Production of Biofuels Using Calcium-based Catalyst

By

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
Universiti Teknologi PETRONAS
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Approved by,

(Dr. Bawadi Bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgement, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(FATIN ELLIYA BINTI ZAILAN)

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ABSTRACT

Biodiesel is gaining more and more importance as an attractive fuel due to the depleting fossil fuel resources. Chemically biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feed stock like vegetable oils and animal fats through transesterification reaction by methanol. Increase in the production of biodiesel is expected in the near future. However, production costs are still rather high, compared to petroleum-based diesel fuel. From a financial point of view, the introduction of a solid heterogeneous catalyst in biodiesel production could reduce its price, becoming competitive with diesel fuel.

In this work, production of biodiesel via transesterification of rubber seed oil using calcium based catalyst is investigated. Catalyst is prepared through incipient wetness impregnation method. The developed catalyst will undergoes catalyst characterization by using various tools to determine the pore volume, surface area, composition of catalyst and also the particle size.

Transesterification reaction used a wide range of catalyst. Experiment will be carry out under the same reacting condition in the presence of calcium carbonate ($CaCO_3$), calcium oxide (CaO), and calcium/zinc oxide (CaO/ZnO).

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CHAPTER 1: INTRODUCTION

1.1 Project Background

In the recent years, there has been increased twin focus on global warming and the depletion of resources caused by the heavy consumption of fossil resources. The depletion of crude oil would cause a major impact on the transportation sector. Among various alternative fuels, biodiesel fuel derived from vegetable oil (VOs) is the most promising alternative fuel to conventional diesel fuel.

The attractive facts in using biodiesel such that it gives lower emission of CO due to better combustion, a better lubricating effect on engines, non-sulphur emission and non-particulate matter. Other than that, it is renewable in nature and can be produced locally. Sharmer et al. have estimated that in the case of using 1 kg of pure biodiesel instead of the fossil fuel, 3.2 kg of CO_2 production could be reduced [1].

1.1.1 Feedstock

There are many resources which are being used as feedstock. Most of biodiesel currently being produced is mainly dependent on edible oil sources. Examples are palm oil, sunflower, soybean and rapeseed. Based on research, more than 95% of the world biodiesel is produced from edible oil. However, large-scale production of biodiesel from edible oils may compete with food supply. Research had been conducted in order to find alternative raw material for the process. Non-edible plant oils have been found as a possible substitute of edible oils. It is because non-edible oils cover a wide range of low cost, underutilized feedstock with potential in large scale production. Throughout this project, rubber seed oil has been chosen. It is non-food oil and low cost feedstock.

1.1.2 Production of biodiesel

Vegetable oils produced high viscosity and low volatility of biodiesel oil. Biodiesel is obtained through transesterification reaction of edible/non-edible oil by alcohol (alcoholysis) which promoted by catalyst. This reaction has been widely used to reduce the high viscosity of triglycerides in the oil [13]. The transesterification reaction can be expressed by the following equation:

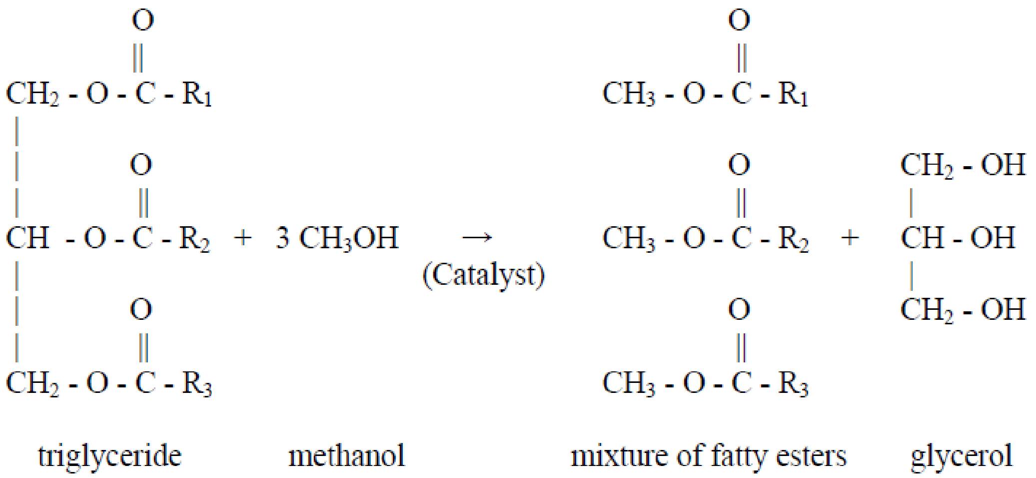


Figure 1.1: Transesterification reaction scheme [26]

The stoichiometry requires 3 mol of alcohol and 1 mol of triglyceride to give 3 mol of fatty acids esters and 1 mol of glycerine [3].

The production of biodiesel using non-edible oils has the drawback since it contains more free fatty acids (FFA). High FFA content reacts with homogeneous catalyst will contribute the formation of soaps, creating difficulties in the biodiesel production process.

Because of that, Ramadhas et al. studied the synthesis of biodiesel from rubber seed oil using two stage transesterification [3]. For the first reaction, acid-esterification is carried out to reduce the acidity of the feed oil before proceeding to alkali transesterification to produce biodiesel [12].

1.1.3 Catalyst

Catalyst can be defined as a substance that increases the rate of reaction without being consumed in the reaction. Catalysts can speed up the reaction by providing new reaction path which has lower activation energy. Relating to the transesterification reaction, it is preferred to the direct esterification of fatty acid because triglycerides are more available than free fatty acids. Biodiesel is produced by transesterification of the triglycerides with short chain alcohols in the presence of a suitable catalyst.

More recently, there has been an increasing development of new catalysts for biodiesel production in order to reduce the cost processing of biodiesel. The use of heterogeneous catalyst could be an attractive solution as it can be separated more easily from reaction products.

Biodiesel is produced using two-stage of reaction. The first one is pre-treatment process called acid-esterification reaction followed by alkali-transesterification. For the first reaction, alcohol reacts with the given oil in the presence of acid catalyst. Sulphuric acid are chosen for initial treatment stage. Sodium and potassium hydroxide are commonly used for alkali-transesterification.

However, transesterification reaction by using a conventional alkali process has several drawbacks; formation of soap, difficulties in purification and separation and reduce production yield. In order to minimize homogeneous process problems, attempts to use heterogeneous catalyst systems in alcoholysis of triglycerides have been made.

Three different calcium based catalyst are synthesize in order to evaluate their potential as heterogeneous catalyst for biodiesel production. Thus, CaO/ZnO catalyst is prepared by impregnation method with 5wt% of ZnO loading while for CaO and $CaCO_3$ catalyst are synthesize through calcination method.

1.2 Problem Statement

Due to the depleting sources of petroleum and environmental concerns, a search for sustainable alternative fuel has gained significant attention. Since diesel engines emit a huge amount of NO_x and particulates, a clean alternative fuel is highly demanded. Among many possible sources, biodiesel fuel derived from vegetable oil (VOs) attracts attention as a promising one to be substituted for conventional diesel fuels.

The used of edible feedstock will increase the price of biodiesel since it needs to compete with cooking oil. Therefore the alternative ways is to use the non-edible oil such as rubber seed oil (RSO) as a feedstock for production biodiesel. However, non-edible oil contains high free fatty acids which cause formation of soap during reaction with homogeneous base catalyst. The unwanted by product create difficulties in post treatment and also suppress the production yield. Therefore, new conception using heterogeneous catalyst in production biodiesel was introduced.

For this project the calcium based catalysts are developed: $CaCO_3$, CaO and CaO/ZnO catalyst to evaluate its potential as heterogeneous in biodiesel production.

1.3 Objectives and Scope of Study

Main objectives of the project are:

1) To develop calcium based catalyst.
2) To characterize the properties of the develop catalyst.
3) To synthesis biodiesel from RSO through transesterification method.

The scope of study is to produce biodiesel from RSO by dual step transesterification process. For this project heterogeneous catalysts are used for simplify the post-treatment of the products (separation and purification). It can be easily separated from the system at the end of the reaction and could also be reused. Other than that, the scope of study for this project also covered the feasibility of calcium based catalyst for production of biodiesel for transesterification process. The success output of this project would indirectly reduce the production cost of biodiesel.

In order to achieve the objectives, this project will be done according to the time frame and planned scheduled in 2 semester period. The schedule is important and acts as guidance in order to ensure this project ends within the time given. As for Final Year Project I (FYP I), project would start with the knowledge gathering and theoretical studies which essential in order to provide the deep insight for the production of biodiesel, catalyst preparation and catalyst characterization method.

For the next stage which is during FYP II, experimental works are carried out to correlate theoretical knowledge with practice. It covers the preparation of catalyst, characterization of the develop catalyst and also the catalytic test for transesterification reaction in production of biodiesel.

1.4 Relevancy of the Project

As mentioned in the problem statement and objective, this project is mainly to produce or synthesis biodiesel form RSO which promising the alternative of diesel fuel and also for environment concern.

High cost of biodiesel production influences by 2 major factors which are the cost of feedstock and cost of processing. New development was introduced by using heterogeneous catalyst to simplify the process operation which later can result in cost reduction. In this project, the calcium based catalyst is chosen to be the one. The availability of calcium carbonate is easy to get and the price is cheapest than other catalyst materials. It is also can be obtain from the waste like shells of oysters, chicken egg and limestone powder. The success output from this project will reduce the price and also increase the biodiesel yield.

1.5 Feasibility of the Project

It is expected the project can be conducted with no difficulty. RSO can be obtained from one of the research centre in UTP conducted by DR.Suzana. The laboratory equipments and chemicals are supplied by the UTP with the specific budget given to the students. The experimental works can be conducted inside UTP by using laboratory as work station. All the facilities inside the UTP can be used to conduct this project with proper procedure. Catalyst that had been develop will go to characteristic analysis using various tool to determine it surface area, porosity, metal distribution and pore volume. Then the catalyst will be tested by transesterification reaction from rubber seed oil.

CHAPTER 2: LITERATURE REVIEW

Biodiesel can be produced from vegetable oils with simple chemical reactions. Based on article in International Conference on Gas-Fuel refer to L. Bournay, D. Casanave , B. Delfort, G. Hillion, J.A. Chodorge said that the reactions of interest today, mainly those producing methyl esters from rapeseed, soybean sunflower and RSO, have been studied and optimized in order to manufacture the high quality diesel fuel [6].

Biodiesel from vegetable oil must meet the standard requirement. The standard used for measurement of properties and the properties values are listed in Table 2.1. The values are comparable with the standard set for biodiesel and also with those for petroleum diesel [11].

Table 2.1: Properties of petroleum, biodiesel standards and ester [14]

Property	**Petroleum**	**Biodiesel Standard**	**Rubber Seed Oil**	**Rape Seed Oil**	**Cotton Seed Oil**	**Soybean Oil**
Specific gravity	0.840	0.87-0.90	0.874	0.882	0.874	0.885
Calorific Value, MJ/kg	42.5	-	36.50	37	40.32	39.76
Viscosity, mm2/s@40°C	2.87	1.9-6.0	5.81	4.5	4.0	4.08
Flash Point, °C	76	Min. 130°C	130	170	70	69
Acid Value, mg KOH/g oil	-	0.8	0.118	NA	NA	NA

Due to competition with food supply, non-edible oil was found to be the alternative. The examples of non-edible oil are jatropha, sea mango, pongamia pinnata, rubber seed, and castor [13].

In present investigation, rubber seed oil has been investigated as a potential source for biodiesel production [14]. Rubber seed kernels (50-60% of seed) contain 40-50% of pale yellow oil. At present, rubber seed oil has not found any major application and hence the natural productions of seeds remain underutilized. The fatty acid composition and properties of rubber seed oil in comparison with diesel is given in Table 2.2 and Table 2.1 respectively.

Table 2.2: Fatty acid composition of rubber seed oil [3]

Fatty Acid	Composition (%)
Palmatic acid	10.2
Stearic acid	8.7
Oleic acid	24.6
Linoleic acid	39.6
Linoleic acid	16.3
Others	0.6

The fatty acid composition of rubber seed oil is not fixed as per Table 2.2 as it is influence depending on the climate and soil condition for different countries. However, the drawback of using non-edible oil as a source of biodiesel is that they contain a high amount of free fatty acids. It will cause difficulties during post treatment.

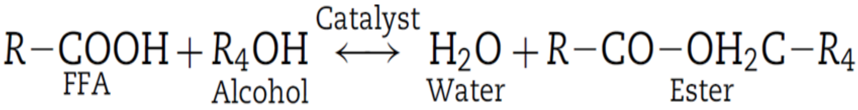
2.1 Acid-Esterification

Non-edible types of oil contain high free fatty acid (FFA) content. Free fatty acid will react with alkaline catalyst to produce soap that inhibits the separation of esters and glycerine. This reduce the conversion efficiency to large extend [11].

Ramadhas found that, unrefined rubber seed oil content high free fatty acid in the oil which is approximately 18%. Transesterification will not occur if the FFA content in the oil is higher than 2% [3].

Thus, it is necessary to reduce the FFA content. Many pre-treatment methods have been proposed for reducing the high FFA content of oil including steam distillation, extraction by alcohol, and esterification by acid catalysis [14]. Acid-esterification is a typical method of producing biodiesel form high FFA.

