

AMERICAN UNIVERSITY OF BEIRUT

CaO/Al₂O₃ CALCINED AEROGELS AND ALCOGELS FOR
HETEROGENEOUS CATALYTIC PRODUCTION OF
BIODIESEL FROM WASTE COOKING OIL

by
FATIMA MOHAMMAD KESSERWAN

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AN ABSTRACT OF THE THESIS OF

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Title: CaO/Al₂O₃ Calcined Aerogels and Alcogels for Heterogeneous Catalytic Production of Biodiesel from Waste Cooking Oil

The depletion of the world's petroleum reserves, increasing energy demand, and rising greenhouse gas emissions led to the search for an alternative and renewable sources of energy. Biodiesel has become the most promising substitute or additive to diesel fuels since it is renewable, clean, and share similar properties to diesel. In this work, CaO/Al₂O₃ calcined aerogels and alcogels were synthesized for the transesterification of WCO using a rapid epoxide-initiated gelation sol-gel method. All synthesized catalysts were characterized using FTIR spectroscopy, nitrogen adsorption-desorption technique, scanning electron microscopy, X-Ray diffraction, and thermogravimetric analysis. Characterization revealed that the calcined aerogels at low CaO content were not as affected by calcination at 700 °C as their corresponding calcined alcogels. Furthermore, calcined aerogels at low CaO content maintained a different structure than their corresponding calcined alcogels. The 3:1 CaO/Al₂O₃ calcined aerogel showed the best catalytic activity using the minimum amount of material to produce high biodiesel yield and conversion with no soap formation. The effect of CaO content, catalyst loading, methanol to oil ratio, and reaction time on biodiesel production was investigated. After optimization of the parameters, a maximum biodiesel yield (89.84 %) with highest purity (98.04 %) was achieved under the following optimum conditions: 1 wt. % 3:1 CaO/Al₂O₃ calcined aerogel, 11:1 methanol to oil molar ratio, 65°C, and 4 hours. The transesterification reaction followed a pseudo first order kinetics. This work compared the activities of calcined aerogels and alcogels for the production of biodiesel from WCO in an economical and eco-friendly process.

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CHAPTER 1

INTRODUCTION

Because of the depletion of the world's petroleum reserves, increasing energy demand, and rising greenhouse gas emissions, the search for alternative and renewable sources of energy has become very crucial. Since the transportation sector consumes 90 % of the total world energy, finding a sustainable ecofriendly substitute for petro-diesel has received most interest ¹. Biodiesel has become the most promising substitute or additive to diesel fuels. In addition to being renewable, sustainable, and biodegradable, biodiesel is free of Sulphur and aromatics, which makes it cleaner and less toxic than diesel. Furthermore, biodiesel can be used in diesel engines directly or with little modification, since its' physiochemical and fuel properties are grouped into the same range as petroleum diesel². The production of biodiesel can be achieved by a number of different processes including blending, pyrolysis, micro emulsion, or transesterification. The most frequently used method is transesterification. This reaction shows high conversion rate and produces low viscosity biodiesel and useful byproducts such as glycerol, which is commonly used for cosmetic and medicinal applications³.

Traditionally, biodiesel is produced from refined edible oil and alcohol with the help of a homogeneous catalyst. However, edible oils are no longer suitable as raw material because of their limited supply and high cost, which in turn increases the cost of biodiesel production⁴. Recently, waste cooking oil (WCO) has been considered as a replacement not only for being a cheap and widely available alternative, but also as a way to minimize food waste and convert it into energy. Unfortunately, WCO contains some water and free fatty acids (FFAs) that form soap when homogeneous base catalysts are used. To eliminate saponification, homogenous acid

catalysts are used instead, but they are very corrosive to equipment. Furthermore, the use of homogeneous catalysts (base/acid) with WCO gives rise to several other problems such as: large amounts of waste water production and separation complications. Since homogeneous catalysts are the same phase as the products (biodiesel and glycerol), further steps are required to separate the catalyst from the products thus producing waste water in the process. This results in the increase of the cost of biodiesel production and the later purification of glycerol³. In addition, the homogeneous catalysts cannot be reused⁵. To overcome these hindrances to the production process of biodiesel, solid heterogeneous catalysts are used instead, since they are noncorrosive and can be easily separated from the products for recycling. Moreover, reusability of heterogeneous catalysts allows for continuous operation, which minimizes product separation and purification costs⁶.

A heterogeneous catalyst is either a heterogeneous solid base catalyst or a heterogeneous solid acid catalyst. However, base catalysts are always preferred to acid catalysts because they are noncorrosive and have higher activity¹. There are several types of basic heterogeneous catalysts: single component metal oxides, mixed metal oxides, zeolites, clay minerals, and supported alkali metal⁷.

One of the most studied catalyst in biodiesel production is calcium oxide (CaO) because of its high availability, activity, and its low cost⁷. Unfortunately, the active species of calcium oxide tend to leach into the reaction media, interfering with the purity of the products. Therefore, a high surface area material, such as alumina or silica, is required to support CaO, to increase the catalyst's stability and to prevent the dissolution of Calcium ions⁸⁻⁹. Umdu et al. showed that the addition of CaO to alumina is more favorable than silica, since it creates a synergetic effect leading to a complete conversion to methyl ester¹⁰. Moreover, alumina support

is known for its extreme thermal stability and high specific surface area¹¹. For these reasons, alumina was chosen to be the CaO support in this study.

Catalyst synthesis determines the catalytic activity of a catalyst. In fact, several methods have been used for the synthesis of catalysts including thermal pretreatment, precipitation (co-precipitation), impregnation, sol-gel, and mechanochemistry⁷. The advantages of the sol-gel method over others is its low temperature processing and mixing at atomic level, which allows for better homogeneity and high purity. It is comprised of three main processes: hydrolysis, condensation, and drying. In the hydrolysis process, the precursors are hydrolyzed in a solvent forming a sol. During the condensation process, the sol turns into a gel. Finally, depending on the drying process, different materials can be obtained. If the gel is dried under ambient conditions, the gel network collapses to a denser structure due to capillary forces forming a xerogel. If the gel is dried under supercritical conditions, the network structure is retained and an aerogel is formed¹². Traditionally, high-surface-area alumina oxide, whether aerogel or xerogel, was prepared from aluminum alkoxide precursors, such as aluminum isopropoxide or aluminum sec-butoxide. However, due to the high reactivity of alkoxides the hydrolysis and condensation rates become difficult to control, requiring the addition of chelating agents. Therefore, using aluminum salts instead of highly reactive and expensive alkoxide precursors would simplify the process of preparing high-surface-area alumina oxide and reduce its cost¹³. Recently, a new method involving the use of epoxides as gelation initiators was developed for the synthesis of sol-gel materials. In this method, the epoxide acts as a proton scavenger increasing the pH in a slow and uniform manner. Hydrolysis and condensation of the inorganic salts are induced by this pH change to form an inorganic oxide framework¹³.

1.1. Objective

Aerogels are rarely used in the production of biodiesel¹⁴. To the best of our knowledge, CaO/Al₂O₃ catalyst in an aerogel form has never been before. In this study, CaO/Al₂O₃ catalyst was prepared using a rapid sol-gel method to produce biodiesel from waste cooking oil. Two drying techniques (supercritical drying and evaporation) were used to produce aerogels and alcogels; their performance was tested in the transesterification reaction. Furthermore, the CaO content was optimized to eliminate saponification. All catalysts were characterized using FTIR spectroscopy, nitrogen adsorption-desorption technique, scanning electron microscopy, Powder X-Ray diffraction, and thermogravimetric analysis. Then, the effect of catalyst loading, methanol to oil ratio, and reaction time were investigated to produce highest yield of biodiesel using the least amount of material for the shortest duration of time. Finally, the kinetics of the catalyst was determined under the optimal reaction conditions.

CHAPTER 2

LITERATURE REVIEW

2.1. Energy sources

The major problem the world faces today is the catastrophic effects of excessive usage of fossil fuels as well as their depletion. Fossil fuels are still the main source of global energy demand; in fact, they provide approximately 87% of the total world energy. It has been estimated by the Energy Information Administration (EIA) 2006 report that the world's total energy consumption will increase by 59% between 1999 and 2020. Indeed, the world energy demand has been increasing drastically over the last few decades due to fast advancement in huge industries and rapid growth in the world's population. It has been reported that at our current usage rate the reserves will last for 218 years for coal, 41 years for oil, and 63 years for natural gas³. In addition, the Organization of the Petroleum Exporting Countries (OPEC) assumes that the peak production date of world crude oil was 2008 as shown in Figure 1.

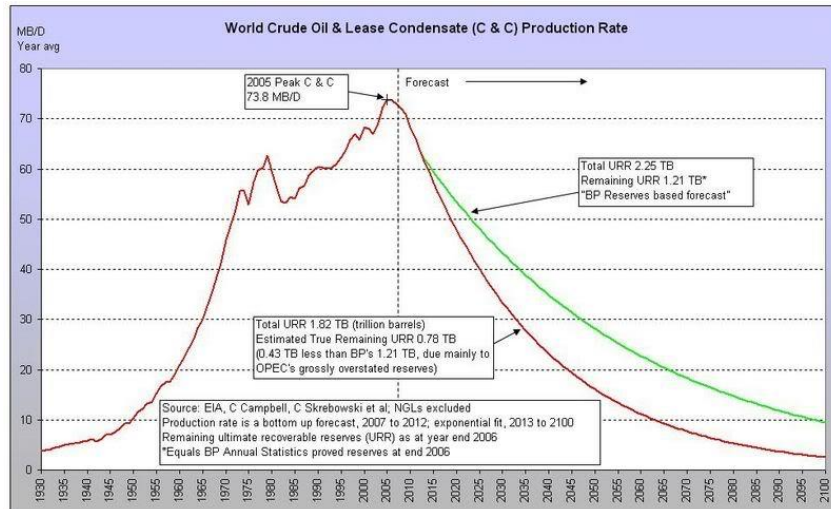


Figure 1 World oil production to 2100^[1]

According to the United States Environmental Protection Agency (EPA), fossil fuel combustion has contributed to about 89 to 92% of the total greenhouse gas emissions since 1990¹⁵(Figure 2). In particular, the transportation sector made up 27 % of the greenhouse gas emissions, which primarily generated from burning fossil fuel, during 2015 (Figure 3). Moreover, the IEA estimated that 8.6 billion metric tons of carbon dioxide (CO₂) will be released to the atmosphere from 2020 to 2035 ¹⁶.

Due to the depletion of world petroleum reserves, increasing energy demand, and rising greenhouse gas emissions, the search for alternative and renewable sources of energy have become very crucial. The fuel used for transportation is over 90 % petroleum based containing gasoline and diesel. As a result finding a sustainable ecofriendly substitute for petro-diesel has been of utmost interest¹⁷.

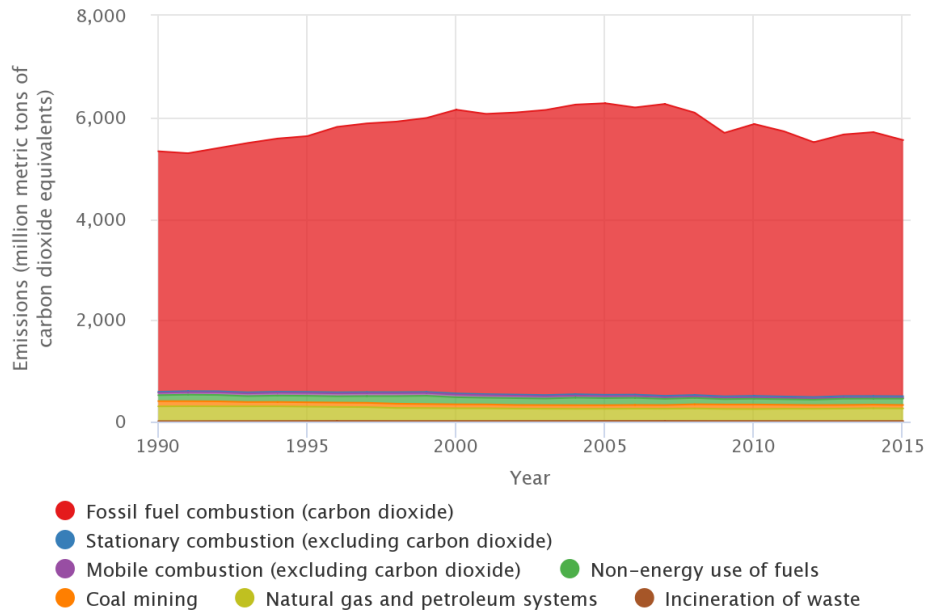


Figure 2 U.S greenhouse gas emission from 1990-2015^[15]

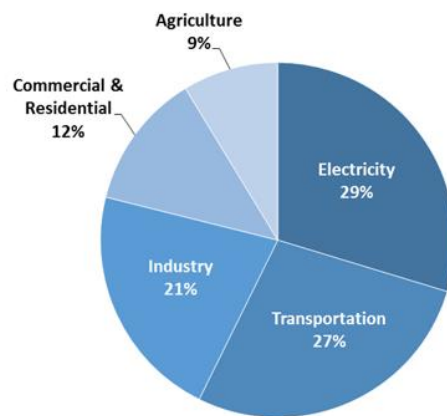


Figure 3 U.S greenhouse gas emission by economic sector in 2015¹⁷

2.2. Biodiesel

In 1893, Rudolph Diesel used vegetable oil (peanut oil) as a fuel in a diesel engine. However, the high viscosity and surface tension of vegetable oil prevent their direct use into

diesel engines because it causes poor atomization, incomplete combustion, and carbonization. In 1937, Charles George Chavanne patented for a method to convert vegetable oils for their use as fuels¹⁶. By converting vegetable oil into biodiesel, the viscosity and boiling point are reduced making it capable of being used in engines. Biodiesel has become the most promising substitute or additive to diesel fuels. It is composed of long chain of carbon atoms, with hydrogen atoms attached, ending with an ester functional group. The chemical formula of biodiesel varies depending on the fatty acid it is produced from; a typical molecule of biodiesel looks like the structure depicted in Figure 4.

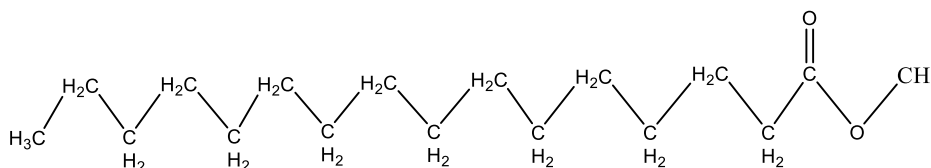


Figure 4 A typical molecule of Biodiesel

Biodiesel is renewable, sustainable, and biodegradable. It is free of Sulphur and aromatics, which makes it cleaner and less toxic than diesel. Moreover, biodiesel can be used in diesel engines directly or with little modification, since its' physicochemical and fuel properties are grouped into the same range as petroleum diesel². The sectors in which biodiesel can be used instead of diesel are listed in Table 1. Compared to diesel, biodiesel emits fewer emissions such as CO₂, CO, SO₂, particulate matter (PM), and hydrocarbon (HC). It also has higher cetane number, lubricity, flash point, and lower toxicity making it safer to handle. Moreover, it is more cost efficient than diesel because it can be produced locally and does not require drilling, transportation, and refinement. However, biodiesel has its drawbacks, such as emitting higher

NO_x emissions. Furthermore, biodiesel's higher viscosity cause difficulties in pumping, combustion, and atomization in the injector system of a diesel engine. In addition, biodiesel reduces power by 5% compared to that of diesel¹⁶.

