SYNTHESIS OF BIODIESEL USING CALCIUM OXIDE CATALYST FROM EGGSHELL WITH 1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE

Mr. JEDSADA JITCHANAK
Miss LAKSANAKORN SAWASDIKOOL
Miss SALINTHIP CHATHEP

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT
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Title	Synthesis of biodiesel using calcium oxide catalyst from eggshell with 1-Ethyl-3-methylimidazolium chloride.	
Students	Mr. Jedsada	Jitchanak
	Miss Laksanakorn	Sawasdikool
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Degree	Bachelor of Science	
Major	Petrochemical Technology	
Academic Year	2011	
Advisor	Asst.Prof.Dr. Vanchat Chuenchom	

ABSTRACT

The aim of this project was to study the transesterification reaction of palm oil and methanol using calcium oxides, both commercial and from egg shell, as catalyst with 1-Ethyl-3-methylimidazolium chloride as co-catalyst. The commercial calcium oxide was calcined at 700°C for 5 hours before used. The egg shell was calcined at 800°C for more than 8 hours before used. The reactions were carried out using 1, 2 and 3%wt of calcium oxide catalyst, 0.074, 0.148, 0.296 and 0.444%wt of 1-Ethyl-3-methylimidazolium chloride, and mole ratio of palm oil to methanol of 1:6 and 1:9 at 65°C for 30 and 60 minutes. It was found that the yields of methyl ester when using 1-Ethyl-3-methylimidazolium chloride were more than that not using 1-Ethyl-3-methylimidazolium chloride. The results showed that 91.82 % yield of methyl ester was reached when 2%wt of calcium oxide with 0.296%wt of 1-Ethyl-3-methylimidazolium chloride, mole ratio of palm oil to methanol of 1:9 were used at 65°C for 60 minutes. When the calcined egg shell was used as catalyst under the optimum condition, the result showed that higher % methyl ester yield of 97.788% was reached. This could be explained by the higher surface area of calcined egg shell as compared to that of commercial calcium oxide which propably led to the higher basicity over that of the commercial catalyst.

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Miss Laksanakorn Sawasdikool
Miss Salinthip Chathep

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Introduction

1.1 Introduction and Motivation

The price of petroleum diesel has soared in the recent years, and the available reserves of this important fuel will eventually be exhausted if large-scale use continues. The greenhouse gas emission by the usage of fossil fuels is also becoming a greater concern.[1] It is necessary to make great efforts at reducing greenhouse gas emissions. Many recent research programs based on energy sector are focused on the development of concepts such as renewable resources, sustainable development, green energy and eco-friendly process.[2] Therefore, It is necessary to develop ecologically clean and safe energy technologies for a sustainable future.

In 1911, for the first time, Rudolph Diesel used peanut oil to run the diesel engine invented by him owing to which different varieties of edible and non edible oil have been studied for the purpose. The interest in energy self sufficiency and periodic petroleum shortages spurred research into vegetable oil as a petroleum diesel substitute. It is known those vegetable oil was investigated as diesel fuel during the energy crisis of the 1970–1980s and were also used as emergency fuels during World War II. The different feedstock that were investigated for biodiesel production includes palm oil, soybean oil, rapeseed oil, cottonseed oil, castor oil, Jatropha oil, etc. In some cases, investigations were also carried out on non vegetable sources such as animal fats and waste cooking oil. The major problem associated with vegetable oil is its high viscosity which leads to poor atomization of the fuel in the engine's combustion chamber and results in operational problem such as engine deposit. The most appropriate way to adjust the viscosity of the vegetable oil and animal fats for use in unmodified diesel engines is by converting the triacylglyceride into lower molecular weight fatty acid monoalkyl ester. Chemically, biodiesel is mono alkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils and animal fats. It has similar physical properties to petroleum diesel. It can be used in its neat form or as a blend with conventional diesel fuel in diesel engine without any modification and can reduce the particulate emissions from engine.[2]

The conventional catalysts for transesterification reaction are homogeneous strong bases (such as alkali metal hydroxides and alkoxides) and homogeneous acids (such as H_2SO_4). However, alkaline catalysts are generally corrosive to equipment, the subsequent separation and purification steps are time-consuming and non-environmentally friendly due to a requirement of several washing stages (amount of highly caustic wastewater is inevitably produced), and also react with free fatty acid to form unwanted soap by-products that require expensive separation; homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems. These drawbacks significantly contribute some additional cost to the final product. To overcome these problems, more environmentally benign routes to the methyl esters have been extensively researched and developed. Using heterogeneous catalysts has received much attention since the reaction proceeds under relatively mild conditions at an acceptable rate and the process can be simplified by facilitating the separation and purification, lack of corrosion or toxicity problem, and omitting the washing stage. The production of biodiesel calls for an efficient and cheap catalyst to make the process economic and fully ecologically friendly, accordingly reducing its price and making it competitive with petroleum diesel. [1, 6]

In part of production of biodiesel which has their widespread applications, the using of metal oxide and ionic liquid catalysts are becoming the focus of current investigation. Since the heterogeneous catalyst process has been extensively researched from the viewpoint of simplifying the production and purification processes, downsizing the process equipment, and, in consequence, reducing the environmental impact and process cost. Heterogeneous catalysts are of two types – acids and bases. Base catalysts exhibit high catalytic activities, and a number of basic heterogeneous catalysts have been developed, e.g., metal oxides. Calcium Oxide (CaO) is one of the well-researched heterogeneous catalysts as it has a higher basicity, lower solubility, lower price, and is easier to handle than KOH. [4]

The ionic liquid catalysts has the prospect to develop the economical and environmental aspects of biodiesel production such as its properties of less corrosion effects, separable, recyclable, direct and continuous processing, less waste water formation and more competitive economical processing and yielding of higher purity of esters[3]. Imidazolium structure is one of ionic liquid catalysts which exhibit good catalytic performances in the transesterification. They have already been used in many researches for synthesis of biodiesel in co-functionalized with other catalysts which got the yield of biodiesel product (methyl ester (ME) content) higher than 93.6%.[3, 5]

Palm oil is one of the most economic viable feedstock for biodiesel production containing equivalent amounts of saturated and unsaturated fatty acids.[3] Therefore, palm oil was chosen for use in this project. Moreover, egg shells were calcined and used as calcium oxide catalyst in this work. They are produced several tons a day. Using wastes as raw materials for catalyst synthesis could eliminate the wastes and simultaneously produces the catalysts with high cost effectiveness, high potential and low-cost biodiesel production catalyst. The optimised %wt. of calcium oxide was determined. The use of a small amount of imidazolium ionic liquid as co-catalyst was studied in order to reach the highest percentage yield of methyl ester product compared with the use of calcium oxide alone.

1.2 Objective

To synthesizes the methyl ester product by using the proper amount of %wt. calcium oxide and imidazolium ionic liquid catalysts, the ratio of palm oil to methanol and time to get the highest yield of product.

1.3 Scope of work

1. Literature Reviews.
2. Preparation of catalysts

   Commercial calcium oxide

   - Pretreatment of calcium oxide by calcinations at 700°C for 5 hours

   Calcium oxide from eggshell

   - Eggshell was collected, rinsed with deionized water, and dried at 105°C for 24 h. It was then grinded, sieved and burnt with frame from Bunsen burner. Finally, calcination was performed at 800°C for more than 8 h under static air.

   Characterizations calcium oxide

   - Characterization of calcium oxide both commercial and from eggshell by using X-ray diffractometry (XRD), scanning electron microscope (SEM), and BET method.

3. Synthesis of the methyl ester from palm oil and methanol via transesterification
    - Using calcium oxide, both commercial and from eggshell, as catalyst from 1.0 to 2.0 and 3.0% by weight of palm oil.
    - Using imidazolium ionic liquid catalyst from 0.074, 0.148, 0.296 and 0.444 % by weight of palm oil.
    - Using the ratio of palm oil to methanol from 1:6 to 1:9
    - Using the reaction time from 60 minutes to 30 minutes.
4. Characterization of the product by using NMR.

1.4 Expected Result

High yield of methyl ester via milder condition by using the combination of proper amount of calcium oxide from egg shell and 1-Ethyl-3-methylimidazolium chloride was reached comparing with CaO alone.

Chepter2

Theory and Literature reviews

2.1 Introduction to bioenergy [7, 8]

The world today is faced with serious global warming and environmental pollution. Beside, fossil fuel will become rare and faces serious shortage in the near future. These crises have triggered the awareness to find alternative energy as their sustainable energy sources.

Biomass energy is expected to resolve these issues and has gained international attention as a source of renewable and environment-friendly energy. To the extent that biomass does get used for energy, the best use is as liquid fuels for transportation if green house effect emissions reduction is the goal. Besides, solid biomass (e.g. wood chips) uses are in limited amounts to burn for building heat.

In Thailand, the Government of Thailand recently has set up a production target of 8.5 million liters per day of palm oil-based biodiesel by 2011. Palm oil has been considered as a prospective feedstock for biodiesel production, particularly due to the fact that it has the highest yielding among Thailand's oil yielding plants. As palm biodiesel is being promoted at the policy level, it is imperative to consider a full chain energy analysis as a first step to address energy gain or loss of renewable energy production. This will also support the Government of Thailand in its policy to promote the use of indigenous and renewable source for transportation fuels.[19]

2.2 Palm oil [3, 7, 9]

Vegetable oil which also known as triglycerides have the chemical structure, as shown in Figure 2.1, comprise of 98% triglycerides and small amounts of mono and diglycerides. Biodiesel is defined as the mono alkyl esters of vegetable oil or animal fats. It is the process of reacting triglyceride with an alcohol in the presence of a catalyst to produce glycerol and fatty acid methyl esters.

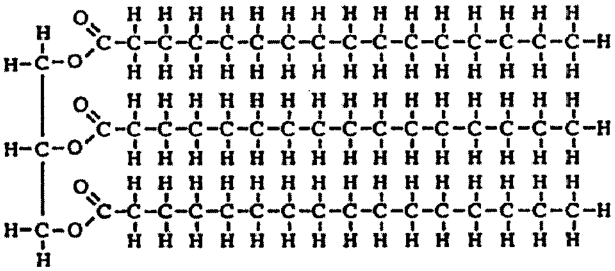


Figure 2.1 Typical structure of a triglyceride molecule.[7]

Vegetable oil contains free fatty acids, phospholipids, phosphatides, carotenes, tocopherols, sulphur compound and traces of water. The fatty acids commonly found in vegetable oil are stearic, palmitic, oleic, linoleic and linolenic and the summary of the fatty acid composition of some the common vegetable oil is shown in Table 2.1.

Table 2.1 Chemical structure for common fatty acids of vegetable oil.[7]

Name	**Chemical name**	**Structure (xx:y)**[a]	**Formula**
Lauric	Lignoceric	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Gadoleic	11-eicosenoic	20:1	$C_{20}H_{38}O_2$
Erucle	cis-13-Docosenoic	22:1	$C_{22}H_{42}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

[a] xx = total number of carbon atoms and y = number of double bonds.

The oil palm is one of the most rapidly growing equatorial crops in the World. Palm oil, unlike other oils, is composed mainly by palmitic acid. Palmitic acid (C16:0) is a saturated (no double bond) fatty acid and containing equivalent amounts of saturated and unsaturated fatty acids is shown in Table 2.2. Palm olein oil is one of the oil palm the most investigated since its availability and purification, ready to be used in any research plan (laboratory tests or large scale continuous research).[3]

Table 2.2 Compositions of fatty acid in palm olein oil.[9]

Fatty acid	Composition (wt %)
C12:0	0.4
C14:0	0.8
C16:0	37.4
C16:1	0.2
C18:0	3.6
C18:1	15.8
C18:2	11.1
C18:3	0.3
C20:0	0.3
C20:1	0.1

2.3 Derivatives from vegetable oil as biofuels

There are four methods which have been investigated to reduce the viscosity of vegetable oil; pyrolysis, dilution with conventional petroleum-derived diesel fuel, micro-emulsification and transesterifcation as shown in Table 2.3.

Table 2.3 An overview of methods in biofuels production.[2]

Methods	Definition	Advantage	Disadvantage
Pyrolysis or thermal cracking	Method of conversion of one substance into another by application of heat with the aid of the catalyst in the absence of air or oxygen.	1. Lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility. 2. The final products are similar to diesel fuel in composition.	Energy intensive
Micro-emulsions	A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles.	1. Fuel viscosity is lowered 2. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles.	Lower cetane number and energy content
Direct use and blending	Either use vegetable oil directly or is blended with diesel.	Liquid nature and portability. Heat content ~80% of diesel fuel readily available; renewability	1. Higher viscosity 2. Lower volatility 3. The reactivity of unsaturated hydrocarbon chains

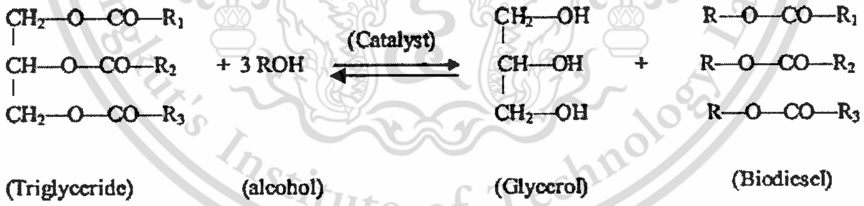
Table 2.3 An overview of methods in biofuels production [2] (Cont'd).

Methods	Definition	Advantage	Disadvantage
Transesterification	Transesterifcation (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol.	Renewability, higher cetane number, lower emissions, higher combustion efficiency.	Glycerol disposal and waste water problem.

Among all these methods, transesterifcation process has been widely used to reduce the high viscosity of triglycerides and produce biodiesel with higher cetane number.

2.4 Catalytic transesterification [2, 10, 11-14]

Transesterification is the process in which the vegetable oil is subjected to chemical reaction with alcohol in presence of a catalyst to form glycerol and ester. The simplified form of this chemical reaction is presented as following.



Where R_1, R_2, R_3 are the fatty acid chains.

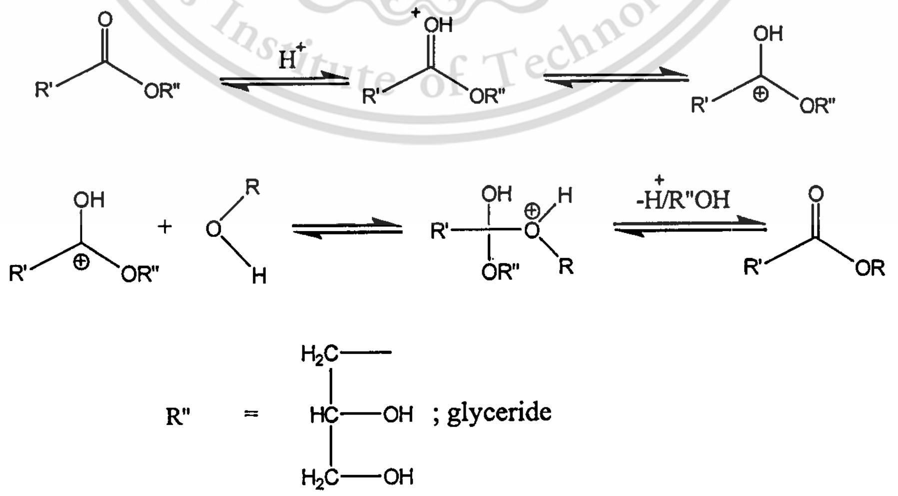
Transesterification is mainly affected by the methanol and oil molar ratio, used to drive the reaction towards forward direction to catalyst, depended on the amount of free fatty acid present in the vegetable oil/animal fat, reaction temperature and reaction time.

2.4.1 Acid-catalyzed transesterification [3, 13, 15-16]

During alcoholysis, the presence of high free fatty acids in the feedstock can easily react with an alkali catalyst producing soaps and water. Consequently, the downstream recovery and purification of the product becomes difficult. Therefore, acid catalyzed by Brønsted acids process is preferred. Generally, the problem can be circumvented by a tranesterification pretreatment of the free fatty acids to alkyl esters in the presence of an acid catalyst.[18]

However, heterogeneous acid catalyts cannot be reused because it is difficult to separate the fine powder catalyst from biodiesel by settlement and filtration. Not only it cannot be reused but also has other disadvantages such as equipment corrosion, more byproducts, tedious work up procedure and environmental problem. Moreover, acid catalyzed process requires relatively high amount of alcohol and high pressure (170–180 kPa), which necessitates an increasing in the size of the reactor, extensive conditioning, and purification steps to recover unreacted alcohol, as well as the catalyst, from the reaction products. All these drawbacks will be adding more cost to the production expense and affecting the biodiesel price.[3, 13, 16]

The mechanism of acid-catalyzed transesterification of vegetable oil for a monoglyceride is shown in Figure 2.2. However, it can be extended to di-and triglycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst.