For this method, free fatty acid are treated by reacts the alcohol with the given amount of alcohol in the presence of acid catalyst. This reaction will form free fatty acid methyl ester and water as by product.



$$\underset{\text{FFA}}{R-COOH} + \underset{\text{Alcohol}}{R_4OH} \overset{\text{Catalyst}}{\longleftrightarrow} \underset{\text{Water}}{H_2O} + \underset{\text{Ester}}{R-CO-OH_2C-R_4}$$

Figure 2.1: Reaction of acid-esterification [13]

For high FFA feedstock, it is insufficient to only involved one step transesterification process. An alternative way of processing the high free fatty acid oil is to undergo pretreatment process called acid-esterification. The first step which is acid-esterification reduces FFA content of oil to less than 2%. The second step involves alkaline transesterification process to convert the products of first step to its mono-esters and glycerol.

Acid-esterification process is catalyzed by Bronsted acids, preferably sulphuric acid. The mechanism of acid catalyzed esterification of fatty acids start as the protonation of the acid to give an oxonium ion (1), which can undergo an exchange reaction with an alcohol to give the intermediate (2), and this, in turn, can lose a proton to become an ester (3). Each step in the process is reversible, but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion. Figure 2.2 shows the mechanism of acid catalyzed transesterification of vegetable oils.

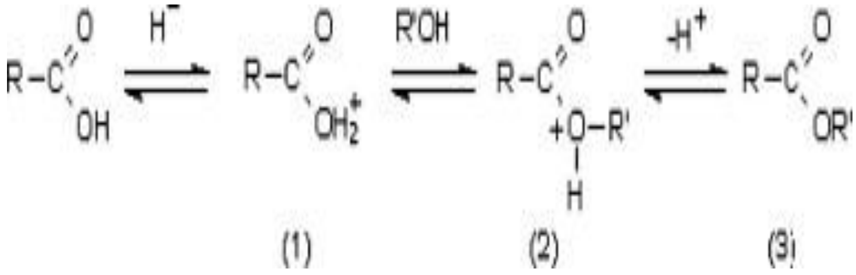


Figure 2.2: Reaction mechanism for acid-transesterification

Free fatty acids should be removed from the feedstock prior to the transesterification to prevent serious damage was caused to the catalyst by reacting with free fatty acids [19].

2.2 Transesterification

Biodiesel form vegetable oils are chemically complex esters of fatty acids. It is naturally present in oil seeds and known as tri-glycerides of fatty acids. The molecular weight of these tri-glycerides is around 800 kg/m^3 or more [15]. The high molecular weight results in unfavourable physical properties on the viscosity. Thus make the viscosity of biodiesel are higher compared to biodiesel. The high viscosity of vegetable oils can cause serious damage in engine. Viscosity reduction is necessary by using several methods such as blending with diesel, emulsification, pyrolysis and transesterification. Looking at the possible methods, transesterification appears to be more suitable in production of this green fuel.

The trigyceride (vegetable oils and fats) are esters of long chain carboxylic acids combined with glycerol. Carboxylic acids $R\text{–}C{=}(O)\text{–}O\text{–}H$ can be converted to methyl esters $R\text{–}C{=}(O)\text{–}O\text{–}CH_3$ by the action of a transesterification agent. Transesterification consists of a number of consecutive, reversible reactions. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol. Based on equations (1), (2), (3) and (4) it is showed that 1 mol of alkyl esters is removed in each step.

$$\text{Fatty acid } (R_1\,COOH) + \text{Alcohol } (ROH) \rightleftarrows \text{Ester } (R_1\,COOR) + \text{Water } (H_2O) \qquad (1)$$

$$\text{Triglyceride} + ROH \rightleftarrows \text{Diglyceride} + RCOOR_1 \qquad (2)$$

$$\text{Diglyceride} + ROH \rightleftarrows \text{Monoglyceride} + RCOOR_2 \qquad (3)$$

$$\text{Monoglyceride} + ROH \rightleftarrows \text{Glycerol} + RCOOR_3 \qquad (4)$$

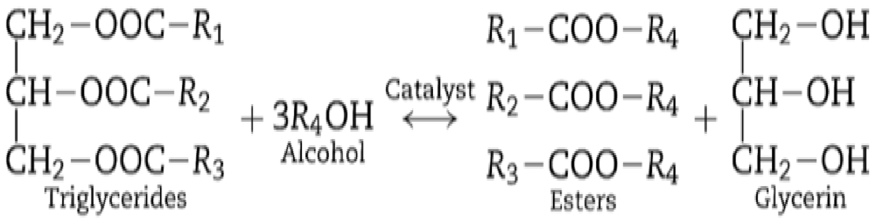


Figure 2.3: Transesterification reaction [13]

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis . Most of the biodiesel is produced from the refined/edible type oils using methanol and an alkaline catalyst [7]. Methanol is especially used because of its lower cost and its physical and chemical advantages. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colourless and odourless. The transesterification is an equilibrium reaction, and the transformation occurs essentially by mixing the reactants.

The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol start another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

2.3 Catalyst

Most of the biodiesel is produced from the refined/edible type oils using methanol and an alkaline catalyst [7]. Methanol is especially used because of its lower cost and its physical and chemical advantages. Methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it.

The difficulty with alkaline-esterification of these oils is that they often contain large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps. The soap formation is an undesirable side-reaction, because it partially consumes the catalyst, decreases the biodiesel yield and complicates the separation and purification steps. The removal of these catalysts is technically difficult and brings extra cost to the final product [5].

Several methods have been proposed to solve these problems, but the most useful seem to be the following [8]:

(a) Use of enzymes.
  - A Lypase enzyme catalyzes both transesterification of triglycerides and esterification of FFA in one step.

(b) Use of acid catalysts.
  - Acid catalyst can also promote esterification and transesterification.

(c) Pre-esterification method.
  - FFAs are first esterified to fatty acids methyl esters (FAMEs) using an acid catalyst, and then, transesterification is performed, as usual, by using an alkaline catalyst.

Based on research done by Canakci and Van Gerpan found that transesterification would not occur if FFA content in the oil were about 3% [26]. The yield of esterification process decreases considerably if FFA value is greater than 2%. It has been found that the alkaline catalyzed transesterification process is not suitable to produce esters from unrefined oils [3].

The transesterification reaction can be catalyzed conducted either using a homogeneous or heterogeneous catalytic process. Attempts to use heterogeneous catalyst systems in alcoholysis of triglycerides have been made. These catalysts greatly simplify the post-treatment of the products (separation and purification). They can be easily separated from the system at the end of the reaction and could also be reused. Besides, the use of heterogeneous catalysts does not produce soaps through free fatty acid neutralization or triglyceride saponification [5]. In addition, solid heterogeneous catalysts can be used with single step transesterification, thus these catalysts are particularly useful for feedstock with high free fatty acid content. The reaction is performed at higher temperature and pressure than homogeneous catalysis processes, with an excess of methanol [6].

P-L Boey et al. was reported that CaO has advantages in terms of catalyst cost and simpler production process [21]. Kawashima and cowerkers found that calcium oxide was so active as to finish transesterification of rapeseed oil with refluxing methanol within a reaction time of 3 hours. According to Gryglewicz, CaO was slightly dissolved in methanol due to its poor mechanical strength [23]. However, as compared to other catalyst, it has a considerably low leaching property and lower solubility in methanol. In order to enhance its performance, CaO are mixed with other oxides in transesterification activity. In this project, CaO are mixed with ZnO in methanolysis of rubber seed oil for biodiesel production.

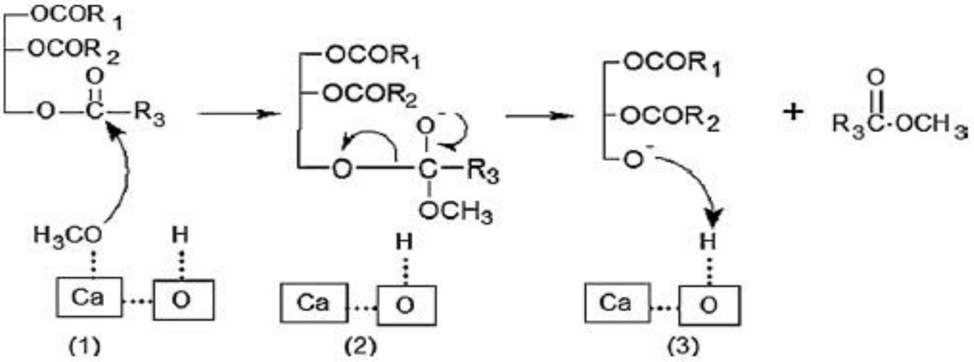


Figure 2.4: Mechanism of CaO catalyzed transesterification [21]

The reaction route of transesterification of triglycerides with methanol using CaO describe in figure above. The methoxide ion that is attached to the catalyst surface attacks the carbonyl carbon of the triglyceride molecule. This results in the formation of a tetrahedral intermediate. The then the intermediate is rearranged to form diglyceride anion and a mole of methyl ester. The charged-anion is then stabilized by a proton from the catalyst surface to diglyceride and at the same time regenerates the catalyst. The cycle continues until all three carbonyl centres of the triglyceride have been attacked by the methoxide ions to give one mole of glycerol and three moles of methyl esters [21].

2.4 Effect of Parameters

The important parameters that influence the process output quantity and quality are methanol to oil ratio, amount of catalyst, and reaction temperature

2.4.1 Acid Esterification

The purpose of this stage is to reduce the FFA content of the feed oil to less than 2% before proceeding to transesterification. FFA reacts with methanol in the presence of sulphuric acid as catalyst. Alcohol to oil molar ratio is the ratio of number of moles of alcohol to number of moles of glycerides in the oil. Theoretically, the reaction requires 3 moles of alcohol for each mole of oil. This reaction is reversible. Excess amount of alcohol are required to shift the equilibrium toward the forward reaction. Insufficient amount of methanol will caused the black layer forming at the bottom instead of at the top while higher consumption of methanol will increase the cost of production [13]. A.S Ramadhas was reported that the optimum condition for methanol to oil molar ratio is 6:1 [3]. Canakci and Ven Gerpan advocate the use of large excess quantity of methanol of 15:1-35:1 while using sulphuric acid as catalyst [26]. Modhar A.Khan found that 15:1 of molar ratio was sufficient in reducing the FFA [12]. Catalyst concentration is one of the important parameter in acid esterification. Sulphuric acid will be used in this stage of reaction. It is recommended to use 0.5 wt% of sulphuric acid. It is observed that, adding excess amount of sulphuric acid resulted in product darkening. The reaction temperature also affects the conversion efficiency of the process. According to A.S Ramadhas, the optimum temperature was found to be in the range of 318±5 K [3]. Modhar A.Khan was reported that lowest FFA content in the product was obtained at 338 K max before exceeding the methanol boiling point [12].

Therefore, in this project, acid esterification will be conducted with methanol to oil ration of 15:1, catalyst concentration of 10% and reaction temperature of 338 K.

2.4.2 Transesterification

According to Mahbub Morshed, the optimum condition for rubber seed oil was 5:1 alcohol to oil ratio, catalyst concentration of 2 wt% and 328 K of reaction temperature [14]. 2 wt% of catalyst concentration is used when using potassium hydroxide (KOH). For this project, heterogeneous catalyst will be used. 30 grams of calcium based catalyst will be prepared with 5 wt% of Zinc Oxide. According to Y.H Taufiq et al., transesterification of Jatropha curcas oil with methanol was conducted under 338 K reaction temperature, 4 wt% amount of Calcium based catalyst, methanol:oil ratio of 15:1 and reaction temperature of 6 hours. Under this condition, Jatropha curcosa oil conversion is more than 80% [23].

For this project, transesterification of rubber seed oil are conducted under reaction condition of methanol to oil ratio of 5:1, catalyst concentration of 5 wt% and reaction temperature of 338 K.

2.5 Analysis Method

At first stage, characterization of $CaCO_3$ is conducted in order to evaluate the calcinations method by Thermogravimetric Analysis (TGA). TGA is used to determine the thermal decomposition of $CaCO_3$ in which the mass of a substance is monitored as a function of temperature or time as the temperature of the sample is increased. Most TGA experiments use an inert sample purge gas. This is done so the sample only reacts to temperature during decomposition. When the sample is heated in an inert atmosphere this is called pyrolysis. Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents. Sample of $CaCO_3$ is analyzed by using temperature program.

Calcium based catalyst were characterize by X-Ray Diffraction (XRD). The purpose of XRD is to analyze the crystalline structure and composition of catalyst samples. The Scanning Electron Microscope (SEM) technique and Transmission Electron Microscope (TEM) was use to obtain the information of the morphology, size of sample and nanostructure of the develop catalyst. The total surface area of the catalyst is obtained by Brunauer-Emmer-Teller (BET) method using nitrogen adsorption at 77K.

Biodiesel production from rubber seed oil will be analyzed by using Gas Chromatography (GC). It is a common type of chromatography used in analytic chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound.

CHAPTER 3: METHODOLOGY

3.1 Chemicals

Calcium carbonate, calcium oxide, zinc nitrate hexahydrate, isopropanol, toluene, phenolphthalein, rubber seed oil, methanol, potassium hydroxide, n-hexane, sodium sulphate.

3.2 Experimental Set Up

250 ml beaker, 500 ml beaker, 50 ml burette, retort stand, pipette, thermometer, stopwatch, hot plate stirrer, magnetic stirrer, 250 ml 3-necked round bottomed flask with reflux condenser, separating funnel, crucible, oven, furnace, water bath shaker.