Table 1 Potential of biodiesel usage as a diesel fuel substitute (adapted from ref.15)

Current fuel usage	Potential biofuel substitute (blend or drop-in)
Light vehicles: gasoline, diesel, LPG	Ethanol, biodiesel, renewable gasoline, renewable diesel, other fuels and additives
Heavy vehicles: diesel	biodiesel, renewable diesel
Equipment/machinery: diesel	biodiesel, renewable diesel
Marine: diesel/fuel oil	biodiesel, renewable diesel
Aviation: aviation fuel	renewable aviation fuel
Remote generation: diesel/natural gas	biodiesel, renewable diesel, bio-synthetic gas

Biodiesel can be produced by blending, pyrolysis, micro emulsion, and transesterification. The most frequently used method is transesterification. This reaction shows high conversion rate and produces low viscosity biodiesel and useful byproducts such as glycerol, which is commonly used for cosmetic and medicinal applications³. The quality of biodiesel should be measured to meet the specifications set by the American Society for Testing and Materials (ASTM) D6751.15 standard¹⁸. Consequently, the identification of the chemical structures of biodiesel is crucial. In fact, several instruments can be used to analyze the purity and compositions of biodiesel including gas Fourier transform infrared spectroscopy (FTIR), high-performance liquid chromatography (HPLC), chromatography-mass spectroscopy (GC/MS), and nuclear magnetic resonance spectroscopy (NMR).

2.3. Transesterification reaction

Transesterification is a chemical reaction used to convert triglycerides into biodiesel by an alcohol with the support of a catalyst. The transesterification reaction is described in Figure (5), where R', R'', and R''' are long chains containing carbon and hydrogen atoms (chain fatty acids). Although the reaction is reversible, the backward reaction is very slow due to the non-miscibility of the glycerol with the product formed. In fact, the products are in separate phases. In addition, a large excess of alcohol is used to shift the equilibrium far to the right in this reaction. Biodiesel is usually produced with homogeneous base catalysts such as NaOH and KOH because they are cheap, widely available, and have rapid reaction rate. There are several parameters that affect the transesterification reaction:

- 1- Temperature: since transesterification is an endothermic reaction, increasing the temperature increases the yield and the rate of the reaction¹⁹. Moreover, the high temperature reduces the viscosity of the oil allowing for better interaction conditions and thus a better yield. However, the temperature is limited by the alcohol used in the reaction and cannot exceed its boiling point.
- 2- Catalyst loading: increasing the catalyst loading increases biodiesel yield and the rate of the reaction. However, increasing the catalyst loading of a basic catalyst may cause saponification and result in low biodiesel yield.
- 3- Alcohol to oil ratio: following Le Chatelier's principle, increasing the methanol concentration will favor the forward reaction, thereby increasing the product. Furthermore, a high methanol ratio reduces the viscosity of the reaction mixture which in turn enhances the mass transfer and eventually, the performance of the catalyst.

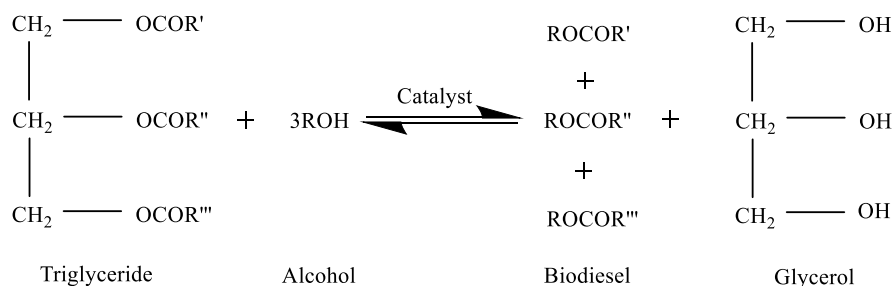


Figure 5 Transesterification of triglycerides in presence of an alcohol

Alcohol is used in the transesterification reaction to convert oil to biodiesel. Thus, the type of alcohol used can influence the properties of biodiesel. Knothe showed that the use of isopropanol produced better biodiesel with superior properties compared to both methanol and ethanol²⁰. However, methanol or ethanol are frequently used because of the high cost of isopropanol.

Biodiesel can either be fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE), depending on which alcohol is used. Unlike methanol, ethanol is safer and completely renewable since it is produced mainly from biomass. However, methanol produces better results in the transesterification of oils and fats since it requires shorter reaction times, smaller catalyst amounts, and lower alcohol/oil molar ratios than other alcohols²¹.

The main problem of biodiesel resides in its high production cost. This is due to its raw materials (refined vegetable oil) whose price can account for 60-75% of the final cost of biodiesel^{6, 22}. Using edible oils as raw material for biodiesel production, not only increases the cost of production, but also competes with the food demand. For these reasons, nonedible oils and waste cooking oils (WCO) have been considered instead to decrease the production costs and eliminate the competition with food supply. Furthermore, WCO represent a large portion of wastes nowadays due to the increase in population and change in lifestyle. According to the

United States Environmental Protection Agency (EPA), hotels and restaurants alone in the United States generate up to 3 billion gallons of WCO per year²³. Hence, producing biodiesel from WCO minimizes food wastes and convert them into usable energy sources. However, the major drawback for using nonedible oil and WCO is their high free fatty acids (FFAs) content, which causes saponification and subsequently leads to low biodiesel yield. In this study, sunflower WCO was used since sunflower oil is the one of the most used oils in Lebanon.

2.4. Types of Catalysis used in transesterification reaction

A catalyst is a substance that speeds up a chemical reaction without being consumed by the reaction. The choice of a catalyst is very essential in determining product yield. In fact, the great challenge that researchers face in production of biodiesel is maximizing biodiesel yield while minimizing the catalyst usage.

Hence, a good catalyst should have high activity, selectivity, surface area, and porosity (if applicable to be measured). It should also tolerate high temperature and temperature fluctuations¹. There are four primary catalysts used for biodiesel production described in the literature: homogeneous base catalysts, homogeneous acid catalysts, enzyme catalysts, and heterogeneous catalysts.

2.4.1. *Homogeneous Base Catalysts*

When edible oil is used as the raw material, base-catalyzed transesterification is the preferable method due to its high efficiency, availability, and low cost⁶. Base catalysts such as sodium hydroxide and potassium hydroxide remove a proton from alcohol to produce alkoxide

and a protonated catalyst, causing a nucleophilic attack of alkoxide to the carbonyl group of triglyceride to release an ester. Figure 6 clearly depicts the process.

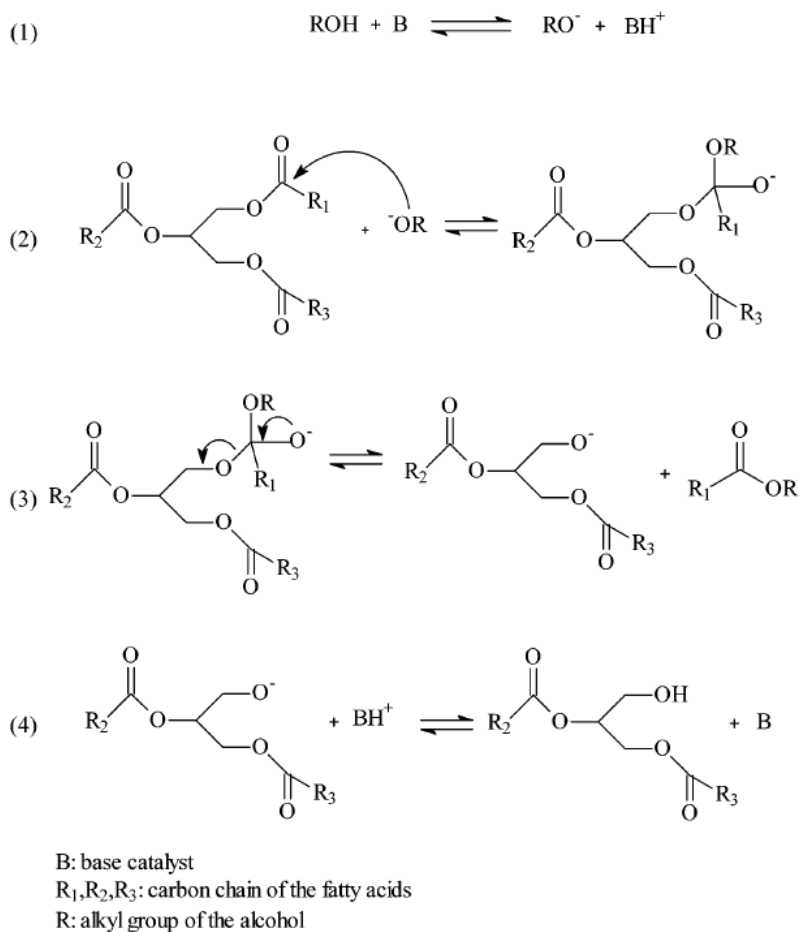


Figure 6 Homogeneous base-catalyzed reaction mechanism for transesterification²²

Awad et al. studied the optimal conditions to enhance the yield of biodiesel. They used three types of waste oils, with different acidities, as raw materials for biodiesel production. Their results showed that alkaline catalysts are sensitive to moisture and to high free fatty acids (FFAs)

levels, which form soap with a strong base. As the acidity of the oil they used increased from 0.8 mg_{KOH}/g to 6.5 mg_{KOH}/g biodiesel production decreased from 97% to 76%²¹.

Therefore, alkaline catalysts do not function well with the use of nonedible and waste cooking oil as raw material, due to their high FFA and water content. When FFA content is above 1 %, the alkaline catalyst leads to the formation of soaps due to either its reaction with free fatty acids or saponification of the triglycerides and biodiesel. Water causes the hydrolysis of biodiesel which leads to subsequent formation of soaps²⁴. These undesired reactions, depicted in Figure 7 and 8, consume the catalyst and results in reduced biodiesel yields.

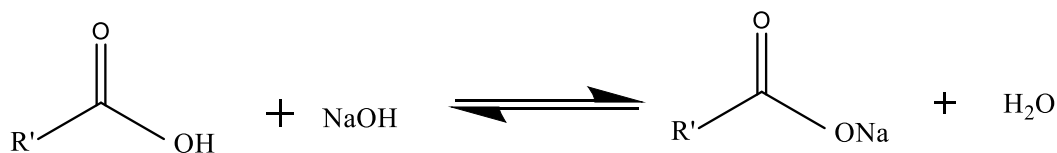


Figure 7 Saponification reaction of FFA

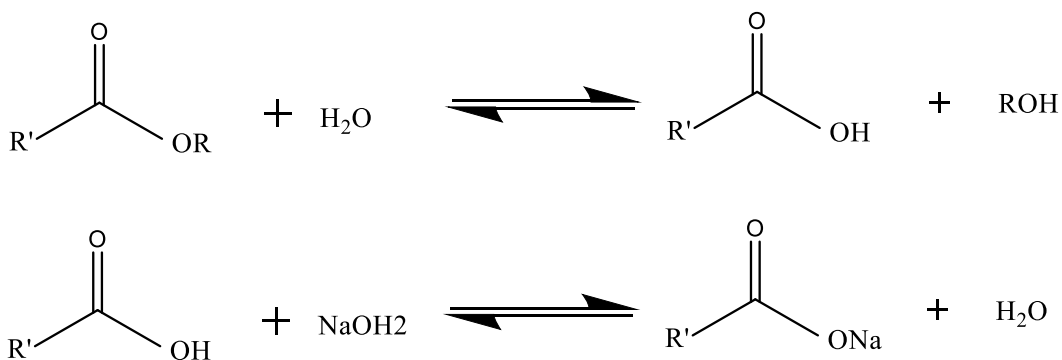


Figure 8 Hydrolysis of ester followed by saponification reaction of produced FFA

Another drawback of alkaline catalysts is the formation of a glycerol salt by-product during the neutralization of the catalyst. As a result, a more expensive purification process of profitable glycerol is required²⁵.

2.4.2. Homogeneous Acid Catalysts

Although base-catalyzed transesterification is almost 4,000 times faster than acid-catalyzed transesterification, the latter is recommended due to high levels of FFA found in WCO²⁶. In fact, acid catalysts can simultaneously catalyze esterification and transesterification; it can also convert FFA into biodiesel. Acid catalyst protonates the carbonyl group, which increases the electrophilicity of the adjoining carbon atom; this makes it more susceptible to nucleophilic attack by the alcohol²²(Figure 9).

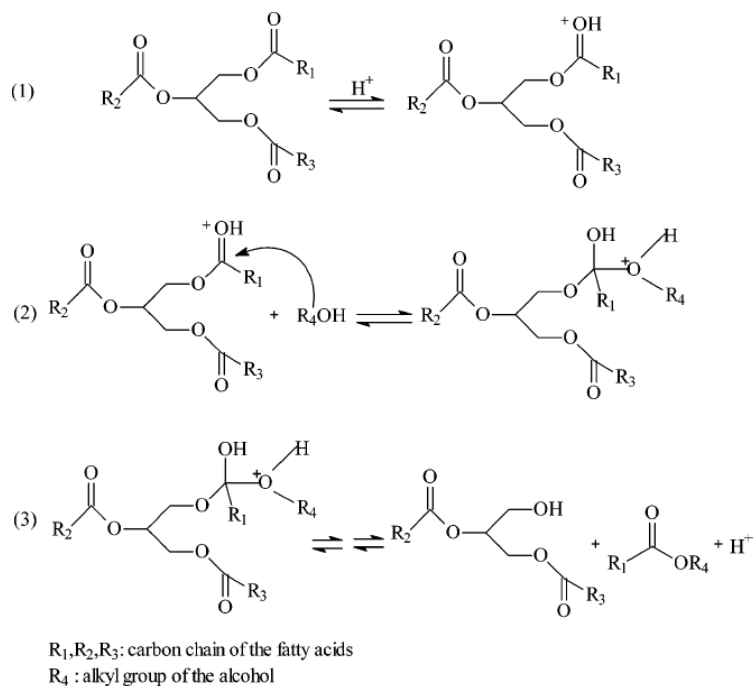


Figure 9 Homogeneous acid-catalyzed reaction mechanism for the transesterification²²

Several studies have successfully demonstrated that the reaction rate as well as biodiesel production can be increased by using higher temperatures, pressure, and catalyst loading²⁷⁻²⁸. However, such harsh conditions result in ether formation due to alcohol dehydration²². Moreover, additional processing steps are required to remove the acid catalyst, increasing waste formation and biodiesel production costs. Other disadvantages of using acid catalysts include the corrosive nature of acids and water formation during acid esterification, which hinders the process.

