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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

DEVELOPMENT OF CALCIUM OXIDE BASED CATALYSTS FOR ETHYL
ESTER PRODUCTION



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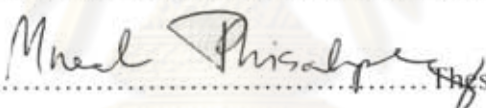
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งานวิจัยนี้ศึกษาการพัฒนาตัวเร่งปฏิกิริยาที่มีแคลเซียมออกไซด์เป็นองค์ประกอบหลักสำหรับปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันของน้ำมันถั่วเหลืองกับเอทานอล สารประกอบที่มีคุณสมบัติเป็นเบสอ่อน (NH_4OH) และสารประกอบที่มีคุณสมบัติเป็นเบสแก่ (NaOH , KOH และ Ca(OH)_2) ถูกนำมาเติมลงบนแคลเซียมออกไซด์ ตัวเร่งปฏิกิริยาทั้งหมดถูกนำไปตรวจสอบลักษณะและสมบัติ ซึ่งอาจมีผลต่อการทำปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันด้วยเครื่อง XRD, BET, TEM, CO_2 -TPD และ TGA จากการศึกษาพบว่าตัวเร่งปฏิกิริยาที่มีแคลเซียมออกไซด์เป็นองค์ประกอบหลักที่ถูกโหลดด้วยแคลเซียมไฮดรอกไซด์ (Ca(OH)_2) และแอมโมเนียมไฮดรอกไซด์ (NH_4OH), แคลเซียมไฮดรอกไซด์ที่ถูกเผา และ แคลเซียมออกไซด์ที่เตรียมจากหินปูนมีศักยภาพในการใช้เป็นตัวเร่งปฏิกิริยาของปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชัน โดยพบว่าแคลเซียมออกไซด์ที่เติมแคลเซียมไฮดรอกไซด์ลงไป 3.7 เปอร์เซ็นต์โดยน้ำหนักมีความสามารถในการเร่งปฏิกิริยาสูงที่สุดเมื่อเทียบกับตัวเร่งปฏิกิริยาทั้งหมดที่มีการตรวจสอบ โดยให้ปริมาณเอทิลเอสเทอร์ที่สูงที่สุดเท่ากับ 96.3 เปอร์เซ็นต์หลังจากการทำปฏิกิริยานาน 10 ชั่วโมง ซึ่งสภาวะที่เหมาะสมที่สุดสำหรับการเกิดปฏิกิริยาก็คือ อัตราส่วนของเอทานอลต่อน้ำมันเท่ากับ 9:1 และปริมาณตัวเร่งปฏิกิริยา 13.8 เปอร์เซ็นต์ (โดยน้ำหนักของน้ำมัน) โดยดำเนินการที่อุณหภูมิ 70 องศาเซลเซียสเป็นเวลา 10 ชั่วโมง ผลจากการศึกษาชี้ให้เห็นว่าความสามารถในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาขึ้นอยู่กับโครงสร้างของผลึกและการรวมกันของผลึก นอกจากนี้สามารถนำตัวเร่งปฏิกิริยามาใช้ซ้ำได้โดยมีความสามารถในการเร่งปฏิกิริยาที่เกือบจะคงที่ได้อย่างน้อย 3 รอบ

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KORNKANOK WATCHARATHAMRONGKUL: DEVELOPMENT OF
CALCIUM OXIDE BASED CATALYSTS FOR ETHYL ESTER
PRODUCTION. ADVISOR: ASSOC. PROF. MUENDUEN
PHISALAPHONG, Ph.D., CO-ADVISOR: ASSOC. PROF. BUNJERD
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This research studied the development of calcium oxide based catalysts for transesterification of soybean oil with ethanol. The weak basic compounds (NH_4OH) and the strong basic compounds (NaOH , KOH and $\text{Ca}(\text{OH})_2$) were used to load on CaO . All catalysts were characterized by XRD, BET, TEM, CO_2 -TPD and TGA to examine the characteristics and properties which could affect transesterification reaction. The results showed that $\text{Ca}(\text{OH})_2$ and NH_4OH loaded CaO based catalysts, calcined $\text{Ca}(\text{OH})_2$ and CaO from limestone had potential to be used as heterogeneous catalysts for transesterification reaction. The CaO loaded with 3.7 wt% of $\text{Ca}(\text{OH})_2$ was found to exhibit the highest catalytic activity among all catalysts investigated. The maximum ethyl esters content achieved was 96.3 wt% after 10 hours of the reaction. The optimum conditions were 9:1 molar ratio of ethanol to oil and 13.8 (wt% by oil) of catalyst operated at 70°C for 10 hours. The results also showed that the catalytic activity of catalysts depended upon the crystal structure and the agglomeration of catalysts. Reusability of the catalyst was investigated and it was found that the conversion of biodiesel maintained the same level after recycling of at least 3 times.

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CHAPTER I

INTRODUCTION

1.1 Motivation

According to the diminishing petroleum reserves and environmental consequences of exhaust gases from petroleum-fueled engines, biodiesel becomes more attractive and promising alternative energy sources. Biodiesel is a renewable energy for diesel engines that is biodegradable, non-toxic and has low emission profiles as compared to petroleum diesel. The most popular method of producing biodiesel is the transesterification reaction between vegetable oils or animal fat with short chain alcohol such as methanol and ethanol. Methanol, however, is at present mainly produced from natural gas. Besides, methanol vapor is toxic, does not produce a visible flame when burning and can be absorbed through the skin. Any methanol spill can quickly vaporize and form flammable vapor/air mixtures. On the other hand, ethanol is the renewable alternative fuel because it is made from agricultural products and not from hydrocarbon-based fossil fuel. Ethanol has better solvent properties than methanol for solubility of oil (Kulkarni et al., 2007). In addition, the use of ethyl ester improves the cold start since its cloud and pour points are lower than those of the methyl ester (Encinar et al., 2007) .

The transesterification can be catalyzed by either homogeneous (acids or bases) or heterogeneous catalysts. The homogeneous catalysts, however, have a problem with the separation of catalysts from the product and the formation of stable emulsion and a large amount of waste water. Alternatively, the heterogeneous catalysts are noncorrosive, environmentally benign and display fewer disposal problems. Meanwhile, they are more easily separated from the

liquid products by filtration and can be developed to give higher activity, selectivity and longer catalyst lifetimes.

In the recent years, many kinds of heterogeneous (acids, bases) catalysts have been extensively applied for transesterification process, such as alkaline earth metal oxides, various alkali metal compounds supported on alumina or zeolite. The solid superacid catalysts of sulfated tin, zirconium oxides and tungstated zirconia were reported for the transesterification of soybean oil with methanol at 200–300 °C and the esterification of n-octanoic acid with methanol at 175–200 °C in a fixed bed reactor (Furuta et al., 2004). Tungstated zirconia–alumina gave the conversion over 90% for both of the esterification and the transesterification process. A heterogeneous base catalyst, Na/NaOH/ γ -Al₂O₃ was developed for transesterification of soybean oil with methanol using n-hexane as a co-solvent with the maximal biodiesel yield of 94 % (Kim et al., 2004). Alumina-supported potassium iodide was later on, reported as a solid base catalyst in a heterogeneous manner with methyl ester at conversion yield of 96 % (Xie et al., 2006).

CaO has also been applied as a solid base catalyst because of its high catalytic activity at mild reaction conditions, long catalyst lifetimes and low catalyst cost. The possibility of using nanocrystalline calcium oxides under room-temperature was investigated (Reddy et al., 2006). A solid super base of CaO prepared by the treatment with an ammonium carbonate solution and calcinations at a high temperature was used for the transesterification (Zhu et al., 2006). The sequence of catalytic activity of calcium oxides for transesterification were reported in order of CaO > Ca(OH)₂ > CaCO₃. The water content and the adsorption of CO₂ strongly deactivated the active sites of catalysts (Kouzu et al., 2008). The alkaline and alkaline-earth metals compounds were used for methanolysis of sunflower oil (Arzamendi et al., 2008). Recently, alkali-doped metal oxide catalysts, Ca (NO₃)₂/CaO, LiNO₃/CaO, NaNO₃/CaO, KNO₃/CaO and LiNO₃/MgO

were examined for transesterification of vegetable oils (Macleod et al., 2008 , Granados et al., 2007). Although many developments of new and effective solid catalysts for methanolysis of vegetable oils were established, only few studies have been done on ethanolysis of vegetable oils.

In the present study, the transesterification reactions between soybean oil and ethanol by calcium oxides as solid base catalysts were investigated. Calcium oxides were prepared by the calcinations of CaO, Ca(OH)₂ and limestone at a high temperature. The catalytic activity was then improved by loading alkali solutions such as calcium hydroxide, ammonium hydroxide, potassium hydroxide and sodium hydroxide on CaO. Catalyst characterizations, were then examined by means of X-ray diffraction, BET surface area, transmission electron microscopy and temperature-programmed desorption of carbon dioxide (CO₂-TPD). The effects of operational parameters, such as a molar ratio of ethanol to oil, a mass ratio of catalyst to oil, reaction time, and type of catalysts on the transesterification were investigated. The results would be of great benefits for the understanding and development of catalytic design for the ethanolysis of vegetable oils.

1.2 Objectives

1. To develop calcium oxide (CaO) based catalysts for ethyl ester production.
2. To investigate the effects of operating conditions on biodiesel production from soybean oil and ethanol using CaO based catalysts.
3. To examine the reusability of CaO based catalysts for ethyl ester production.

1.3 Scope of work

By following the research objectives, the scope of work is,

1. Using CaO, limestone, Ca(OH)₂/CaO, NH₄OH/CaO, KOH/CaO and NaOH/CaO as base catalysts for ethyl ester production.
2. Ethyl ester production from soybean oil and 99.9% ethanol.
3. Catalyst characterization by X-ray diffraction (XRD), Nitrogen physisorption BET surface area, Transmission electron microscopy (TEM), Temperature programmed desorption (TPD) and Thermal gravimetric analysis (TGA).
4. Investigation of the effects of operating conditions on ethyl ester production such as molar ratio of ethanol to oil, mass ratio of catalyst to oil, Ca(OH)₂, NH₄OH, KOH and NaOH loading on CaO, and reaction time.
5. Examination of the reusability and deactivation of CaO based catalysts.

1.4 Expected benefits

1. This study will indicate the strategic development of CaO based catalysts for ethyl ester production.
2. This investigation will provide the suitable conditions for ethyl ester production using CaO based catalysts.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Biodiesel

Biodiesel is one of clean burning alternative fuels, produced from domestic, renewable resources. It is comprised of monoalkyl ester of long chain fatty acids derived from vegetable oil and animal fats. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. The well-known advantages of biodiesel, comparing to petro-diesel are: lower dependence on foreign crude oil, renewable resource, reduction of greenhouse gas emissions due to the closed CO₂ cycle, lower combustion emission profile (especially SO_x) and potential improvement of rural economics.

2.2 The production of biodiesel

2.2.1 Direct use and blending

There was considerable discussion regarding use of vegetable oil as fuel in 1981 (Bartholomew, 1981). Caterpillar Brazil in 1980 used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alteration or adjustments to the engines. At that point, it was not practical to substitute 100 % vegetable oil for diesel fuel. But a blend of 20 % vegetable oil and 80 % diesel fuel was successful. Some short-term experiments were successfully carried out using up to 50:50 ratio. Nevertheless, the problem appeared after the engine has been operating on vegetable oil for longer period of time.

Therefore, direct use of vegetable oil and/or the use of blends of the oils has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines (Petchmala, 2008). Moreover, it was concerned for the high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and composition carbon deposits and lubricating oil thickening. The probable problems and the potential solutions for using vegetable oils as engine fuels are shown in Table 2.1

Table 2.1 Problems and potential solutions for using vegetable oils as engine fuels (Harwood, 1984, Ma et al., 1999).

Problem	Probable cause	Potential solution
<u>Short-term</u>		
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2. Plugging and gumming filters, lines and injectors	Nature gums (phosphatides) in vegetable oil. Other ash	Partially refine the oil to remove gums. Filter to 4 microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester.
<u>Long-term</u>		
4. Coking of injectors on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
5. Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester

Problem	Probable cause	Potential solution
6. Excessive engine wear	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation
7. Failure of engine lubricating oil due to polymerization	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation

2.2.2 Microemulsions

To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol, and 1-butanol have been studied. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimension generally in the 1-150 nm range, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Schwab et al., 1987). Pryde (1984) found that microemulsions can improve spray characteristic by explosive vaporization of the low boiling constituent in the micelles. In short term performances, Goering et al. (1984) found that ionic and non-ionic microemulsions of aqueous ethanol in soybean oil were nearly as good as that of No. 2 diesel. However, fuels formulated as microemulsions have low cetane numbers and low heating values as compared with No. 2 diesel fuel (Bagby, 1987).

2.2.3 Pyrolysis

Pyrolysis or thermal cracking can be used to produce triglyceride based biodiesel. Pyrolysis is the thermal degradation of vegetable oils by heat in the absence of oxygen, which results in the production of alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small amounts of gaseous products (Schwab et al. 1988). The starting material can be vegetable oils, animal fats, fatty acids and methyl esters of fatty acids. The mechanism of pyrolysis of triglycerides for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids is shown in Figure 2.1 (Schwab et al., 1988). Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism. Formation of homologous series of alkanes and alkenes is accountable from the generation of the RCOO radical from the triglyceride cleavage and subsequent loss of carbon dioxide. The R radical, upon disproportionation and ethylene elimination, gives the odd-numbered carbon alkanes and alkenes. However, while pyrolyzed vegetable oils possess acceptable amounts of sulphur, water, and sediment, as well as giving acceptable copper corrosion values, they are unacceptable in terms of ash, carbon residues, and pour point. In addition, disadvantages of this process include high equipment cost and need for separate distillation equipment for separation of various fractions. (Sawangpanya, 2009)

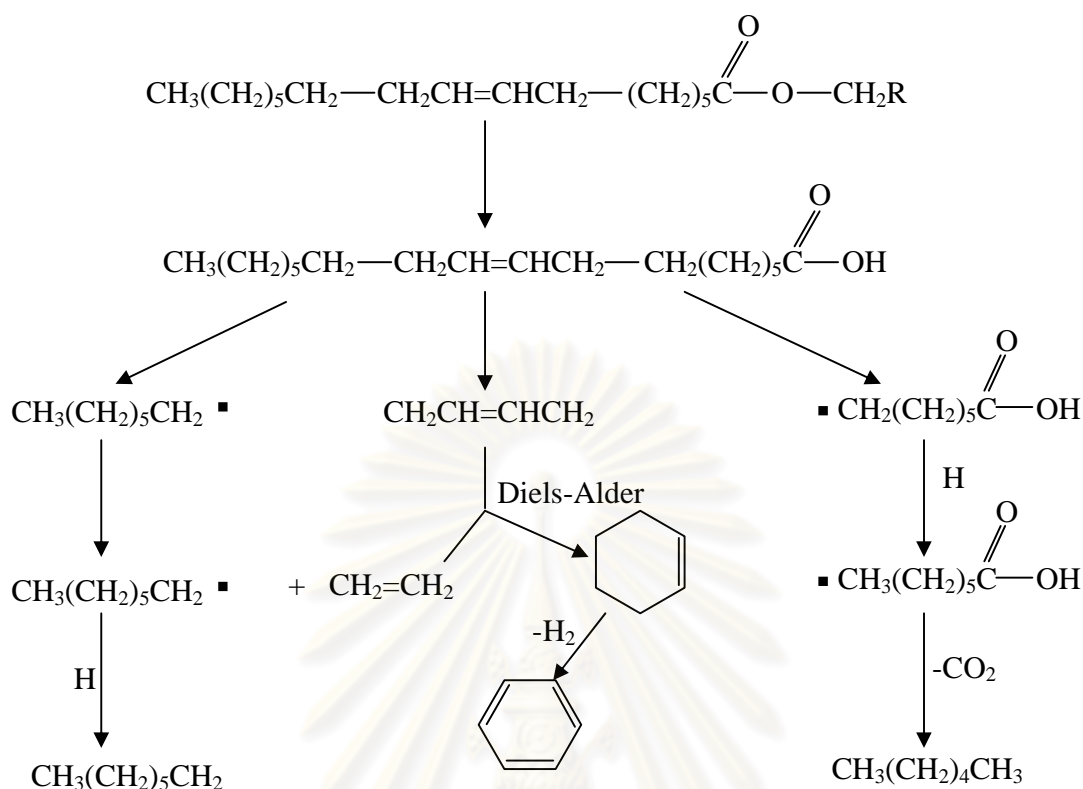


Figure 2.1 The mechanism of pyrolysis of triglycerides (Schwab et al., 1988).

2.2.4 Esterification

The formation of ester occurs through a condensation reaction known as esterification. This requires two reactants, carboxylic acids (fatty acids) and alcohol. Esterification reactions are acid catalysed and proceed slowly in the absence of strong acids such as sulphuric acid, phosphoric acid, organic sulfonic acids and hydrochloric acid. The equation for esterification reaction can be seen in Figure 2.2.

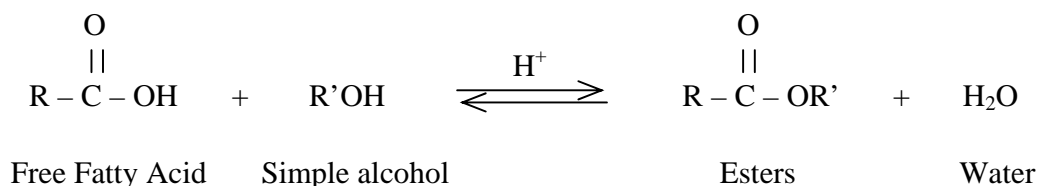


Figure 2.2 Esterification reaction

Esterification can also be carried out without a catalyst in supercritical condition. Similar to the supercritical transesterification, the advantages of carrying out the methyl esterification is the rapid reaction and the ease of product separation.

2.2.5 Transesterification

Transesterification (also called alcoholysis) is a reaction of vegetable oils such as soybean oil, sunflower oil, coconut oil, rapeseed oil, palm oil, or animal fat (or known as triglycerides) to produce fatty acid esters (biodiesel), and glycerol as a co-product. This reaction takes a long time to complete, and thus generally requires some base or acid catalyst to improve reaction rate and yield. Examples of these catalysts are sodium or potassium hydroxide, or sulfuric acid. General equation of this reaction is shown in Figure 2.3. R_1 , R_2 , and R_3 of the oil molecules are long chain of hydrocarbon constituting fatty acids which may be the same or different.

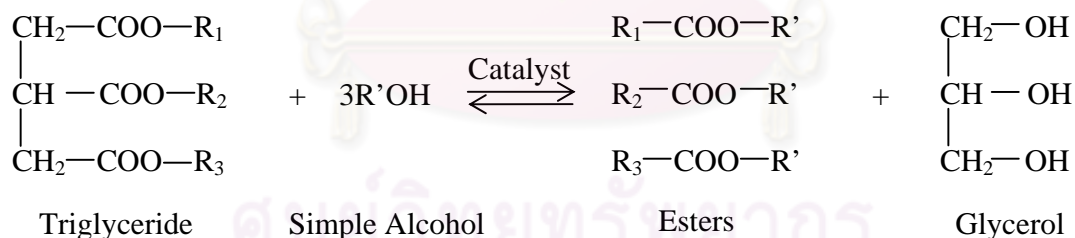


Figure 2.3 Chemical reaction of transesterification reaction

The stoichiometry requires three moles of alcohol and one mole of triglyceride to produce three moles of fatty esters and one mol of glycerol. However, this reaction is reversible, and therefore excess alcohol is used in reaction to shift the equilibrium to the right side (products). Typically, the variables affecting reaction rate and yield include: type and amount of

catalyst, type of alcohol, reaction temperature, reaction time, molar ratio of vegetable oil and alcohol, glycerol separation and quality of vegetable oil such as fatty acid composition.

The transesterification reaction shown in Figure 2.3 is indeed the overall reaction for three stepwise reactions with intermediate formation of diglyceride and monoglyceride (Figure 2.4). In the first reaction, triglyceride (TG) reacts with alcohol to produce diglyceride (DG), then in the second reaction, diglyceride (MG) reacts with alcohol to form monoglyceride (MG). Finally, in the third reaction, monoglyceride (MG) reacts with alcohol to give glycerol.