3.3 Experimental methods

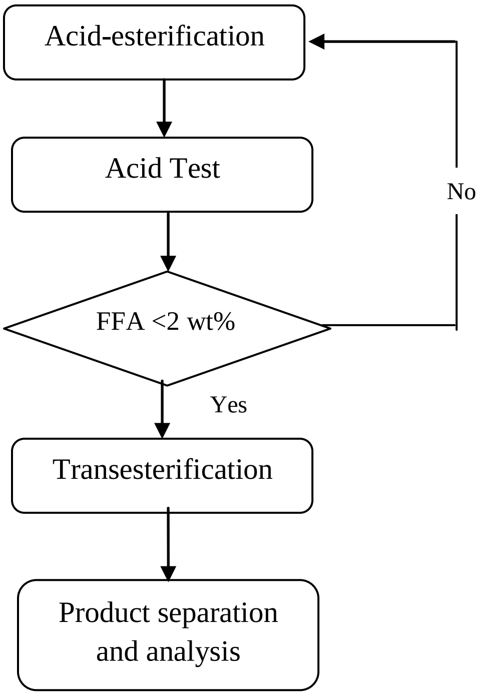


Figure 3.1: Summary of experimental method

3.3.1 Catalyst Preparation

In this project mixed oxide (CaO/ZnO) catalyst are prepared by incipient wetness impregnation method. Zinc nitrate hexahydrate is dissolve into aqueous solution by using distilled water. Impregnation method has been done by impregnating a calcium oxide with a solution of the active substance precursor. Capillary action draws the solution into the pores. The catalyst can then be dried by using oven as the elimination of the solvent (usually water) from the pores. Finally, the catalyst will undergo calcinations process at temperature 1173 K to activate the catalyst.

While for calcium oxide (CaO) catalyst, it was obtained after calcinations of calcium carbonate ($CaCO_3$) at 1173 K for 2 hours. Calcium carbonate catalyst was prepared in the same way of CaO catalyst with temperature of 873 K for 3 hours.

The dried and calcined catalysts are characterized with X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) technique, Transmission Electron Microscope (TEM) and Brunauer-Emmer-Teller (BET) method.

<u>Experimental Procedure:</u>

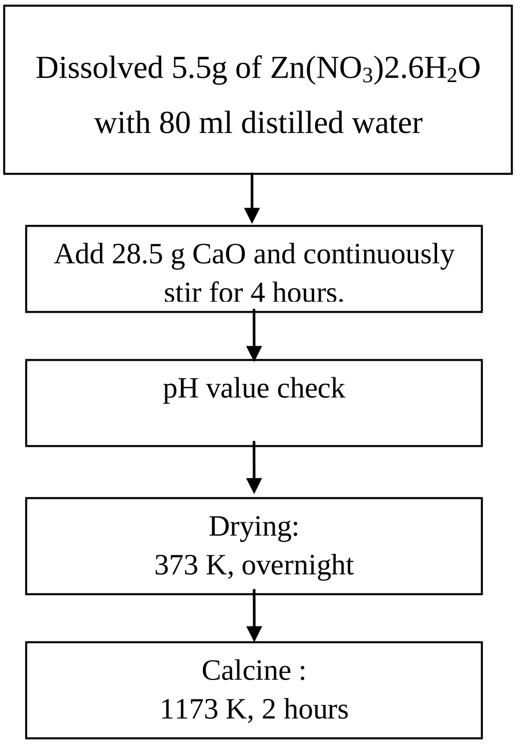


Figure 3.2: Experimental procedure for impregnation method

(Refer Appendix A)

3.3.2 Acid Value Test (EN 14104)

Principle: Test portion is dissolved in a mixed solvent and titrated with a diluted solution of potassium hydroxide (KOH) using phenolphthalein as an indicator.

Experimental Procedure:

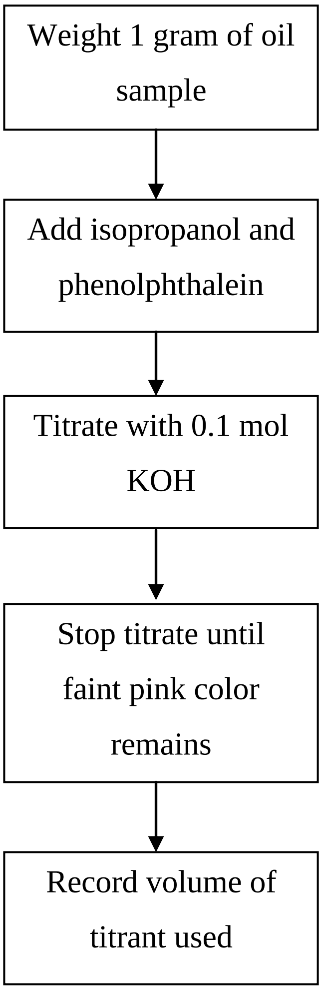


Figure 3.3: Experimental procedure of acid titration EN 14104

3.3.3 Acid Esterification

RSO will undergo pretreatment of acid esterification. The purpose of acid esterification is to reduce the FFA content less than 2 wt% prior transesterification reaction.

<u>Experimental Procedure:</u>

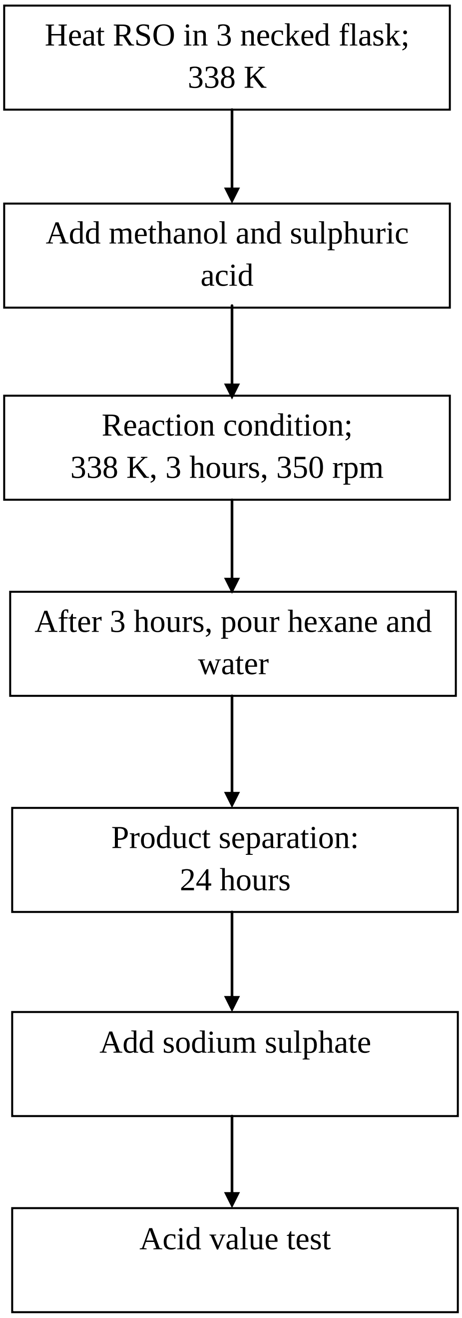


Figure 3.4: Experimental procedure of acid esterification

(Refer Appendix B)

3.3.4 Transesterification Reaction

Transesterification is conducted after the pretreatment under reaction condition; methanol to oil ratio of 5:1, catalyst concentration of 5 wt% and reaction temperature of 338 K for 3 hours.

Experimental Procedure:

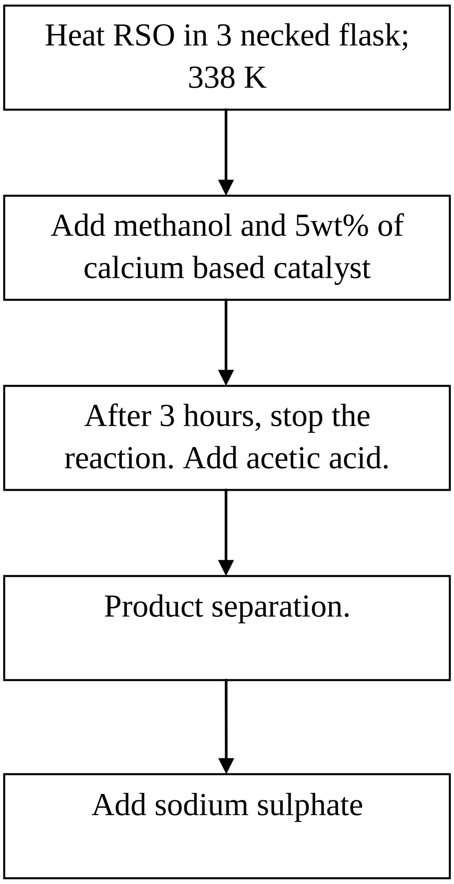
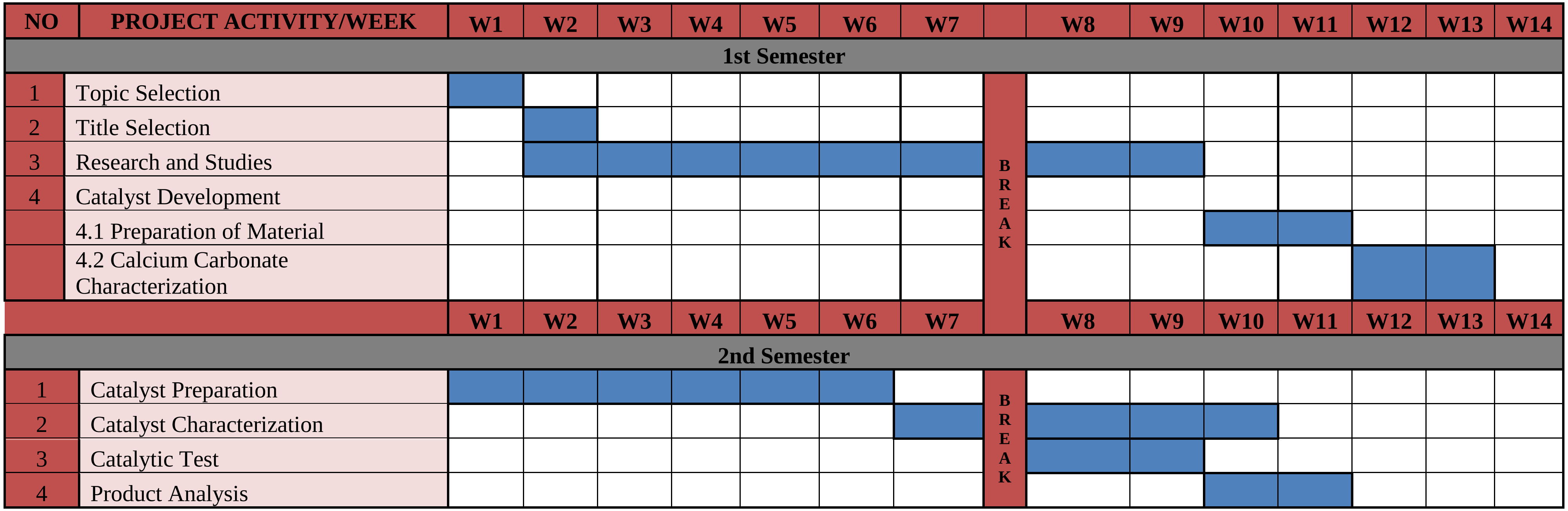


Figure 3.5: Experimental procedure of transesterification

(Refer Appendix C)

3.4 Project Gantt Chart and Key Milestone



PROJECT GANTT CHART
PRODUCTION OF BIOFUELS USING CALCIUM-BASED CATALYST

NO	PROJECT ACTIVITY/WEEK	W1	W2	W3	W4	W5	W6	W7		W8	W9	W10	W11	W12	W13	W14
1st Semester																
1	Topic Selection	■							BREAK							
2	Title Selection		■													
3	Research and Studies		■	■	■	■	■	■		■	■					
4	Catalyst Development															
	4.1 Preparation of Material											■	■			
	4.2 Calcium Carbonate Characterization													■	■	
		W1	W2	W3	W4	W5	W6	W7		W8	W9	W10	W11	W12	W13	W14
2nd Semester																
1	Catalyst Preparation	■	■	■	■	■	■		BREAK							
2	Catalyst Characterization							■		■	■	■				
3	Catalytic Test									■	■					
4	Product Analysis											■	■			

Figure 3.6: Gantt chart and key milestone

CHAPTER 4: RESULT AND DISCUSSION

4.1. Result and Discussion on Catalyst Characterization

4.1.1. Thermogravimetric (TG) Analysis

Three different calcium-containing catalysts have been prepared. Before the catalysts are synthesized, TGA had been conducted in order to evaluate the calcinations method.