2.4.3. *Enzyme Catalysts*

The use of enzymes as biocatalysts gained interest due to their high activity and selectivity under mild and environmental friendly conditions²⁹. Unlike homogeneous (acid/base) catalysts, enzyme catalysts- such as lipases- allows for simple recovery and reuse of glycerol without complicated purification, simple separation process of methyl/ethyl esters from other compounds, and almost no chemical waste liquid produced⁵. However, enzyme catalysts are expensive and sensitive to temperature. They are also sensitive to high level of FFAs and short chain alcohols (such as methanol and ethanol), which denature the enzyme to a certain extent. Moreover, the glycerol produced from the reaction negatively affects the enzyme³⁰.

2.4.4. *Heterogeneous Catalysts*

The use of homogeneous catalysts (base/acid) with WCO causes several problems such as: large amounts of waste-water production and separation complications; therefore, increasing the cost of biodiesel production³. In addition, homogeneous catalysts (acid/base) are removed

together with the glycerol layer after the reaction, making purification of glycerol more expensive. Moreover, the catalyst cannot be reused⁵. Consequently, Heterogeneous catalysts offer several advantages over their homogeneous counterparts. In addition to having high catalytic activity, being environmentally benign, and easily separable, heterogeneous catalysts can be reused or regenerated^{24, 31}. Furthermore, they are operative in continuous processes by simple filtration on contrary to homogeneous catalysts, which require neutralization by quenching the reaction²⁴. However, they have lower reaction rates than homogeneous catalysts due to diffusion problems. Since transesterification is considered a three phase process (oil, methanol, and solid), the reactants need time to diffuse to the catalyst⁷.

The steps that occur in a chemical reaction involving a heterogeneous catalyst is as follows:

1. Reactants diffusion to the catalyst.
2. Reactants diffusion into the pores of the catalyst.
3. Reactants adsorption on the inner surface of the pores. The process can be by physical (physisorption) or chemical (chemisorption) means.
4. Chemical reaction occurs on the catalyst surface, by the formation and decomposition of intermediate adsorbed species.
5. Products desorption from the catalyst surface, to empty the active site for a new set of molecules to be adsorbed to and react.
6. Products diffusion out of the pores away from the catalyst's surface through the boundary layer into the gas phase.

A heterogeneous catalyst is either heterogeneous solid base catalyst or heterogeneous solid acid catalyst. However, base catalysts are always preferred to acid catalysts because they

have higher activity¹. There are several types of basic heterogeneous catalysts including: single component metal oxides, mixed oxides, zeolites, supported alkali metal, and clay minerals⁷.

2.5. Choice of catalyst

CaO was chosen as the active metal for this study because it's economical, highly active, and readily available. Figure 10 shows the proposed mechanism of CaO catalyzed transesterification. As shown, the methoxide attacks the carbonyl carbon in the triglyceride forming a tetrahedral intermediate, which eventually destabilizes and breaks down to diglyceride and methyl ester. The process keeps repeating until the triglyceride is converted to one mole of glycerol and three moles of methyl esters⁷.

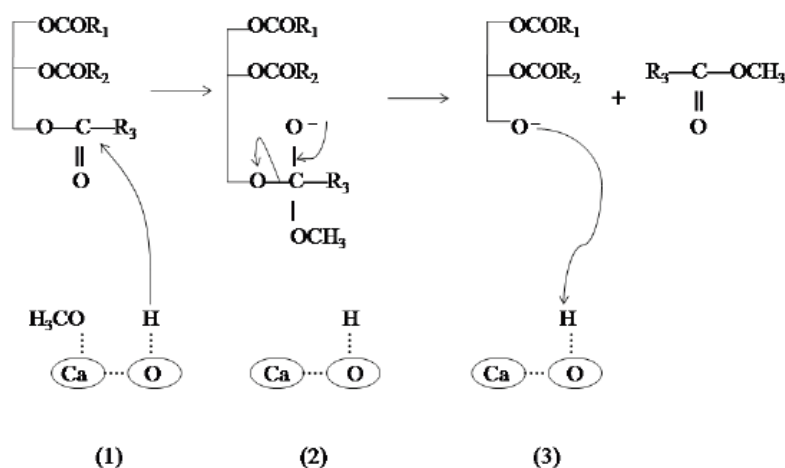


Figure 10 Mechanism of CaO-catalyzed transesterification⁷

However, during the transesterification reaction, a partial dissolution of Ca²⁺ from the CaO surface occurs causing separation problems of Ca²⁺ from the products. This was observed by Granados et al.³² who used calcium oxide for the production of biodiesel from sunflower oil.

Although they were able to reach a conversion of 94%, but the active species of calcium oxide was leached into the reaction medium. This leaching phenomena was also observed by Colombo et al.³³ who also used CaO as heterogeneous catalyst for the transesterification of vegetable oil. Since calcium concentration affects the quality of biodiesel, Colombo et al. had to determine the calcium concentration found in the produced biodiesel. They concluded that the calcium concentration was high enough to exceed the maximum limit set by the Brazilian National Petroleum Agency (ANP) and a secondary operation was required to purify the biodiesel obtained. Therefore, using a high surface area material, such as alumina or silica, to support CaO will increase the catalyst stability and prevent dissolution of Ca^{2+} , thus eliminating the need for biodiesel purification step. Moreover, a high surface area support allows for a decent dispersion of the metal oxide leading to an increased catalytically active surface³⁴. This was proved by Umdu et al. who investigated the production of biodiesel from algal lipids using pure CaO and alumina supported CaO⁸. In the study, alumina supported CaO catalyst was more active than pure CaO⁸⁻⁹ and no leaching of Ca^{2+} was observed. Furthermore, in another study Umdu et al investigated the effect of silica and alumina as supports for CaO during the transesterification of vegetable oil. The study showed that the addition of CaO to alumina created a synergetic effect leading to a 100 % yield (complete conversion to methyl ester) while a silica support gave only 8.27 % yield¹⁰. Moreover, alumina support has been extensively used in catalysis due to its extreme thermal stability and high specific surface area¹¹. For these reasons, alumina was chosen to be the support for CaO in this study. Previous work done using CaO/ Al_2O_3 catalyst as a heterogeneous catalyst for biodiesel production is summarized in Table 2 along with their method of preparation and calcination.

Table 2 Summary of CaO/Al₂O₃ catalysts used in transesterification reactions

Catalyst	Catalyst preparation and calcination	Oils and fats used	Temperature (°C)	Methanol to oil molar ratio	Catalyst loading (wt.%)	Reaction time (h)	Yield (Y) or conversion (C) in (%)	Ref.
CaO/Al ₂ O ₃ ³⁵	Impregnation method, T _{calc.} = 718 °C for 5 h	Palm oil	65	12:1	3.5	5	Y = 95	[35]
CaO/y-Al ₂ O ₃ ³⁶ (5.5 wt. % of CaO)	Impregnation method, T _{calc.} = 700 °C for 4 h	Sunflower oil	60	9:1	0.51	5	C = 35	[36]
CaO/Al ₂ O ₃ ³⁷	Wet impregnation of CaO on acidic, basic and neutral Al ₂ O ₃ , T _{calc.} = 550 °C for 6 h (under N ₂ atmosphere)	Soybean oil	150	9:1	3	6	Y = 90	[37]
80 wt.% CaO/Al ₂ O ₃ ⁸	Single step sol-gel method, T _{dry} = 120 °C for 18 h, T _{calc.} = 500 °C for 6 h	lipid of yellow green microalgae, Nannochloropsis oculata	50	3.6:1	2	4	Y = 97.5	[8]
40 wt.% CaO/Al ₂ O ₃ ³⁸	sol-gel method, T _{dry} = 120 °C for 18 h, T _{calc.} = 500 °C for 6 h	Soybean oil	70	12:1	6	8	C = 90	[38]
40 wt.% CaO/y-Al ₂ O ₃ ³⁴	sol-gel method, T _{dry} = 120 °C for 18 h, T _{calc.} = 500 °C for 6 h	Corn oil	65	12:1	6	5	Y = 79.1	[34]
Nano CaO/Al ₂ O ₃ ³⁹	Nanoparticles of CaO and Al ₂ O ₃ prepared by the Ball milling	Jatropha oil	100	5:1	0.1	3	Y = 82.3%	[39]

	process $T_{\text{calc.}} = 500$ °C for 3 h							
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2.6. Catalyst Preparation

Catalyst synthesis defines the catalytic activity of a catalyst. There are several methods for the synthesis of catalysts including thermal pretreatment, precipitation (co-precipitation), impregnation, sol-gel, and mechanochemistry⁷. However, as seen in Table 2 most commonly used methods for CaO/Al₂O₃ synthesis are wet impregnation and sol-gel method. Comparison between both methods was investigated by several studies, they showed that the sol-gel method provides a catalyst with better distribution of particles as well as higher activity and selectivity⁴⁰⁻⁴¹. In addition, Moradi et al. compared both methods in the synthesise of CaO/ γ -Al₂O₃ catalyst. The study showed that the percentage of Ca²⁺ leaching was higher in impregnation compared to sol-gel method. Consequently, the catalyst synthesized by the impregnation method lost activity significantly faster than the sol-gel catalyst³⁴.

2.6.1. The sol-gel method

In the current study, the sol–gel method was chosen due to low temperature processing and mixing at atomic level, which allows for better homogeneity and high purity. It is also a very versatile technique allowing for the control of porosity and particle size⁴². The sol-gel process, depicted in Figure 11, is the production of inorganic polymers by converting precursors into a sol (colloidal solution) and finally to a network structure called gel⁴³. It is comprised of three main processes: hydrolysis, condensation, and drying. In the hydrolysis process, the precursors are hydrolyzed in a solvent forming a sol. During condensation process, the sol turns into gel.

Finally, the drying process can lead to different material. If the gel is dried under ambient conditions, the gel network collapses to a denser structure due to the capillary forces forming a xerogel. If the gel is dried under supercritical conditions, the network structure is retained and an aerogel is formed¹².

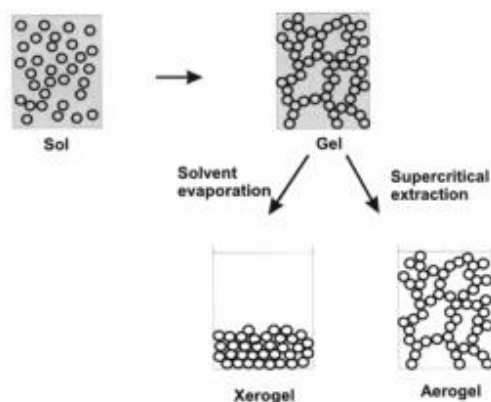


Figure 11 sol-gel method¹²

Traditionally, high surface area alumina oxide, including aerogels and xerogels, was prepared from aluminum alkoxide precursors, such as aluminum isopropoxide or aluminum sec-butoxide. However, due to the high reactivity of alkoxides the hydrolysis and condensation rates becomes difficult to control, requiring the addition of chelating agents. Therefore, using simple aluminum salts instead of highly reactive and expensive alkoxide precursors would simplify and reduce the cost of preparing high surface area alumina oxide. Recently, a new method involving the use of epoxides as gelation initiators was developed for the synthesis of sol-gel materials, such as transition and main-group metal oxide xerogels, aerogels, and nanocomposites. In this method, the epoxide acts as a proton scavenger increasing the pH in a slow and uniform manner.

Hydrolysis and condensation of the inorganic salts are induced by this pH change forming an inorganic oxide framework (gel). As for the epoxide, it is consumed during gelation creating a ring-opened byproducts (Figure 12). For this study, the alumina support was synthesized through the sol-gel polymerization of hydrated aluminum salts (aluminum nitrate nonahydrate) using propylene oxide as the gelation initiator¹³.

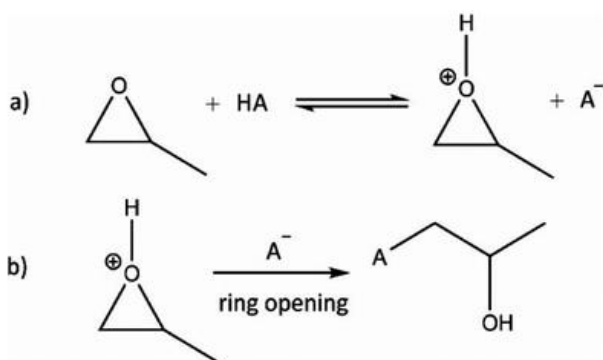


Figure 12 reaction mechanism of propylene oxide⁴⁴

2.6.2. Calcination temperature

The method of catalyst activation affects its catalytic activity. Heterogeneous catalysts are usually thermally activated through calcination. Many studies have investigated the optimum calcination temperature for CaO to increase biodiesel yield. According to Granados et al, the calcination of CaO at 700 °C gave the highest activity during the transesterification of sunflower oil³². Furthermore, Marinković et al studied effect of different calcination temperature (500-750 °C) on the catalytic activity of CaO/ γ -Al₂O₃ catalyst during the methanolysis of sunflower oil. The study showed that CaO/ γ -Al₂O₃ calcined at 700 °C produced the highest FAME content for the shortest reaction time³⁶. For these reasons and the fact that we are using sunflower WCO, the

CaO/Al₂O₃ catalyst prepared in this study was calcined at 700 °C. After calcination, the catalyst was stored in a desiccator to prevent atmospheric CO₂ and moisture poisoning^{7, 36}.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

In this study, the chemicals were received from their corresponding companies and used without any further modification. Aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$, ACS reagent, Sigma-Aldrich) and calcium chloride CaCl_2 (anhydrous, BDH chemicals) were used as precursors for alumina and calcium oxide. Ethanol $\text{CH}_3\text{CH}_2\text{OH}$ ($\geq 99.8\%$, Sigma-Aldrich) was used to dissolve the precursors, and propylene oxide $\text{C}_3\text{H}_6\text{O}$ (99%, Acros Organics) was used as the gelation initiator. The alcogels were immersed in acetone (extra pure) for 24 hours before drying under supercritical conditions using CO_2 .

Methanol CH_3OH ($\geq 99.9\%$, Sigma-Aldrich) was the alcohol used for the transesterification reaction. The sunflower WCO was retrieved from a household after 5-time usage. The free fatty acid content in WCO was determined by titration using the following reagents: 0.1 M alcoholic sodium hydroxide (NaOH in ethanol), phenolphthalein (Baker Chemicals), toluene C_7H_8 (Fisher Scientific), and 2-propanol $(\text{CH}_3)_2\text{CHOH}$ (BDH chemicals). The chloroform-d CDCl_3 (99.8%) was used as the solvent for the $^1\text{H-NMR}$ analysis to determine the conversion of WCO to methyl ester.