R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Figure 2.2 Mechanism of the acid-catalyzed transesterification of triglycerides.[15]

2.4.2 Alkali-catalyzed transesterification [6, 10, 11-14]

For the existent biodiesel production process, the base-catalyzed transesterification is faster than the acid-catalyzed. Moreover, it should be noted that methanol is the alcohol appropriate to biodiesel production from an economical and available point of view. Additionally, methanol brings about the larger reaction rate than ethanol and propanol. Some technological problem resulting in costly production of biodiesel, these typical problems are the massive amount of the waste water which is due to the purification to wash the homogeneous catalyst off the crude biodiesel with water, and the emulsification of biodiesel occurs during the purifying operation which causes not only obstruction of the process operation but also loss of biodiesel. [6]

Even though homogeneous catalyzed biodiesel production processes are relatively faster and show high conversions, their utilization in vegetable oil transesterification results in soap formation which is an undesirable side-reaction. But they cannot be reused or regenerated, since the catalyst is consumed in the reaction which makes the separation of catalyst from products very difficult requiring more equipment resulting in higher production costs.

Biodiesel synthesis using heterogeneous catalyst could potentially lead to cheaper production costs by enabling reuse of the catalyst and opportunities to operate in a fixed bed continuous process. The use of heterogeneous catalytic system in the transesterification of triglyceride also implies the elimination of several washing steps. A variety of solid catalysts have been examined for the transesterification reaction.

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap as shown in Figure 2.3. The soap lowers the yield of esters and renders the separation of ester and glycerol and difficultly washed by water. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid catalyzed transesterification can be used.

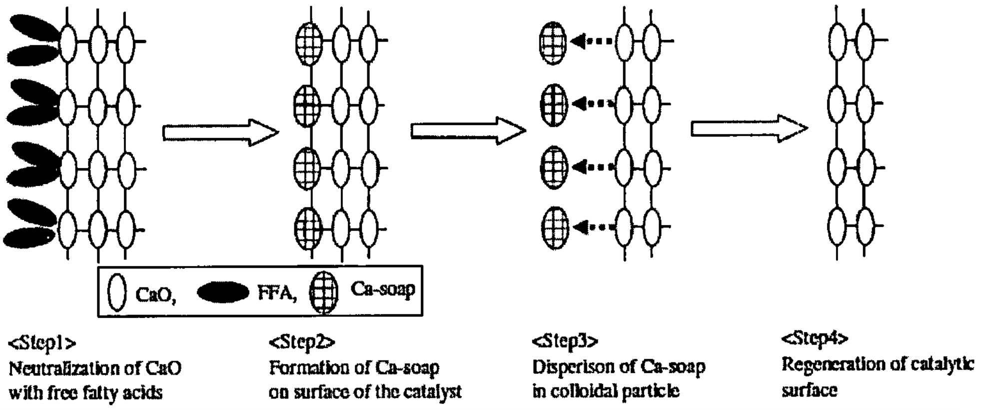
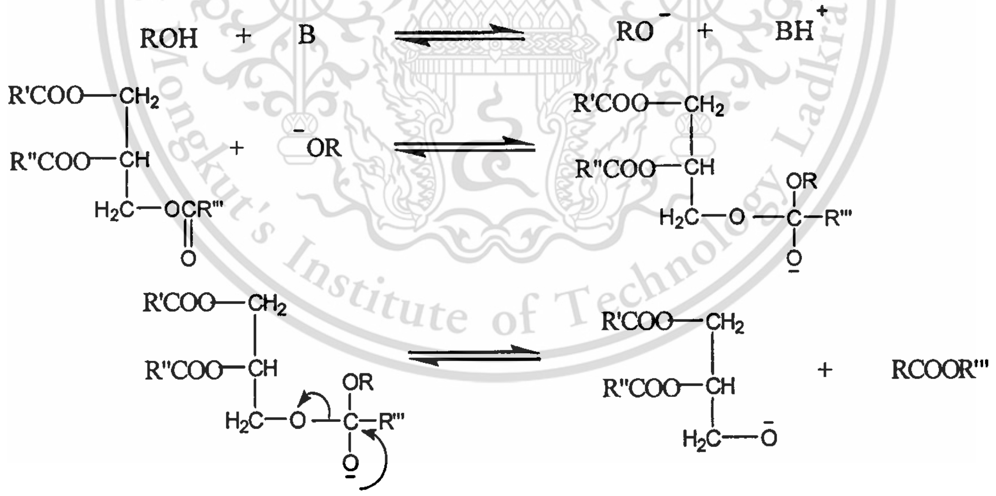


Figure 2.3 Mechanism on influence of free fatty acids on calcium oxide used as a catalyst for transesterification of palm oil.

The mechanism of alkali-catalyzed transesterification is described in Figure 2.4. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step, the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride.



R', R", R''' = carbon chain of the fatty acid R = alkyl group of the alcohol

Figure 2.4 Mechanism of the base-catalyzed transesterification of triglycerides.[15]

Among the different routes mentioned, the preferred method is the base-catalyzed (CaO) transesterifcation of vegetable oils with simple alcohol where one can achieve high purity and yield of biodiesel. The heterogeneous catalytic process overcomes the homogeneous one since the solid catalysts can be easily recovered and therefore potentially be reusable.

2.4.2.1 CaO as catalysts for tranesterification [15, 17]

The use of the waste matters is not only effective in enhancing the cost advantage of CaO catalyst but also related to recycle of the naturally mineral resources. In addition to the economical advantage, the superior catalytic performance of CaO is described in a number of researches reviewing utilization of solid base for the heterogeneous catalytic reaction to produce biodiesel. CaO catalyst was more active in transesterification of vegetable oil with methanol. [15]

A mechanism on the catalyzed transesterification using calcium oxide as the solid base is shown below. From no appreciable difference in the surface area among the employed calcium compounds, it was probable that the nucleophilic reaction was accelerated by an enhancement of the basic properties. [17]

Step 1: Dissociation of CaO and methanol while activation of the catalyst (Equation (2.1) and (2.2)).

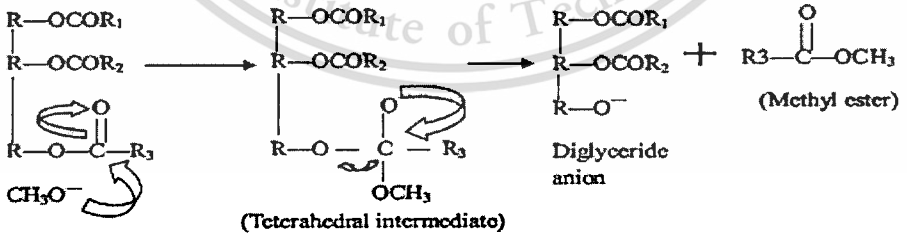
$$CaO \rightleftharpoons Ca^{2+} + O^{2-} \tag{2.1}$$

$$O^{2-} + CH_3OH \rightleftharpoons OH^- + CH_3O^- \tag{2.2}$$

Step 2: Methanol and hydroxide ion reacts to form methoxide anion (Equation (2.3)).

$$OH^- + CH_3OH \rightleftharpoons H_2O + CH_3O \tag{2.3}$$

Step 3: Carbonyl carbon of triglyceride is attacked by the methoxide anion formed in the previous reaction to form tetrahedral intermediate. This is followed by the rearrangement of the intermediate molecule to form methyl ester and diglyceride (Equation (2.4)).



(2.4)

Step 4: The methoxide anion attack on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. This continues till a total of three moles of methyl esters and a mole of glycerol is formed during the reaction.

2.5 Biodiesel [10]

Biodiesel as a cleaner renewable fuel has been considered as the best substitution for diesel fuel due to it being used in any compression ignition engine without any modification. The main advantages of using biodiesel are its renewability and better quality of exhaust gas emission.

Biodiesel fuel, fatty acid methyl ester (FAME), produced by the transesterification of vegetable oils and animal fats with methanol has the following characteristics: it is a biomass-derived fuel and is free from aromatic compounds, and it has high biodegradability and low SO_X and particulate matter content in diesel fumes.

2.5.1 Advantages of biodiesel [8, 18]

1 The main advantages of using biodiesel are its renewability and good quality of exhaust gas emission in conventional diesel engines. That results in substantial reduction of un-burnt hydrocarbons, carbon monoxide and particulate matter. Biodiesel is considered a clean fuel since it has almost no sulfur, no aromatics and has about 10 % built-in oxygen, which helps it to burn fully. Its higher cetane number improves the ignition quality even when blended in the petroleum diesel.

2 Biodiesel is safer to use than petroleum diesel. The flash point for biodiesel in its pure form is more than 149°C versus about 52°C for regular diesel.

3 Just like petroleum diesel, biodiesel can be used in conventional diesel engines. Essentially, no engines modification is required.

4 Biodiesel exhaust is less offensive, when compared with diesel oil, and does not require special storage. In fact, in its pure form or in blends, biodiesel can be stored wherever petroleum diesel is stored.

5 Neat biodiesel fuel is non-toxic and biodegradable.

6 Biodiesel provides significant lubricity improvement over petroleum diesel fuel.

2.5.2 Disadvantages of biodiesel [8]

1 The major problem associated with vegetable oil because of its high viscosity due to its large molecular weight and chemical structure .The viscosity of biodiesel is higher (1.9 to 6.0 cSt) and reported to result in gum formation on injector, cylinder liner, etc. if used in neat form. However, blending should not give any problem.

2 In general, biodiesel will soften and degrade certain types of elastomers and natural rubber compounds overtime. Using high percent, blending can impact fuel system components that contain elastomeric compounds incompatible with biodiesel.

3 Neat biodiesel will get faster than petro diesel in cold weather operation.

4 Biodiesel is more expensive to produce than petroleum diesel.

2.5.3 Performance of biodiesel

Although the major problem associated with vegetable oil because of its high viscosity but palm oil is one of the most economic viable feedstock for biodiesel production because it presents low viscosity, good combustion and little deposit when heated at 100 °C. However, the specific fuel consumption of palm oil in diesel engine is slightly higher than diesel fuel and provided smooth fuel flow but does not affect the injection system. The other properties of palm oil under steady state to compare with biodiesel standard testing materials (American standards ASTM D6751) are shown in Table 2.4.

Table 2.4 Summary of fuel properties of palm oil compared with the biodiesel standard testing materials.

Properties	**Unit**	**Palm biodiesel**	**ASTMD6751-06 standard**
Density at 15 °C	kg/m^3	879.3	860–900
Cetane number	–	52	47 min
Viscosity at 40 °C	mm^2/s	4.9	1.9–6.0
Flash point	°C	181	130 min
Cloud point	°C	15	3 to 12
Pour point	°C	14	15 to 10
Calorific value	kJ/kg	–	–
Distillation 90%	°C	335	360max
Water content	wt%	0.03	0.030max
Ash content	wt%	0.0066	0.020max
Carbon residue	wt%	0.07	–
Acid value	mgKOH/g	0.33	0.8max

The physicochemical and fuel properties of biodiesel are categorized into the same range of petroleum diesel. Thus, it can be applied to compression–ignition diesel engines with little or no modifications.

2.5.4. Biodiesel effect to engine

Biodiesel which has combustion characteristics similar to diesel and biodiesel blends has shorter ignition delay, higher ignition temperature and pressure as well as peak heat release compare to diesel fuel. Moreover, the engine power output and brake power efficiency was found to be equivalent to diesel fuel. Biodiesel and diesel blends can reduce smoke opacity, particulate matters, un-burnt hydrocarbons, carbon dioxide and carbon monoxide emissions but nitrous monoxide emissions have slightly increased. However, the main drawback of biodiesel fuel is their high viscosity and low volatility, which causes poor combustion in diesel engines including formation of deposits and injector cocking due to poorer atomization upon injection into the combustion chamber. The summary of research findings related to emissions from palm oil is shown in Table 2.5.

Table 2.5 The summary of research findings related to emissions from palm biodiesel [7]

Emissions	**Palm oil (Processing)**
CO_2 increase	-
CO_2 decrease	-
NO_x increase	Preheated
NO_x decrease	NPAA additive Corrosion inhibitor additive
HC/CO increase	NPAA additive Preheated
HC/CO decrease	-
Smoke opacity increase	-
Smoke opacity decrease	-

2.6 Egg shell [1, 2]

The chemical composition (by weight) of eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%). Reuse of eggshell as low-cost catalyst for biodiesel production was investigated in the viewpoint of the recycle of eggshell waste, minimization of contaminants, reducing the production costs of biodiesel and making the process to produce biodiesel fully ecologically friendly. Due to its intrinsic pore structure in the calcified eggshell, when calcined at a proper temperature, calcium carbonate converts into CaO. Researchers have found that the CaO prepared from the waste shells can be used as catalyst in biodiesel production process.

2.7 Ionic liquids catalysts [3, 18, 19, 20]

The ionic liquid (ILs) have been accepted as a new green chemical revolution which has attracted much attention for synthetic and catalytic application because of their important attributes such as wide liquid range, negligible vapor pressure, high catalytic activity, excellent chemical and thermal stabilities, potential recoverability, design possibilities, and ease of separation of the products from reactants. This new chemical group can reduce the use of hazardous and pollution organic solvents due to their unique characteristics as well as taking part in various new syntheses.

In recent years, room-temperature ionic liquids (ILs), up to now investigated can be broadly divided into two types:

1 Chlorometallate anions such as $Al_2Cl_7^-$

2 The others on non-metal-containing anions such as PF_6^-

Preparing composite catalyst from alkali or acidic IL and other alkalis (sodium hydroxide, etc.) or acid (concentrated sulfuric acid, etc.) to catalyze soybean oil to biodiesel, catalyzed biodiesel from cottonseed with BrØnsted acidic ILs, these ILs above-mentioned were mostly belonged to imidazole and pyridines ILs. However, the cost of imidazolium ILs is relatively high for bulk application, whilst chloroaluminate ILs should be used under anhydrous and oxygen-free condition due to their low tolerance to moisture.

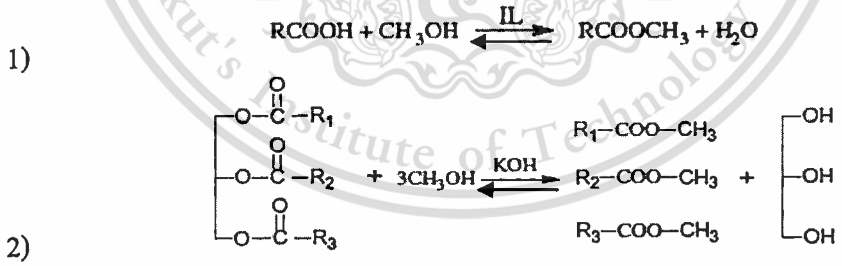
ILs are known as salts that are liquid at or below 100°C in contrast to high-temperature molten salts. As solvent, their ability to dissolve many different organic, inorganic, and organometallic materials and their high polarity. They are immiscible with many organic solvent;

moreover, the salvation properties of ILs can be tuned for a specific application by varying the anion-cation combinations.

From researches reviewing, using of ionic liquid as catalysts or solvents for the esterification of fatty acids or tranesterification of vegetable oils and animal fats, as well as other chemical reactions, has increased significantly in recent years. Indeed, ionic liquids, especially those not only functionalized with Lewis and BrØnsted acid sites, that has found numerous application has been applied to the synthesis of biodiesel from vegetable oil, resolved the effect of the saturation degree of the oil and the alkyl chain of the alcohols on the catalytic activity of these ionic liquids in the tranesterification reaction.[3]

The alkaline catalysts exhibit higher catalytic performances than the acid catalysts in the preparation of biodiesel; alkaline ionic liquids were also reported as catalysts for the preparation of biodiesel. The research reviewing was supported to be a novel and green catalysts in the synthesis of biodiesel.

The alkaline catalysts preferably uses in the preparation of biodiesel by a two-step catalytic process is shown which has been applied to produce biodiesel from crude palm oil (CPO). Firstly, the FFA in the CPO was esterified with methanol in the presence of IL ($BMIMHSO_4$). At the second step, potassium hydroxide (alkaline catalysts) was introduced to catalyze the transesterification of the triglycerides in the CPO with methanol.



$$RCOOH + CH_3OH \xrightleftharpoons{IL} RCOOCH_3 + H_2O$$

Figure 2.5 Mechanism of biodiesel preparation via two-step catalyzed process.[3]

The objective of IL-catalyzed esterification of CPO was to reduce the acid value or FFA contents of vegetable oil. Increasing the side chains has a great effect in the ILs nature and it may rule their acidity or basicity, effecting the FFA conversion.[3]

The reaction mechanism of the catalyzed transesterification of soybean oil using $ZnCl_2$ ionic liquid as Lewis-acidic ionic is shown in Figure 2.6. FT-IR investigation demonstrated that Lewis acid strength of ILs increased with the increase of ionic liquid, which was in agreement with the activities observed in the preparation of biodiesel. $Zn_2Cl_5^-$ is the predominant species in IL so that the transesterification is mainly catalyzed by $Zn_2Cl_5^-$. Therefore, the main method increasing the conversion is to improve the acidity of catalyst. Choline chloride·$2ZnCl_2$ exists in methanol phase with glycerol. Glycerol was separated from ILs by vacuum distillation. However, the high boiling point and high viscosity of glycerol make the separation between ILs and glycerol difficult. Furthermore, the requirement for equipment is high in vacuum distillation, which has not been realized in industry. Therefore, the separation between glycerol and ILs may become the bottleneck problem. Thus, the ILs immobilized on some solid materials such as resin to catalyze transesterification to biodiesel or purification of ILs by solvent extraction is proposed and further studied.