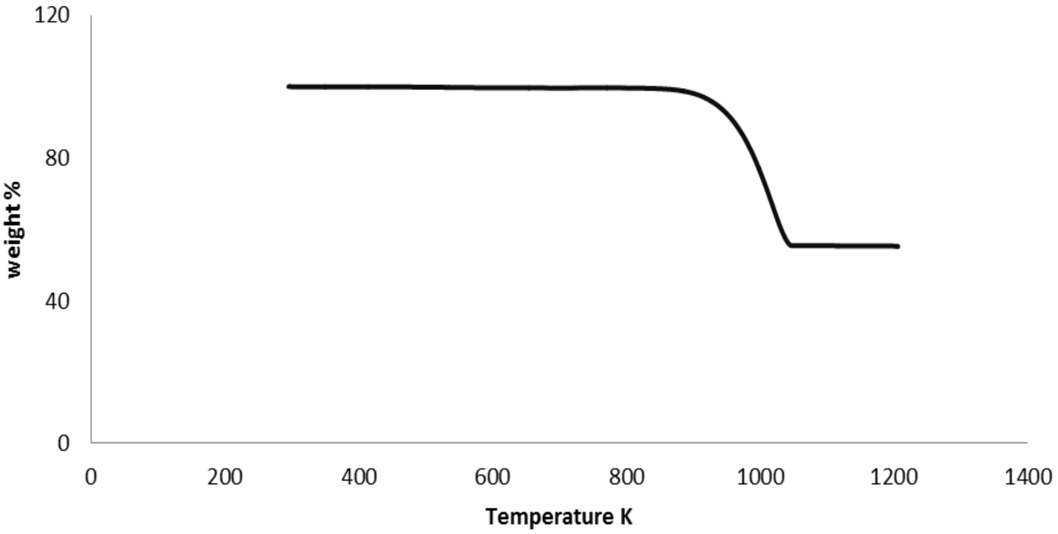


Figure 4.1: TGA result for calcium carbonate

Sample of $CaCO_3$ is analysed by using temperature Program; Heat from 373 K to 1173 K @ 283 K/minute in Argon atmosphere with a purge rate of 20mL/minute. A plot of mass as a function of time is called thermogram is obtained.

The descending TGA thermal curve indicates a weight loss occurred at temperature range of 873 K-1043 K. As the temperature increase beyond 1043 K, it is predicted $CaCO_3$ decomposes into CaO by the following reaction: $CaCO_3 \rightarrow CaO+CO_2$. Thus it can be conclude that the decomposition temperature for calcium carbonate is at 1073 K.

4.1.2. Calcination Condition

Calcium/zinc oxide catalyst is prepared by incipient wetness impregnation method. While for calcium oxide and calcium carbonate catalyst, it is develop from calcinations of neat calcium carbonate powder. The temperature during calcination for each catalyst is different. The application of TGA result is used for determination of calcinations temperature. The mass of catalyst are also been recorded after and before the calcinations.

Table 4.1: Calcination condition

Catalyst	**Calcination**			
	Temperature (K)	**Time (hour)**	**Mass Before (g)**	**Mass After (g)**
$CaCO_3$	873	3	32	32
CaO	1173	2	32	19.4
CaO/ZnO	1173	2	28.5	20.3

Based on information above, calcium carbonate is calcined at temperature 873 K to prevent it from decompose. It is observed that there is no weight loss occurred. Calcium oxide catalyst is obtained from calcination of calcium carbonate at 1173 K for 2 hours [19]. Upon heating calcium carbonate at 1173 K, it undergoes a reaction where bound CO_2 is released from the material and only calcium oxide remains after calcined. Weight loss is observed by 12.6 grams. Theoretically, weight loss occurred from the decomposition of calcium carbonate to calcium oxide is about 44%. For this experiment, the weight loss is 39.4%. Thus, the deviation is about 10.25% and it is acceptable *(Refer Appendix D for calculation*).

The calcination condition for CaO/ZnO is obtained based on literature review. It is reported by Y.H Taufiq Yap et al that the calcination temperature for calcium-based mixed oxide was at 1173 K [23]. Small mass reduction is also observed.

Figure 4.2: Calcined catalyst, CaO/ZnO

Figure 4.3: Calcined catalyst, CaO

Figure 4.4: Calcined catalyst, $CaCO_3$

4.1.3. pH Value

In the case of incipient wetness impregnation method, pH value is important in order to where surfactant adsorption should occur. At a pH value of the so-called Point of Zero Charge (PZC) of the surface is electrically neutral. At pH values above PZC, the surface is negatively charged, while at pH values below PZC the surface is positively charged. According to P. Rungruang et al. studied for colloids and surface investigate that the PZC value of calcium ($CaCO_3$ and CaO) is 8 [20].

Table 4.2: Relationship between PZC and surface charge

pH	pH < PZC	pH = PZC	pH > PZC
Surface Charge	Positive	Neutral	Negative
Species	MOH_2^+	MOH	MO
Adsorption	anions		Cations
pH increase	⟶		

Table 4.3: pH value

Catalyst	pH value
$CaCO_3$	9.73
CaO	12.48
CaO/ZnO	11.71

For calcium based catalyst, the PZC is at pH = 8, the surface is neutral. The catalysts are prepared and the pH values are measured in table above. The pH value for three catalysts is higher than the PZC. The surface is negatively charged. Thus the cations are to be deposited.

4.1.4. X-Ray Diffraction

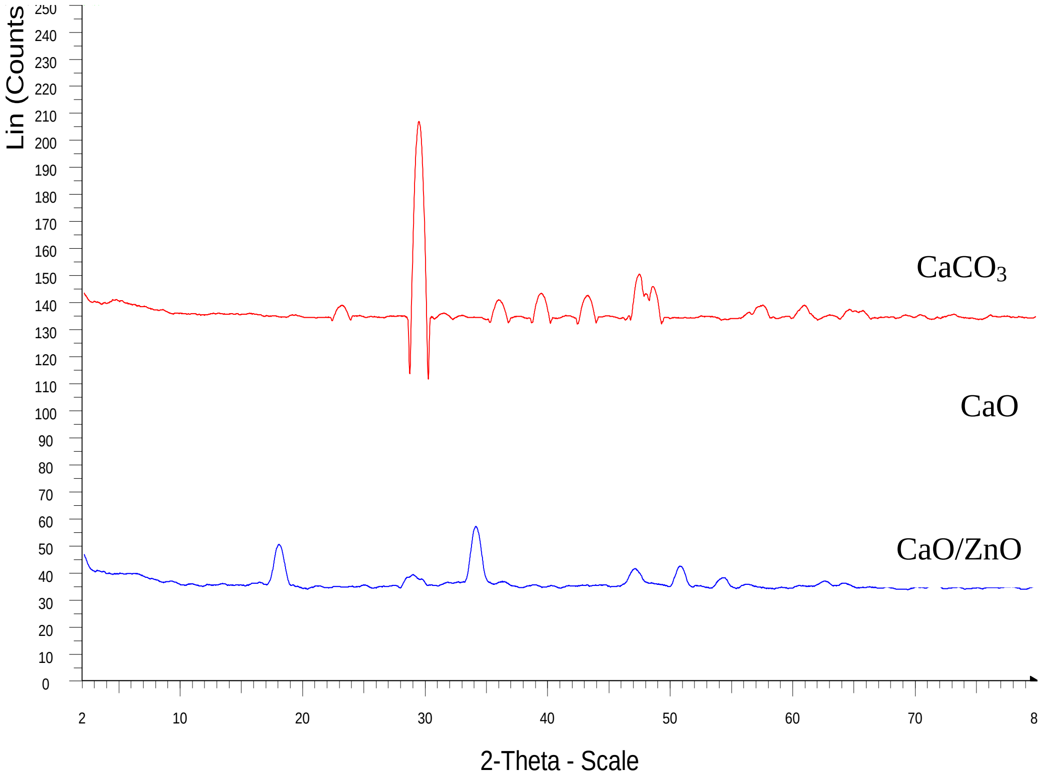


Figure 4.5: XRD pattern of $CaCO_3$, CaO and CaOZnO

The powder X-ray diffraction analysis was carried out for all prepared catalyst. It is conducted to analyse the elemental exist and crystallites of the catalyst structure. The XRD results are displayed in the form of diffraction pattern. The diffraction pattern of catalysts ($CaCO_3$, CaO and CaO/ZnO) was compared to literature powder X-ray diffraction data confirming the correct pattern.

Figure 4.5 shows the diffraction pattern of $CaCO_3$ was compared with library pattern. It is observed that the pattern is the same. The result indicated that $CaCO_3$ compound presence in the catalyst. The diffraction pattern for $CaCO_3$ clearly observed at 2ϴ angles of ≈ 30°, 36°, 40°, 44° and 48°. The result indicated $CaCO_3$ is in crystalline phase. Diffraction pattern for CaO and CaO/ZnO shows the narrowed peaks at angles of ≈ 28°, 34°, and 51° indicating that $CaCO_3$ was fully converted to CaO after calcination and ZnO at 2ϴ angles of ≈ 32°, 35°, and 36° with wurzite structure [23]. The crystalline structures are also presence in both CaO and CaO/ZnO catalyst

4.1.5. Surface Area and Pore Size

The total surface area of the catalysts was obtained by Brunauer-Emmer-Teller (BET) method using nitrogen adsorption at 77 K. Instead surface area, pore volume and pore size can also be obtained through this method *(Refer Appendix E)*. The surface are for $CaCO_3$, CaO and CaO/ZnO were shown in Table 4.4.

Table 4.4: BET result for calcium-based catalyst

	$CaCO_3$	**CaO**	**CaO/ZnO**
Surface area, m^2/g	2.4728	9.8208	2.8718
Pore volume, cm^3/g	0.002294	0.053803	0.007086
Pore size, Å	37.1002	219.1412	98.7028

Based on result obtained, it was found that with has the highest surface area and pore size is CaO catalyst followed by CaO/ZnO and $CaCO_3$.

Physical properties of catalyst give influence during transesterifiaction reaction. Catalyst which has a small pore size will limited the diffusion of the oil molecules into the catalytic sites situated inside the porous channel thereby reduced the conversion of biodiesel. The large pore size rendered the active site so they were accessible by the bulky triglyceride molecule [17].

Other than that, surface area also gives influence during transesterification reaction. Catalyst with high surface area could make the reactions proceed at high rate thus improved the efficiency of the tranesterification [17]. So, the high yield for biodiesel could be obtained by large surface area of catalyst occupied by pore of relatively large size.

From this argument, it is expected that CaO gives high yield of biodiesel since it has large surface area with large pore size.

4.1.6 Scanning Electron Microscope (SEM)

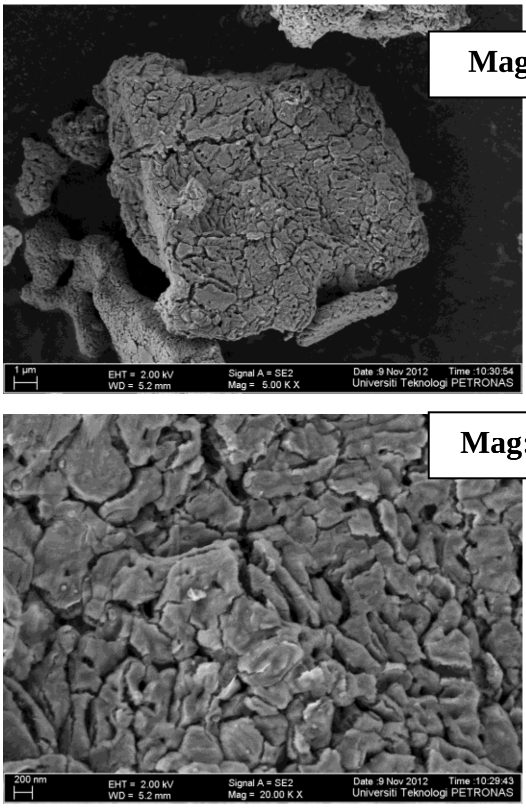


Figure 4.6: SEM images of CaO catalyst

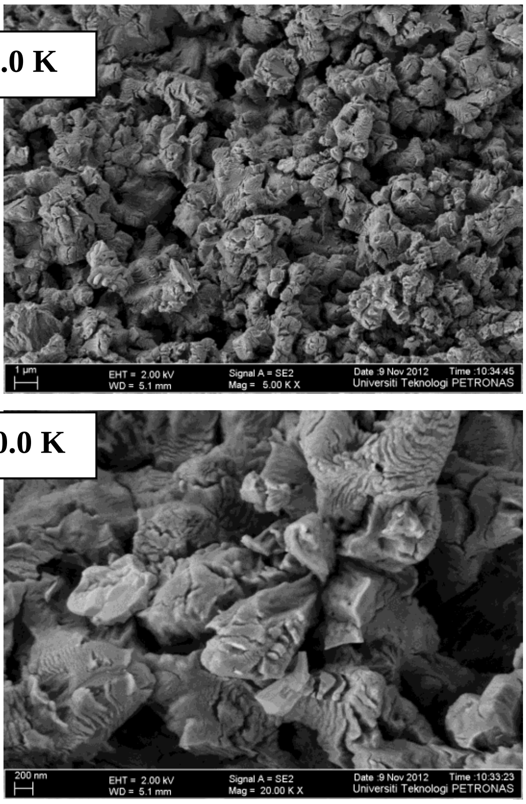


Figure 4.7: SEM images of CaO/ZnO catalyst

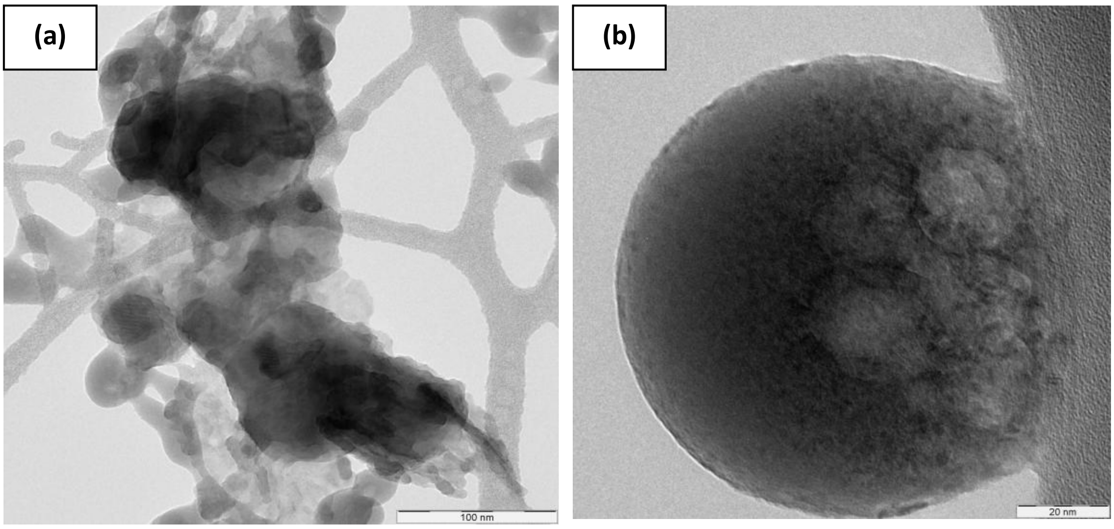


Figure 4.8: TEM images of CaO (a) and CaO/ZnO (b) catalysts

The morphology of the catalyst was studied by scanning electron microscope (SEM). Due to the limitation of equipment, students can only send only for 2 samples. Figures 4.6-4.8 shows the SEM and TEM image for CaO and CaO/ZnO.