3.2. Catalyst preparation

In this study, the $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst was prepared using a rapid sol-gel method. In this method, the required amount of aluminum nitrate nonahydrate, calcium chloride, and ethanol were mixed together for 20 minutes at room temperature. The required amount of propylene

oxide was added, and the solution was stirred for 25 seconds. The solution was transferred into closed plastic vials, where gelation was observed after few seconds, and left to age. After 24 hours, the formed alcogels were divided into two batches. The first batch was immersed in acetone for another 24 hours for solvent exchange, where the ethanol was exchanged with acetone, since liquid CO₂ is more miscible with acetone than ethanol. Then, they were dried using CO₂ supercritical drying process, above T_c = 31.1 °C and P_c = 1071 psi, to keep the porous texture of the alcogels intact forming aerogels. While the second batch was aged for another 24 hours. Finally, the aerogels and alcogels were calcined using a temperature program with a heating rate of 2 °C/min and holding time of 5 hours at peak temperature 700 °C to produce calcined aerogels and alcogels.

The calcium chloride to aluminum nitrate nonahydrate molar ratio was varied to produce catalysts with different CaO content. The calcium chloride to aluminum nitrate nonahydrate molar ratio was varied from 2 to 6. The 2:1 CaO/Al₂O₃ (equivalent to 62 wt. % CaO loading) was the lowest molar ratio prepared because according to previous work (Table 2), highest biodiesel yield (97 %) achieved was with 80 wt. % CaO loading. Table 3 shows the molar ratios used for the synthesis of CaO/Al₂O₃ catalysts and alumina support, where Al:PO:CaCl₂:Eth stands for: aluminum nitrate nonahydrate, propylene oxide, calcium chloride, and ethanol respectively. As seen in Table 3, the ethanol molar ratio increased with the addition of CaCl₂. The additional ethanol added was calculated according to the solubility of CaCl₂ in ethanol.

Table 3 Molar ratios used for the preparation of CaO/Al₂O₃ aerogels and alcogels

Catalyst	Chemical composition	Molar ratios
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Al ₂ O ₃	Al:PO:Eth	1:10:33.3
2:1 CaO/Al ₂ O ₃	Al:PO:CaCl:Eth	1:10:2:51.7
3:1 CaO/Al ₂ O ₃	Al:PO:CaCl:Eth	1:10:3:61.7
4:1 CaO/Al ₂ O ₃	Al:PO:CaCl:Eth	1:10:4:70
5:1 CaO/Al ₂ O ₃	Al:PO:CaCl:Eth	1:10:5:80
6:1 CaO/Al ₂ O ₃	Al:PO:CaCl:Eth	1:10:6:90

3.3. Free fatty acid calculation

Before using the WCO in transesterification reaction, its free fatty acid content was determined according to the British-Adopted European Standard (BS EN 14104:2003). Equal volumes of toluene (50 mL) and 2-propanol (50 mL) were mixed and added to 20 grams of WCO along with 2 drops of phenolphthalein indicator (Noted as mixture). A blank was prepared by mixing 50 mL of toluene with 50 mL of 2-propanol with 2 drops of phenolphthalein indicator. The titration solution prepared was 0.1 M alcoholic NaOH, since the mixture is more miscible in ethanol than water. The blank and mixture were titrated against the titration solution from a burette until it reached the equivalence point (pink color). The FFA% was calculated using the following equation below⁴⁵:

$$\text{FFA}\% = \frac{(v - b) \times N \times 28.2}{w} \quad (\text{Eq. 1})$$

v is the volume in mL of titration solution (0.1 M alcoholic NaOH) that was added to the mixture to reach the equivalence point.

b is the volume in mL of titration solution that was added to the blank to reach the equivalence point.

N is the normality of the titration solution which is 0.1

28.2 is the molecular weight of oleic acid divided by ten.

w is the weight of the sample of oil in grams (20 g)

3.4. Transesterification reaction

The experiment was performed in a 50 mL round bottom flask equipped with a water-cooled condenser and a magnetic stirrer. The WCO (16.67 grams, 0.02 moles) was preheated up to a 65 °C by means of a water bath; then the methanol and catalyst were added to the reaction. The mixture was stirred for 5 h under reflux (65 °C). After stopping the reaction, the mixture was centrifuged at 4000 rpm for 10 minutes to remove the catalyst and separate the liquid phase into a lower layer containing glycerol and an upper layer containing methyl esters and methanol. The upper layer was transferred to a rotatory evaporator to remove the methanol. Finally, the product remaining (represents biodiesel yield) was weighed and a sample was taken to ¹H-NMR analysis to determine the purity of the product.

An optimum condition was reached after varying the parameters (CaO content, catalyst loading, methanol to oil ratio, and reaction time) while keeping the temperature (65 °C) constant. The initial conditions used were 12:1 methanol to oil molar ratio (methanol = 0.24 moles, 7.7 grams), 2 wt. % catalyst loading (0.3334 grams), and 5 hr reaction time. These conditions were adopted based on previous studies' optimum conditions, depicted in Table 2, which used 12:1 methanol to oil molar ratio for 5 hr at 65 °C temperature³⁴⁻³⁵. However, for economical purposes the catalyst loading was adopted from the least catalyst loading used in the previously mentioned studies at atmospheric pressure⁸. For the kinetic study, identical sets of the transesterification reaction using the optimum condition were performed. The reactions were stopped at different reaction times (15, 30, 45, 60, 90, 120, 180, 210, 240, 270, and 300 min) and the biodiesel yields and conversions (purity) were calculated.

3.5. Methyl ester analysis

The yield of biodiesel was calculated by the following equation⁴⁶:

$$\text{Yield} = \frac{\text{weight of biodeisel}}{\text{weight of oil}} \quad (\text{Eq. 2})$$

Where, the weight of biodiesel represents the weight of the final product after the catalyst is removed, lower glycerol layer is decanted, and the methanol is evaporated. While, the weight of the oil is the weight of the WCO used as the starting material for the reaction. A sample of the final product (biodiesel) is dissolved in CDCl_3 solvent for Nuclear Magnetic Resonance ($^1\text{H-NMR}$) analysis. The $^1\text{H-NMR}$ analysis was performed to determine the conversion of sunflower WCO to methyl ester, which represents the purity of the obtained biodiesel. The conversion of WCO into methyl esters was calculated using the equation given below⁴⁷

$$C = \frac{2 \times A_{\text{ME}}}{3 \times A_{\alpha\text{-CH}_2}} \times 100 \quad (\text{Eq. 3})$$

Where C is the conversion of methyl esters (in percentage); A_{ME} is area from the integration value of the protons at 3.6 ppm corresponding to methoxy groups in the methyl ester, and $A_{\alpha\text{-CH}_2}$ is area from the integration value of protons at 2.3 ppm corresponding to the methylene protons. The signals corresponding to CDCl_3 , methoxy protons, and methylene protons are represented as red arrows in Figure 13.

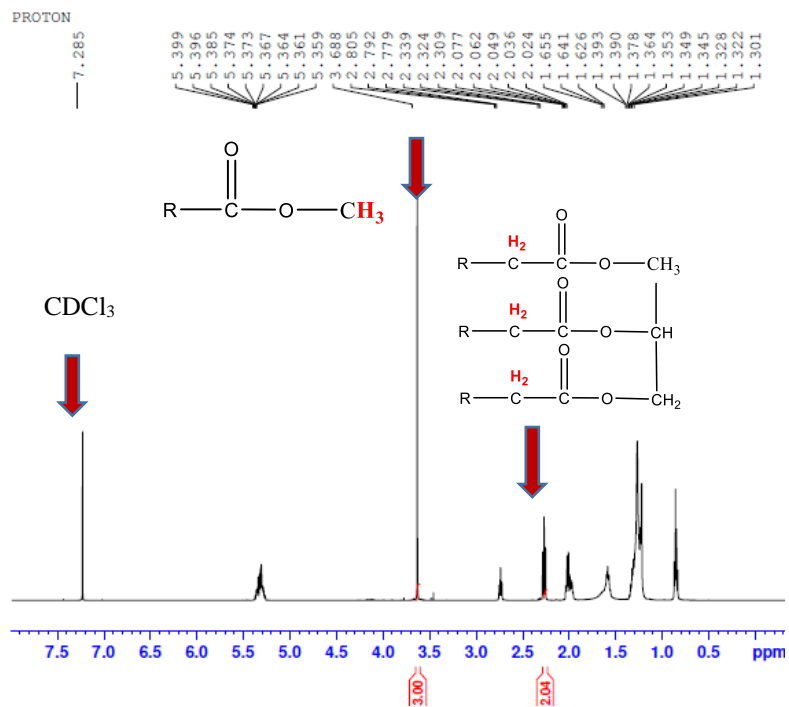


Figure 13 ^1H NMR spectrum of sample collected after using the optimum condition: 4 hours reaction time at 65°C ; alcohol to oil mole ratio of 11:1; catalyst amount of 1 wt% with respect to oil.

3.6. Characterization techniques:

After synthesis and calcination, the catalysts were characterized using Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption technique, scanning electron microscopy (SEM), Powder X-Ray diffraction (PXRD), and thermogravimetric analysis (TGA).

3.6.1. Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) is used to identify the functional groups existing on the catalyst surface. The infrared spectra were recorded on FT-IR

spectrometer Thermo-Nicolet working in the transmittance mode, in the 400-4000 cm^{-1} range with the resolution of 4 cm^{-1} using 12 scans. The potassium bromide (KBr) pellet method is used for the sample preparation.

3.6.2. Nitrogen adsorption-desorption technique

The surface area and pore volume was determined by Nitrogen adsorption-desorption technique in order to evaluate the effect of increasing CaO content on alumina support using an autosorb iQ-Microscope-XR (Quantachrome Instruments, Boynton Beach, FL, USA) gas analyser. The Brunauer-Emmett-Teller (BET) theory was used to calculate the surface area, while the Barrett-Joyner-Halenda (BJH) method was used to determine the pore volume of the catalysts. Prior to analysis, the catalyst was calcined at 700 °C and then degassed at 120°C for three hours to activate and remove moisture and other adsorbed gases from the catalyst surface and pores.

3.6.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed using a MIRA3 Tescan electron microscope. SEM images shows the morphology, grain size, and grain shape of the catalyst. Prior to analysis, the samples were coated with a thin layer (40 nm) of Gold.

3.6.4. Powder X-Ray Diffraction (PXRD)

As the catalysts are in powder form, a Powder X-ray diffraction (PXRD) was used for analysis. PXRD is a non-destructive analytical tool used to determine the crystallinity of the

catalyst. The analysis was obtained using a Bruker D8 advance X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany). The conditions used for all samples were: 40 kV, 40 mA (1600 W) using Cu K α radiation source ($k = 1.5418 \text{ \AA}$), scan speed of 1 degree/minute, 2θ scan range of $5 - 80^\circ$, and step width of 0.01° .

XRD patterns were analyzed to check the catalysts structure and calculate the average crystallite sizes. The crystallite size was obtained using the Scherrer equation given below⁸:

$$T = \frac{K \lambda}{(\beta \cos \theta)} \quad (\text{Eq. 4})$$

K = Shape Factor

β = FWHM = line broadening at half the maximum intensity

λ = wavelength of x-rays, and

θ = Bragg's diffraction angle

Note that the Scherrer equation gives the size of the apparent or average particle-size of the material. As mentioned before, the catalysts used are powders that are usually aggregates of smaller particles, and consequently contain a distribution of particle sizes.

3.6.5. Thermogravimetric Analysis (TGA)

TGA is used to determine the thermal stability of the CaO/Al₂O₃. This technique records the change of mass of a substance with respect to temperature while being heated using a controlled heating rate, gas atmosphere, and flow rate. Thermogravimetric Analysis (TGA) was performed with a Netzsch TG 209 F1 Libra apparatus. The analysis was recorded in N₂ flow from 30 to 1100°C at a heating rate of 5 K/min.

Prior to analysis, the catalyst was calcined at 700 °C, then around 6 mg of the catalyst was weighed and transferred to crucibles used for the machine.

TGA has been used to identify the thermal reaction conditions that the catalysts could handle and the optimum calcination temperature required. In fact, Umdu et al. used TGA analysis to determine the temperature required to remove water and carbon dioxide from pure CaO and used his optimal calcination temperature accordingly⁸.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Catalyst characterization

The synthesized CaO/Al₂O₃ calcined aerogels and alcogels were characterized by nitrogen adsorption-desorption technique known as BET, Fourier-transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM).

4.1.1. Nitrogen Adsorption-Desorption Technique Analysis

The specific surface area (SSA) and porosity analysis for CaO/Al₂O₃ and alumina calcined aerogels and alcogels are grouped in Tables 4 and 5.

Table 4 Specific surface area and pore volume of CaO/Al₂O₃ calcined aerogels with different CaO loading

Catalyst	Specific Surface area (m ² /g)	Pore volume (cc/g)
Al ₂ O ₃	369	3.87
2-1 CaO/Al ₂ O ₃	44	0.19
3-1 CaO/Al ₂ O ₃	24	0.08
4-1 CaO/Al ₂ O ₃	21	0.07
5-1 CaO/Al ₂ O ₃	10	0.04
6-1 CaO/Al ₂ O ₃	14	0.03

Table 5 Specific surface area and pore volume of CaO/Al₂O₃ calcined alcogels with different CaO loading

Catalyst	Specific Surface area (m ² /g)	Pore volume (cc/g)
Al ₂ O ₃	303	0.41
2-1 CaO/Al ₂ O ₃	21	0.07
3-1 CaO/Al ₂ O ₃	16	0.07
4-1 CaO/Al ₂ O ₃	15	0.07
5-1 CaO/Al ₂ O ₃	16	0.03
6-1 CaO/Al ₂ O ₃	16	0.05

The calcined alumina aerogels have a significantly higher SSA and pore volume (369 m²/g and 3.87 cm³/g) than calcined alumina alcogels (303 m²/g and 0.41 cm³/g). Furthermore, alumina calcined aerogel and alcogel have a significantly higher SSA than all the CaO/Al₂O₃ calcined aerogels (with highest SSA and pore volume of 44 m²/g and 0.19 cm³/g) and alcogels (with highest SSA and pore volume of 19 m²/g and 0.19 cm³/g). As a matter of fact, the SSA and pore volume of CaO/Al₂O₃ calcined aerogels decreased even further as CaO content increased, which is in agreement with results obtained from a study done by Umdu et al.⁴⁸. This is probably because the increased CaO content enters and blocks the pore volume of the alumina support leading to a lower specific surface area and pore volume¹. However, the SSA of CaO/Al₂O₃ calcined alcogels stayed relatively the same ~ 15 m²/g as CaO content increased, although the pore volume still decreased from 0.19 cm³/g for 2:1 CaO/Al₂O₃ to 0.04 cm³/g for 6:1 CaO/Al₂O₃. Nevertheless, the CaO/Al₂O₃ calcined aerogels show a higher SSA than their corresponding CaO/Al₂O₃ calcined alcogels. This shows that even after calcining at 700 °C, aerogels still maintained the capacity to have a higher SSA and pore volume than alcogels. Furthermore, the

calcined aerogel exhibits a linear trend as depicted in Figure 14 between the pore volume and SSA, which is not seen in calcined alcogels.