Stepwise Reaction:

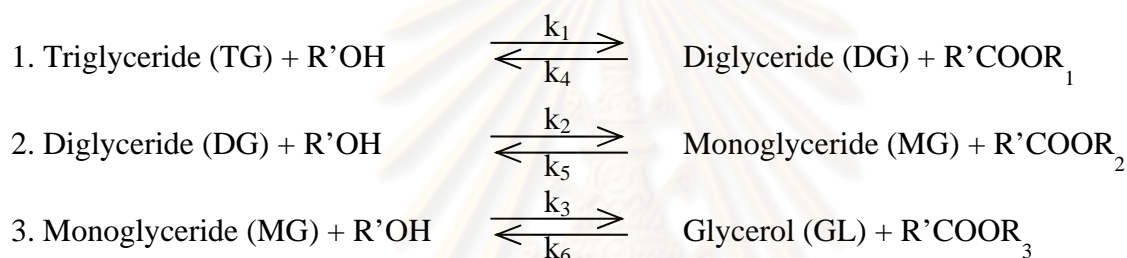


Figure 2.4 The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986).

2.2.5.1 Non-Catalytic transesterification method (Supercritical Methanol)

When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. Firstly, there no longer is a distinct liquid and vapor phase, but a single, fluid phase presents. Secondly, solvent containing a hydroxyl (OH) group, such as water or primary alcohol, takes on the properties of superacids. For this reason, transesterification in supercritical alcohol can be achieved without use of catalyst for production of biodiesel. With this process, used oil with high amount of free fatty acids can be used as a raw material. The only products are the ester or biodiesel (the upper phase) and glycerol (the lower phase). No soap is produced, thus the separation process is simple. In addition, alcohol used in biodiesel production such as methyl or ethyl alcohol

are polar solvents and have hydrogen bonding to which normally form cluster of these molecules, separating them from other non-polar compounds such as glyceride. Because the degree of hydrogen bonding decreases with increasing temperature, the polarity of alcohol would decrease in supercritical state. Thus, supercritical alcohol has a hydrophobic nature with the lower dielectric constant. As a result, non-polar triglycerides can dissolve in the supercritical alcohol to form a single phase of vegetable oil/methanol mixture (Kusdiana and saka, 2001).

2.2.5.2 Catalytic transesterification method

Alkali catalyzed process

All commercial biodiesel production today employs an alkali-catalyzed transesterification process. This process is accomplished by mixing alcohol (methanol) with sodium hydroxide or potassium hydroxide to make sodium methoxide. Then the sodium methoxide is added to vegetable oil in a reactor at molar ratio of oil and alcohol 6:1. The mixture was stirred and heat at 60-63 °C. After complete reaction, the mixture is allowed to cool to room temperature, and ester and glycerol were separated. Glycerol is left on the bottom and methyl esters, or biodiesel, is left on top. The ratio of 6:1 was found to be the best condition because methanol/oil molar ratio less than 6:1 resulted in incomplete reaction, and that above 6:1 makes the separation of glycerol difficult. The excess methanol can hinder the decantation by gravity. The apparent yield of esters decreases because some part of the glycerol remained in the biodiesel phase (Freedman et al., 1984).

The mechanisms of alkaline catalyzed transesterification are depicted in Figure 2.5. The first step (equation 1) is the reaction of the base (B) with alcohol (ROH), producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (equation 2) from which the

alkyl ester and the corresponding anion of the diglyceride are formed as shown in equation 3. The latter deprotonates the catalyst, thus regenerating the active species (equation 4) which is now able to react with a second molecule of the alcohol, starting another catalyst cycle. Diglycerides and monoglycerides are converted by the same mechanism to form a mixture of alkyl esters and glycerol.

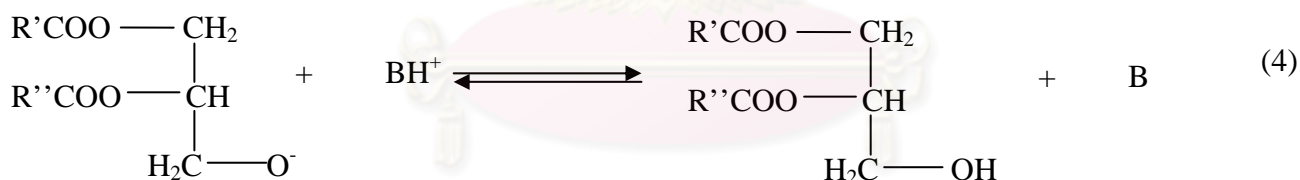
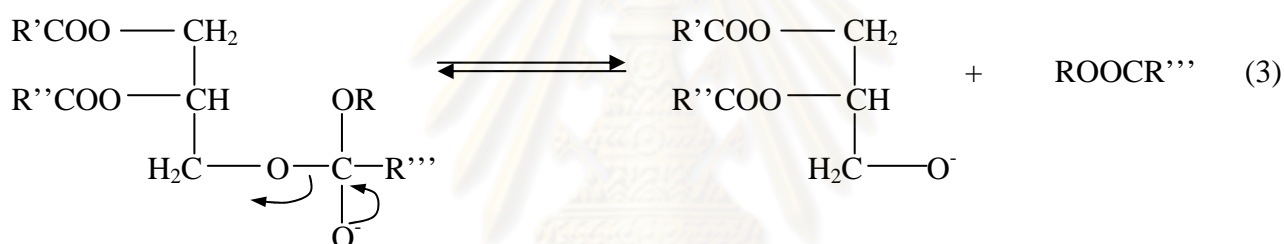
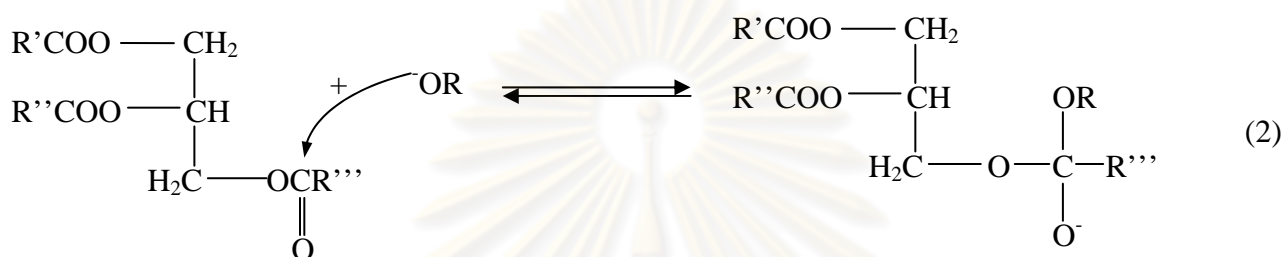


Figure 2.5 Mechanism of the alkali-catalyzed transesterification of vegetable oils

(Demirbas, 2005)

Alkali metal alkoxides (denoted as CH_3ONa for the methanolysis) are the most active catalyst, since they give very high yields (> 98 %) in short reaction time, about 30 minute even if they are applied at low molar concentrations (0.5 mol %). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxide, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of

vegetable oils just by increasing the catalyst concentration to 1 or 2 mol %. However, even if a water free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably caused difficulty for the recovery of glycerol due to the formation of emulsions.

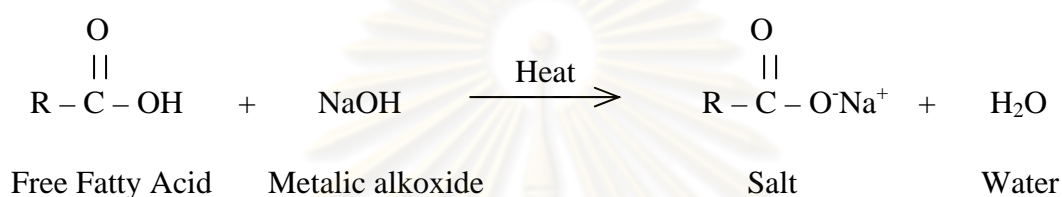


Figure 2.6 Saponification from free fatty acid

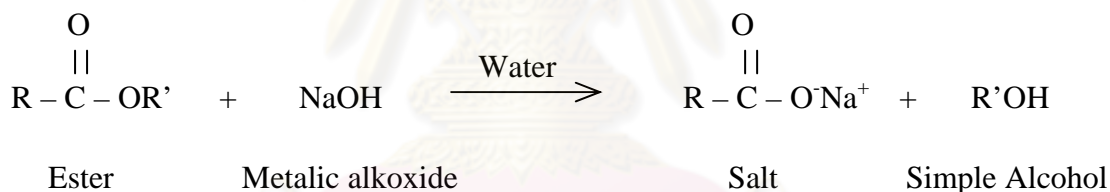


Figure 2.7 Saponification from ester

Acid catalyzed process

The transesterification process can be catalyzed by acids such as sulfuric or hydrochloric acids (Freedman et al., 1986). These catalysts give very high yield in alkyl esters, but the acid catalyzed reactions are generally slow, requiring, typically, temperatures above 100 °C and more than several hours to complete. Methanolysis of soybean oil, in the presence of 1 mol % of H₂SO₄ with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (>99 %) while the butanolysis (at 117°C) and

ethanolysis (at 78°C) using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively (Freedman et al., 1986).

The alcohol/vegetable oil molar ratio is one of the main factors that influences transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid catalyzed transesterification of vegetable oils is shown in Figure 2.8 for a monoglyceride. However, it can be extended to diglyceride and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III. Elimination of glycerol from the new ester IV, and regenerates the catalyst H^+ (Naik et al., 2006).

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid catalyzed transesterification should be carried out in the absence of water in order to avoid the competitive formation of carboxylic acid which reduces the yield of alkyl esters.

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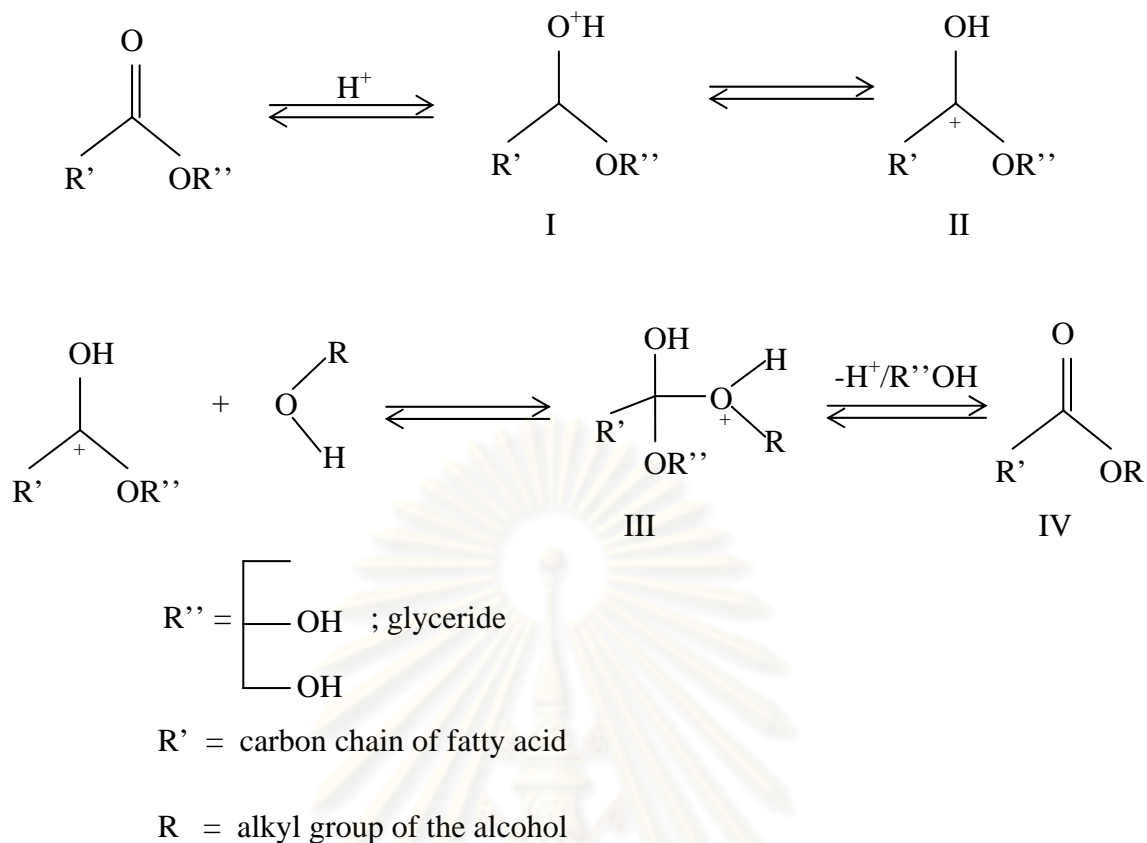


Figure 2.8 Mechanism of acid catalyzed transesterification (Naik et al., 2006).

Acid- and Alkali-catalysed two-step transesterification.

Two step transesterification in which the first acid catalyzed step was followed by the second alkali catalyzed step was developed for the production of biodiesel from oil with high FFA content. Initially, acid catalyst can be used to convert FFA to esters and to decrease FFA level. In the second step, alkali catalyst can be performed for the transesterification of oil. The technique overcomes the problem of a slow reaction rate with acid catalyst and the formation of soap with an alkaline catalyst and increases the ester yield. However, the problem with the removal of the catalysts is still a big issue for the two-step method (Dalai et al., 2006).

Enzymatic transesterification

Enzymatic transesterification of triglycerides has been suggested as a realistic alternative to the conventional physiochemical methods. Lipase is an effective enzyme for the transesterification of triglyceride. It is generally effective biocatalyst due to its substrate specificity, functional group specificity and stereo specificity in aqueous media. Lipases in living organisms hydrolyse triacylglycerols. This ability has been used until now for the synthesis of many compounds in very mild conditions. Through the use of these enzymes in water media, esterification and transesterification reactions can also be carried out. The major problem with this process however, is the enzyme stability and recovery. Therefore, immobilization is the most widely used method for achieving favorable stability of lipases and to make them more attractive for reaction (Clark, 1994). Moreover immobilization provides enzyme reuse and eliminates the costly processes of enzyme recovery and enzymes recycle. The reaction generally requires the following conditions: 30% enzyme based on oil weight; oil/alcohol molar ratio of 1:4; the temperature of 50 °C; and the reaction time of 7 h (Kose et al., 2002). Transesterification of rapeseed oil with 2-ethyl-1-hexanol and using *Candida rugosa* lipase powder gave 97 % conversions of ester (Linko et al., 1998). The stepwise addition of methanol into the reaction to avoid lipase inactivation converted 98.4% of the oil to methyl esters at 30 °C after 48 h (Kaieda et al., 1999). In this method, the recovery of glycerol is easy without any complex process and free fatty acid contain in waste oil or fat can be completely converted to methyl ester. However, the production of biodiesel fuel by enzymatic method has not often been used in industry because of the high cost of enzyme catalysts.

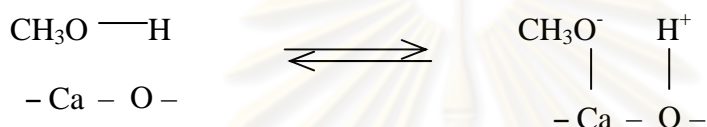
Heterogeneous catalysts process

Although homogeneous catalyzed biodiesel processes are relatively fast and gives high conversions with minimal side reaction, they still have several problems such as; (1) the catalyst cannot be recovered and must be neutralized at the end of the reaction, (2) there is limited use of continuous process, and (3) the processes are very sensitive to the presence of water and FFA which give rise to competing hydrolysis and saponification reactions. Nowadays, heterogeneous reaction is being considered in which the liquid catalyst is replaced by solid catalysts. This process could potentially lead to cheaper production costs because it is possible to reuse the catalysts and carry out both transesterification and esterification simultaneously (Goodwin et al., 2005). The ideal synthesis of fatty acid methyl esters need to involve continuous processing in a flow system, have as few reaction steps as possible, limit the number of separation processes, and use a robust heterogeneous catalyst (such as metal oxides). The appropriate solid catalysts could be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. Therefore, heterogeneous catalysts such as nickel, palladium, calcium carbonate and calcium oxide are new developed catalysts to lower the cost of production and reduce the amount of waste water. These heterogeneous or solid catalysts can be removed easily by filtration and can be used in a large scale production. Moreover, they can be reused, recycled and regenerated making the production cost more efficient. Many heterogeneous catalysts have been developed for transesterification of vegetable oil with methanol as shown in the part of literature reviews. The strong basic sites of calcium methoxide can catalyze the reaction with high methyl esters yield of 98% (Lui et al., 2008).

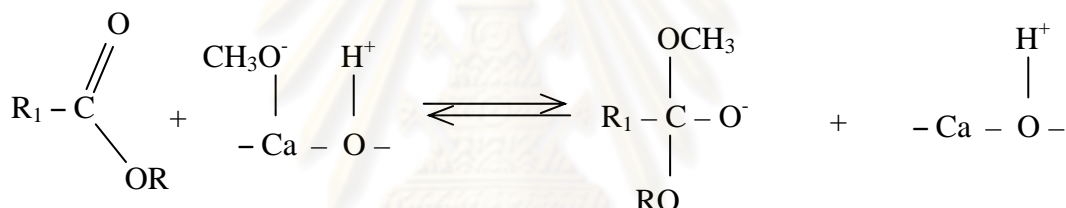
Although the heterogeneous catalysts have many advantages, lower methyl esters content and yield is still a problem. For this reason, improving the methyl esters content and yield in this catalytic system is of interest. The mechanism of transesterification of glyceride

to methyl esters in the presence of methoxide anion is as shown in figure 2.9. In the first step, the methoxide anion attaches to the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate (step 1a and 1b). In the second step, the tetrahedral intermediate picks up an H^+ atom from the surface of CaO (step2). The tetrahedral intermediate also can react with methanol to generate methoxide anion (step3). In the last step, the rearrangement of the tetrahedral intermediate results in the formation of biodiesel and glycerol (step4).

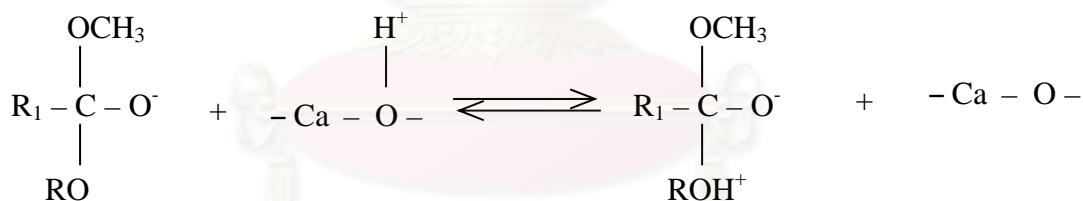
Step 1a



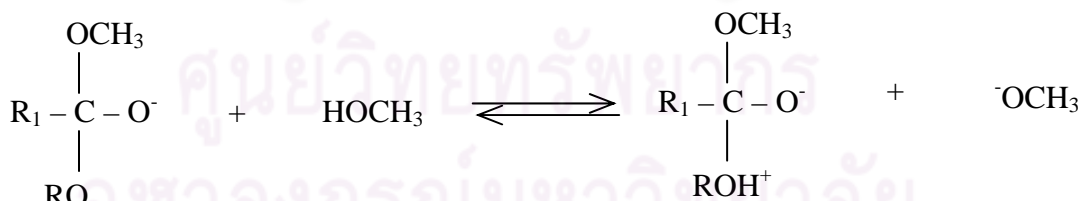
Step 1b



Step 2



Step 3



Step 4

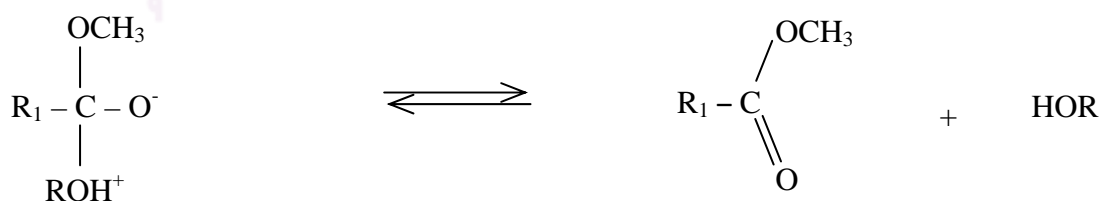


Figure 2.9 Reaction mechanisms of transesterification reaction over CaO by Lui et al. (2008)

2.3 Variables affecting transesterification and esterification

The process of transesterification and esterification are affected by various factors depending upon the reaction condition used. The effects of these factors are described below.

2.3.1 Ratio of alcohol to oil or fatty acids

For transesterification, it is generally known that one of the most important variables affecting the yield of ester is molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. However, the too high molar ratio of alcohol to vegetable oil can interfere with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it drives the equilibrium to back to the left, lowering the yield of esters.

For esterification, the molar ratio of alcohol to fatty acids is also of importance. In this case however, the stoichiometric ratio requires 1 to 1 mole ratio of the two reactants. Furthermore, no glycerol is produced. As a result, it is expected that lower alcohol to fatty acids molar ratio would be needed compared with triglyceride transesterification.