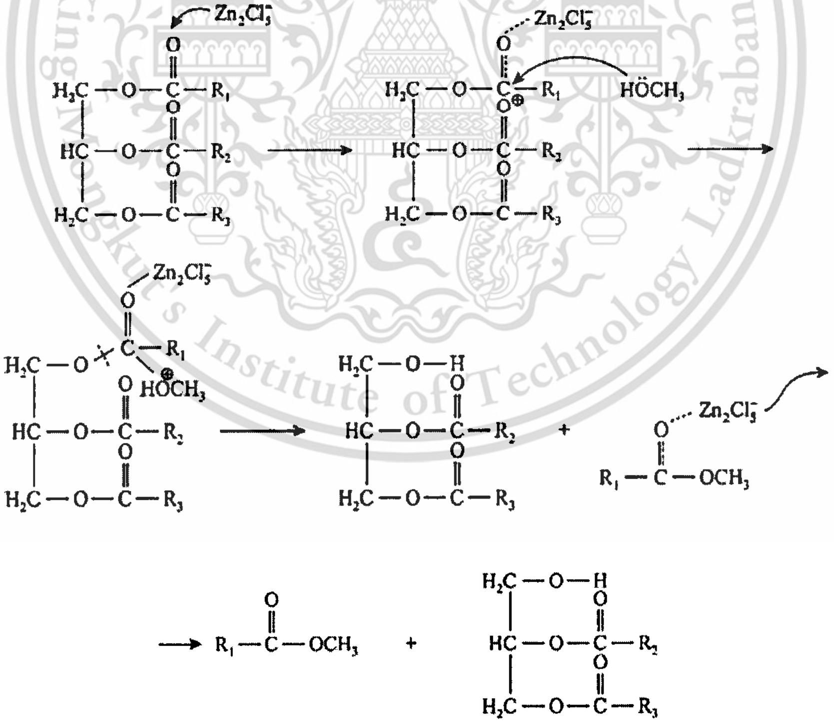


Figure 2.6 Mechanism of biodiesel preparation using $ZnCl_2$ ionic liquid as catalyst[23]

2.8 Literature reviews

In 2011, Y.A. Elsheikh, Zakaria Man, M.A. Bustam and Suzana Yusup studied the preparation of biodiesel via a two-step transesterification process. The high free fatty acids (FFA) value contained in the crude palm oil (CPO), which cause several problems with the straight alkaline-catalyzed, were converted to fatty acid methyl esters (FAME) before introducing KOH-catalyzed transesterification step. In order to evaluate their catalytic activities, three BrØnsted acidic imidazoliums were investigated. These ionic liquids (ILs) appeared to be promising candidates to replace conventional acidic catalyst for biodiesel production due to their unique properties. Among them, a longer side chains 1-butyl-3-methyl-imidazolium hydrogen sulfate ($BMIMHSO_4$) was found to be more superior to the other two catalysts. Based on the experimental results, a catalyst (BIMHSO4) concentration of 4.5 wt.%, methanol/CPO molar ratio of 12:1, a temperature of 160°C, and agitation speed of 600 rpm provided a final CPO acid value lower than 1.0 mg KOH/CPO within 120 min. The second alkalicatalyze step was performed at agitation speed of 600 rpm, 60°C, 1.0% KOH for 50 min. The final biodiesel product in 98.4% yield was analyzed by gas chromatography (GC). The determined physicochemical important properties of POME were confirmed with American Standards for Testing Material (ASTM).[3]

In 2012, Jutika Boro, Dhanapati Deka, Ashim J. Thakur reported that the CaO prepared from the waste shells can be used as catalyst in biodiesel production process. Utilization of waste shells as a source of CaO not only gives an opportunity to use it as catalyst but also adds value to the waste generated. A brief discussion with recent development on biodiesel production using waste shell derived solid oxide as catalyst was presented.[2]

In 2011, Masato Kouzu and Jyu-suke Hidaka studied CaO catalyst for the vegetable oil transesterification. After catalytic properties of the basic sites generated on CaO were described preliminarily, a mechanism on the vegetable oil transesterification catalyzed by CaO was explained. Then, procedure to prepare the active CaO catalyst, its deactivation occurring under the reacting condition and modification of CaO catalyst were discussed. Finally, the practical use of CaO catalyst for industrial biodiesel production was studied with pointing out the required future work.[15]

In 2011, Chawalit Ngamcharussrivichai, Pramwit Nunthasanti, Sithikorn Tanachai and Kunchana Bunyakiat studied transesterification of palm kernel oil (PKO) with methanol over various natural calciums, including limestone calcite, cuttlebone, dolomite, hydroxyapatite, and dicalcium phosphate at 60°C and 1 atm. The study showed that dolomite, mainly consisting of $CaCO_3$ and $MgCO_3$, was the most active catalyst. The calcination temperature largely affected the physicochemical properties, as evidenced by N_2 adsorption–desorption measurement, TGA, SEM and XRD, and the transesterification performance of the resultant catalysts. It was found that the calcination of dolomite at 800°C resulted in a highly active mixed oxide. CaO was suggested to be the catalytically active site responsible for the methyl ester formation. Under the suitable reaction conditions, the amount of dolomite calcined at 800°C=6 wt.% based on the weight of oil, the methanol/oil molar ratio=30, and the reaction time=3 h, the methyl ester content of 98.0% can be achieved. The calcined dolomite can be reused many times. The analyses of some important fuel properties indicated that the biodiesel produced had the properties that meet the standard of biodiesel and diesel fuel issued by the Department of Energy Business, Ministry of Energy, Thailand.[6]

In 2009, Ziku Wei, Chunli Xu and Baoxin Li studied the effect of calcination temperature on structure and activity of eggshell catalysts. Reusability of eggshell catalysts was also examined. It was found that high active, reusable solid catalyst was obtained by just calcining eggshell. Utilization of eggshell as a catalyst for biodiesel production not only provides a cost-effective and environmental friendly way of recycling this solid eggshell waste, significantly reducing its environmental effects, but also reduces the price of biodiesel to make biodiesel competitive with petroleum diesels.[1]

Chapter 3

Experimental details

3.1 Chemicals

1. Refined palm oil olein cooking oil (OLEEN Company)
2. Methanol; analytical reagent from Carlo Erba Company
3. Distilled Water
4. Paraffin oil
5. Sodium sulfate anhydrous; analytical reagent from Rankem company
6. 1-ethyl-3 methylimidazolium chloride; analytical reagent from Acros organics company
7. Calcium oxide analytical reagent from Unilab company
8. Egg shell

3.2 Apparatus and instruments

1. X-ray diffraction XRD type D8 advance, SIEMENS
2. Scanning electron microscope SEM type Leo 1450 VP, LEO
3. Nuclear Magnetic Resonance Spectrometer NMR Avance DPX 300, BRUKER
4. Autosorb-1b, Quantachrome
5. Hotplate/Stirrer
6. Water bath
7. Laboratory glasswares
8. Thermometer
9. Spatula
10. Clamp and clamp holder
11. Oven
12. Furnace
13. Bunsen burner
14. Tripod
15. Porcelain crucible
16. Wire gauze

17. Filter paper
18. Universal indicator paper
19. Blender
20. Aluminium foil
21. Centrifuge
22. Desiccator
23. Sieve and sieve shakers

3.3 Experimental procedures

3.3.1 Preparation and characterization of calcium oxide catalysts

3.3.1.1 Pretreatment of commercial calcium oxide

Commercial calcium oxide catalyst was calcined in air at 700°C for 5 hours. To determine the structure, surface area, basicity and basic strength, and morphology, the catalyst was subjected to X-ray Diffractometer (XRD), Gas Adsorption Analyzer (Autosorb-1b), and Scanning Electron Microscope (SEM), respectively. It was kept in a desiccator until used.

3.3.1.2 Preparation of calcium oxide from egg shell

1. Raw egg shells were washed with tap water, and then dried in the oven at 105°C for 48 hours.

2. Afterwards, they were crushed into powder using the blender and was sieved (MESH NO. 100) for 1 hour to collect the particle size smaller than 0.150 mm.

3. The egg shell powder was calcined in air at 800°C for more than 8 hours, characterized by the same method as commercial calcium oxide and then kept in a desiccator until used.

3.3.1.3 Characterization of calcium oxide catalysts

1. Determination of the structure using X-ray Powder Diffractometer (XRD).

The structure of calcium oxide was determined by X-ray powder diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre; KMITL). The sample was prepared by packing calcium oxide in the sample holder. CuK_{α} X-ray beam was used for analysis at 40 kV, 40 mA. The sample was scanned from 2θ angle 10° to 80° with 1 second/step time and 0.04 2θ/step increment. X-ray diffraction pattern of the sample was compared with the pattern of standard calcium oxide for structure determination.

2. Determination of the surface area using Gas Adsorption Analyzer (Autosorb-1b).

The surface area (S_{BET}) of calcium oxide was determined by nitrogen adsorption with Gas Adsorption Analyzer (Autosorb-1b, Quantachrome). The sample was prepared by weighing approximately 20 mg of calcium oxide sample into the cleaned and dried sample cell. The sample cell was attached to the out gassing station. The temperature was raised to 350°C under vacuum. The sample was out-gassed for 24 hours. The sample cell was then removed from the out gassing station. After that, nitrogen gas was filled and was attached to the analysis station. The equilibration time was set to 3 minutes and the gas adsorption was measured at the partial pressure (P/P_0) ranged from 10^{-6} to 1.0 at 77.4 K.

3. Determination of the morphology using Scanning Electron Microscope (SEM).

The analysis was performed at 2θ angle ranging from 20° to 80° at a scanning speed of 1° min^{-1}. The surface morphology of the developed catalyst was determined using scanning electron microscope (SEM) at 15 kV. The prepared sample was placed on stub and coated with gold before analyzed.

3.3.2 Synthesis of methyl ester

The transesterification reactions were carried out at 65°C for 60 minutes using the ratio of palm oil to methanol of 1:6 and 1:9, 1 to 3 %wt of calcium oxide by weight of palm oil, and 0.074, 0.148, 0.296, 0.444 %wt of 1-Ethyl-3-methylimidazolium chloride. The catalysts were separated from the mixture after the reaction. The ^1H-NMR spectrum of a complete reaction is illustrated in Figure 3.1

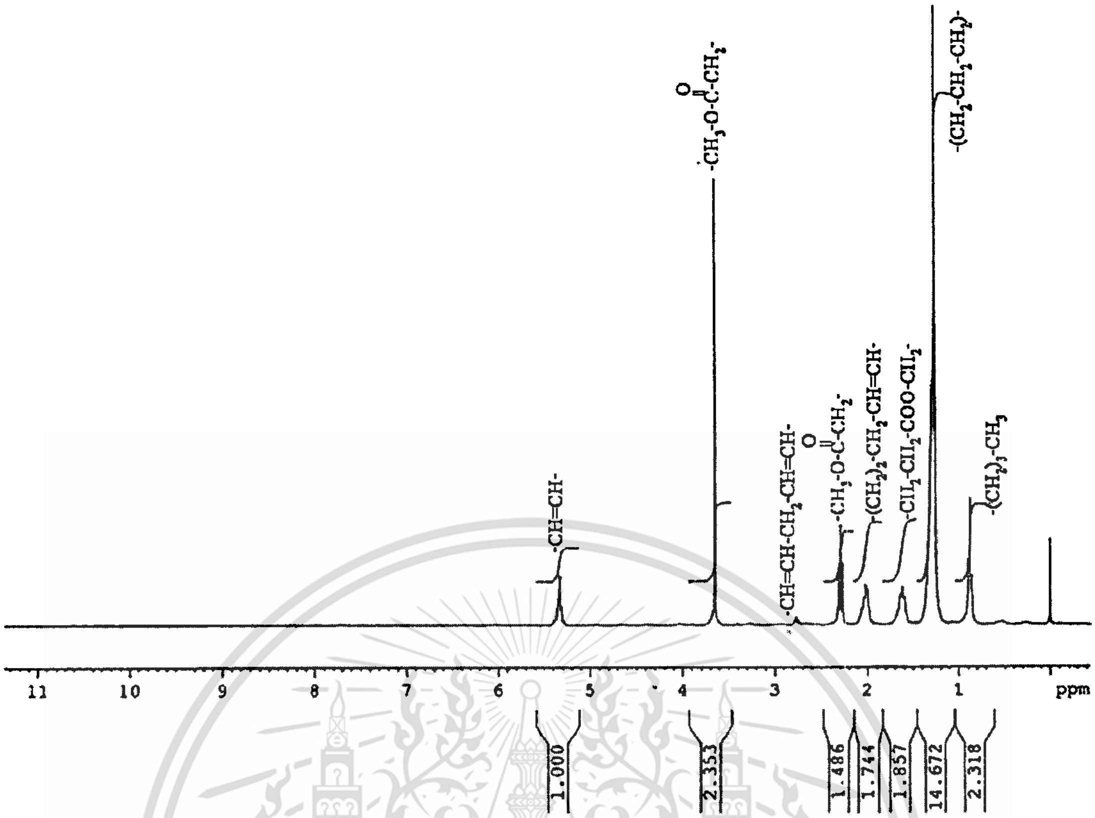


Figure 3.1 ^{1}H-NMR spectrum (CDCl$_3$) of a complete reaction between palm oil and methanol.

From Figure 3.1, ^{1}H-NMR spectrum of a complete reaction between palm oil and methanol shows the signals of methyl protons (CH$_3$-C-) and methylene protons (-C-CH$_2$-C-) at δ 0.88 and 1.3 ppm, respectively. The signal of –CH$_2$-C-COO-C- appears at δ 1.61 ppm. The signal of –CH$_2$-C=C- appears at δ 2.05 ppm. The signal of α-CH$_2$-appears at δ 2.3 ppm. The signal of –C=C-CH$_2$-C=C- appears at δ 2.76 ppm. The signal of –OCH$_3$ appears at δ 3.7 ppm. The signal of CH=CH- appears at δ 5.35 ppm. The yields of methyl ester were calculated from the peak area of NMR spectra by the equation show below.

Example

$$\text{Yield (\%)} = \frac{2\times\text{Area under peak of }-\text{OCH}_3\text{ at }\delta\text{ 3.7 ppm}}{3\times\text{Area under peak of }\alpha-\text{CH}_2\text{at }\delta\text{ 2.3 ppm}} \times 100$$

3.3.2.1 Synthesis of methyl ester using commercial calcium oxide

1. Palm oil (44.61 g, 50 ml) and methanol (19.6 ml, palm oil: methanol of 1:9) were measured by using a graduated cylinder. Palm oil was then poured into a round bottom flask.

2. 0.446g (1.0 %wt) of commercial calcium oxide was added to methanol.

3. Afterwards, the mixture of commercial calcium oxide and methanol was added into palm oil and was stirred with hotplate stirrer.

4. The mixture was refluxed at 65 °C with 340 rpm stirring for 60 min.

5. After cooled down at room temperature, the mixture was centrifuged at 3400 rpm for 15 minutes for glycerol separation.

6. The mixture was poured into a separation funnel. Biodiesel phase was collected and glycerol phase was drained out.

7. Biodiesel was washed with 0.5 ml of 0.1 HCl twice followed by 50 ml of distilled water for 5 times. The remaining distilled water in biodiesel phase was removed with anhydrous Na_2SO_4.

8. The sample of biodiesel product was collected in a vial and characterized by using NMR spectroscopy

9. Step 1 to 8 were repeated by changing the amount of calcium oxide catalyst from 1to 2 and 3 % wt of palm oil, and oil to methanol ratio from 1:9 to 1:6.

3.3.2.2 Synthesis of methyl ester using commercial calcium oxide with ionic liquid

Using the same procedure described in section 3.3.2.1, the experiments were repeated by adding 1-ethyl-3 methylimidazolium chloride to methanol in Step 2 from 0.074 to 0.148, 0.296 and 0.444 %wt by weight of palm oil together with commercial calcium oxide.

3.3.2.3 Synthesis of methyl ester using calcium oxide from egg shell with ionic liquid

The best condition from the previous reactions was chosen. It was repeated by changing the commercial calcium oxide to calcium oxide from calcined egg shell to compare the yield of methyl ester.

Chapter 4

Results and Discussion

This special project is the study of methyl ester synthesis from palm oil and methanol by using calcium oxide catalysts and 1-Ethyl-3-methylimidazolium chloride as co-catalyst. The results and discussion is categorized into 3 parts. The first part is the characterization of palm oil. On the second part, the catalysts are studied for structure, compositions and surface area. The third part is the methyl ester synthesis and studies on the parameters which affect the yield of methyl ester in transesterification. These are the amount of calcium oxide, amount of 1-Ethyl-3-methylimidazolium chloride, ratio of palm oil to methanol, and time. The comparison between the use of commercial calcium oxide and the one from egg shell is also discussed.

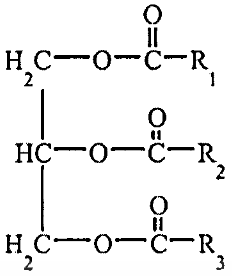
4.1 Characterization of palm oil

The vegetable oil used in this study was palm oil. Its composition was confirmed by analyzing the fatty acid compositions of the oil using gas chromatography–mass spectrometer.[22] As shown in Table 4.1, the major fatty acid components of palm oil are myristic, palmitic, stearic, oleic and linoleic acid. Based on these compositions, the average molecular weight of palm oil used in this study is 854 g/mol.