Image of SEM and TEM shown that CaO showed a compact agglomeration and aggregated block with clear edges which gives it has large surface area. It is shown an agreement in BET result. While for CaO/ZnO, it gaves round-shape particles on its surface.

4.2 Results and Discussion on Transesterification Reaction

4.2.1 Acid Value Test

RSO contain high amount of free fatty acids. Acid-esterification is performed in order to reduce the FFA contents. Reduction in FFA can be determined by conducting acid value method using standard EN 14104. FFA content after and before acid esterification is determined by using this method.

Table 4 5: Acid value test

	Code	**Oil weight (g)**	**Volume titrant used (ml of KOH)**	**Acid value**	**Free fatty acid**
Before acid esterification	A	1.0419	17.94	96.596	34.376
	B	1.0425	17.70	95.249	33.896
	C	1.0693	18.01	94.488	33.626
			AVERAGE:	**95.444**	**33.966**
After acid esterification	D	1.0129	0.54	2.991	1.064
	E	1.0540	0.36	1.916	0.682
	F	1.0035	0.4	2.236	0.796
			AVERAGE:	**2.381**	**0.847**

After conducting acid esterification, it is observed that FFA contents are reduced from 33.966 to 0.847 *(Refer Appendix F).*

4.2.2 Product Analysis

Standard method E 14103 used to verify the ester content of fatty acid methyl esters (FAMEs) between C_{14} and C_{24}. This standard method requires GC analysis with split/splitless inlet and FID and wax column for a detailed separation of FAMEs. From this analysis, percentage of ester content is obtained with a solution of methyl heptadecanoate as internal standard.

The FAMEs content in biodiesel is expressed in percentage of mass fraction, calculated using the following formula:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\%$$

Where:

$\sum A$ Total peak area from methyl ester C14 to C24

A_{EI} Peak area corresponding to methyl heptadecanoate

C_{EI} Concentration of methyl heptadecanoate, mg/ml

V_{EI} Volume of methyl heptadecanoate, ml

m mass of sample

Table 4 6: FAMEs content in biodiesel

Catalyst Used	**∑A**	**FAMEs (%)**
CaO/ZnO	2501172	79
CaO	2878500	92
$CaCO_3$	1841707	61
KOH	2424612	78

For this experiment 4 runs of transesterification reaction with different catalysts ($CaCO_3$, CaO, CaO/ZnO and KOH) are conducted under same reaction condition;

3 hours of reaction time, 338 K of reaction temperature, methanol to oil ratio 5:1, and with rate of stirring of 350 rpm.

Based on chromatogram in Appendix G, it shows 5 main peaks which represent the FAMEs content of myristate, palmitate, oleate, linoleate and stearate. Peak with retention time 10.52 is belong to internal standard, methyl heptadecanoate.

Comparisons are made based on the percentage of ester content produced by using 4 different type of catalyst including the conventional catalyst, KOH. Table 4.6 shows the percentage of FAMEs content in biodiesel produced by using calcium-based catalyst. CaO catalyst produced the highest percent of FAMEs content of 92% followed by CaO/ZnO, KOH and $CaCO_3$ *(Refer Appendix G).*

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The first objective of this project which is to develop calcium-based catalyst was done. Catalysts are prepared with impregnation method (CaO/ZnO) and calcination method (CaO and $CaCO_3$).

The prepared catalysts were characterized by TGA, XRD, BET, FESEM and TEM. Based on the TGA result, decomposition temperature of $CaCO_3$ is obtained which is at 1043 K. The application of TGA is used in deciding the calcination temperature of catalyst. The prepared catalysts are being measured for pH value to determine the surface charge. The pH values of catalysts are higher than PZC. The surface is negatively charged and the cations are to be deposited. The diffraction pattern obtained from XRD analysis shows that the element for each catalyst are presence. BET result shown that the CaO has high surface area and pore size compared to the others. The morphology of the catalysts is also studied by FESEM and TEM.

The final objective is to produce biodiesel by using calcium-based catalyst. Transesterififcation of RSO have been investigated in presence of calcium-based catalyst and compared with conventional catalyst, KOH. The percentage of Ester content have been identified and were arrange in sequence of CaO > CaO/ZnO > KOH > $CaCO_3$.

This project has achieved the objectives and it is proven that the calcium-based catalyst has the potential to become as heterogeneous catalyst in production biofuels.

5.2. Recommendations:

1. Conversion yield of biodiesel using different type of catalyst can be obtained by using standard method EN 4105 and ASTM D6584. This standard method provides results for free and total glycerine and mono-, di- and triglyceride content.
2. Optimum reaction condition (methanol to oil ratio, reaction time and temperature, and amount of catalyst) for transesterification using calcium-based catalyst should be studied.
3. The effect of calcinations time and temperature should be varies to study the effect in transesterification.
4. Catalyst reusability should be study as it is one of the most important features for a catalyst to be industrially useful.

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APPENDICES

Appendix A: Calculation for Catalyst Preparation

Calculation:

5 weight percent (5wt%) of zinc oxide loading for 30 grams of CaO/ZnO catalyst.

- Mw Zn(NO3)2.6H2O : 297.49
- Mw ZnO: 81.4

Equations that are used:

$$2Zn(NO_3)_2 \rightarrow 2ZnO + 4NO_2 + O_2$$

The amount of Zn(NO3)2.6H2O needed:

a. 5 wt% of ZnO from 30 g of CaO/ZnO catalyst

$$\left(\frac{5}{100}\right)\times 30 = 1.5 \text{ g of ZnO}$$

b. $mole = \dfrac{mass}{molarmass} = \dfrac{1.5}{81.4} = 0.02 mole$

0.02 mole of ZnO ≈ 0.02 mole of $Zn(NO_3)_2$

c. To get the amount of Zn(NO3)2.6H2O ;

$$mass = mole \times molarmass$$

= 0.02 × 297.49

= 5.5 g of Zn(NO3)2.6H2O

Thus, 5.5 grams of Zn(NO3)2.6H2O and 28.5 grams of CaO powder are needed to produce 30 grams CaO/ZnO catalyst.

Pictures of experiment:

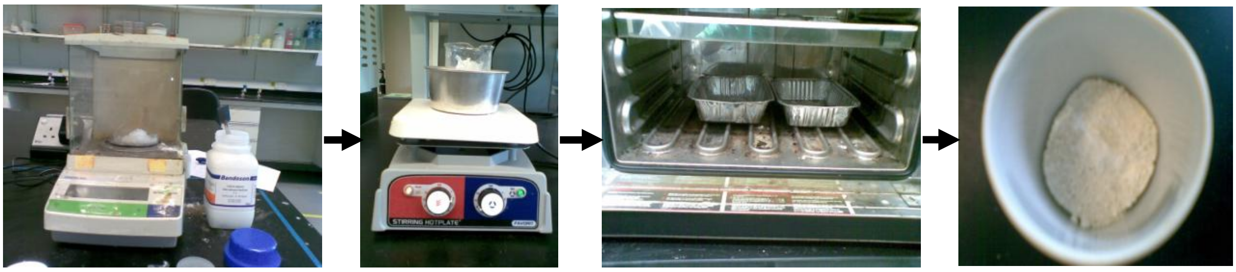


Figure 6 1: Catalyst preparation

Appendix B: Calculation for Acid Esterification

Calculation:

a) Run 1: $CaCO_3$ Catalyst

Reaction parameter		RSO
Methanol:oil ratio	15:1	Mass of RSO: 50 g MW of RSO: 877.19 g/mol Mole of RSO: 0.057 mole $\text{Mole of methanol} = 0.057 \times 15 = 0.855$ $\text{Mass of methanol} = 0.855 \times 32.04 = 27.39g$
Catalyst (H_2SO_4)	10 wt%	$0.10 \times 50 = 5g$
Reaction Temperature	338 K	-

b) Run 2 and Run 3: CaO and CaO/ZnO Catalyst

Reaction parameter		RSO
Methanol:oil ratio	15:1	Mass of RSO: 102.55 g MW of RSO: 877.19 g/mol Mole of RSO: 0.117 mole $\text{Mole of methanol} = 0.117 \times 15 = 1.754$ $\text{Mass of methanol} = 0.855 \times 32.04 = 56.19g$
Catalyst (H_2SO_4)	10 wt%	$0.10 \times 102.55 = 10.26g$
Reaction Temperature	338 K	-

c) Run 4: KOH Catalyst

Reaction parameter		RSO
Methanol:oil ratio	15:1	Mass of RSO: 50 g MW of RSO: 877.19 g/mol Mole of RSO: 0.057 mole Mole of methanol $= 0.057 \times 15 = 0.855$ Mass of methanol $= 0.855 \times 32.04 = 27.39g$
Catalyst (H_2SO_4)	10 wt%	$0.10 \times 50 = 5g$
Reaction Temperature	338 K	-

MW of RSO : 877.19 g/mol

MW of Methanol : 32.04 g/mol

Pictures of experiment:

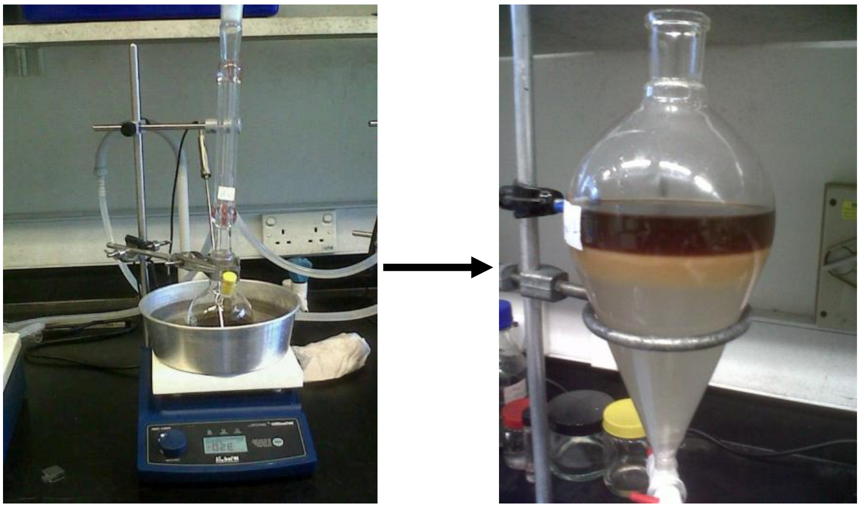


Figure 6 2: Acid esterification

Appendix C: Transesterification

Calculation:

a) Run 1: $CaCO_3$ Catalyst

Reaction parameter		RSO
Methanol:oil ratio	5:1	Mass of RSO: 40.4 g MW of RSO: 877.19 g/mol Mole of RSO: 0.0461 mole Mole of methanol $= 0.0461 \times 5 = 0.2305$ Mass of methanol $= 0.2305 \times 32.04 = 7.3852\,g$
Catalyst (H_2SO_4)	5 wt%	$0.05 \times 40.4 = 2.02\,g$
Reaction Temperature	338 K	-

b) Run 2: CaO Catalyst

Reaction parameter		RSO
Methanol:oil ratio	5:1	Mass of RSO: 39.937 g MW of RSO: 877.19 g/mol Mole of RSO: 0.0455 mole Mole of methanol $= 0.0455 \times 5 = 0.228$ Mass of methanol $= 0.228 \times 32.04 = 7.294\,g$
Catalyst (H_2SO_4)	5 wt%	$0.05 \times 39.937 = 1.997\,g$
Reaction Temperature	338 K	-

c) Run 3: CaO/ZnO Catalyst

Reaction parameter		RSO
Methanol:oil ratio	5:1	Mass of RSO: 39.3064 g MW of RSO: 877.19 g/mol Mole of RSO: 0.0448 mole Mole of methanol $= 0.0448 \times 5 = 0.224$ Mass of methanol $= 0.224 \times 32.04 = 7.178\,g$
Catalyst (H_2SO_4)	5 wt%	$0.05 \times 39.3064 = 1.9653\,g$
Reaction Temperature	338 K	-

d) Run 4: KOH Catalyst

Reaction parameter		RSO
Methanol:oil ratio	5:1	Mass of RSO: 20.3505 g MW of RSO: 877.19 g/mol Mole of RSO: 0.0232mole Mole of methanol $=0.0232\times 5=0.116$ Mass of methanol $=0.116\times 32.04=3.7166\,g$
Catalyst (H_2SO_4)	5 wt%	$0.05\times 20.3505=1.0175\,g$
Reaction Temperature	338 K	-