2.3.2 Reaction temperatures

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the catalytic reactions are conducted close to the boiling point of alcohol (60 to 70 °C), under atmospheric pressure. However, for supercritical conditions, the reaction is carried out under high pressure (45 MPa) and high temperature (above 300°C) (Kusdiana and saka, 2001).

2.3.3 Reaction time

The conversion increases with reaction time. For example, Freedman et al. (1984) studied the transesterification of peanut, cotton-seed, sunflower and soybean oil under the condition of methanol to oil molar ratio of 6:1, 0.5 % sodium methoxide catalyst, and at 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same (93-98%) for all four oils.

2.3.4 Use of organic co-solvent

An improved process by using of organic co-solvent was investigated by Krisnangkura and Simamaharnnop (1992) for methanolysis and ethanolysis of fatty acid glycerides. The processes comprise solubilizing oil or fat in methanol or ethanol by addition of toluene as co-solvent in order to form a one phase reaction mixture. The processes proceed quickly, usually in less than 20 min, at ambient temperature, atmospheric pressure, and without agitation. The co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactant. The lower alkyl fatty acid monoesters produced by the process can be used as biofuels and are suitable as diesel replacement or additives.

2.3.5 Purity of reactant

Impurities in the oil also affect conversion levels. Under the same condition, 67 to 84 % conversion into ester using crude vegetable oils can be obtained, compared with 94 to 97 % when using refined oils. The free fatty acids in the original oils interfere with catalyst, however, under conditions of high temperature and pressure this problem can be overcome (Freedman et al., 1984).

2.3.6 Catalyst type and concentration

Catalysts used for transesterification of triglyceride are classified as alkaline, acid, enzyme or heterogeneous catalyst, among which alkaline are the most effective transesterification catalyst compared to acidic catalyst. Sodium alkoxides are among the most efficient catalyst used, although KOH and NaOH can also be used. The alkaline catalyst concentration in range of 0.5 to 1 % by weight yields 94 to 99%. The acid could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Acid catalyst transesterification was widely studied with waste vegetable oil. In presence of 100 % excess alcohol, sulfuric acid (H_2SO_4) was found to have superior catalyst activity in the range of 1.5-2.25 M concentration (Mohamad, 2002).

2.3.7 Presence of water

In biodiesel production, it is well known that the vegetable oils used as raw material for the transesterification should be water free since water has a negative effect on the reaction. Water can consume the catalyst and reduce catalyst efficiency and it is believed that the presence of water has a greater negative effect than that of the free fatty acids. Therefore, it is generally recommended that for typical transesterification of vegetable oil, the water content should be kept below 0.06 % (Ma et al., 1999).

2.4 Literature reviews

A number of studies on preparation of biodiesel from vegetable oils have been reported using a variety of oils, alcohols, different catalysts, and reaction conditions. For alkali catalyzed process, Aracil et al., (2004) used different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for transesterification of sunflower oil. The biodiesel purity 90-100 wt.% was obtained for all

catalysts. However, biodiesel yields near 100 wt.% were only obtained with the methoxide catalysts. The reactions using sodium hydroxide turned out to be the fastest. Encinar et al., (2007) carried out a study on the transesterification of used frying oil and ethanol for the applications as biodiesel in internal combustion engines. 74.2% of ester yield was obtained using an ethanol/oil molar ratio of 12:1, potassium hydroxide as catalyst (1%), and 78 °C temperature. The transesterification of karanja oil with methanol was carried out using alkaline catalyst in a batch type reactor at 65 °C, with a molar ratio of 1:6 of the karanja oil to methanol, using KOH as catalyst (Meher et al., 2006). The 97% conversion to methyl esters was obtained after 3 h. Although high purity and yield of biodiesel can be achieved in a short time with the alkali process. However, it is very sensitive to the purity of reactants. The starting material (oil or fat) must be dried (moisture level <0.06%) and free of free fatty acid (FFA) (<0.5%). The presence of minor amount of FFA and moisture in the reaction mixture produces soap, which lower the yield of ester and renders the separation of ester and glycerol. FFA also consumed the catalyst and reduced catalyst efficiency (Zullaikah et al., 2005).

Another option to the alkali process is the acid catalyzed process. Mohamad et al., (2002) determined the effects of excess levels of ethanol, types of acid catalysts (H_2SO_4 , HCl) for transesterification of waste palm oil. It was found that H_2SO_4 performed better than HCl and at 100% excess ethanol, the reaction time was significant reduced. The experimental parameters such as amount of catalyst, temperature and time noticeably affected the biodiesel production. Zheng et al., (2006) studied the reaction kinetic of acid catalyzed (H_2SO_4) transesterification of waste frying oil in excess methanol to form fatty acid methyl esters for possible use as biodiesel. The oil:methanol:acid molar ratios and temperature were the most significant factors affecting the yield of fatty acid methyl ester. As a result of the large excess of methanol, the reaction completed (99±1% conversion) in 4 h. Although acid catalyzed process does have advantages such as reduced purification costs, the reaction is much slower.

Ramadhas et al., (2005) proposed a two-step transesterification process to convert the high free fatty acid (FFA) oil to its mono-ester in the first step via acid catalyzed esterification to reduce FFA content of the oil to less than 2%. Then, in the second step, alkaline catalyzed transesterification process converts the product of the first step to its mono-esters and glycerol. The major factors affecting the conversion efficiency of the process are such as oil to methanol molar ratio, the amount of catalyst, reaction temperature, and reaction time. However, for this two-step process, long reaction time, no recovery of catalyst, and high cost of reaction equipment were still the major disadvantages (Wang et al., 2007).

Recently, many kinds of heterogeneous catalysts have been applied for transesterification process, such as alkaline earth metal oxides, various alkali metal compounds supported on alumina or zeolite. Gorzawski et al. (1999), suggested that the production of alkyl ester would be simplified when heterogeneous catalysts were utilized. Furuta et al., (2004) prepared the solid superacid catalysts of sulfated tin, zirconium oxides and tungstated zirconia for the transesterification of soybean oil with methanol at 200–300 °C and the esterification of n-octanoic acid with methanol at 175–200 °C in a fixed bed reactor. The best solid superacid catalyst, Tungstated zirconia–alumina gave the conversion over 90% for both of the esterification and the transesterification process. Kim et al., (2004) developed Na/NaOH/ γ -Al₂O₃ heterogeneous base catalyst for transesterification of soybean oil with methanol using n-hexane as a co-solvent. The maximum biodiesel production yield reached to 94%, and the Na/NaOH/ γ -Al₂O₃ heterogeneous base catalyst showed almost the same activity under optimum conditions compared to the conventional homogeneous NaOH catalyst. Baba et al., (2005) studied transesterification of triolein with methanol and glycerolysis of triolein with glycerol are performed using this alkali metal salt-loaded alumina catalyst. A K₂CO₃-loaded alumina catalyst prepared by evacuation at 823 K gives methyl oleate and glycerol in the highest yields of 94 and 89%, respectively, at 333 K in 1

hour. This catalyst also effectively catalyzes the glycerolysis of triolein with glycerol to give dioleoyl glycerol at 71% yield at 453 K in 5 hour. A process for transesterification of soybean oil to methyl esters using alumina loaded with potassium as a solid base catalyst in a heterogeneous manner was reported [Xie et al.,(2006)] ; methyl ester at conversion yield of 96% could be obtained after 3 h using 35 wt%KI/Al₂O₃. Arzamendi et al., (2008) investigated the catalytic activity and selectivity of several compound of the alkaline and alkaline-earth metals in the transesterification of 12:1 of methanol to sunflower oil ratio, at 50 °C in a batch reactor. The result showed that the hydroxides of the alkaline metals (Li, Na, K, Rb, and Cs) were completely soluble in methanol and behaved as homogeneous catalysts and achieved the conversion of sunflower oil above 90% after 100 min of reaction. Alonso et al., (2009) studied the influence of the lithium content supported on CaO by using lithium amount above 4.5 wt% to promote the catalytic activity of CaO in the transesterification of sunflower oil. When activation temperature was above the melting point of LiNO₃ (492 K), the catalyst started to be active. Moreover the leaching of lithium and homogeneous contribution was significant for activation temperatures ≥ 973 K (87% in 3 h). Li₂O was shown in the sample, whereas the homogeneous contribution was relevant at activation temperatures above 773 K. Kansedo et al., (2009) studied the transesterification of palm oil by using montmorillonite KSF as a catalyst. With various conditions, the result showed that the yield of palm oil fatty acid methyl esters (FAME) could reach to 79.6% by using 3 wt% catalyst loading, 8:1 mol mol⁻¹ methanol to oil molar ratio, reaction temperature at 190 °C with period at 180 min. Karavalakis et al., (2010) studied the transesterification of cottonseed oil and used frying oil by using tetramethyl ammonium hydroxide and benzyltrimethyl ammonium hydroxide as catalyst. It was found that biodiesel ester content was related with the type of feedstock and the reaction variables i.e. catalyst concentration, methanol to oil molar ratio and reaction time. The results suggested that both catalysts activated high

conversion rates in transesterification process of cottonseed oil. Meanwhile, with waste oil as a substrate, lower ester yields were obtained, which were probably due to amide formation during the transesterification reaction. Baroutian et al., (2010) proved that palm shell activated carbon supported potassium hydroxide was an effective catalyst for transesterification of palm oil. The highest yield was found at 30.3 wt% catalyst loading, 64.1 °C reaction temperature and 24:1 methanol to oil molar ratio. Under these conditions 98.03% production yield was obtained with catalyst leaching of 0.53 ppm. Also this study showed that the physical and chemical properties of the produced biodiesel by using potassium hydroxide catalyst supported on palm shell activated carbon met the ASTM standard.

CaO has been studied as a solid strong base catalyst by many researchers because CaO has higher activity, mild reaction conditions, long catalyst lifetimes and low catalyst cost. Reddy et al., (2006) investigated the possibility of using nanocrystalline calcium oxides under room-temperature. They found that the reaction rate was slow and it required 6–24 h to obtain high conversion with the most active catalyst. The deactivation of the catalyst was observed after eight cycles when using soybean oil as a substrate and after three cycles with poultry fat. Zhu et al., (2006) obtained a 93% conversion of jatropha curcas oil using treated CaO treated with an ammonium carbonate solution and calcinated at high temperature. Kouzu et al., (2008) studied the synthesis of methyl esters using CaCO_3 , Ca(OH)_2 and CaO catalysts that calcined at 900 °C for 1.5 h with waste cooking oil ratio of methanol/oil of 42:1, used 1 %wt of catalysts, 65°C and 4 h for the reaction. The results showed that the catalytic activity was in the sequence of $\text{CaO} > \text{Ca(OH)}_2 > \text{CaCO}_3$. The yield of fatty acid methyl esters was 93% for CaO, 12% for Ca(OH)_2 and 0% for CaCO_3 under the same reacting condition after 1 h of reaction time. Macleod et al., (2008) evaluated the activity of LiNO_3/CaO , NaNO_3/CaO , KNO_3/CaO and LiNO_3/MgO for transesterification of rapeseed oil. All series of alkali-doped metal oxide catalyst exhibited more than 90% conversion in 3

h. Albuquerque et al, (2009) used MgO/CaO as a model reaction to test the potential of these catalysts in triglycerides transesterification of ethyl butyrate with methanol at 333K and atmospheric pressure. These catalysts showed the conversion close to 60% when increasing CaO content in the mixture up to 1:3 molar ratio of Mg to Ca. Bai et al, (2009) reported CaO microsphere catalyzed the transesterification reaction of soybean oil for biodiesel with the high transesterification yield of 98.72%. The simply synthetic process, low cost and high potential of production were the advantages of the porous CaO microsphere. Chakraborty et al., (2010) developed a fly ash supported CaO catalyst derived from waste egg shell for transesterification of soybean oil into biodiesel, in which high catalytic performance was reported corresponding to 96.97% fatty acid methyl ester (FAME) yield upon 30 wt% CaO loading, 1.0 wt% catalyst concentration and 6.9:1 methanol to oil molar ratio. Under the utilization of waste products, fly ash and egg shell, this process created an effective avenue of waste valorization for the green energy. Hsiao et al., (2011) tested that nano CaO significantly improved the transesterification efficiency of soybean oil to biodiesel assisted by microwave irradiation. It was found that microwave irradiation was more efficient than the conventional bath for biodiesel production catalyzed by nano CaO. Achieving a conversion rate of 96.6% was subjected to 60 min transesterification reaction, 7:1 methanol to oil molar ratio, 3.0 wt% catalyst loading and reaction temperature at 333K. Hu et al., (2011) indicated that a nano-magnetic catalyst KF/CaO-Fe₃O₄ could be prepared by a facile impregnation method. The results which were tested by vibrating sample magnetometer (VSM) showed that the catalyst has a unique porous structure with an average particle diameter of 50 nm. With its ferromagnetic property, the catalyst could be recovered by magnetic separation. The best activity was obtained by using 25 wt% KF loading, 5 wt% Fe₃O₄ and 600 °C for 3 h. Moreover, the catalyst recovery was more than 90% when testing at 65 °C, 12:1 methanol to oil molar ratio and 4 wt% catalyst concentration. Under the optimal conditions, the biodiesel

yield over 95% at 3 h of reaction time was obtained. This study showed that the nano magnetic solid base catalyst, $\text{KF}/\text{CaO}-\text{Fe}_3\text{O}_4$, used in the preparation of biodiesel could also be a good prospect of development and application.



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Table 2.2 Review studies production of biodiesel.

Reference	Material	Catalyst	Method	Temp. (°C)	Condition Molar ratio Alcohol:oil	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Ma et al. (1999)	beef tallow methanol	NaOH	Transesterification (alkali catalyst) (0.3 wt% cat.)	80	6:1	110-330 1-3 min	30 min	450	GC	To determine the effect of mixing (the stirring speeds and the stirring time) on transesterification of beef tallow with NaOH-MeOH.
Vicente et al. (2004)	sunflower oil methanol	KOH NaOH CH ₃ OK CH ₃ ONa	Transesterification (alkali catalyst) (1 wt% cat.)	65	6:1	600	4	100	GC	To compare the different types of base catalysts for transesterification of sunflower oil.
Meher et al. (2006)	karanja oil methanol	KOH	Transesterification (alkali catalyst) (0.25-1.5 wt% cat.)	37-65	6:1-24:1	180-600	3	1000	HPLC ¹ H NMR	To investigate the optimum conditions that influenced the yield of biodiesel from transesterification of karanja oil with methanol.
Rashid et al. (2008)	rapeseed oil methanol	KOH NaOH CH ₃ OK CH ₃ ONa	Transesterification (alkali catalyst) (0.25-1.5 wt% cat.)	35-65	3:1-21:1	180-600	2	-	GC	To optimize the operating conditions for the production of biodiesel with the alkali catalysts and rapeseed oil.
Mohamad et al. (2002)	waste palm oil ethanol	H ₂ SO ₄ HCl	Transesterification (acid catalyst) (0.5-2.25 M cat. conc.)	90	-	-	30	-	-	To find the effect of access levels of ethanol, types of acid catalysts and different concentration of HCl for transesterification of waste palm oil.

Reference	Material	Catalyst	Method	Temp. (°C)	Condition Molar ratio Alcohol:oil	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Zheng et al. (2006)	waste frying oil methanol	H ₂ SO ₄	Transesterification (acid catalyst) (0.5-1 M cat. conc.)	70-80	50:1-250:1	100-600	4	5000	*GPC	To determine the reaction kinetics of acid catalyzed transesterification of waste frying oil in excess methanol to form fatty acid methyl esters.
Chongkhong et al. (2007)	palm fatty acid distillate (PFAD) methanol	H ₂ SO ₄	Esterification (acid catalyst) (0-5.502 wt% cat.) (batch-CSTR)	70-100	0.4:1-12:1	-	15-240 min	22400	*TLC	To produce the fatty acid methyl ester (FAME) from palm fatty acid distillate (PFAD) having high free fatty acids (FFA) in esterification process with acid catalyst.
Bhatti et al. (2008)	waste tallow methanol	H ₂ SO ₄ KOH	Transesterification (acid-base catalyst)	30-60	30:1	-	24	250	GC	To compare the types of catalysts between acid catalyst and base catalyst from transesterification of waste tallow with methanol.
Furata et al. (2004)	soybean oil n-octanoic acid methanol	SZA WZA STO	Transesterification Esterification (solid catalyst) (4 g. cat.)	200-300 175-200	40:1 4.5:1	- -	20 20	- -	GC-MS GC	To compare three types of solid superacid catalysts in the transesterification of soybean oil with methanol and the esterification of n-octanoic acid with methanol.

*GPC = Gel Permeation Chromatography

*TLC = Thin Layer Chromatography

Reference	Material	Catalyst	Method	Temp. (°C)	Condition Molar ratio Alcohol:oil	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Kim et al. (2004)	soybean oil methanol n-hexane	Na/NaOH/ γ -Al ₂ O ₃	Transesterification (solid catalyst)	60	9:1	300	2	100	GC	To study for optimizing the reaction conditions such as the reaction time, the stirring speed, the use of co-solvent, the oil to methanol ratio and the amount of catalyst and compare with the conventional NaOH catalyst.
Xie et al. (2006)	soybean oil methanol	Mg-Al hydrotalcite	Transesterification (solid catalyst) (1-9 wt% cat.)	*MR	2:1-20:1	600	2-20	250	¹ H NMR	To Find the suitable catalyst and conditions for the methanolysis of soybean oil.
Xie et al. (2006)	soybean oil methanol	Al ₂ O ₃ KF/Al ₂ O ₃ KCl/Al ₂ O ₃ KBr/Al ₂ O ₃ KI/Al ₂ O ₃ K ₂ CO ₃ /Al ₂ O ₃ KNO ₃ /Al ₂ O ₃ KOH/Al ₂ O ₃ KI/ZrO ₂ KI/ZnO KI/NaX KI/KL	Transesterification (solid catalyst) (1.0-35 wt% KI/Al ₂ O ₃)	MR	9:1-24:1	-	1-10	250	¹ H NMR	To determine the amount of potassium iodide loading on alumina for biodiesel production from soybean oil and find the reaction variables for the suitable conditions.

*MR = methanol reflux temperature

Reference	Material	Catalyst	Method	Temp. (°C)	Condition Molar ratio Alcohol:oil	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Zhu et al. (2006)	jatropha curcas oil methanol	CaO	Transesterification (solid catalyst) (0.5-2.5 wt% cat.)	50-70	9:1	-	1-4	100	Spectro- photo- meter	To study for optimizing the reaction conditions for the transesterification of jatropha curcas oil with calcium oxide.
Xie et al. (2007)	soybean oil methanol	KOH/NaX zeolites	Transesterification (solid catalyst) (1.0-6.0 wt% cat.)	65	2:1-16:1	200-800	4-12	100	NMR	To study the transesterification of soybean oil to methyl ester using KOH/NaX zeolites at methanol reflux temperature.
Liu et al. (2007)	soybean oil methanol	SrO	Transesterification (solid catalyst) (0.5-3 wt% cat.)	55-70	6:1-18:1	1000	5-30 min	100	GC	To investigate the reaction mechanism and the suitable operating conditions for transesterification of soybean oil using SrO as a solid catalyst.
Kouzu et al. (2008)	soybean oil methanol	CaO	Transesterification (solid catalyst) (0.78 g of CaO)	MR	12:1	500	0.5-1.0	500	¹³ C NMR	To develop a process of biodiesel production using active phase of calcium oxide as a solid base catalyst.
Kouzu et al. (2008)	soybean oil waste cooking oil methanol	CaO Ca(OH) ₂ CaCO ₃	Transesterification (solid catalyst) (0.78 g of CaO)	MR	12:1	500	0.5-2.0	500	¹³ C NMR	To compare solid base catalysts for biodiesel production with refluxing methanol.

Reference	Material	Catalyst	Method	Temp. (°C)	Condition Molar ratio Alcohol:oil	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Liu et al. (2008)	soybean oil methanol	CaO K ₂ CO ₃ /g-Al ₂ O ₃ KF/g-Al ₂ O ₃	Transesterification (solid catalyst) (8 wt% cat.)	50-80	3:1-18:1	800	0-3.0	100	GC	To propose the transesterification reaction mechanism in the presence of a little water in methanol and find the effects of the reaction conditions and the catalyst lifetime.
Singh et al. (2008)	soybean oil methanol	PbO PbO ₂ Pb ₃ O ₄ MgO ZnO CaO Ti ₂ O ₃	Transesterification (solid catalyst) (0.5-3 wt% cat.)	75, 150, 225	7:1	-	2	-	GC	To study seven different solid catalysts (metal oxide) with different surface area, acidity/basicity and temperature for transesterification of soybean oil.
Alonso et al. (2009)	Sunflower Oil Methanol	Li/CaO	Transesterification solid catalyst (0.2 wt% cat.)	60	14 : 1	1000	3	100	GC	To study the influence of using Li/CaO catalysts in the transesterification reaction by
Bai et al. (2009)	Soybean Oil	porous CaO microsphere CaCO ₃ CaCl ₂ Na ₂ CO ₃	Transesterification (Solid catalyst) (3 wt% cat.)	65	9 : 1	-	3	250	GC	To develop a simple and low cost route for porous CaO microsphere in catalyzing transesterification reaction of vegetable oil for biodiesel product.