Table 4.1 Fatty acid compositions of palm oil[22]

Fatty acid	Formular	Percent in refined palm oil (%)
Myristic acid	$C_{14}H_{28}O_2$	1.07
Palmitic acid	$C_{16}H_{32}O_2$	35.32
Stearic acid	$C_{18}H_{36}O_2$	5.30
Oleic acid	$C_{18}H_{34}O_2$	46.30
Linoleic acid	$C_{18}H_{32}O_2$	12.01
	Total	100

Palm oil has a general structure shown in Figure 4.1. It was characterized using Nuclear Magnetic Resonance Spectrometer (NMR).



R_1 R_2 and R_3 = CH_3-$(CH_2)_{12}$-(myristic acid), CH_3-$(CH_2)_{14}$- (palmitic acid), CH_3-$(CH_2)_{16}$- (stearic acid), CH_3-$(CH_2)_7$-CH=CH-$(CH_2)_7$- (oleic acid), and CH_3-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$- (linoleic acid)

Figure 4.1 The general structure of palm oil

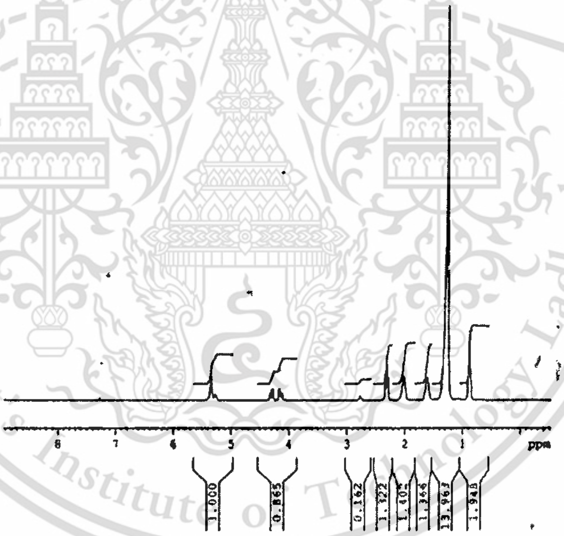


Figure 4.2 ^{1}H-NMR spectrum of palm oil

^{1}H-NMR spectrum of palm oil (Figure 4.2) shows the signals of methyl protons (CH_3-C-) and methylene protons (-C-CH_2-C-) at δ 0.85-0.88 and 1.25-1.30 ppm, respectively. The signal of -CH_2-C-COO-C- appears at δ1.61 ppm. The signal of -CH_2-C=C- appears at δ2.01-2.05 ppm. The signal of -CH_2-COO-C- appears at δ 2.28-2.33 ppm. The signal of -C=C-CH_2-C=C- appears at δ 2.74-2.76 ppm. The signal of -CH_2-OOC-R- and -CH-OOC-R appear at δ 4.11-4.17 and 4.27-4.32 ppm, respectively. The signal of -CH=CH- appears at δ 5.26-5.35 ppm.

4.2 Characterization of calcium oxide catalysts.

4.2.1 X-ray Powder Diffractometer (XRD).

Two types of catalysts were used in this special project, commercial calcium oxide and calcium oxide from calcined egg shell. Both types of catalysts were characterized by X-ray diffractometry (XRD) as shown in Figure 4.3 and 4.5.

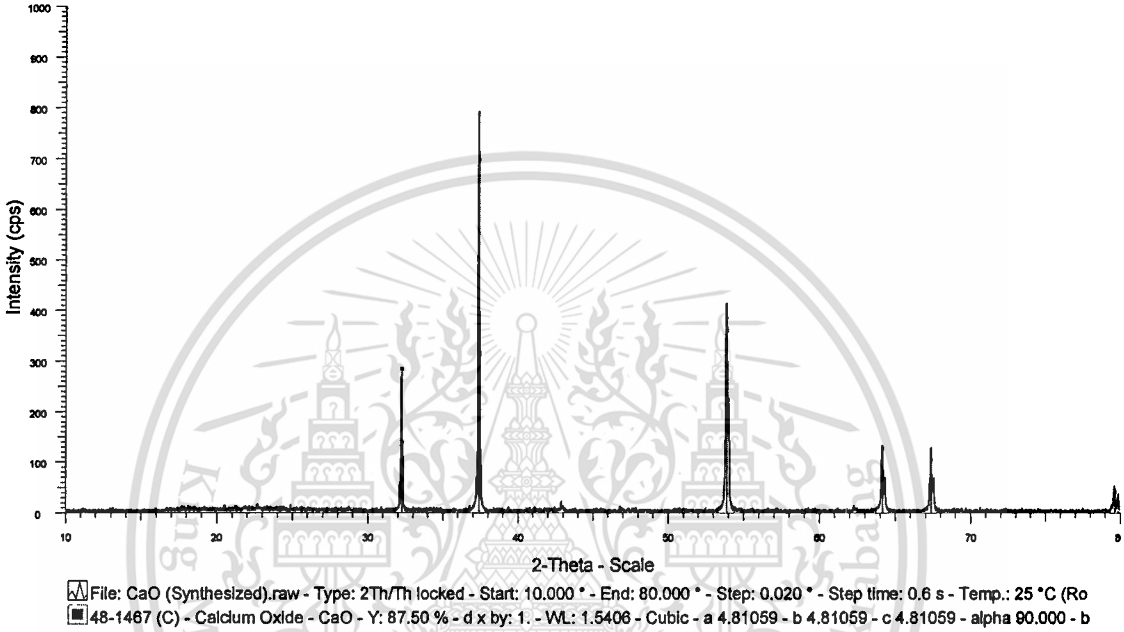


Figure 4.3 XRD pattern of commercial calcium oxide calcined at 700 °C for 5 hour

From Figure 4.3, the commercial calcium oxide catalyst calcined at 700 °C for 5 hour shows the signals at 2θ angle = 32.2°, 37.4°, 53.8°, 64.2°, 67.4°, and 79.5°. Those are corresponding to the pattern of highly crystalline calcium oxide.

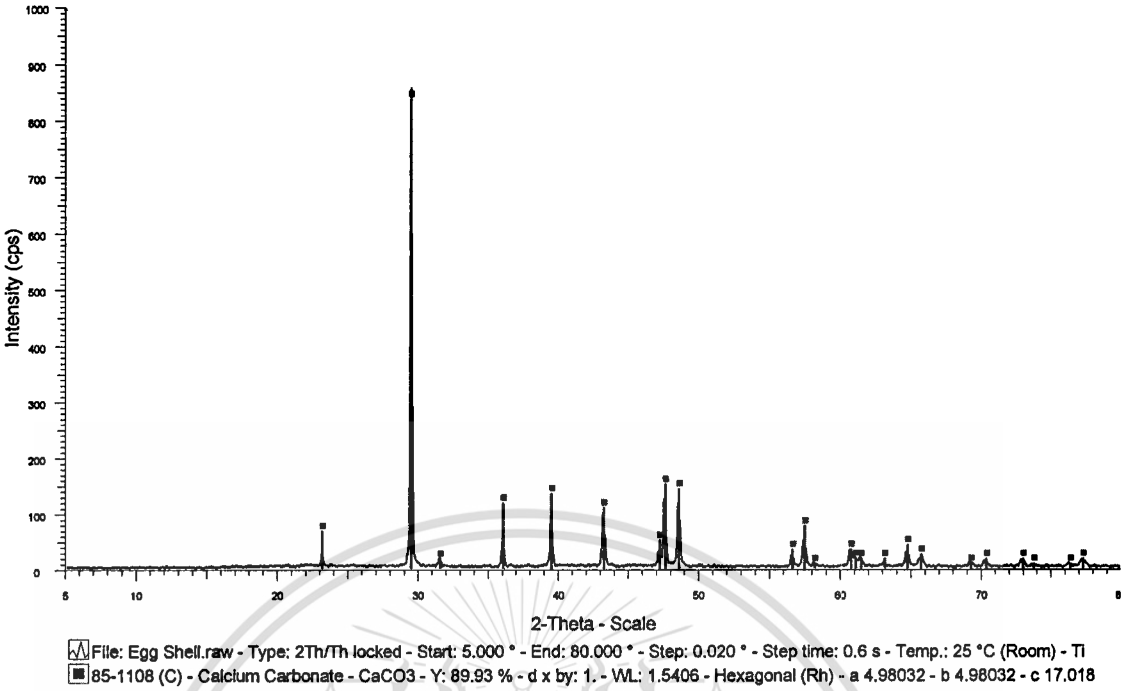


Figure 4.4 XRD pattern of egg shell before calcinations

From Figure 4.4 the egg shell before calcination shows the signals at 2θ angle = 23.2°, 29.5°, 31.5°, 36.0°, 39.5° 43.2°, 47.2°, 47.8°, 48.5°, 56.5°, 57.5°, 58.2°, 60.7°, 61.0°, 61.5°, 63.2°, 64.9°, 65.7°, 69.2°, 71.4°, 73.0°, 73.8°, 76.3°, and 77.2°. Those are corresponding to the pattern of highly crystalline calcium carbonate.

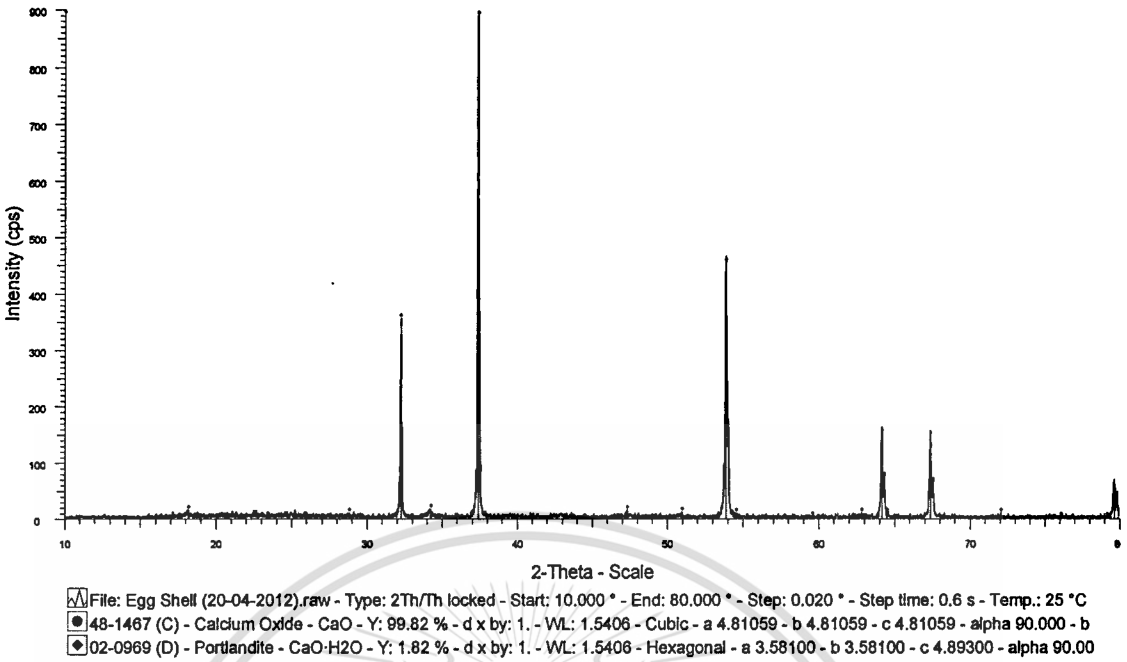


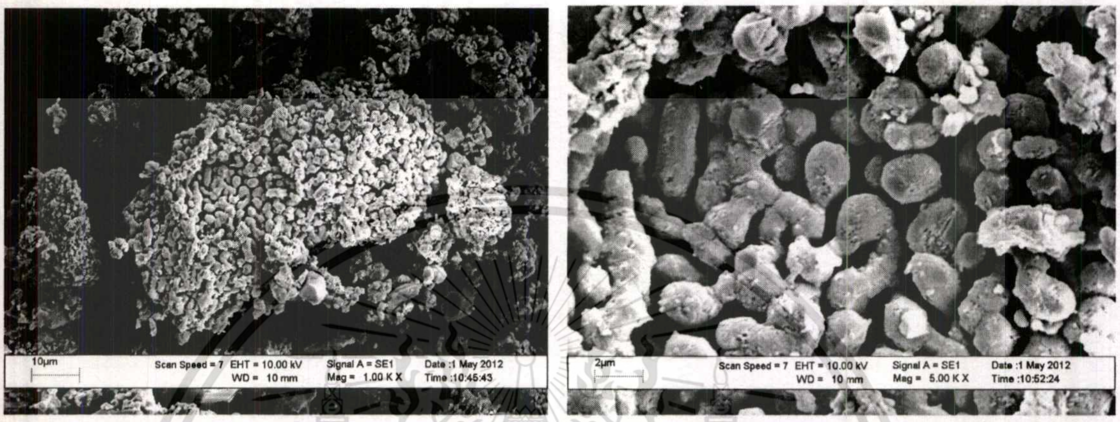
Figure 4.5 XRD pattern of calcium oxide from egg shell calcined at 800°C for more than 8 hours.

From Figure 4.5, the egg shell calcined in air at 800°C for more than 8 hours shows the signals at 2θ angle = 32.2°, 37.4°, 53.8°, 64.2°, 67.4, and 79.5°. Those are corresponding to the pattern of highly crystalline calcium oxide.

From Figure 4.3-4.5, the main component in egg shell is calcium carbonate. After it was calcined in air at 800°C for more than 8 hours, calcium carbonate was completely changed into calcium oxide with a very small amount of calcium hydroxide remaining. The signals at 2θ angle = 18.1°, 28.7°, 34.1°, 47.2°,50.9°, 59.5°, 62.7°, 64.1°, and 71.8° are agreed with the pattern of highly crystalline calcium hydroxide.

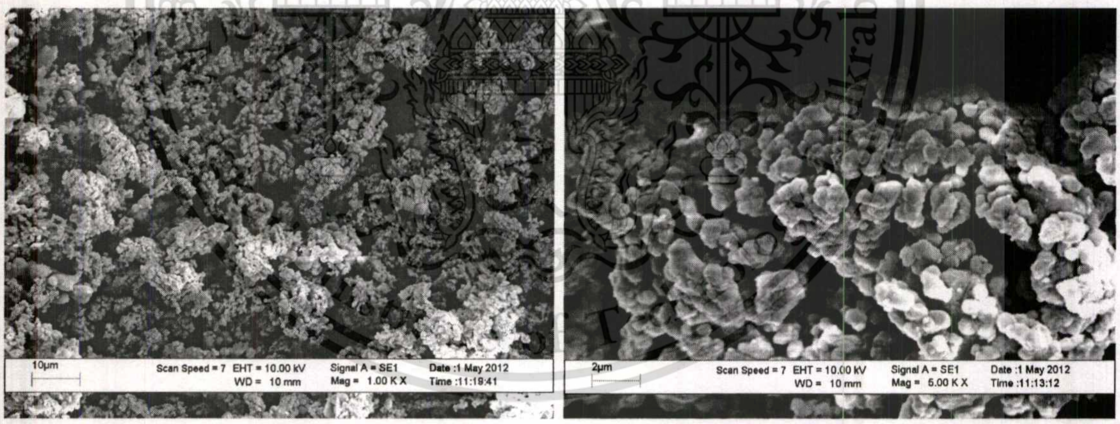
4.2.2 Scanning Electron Microscope (SEM)

The morphology of catalysts was studied by using scanning electron microscope (SEM) with (a) 1,000 times magnification and (b) 5,000 times magnification. Figure 4.6 shows the morphology of commercial calcium oxide calcined at 700°C for 5 hours, and Figure 4.7 shows the morphology of egg shell calcined in air at 800°C for more than 8 hours.



(a) Magnification 1,000 times **(b)** Magnification 5,000 times

Figure 4.6 The morphology of commercial calcium oxide calcined at 700°C for 5 hours



(a) Magnification 1,000 times **(b)** Magnification 5,000 times

Figure 4.7 The morphology of egg shell calcined in air at 800°C for more than 8 hours

From Figure 4.6 and 4.7, it was found that the both types of calcium oxide have similar morphology. Furthermore, it can also be noticed that calcium oxide from the calcined egg shell has smaller particle size (1.04µm) than commercial calcium oxide (2.11µm). This will lead to higher surface area and probably higher basicity, hence higher yield of methyl ester from transesterification reaction.

4.2.3 Gas Adsorption

Surface area of calcium oxides was determined by Gas Adsorption Analyzer (Autosorb-1C, Quantachrome). The nitrogen adsorption was measured at the partial pressure (P/P0) ranged from 10^{-4} to 1.0 at 77.4 K. The BET analysis of commercial calcium oxide calcined at 700°C for 5 hours and egg shell calcined in air at 800°C for more than 8 hours are shown in Table 4.2.

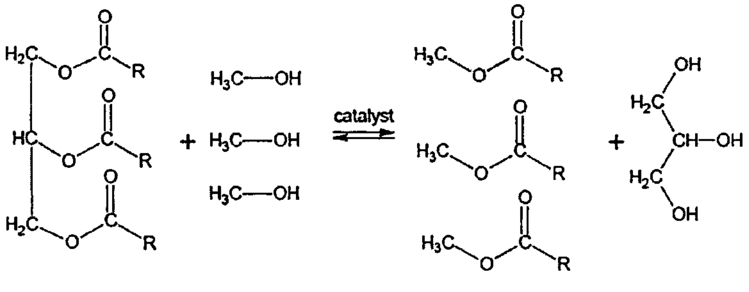
Table 4.2 The specific surface area of calcium catalysts

Catalyst	Specific surface area (m^2/g)	Pore Volume (cc/g)	Pore Size (A°)
Commercial calcium oxide	16.88	3.633×10^{-2}	37.91
Calcium oxide from egg shell	21.56	5.015×10^{-2}	37.73

After the catalysts were characterized by gas adsorption analyzer for determining the surface area, it was found that the calcined egg shell has indeed higher surface area than commercial calcium oxide. This surface area result is a match with the morphology.