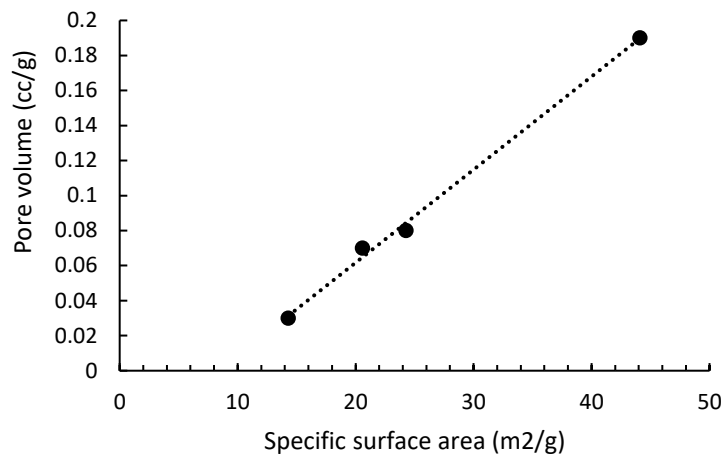


Figure 14 Surface area vs. pore volume in calcined CaO/Al₂O₃ aerogels

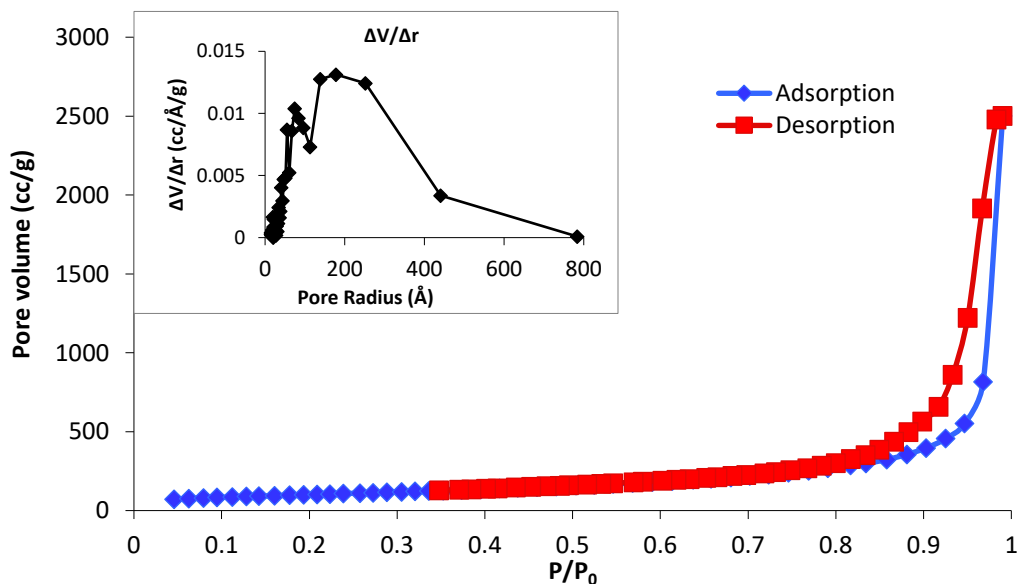


Figure 15 Nitrogen adsorption-desorption isotherms of alumina calcined aerogel with corresponding pore size distribution

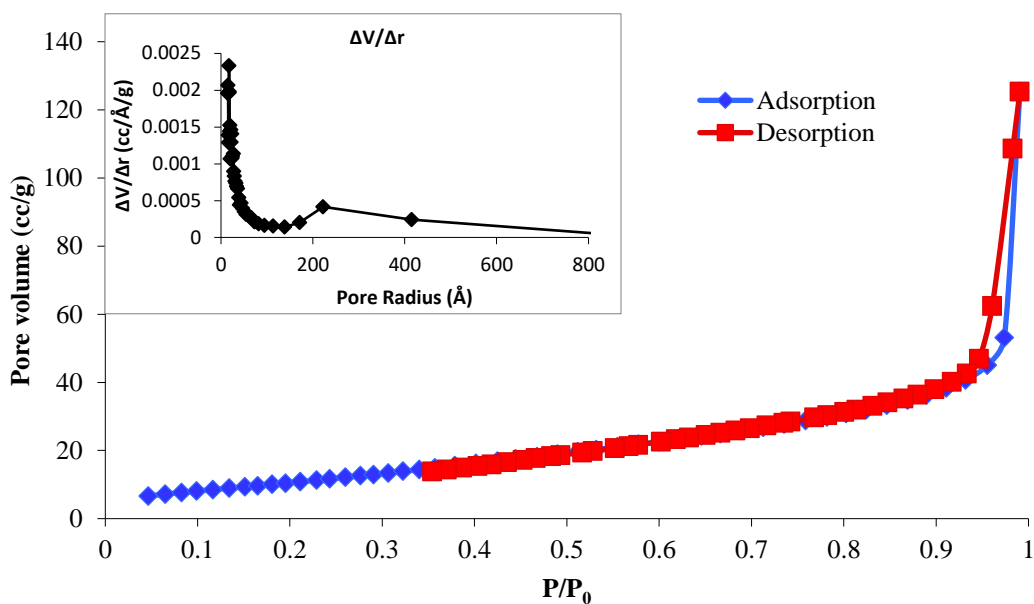


Figure 16 Nitrogen adsorption-desorption isotherm of 2:1 CaO/Al₂O₃ calcined aerogel with corresponding pore size distribution

All the catalysts synthesized have similar isotherm as depicted in Figure 15 and 16. According to the IUPAC classification of adsorption isotherms, all the catalysts are mesoporous since their isotherms follow Type V isotherm. In particular, the hysteresis loop in Type V isotherm represents the capillary condensation that takes place in mesopores⁴⁹. Furthermore, the hysteresis loop for all catalysts is a Type H1 hysteresis representing a porous material containing agglomerates of relatively uniform spheres⁵⁰. As for the pore size distribution, the highest pore radius corresponds to calcined alumina aerogel, which also has the broadest pore size distribution. While, the calcined CaO/Al₂O₃ alcogels and aerogels share a narrow and similar pore size distribution profile, as exhibited in Figure 16.

4.1.2. *Fourier-transform infrared spectroscopy (FTIR) analysis*

As mentioned in the literature review, CaO/Al₂O₃ catalysts are very sensitive to moisture and atmospheric CO₂^{7, 36}. This is clearly supported by the FTIR results shown in Figures 17 and 18. Where, the broad band ranging from 3643 cm⁻¹ to 3438 cm⁻¹ corresponds to the stretching of hydroxyl groups, while the sharp peak around 1630 cm⁻¹ is attributed to hydroxyl group bending⁵¹⁻⁵². The absorption band ranging from 1488 cm⁻¹ to 1415 cm⁻¹ seen in all catalysts, except the calcined alumina aerogel and alcogel, corresponds to the symmetric stretching of unidentate carbonate. Furthermore, the presence of carbonate is clearly exhibited by the weak absorption bands ranging from 819 cm⁻¹ to 842 cm⁻¹. These hydroxyl and carbonate groups are formed due to the exposure to air while measuring, which contains humidity and CO₂. As for the peak around 455 cm⁻¹ corresponds to the lattice vibrations of CaO⁵¹. Finally, the peak at 569 and 668 cm⁻¹, it is attributed to the stretching of Al-O bond⁵³. For calcined aerogels, the Al-O (569 cm⁻¹) and CaO peaks were not observed at low CaO concentration (2:1 CaO/Al₂O₃), but they were seen after increasing the CaO content (3:1 to 6:1 CaO/Al₂O₃). However, these peaks were observed in all calcined alcogels even at low CaO content (2:1 CaO/Al₂O₃). Moreover, the 668 cm⁻¹ peak seen in both 2:1 and 3:1 CaO/Al₂O₃ calcined aerogels is not seen in their corresponding (2:1 and 3:1 CaO/Al₂O₃) calcined alcogels. This shows that the calcined aerogels at low CaO content shows a different structure than their corresponding calcined alcogels.

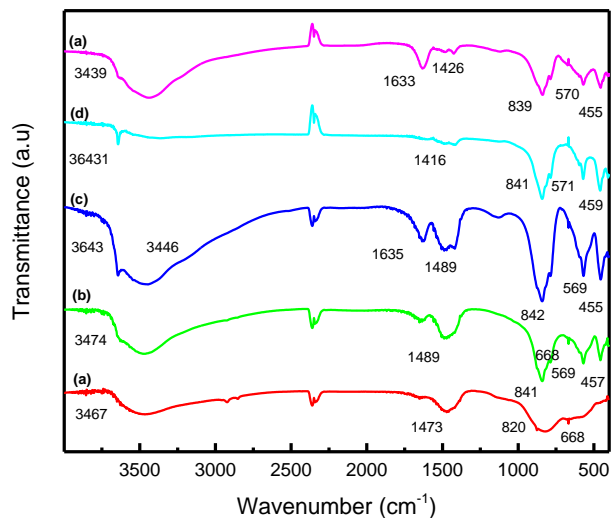


Figure 17 FTIR spectra of the a) 2:1 CaO/Al₂O₃, b) 3:1 CaO/Al₂O₃, c) 4:1 CaO/Al₂O₃, d) 5:1 CaO/Al₂O₃, and e) 6:1 CaO/Al₂O₃ calcined aerogels as a function of wavenumbers at different calcium chloride compositions.

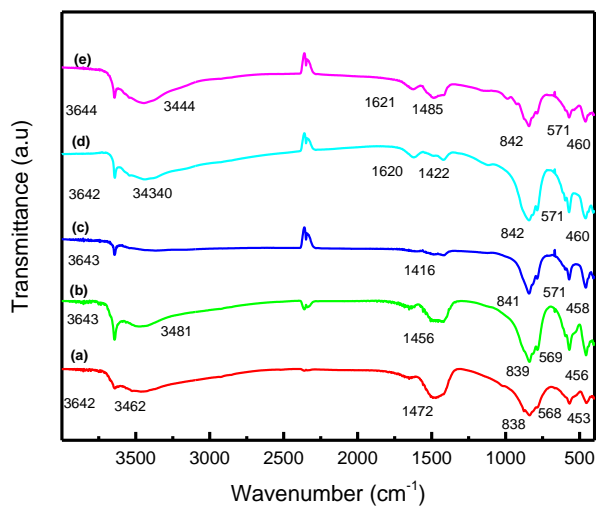


Figure 18 FTIR spectra of the a) 2:1 CaO/Al₂O₃, b) 3:1 CaO/Al₂O₃, c) 4:1 CaO/Al₂O₃, d) 5:1 CaO/Al₂O₃, and e) 6:1 CaO/Al₂O₃ calcined alcogels as a function of wavenumbers at different calcium chloride compositions.

The hydroxyl group was also seen in both calcined alumina aerogel and alcogel, and the 2102 corresponds to H–O–H bonds (Figure 19). As for the peak at 623 cm^{-1} , which is attributed to the stretching of Al-O bond, was only perceived in calcined alumina aerogel, but not in the calcined alcogel support⁵³. This explains why the 668 peak was seen only in the calcined CaO/Al₂O₃ aerogels and in none of the calcined CaO/Al₂O₃ alcogels.

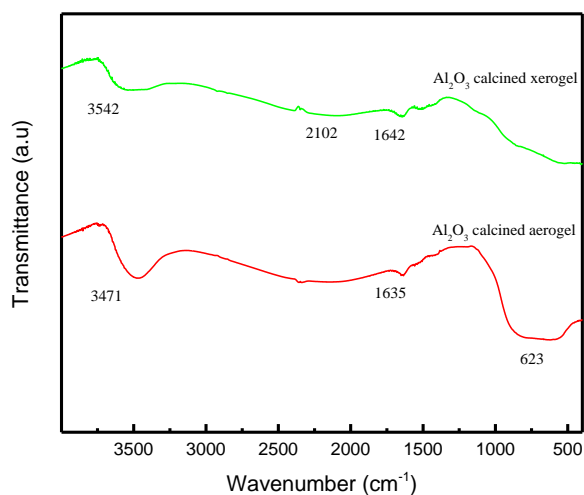


Figure 19 FTIR spectra of the alumina calcined alcogel and aerogel

4.1.3. Powder X-Ray diffraction (XRD)

PXRD patterns of CaO/Al₂O₃ calcined aerogels and alcogels samples obtained at different CaO contents are presented in Figure 20 and 21 respectively, while alumina calcined aerogel and alcogel are depicted in Figure 22. The powder XRD pattern of the CaO shows the main characteristic peak corresponding to 2θ values of 32.2, 37.3, and 53.8°, respectively⁵⁴.

The major diffraction peak of calcium oxide at 2θ angle of 37° was observed on all the catalysts except 2:1 CaO/Al₂O₃ calcined aerogel, since its amorphous. In fact, this peak (at 37° 2θ)

was used to calculate the crystallite size of all the catalysts. The diffraction peaks attributed to calcium hydroxide and CaCO_3 are due to the moisture and CO_2 exposure from air during the measurement⁵⁵⁻⁵⁸. The diffraction peaks are assigned according to the simulated X-ray patterns of CaO , Ca(OH)_2 , and CaCO_3 represented in Figure 23.

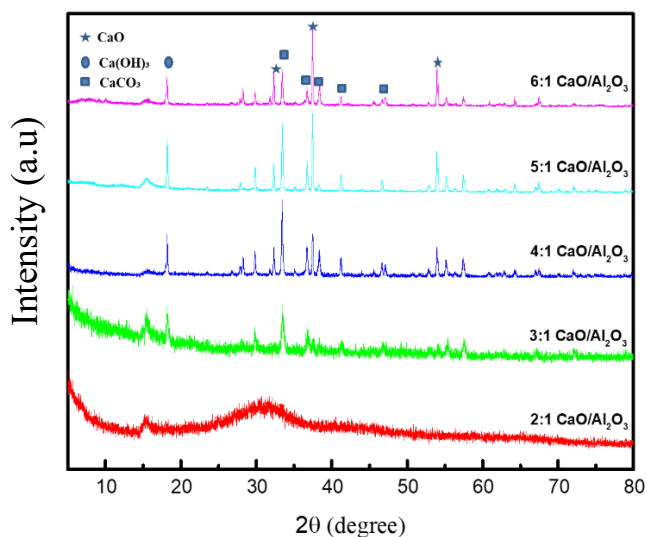


Figure 20 Comparison of powder XRD patterns of the $\text{CaO}/\text{Al}_2\text{O}_3$ calcined aerogels at different calcium chloride compositions calcined at 700 degrees.