Reference	Material	Catalyst	Method	Temp.	Condition Molar ratio Alcohol:oi	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Kansedo et al. (2009)	Palm Oil	Montmorillonite KSF	Transesterification (Solid catalyst) (1-5 wt% cat.)	50	4:1-12:1	-	1 - 5	-	GC	To study the optimal reaction conditions by using montmorillonite KSF as a
Albuquerque et al. (2009)	Ethyl Butyrate Methanol	MgO/CaO	Transesterification (Solid catalyst)	60	4 : 1	1250	1	-	GC	To study for MgCa metal oxide catalysts with different Mg/Ca
Baroutian et al. (2010)	Palm Oil	KOH/Palm shell Activated Carbon	Transesterification (Solid catalyst)	50-60	6:1 - 24:1	700	1	150	GC	To study the optimal conditions and catalyst reusability of biodiesel production from palm oil using KOH catalyst supported on palm shell
Chakraborty et al. (2010)	Soybean Oil Methanol	Fly ash/egg shell/CaO	Transesterification (Solid catalyst) (1 - 5 wt% cat.)	70	5.5:1 - 6.9:1	500	5	100	GC	To develop the industrial waste i.e. fly ash and municioal waste i.e. egg shell to be utilized in converting soybean oil into fuel grade biodiesel with low-cost, high efficiency and the generation of green energy.
Karavalakis et al. (2010)	Cottonseed oil Used frying oil	tetramethyl NH ₄ OH benzyltrimethyl NH ₄ OH	Transesterification (Solid catalyst) (1 - 3.5% wt cat)	65	6 : 1, 9 : 1 and 12 : 1	-	1.5	-	GC	To investigate the optimal conditions for biodiesel production using amine-based liquid catalysts.

Reference	Material	Catalyst	Method	Temp.	Condition Molar ratio Alcohol:oi	Stirring speed (rpm)	Time (h)	Volume reactor (ml)	Analysis	Objective
Hsiao et al. (2011)	Soybean Oil Methanol Microwave Irradiation	Nano CaO	Transesterification (Solid catalyst) 1.0 - 5.0 wt% cat.	50 - 70	6:1 - 10:1	350	15, 30, 45, 60 and 75 Min	250	GC	To examine the effect of nano CaO and suitable reaction conditions on the transesterification of soybean oil assisted by microwave irradiation.
Hu et al. (2011)	Stillingia Oil Methanol	KF/CaO-Fe ₃ O ₄	Transesterification (Solid catalyst)	65	12 : 1	-	3	100	GC	To determine the effect of using nano magnetic solid base catalyst and the reusability for biodiesel production.

CHAPTER III

MATERIALS AND METHODS

This chapter is categorized in five parts: chemicals, catalyst preparation, catalyst characterization biodiesel production and ethyl ester analysis.

3.1 Chemicals

Soybean oil used in the experiments was obtained from Thanakorn Vegetable Oil Products Co. Ltd. (SamutPrakan, Thailand), which consisted of linoleic acid 49.4%, oleic acid 26.5%, palmitic acid 12.3%, linolenic acid 5.9%, stearic acid 5.8%, and traces of other acids. CaO, NaOH, KOH, NH₄OH and Ca(OH)₂ were purchased from Ajax Finechem (New South Wales, Australia). Limestone was obtained from a local cement factory (Saraburi, Thailand).

3.2 Catalyst preparation

3.2.1 Preparation of catalyst without loading modified agent

30 grams of CaO, limestone and Ca(OH)₂ were calcined in a muffle furnace at 800 °C for 24 h without gas purge.

3.2.2 Preparation of CaO loaded with Ca(OH)₂, NH₄OH, NaOH and KOH

The catalysts were prepared by an impregnation method using aqueous solutions of basic compounds investigated (e.g. Ca(OH)₂, NH₄OH, NaOH and KOH), according to the following procedure.

1. About 25 ml of the aqueous solution of the basic compound with the predetermined concentration was added into 30 grams of CaO powder. The mixture was stirred.
2. The products were dried for 6 h at room temperature.
3. The resulting powder was further dried in an oven at 100 °C overnight.

4. Prior to the reaction, the thus-obtained powder was calcined in a muffle furnace at 800 °C for 24 h without gas purge.

5. All catalysts were kept in a desiccators before using in the experiment.

The method for preparing all catalysts are presented in Table 3.1.

Table 3.1 The Methods for preparing all catalysts.

Sample No.	Sample Name	Drying		Calcination	
		Temp. (°C)	Time (h)	Temp. (°C)	Time (h)
1	commercial CaO	-	-	-	-
2	commercial Ca(OH) ₂	-	-	-	-
3	CaO*	100	12	800	24
4	Ca(OH) ₂ *	100	12	800	24
5	CaO* from limestone	100	12	800	24
6	[H ₂ O/CaO]*	100	12	800	24
7	[0.4M Ca(OH) ₂ /CaO]*	100	12	800	24
8	[1.0M Ca(OH) ₂ /CaO]*	100	12	800	24
9	[0.5M NH ₄ OH/CaO]*	100	12	800	24
10	[1.0M NH ₄ OH/CaO]*	100	12	800	24
11	[0.5M NaOH/CaO]*	100	12	800	24
12	[1.0M NaOH/CaO]*	100	12	800	24
13	[0.5M KOH/CaO]*	100	12	800	24
14	[1.0M KOH/CaO]*	100	12	800	24

* Identified for the catalysts under the activation treatment by the calcination at 800°C for 24 h without gas purge.

3.3 Catalyst characterization

Various characterization techniques were used in this study in order to clarify the catalyst structure and morphology, basic strength and surface composition of various catalysts.

3.3.1 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns of powder were recorded using a Bruker D8 Advance X-ray diffractometer (Baden-Wurttemberg, Germany) with Cu K_{α} radiation ($\lambda = 0.15064$ nm) operating at 40 kV and 30 mA. The spectra were scanned at the rate 0.02 °/step from $2\theta = 10^{\circ}$ to 80° . The XRD analysis of samples have been performed to obtain more information about the catalysts structure. In addition, the crystallite size was estimated from line broadening according to the Scherrer equation.

3.3.2 Nitrogen physisorption (BET surface area)

The specific surface area, pore size and pore volume were measured via the Brunauer-Emmet-Teller (BET) technique, using Nitrogen as the adsorbate at liquid N₂ temperature (-196 °C) on a Micromeritics ASAP 2020 automated instruments (Atlanta, USA). 0.3 g of sample was degassed at 150 °C under vacuum. After degassing the sample was run at -196 °C for 3 h.

3.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was performed to study catalyst crystal size and the diffraction pattern using a JEOL JEM-2010 (Tokyo, Japan) transmission electron microscope operated at 200 kV with an optical point to point resolution of 0.23 nm. The sample was dispersed in ethanol prior to the TEM measurement.

3.3.4 Temperature programmed desorption (TPD)

Temperature-programmed desorption of carbon dioxide (CO₂-TPD) was used to determine the base properties of catalysts. TPD experiments were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at its calcination temperature (800 °C) in a

helium flow for 1 h, and then saturated with a pure CO₂ flow (50 mLmin⁻¹) after cooling to 100 °C. After that, it was purged with the helium at 100 °C for 1 h to remove weakly physisorbed CO₂. The TPD of CO₂ was carried out at temperature between 100 °C and 800 °C under a helium flow (10 °C min⁻¹, 30 mLmin⁻¹). The areas of desorption profiles were obtained from a Micromeritics ChemiSorb 2750 pulse chemisorption system analyzer (Atlanta, USA). For the broad desorption peak, it was separated into many sub-peaks by using the Fityk program for peak fitting. All areas of sub-peaks were summed to calculate the total amount of base sites.

3.3.5 Thermal gravimetric analysis (TGA)

TG measurement was carried out with a instruments SDTQ600 analyzer. The prepared catalysts were subjected to a differential thermal analysis to determined the temperature of possible decomposition and phase change in the range of 25-800 °C. The samples of 10–20 mg and temperature ramping at 5 °C min⁻¹ were used in the operation. The carrier gas was N₂ Ultra High Purity.

3.4 biodiesel production

The transesterification reactions were carried out in 250 ml one-necked glass flask containing the mixtures of soybean oil/ethanol in an incubator. The working scopes are as follows:

- Molar ratio of ethanol to soybean oil (3:1, 6:1, 9:1, 12:1, 15:1, 18:1)
- Mass ratio of catalyst to soybean oil (1.4%-34.5wt% oil)
- The resident time of reaction from 2-21 h.
- Basic compounds for loading : Ca(OH)₂, NH₄OH, NaOH and KOH
- The reusability of solid catalysts (For 1- 3 recycle use)

The samples were taken out from the reaction mixture every 2 h. After the sample was centrifuged, it formed two phases. The upper layer was primarily composed of biodiesel, glycerol and excess ethanol, and the lower layer was a mixture of solid catalyst and glycerol. Once the mixture in the upper layer was separated, the biodiesel was purified by washing with warm water to remove glycerol and excess ethanol. Then, all contents were decanted to separate biodiesel from the mixture.

3.5 Ethyl ester analysis

The biodiesel samples were analyzed by gas chromatography (GC) (Shimadzu 14B, Tokyo, Japan) with consist of a column (Rtx 5, 30 m, 0.25 mm ID, 0.25 μm) and flame ionization detector (FID). The parameters for the oven temperature program consisted of: start at 150 $^{\circ}\text{C}$, ramp at 5 $^{\circ}\text{C min}^{-1}$ to 250 $^{\circ}\text{C}$. The sample for the GC was prepared by adding 0.1 ml of biodiesel sample.

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CHAPTER IV

RESULTS AND DISCUSSION (PART I)

This chapter presents the results of ethyl ester productions from soybean oil using calcium oxide based catalysts. The catalysts are commercial CaO, CaO* from limestone, commercial Ca(OH)₂, calcined CaO and calcined Ca(OH)₂. The effects of operational parameters such as a molar ratio of ethanol to oil, a mass ratio of catalyst to oil, reaction time and type of catalysts on the transesterification were examined.

4.1 Characterization of vegetable oils

The raw material for based catalyst transesterification must be free of water content because it causes soap formation, which consumed the catalyst and reduced the catalyst efficiency. Soap also causes an increase in viscosity, formation of gels and makes the separation of glycerol difficult. The basicity on the catalyst is compensated by the acidity and results in catalyst deactivation when there is high free fatty acid content. The acid value and moisture content of soybean oil are summarized in Table 4.1.

Table 4.1 The properties of soybean oil (Thanakorn Vegetable Oil Products Co. Ltd.)

Properties	Soybean oil
Acid value, mgKOH/g	0.2
Moisture Content, %	0.1

The commercially available edible grade soybean oil are categorized as linoleic acid oils. The fatty acid composition of soybean oils analyzed by gas chromatography is shown in

Table 4.2. (Zhenqiang et al., 2007) The major fatty acid components are linoleic acid (49.4%), oleic acid (26.5%) and palmitic acid (12.3%). The average molecular weight of soybean oil calculated from the saponification value are 874 g/mole.

Table 4.2 Fatty acid composition of soybean oil (Zhenqiang et al., 2007)

Fatty acid	Composition (%)
Palmitic acid	12.3
Stearic acid	5.8
Oleic acid	26.5
Linoleic acid	49.4
Linolenic acid	5.9
Molecular Weight, g/mole	874

4.2 Characterization of catalysts

In this study, the modified catalysts were prepared by the impregnation of calcium hydroxide over calcium oxide support. All catalysts except commercial CaO and commercial Ca(OH)₂ were dried in the oven at 100°C overnight and calcined in a muffle furnace at 800°C for 24 h without gas purge. After that all catalysts were kept in desiccators before using in the experiment.

4.2.1 X-ray diffraction analysis

The XRD patterns of commercial CaO, CaO*, commercial Ca(OH)₂, Ca(OH)₂*, CaO* from limestone and modified CaO* catalysts with different amount of Ca(OH)₂ loading are shown in Figure 4.1. The diffraction peaks at 32.3°, 37.4°, 54.0°, 65.2° and 67.5° were those of calcium oxide being similar to those from previous reports (Zhu et al., 2006;

Granados et al., 2007; Kouzu et al., 2008; Ngamcharussrivichai et al., 2008). The diffraction peaks at 18.1° , 28.8° , 34.1° , 47.1° and 50.8° in all catalyst series represented calcium hydroxide (Granados et al., 2007). No peak of calcium carbonate was observed in any of these XRD patterns. Ca(OH)_2 is an ionic solid that is slightly soluble in water. By loading Ca(OH)_2 , which was dispersed in water on CaO particles, the CaO particles were soaked in a saturated Ca(OH)_2 aqueous solution and were covered with a thin layer of Ca(OH)_2 . It was suggested that due to the interaction of CaO and Ca(OH)_2 in the granular, it was relatively more difficult to oxidize Ca(OH)_2 . The XRD result indicated the existence of Ca(OH)_2 dispersed on CaO catalysts prepared by the calcinations of limestone and $[\text{Ca(OH)}_2/\text{CaO}]^*$, but not the one from Ca(OH)_2^* . However, the Ca(OH)_2 peaks were considerably smaller than those of the CaO. Therefore, in these particles, Ca(OH)_2 might not be completely decomposed to CaO.

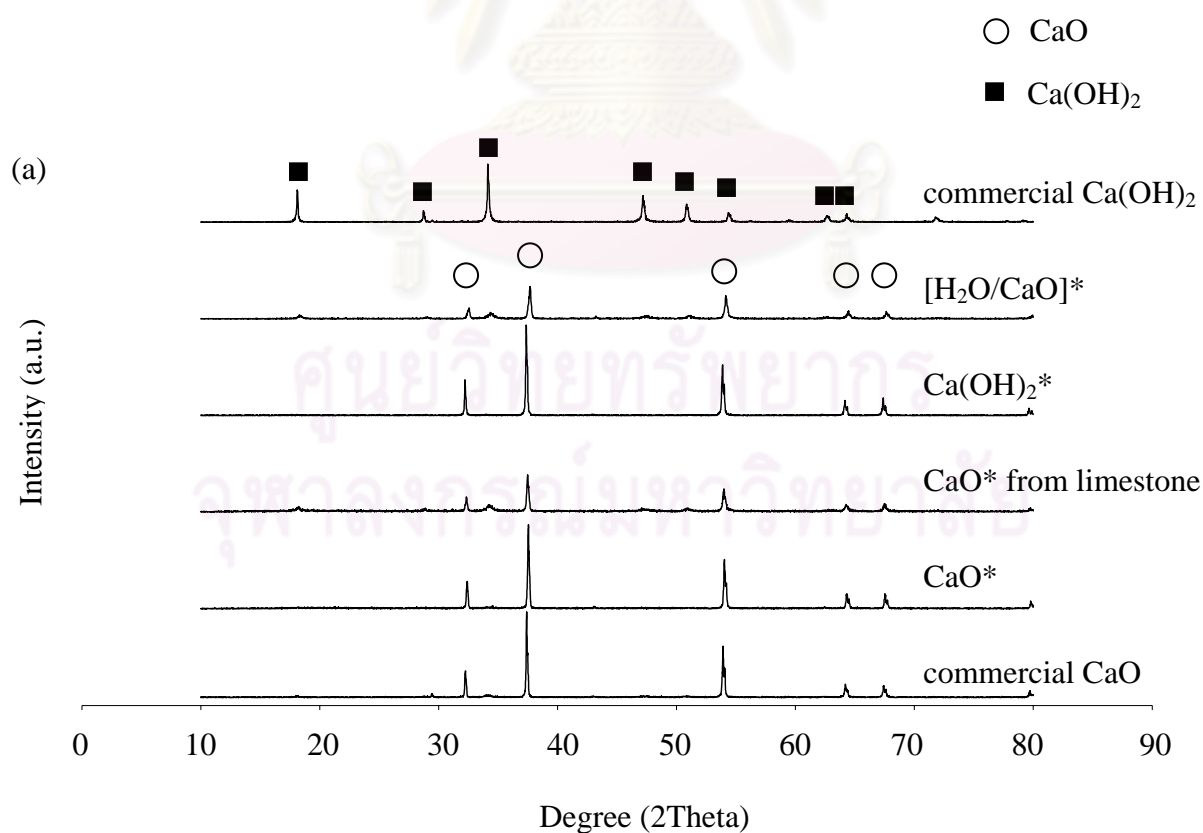


Figure 4.1 XRD patterns of the employed catalysts. CaO (○), Ca(OH)_2 (■).

4.2.2 Nitrogen physisorption (BET surface area)

The BET surface area, pore volume and pore diameter of all catalysts are presented in Table 4.3. The BET surface areas of the $[\text{Ca}(\text{OH})_2/\text{CaO}]^*$ were 6.2-7.4 m^2/g , which was about 3 folds that of CaO^* owing to the deposit of $\text{Ca}(\text{OH})_2$ on the surface areas. Since the pore volumes of them were all less than 0.03 cm^3/g , the materials appeared to have nonporous structures. The detected pore size and pore volume should belong to the interparticle voids. From the previous reports, the BET surface areas of CaO were 6-13 m^2/g , (Zhu et al., 2006; Arzamendi et al., 2008; Kouzu et al., 2008) whereas, those of CaCO_3 were 0.6-10 m^2/g (Arzamendi et al., 2008; Kouzu et al., 2008) and that of $\text{Ca}(\text{OH})_2$ was 16 m^2/g (Kouzu et al., 2008). The variations in the values could be according to individual differences in material source and treatment.

Table 4.3 Comparison of BET surface area, pore volume and average pore diameter of various types of catalysts.

Sample No.	Catalyst	Total	Average	
		surface area ^a (m^2/g)	pore volume ^a (cm^3/g)	pore diameter ^a (nm)
1	commercial CaO	1.6	0.013	9
2	commercial $\text{Ca}(\text{OH})_2$	5.5	0.020	15
3	CaO^*	2.4	0.006	10
4	$\text{Ca}(\text{OH})_2^*$	6.2	0.019	13
5	CaO^* from limestone	5.9	0.016	11
6	$[\text{0.4M Ca}(\text{OH})_2/\text{CaO}]^*$	7.4	0.027	14
7	$[\text{1.0M Ca}(\text{OH})_2/\text{CaO}]^*$	6.2	0.021	14

^a Calculated by BET method.

4.2.3 Transmission electron microscopy (TEM)

The TEM micrographs of all catalysts are demonstrated in Figure 4.2. The TEM images showed that all of the applied catalysts were in sizes of 30-300 nm. It was found that the crystal sizes of CaO* and Ca(OH)₂* were considerably larger than the untreated ones and the crystal size of [Ca(OH)₂/CaO]* was much larger than that of CaO*. After loading calcium hydroxide on CaO, the morphologies of the particle became similar to the calcined CaO* from limestone and Ca(OH)₂*. The crystallite sizes determined by XRD patterns of CaO* from limestone, Ca(OH)₂* and [Ca(OH)₂/CaO]* were all in the range of 30-40 nm (Table 4.4). When compared the crystallite size calculated from XRD line broadening with those obtained from TEM micrographs, it was found that the crystallite size obtained from TEM were much larger due to the accumulation of single crystals.