4.3 Effect of parameters on transesterification

The transesterification reaction of palm oil was carried out under various conditions. Alkali earth metal oxide catalysts; namely calcium oxide, was used. The variables affecting the methyl ester yield during the transesterification, such as amount of calcium oxide catalysts, amount of 1-Ethyl-3-methylimidazolium chloride, the molar ratio of methanol to palm oil, and reaction time were investigated. The results were also compared with the reaction using calcium oxide catalyst from calcined egg shell.



Triglycerides + Methanol **Methyl Ester + Glycerol** **(4.1)**

The biodiesel production by transesterification reaction is expressed in Equation (4.1). By the transesterification in heterogeneous process, the palm oil or triglyceride is mixed with methanol and catalyzed by calcium oxide and 1-Ethyl-3-methylimidazolium chloride in this case. Such triglyceride is reacted to be di- and mono-glyceride, subsequently (Figure 4.8), while product methyl ester is produced in every part during the conversion as well. The biodiesel and glycerol were the final products when the reaction is completed. From the mechanism in the transesterification, calcium methoxide species, Ca $(CH_3O)_2$, was reported to form on the surface of calcium oxide catalyst for increase the reaction between palm oil and methanol.

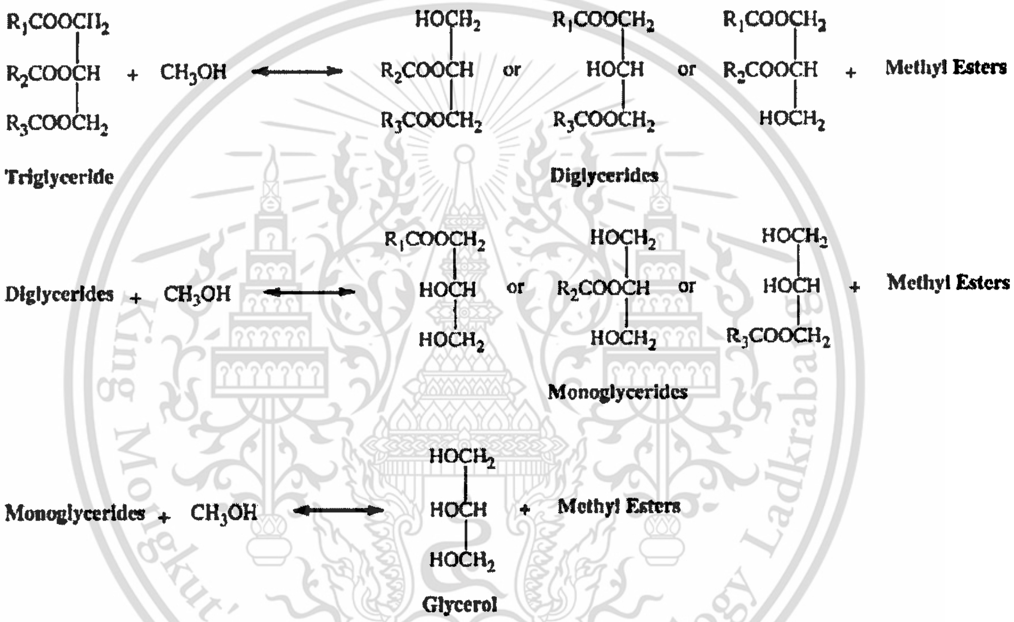


Figure 4.8 Transesterification of representative triglyceride to methyl esters and diglycerides, monoglycerides and glycerol, respectively.[6]

4.3.1 Effect of the amount of commercial calcium oxide.

In this special project, the amount of commercial calcium oxide catalyst was varied from 1.0 to 2.0 and 3.0%wt, respectively. The effects of the amount of catalyst on yield are shown in Table 4.3 and Figure 4.9. The reaction condition was fixed at 65 °C, 1:9 mole ratio of palm oil to methanol, and 60 minutes of reaction.

Table 4.3 Effect of the amount of commercial calcium oxide on percent yield of methyl ester

Percent of calcium oxide (%wt)	Ratio of palm oil to methanol	Percent of [EMIM] Cl (%wt)	Reaction time (min)	Percent yield of methyl ester
1.0	1:9	-	60	6.033
2.0	1:9	-	60	5.186
3.0	1:9	-	60	100.000

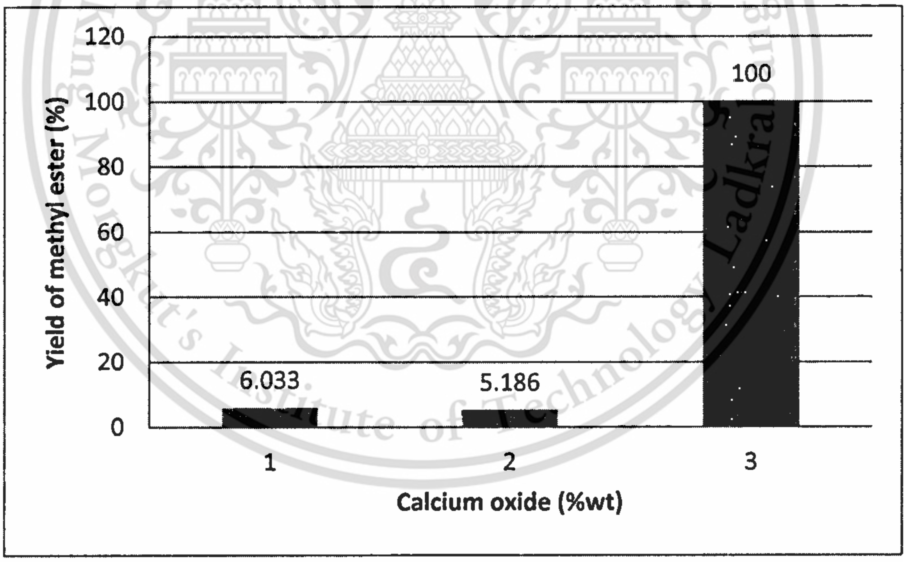


Figure 4.9 Effect of the amount of commercial calcium oxide on percent yield of methyl ester.

Figure 4.9 shows the relationship between the amount of commercial calcium oxide and the percent yield of methyl ester. It can be assure that calcium oxide can evidently accelerate the methyl ester yield even if a small amount was added. The transesterification rate was largely improved as the amount of catalysts increased from 1.0 to 3.0%wt. When the amount of catalysts increased to 3.0% wt, the yield of 100% was reached. Then, 1.0 and 2.0%wt of calcium oxide were used with 1-Ethyl-3-methylimidazolium chloride to study the yield of methyl ester via milder conditions.

Concerning the transesterification of palm oil with methanol using solid base catalyst, the abstraction of proton from methanol by the basic sites to form methoxide anion is the first step of the reaction. The methoxide anion attacks carbonyl carbon in a molecule of triglyceride, which leads to the formation of alkoxycarbonyl intermediate. Then, the alkoxycarbonyl intermediate divides into two molecules: methyl ester and anion of diglyceride. The methoxide anion attacks on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. This continues till a total of three moles of methyl esters and a mole of glycerol is formed during the reaction. Figure 4.10 illustrates a mechanism on the catalyzed transesterification using calcium oxide as the solid base. It can be accelerated by an enhancement of the basic properties.

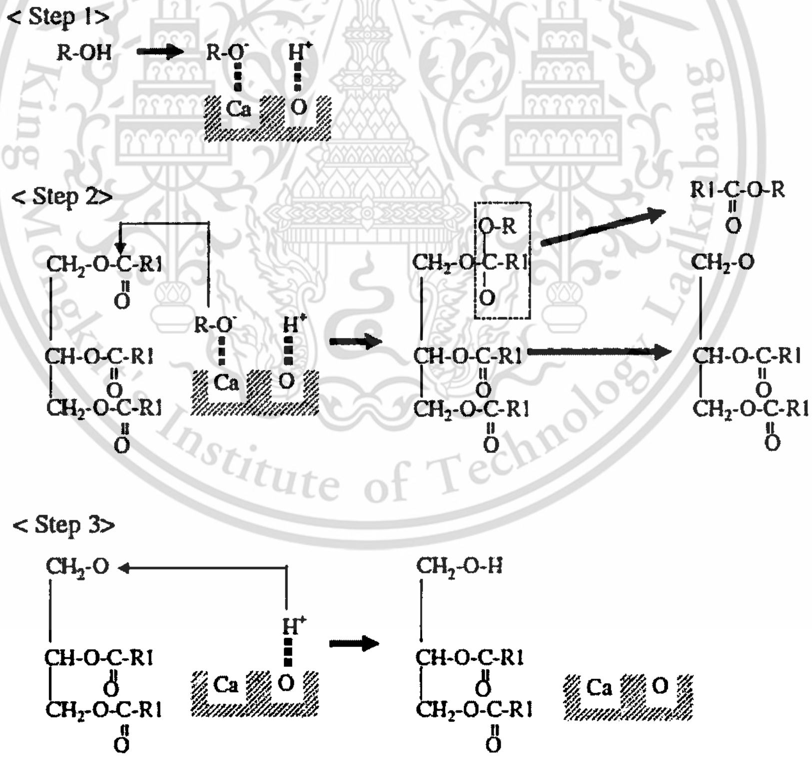


Figure 4.10 Mechanism on the catalyzed transesterification using calcium oxide as the solid base.

4.3.2 Effect of the amount of 1-Ethyl-3-methylimidazolium chloride.

Imidazolium ionic liquid that was used in this special project is 1-Ethyl-3-methylimidazolium chloride or [EMIM] Cl as illustrated in Figure 4.11.

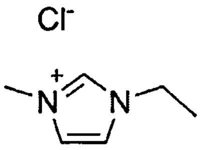


Figure 4.11 1-Ethyl-3-methylimidazolium chloride or [EMIM] Cl

1.0 and 2.0%wt of calcium oxide were chosen to be used with 1-Ethyl-3-methylimidazolium chloride for determining the proper amount of co-catalyst in transesterification reaction. The temperature and ratio of palm oil to methanol were fixed at 65°C and 1:9, respectively, with reaction time of 60 minutes. Table 4.4 shows the effect of different amount of 1-Ethyl-3-methylimidazolium chloride on percent yield of methyl ester.

Table 4.4 Effect of the amount of 1-Ethyl-3-methylimidazolium chloride on percent yield of methyl ester

Percent of calcium oxide (%wt)	Ratio of palm oil to methanol	Reaction time (min)	Percent of [EMIM] Cl (%wt)	Percent yield of methyl ester
1.0	1:9	60	-	6.033
			0.148	3.76
			0.296	27.88
			0.444	29.69
2.0	1:9	60	-	5.186
			0.148	87.571
			0.296	91.816
			0.444	80.125

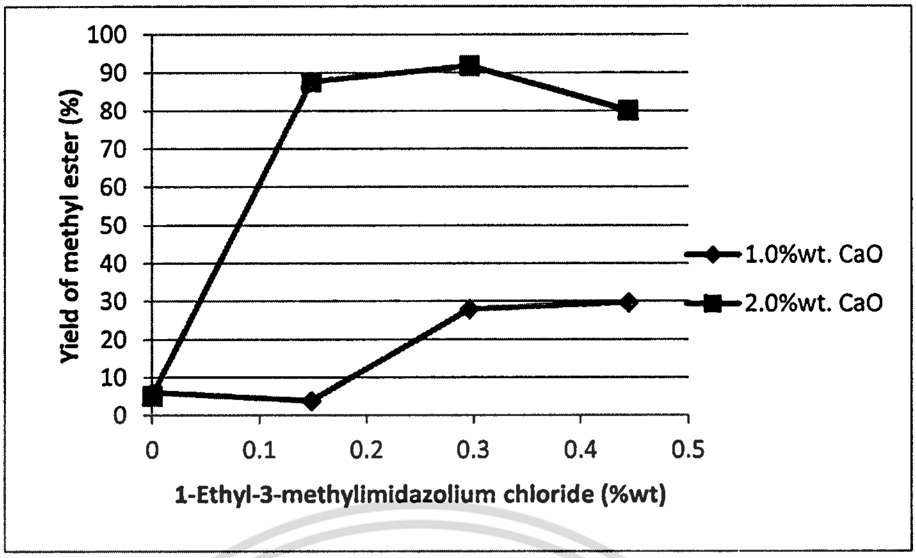
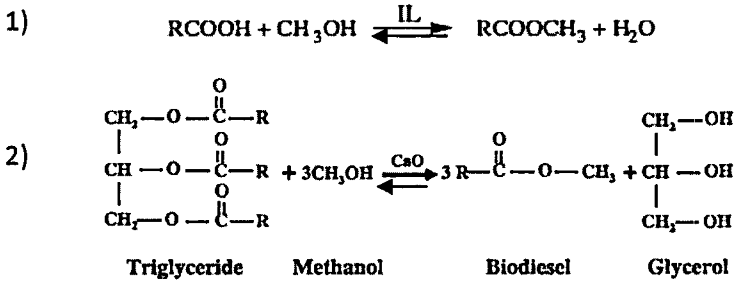


Figure 4.12 Effect of the amount of 1-Ethyl-3-methylimidazolium chloride on percent yield of methyl ester.

The percent yield of methyl ester increased when 1-Ethyl-3-methylimidazolium chloride was added into the reactions. There are two reasons of the increasing yields from using 1-Ethyl-3-methylimidazolium chloride. The first reason is that 1-Ethyl-3-methylimidazolium chloride can act as a catalyst for the esterification of fatty acids and as co-catalyst for the tranesterification of vegetable oils as illustrated in Figure 4.13. Calcium oxide catalyst preferably used in the preparation of biodiesel by a two-step catalytic process has been applied to produce biodiesel palm oil. Firstly, the free fatty acid in the palm oil was esterified with methanol in the presence of 1-Ethyl-3-methylimidazolium chloride. At the second step, calcium oxide was introduced to catalyze the transesterification of the triglycerides in the palm oil with methanol. However, in this project, it mainly acted as catalyst for transesterification since the refined palm oil used in this work had insignificant amount of free fatty acids to begin with.



$$\mathrm{RCOOH + CH_3OH \underset{}{\overset{IL}{\rightleftharpoons}} RCOOCH_3 + H_2O}$$

Figure 4.13 Two step biodiesel preparation using calcium oxide and ionic liquid as catalysts.

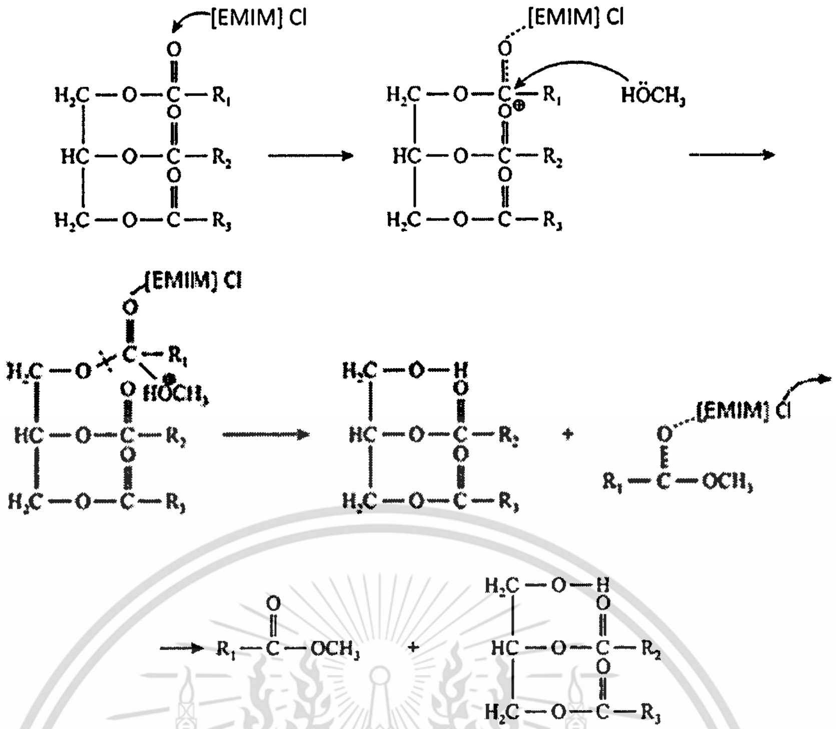


Figure 4.14 Mechanism of biodiesel preparation using 1-Ethyl-3-methylimidazolium chloride as catalyst

The proposed reaction mechanism of the catalyzed transesterification of palm oil using 1-Ethyl-3-methylimidazolium chloride as Lewis-acidic catalyst is shown in Figure 4.14. The cations from IL interact with the oxygen of carbonyl groups from triglyceride making the carbon a better electrophile which then accelerate the attack by nucleophilic oxygen from methanol. The reaction rate would certainly be boosted up from that using calcium oxide as catalyst alone.