MW of RSO : 877.19 g/mol

MW of Methanol : 32.04 g/mol

Pictures of experiment:

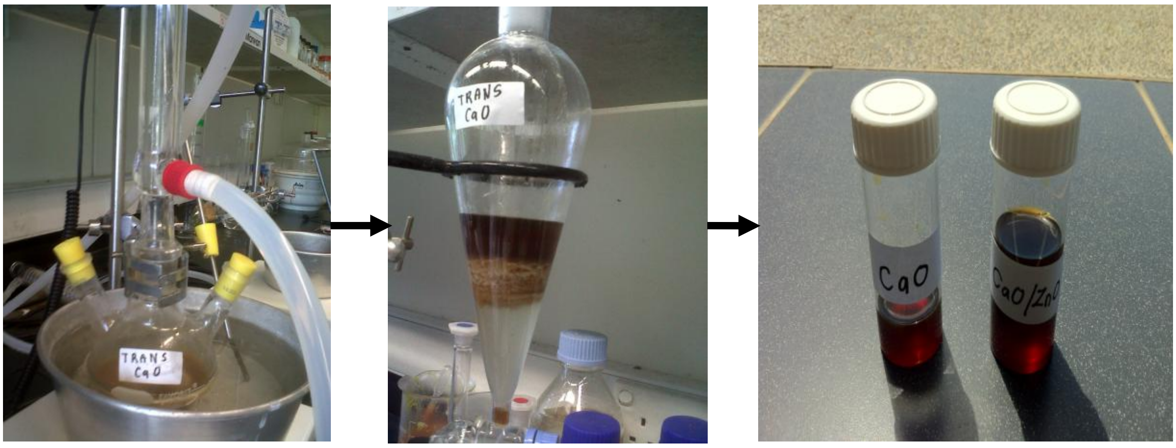


Figure 6 3: Transesterification

Appendix D: Weight Loss Calculation

Calculation:

Table 6 1: Calcination condition

Catalyst	**Calcination**				
	Temperature (°C)	**Time (hour)**	**Mass Before (g)**	**Mass After (g)**	**Mass reduction (g)**
$CaCO_3$	600	3	32	32	-
CaO	900	2	32	19.4	12.6
CaO/ZnO	900	2	28.5	20.3	5.2

a) Mass reduction = mass before – mass after

b) Theoretical mass reduction for decomposition of $CaCO_3$

c) Mw $CaCO_3$: 100.08

Mw CaO: 56.08

$CaCO_3 \rightarrow CaO + CO_2$

Assume mass of $CaCO_3$ is 100. Then number of moles will be;

$$\text{Mole} = \frac{mass}{molarmass}$$

$$= \frac{100}{100.08}$$

= 1 mole of $CaCO_3$

1 mole of $CaCO_3$ ≈ 1 mole of Cao

Mass of CaO will be 56.08 grams

$$\text{Weight loss \%} = \frac{43.9}{100} \times 100$$

$$= 43.9\%$$

d) Measured value

For this project, 32 g of $CaCO_3$ is used. After heating at 900°C, it decomposes into CaO. The obtained CaO is 19.4 g.

Weight loss = 32 – 19.4

= 12.6 g

Weight loss % = $\frac{12.6}{32} \times 100$

= 39.4%

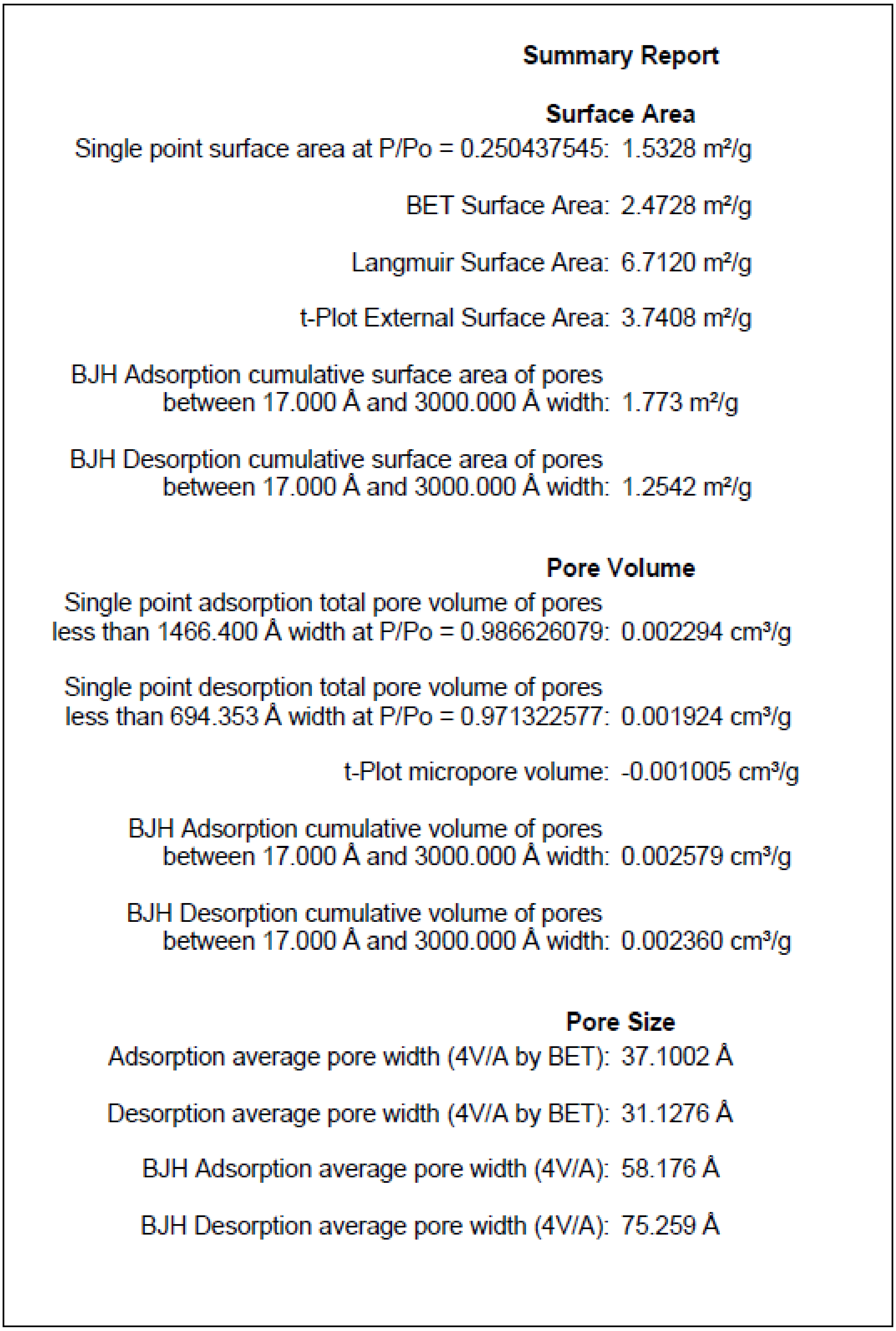
Thus, percent of deviation between theoretical and measured value;

% Deviation = $\frac{theoritical - measured}{theoritical} \times 100$

= $\frac{43.9 - 39.4}{43.9} \times 100$

= 10.20%

Appendix E: BET Results



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                                   Summary Report

                                    Surface Area
 Single point surface area at P/Po = 0.250437545:  1.5328 m²/g

                               BET Surface Area:  2.4728 m²/g

                          Langmuir Surface Area:  6.7120 m²/g

                     t-Plot External Surface Area:  3.7408 m²/g

 BJH Adsorption cumulative surface area of pores
           between 17.000 Å and 3000.000 Å width:  1.773 m²/g

 BJH Desorption cumulative surface area of pores
           between 17.000 Å and 3000.000 Å width:  1.2542 m²/g


                                    Pore Volume
 Single point adsorption total pore volume of pores
less than 1466.400 Å width at P/Po = 0.986626079:  0.002294 cm³/g

 Single point desorption total pore volume of pores
 less than 694.353 Å width at P/Po = 0.971322577:  0.001924 cm³/g

                           t-Plot micropore volume:  -0.001005 cm³/g

       BJH Adsorption cumulative volume of pores
           between 17.000 Å and 3000.000 Å width:  0.002579 cm³/g

       BJH Desorption cumulative volume of pores
           between 17.000 Å and 3000.000 Å width:  0.002360 cm³/g