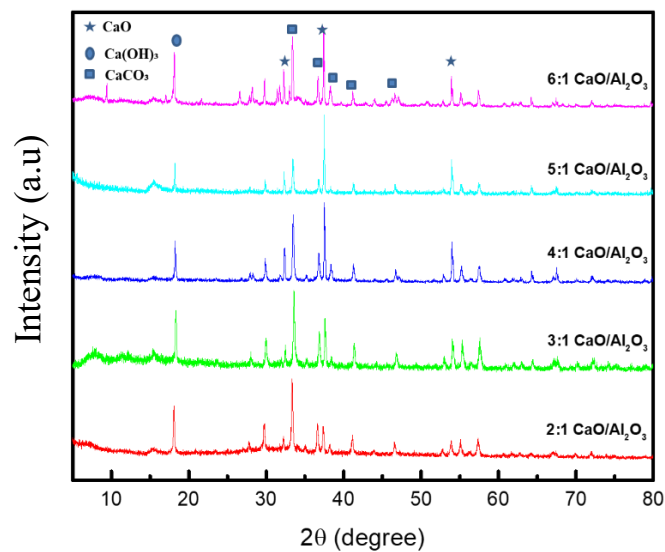


Figure 21 Comparison of powder XRD patterns of the CaO/Al₂O₃ calcined alcogels with different calcium chloride compositions calcined at 700 degrees.

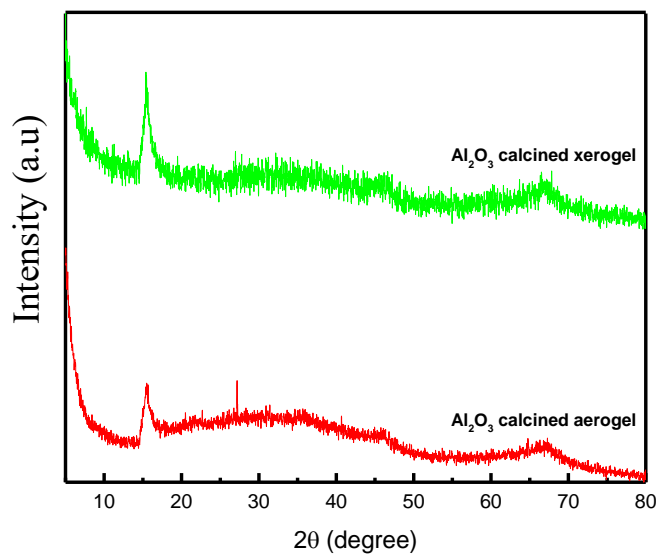


Figure 22 Comparison of powder XRD patterns of the alumina aerogel and alcogel calcined at 700 degrees.

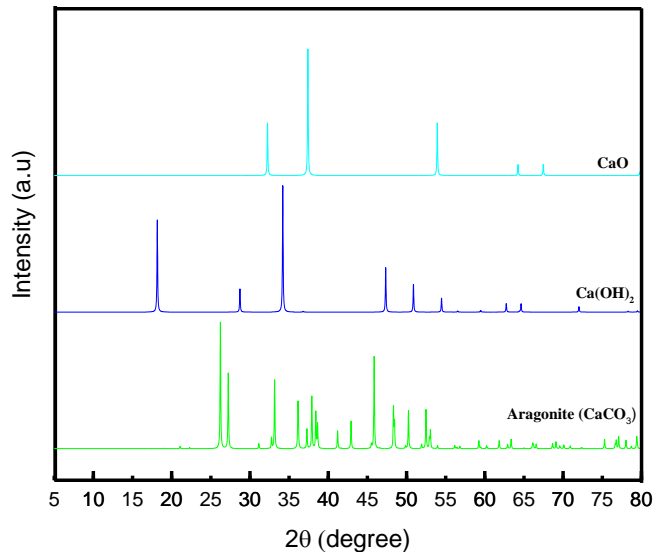


Figure 23 Powder X-ray patterns of CaO, Ca(OH)₂, and CaCO₃ (reproduced from the crystallography database⁵⁹)

Alumina aerogels, alcogels, and 2:1 CaO/Al₂O₃ calcined aerogel were amorphous. As for the rest of CaO/Al₂O₃ calcined aerogels, they showed better crystallinity with increased CaO content. However, all the CaO/Al₂O₃ calcined alcogels were crystalline. This shows that aerogels were not as affected by calcination as the alcogels were, and they maintained their structure at low CaO content.

As shown in Table 6 and 7, as the CaO content increased in both CaO/Al₂O₃ calcined aerogel and alcogels the crystallite size of the catalyst increased as well. However, the crystallite sizes of the calcined alcogels were larger than their corresponding calcined aerogels.

Table 6 Crystallite size of CaO/Al₂O₃ calcined aerogel catalysts with different calcium chloride composition.

Catalyst	Crystallite size (nm)
3:1 CaO/Al ₂ O ₃	33.6

4:1 CaO/Al ₂ O ₃	128.3
5:1 CaO/Al ₂ O ₃	155.7
6:1 CaO/Al ₂ O ₃	193.7

Table 7 Crystallite size of CaO/Al₂O₃ calcined alcogel catalysts with different calcium chloride composition.

Catalyst	Crystallite size (nm)
2:1 CaO/Al ₂ O ₃	75.7
3:1 CaO/Al ₂ O ₃	124.1
4:1 CaO/Al ₂ O ₃	157.9
5:1 CaO/Al ₂ O ₃	173.9
6:1 CaO/Al ₂ O ₃	197.2

As seen in Figure 24, both calcined aerogels and alcogels showed a linear trend between crystallite size and CaO content, with calcined aerogels showing a better linearity.

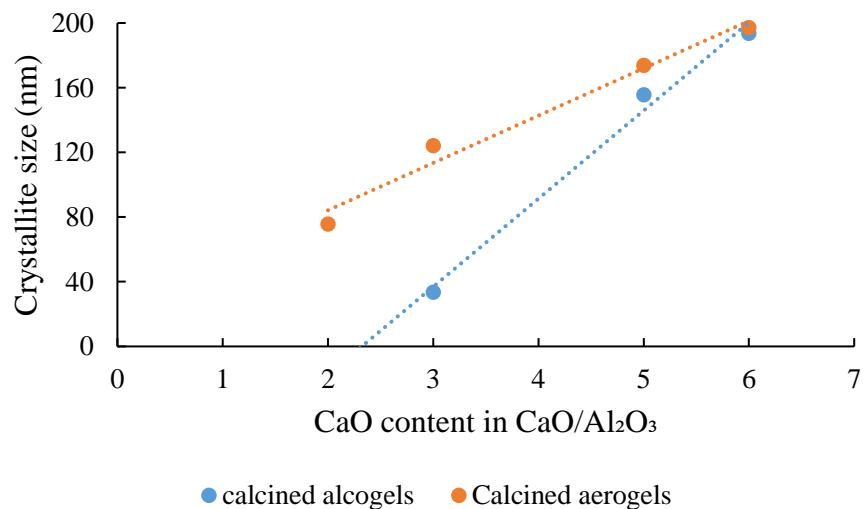


Figure 24 crystallite size vs CaO content in calcined CaO/Al₂O₃ aerogels and alcogels

4.1.4. Thermogravimetric analysis (TGA) analysis

According to TGA analysis, the least stable catalyst suffering the largest % weight loss (around 8 %) in both aerogels and alcogels is the 6:1 CaO/Al₂O₃ catalyst. In all catalysts, the % weight loss below 200° C is due to the physisorbed moisture from air. Moreover, the % weight loss around 300° C is attributed to the decomposition of hydroxyl group from Ca(OH)₂. While, the weight loss between 400° to 600° C is due to decomposition of carbonates and removal of CO₂^{10, 60}.

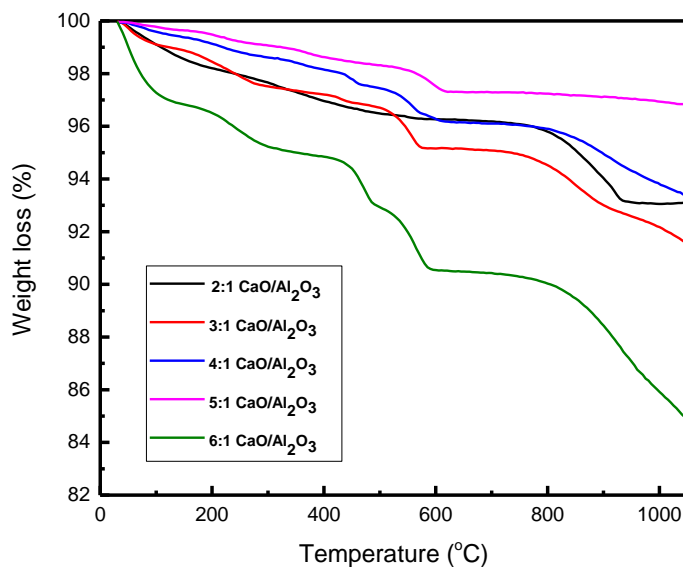


Figure 25 TGA curves of the CaO/Al₂O₃ calcined aerogels with different calcium chloride compositions

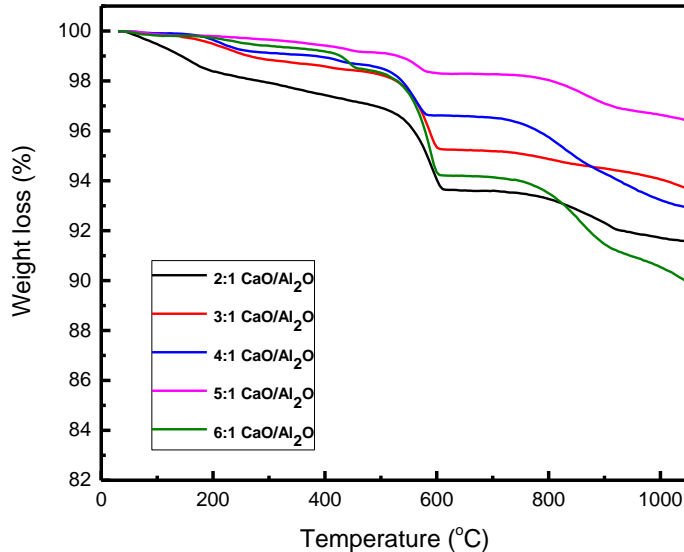


Figure 26 TGA curves of the CaO/Al₂O₃ calcined alcogels with different calcium chloride compositions

This shows that the synthesized catalysts are thermally stable at very high temperatures, that are significantly higher than the temperature used for this study (65°C).

4.1.5. Scanning electron microscopy (SEM)

The SEM micrographs for the CaO/Al₂O₃ catalysts with different CaO content and alumina support showed their surface morphology. Both alumina calcined aerogel and alcogel show an amorphous structure which validates the PXRD results. As seen in Figure 27, in CaO/Al₂O₃ calcined aerogels as the CaO content increased the crystalline form of CaO was more exhibited. However, in CaO/Al₂O₃ calcined alcogels, rod shaped and spherical crystal phases of CaO are clearly seen in all CaO/Al₂O₃ calcined alcogels even at 2:1 CaO/Al₂O₃ calcined alcogel. These results further confirm the PXRD results. Moreover, agglomerates of compact spheres

represented in the SEM micrographs further validates the type H₁ hysteresis observed in the nitrogen adsorption-desorption isotherms.

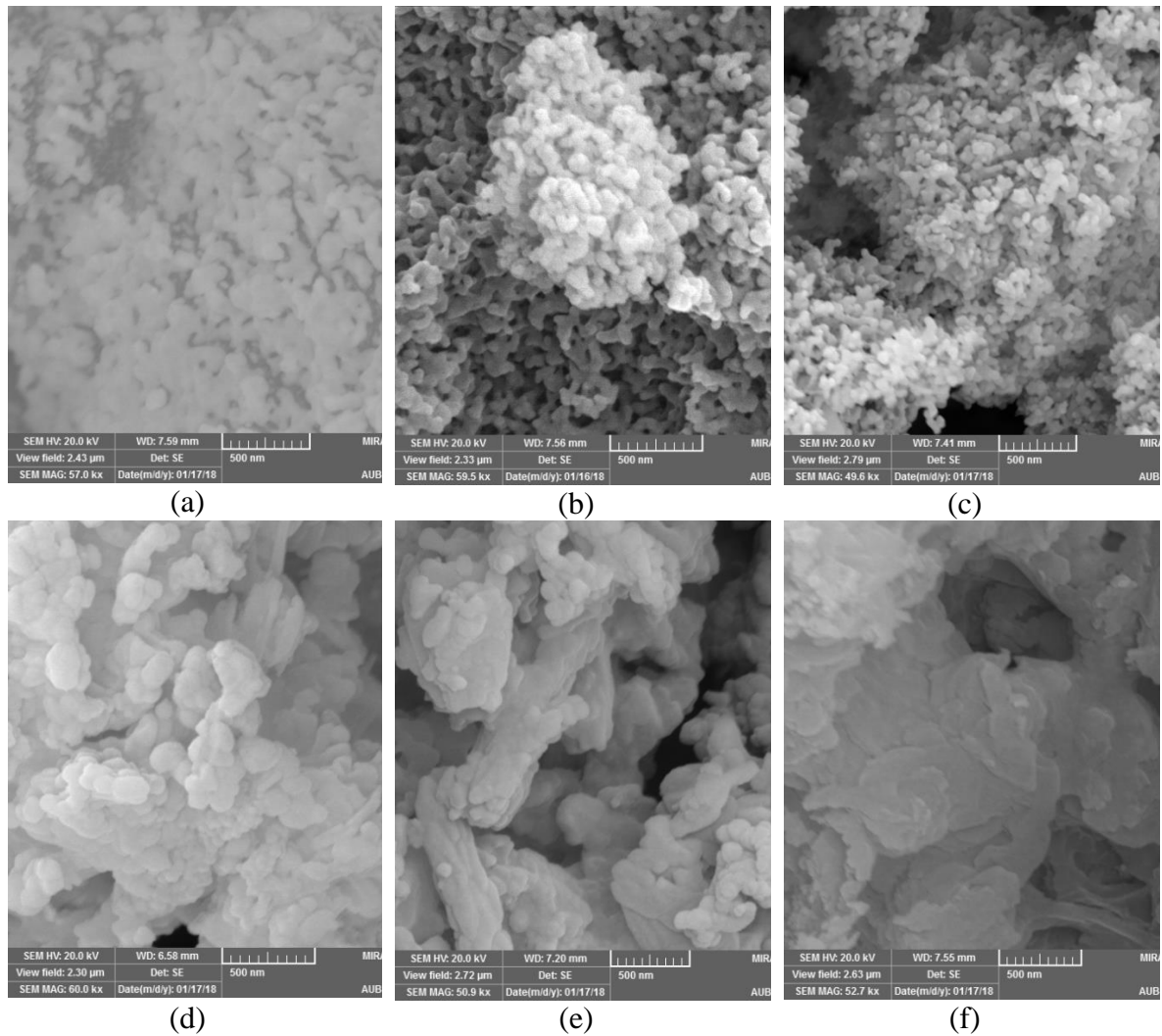


Figure 27 SEM micrographs for a) alumina, b) 2:1 CaO/Al₂O₃, c) 3:1 CaO/Al₂O₃, d) 4:1 CaO/Al₂O₃, e) 5:1 CaO/Al₂O₃, and f) 6:1 CaO/Al₂O₃ aerogels calcined at 700 °C.