The second reason is that 1-Ethyl-3-methylimidazolium chloride also acts as an accelerator for phase separation with its high polarity. In this case, glycerol could be removed more efficiently from the organic phase. This glycerol removal could thus shifts the reaction to give more methyl ester products.

However, from Figure 4.12, some lower yields of methyl ester were also found while increasing the amount of 1-Ethyl-3-methylimidazolium chloride. These occurred probably because the transesterification is a reversible reaction; it is possible for the product methyl ester to be reversed back to fatty acids.

The comparison of using calcium oxide between 1.0% and 2.0%wt of palm oil under the same conditions showed that 2.0%wt of calcium oxide gave higher yield than 1.0%wt. This amount was then chosen for the next experiments.

4.3.3 Effect of the ratio of palm oil to methanol.

The effect of mole ratio of palm oil to methanol on the yield of methyl ester was determined by using the mole ratio of palm oil to methanol of 1:6 and 1:9 with 2.0%wt of calcium oxide catalyst, 0.074, 0.148, 0.296, 0.444% wt of 1-Ethyl-3-methylimidazolium chloride, and reaction time of 60 minutes. Table 4.5 and Figure 4.15 show the result and trend of percent yield of methyl ester.

Table 4.5 Effect of the mole ratio of palm oil to methanol

Percent of calcium oxide (%wt)	Reaction time (h)	Ratio of palm oil to methanol	Percent of [EMIM] Cl (%wt)	Percent yield of methyl ester
2.0	60	1:6	-	8.51
			0.148	75.957
			0.296	82.10
			0.444	79.015
		1:9	-	5.186
			0.148	87.571
			0.296	91.816
			0.444	80.125

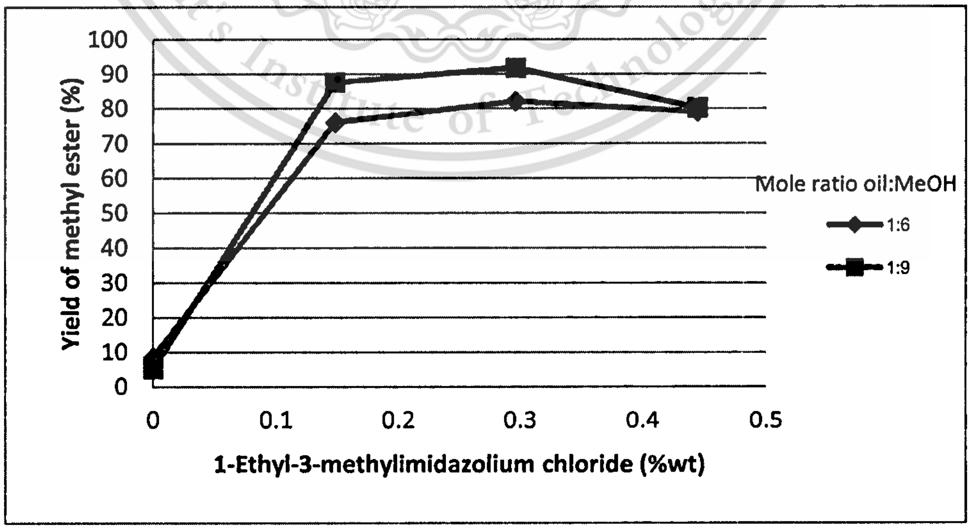


Figure 4.15 Effect of the mole ratio of palm oil to methanol on percent yield of methyl ester using 2.0%wt of calcium oxide.

Figure 4.15 shows the effect of the mole ratio of palm oil to methanol on percent yield of methyl ester in transesterification over 2.0%wt of calcium oxide and various %mole of 1-Ethyl-3-methylimidazolium chloride catalyst. By increasing the mole ratio of palm oil to methanol from 1:6 to 1:9, the methyl ester content increased significantly. It was considered that the higher yields of product methyl ester could be produced from higher methanol content in transesterification reaction. Since the transesterification is reversible reaction between the methyl ester product and glycerol to form monoglycerides and diglycerides, the reversible reaction is prevented by using the excess methanol. In the present study, the optimum mole ratio of palm oil to methanol was 1:9. This ratio was higher than that generally used in homogeneous transesterification having the mole ratio of palm oil to methanol of 1:6.

As a result, 2% wt of calcium oxide, 0.296% wt of 1-Ethyl-3-methylimidazolium chloride, and mole ratio of palm oil to methanol 1:9 were the optimum condition to be further studied.

4.3.4 Effect of the reaction time.

The reaction time of 30 and 60 minutes were used for the study on the effect of reaction time. The yields of methyl ester in transesterification reaction were determined using 2.0%wt of calcium oxide catalyst, 0.296% wt of 1-Ethyl-3-methylimidazolium chloride, and mole ratio of palm oil to methanol of 1:9 at 65°C. The results are listed in Table 4.6.

Table 4.6 Effect of reaction time

Percent of calcium oxide (%wt)	**Ratio of palm oil to methanol**	**Percent of [EMIM] Cl (%wt)**	**Reaction time (min)**	**Percent yield of methyl ester**
2.0	1:9	0.296	30	14.20
2.0	1:9	0.296	60	91.816

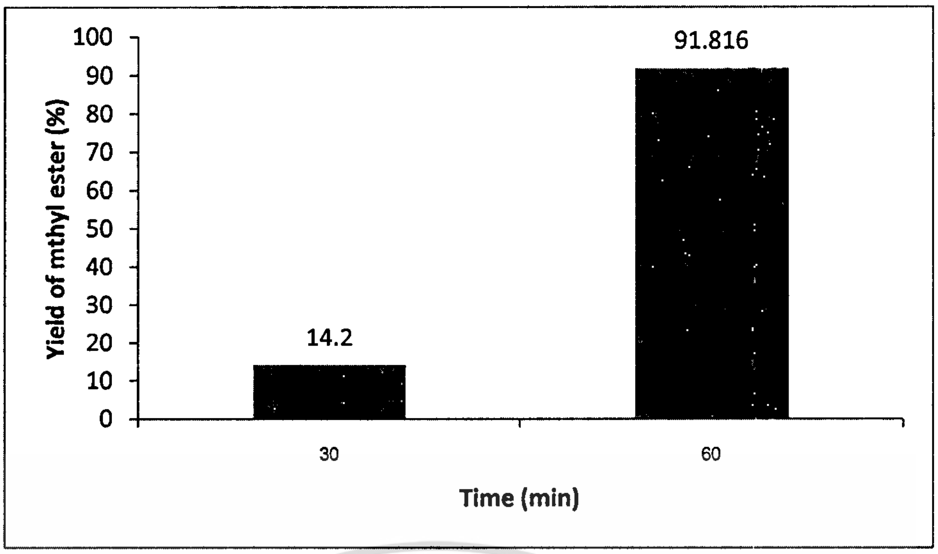


Figure 4.16 Effect of reaction time using 2.0%wt of calcium oxide with 0.296% wt of 1-Ethyl-3-methylimidazolium chloride.

Figure 4.16 shows the relationship between the yield of methyl ester and reaction time. It was found that the reaction time of 60 minutes was the optimum. So, the reaction time of 60 minutes was chosen for the next experiments.

4.3.5 The comparison between commercial calcium oxide and calcium oxide from eggshell.

In this experiment, the calcium oxide from calcined eggshell was used to compare the yield of methyl ester with the commercial calcium oxide. 2%wt of calcium oxides were used with 0.296% wt of 1-Ethyl-3-methylimidazolium chloride, 1:9 mole ratio of palm oil to methanol at 65°C for 60 minutes. The results are shown in Table 4.7.

Table 4.7 Effect of the types of calcium oxides.

Types of calcium oxide catalysts	Percent of calcium oxide (%wt)	Ratio of palm oil to methanol	Percent of [EMIM] Cl (%wt)	Reaction time (min)	Percent yield of methyl ester
Commercial	2.0	1:6	0.296	60	91.816
Calcined eggshell	2.0	1:6	0.296	60	97.788

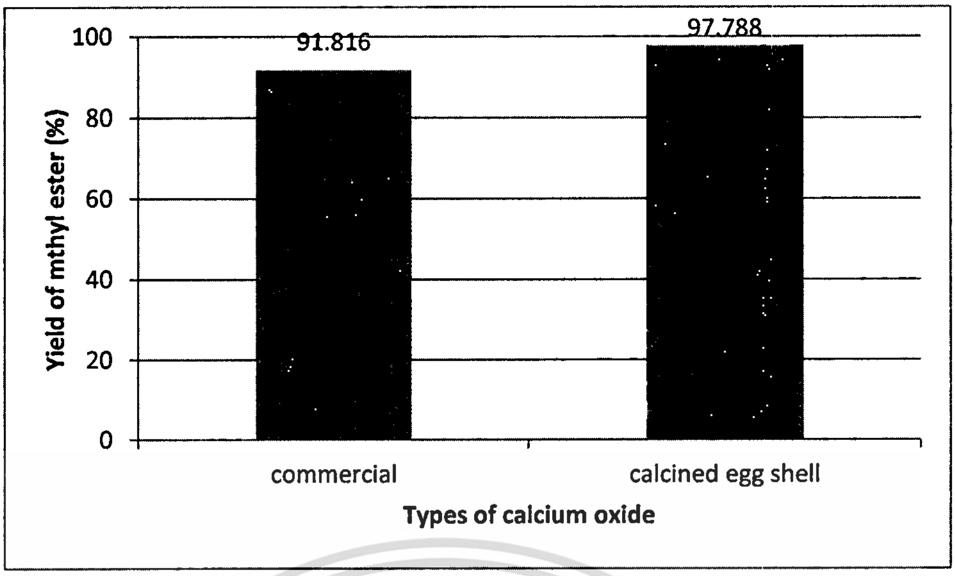


Figure 4.17 The comparison between % methyl ester yield using the 2%wt commercial calcium oxide and calcined eggshell with 0.296%wt of 1-Ethyl-3-methylimidazolium chloride and mole ratio palm oil to methanol of 1:9 at 65 °C for 60 minutes.

From Figure 4.17, it was found that the yield of methyl ester from calcined egg shell catalyst was higher than that of the commercial calcium oxide catalyst. This could be explained by the result from scanning electron microscope (SEM) that the particle sizes of CaO from calcined egg shell is smaller than commercial calcium oxide. Gas Adsorption Analyzer also shows a higher surface area of CaO from calcined egg shell as compared to that of commercial calcium oxide. Hence, the basicity of the calcined egg shell catalyst is higher than that of the commercial catalyst.

Chapter 5

Conclusion and Suggestions

5.1 Conclusion

This special project is the study of the transesterification reaction of palm oil and methanol by using calcium oxide catalysts and 1-Ethyl-3-methylimidazolium chloride as co-catalyst. The variables affecting the methyl ester yield during the transesterification, such as amount of calcium oxide catalysts, amount of 1-Ethyl-3-methylimidazolium chloride, the molar ratio of methanol to palm oil, and reaction time were investigated. The amount of commercial calcium oxide catalyst was varied from 1.0 to 2.0 and 3.0%wt, respectively. The reaction temperature was fixed at 65°C. 1-Ethyl-3-methylimidazolium chloride was used from 0.074 to 0.148, 0.296 and 0.444%wt. The mole ratio of palm oil to methanol was varied from 1:6 to 1:9. The reaction time of 30 and 60 minutes were used.

From the results, it was found that using the reaction time of 60 minutes would give the higher methyl ester yield than 30 minutes. When the mole ratio of palm oil to methanol was increased from 1:6 to 1:9, the product methyl ester was increased. Increasing the percent by weight of calcium oxide from 1.0 to 2.0 and 3.0 resulted in the higher methyl ester yield. The percent yield of methyl ester increased when 1-Ethyl-3-methylimidazolium chloride was added into the reactions. There are two reasons of the increasing yields from using 1-Ethyl-3-methylimidazolium chloride. The first reason is that 1-Ethyl-3-methylimidazolium chloride can act as a co-catalyst for the tranesterification of vegetable oils. The cations from IL interact with the oxygen of carbonyl groups from triglyceride making the carbon a better electrophile which then accelerate the attack by nucleophilic oxygen from methanol. The reaction rate would certainly be boosted up from that using calcium oxide as catalyst alone. The second reason is that 1-Ethyl-3-methylimidazolium chloride also acts as an accelerator for phase separation with its high polarity. In this case, glycerol could be removed more efficiently from the organic phase. This glycerol removal could thus shifts the reaction to give more methyl ester products. The optimum condition which gave the highest yield of methyl ester in this project was by using 2%wt calcium oxide with 0.296% wt of 1-Ethyl-3-methylimidazolium chloride, mole ratio of palm oil to methanol of 1:9 at 65°C for 60 minutes.

For the comparison between the use of commercial calcium oxide and calcined egg shell via the optimum condition, it was found that the yield of methyl ester from calcined egg shell catalyst was higher than that of the commercial calcium oxide catalyst. This could be explained by a higher surface area of calcined egg shell as compared to that of commercial calcium oxide. Hence, the basicity of the calcined egg shell catalyst are higher than that of the commercial catalyst.

5.2 Suggestions

1. The reactions using the other metal oxide or ionic liquids could be attempted.
2. The reversible reaction is prevented by using the excess methanol. The mole ratio of palm oil to methanol higher than 1:9 could be studied.
3. The recovery of ionic liquids could be studied.
4. The recovery and reuse of calcium oxide from calcined egg shell could be studied

References

[1] Ziku Wei [a,b], Chunli Xu [a,b],*, Baoxin Li [c], Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresource Technology 100 (2009) 2883–2885

[2] Jutika Boro[a], Dhanapati Deka[a], Ashim J. Thakur[b], A review on solid oxide derived from waste shells as catalyst for biodiesel production. Renewable and Sustainable Energy Reviews 16 (2012) 904– 910.

[3] Y.A. Elsheikh , Zakaria Man, M.A. Bustam, Suzana Yusup, C.D. Wilfred, Brønsted imidazolium ionic liquids: Synthesis and comparison of their catalytic activities as pre-catalyst for biodiesel production through two stage process, Universiti Teknologi PETRONAS (UTP), Department of Chemical Engineering, 31750 Tronoh, Perak, Malaysia, Energy Conversion and Management 52 (2011) 804–809.

[4] Ayato Kawashima[*], Koh Matsubara, Katsuhisa Honda, Acceleration of catalytic activity of calcium oxide for biodiesel production. Bioresource Technology 100 (2009) 696–700.

[5] Maan Hayyan , Farouq S. Mjalli , Mohd Ali Hashim , Inas M. AlNashef , A novel technique for separating glycerine from palm oil-based biodiesel using ionic liquids, University of Malaya, Chemical Engineering Dept., Kuala Lumpur, Malaysia King Saud University, Chemical Engineering Dept., Riyadh, Saudi Arabia, Fuel Processing Technology 91 (2010) 116–120.

[6] Chawalit Ngamcharussrivichai, Pramwit Nunthasanti, Sithikorn Tanachai, Kunchana Bunyakiat, Biodiesel production through transesterification over natural calciums. Fuel Processing Technology 91 (2010) 1409–1415.

[7] H.C. Ong, T.M.I. Mahlia, H.H. Masjuki, R.S. Norhasyima, “Comparison of palm oil, Jatropha curcas and Calophyllum inophyllum for biodiesel: A review”, Renewable and Sustainable Energy Reviews Vol.15 ,pp. 3501–3515,2011.

[8] Schimel, “ Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems”,. Nature , pp.169-172, 2001.

[9] N. Viriya-empikul, P. Krasae , B. Puttasawat , B. Yoosuk, N. Chollacoop, K. Faungnawakij , “Waste shells of mollusk and egg as biodiesel production catalysts”.Bioresource Technology Vol.101,pp.3765–3767,2010.

[10] N. Viriya-empikul , P. Krasae, W. Nualpaeng , B. Yoosuk , K. Faungnawakij, “Biodiesel production over Ca-based solid catalysts derived from industrial wastes”, Fuel,Vol.92,pp. 239–244,2012.

[11] M. Fangrui and A.H. Milford, "Biodiesel production : a review," Bioresource Technology, Vol. 70, pp. 1-15, 1999.

[12] A. Srivastava and R. Prasad, "Triglycerides-based diesel fuels," Renewable and Sustainable Energy Reviews, pp. 111-133, 2000.

[13] H. Fukuda, A. Kondo and H. Noda, "Review Biodiesel Production by transesterification of Oils," Journal of Bioscience and Bioengineering, Vol. 92, pp. 405-416, 2001.

[14] D. Ayhan, "Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification method," Process in Energy and Combustion Science, Vol. 30, pp. 466-487, 2005.

[15] Masato Kouzu , Jyu-suke Hidaka , "Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review".Fuel,2011.

[16] Lei Zhang , Mo Xian, Yucai He , Liangzhi Li , Jianming Yang, Shitao Yu, Xin Xu, "A BrØnsted acidic ionic liquid as an efficient and environmentally benign catalyst for biodiesel synthesis from free fatty acids and alcohols", Bioresource Technology ,Vol.100 ,pp. 4368–4373,2009.

[17] Kawashima A, Matsubara K, Honda K, "Acceleration of catalytic activity of calcium oxide for biodiesel production". Bioresource TechnologyVol100,pp.696–700,2009.

[18] M. Ghiaci, B. Aghabarari, S. Habibollahi and A. Gil, "Highly efficient BrØnsted acidic ionic liquid-based catalysts for biodiesel synthesis from vegetable oils", Bioresource Technology Vol 102, pp.1200–1204, 2004.