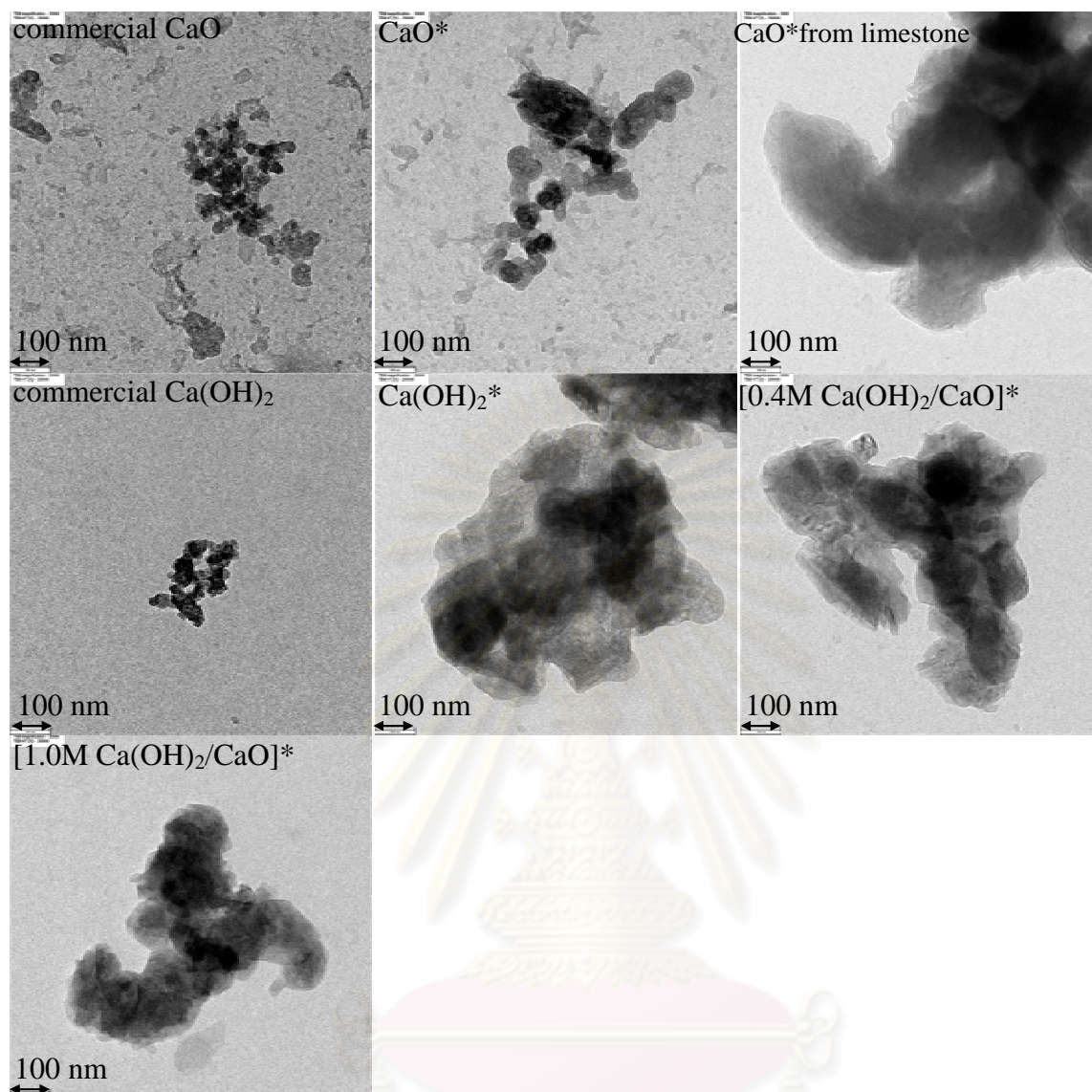


Figure 4.2 TEM micrographs of catalysts

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Table 4.4 Comparison of crystallite size and based sites of various types of catalysts.

Sample No.	Catalyst	Crystallite size ^a (nm)		Base sites ^b ($\mu\text{mole/g}$)
		CaO	Ca(OH) ₂	
1	commercial CaO	41	13	n.d.
2	commercial Ca(OH) ₂	0	36	10,611
3	CaO*	39	0	1,129
4	Ca(OH) ₂ *	36	0	2,868
5	CaO* from limestone	33	15	2,966
6	[0.4M Ca(OH) ₂ /CaO]*	37	19	2,590
7	[1.0M Ca(OH) ₂ /CaO]*	38	40	3,145

^a Determined by XRD patterns using Scherrer's equation.

^b Measured by CO₂ -TPD.

n.d. = not determined

4.2.4 Temperature-programmed desorption of carbon dioxide (CO₂-TPD)

The base properties of the catalysts could be measured by using CO₂-TPD techniques (Albuquerque et al., 2007; Kouzu et al., 2008). The CO₂-TPD profiles of catalysts are shown in Figure 4.3. The amounts of base sites summarized in Table 4.4 are calculated from the area below the curve of TPD profiles. The characteristic peaks of these profiles are assigned to their desorption temperatures indicating the strength of basic sites. For CO₂-TPD profiles (Figure 4.3), the CO₂ desorption peaks at high temperature (500-650°C) (Albuquerque et al., 2007) appear in all profiles, suggesting that all catalysts have strong base sites. The order of base sites of the catalysts after calcinations are: CaO* < [0.4M Ca(OH)₂/CaO]* < Ca(OH)₂* < CaO* from limestone < [1.0M Ca(OH)₂/CaO]*. The basicity of [Ca(OH)₂/CaO]* increased with the amount of Ca(OH)₂ loading. The untreated Ca(OH)₂ was more base sites than its oxide (about 3.7 folds). The basic sites can be either Bronsted or Lewis bases, which cannot be differentiated by CO₂ TPD technique.

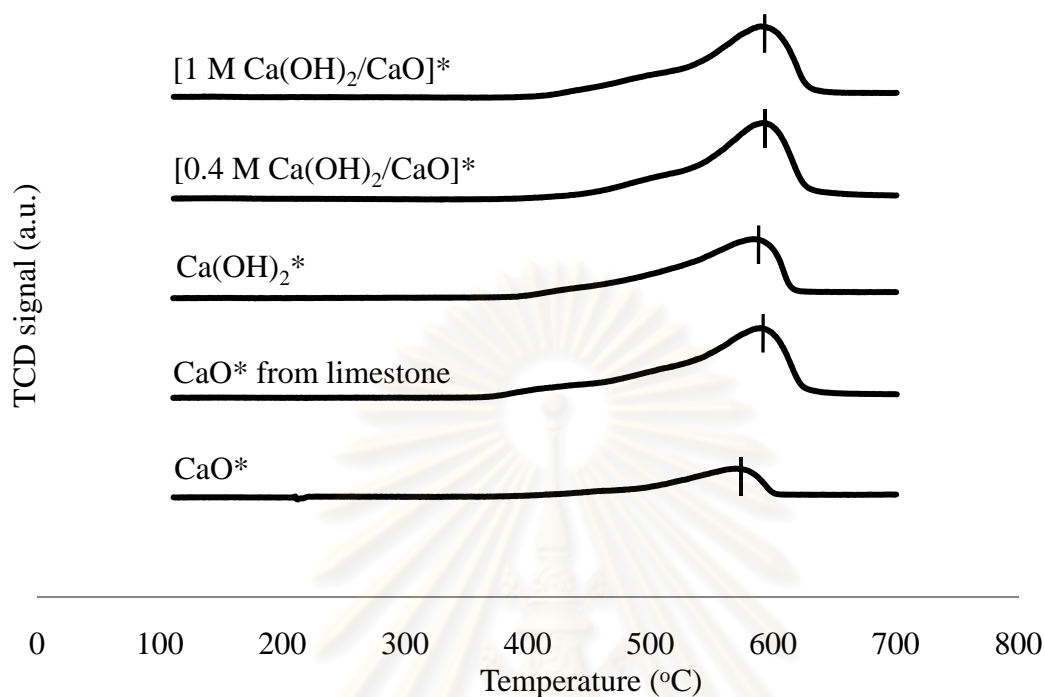


Figure 4.3 CO₂-TPD profiles of catalysts with no loaded modified agents.

4.3 Effect of parameters on biodiesel yield

4.3.1 Molar ratio of ethanol to oil

The effects of molar ratio of methanol to oil on transesterification were presented previously (Xie and Li, 2006; Zhu et al., 2006; Yang and Xie, 2007; Liu et al., 2008). Similarly, the conversion of ethyl ester could be improved by introducing excess amounts of ethanol to shift the equilibrium to the right-hand side. In order to determine the effect of molar ratio of ethanol to oil on the reaction rate without interference by mass transfer, the transesterification was performed by using CaO* at low concentration (1.4 wt% of catalyst in oil). The result as shown in Figure 4.4 indicated that the molar ratio of ethanol to oil has a significant impact on the conversion yield. After 21 h at the reaction temperature of 70 °C, the ethyl ester yield increased from 7.0% to 14.7% with the increase of the molar ratio from

3:1 to 9:1. However, the conversions were steady when the ratio further increased up to 12:1 and 15:1 and comparatively decreased when the ratio was up to 18:1. From the previous reports, high excessive amount of ethanol could cause a negative effect on the conversion rate as it diluted the concentration of catalyst in the system and might cause the catalyst deactivation (Modi et al., 2007; Liu et al., 2008). In this system, the optimal molar ratio of ethanol to soybean oil was 9:1, which corresponded to three times of the stoichiometry.

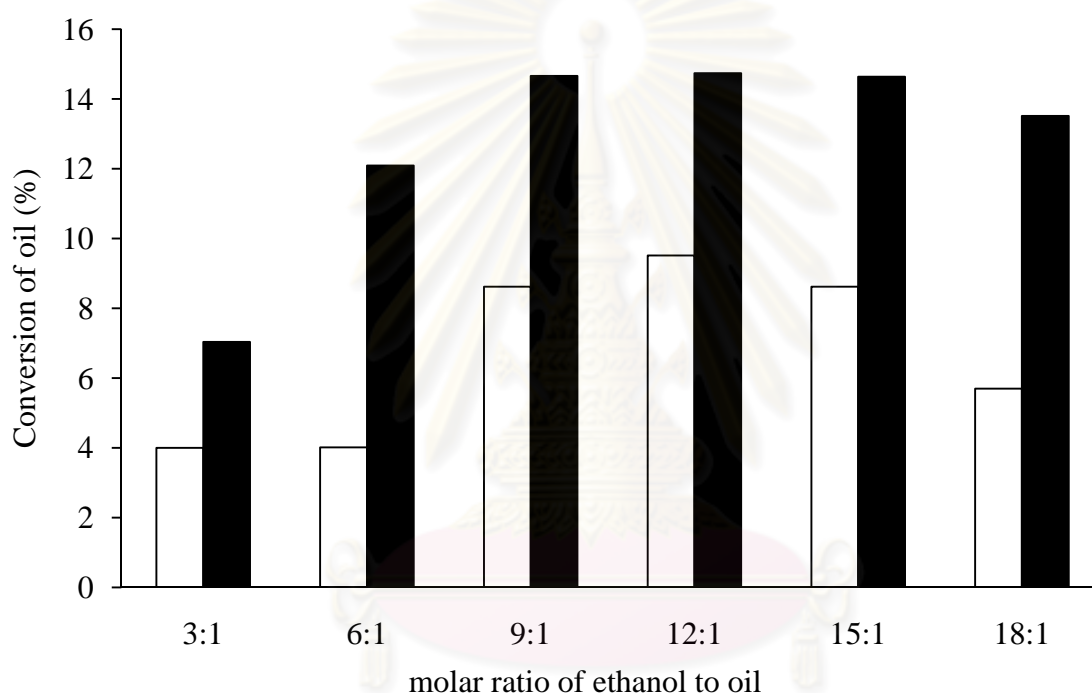


Figure 4.4 The effect of molar ratio of ethanol to oil on the conversion of soybean oil using 1.38 wt% of CaO, reaction temperature at 70 °C and reaction time of 10 h (□) and 21 h (■).

4.3.2 Mass ratio of catalyst to oil

In the case of homogeneous catalysts, it has been reported that the amount of catalysts in the system has a strong influence on the conversion to methyl esters (Ma and Hannab, 1999; Yang and Xie, 2007). The effect of $[\text{H}_2\text{O}/\text{CaO}]^*$ concentration in the range of 1.4%-34.5%wt of oil was investigated at a 9:1 molar ratio of ethanol to oil at the reaction temperature of 70 °C for 21 h. As demonstrated in Figure 4.5, the conversion of soybean oil

to ethyl ester was strongly enhanced with the increase of $[\text{H}_2\text{O}/\text{CaO}]^*$ up to 13.8%wt. The transesterification reached a steady state with the biodiesel conversion of 64.8% after 10 h of the reaction time. The effect of catalyst concentration on the conversion of oil was negligible when the mass ratio of $[\text{H}_2\text{O}/\text{CaO}]^*$ to oil was increased above 13.8 wt%. As a result of increasing catalyst concentration, the mixture of catalyst and reactants could become too viscous leading to a mixing problem and a demand of higher power consumption for enough stirring. On the other hand, when the catalyst loading amount was not enough, the maximum production yield could not be reached (Kim et al., 2004). The external mass-transfer resistance becomes more important at high amount of catalyst. It was found that, the optimal catalyst concentration was 13.8 %wt of oil.

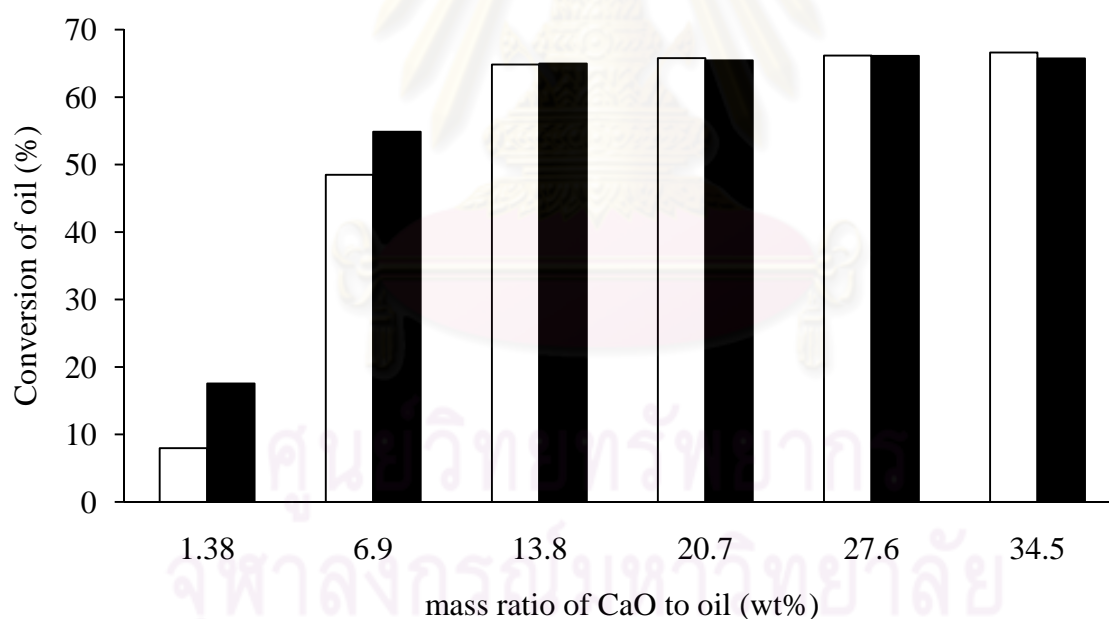


Figure 4.5 The effect of mass ratio of $[\text{H}_2\text{O}/\text{CaO}]^*$ to oil on the conversion of soybean oil using molar ratio of ethanol to oil of 9:1, reaction temperature at 70 °C and reaction time of 10 h (□) and 21 h (■).

4.3.3 Reaction time

The optimum reaction time for the biodiesel production was determined by performing reactions up to 10 h. Compared to a homogeneous reaction, the transesterification using a heterogeneous reaction presented relatively slow reaction rate (Zhu et al., 2006; Liu et al., 2008). The experimental results as reported in Figure 4.6 indicated that the conversion of soybean oil to ethyl ester was very low in the first 4 h, however, the conversion increased rapidly during the reaction time of 4-8 h. The conversion remained almost constant or gradually increased as a result of a nearly equilibrium conversion after 8 h. It is possible that the presence of too much hydroxyl group on our catalyst samples would hinder the access of reactants to the active sites, thus limiting the maximum conversion which could be attained under the experimental conditions used in the present work.

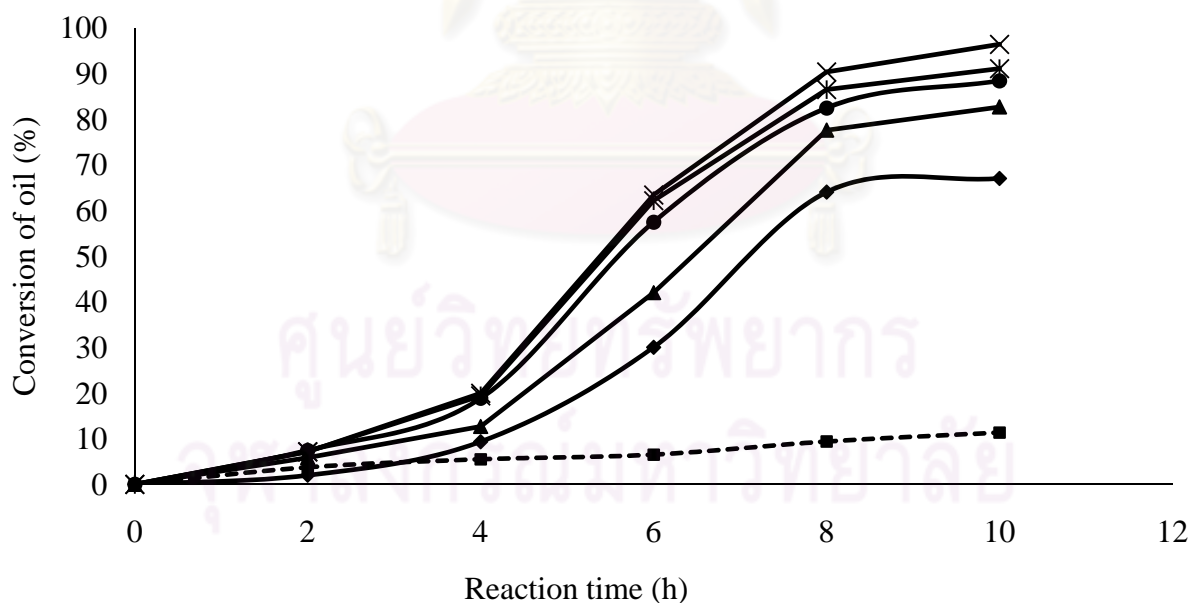


Figure 4.6 The effect of the reaction time on the conversion of soybean oil using 13.8 wt% of catalyst, molar ratio of ethanol to oil of 9:1, reaction temperature at 70 °C

commercial $\text{Ca}(\text{OH})_2$, (■); $[\text{H}_2\text{O}/\text{CaO}]^*$, (◆); CaO^* from limestone, (▲); $\text{Ca}(\text{OH})_2^*$, (●); $[1\text{M } \text{Ca}(\text{OH})_2/\text{CaO}]^*$, (*); $[0.4\text{M } \text{Ca}(\text{OH})_2/\text{CaO}]^*$, (x).

4.3.4 Type of catalysts

The set of CaO* from different preparation and the CaO loaded with Ca(OH)₂ were examined for the transesterification at 9:1 ethanol to soybean oil molar ratio, 13.8 wt% of catalyst in incubator shaker under stirring (150 rpm) and reaction temperature at 70°C. It was previously reported that calcium hydroxide was much less active in the transesterification of oil with methanol than calcium oxide (Kouzu et al., 2008). In this study (Figure 4.6), the catalytic activities of catalysts were in the following order: [0.4M Ca(OH)₂/CaO]* > [1.0M Ca(OH)₂/CaO]* > Ca(OH)₂* > CaO* from limestone > CaO* > commercial Ca(OH)₂. It was found that [0.4M Ca(OH)₂/CaO]* showed the highest catalytic activity among other samples and obtained the highest ethyl ester conversion at 96.3 % after 10 h, whereas the untreated Ca(OH)₂ showed the lowest catalytic activity. The untreated CaO also exhibited a low activity (not shown). It has been previously reported that the active surface sites of CaO could possibly be poisoned by the atmospheric H₂O and CO₂, and its catalytic activity could be improved by activation treatment at high temperature (≥700°C) (Granados et al., 2007; Kouzu et al., 2008). In this study, the catalytic activity could also be improved by loading Ca(OH)₂ on CaO to form basic sites on CaO*.

4.3.5 Amount of Ca(OH)₂ loading on CaO

The effect of the amount of Ca(OH)₂ loading on CaO on the catalytic activity of the transesterification is shown in Table 4.5. It was demonstrated that the conversion was over 90% with the use of the calcined CaO loading with 0.9-4.6wt% Ca(OH)₂. Although the catalytic activity was extremely attractive by alkalinity, however, further increasing in the amount of loaded Ca(OH)₂ beyond 5wt%, led to a decrease in the ethyl ester yield. It could

be possibly explained that the excessive load of Ca(OH)_2 could cover the surface area, and thus cause the decreased catalytic activity. When the active sites are inaccessible to incoming reactants, it is accountable for the decrease in the conversion. The highest ethyl ester conversion of 96.3% was obtained after 10 h of the reaction at 70 °C with the use of $[\text{0.4M Ca(OH)}_2/\text{CaO}]^*$ as the catalyst.