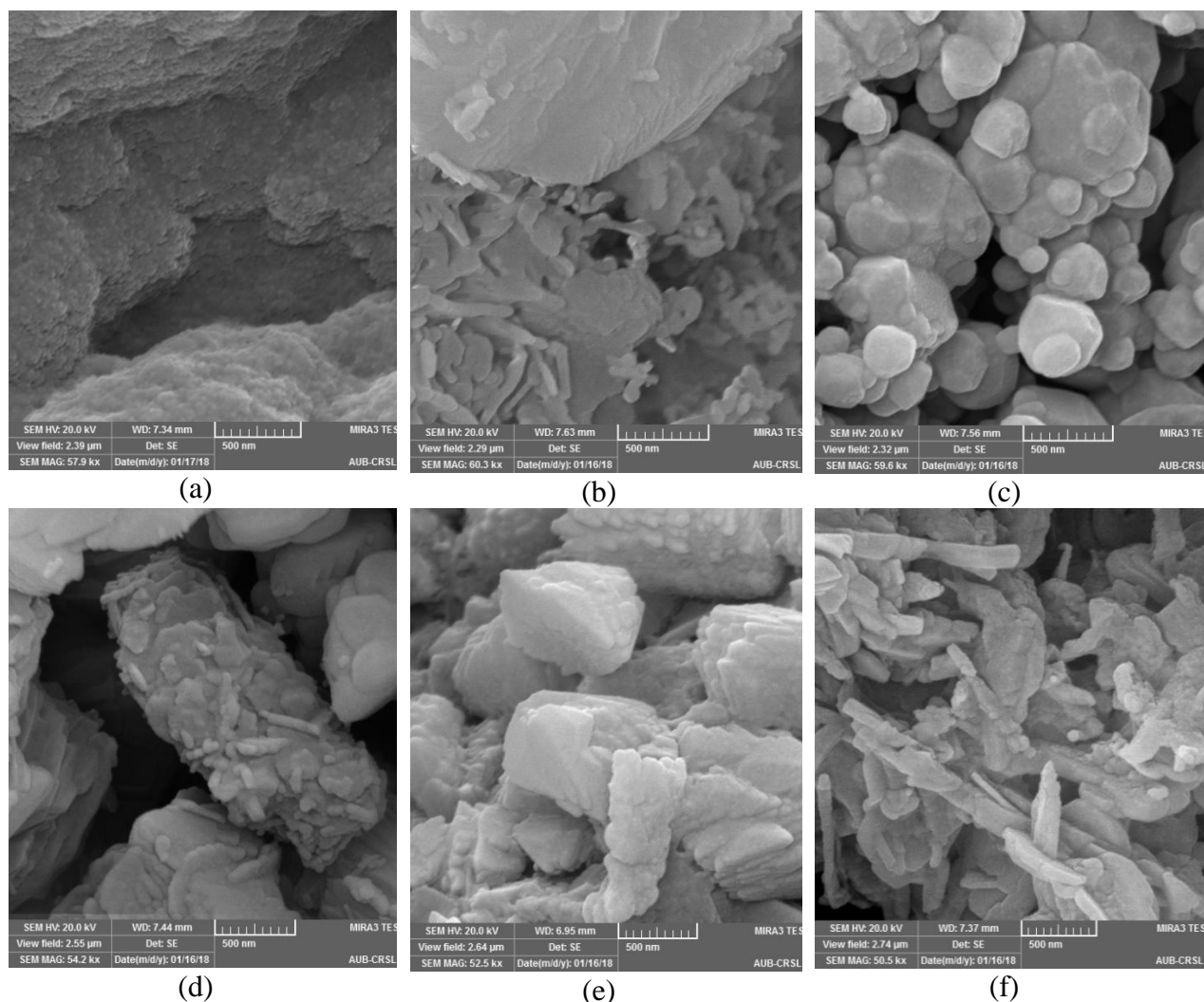


Figure 28 SEM micrographs for a) alumina, b) 2:1 CaO/Al₂O₃, c) 3:1 CaO/Al₂O₃, d) 4:1 CaO/Al₂O₃, e) 5:1 CaO/Al₂O₃, and f) 6:1 CaO/Al₂O₃ alcohels calcined at 700 °C.

4.1.6. Conclusion

To conclude, nitrogen adsorption-desorption isotherms showed that aerogels have a higher surface area than alcohels, and that the addition of CaO to alumina support significantly decreases the surface area and pore volume. Moreover, the type H1 hysteresis of type V isotherm indicates that the catalyst synthesized is a mesoporous material composed of agglomerates of compact spheres, which was clearly represented in the SEM micrographs collected. TGA, FTIR, and PXRD proved that all the synthesized catalysts are all very sensitive to moisture and CO₂

adsorbed from the atmosphere. The PXRD analysis showed that the crystallite sizes of CaO/Al₂O₃ calcined alcogels are significantly larger than their corresponding CaO/Al₂O₃ calcined aerogels. Moreover, as the CaO content increases in both CaO/Al₂O₃ calcined aerogels and alcogels the crystallite size increases as well in a linear way, with aerogels showing more linearity than alcogels. Both PXRD and FTIR showed that even after calcining at 700 °C aerogels had a different structure than their corresponding alcogels. In PXRD, 2:1 CaO/Al₂O₃ calcined aerogel was amorphous, and the crystallinity increased with increased CaO content. However, all the CaO/Al₂O₃ calcined alcogels were crystalline, even the 2:1 CaO/Al₂O₃ calcined alcogel. This shows that aerogels were not as affected by calcination as the alcogels were. The FTIR showed that the Al-O (569 cm⁻¹) and CaO peaks were not observed in 2:1 CaO/Al₂O₃ calcined aerogel, but they were seen after increasing the CaO content (3:1 to 6:1 CaO/Al₂O₃). However, these peaks were observed in all calcined alcogels even 2:1 CaO/Al₂O₃ calcined alcogel. Moreover, the 668 cm⁻¹ peak seen in both 2:1 and 3:1 CaO/Al₂O₃ calcined aerogels is not seen in their corresponding (2:1 and 3:1 CaO/Al₂O₃) calcined alcogels; it is only seen in the calcined alumina aerogel. This further proves that the calcined aerogels at low CaO content shows a different structure than their corresponding calcined alcogels. Finally, TGA revealed that all the synthesized catalysts are thermally stable at very high temperature. In addition, the 6:1 CaO/Al₂O₃ calcined aerogels and alcogels were the least thermally stable catalysts synthesized.

4.2. Influence of reaction conditions on the transesterification of WCO

The WCO was not treated for the transesterification reaction because the average of % FFA in it was $0.17 \pm 0.005\%$, which was very low. However, the WCO was preheated to 65 °C

to reduce its viscosity and allow for better mixing conditions for the reaction. The prepared CaO/Al₂O₃ calcined aerogels and alcogels were used for the transesterification of WCO. The reaction conditions were optimized to eliminate soap formation and achieve highest biodiesel yield and purity in an economical process. Transesterification reactions were carried out at 65 °C for five hours by varying one parameter at a time, including the following by order: CaO concentration, catalyst loading, methanol to oil molar ratio, and reaction time. Moreover, the kinetics of the catalyst was determined under the optimal reaction conditions.

4.2.1. Effect of CaO concentration on biodiesel production

The prepared calcined CaO/Al₂O₃ aerogels and alcogels with different CaO content were used in transesterification reaction to check their activity. The reaction conditions used were 12:1 methanol/oil molar ratio, 2 wt. % catalyst loading, 65°C, and 5-hour reaction time under magnetic stirring, otherwise it is mentioned in the corresponding section. If saponification occurred, the soap is weighed and divided by the total mass of oil.

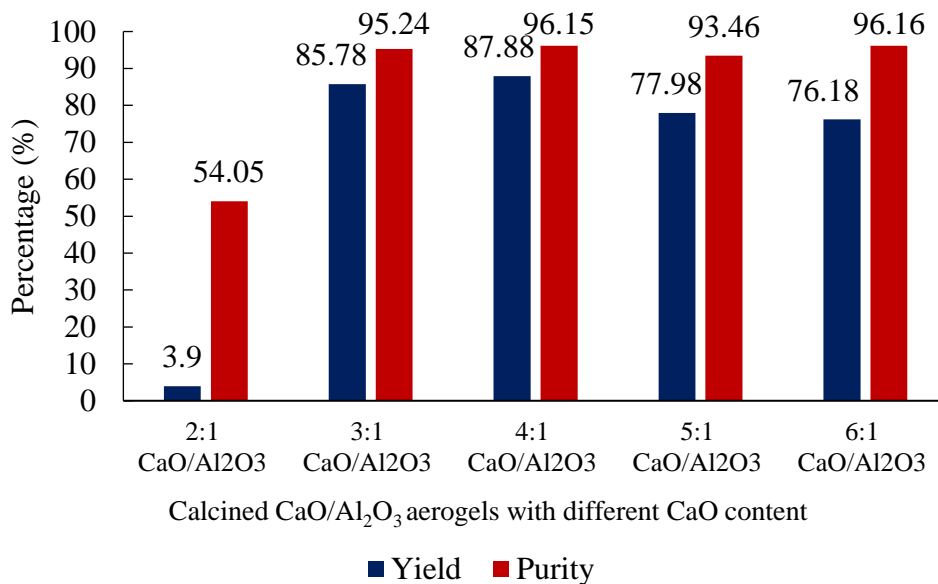


Figure 29 Effect of calcium chloride concentration on calcined CaO/Al₂O₃ aerogel activity towards transesterification of WCO (reaction conditions: methanol/oil molar ratio = 12:1; catalyst amount = 2 wt%; temperature = 65°C, and reaction time = 5 hours)

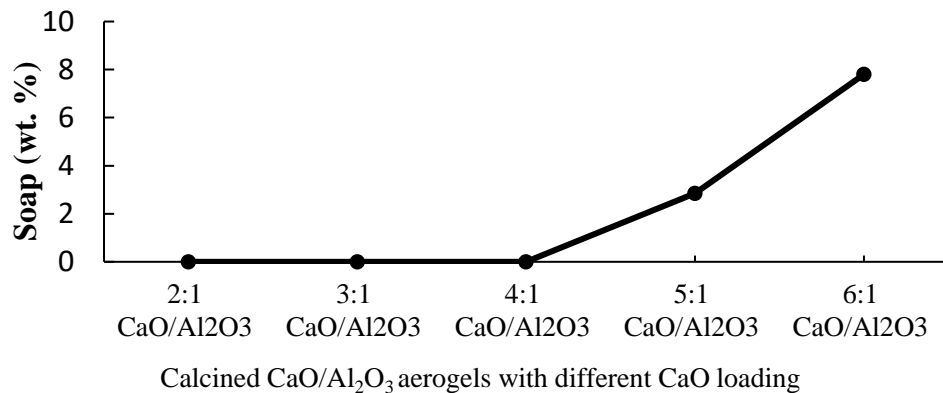
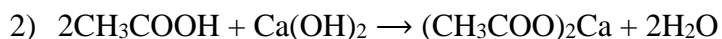


Figure 30 Soap formation (wt. %) for different calcium chloride concentration in calcined CaO/Al₂O₃ aerogels (reaction conditions: methanol/oil molar ratio = 12:1; catalyst amount = 2 wt%; temperature = 65°C, and reaction time = 5 hours)

As depicted in Figure 29 and 30, for CaO/Al₂O₃ calcined aerogels the biodiesel yield decreased as the CaO content increased, while saponification was observed at 5:1 and increased even further at 6:1 CaO/Al₂O₃. This is expected since excess CaO reacts with water in WCO producing calcium hydroxide, which causes saponification that leads to lower biodiesel yield.



The highest biodiesel yield was achieved at 3:1 and 4:1 CaO/Al₂O₃. Although 4:1 CaO/Al₂O₃ has approximately similar biodiesel yield to 3:1 CaO/Al₂O₃, 3:1 CaO/Al₂O₃ was chosen as the optimum case because it uses the least amount of material making the process more economic and eco-friendly.

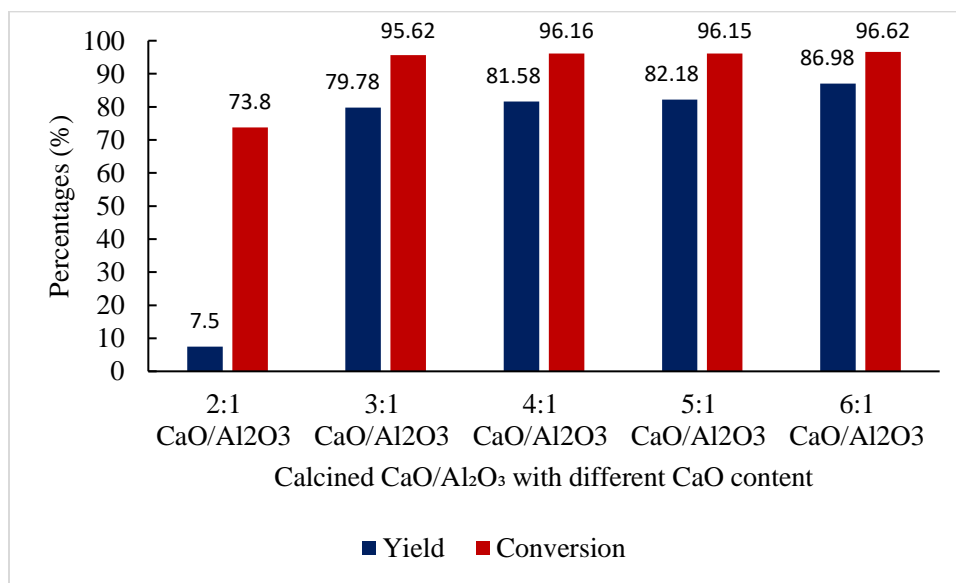


Figure 31 Effect of calcium chloride concentration on calcined CaO/Al₂O₃ aerogel activity towards transesterification of WCO (reaction conditions: methanol/oil molar ratio = 12:1; catalyst amount = 2 wt%; temperature = 65°C, and reaction time = 5 hours)

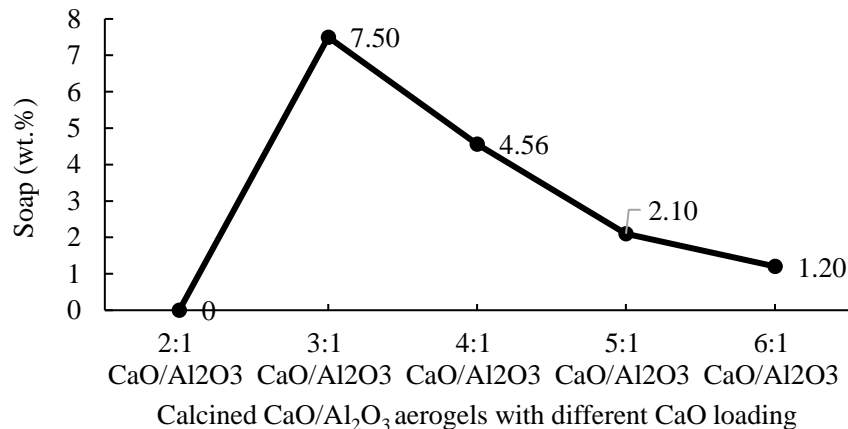


Figure 32 Soap formation (wt. %) for different calcium chloride concentration in calcined CaO/Al₂O₃ alcogels (reaction conditions: methanol/oil molar ratio = 12:1; catalyst amount = 2 wt%; temperature = 65°C, and reaction time = 5 hours)

As for CaO/Al₂O₃ calcined alcogels, shown in Figure 31 and 32, the biodiesel yield increased and saponification decreased as the CaO concentration increased. This could be explained by the gel network collapse that occurs in all alcogels during calcination, unlike aerogels which was still able to retain its structure at low CaO content. Therefore, at low CaO concentration some of the CaO particles do not attach properly to the alumina support leading to the leaching of Ca²⁺ into the reaction, where it reacts with water molecules and forms soaps. However, as the CaO content increased the CaO particle established a better distribution and attachment to the alumina support; consequently, less amounts of Ca²⁺ particles are leached producing small amounts of soap.