[19] LIANG Jin-hua1, REN Xiao-qian, WANG Jin-tang3, JINAG ming1, LI Zheng-jinag, "Preparation of biodiesel by transesterification from cottonseed oil using the basic dication ionic liquids as catalysts", Journal of fuel chemistry and technology,Vol.38, 3, ,2010.

[20] LONG Tao, DENG Yuefeng, GAN Shucai and CHEN Ji, "Application of Choline Chloride·xZnCl2 Ionic Liquids for Preparation of Biodiesel" Biotechnologe and bioengineering,Vol 18, pp.322-327, 2010.

[21] A. Srivastava and R. Prasad, "Triglycerides-based diesel fuels," Renewable and Sustainable Energy Reviews, pp. 111-133, 2000.

[22] Witchuta Trakoonrat, "synthesis of biodiesel from refined palm oil using alkali earth metal oxide as catalyst under critical temperature and pressure"

[23] LONG Tao, DENG Yuefeng, GAN Shucai and CHEN Ji, "Application of Choline Chloride·x$ZnCl_2$ Ionic Liquids for Preparation of Biodiesel". BIOTECHNOLOGY AND BIOENGINEERING, Chinese Journal of Chemical Engineering, 18(2) 322-327 (2010)

Appendices

Appendix A

Calculations

1. Molecular weight of palm oil

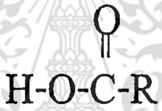
The data from Table 4.1 could be used for the calculation of an average molecular weight of fatty acids in palm oil.

Step 1: Calculation of average molecular weight of fatty acid.

$$\text{Molecular weight of fatty acid} = \frac{(228x1.07)+(256x35.32)+(284x5.30)+(282x46.30)+(280x12.01)}{100}$$

$$= 272.10 \text{ g/mol}$$

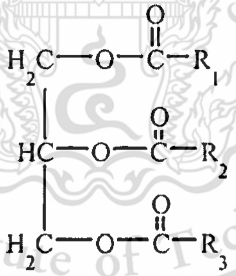
The weight of 272.10 g/mole is an average molecular weight of fatty acids in palm oil.



$$\overset{O}{\overset{\|}{\text{H-O-C-R}}}$$

Step 2: Calculation of molecular weight of palm oil

The structure of palm oil:



Therefore;

Molecular weight of palm oil = ((272.10-1H) x 3) + (3C) + (5H)

= ((272.10 - 1) x 3) + (12x3) + 5

= 854.3 g/mole

Where; Molecular weight of C = 12 g/mole

Molecular weight of H = 1 g/mole

2. Weight percentage of 1-Ethyl-3-methylimidazolium chloride

Molecular weight of palm oil = 854.3 g/mole

Weight of palm oil = 44.61 g

Mole of palm oil = $\frac{44.61g}{MW854.3g/mole}$ = 0.052 mole

Molecular weight of 1-Ethyl-3-methylimidazolium = 146.62 g/mole

Weight of imidazolium = 0.066 g

Then, percent weight of 1-Ethyl-3-methylimidazolium by weight of palm oil:

In palm oil 44.61 g => weight of [EMIM] Cl = 0.066 g

In palm oil 100 g => weight of [EMIM] Cl = $\frac{0.066x100}{44.61}$ = 0.148%

Weight of palm oil (g)	**Mole of palm oil (mole)**	**Weight of [EMIM] Cl (g)**	**%weight of [EMIM] Cl**
44.61	0.052	0.033	0.074
		0.066	0.148
		0.132	0.296
		0.198	0.444

Appendix B

NMR Spectra

Figure B1 ^{1}H-NMR spectrum of biodiesel using 1:6 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil at 65°C for 60 minutes.

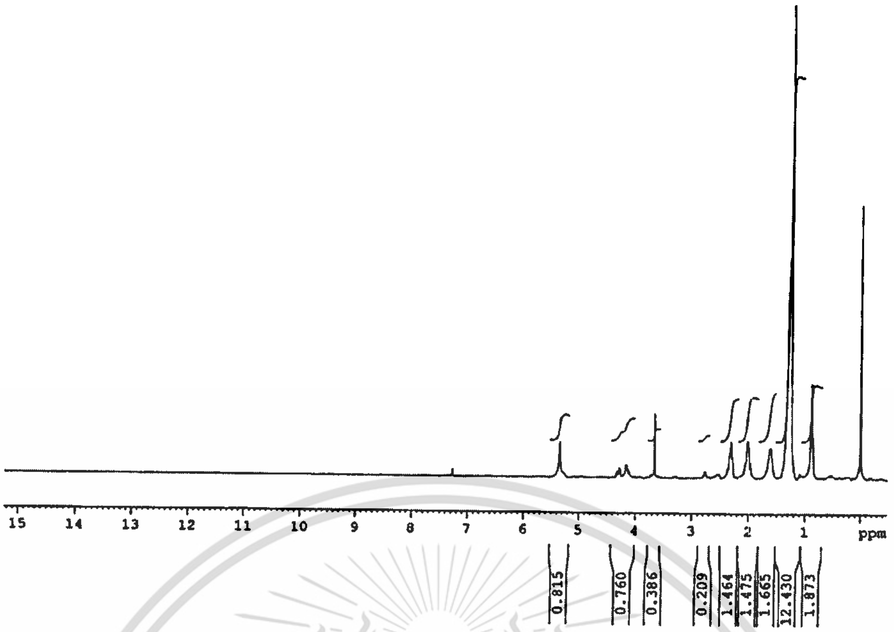


Figure B2 ^{1}H-NMR spectrum of biodiesel using 1:6 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.0005% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

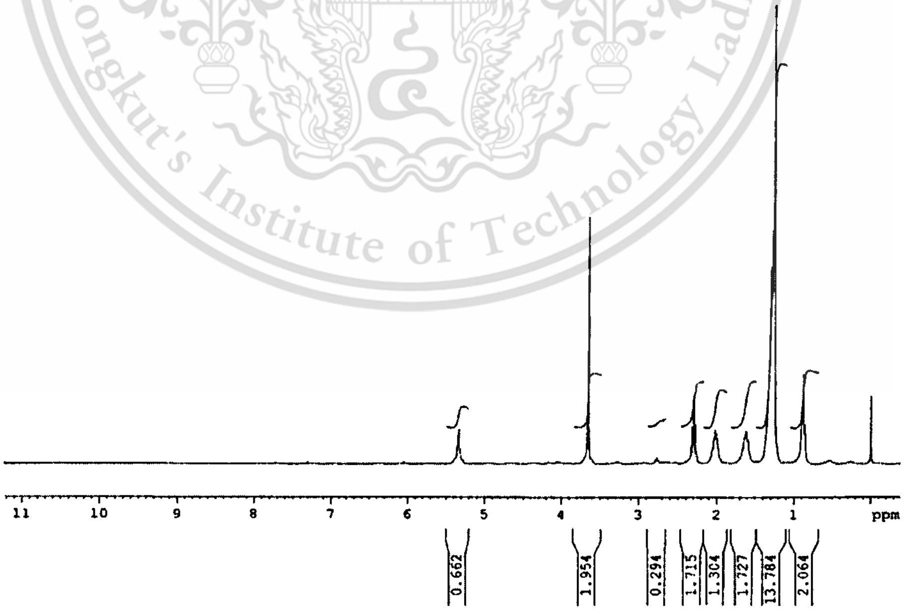


Figure B3 ^{1}H-NMR spectrum of biodiesel using 1:6 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.001% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

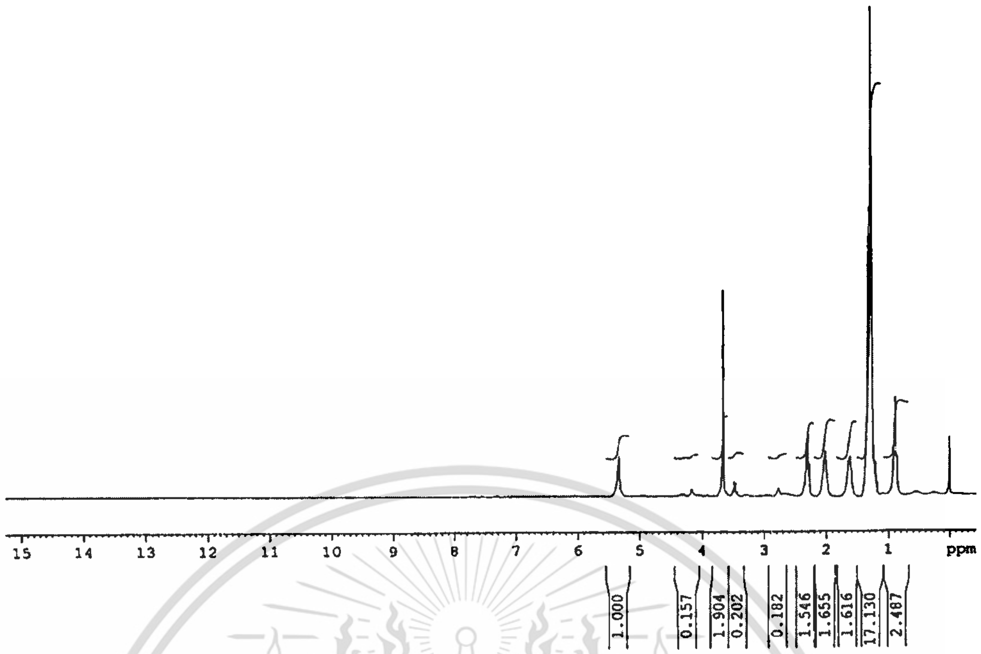


Figure B4 ^{1}H-NMR spectrum of biodiesel using 1:6 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.002% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

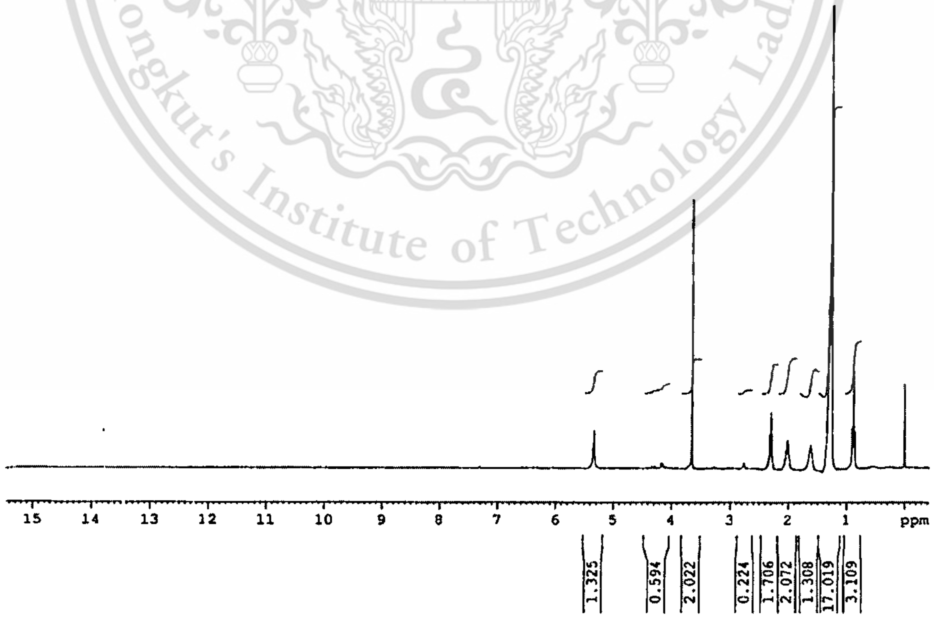


Figure B5 ^{1}H-NMR spectrum of biodiesel using 1:6 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.003% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

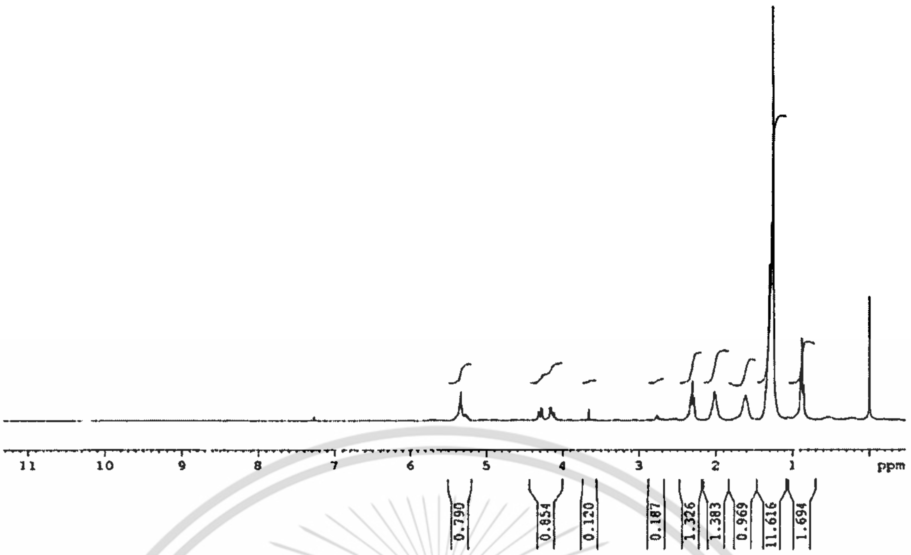


Figure B6 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 1%wt of calcium oxide by weight of palm oil at 65°C for 60 minutes.

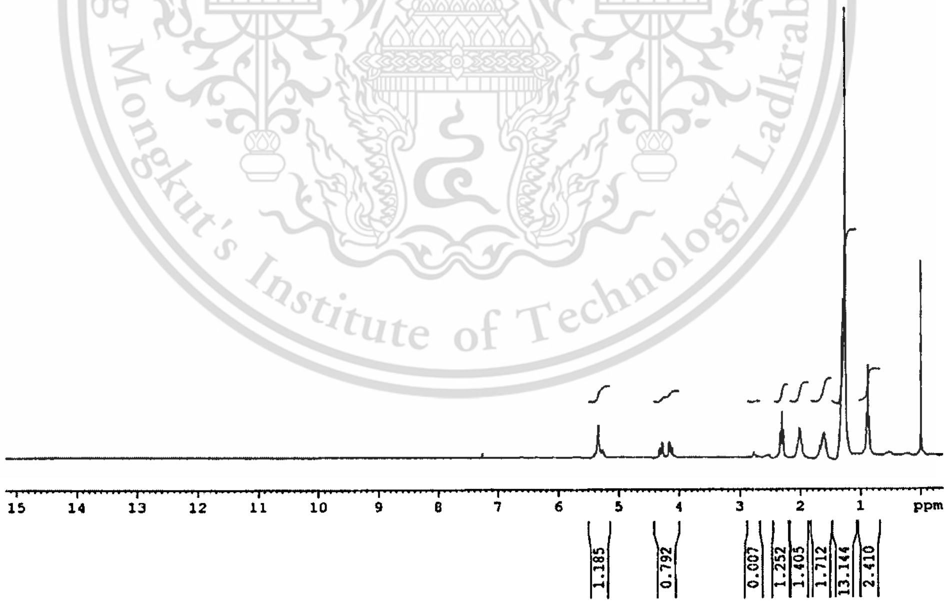


Figure B7 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 1%wt of calcium oxide by weight of palm oil with 0.0005% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

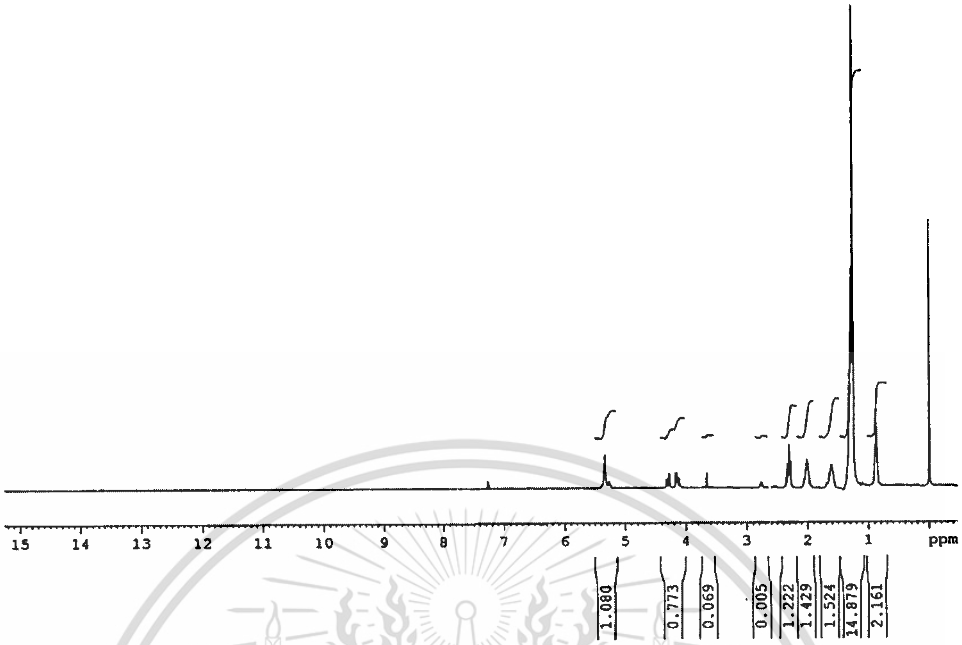


Figure B8 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 1%wt of calcium oxide by weight of palm oil with 0.001% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