Table 4.5 The effect of the amount of Ca(OH)_2 loading on CaO on the conversion of soybean oil using 13.8 wt% of catalyst, molar ratio of ethanol to oil of 9:1, reaction temperature at 70 °C and reaction time of 10 h.

	The amount of Ca(OH)_2 loading on CaO (wt%) ^a					
	0	0.9	2.3	3.7	4.6	9.3
Conversion of oil (%)	67.8	93.7	96.2	96.3	95.7	88.9

^a The amount of Ca(OH)_2 loading on CaO of 0.9, 2.3, 3.7, 4.6 and 9.3 (wt%) prepared by the impregnation of Ca(OH)_2 solution at concentrations of 0.1, 0.25, 0.4, 0.5 and 1.0 M, respectively.

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CHAPTER V

RESULTS AND DISCUSSION (PART II)

According to the experimental studies in Part I, the increase in CaO* catalytic performance was achieved by loading Ca(OH)₂ on CaO. The ethanolysis activities of the applied catalysts were in the following order: [0.4 M Ca(OH)₂/CaO]* > [1.0 M Ca(OH)₂/CaO]* > Ca(OH)₂* > CaO* from limestone > [H₂O/CaO]* > commercial Ca(OH)₂. The maximum ethyl ester conversion at 96.3% was obtained by the transesterification of soybean oil and ethanol after 10 h of the reaction at 70 °C using [0.4 M Ca(OH)₂/CaO]* as the catalyst at a 9:1 molar ratio of ethanol to oil.

In order to investigate the effect of basic compounds loaded on CaO on the catalytic properties that stimulate the transesterification reaction. The basic compounds such as calcium hydroxide (Ca(OH)₂), ammonium hydroxide (NH₄OH) and sodium hydroxide (NaOH) and potassium hydroxide (KOH) were loaded on CaO. All experiments of transesterification reaction using 13.8wt% of CaO based catalysts were conducted at 60°C, ambient pressure and the alcohol to oil ratio of 9:1.

5.1. Characterization of catalysts

In the experimental studies of part II, the modified catalysts were prepared by the impregnation with aqueous solutions of basic compounds of NH₄OH, Ca(OH)₂, NaOH and KOH on CaO support. All catalysts were dried in the oven at 100°C overnight and calcined in muffle furnace at 800°C for 24 h without gas purge. After that all catalysts were kept in desiccators before using in the experiment.

5.1.1. X-ray diffraction analysis

The XRD patterns of samples have been examined to obtain more information about the catalysts structure. Figure 5.1.a and Figure 5.1.b show the XRD patterns of CaO*, [H₂O/CaO]* and CaO loaded with Ca(OH)₂, NH₄OH, NaOH and KOH at different concentrations. Zhu et al., 2006; Granados et al., 2007; Kouzu et al., 2008; and Ngamcharussrivichai et al., 2008 reported that the diffraction peaks at 32.3°, 37.4°, 54.0°, 65.2° and 67.5° in all catalyst were CaO. Granados et al., 2007 found the diffraction peaks at 18.1°, 28.8°, 34.1°, 47.1° and 50.8° stand for Ca(OH)₂. In this work, the CaO and Ca(OH)₂ peaks were also observed in the XRD patterns of basic compounds loaded CaO catalysts. However, no peaks of NaOH or KOH were observed in any of these XRD patterns. In aqueous solutions, NaOH and KOH could split to Na⁺ or K⁺ and OH⁻ ion. OH⁻ ions could react with CaO to form Ca(OH)₂ on CaO support. However, from the XRD patterns, the Ca(OH)₂ peaks were considerably smaller than those of the CaO. The small Ca(OH)₂ crystals forming on the CaO support, might be generated from the incomplete decomposition of Ca(OH)₂ crystals in the agglomerated CaO crystal grains during the calcinations.

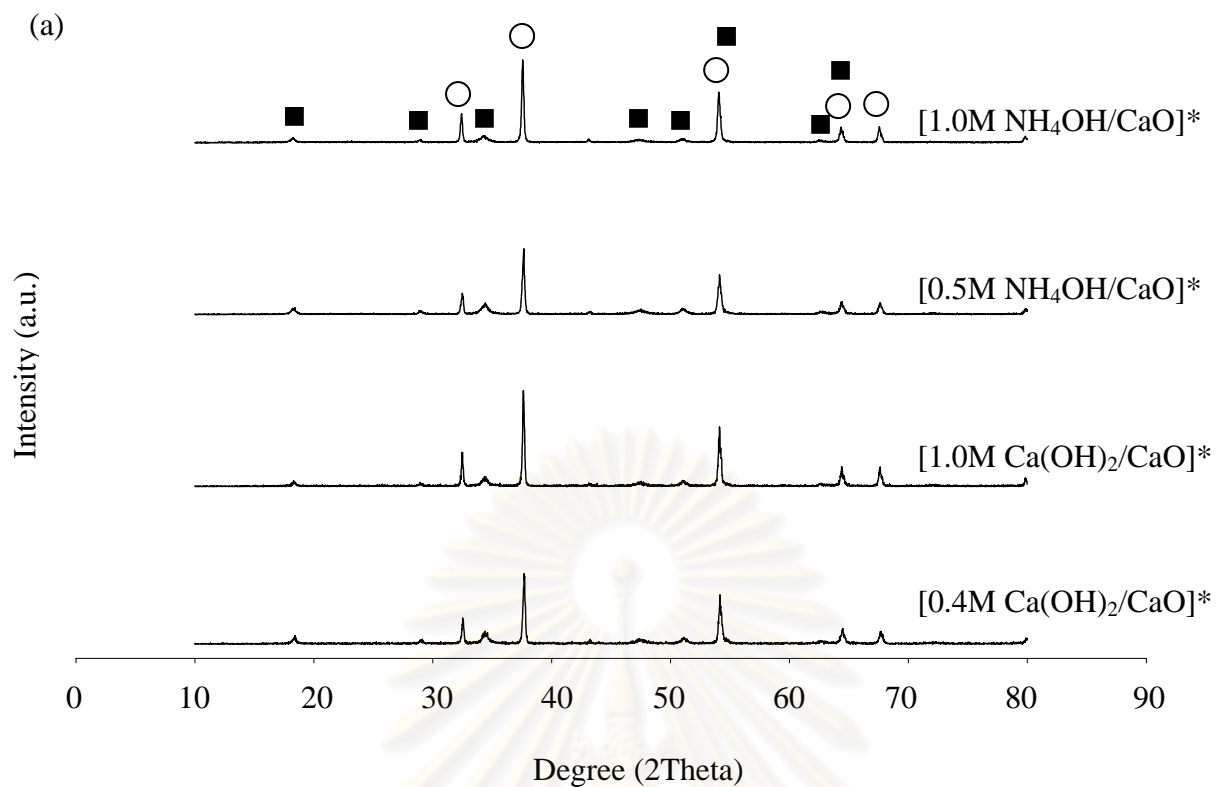


Figure 5.1.a XRD patterns of the employed CaO based catalysts loaded with aqueous solutions of NH_4OH and $\text{Ca}(\text{OH})_2$: CaO (\circ), $\text{Ca}(\text{OH})_2$ (\blacksquare).

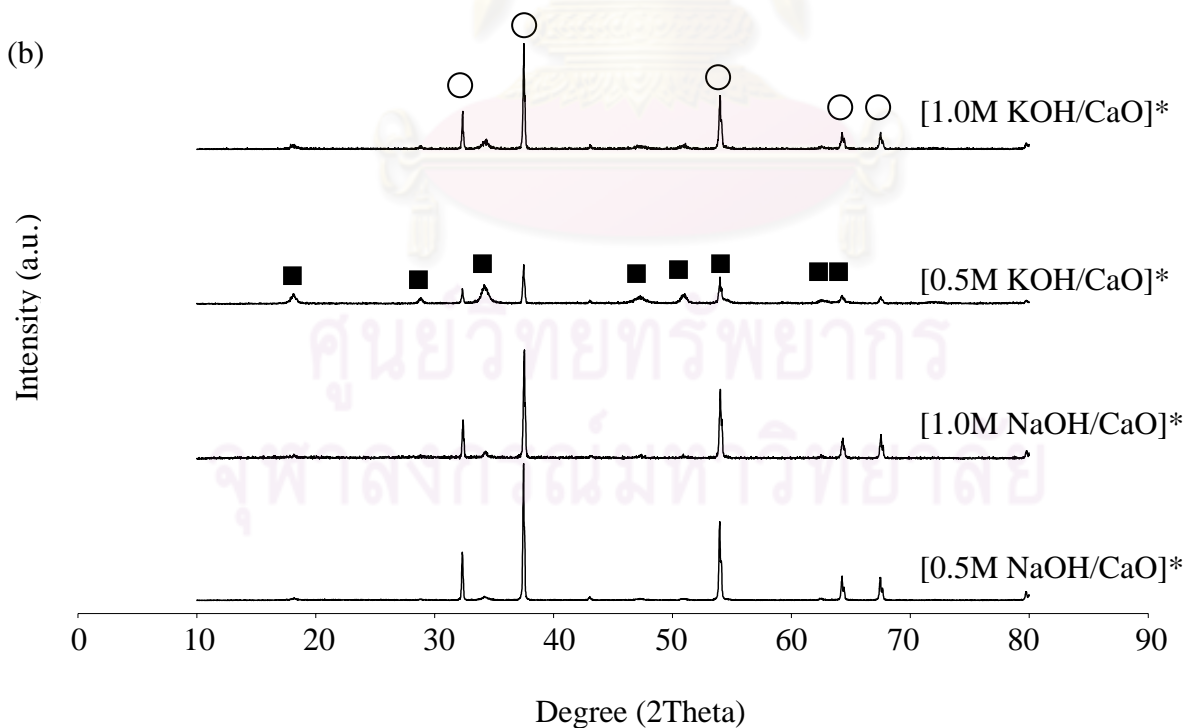


Figure 5.1.b XRD patterns of the employed CaO based catalysts loaded with aqueous solutions of NaOH and KOH : CaO (\circ), $\text{Ca}(\text{OH})_2$ (\blacksquare).

5.1.2. Nitrogen physisorption (BET surface area)

The BET surface area, pore volume and average pore diameter are presented in Table 5.1. For the catalysts prepared by different loader, the surface area could be changed because the modified agents affected crystallization and porosity of the supports (Yan et al., 2009; Wen et al., 2010). Since the pore volumes of them were all less than $0.2 \text{ cm}^3/\text{g}$, the materials appeared to have nonporous structures. The detected pore size and pore volume should belong to the interparticle voids. From the previous reports, the BET surface areas of CaO were $6\text{-}13 \text{ m}^2/\text{g}$, (Zhu et al., 2006; Arzamendi et al., 2008; Kouzu et al., 2008). The BET surface areas of the modified catalysts in this study were $3.7 - 19.7 \text{ m}^2/\text{g}$. The variations in the values could be according to individual differences in material source and treatment.

Table 5.1 Comparison of BET surface area, pore volume and average pore diameter of various types of catalysts.

Sample No.	Catalyst	Total		Average
		surface area ^a (m^2/g)	pore volume ^a (cm^3/g)	pore diameter ^a (nm)
1	CaO*	5.2	0.085	65
2	[H ₂ O/CaO]*	19.7	0.146	30
3	[0.4M Ca(OH) ₂ /CaO]*	13.7	0.182	53
4	[1.0M Ca(OH) ₂ /CaO]*	18.6	0.134	29
5	[0.5M NH ₄ OH/CaO]*	3.7	0.004	5
6	[1.0M NH ₄ OH/CaO]*	n.d	n.d	n.d
7	[0.5M NaOH/CaO]*	15.7	0.042	11
8	[1.0M NaOH/CaO]*	8.0	0.030	15
9	[0.5M KOH/CaO]*	n.d.	n.d.	n.d.
10	[1.0M KOH/CaO]*	12.2	0.084	28

^a Calculated by BET method.

n.d. = not determined.

5.1.3 Transmission electron microscopy (TEM)

The TEM micrographs of all catalysts are demonstrated in Figure 5.2. The TEM images showed that all of the applied catalysts were in sizes of 100-300 nm. It was found that the crystal sizes of Ca(OH)_2 and NH_4OH loaded catalysts were considerably larger than those of NaOH and KOH loaded catalysts. After loading calcium hydroxide or ammonium hydroxide on CaO , the morphologies of particle were similar to those with water loading, but being different from the morphologies of sodium hydroxide or potassium hydroxide loaded on CaO . The TEM photograph showed that the catalyst was granular and porous with evenly distributed granules and abundant large pores. As shown in Figure 5.2, the granules were made up of several smaller granules with 30–100 nm in diameter which formed a porous net-like structure (Wen et al., 2010). These results showed that the catalyst was porous which increased the contact between the substrates and the catalyst. These improved catalytic ability and increased transesterification efficiency. The crystallite sizes determined from XRD measurement of CaO^* , $[\text{H}_2\text{O}/\text{CaO}]^*$, $[\text{Ca(OH)}_2/\text{CaO}]^*$, $[\text{NH}_4\text{OH}/\text{CaO}]^*$, $[\text{NaOH}/\text{CaO}]^*$ and $[\text{KOH}/\text{CaO}]^*$ were all in the range of 32-46 nm as showed in Table 5.2. When compared the crystallite sizes calculated from XRD line broadening with those obtained from TEM micrographs, it was found that the crystallite sizes obtained from TEM were much larger due to the agglomeration of single crystals.

Table 5.2 Comparison of crystallite size and based sites of various types of catalysts.

Sample No.	Catalyst	Crystallite size ^a (nm)		Base sites ^b ($\mu\text{mole/g}$)
		CaO	Ca(OH) ₂	
1	CaO*	39	0	7,971
2	[H ₂ O/CaO]*	32	16	14,977
3	[0.4M Ca(OH) ₂ /CaO]*	36	22	11,195
4	[1.0M Ca(OH) ₂ /CaO]*	44	24	6,136
5	[0.5M NH ₄ OH/CaO]*	36	21	13,977
6	[1.0M NH ₄ OH/CaO]*	36	24	8,680
7	[0.5M NaOH/CaO]*	40	16	22,372
8	[1.0M NaOH/CaO]*	39	27	3,839
9	[0.5M KOH/CaO]*	36	13	n.d.
10	[1.0M KOH/CaO]*	39	15	4,332

^a Determined by XRD patterns using Scherrer's equation.

^b Measured by CO₂ -TPD.

n.d. = not determined.

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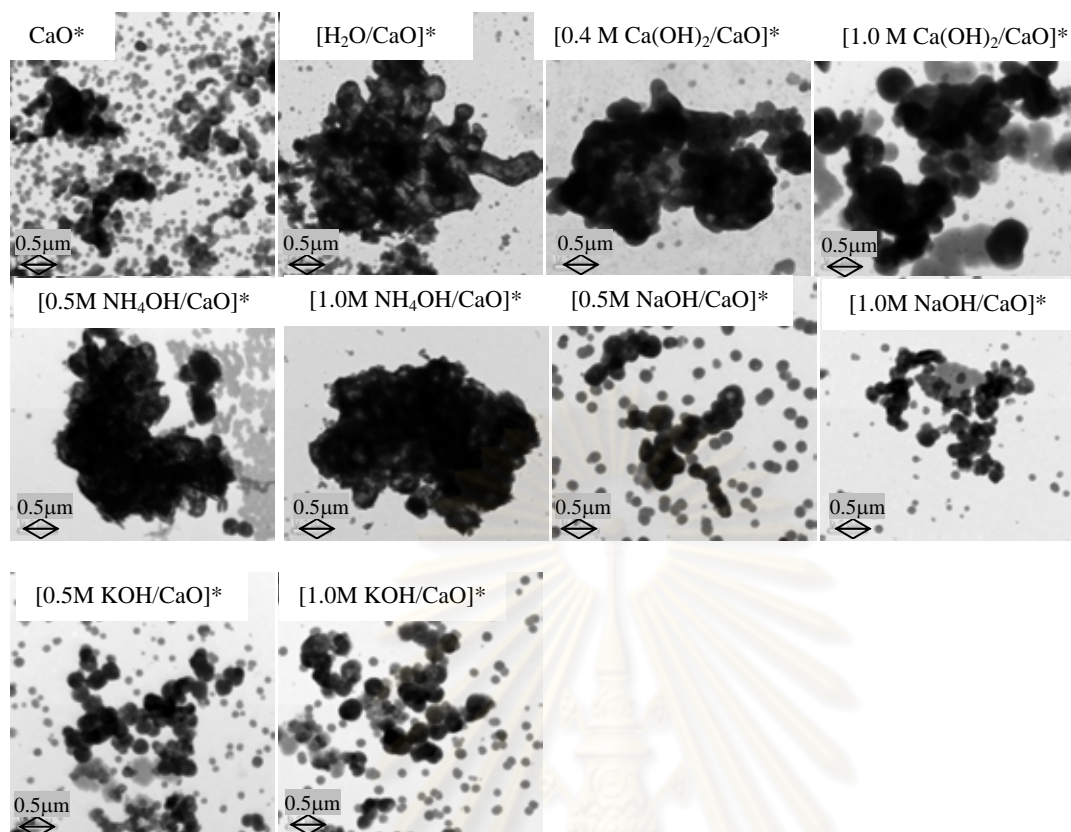


Figure 5.2. TEM micrographs of modified catalysts.

5.1.4 Temperature-programmed desorption of carbon dioxide (CO₂-TPD)

The CO₂-TPD technique (Albuquerque et al., 2007; Kouzu et al., 2008) was used to measure the base properties of the catalysts. The amounts of base sites summarized in Table 5.2 are calculated from the area below the curve of TPD profiles and the CO₂-TPD profiles of catalysts are shown in Figure 5.3. The characteristic peaks of these profiles are assigned to their desorption temperatures indicating the strength of basic sites. For CO₂-TPD profiles all catalysts have strong base sites because of CO₂ desorbed at high temperature (600-750°C) (Albuquerque et al., 2007). However, in this study, the basicity obtained from TPD measurement of all catalysts was not shown the effect on the transesterification of soybean oil

with ethanol because the range of temperature of desorption by CO_2 was much higher than the reaction temperature.