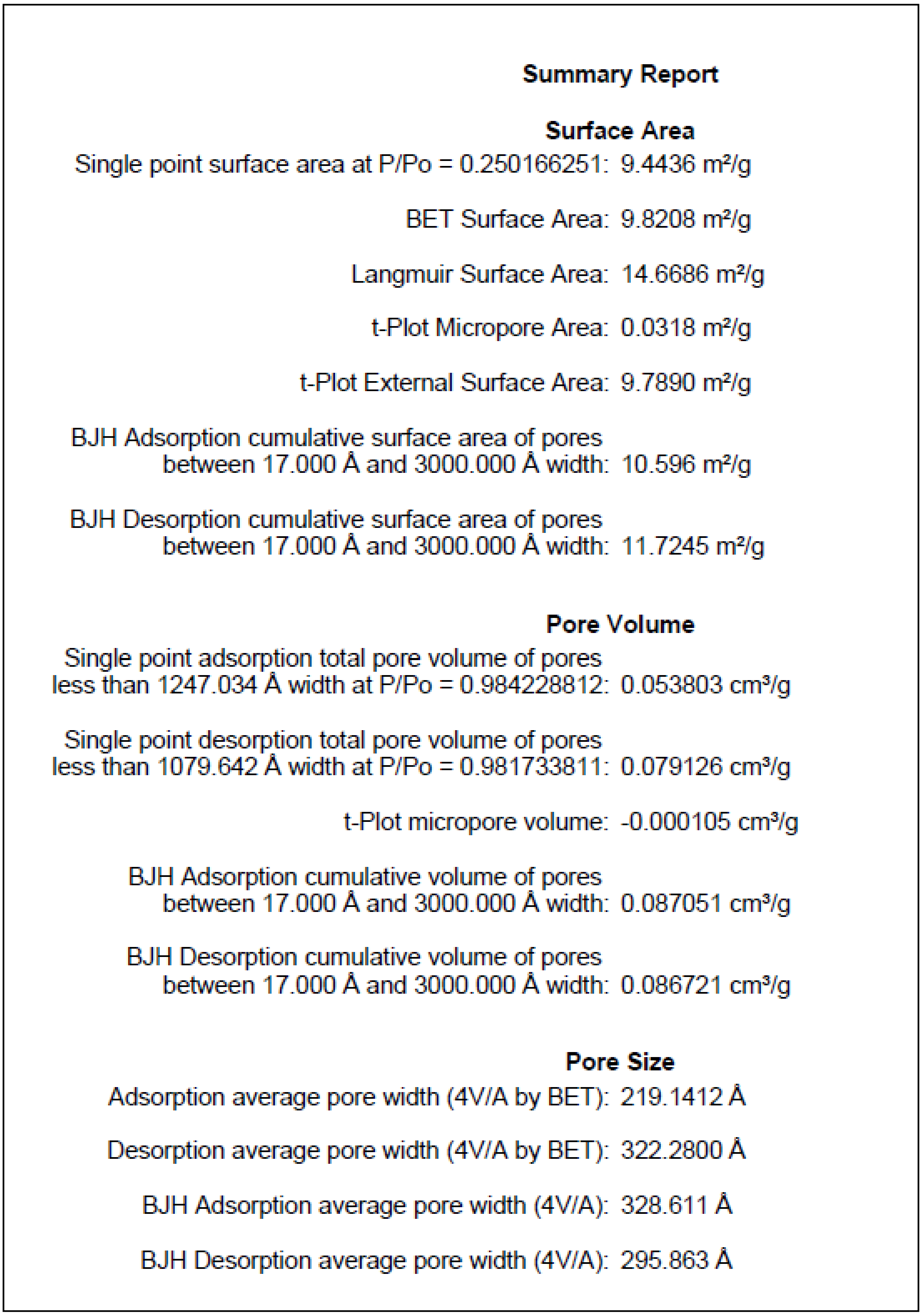

                                     Pore Size
     Adsorption average pore width (4V/A by BET):  37.1002 Å

     Desorption average pore width (4V/A by BET):  31.1276 Å

          BJH Adsorption average pore width (4V/A):  58.176 Å

          BJH Desorption average pore width (4V/A):  75.259 Å
```

Figure 6 4: BET result for $CaCO_3$ catalyst



Summary Report

Surface Area

Single point surface area at P/Po = 0.250166251: 9.4436 m^2/g

BET Surface Area: 9.8208 m^2/g

Langmuir Surface Area: 14.6686 m^2/g

t-Plot Micropore Area: 0.0318 m^2/g

t-Plot External Surface Area: 9.7890 m^2/g

BJH Adsorption cumulative surface area of pores
between 17.000 Å and 3000.000 Å width: 10.596 m^2/g

BJH Desorption cumulative surface area of pores
between 17.000 Å and 3000.000 Å width: 11.7245 m^2/g

Pore Volume

Single point adsorption total pore volume of pores
less than 1247.034 Å width at P/Po = 0.984228812: 0.053803 cm^3/g

Single point desorption total pore volume of pores
less than 1079.642 Å width at P/Po = 0.981733811: 0.079126 cm^3/g

t-Plot micropore volume: -0.000105 cm^3/g

BJH Adsorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.087051 cm^3/g

BJH Desorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.086721 cm^3/g

Pore Size

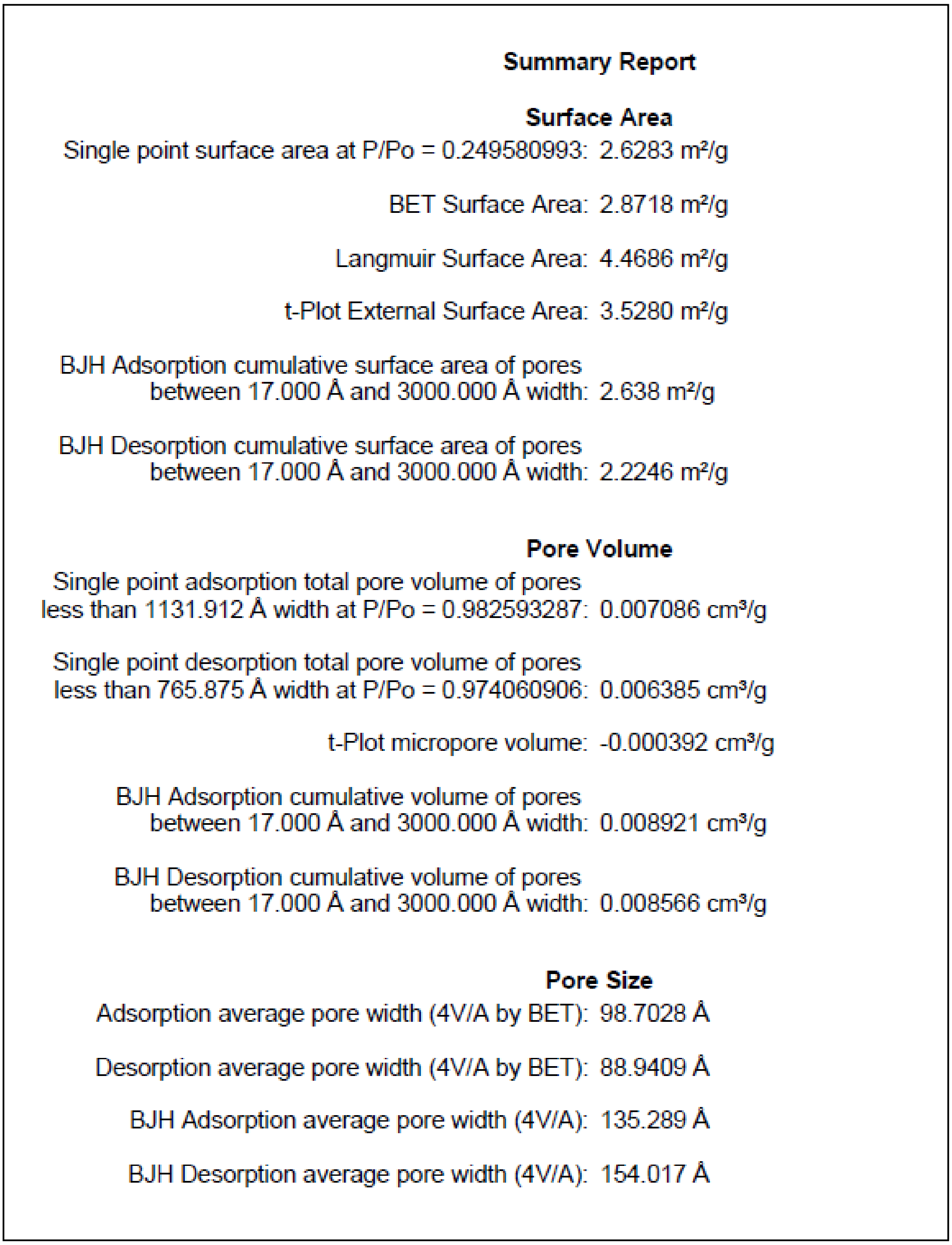
Adsorption average pore width (4V/A by BET): 219.1412 Å

Desorption average pore width (4V/A by BET): 322.2800 Å

BJH Adsorption average pore width (4V/A): 328.611 Å

BJH Desorption average pore width (4V/A): 295.863 Å

Figure 6 5: BET result for CaO catalyst



```
                                   Summary Report

                                    Surface Area
  Single point surface area at P/Po = 0.249580993:  2.6283 m²/g

                                BET Surface Area:  2.8718 m²/g

                           Langmuir Surface Area:  4.4686 m²/g

                     t-Plot External Surface Area:  3.5280 m²/g

  BJH Adsorption cumulative surface area of pores
          between 17.000 Å and 3000.000 Å width:  2.638 m²/g

  BJH Desorption cumulative surface area of pores
          between 17.000 Å and 3000.000 Å width:  2.2246 m²/g


                                    Pore Volume
  Single point adsorption total pore volume of pores
 less than 1131.912 Å width at P/Po = 0.982593287:  0.007086 cm³/g

  Single point desorption total pore volume of pores
  less than 765.875 Å width at P/Po = 0.974060906:  0.006385 cm³/g

                          t-Plot micropore volume:  -0.000392 cm³/g

       BJH Adsorption cumulative volume of pores
          between 17.000 Å and 3000.000 Å width:  0.008921 cm³/g

       BJH Desorption cumulative volume of pores
          between 17.000 Å and 3000.000 Å width:  0.008566 cm³/g