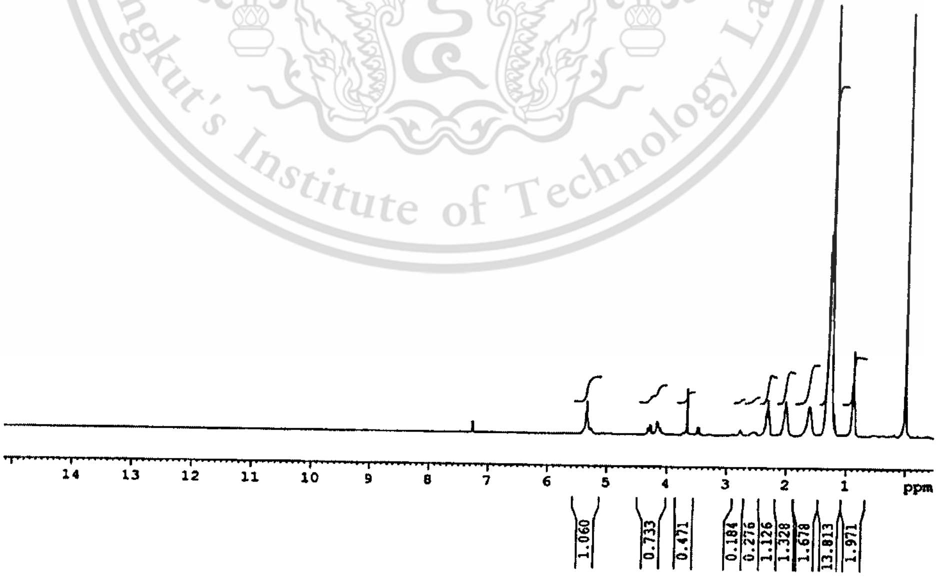


Figure B9 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 1%wt of calcium oxide by weight of palm oil with 0.002% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

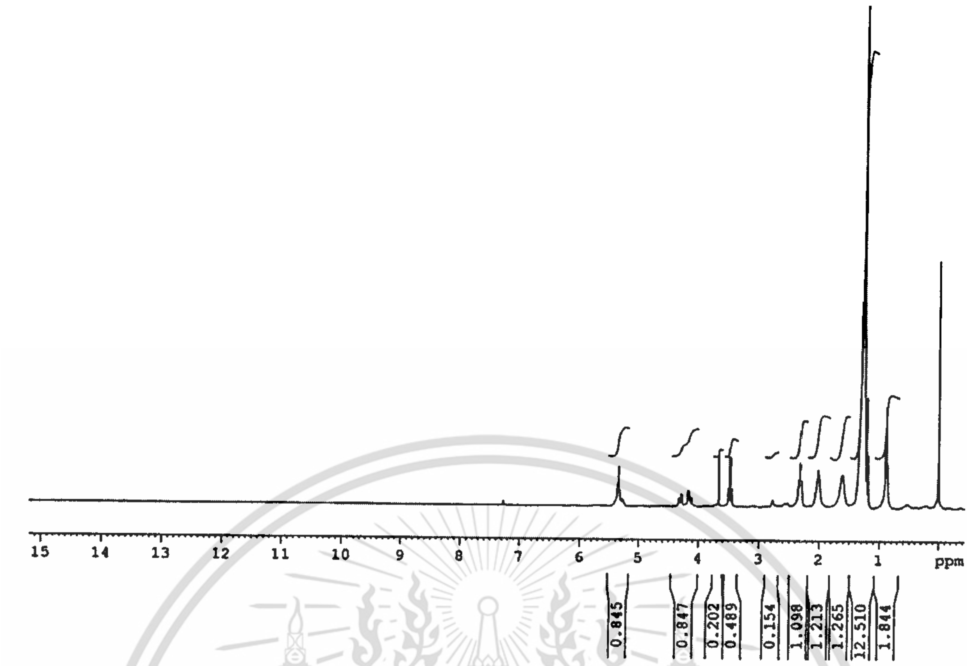


Figure B10 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 1%wt of calcium oxide by weight of palm oil with 0.003% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

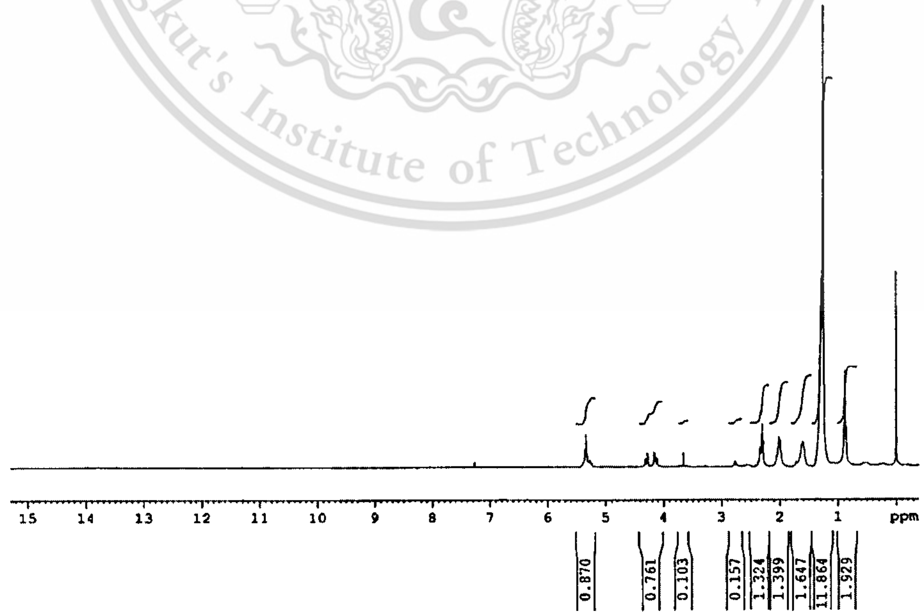


Figure B11 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil at 65°C for 60 minutes.

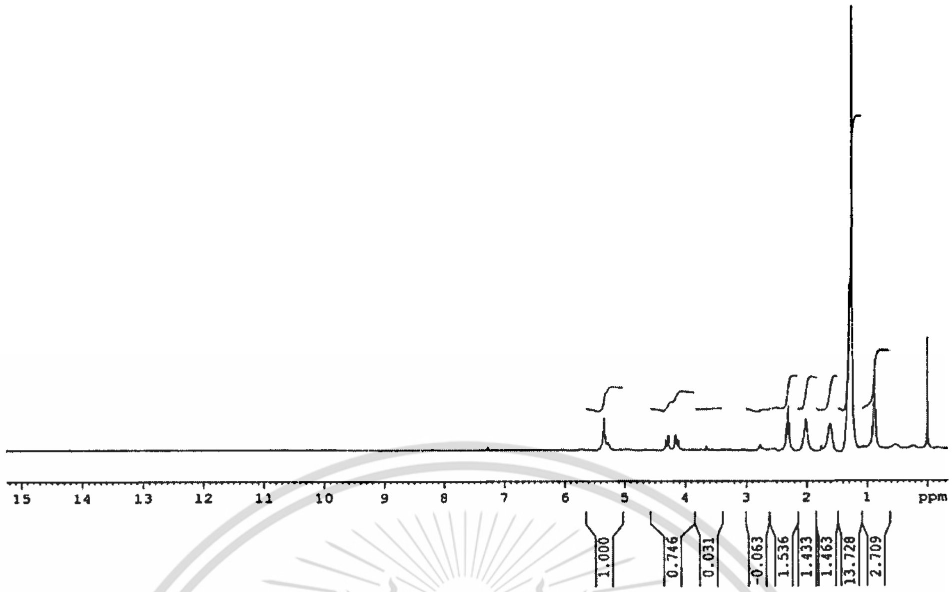


Figure B12 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.0005% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

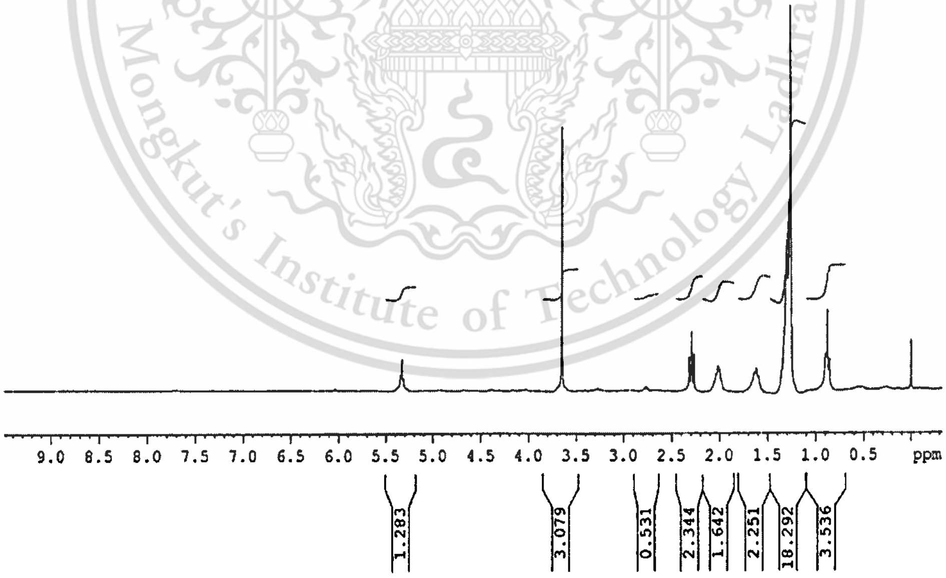


Figure B13 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.001% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

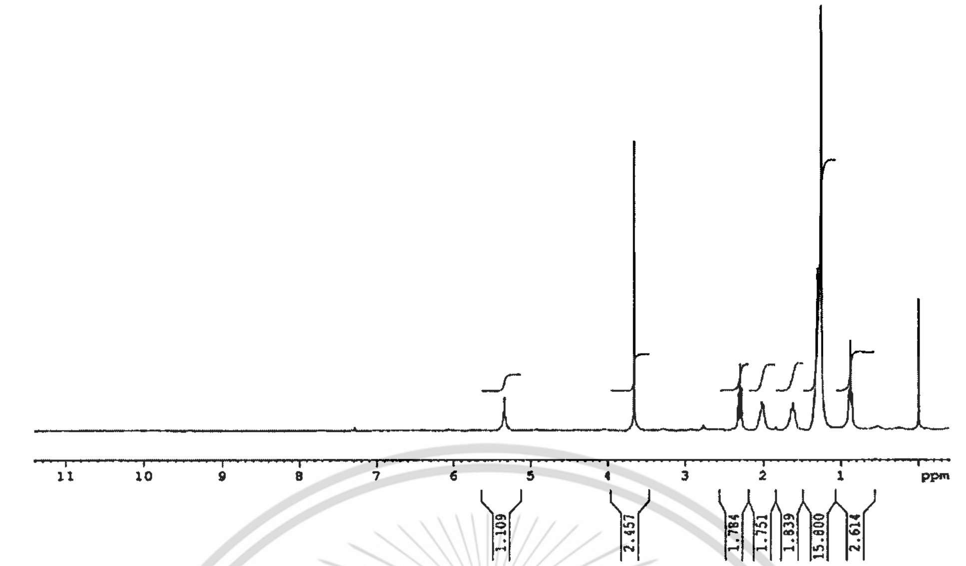


Figure B14 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.002% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

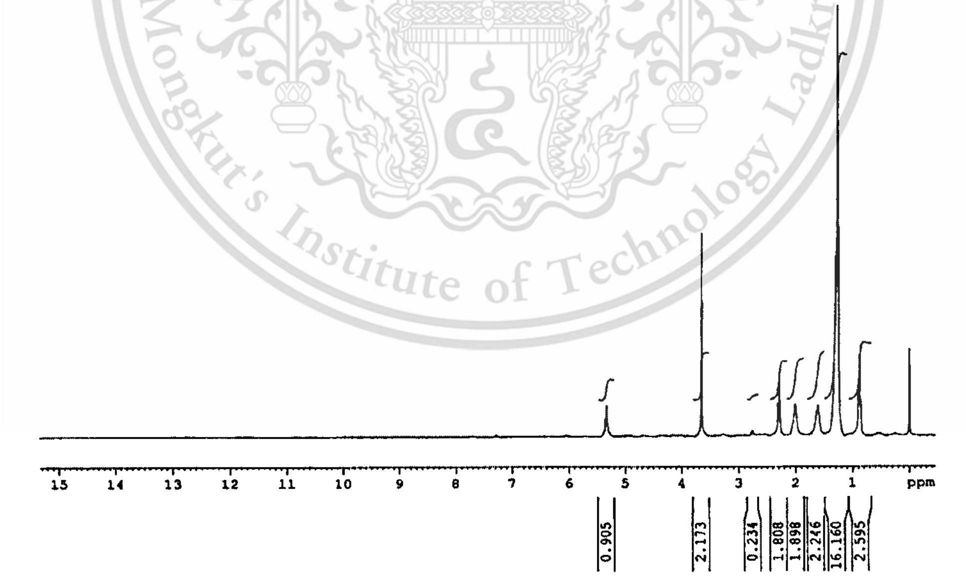


Figure B15 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.003% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.

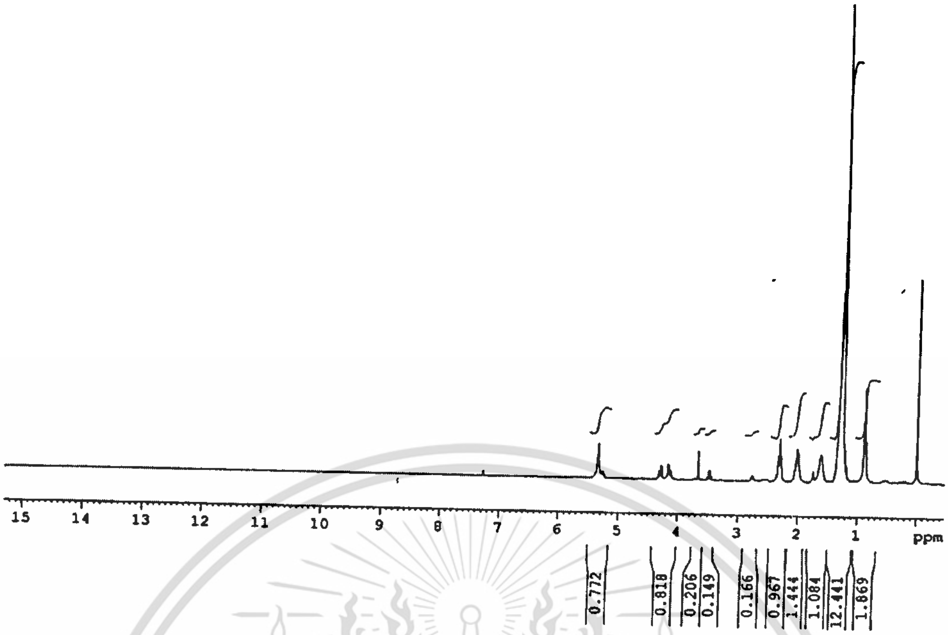


Figure B16 ^{1}H-NMR spectrum of biodiesel using 1:9 mole ratio of palm oil to methanol, 2%wt of calcium oxide by weight of palm oil with 0.002% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 30 minutes.

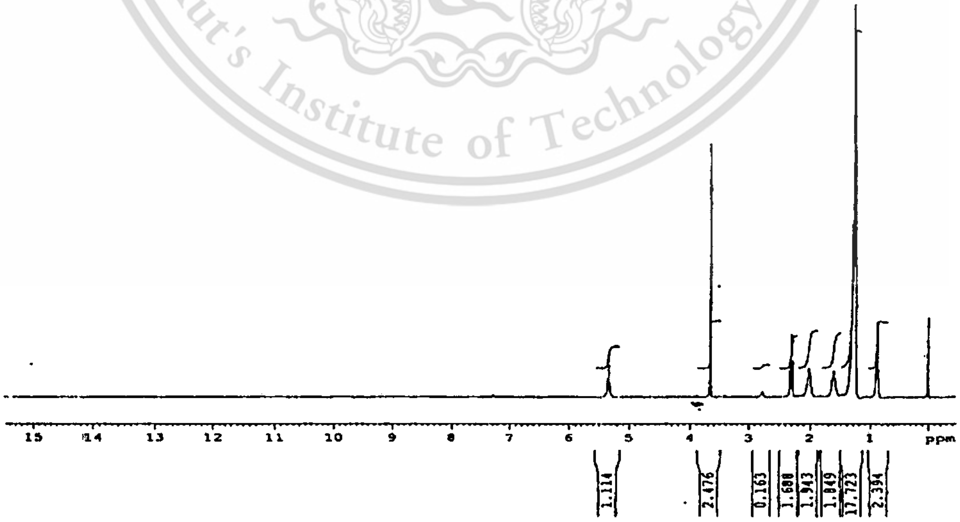


Figure B17 ^{1}H-NMR spectrum of biodiesel using 1:6 mole ratio of palm oil to methanol, 2%wt of calcium oxide from eggshell by weight of palm oil with 0.002% by mole of 1-ethyl-3 methylimidazolium chloride at 65°C for 60 minutes.