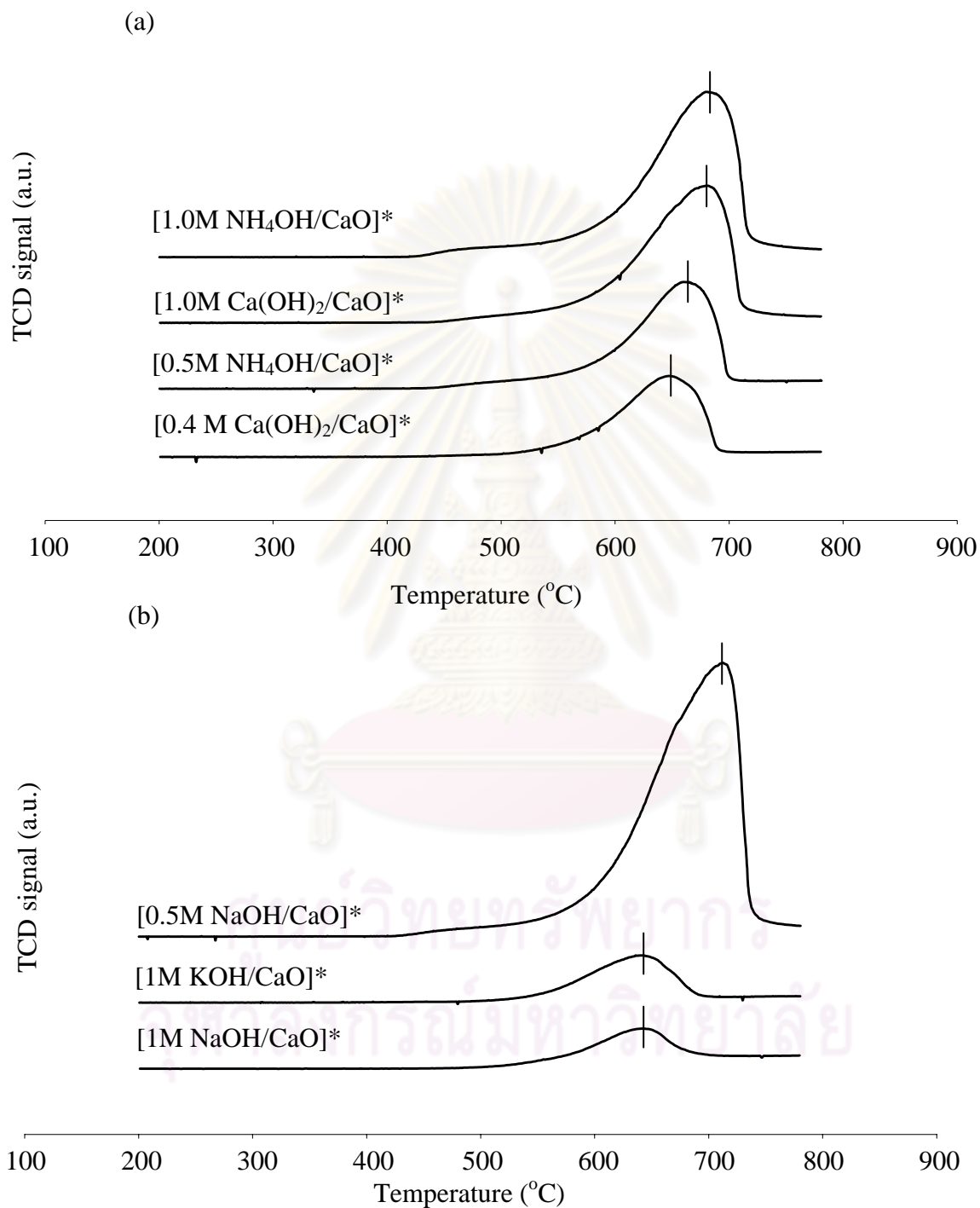
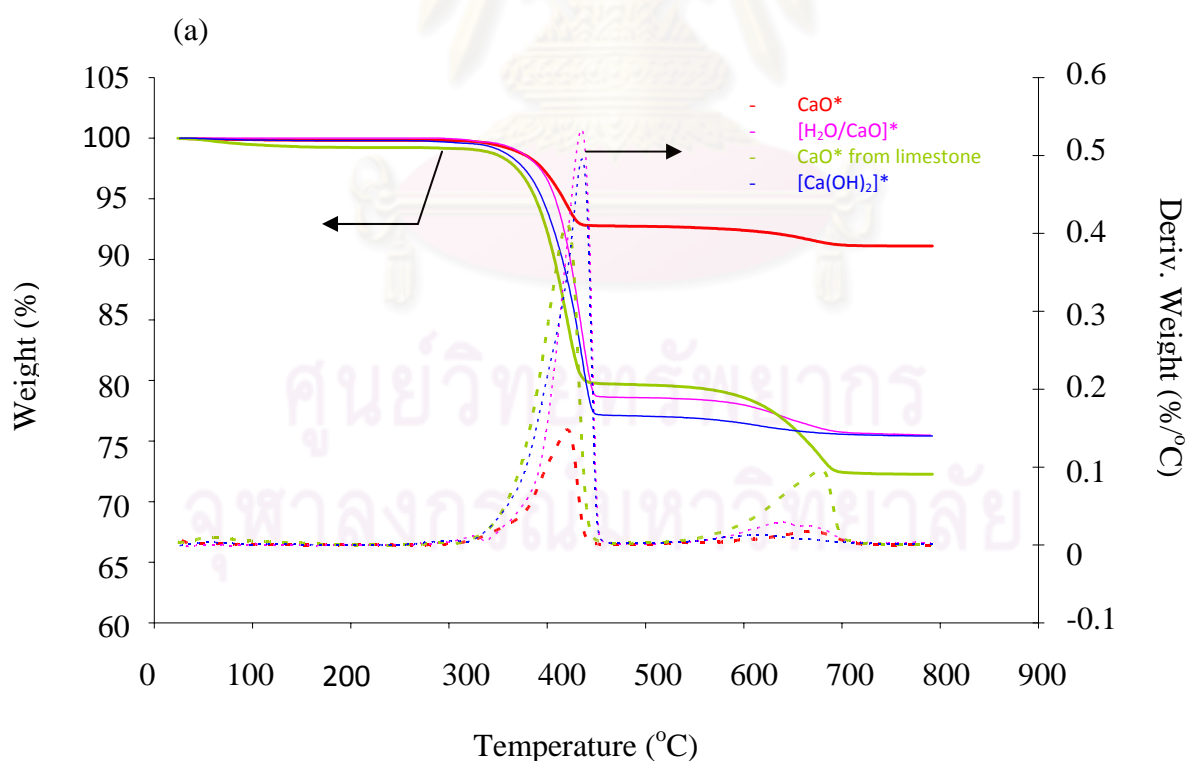


Figure 5.3 CO_2 -TPD profiles of catalysts (a) Ca(OH)_2 and NH_4OH loaded on CaO , (b) NaOH and KOH loaded on CaO

5.1.5 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was used to confirm the optimal calcination temperature for the modified agents (calcium hydroxide, ammonium hydroxide, sodium hydroxide and potassium hydroxide) loaded on CaO catalysts. The TGA profiles for all catalysts are illustrated in Figure 5.4(a)-(c), showing two derivative weight peaks in the range of 25-800 °C. The first exothermic peak around 400 °C, which is accompanied by mass loss of 25% except for CaO* (mass loss only 7%), may be associated to the decomposition of Ca(OH)_2 . The second exothermic peak around 680 °C, may be originated from CaCO_3 . Moreover, the profile showed approximately no weight loss after the temperature around 700 °C suggesting that from this temperature, all the residue components have been removed from catalyst. Therefore, the temperature at 800 °C was selected for the calcination of the corresponding CaO.



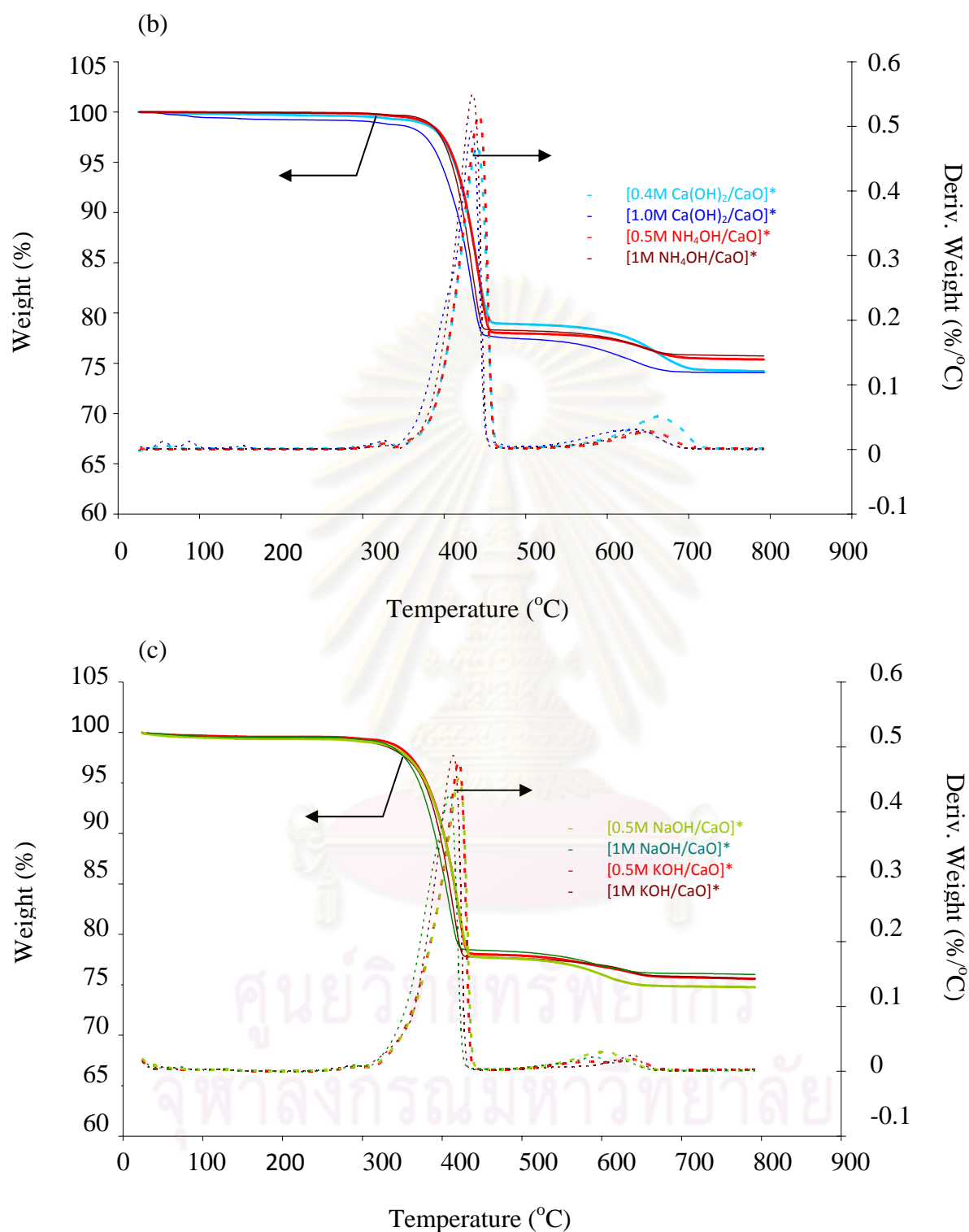


Figure 5.4 Thermal analysis of the employed catalysts. (a) no loaded modified agents, (b)

Ca(OH)₂ and NH₄OH loaded on CaO, (c) NaOH and KOH loaded on CaO

5.2 Effect of parameters on biodiesel conversion

5.2.1 Type of catalysts

From the experimental results in part I, the $[\text{Ca}(\text{OH})_2/\text{CaO}]^*$ was much active in the transesterification of oil with ethanol than CaO^* . In the experimental studies in part II, all of the modified CaO based catalysts were examined for the transesterification at 9:1 ethanol to soybean oil molar ratio, 13.8 wt% of catalyst in the incubator under stirring (300 rpm) and reaction temperature at 60°C . Figure 5.5 presents the enhanced catalytic activities of $\text{Ca}(\text{OH})_2$, NH_4OH and water loaded on CaO, which were in the following order: $[0.4\text{M Ca}(\text{OH})_2/\text{CaO}]^* > [1.0\text{M Ca}(\text{OH})_2/\text{CaO}]^* > [0.5\text{M NH}_4\text{OH}/\text{CaO}]^* > [1.0\text{M NH}_4\text{OH}/\text{CaO}]^* > [\text{H}_2\text{O}/\text{CaO}]^* > \text{CaO}^*$. It was found that $[0.4\text{ M Ca}(\text{OH})_2/\text{CaO}]^*$ showed the highest catalytic activity among other CaO based catalysts with the maximal ethyl ester conversion at 90.8 % after 10 h, whereas no loaded CaO^* showed the lowest catalytic activity. Table 5.3 shows the conversion of oil from transesterification of soybean oil with ethanol using NaOH and KOH loaded on CaO and no loaded CaO^* . The results showed the significant decrease in conversion of oil with the use of NaOH and KOH loaded on CaO support. In this study, the catalytic activity of CaO based catalysts on transesterification could be improved by loading 0.4 – 1.0 M $\text{Ca}(\text{OH})_2$, NH_4OH or water on CaO support to form basic sites on CaO^* , however, the loading of NaOH and KOH on CaO caused significant deactivation of the catalysts. It is important to note that NaOH and KOH are strong bases which are 100% dissociated into the cation and OH^- (hydroxide ion) in water. $\text{Ca}(\text{OH})_2$ in water is chemically classified as strong base because of its high degree of dissociation. However, $\text{Ca}(\text{OH})_2$ is slightly soluble in water. Therefore $\text{Ca}(\text{OH})_2$ produce low concentrations of OH^- ion in water. NH_4OH is chemically classified as weak base with low degree of dissociation.

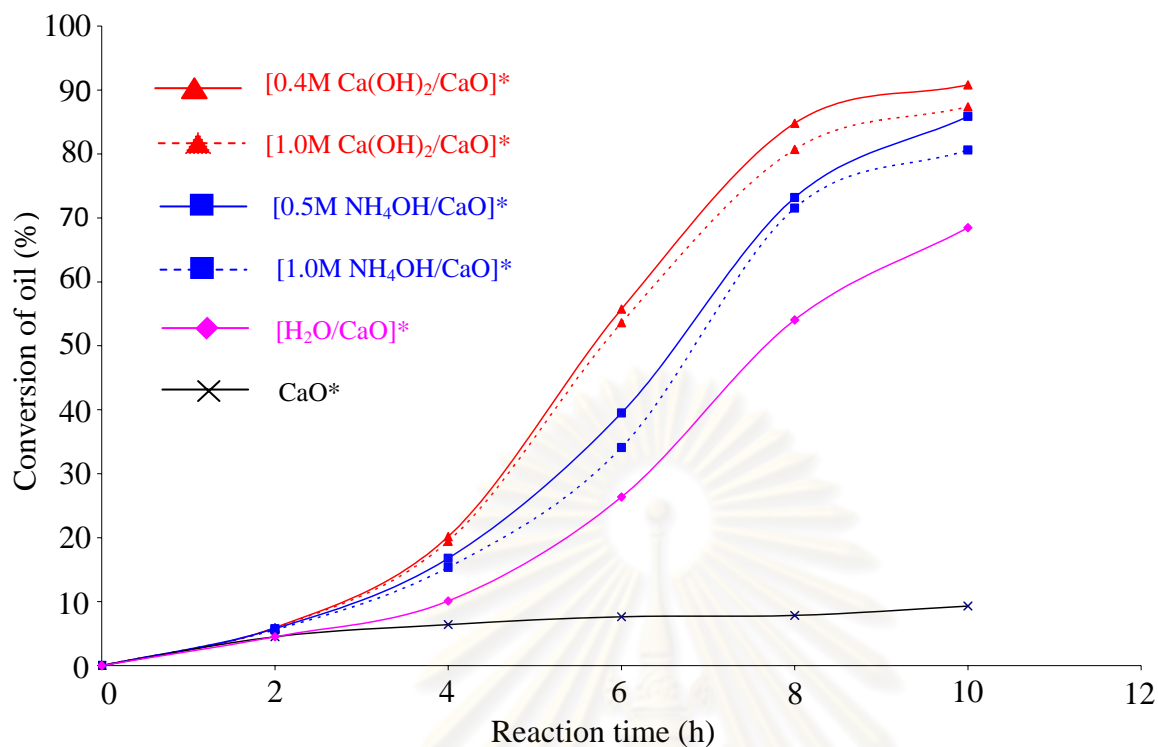


Figure 5.5 Effect of the types of Ca(OH)_2 and NH_4OH loaded on the conversion of soybean oil using 13.8wt% of catalysts, molar ratio of ethanol, to oil of 9:1, reaction temperature at 60°C and reaction time of 10 h.

Table 5.3 Effect of the types of NaOH and KOH loaded on the conversion of soybean oil using 13.8wt% of catalysts, molar ratio of ethanol, to oil of 9:1, reaction temperature at 60°C and reaction time of 10 h.

Reaction time (h)	Conversion of oil (%)				
	CaO*	[0.5 M NaOH/CaO]*	[1.0 M NaOH/CaO]*	[0.5 M KOH/CaO]*	[1.0 M KOH/CaO]*
0	0.0	0.0	0.0	0.0	0.0
2	4.5	0.5	0.8	0.0	0.3
4	6.4	1.0	1.1	0.6	1.2
6	7.6	1.5	1.9	1.2	2.0
8	7.9	2.2	2.5	1.9	3.2
10	9.3	2.7	2.9	2.2	3.7

5.2.2 Reusability of Catalyst

In this work, weak based catalysts, $[\text{H}_2\text{O}/\text{CaO}]^*$ and CaO^* were used as heterogeneous base catalysts for transesterification of soybean oils with ethanol. After the end of the transesterification, the catalysts were separated from the product by centrifuging at 4000 rpm for 30 min. Then the catalysts were reused for the next cycle. The results as shown in Figure 5.6 demonstrates that the catalysts could be recycled at least for 3 times without significant loss in activity. Therefore, the CaO based catalysts has good durability and stability for long-term use.

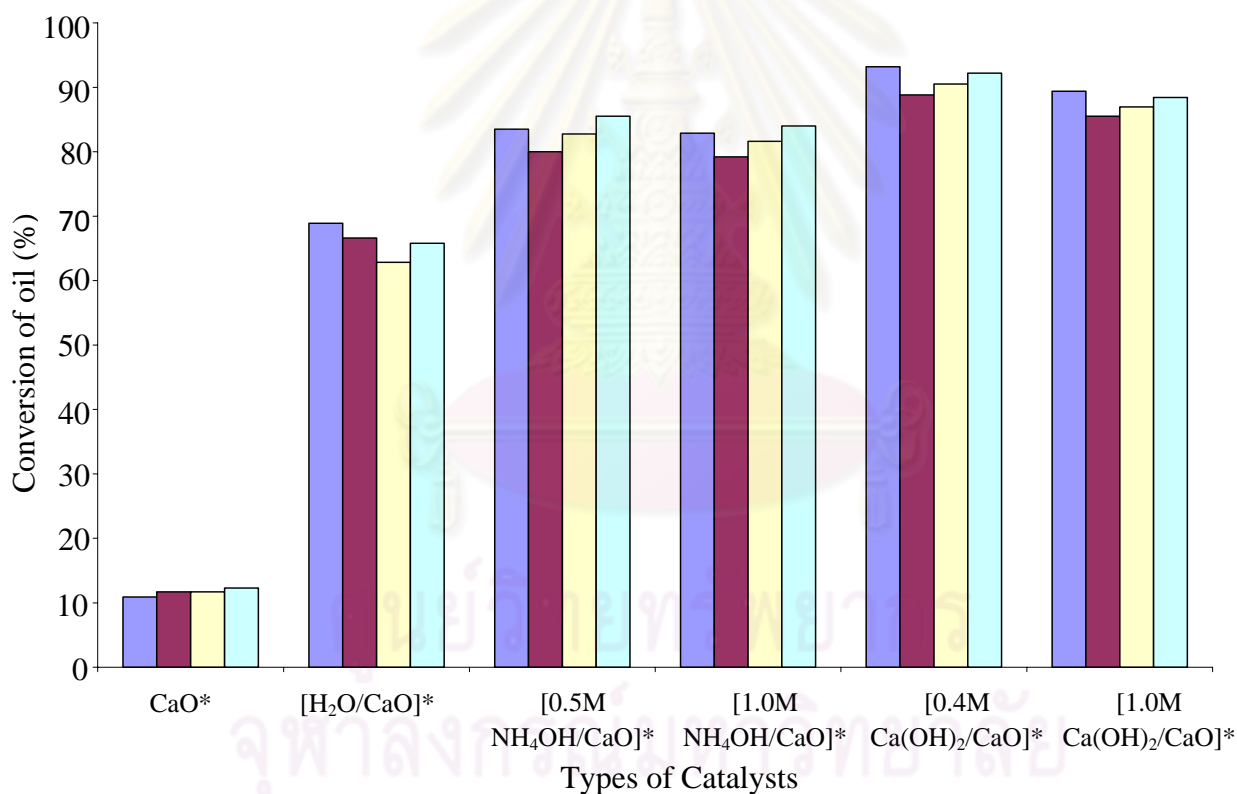


Figure 5.6 Effect of reusability of catalysts on the conversion of soybean oil using 13.8wt% of catalysts, molar ratio of ethanol, to oil of 9:1, reaction temperature at 60 °C and reaction time of 10 h. [■ fresh catalyst, ■ 1st recycle use, ■ 2nd recycle use, ■ 3rd recycle use]

5.2.3 Effect of type of oil and alcohol

In order to investigate the effect of type of oil and alcohol on the catalytic activity of CaO based catalysts, this experimental study was carried out using palm oil and methanol instead of soybean oil and ethanol. Figure 5.7 presented the effect of the reaction time on conversion of palm oil with methanol using molar ratio of methanol to oil of 9:1 and reaction temperature 60°C. Compare to the transesterification of soybean oil with ethanol, the trend of the conversion of oil in Figure 5.7 was as same as in Figure 5.5. The reusability of selected CaO based catalysts applied with palm oil and methanol is shown in Figure 5.8. The conversion of palm oil nearly 95% in the first, second and third round and slightly decreased in the fourth round. It means that $[\text{NH}_4\text{OH}/\text{CaO}]^*$ can use as a heterogeneous catalyst in transesterification of soybean oil with ethanol or palm oil with methanol as well.