The drastic increase in biodiesel yield between 2:1 CaO/Al₂O₃ and 3:1 CaO/Al₂O₃ seen in both calcined aerogels and alcogels is probably due to a better dispersion of CaO on the support and increased basicity of the catalyst. This is in agreement with the study done by Umdu et al which showed that 85 wt.% CaO supported alumina catalyst having the highest basicity gave the highest biodiesel yield⁴⁸. To conclude, 3:1 CaO/Al₂O₃ calcined aerogel was used for this

study because it uses minimum amount of material to produce highest biodiesel yield with no soap formation.

4.2.2. Effect of catalyst loading on biodiesel production

To determine the optimum catalyst loading, the 3:1 CaO/Al₂O₃ calcined aerogel was used in transesterification reactions with different loadings (from 0.25 to 2 wt. %). As shown in Figure 33, approximately equal biodiesel yield and purity were observed at 1, 1.5, and 2 wt. % catalyst loading. However, at low catalyst loading (0.25 and 0.5 wt. %) the yield was significantly low, which is expected because there is not enough amount of catalyst to sufficiently convert the WCO into biodiesel⁶¹. Hence, 1 wt. % of 3:1 CaO/Al₂O₃ calcined aerogel was used in the transesterification reaction for further optimization of other parameters.

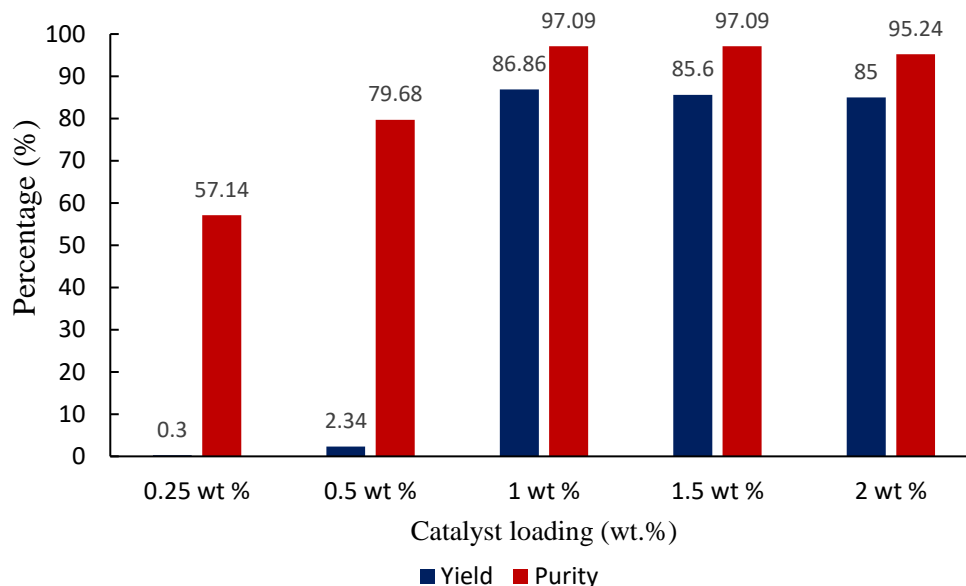


Figure 33 Effect of catalyst loading on WCO conversion and yield (reaction conditions: methanol to oil molar ratio 12:1; temperature = 65°C, and reaction time = 5 hours)

4.2.3. Effect of methanol to oil molar ratio on biodiesel production

As mentioned earlier and seen in Figure 5, the transesterification reaction requires three moles of alcohol for one mole of triglyceride to produce three moles of methyl esters and one mole of glycerol. However, an excess of methanol is required to drive the reaction forward, since it is reversible, as per Le Chatelier's principle. Moreover, methanol reduces the viscosity of oil which in turn enhances the mass transfer and eventually, the performance of the catalyst. Consequently, methanol to oil molar ratio was varied between 9 to 12 in transesterification reactions, where 1 wt. % of 3:1 CaO/Al₂O₃ calcined aerogel was used at 65°C for 5 hours. Although Figure 34 showed that 9:1 and 10:1 methanol to oil molar ratio exhibited high biodiesel yield, their purity was lower than for those with higher methanol to oil molar ratio. The results showed that the maximum biodiesel yield with highest purity was obtained at 11:1 methanol to oil ratio.

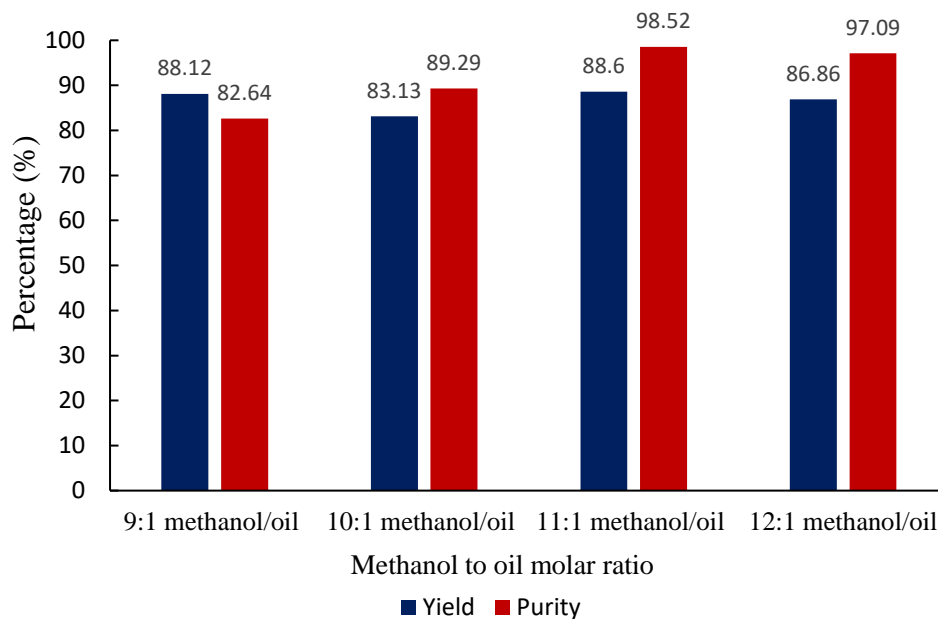


Figure 34 Effect of alcohol to oil molar ratio on WCO conversion and yield (reaction conditions: catalyst loading = 1 wt%; temperature = 65°C, and reaction time = 5 hours)

4.2.4. Effect of reaction time on biodiesel production

Although Figure 35 shows that the biodiesel reaches a complete conversion after 3 hours, but the yield obtained was very low (3.5 %). This shows that 3 hours was insufficient to convert all the WCO to biodiesel. As a matter of fact, it took 4 hours to achieve the maximum biodiesel yield (89.84 %) with highest purity (98.04 %).

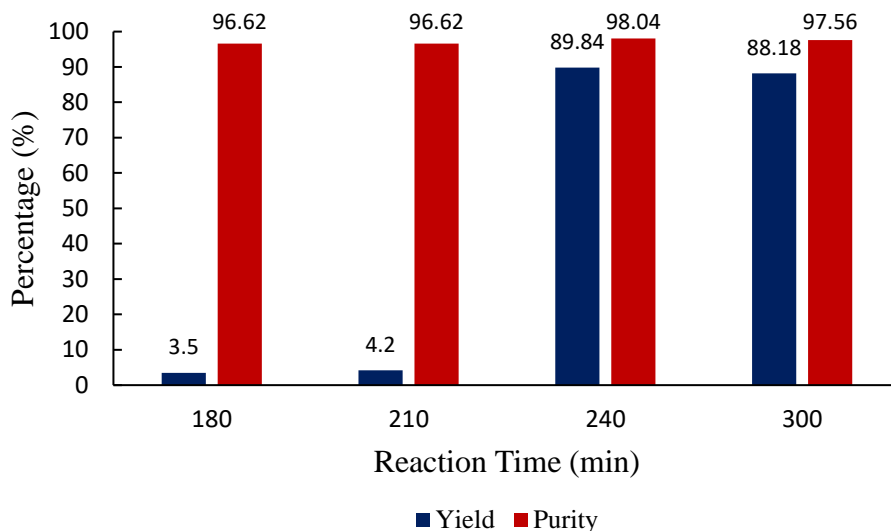


Figure 35 Effect of reaction time on WCO conversion (reaction conditions: catalyst loading = 1 wt%; temperature = 65 °C, and methanol to oil molar ratio 11:1)

The results mentioned above showed that maximum biodiesel yield (89.84 %) with highest purity (98.04 %) is produced under the optimum conditions of 1 wt. % 3:1 CaO/Al₂O₃ calcined aerogel with 11:1 methanol to oil molar ratio at 65°C for 4 hours. This study can be compared to previous studies depicted in Table 2 of biodiesel production catalyzed by heterogeneous CaO/Al₂O₃. It can be concluded that this study achieved a higher yield and conversion than Moradi et al.³⁴ and Moradi et al.³⁸ respectively, under lower methanol to oil molar ratio, catalyst loading, and reaction time. On the other hand, Zabeti et al.³⁵ achieved a better yield (95 %) than our yield. However, they used more than triple the catalyst loading used in this study. It should be emphasized that these studies used edible oil, unlike the household WCO used in this study.

4.3. Kinetics of 3:1 CaO/Al₂O₃ calcined aerogel in transesterification

An excess amount of alcohol is usually used to drive the reaction forward and regenerate the catalyst. In fact, the optimum methanol to oil molar ratio obtained for this study was 11:1. Therefore, the methanol is expected to remain constant and the rate of the reaction should depend only on one reactant, which is oil in this case³. Thus the reaction should follow a pseudo first order kinetic, which has the following equation:

$$-\ln(1 - X) = kt \quad (\text{Eq. 5})^4$$

where X is the FAME conversion at time "t".

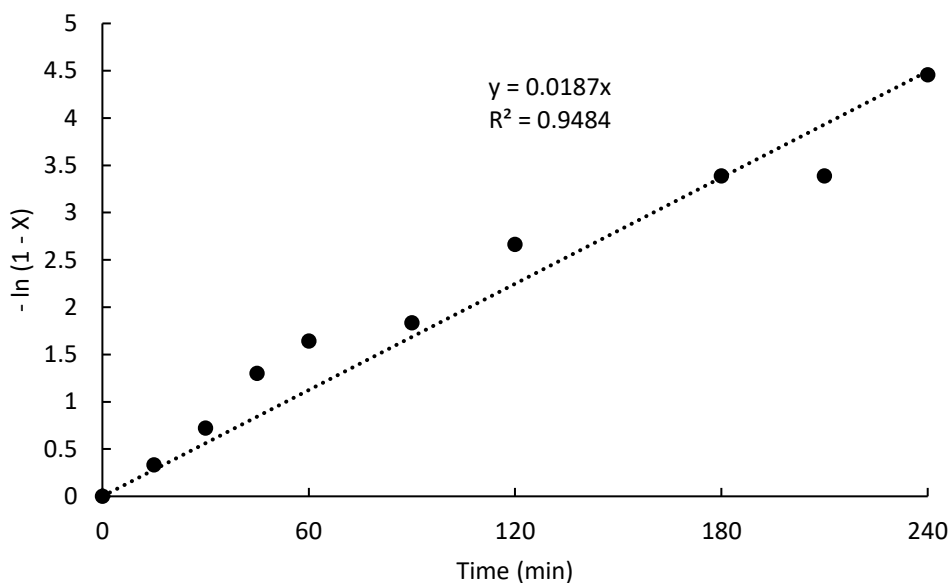


Figure 36 Plot of $-\ln(1-X)$ vs time

As seen in Figure 36, the plot between $-\ln(1-X)$ versus time is linear, which supports the hypothesis that the reaction is indeed of pseudo first order with $k = 0.019 \text{ min}^{-1}$.

CHAPTER 5

CONCLUSION AND FUTURE WORK

In this study, CaO/Al₂O₃ calcined aerogels and alcogels with different CaO content were prepared using a rapid epoxide-initiated gelation sol-gel method to produce biodiesel, an eco-friendly substitute for diesel, from WCO. All catalysts were characterized using FTIR spectroscopy, nitrogen adsorption-desorption technique, scanning electron microscopy, X-Ray diffraction, and thermogravimetric analysis. The TGA, FTIR, and PXRD analysis proved that all the synthesized catalysts are very sensitive to moisture and CO₂ adsorbed from the atmosphere. Furthermore, the nitrogen adsorption-desorption technique, FTIR, SEM, and PXRD showed that calcined aerogels with low CaO content were still able to maintain their structure after calcining at 700 °C, and that their structures are different than their corresponding calcined alcogels. In the transesterification reaction, calcined aerogel showed a better catalytic activity at lower CaO concentration than calcined alcogels. Furthermore, aerogels did not form soap at low CaO concentration, while a significant amount of soap was observed in alcogels. For economic reasons, 3:1 CaO/Al₂O₃ calcined aerogel was chosen because it uses minimum amount of material to produce high biodiesel yield with no soap formation. After optimizing the parameters, a maximum biodiesel yield (89.84 %) with highest purity (98.04 %) was achieved under the following optimum conditions: 1 wt. % 3:1 CaO/Al₂O₃ calcined aerogel, 11:1 methanol to oil molar ratio, 65°C, and 4 hours. Finally, under these optimum condition the reaction followed a pseudo first order kinetics. Future work will focus on testing the reusability or regeneration of the catalyst to allow for even more economical and eco-friendly process for the use in large biodiesel production industrial plants.

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