                                     Pore Size
    Adsorption average pore width (4V/A by BET):  98.7028 Å

    Desorption average pore width (4V/A by BET):  88.9409 Å

         BJH Adsorption average pore width (4V/A):  135.289 Å

         BJH Desorption average pore width (4V/A):  154.017 Å
```

Figure 6 6: BET result for CaO/ZnO catalyst

Appendix F: Acid Value Test

Calculation:

Acid value can be calculated using formula:

$$AV = \frac{56.1 \times vol \times 0.1}{m}$$

Where:

Vol : volume of titrant used

0.1N : normality of KOH

m : mass of sample

56.1 : MW of KOH

Free fatty acid can be calculated using formula:

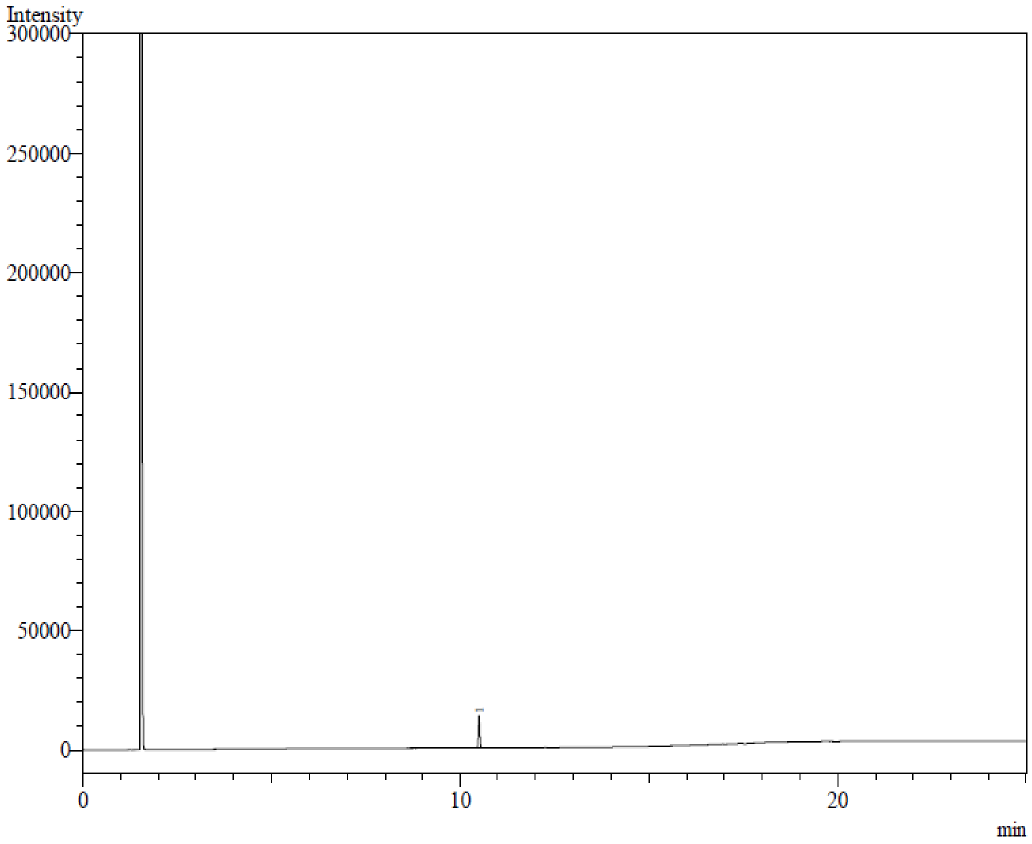
$$FFA = \frac{AV}{f}$$

Where *f* is conversion value factors for RSO =2.81

Table 6 2: Acid value test

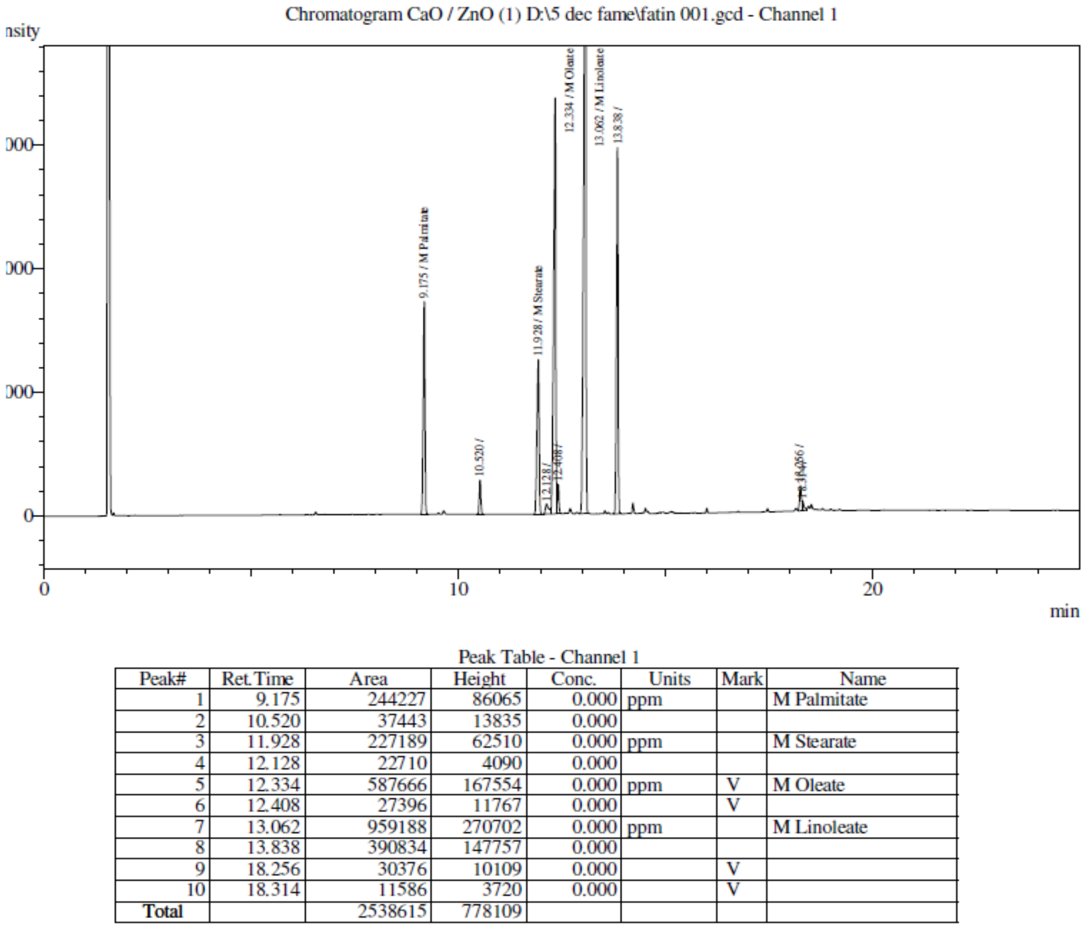
	Code	**Oil weight (g)**	**Volume titrant used (ml of KOH)**	**Acid value**	**Free fatty acid**
Before acid esterification	A	1.0419	17.94	96.596	34.376
	B	1.0425	17.70	95.249	33.896
	C	1.0693	18.01	94.488	33.626
			AVERAGE:	**95.444**	**33.966**
After acid esterification	D	1.0129	0.54	2.991	1.064
	E	1.0540	0.36	1.916	0.682
	F	1.0035	0.4	2.236	0.796
			AVERAGE:	**2.381**	**0.847**

Appendix G: Product analysis by GC



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	10.502	36058.29	13638.68	0.0000		
Total		36058.29		0.0000		

Figure 6 7: Chromatogram of methyl heptadecanoate



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Units	Mark	Name
1	9.175	244227	86065	0.000	ppm		M Palmitate
2	10.520	37443	13835	0.000			
3	11.928	227189	62510	0.000	ppm		M Stearate
4	12.128	22710	4090	0.000			
5	12.334	587666	167554	0.000	ppm	V	M Oleate
6	12.408	27396	11767	0.000		V	
7	13.062	959188	270702	0.000	ppm		M Linoleate
8	13.838	390834	147757	0.000			
9	18.256	30376	10109	0.000		V	
10	18.314	11586	3720	0.000		V	
Total		2538615	778109				

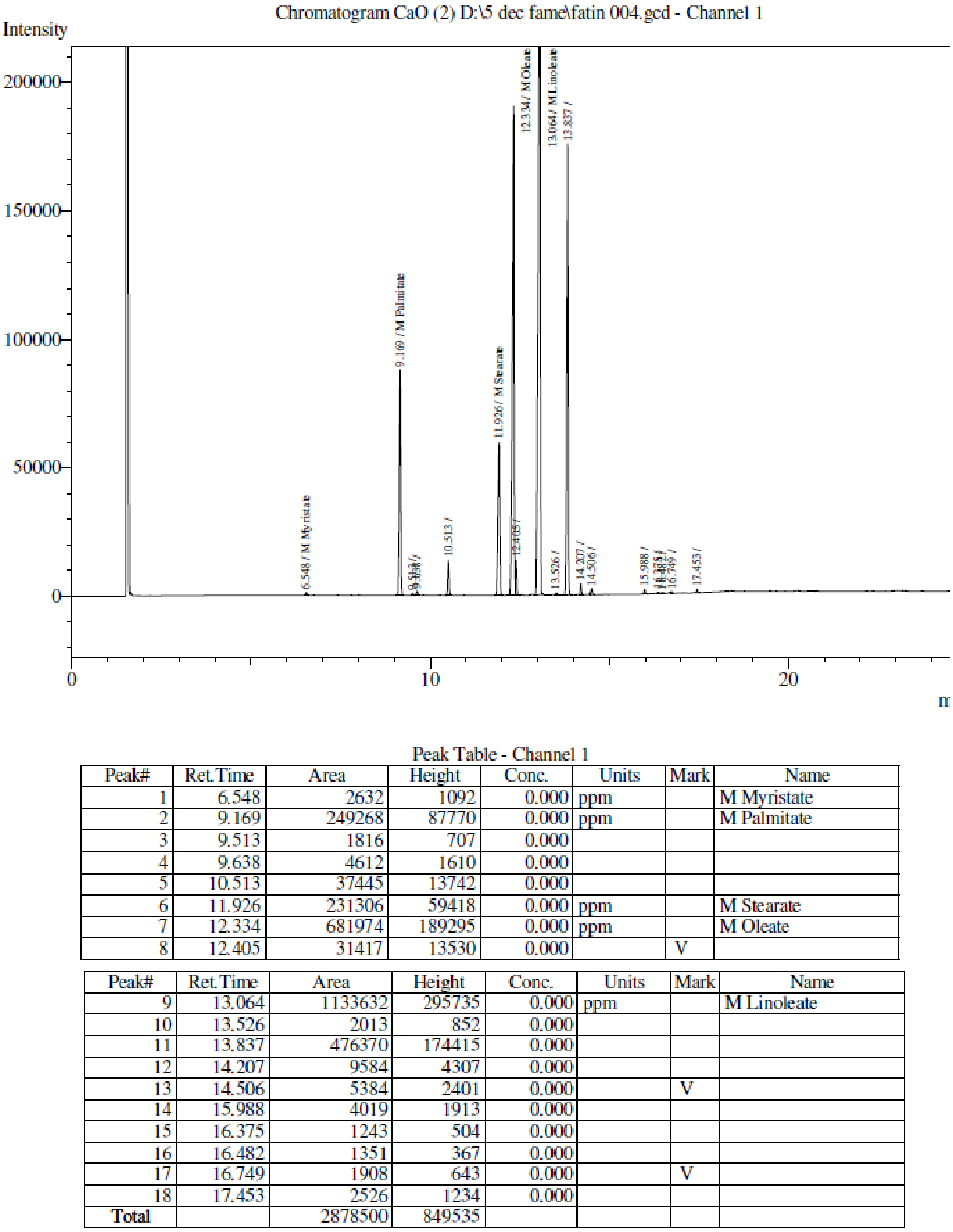
Figure 6 8: Chromatogram of biodiesel using CaO/ZnO catalyst

The ester content can be calculated using the following formula:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% = \frac{2538615 - 37443}{37443} \times \frac{0.648 \times 1}{54.8} \times 100\% = 79\%$$

Where:

∑A	Total peak area from methyl ester C14 to C24
AEI	Peak area corresponding to methyl heptadecanoate
CEI	Concentration of methyl heptadecanoate, mg/ml
VEI	Volume of methyl heptadecanoate, ml
m	mass of sample



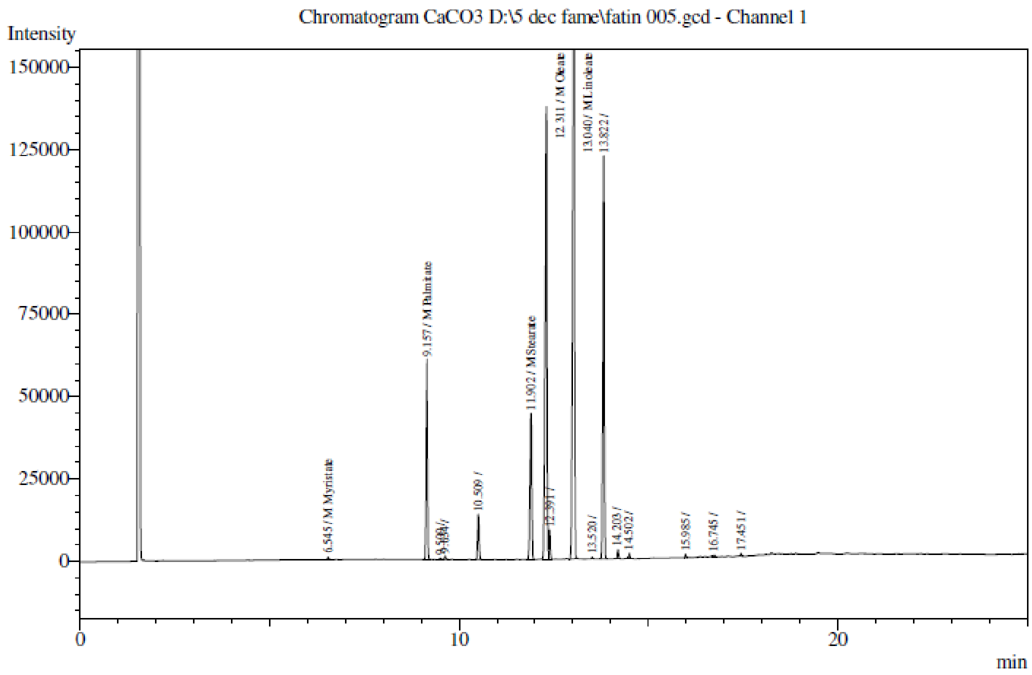
Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Units	Mark	Name
1	6.548	2632	1092	0.000	ppm		M Myristate
2	9.169	249268	87770	0.000	ppm		M Palmitate
3	9.513	1816	707	0.000			
4	9.638	4612	1610	0.000			
5	10.513	37445	13742	0.000			
6	11.926	231306	59418	0.000	ppm		M Stearate
7	12.334	681974	189295	0.000	ppm		M Oleate
8	12.405	31417	13530	0.000		V	
9	13.064	1133632	295735	0.000	ppm		M Linoleate
10	13.526	2013	852	0.000			
11	13.837	476370	174415	0.000			
12	14.207	9584	4307	0.000			
13	14.506	5384	2401	0.000		V	
14	15.988	4019	1913	0.000			
15	16.375	1243	504	0.000			
16	16.482	1351	367	0.000			
17	16.749	1908	643	0.000		V	
18	17.453	2526	1234	0.000			
Total		2878500	849535				

Figure 6 9: Chromatogram of biodiesel using CaO catalyst

Ester content:

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% = \frac{2878500 - 37445}{37445} \times \frac{0.648 \times 1}{53.4} \times 100\% = 92\%$$



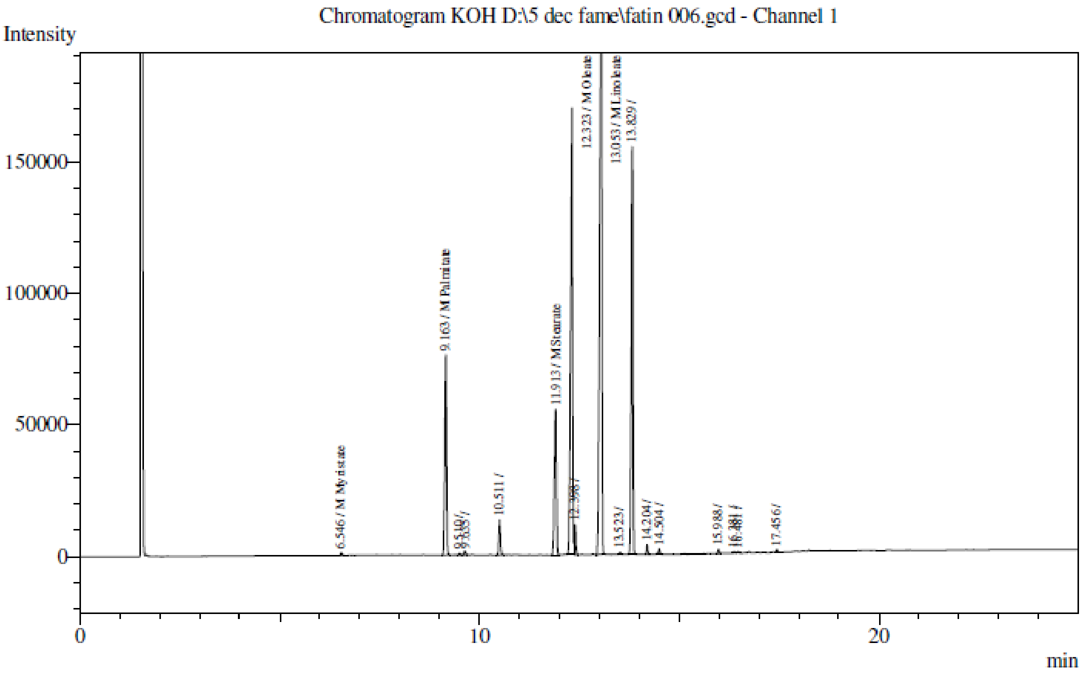
Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Units	Mark	Name
1	6.545	1742	739	0.000	ppm		M Myristate
2	9.157	165798	60643	0.000	ppm		M Palmitate
3	9.509	1180	464	0.000			
4	9.634	3203	1089	0.000			
5	10.509	37048	13693	0.000			
6	11.902	142998	44323	0.000	ppm		M Stearate
7	12.311	443259	136742	0.000	ppm		M Oleate
8	12.391	21855	8895	0.000		V	
9	13.040	739712	227406	0.000	ppm		M Linoleate
10	13.520	1296	572	0.000			
11	13.822	305985	121850	0.000			
12	14.203	5959	2671	0.000			
13	14.502	3408	1556	0.000		V	
14	15.985	2188	1053	0.000			
15	16.745	1501	490	0.000		V	
16	17.451	1623	770	0.000			
Total		1878755	622956				

Figure 6 10: Chromatogram of biodiesel using CaCO3 catalyst

Ester content:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% = \frac{1878755 - 37048}{37048} \times \frac{0.648 \times 1}{52.8} \times 100\% = 61\%$$



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Units	Mark	Name
1	6.546	2273	925	0.000	ppm		M Myristate
2	9.163	211848	75787	0.000	ppm		M Palmitate
3	9.510	1519	587	0.000			
4	9.635	3672	1346	0.000			
5	10.511	36569	13191	0.000			
6	11.913	196202	55320	0.000	ppm		M Stearate
7	12.323	582677	169047	0.000	ppm		M Oleate
8	12.398	27256	11447	0.000		V	
9	13.053	971139	272941	0.000	ppm		M Linoleate
10	13.523	1733	738	0.000			
11	13.829	405682	154539	0.000			
12	14.204	7877	3540	0.000			
13	14.504	4610	2039	0.000		V	
14	15.988	3679	1639	0.000			
15	16.381	1161	540	0.000			
16	16.481	1271	527	0.000			
17	17.456	2013	999	0.000			
Total		2461181	765152				

Figure 6 11: Chromatogram of biodiesel using KOH catalyst

Ester content:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% = \frac{2461181 - 36569}{36569} \times \frac{0.648 \times 1}{55.4} \times 100\% = 78\%$$

Pictures of experiment:

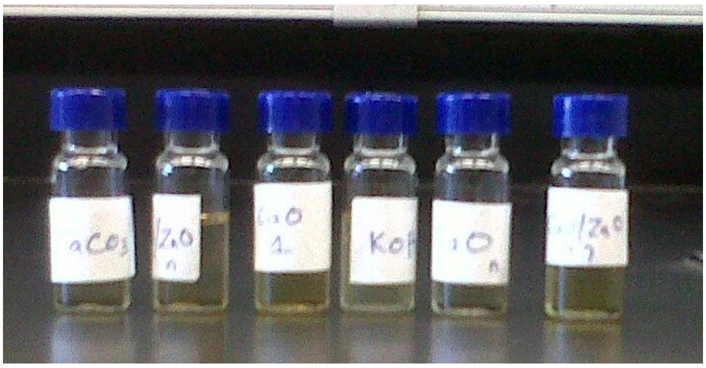


Figure 6 12: Biodiesel sample for GC analysis

Figure 6 13: GC-FID