is also suggested.
- In this studying there is some problem for characterizing of the Catalysts and produced biodiesel, such as, ^{1}HNMR,TGA,SEM, Surface area, pore Volume, particle size and elemental analysis due to there is no equipment's and the unfunctional equipment's in Adama Science and Technology University(ASTU) and generally most of other institutions of Ethiopia. I seriously recommend the ASTU institution to install carefully the equipment's in the laboratory for further characterization.

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APPENDIX

Supplementary data

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes $\left(>C=C<^{H}\right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

- **Methanol to oil molar ratio calculation**

The following basic formula works for all cases:

$$\text{Methanol to oil molar oil} = \frac{\text{number of mole of methanol}}{\text{number of mole of oil}}$$

$$\text{Number of mole} = \frac{Given\ mass}{\text{Molecular mass}}$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Substitute Number of mole and Density in to methanol to oil molar ratio equation:

$$\text{Methanol to oil molar ratio} = \frac{\left(Density * \frac{Volume}{Molecular\ Mass}\right) of\ methanol}{\left(\text{Density} * \frac{\text{Volume}}{\text{Molecular mass}}\right) of\ oil}$$

Then, solving for Volume of methanol:

$$\text{Volume of Methanol} = \frac{\left(Density * \frac{Volume}{Molecular\ Mass}\right) of\ methanol}{\left(\text{Density} * \frac{\text{Volume}}{\text{Molecular mass}}\right) of\ oil} * (\text{methanol oil ratio})$$

Where, Density of methanol=0.79g/ml

Molecular mass of methanol=32.04g/mol

Density of oil=0.960g/ml

Volume of oil=50ml

Molecular mass of oil=876.16g/mol

- **Catalyst to oil weight ratio calculation**

As it was cited before, from Density and Volume of oil, mass of Oil can easily be calculated.

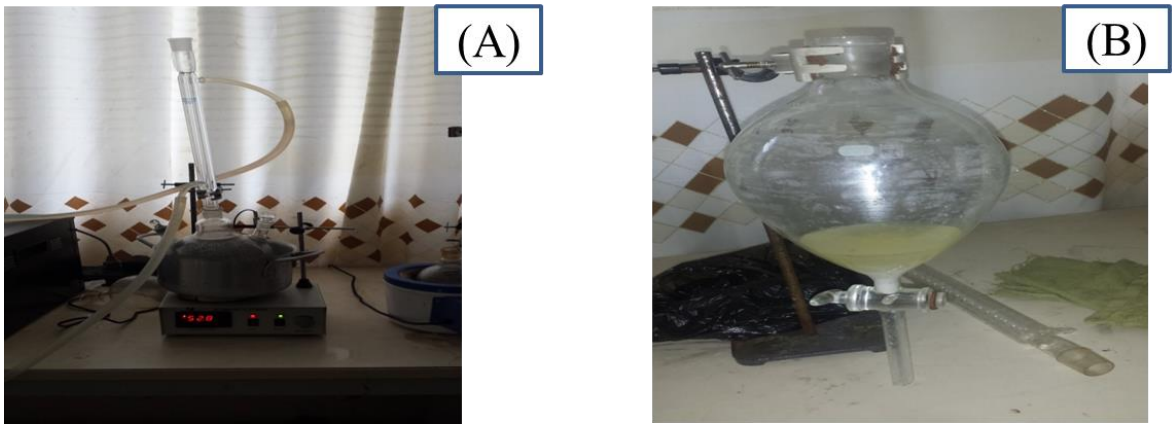
Mass of catalyst was calculated as follow:

$$\text{Catalyst weight} = \frac{\text{Mass of catalyst}}{\text{Mass of oil}}$$

Then;

Mass of catalyst=catalyst weight*mass of oil

Calcination in Muffle furnace at various temperatures



Transesterification reaction (A) Transesterification reaction (B) separation funnel