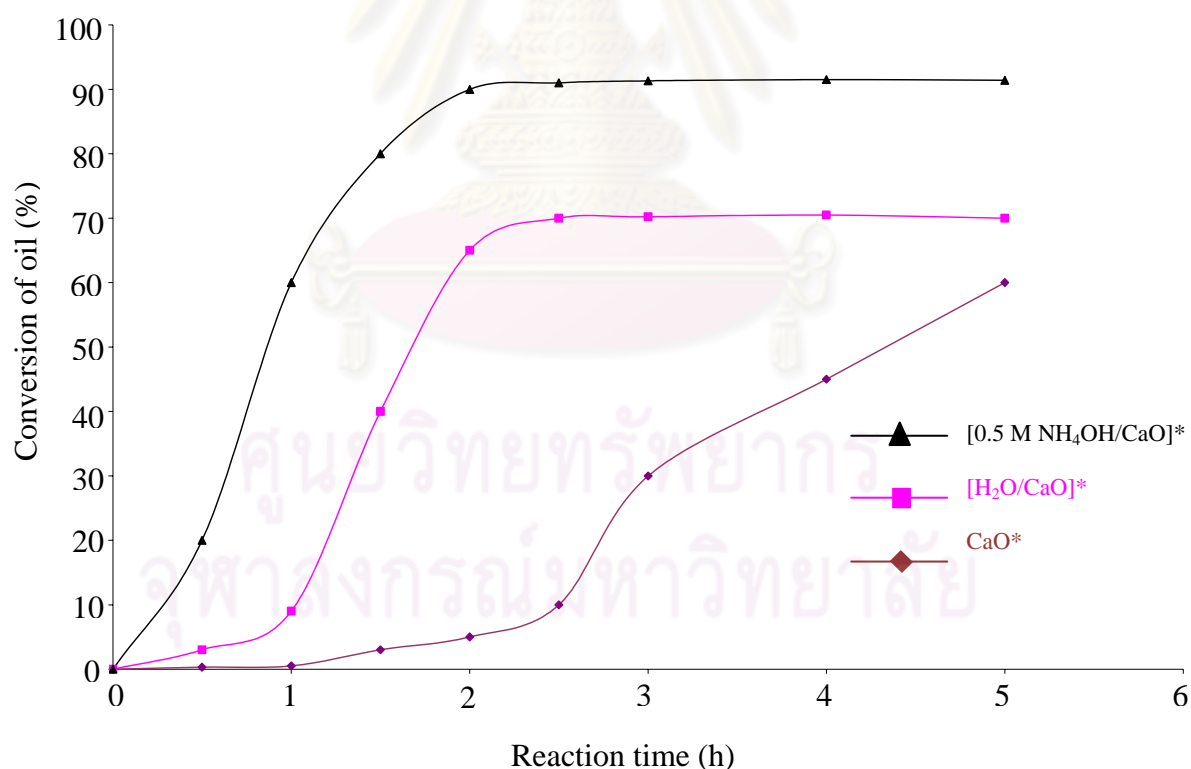


Figure 5.7 The effect of the reaction time on the conversion of palm oil with methanol using molar ratio of methanol to palm oil of 9:1 and reaction temperature 60 °C.

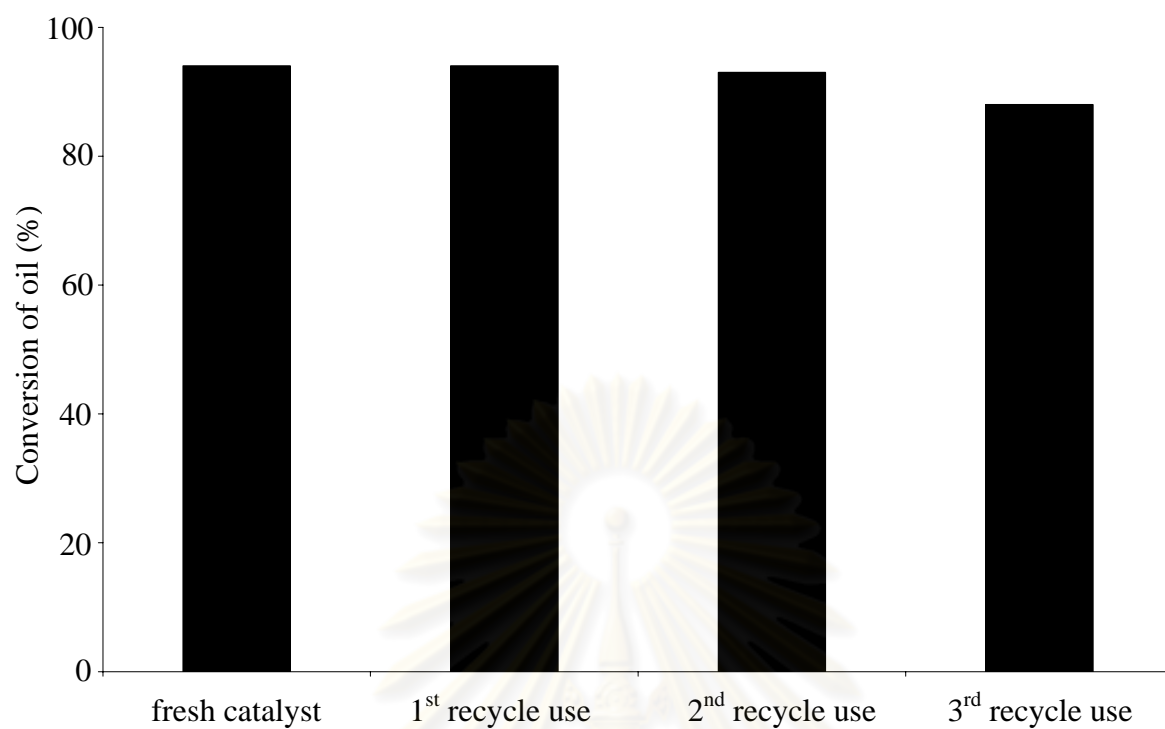


Figure 5.8 Effect of reusability of catalysts on the conversion of palm oil with methanol using $[0.5\text{M NH}_4\text{OH/CaO}]^*$, molar ratio of methanol to palm oil of 9:1, reaction temperature at $60\text{ }^\circ\text{C}$ and reaction time of 3 h.

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CHAPTER VI

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The conclusions of the present research are the following:

1. Ethyl ester could be produced by solid based catalyzed transesterification of soybean oil with ethanol. The reactions were found to be completed in 10 h. Compared with the homogeneous reaction, the separation of products is much simpler and the process is more environmentally friendly.
2. In this work, the suitable preparation condition of calcium oxide based catalysts was to impregnated based agents in 30 g of CaO, after that the catalysts were dried in the oven at 100°C 12 h, and was calcined in a muffle furnace at 800°C for 24 h without gas purge.
3. The most suitable conditions for transesterification reaction of soybean oil with ethanol were the molar ratio of ethanol to oil of 9:1, the catalyst to oil mass ratio of 13.8 wt% at 70 °C and reaction time of 10 h.
4. $[\text{Ca}(\text{OH})_2/\text{CaO}]^*$ and $[\text{NH}_4\text{OH}/\text{CaO}]^*$ can considerably improve the transesterification reaction of soybean oil with ethanol more than $[\text{NaOH}/\text{CaO}]^*$ and $[\text{KOH}/\text{CaO}]^*$. It is probable that the crystal structure and the agglomeration of catalysts are the main for increasing the biodiesel conversion.
5. This study shows that $[\text{Ca}(\text{OH})_2/\text{CaO}]^*$ and $[\text{NH}_4\text{OH}/\text{CaO}]^*$ have a potential to be used for transesterification. Based on the conversion of oil, the order of activity of CaO based catalysts for transesterification is $[0.4\text{M Ca}(\text{OH})_2/\text{CaO}]^* > [1.0\text{M}$

$\text{Ca}(\text{OH})_2/\text{CaO}^* > [0.5\text{M NH}_4\text{OH}/\text{CaO}]^* > [1.0\text{M NH}_4\text{OH}/\text{CaO}]^* > [\text{H}_2\text{O}/\text{CaO}]^* > \text{CaO}^*$. The activity of Commercial $\text{Ca}(\text{OH})_2$, $[0.5\text{M NaOH}/\text{CaO}]^*$, $[1.0\text{M NaOH}/\text{CaO}]^*$, $[0.5\text{M KOH}/\text{CaO}]^*$, $[1\text{M KOH}/\text{CaO}]^* < \text{CaO}^*$. It was found that $[0.4\text{M Ca}(\text{OH})_2/\text{CaO}]^*$ showed the highest catalytic activity among other CaO based catalysts with the maximal ethyl ester conversion at 90.8 %

6. Reusability of the catalyst was performed and found that the activity of the reused catalyst is slightly decreased after recycling 3 times. Therefore, the CaO based catalysts has good durability and stability for long-term use.
7. $[0.5\text{ M NH}_4\text{OH}/\text{CaO}]^*$ can apply to use as a heterogeneous based catalyst for transesterification of palm oil with methanol.

6.2 Recommendations

From the previous conclusions, the following recommendations for future studies can be proposed.

1. The catalyst leaching and deactivation should be investigated for the transesterification of soybean oil with ethanol.
2. The possibility regenerate catalyst by re-impregnation and re-calcinations could be investigated to increase the reusability of catalyst for transesterification of soybean oil with ethanol
3. Since the $[\text{Ca}(\text{OH})_2/\text{CaO}]^*$ and $[\text{NH}_4\text{OH}/\text{CaO}]^*$ showed good results, it is suggested to try and look for another weak based agents loaded on CaO support

for this reaction. It is also interesting to develop a good understanding of systems kinetics by studying a wide range of temperature to determine the best condition.



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APPENDIX

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APPENDIX A

Raw Data for heterogeneous Transesterification

A.1 Calculation of catalyst

Example

Base on volume of soybean oil is 60 g. The catalyst to soybean oil mass ratio of 13.8wt%

Weight of catalyst = Weight of purified palm oil x Catalyst to purified palm oil mass ratio

$$= \frac{60 \times 13.8}{100} = 8.28 \text{ g}$$

A.2 Calculation of the percent ethyl ester conversion

The percent ethyl ester conversion is defined as

$$\text{Conversion} = \frac{\text{consumed oil}}{\text{total oil}} \times 100\% \dots\dots\dots(A1)$$

The rate of ethyl esters for each fatty acid can be determined from GC data with corresponding calibration equation. Below are standard calibration curves for the key ethyl esters (Figure A.1-A.3).

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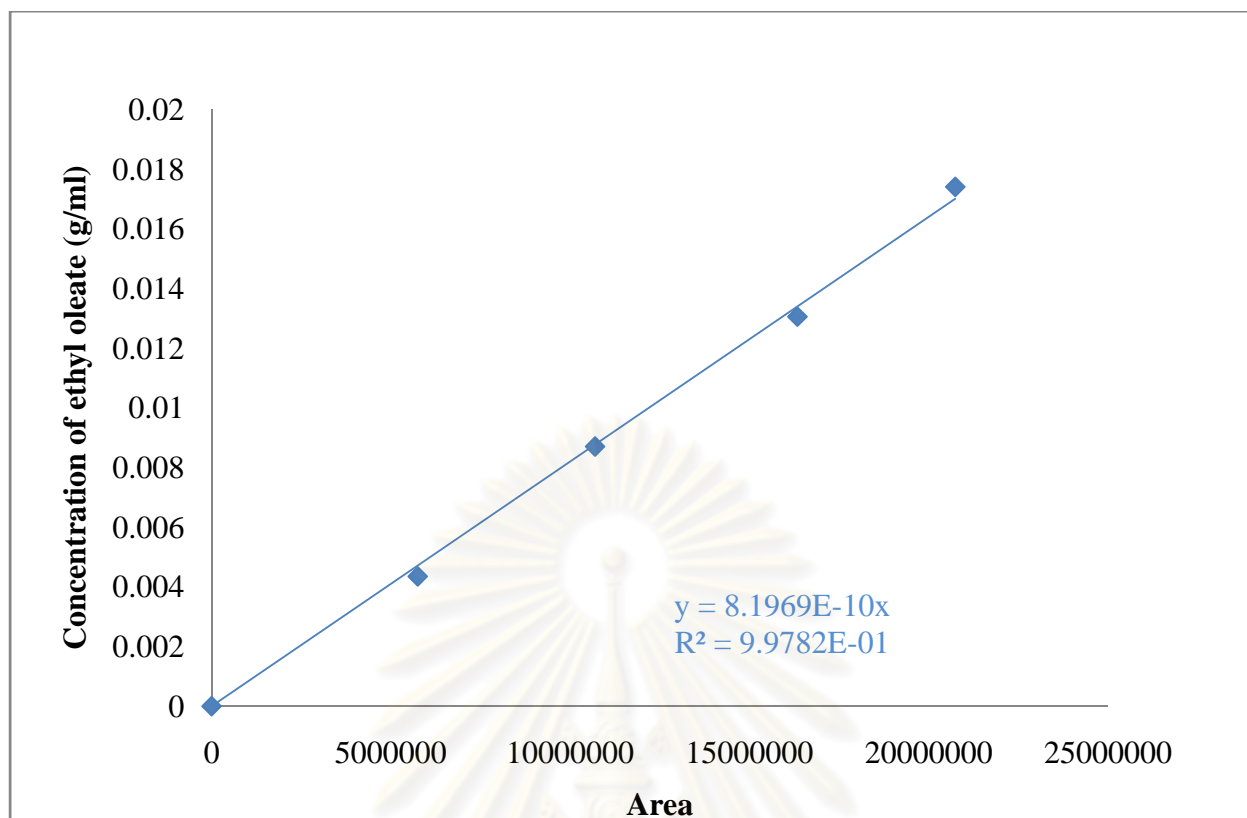


Figure A.1 Standard calibration curve for ethyl oleate.

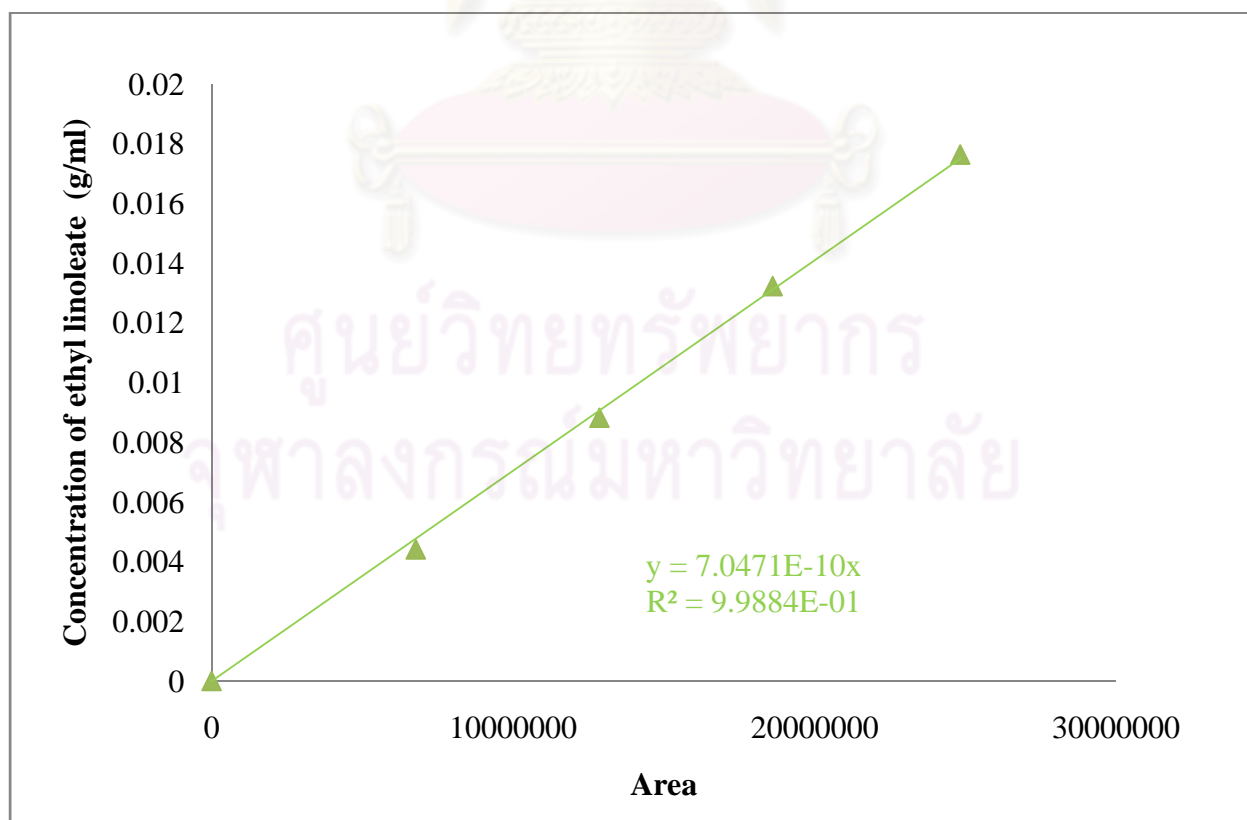


Figure A.2 Standard calibration curve for ethyl linoleate.

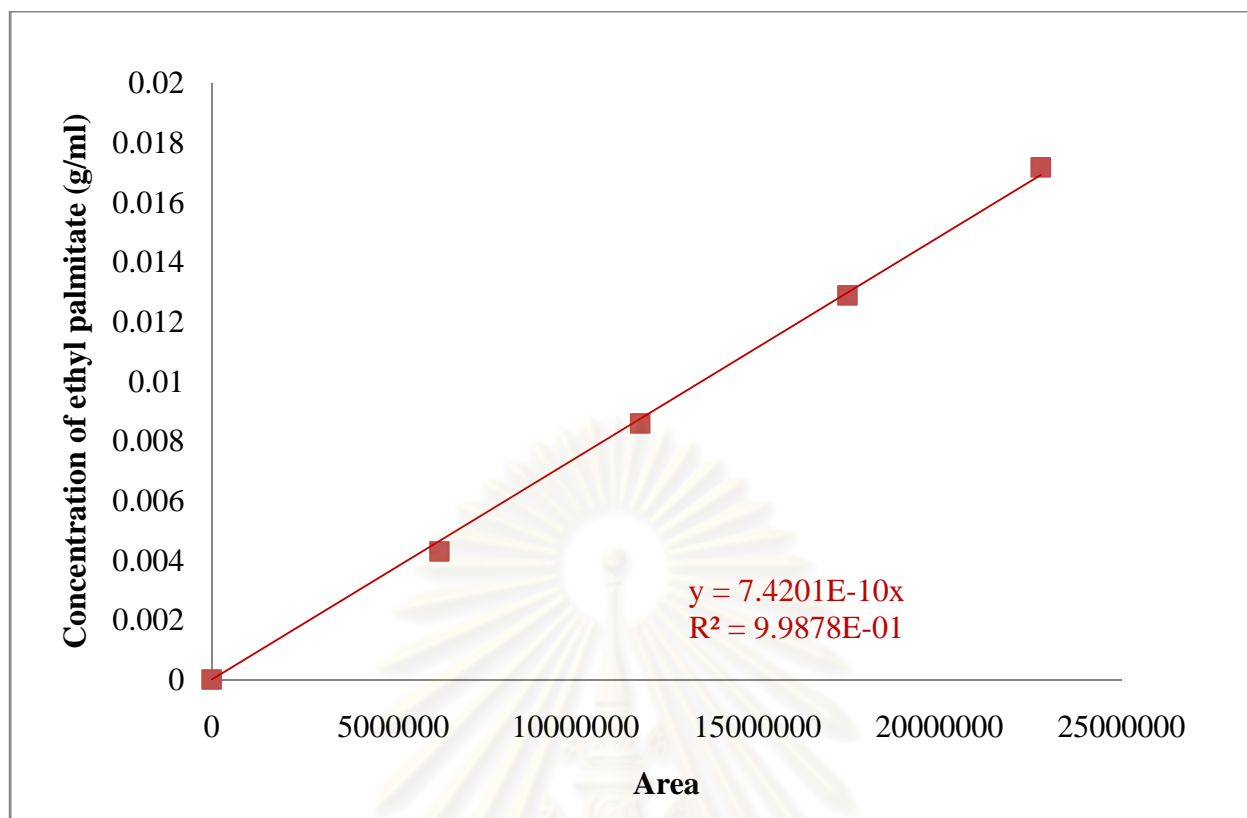


Figure A.3 Standard calibration curve for ethyl palmitate.

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Table A.1 Raw data of CaO based catalysts with weak based compounds for transesterification reaction.

Reaction time (h.)	Conversion of oil (%)					
	CaO*	[H ₂ O/CaO]*	[0.5 M NH ₄ OH/CaO]*	[1 M NH ₄ OH/CaO]*	[0.4 M Ca(OH) ₂ /CaO]*	[1 M Ca(OH) ₂ /CaO]*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	4.5	4.5	5.8	5.6	5.9	5.9
4	6.4	10.1	16.8	15.3	20.2	19.4
6	7.6	26.4	39.5	34.1	55.8	53.6
8	7.9	54.1	73.2	71.5	84.8	80.7
10	9.3	68.5	85.9	80.6	90.8	87.4

Table A.2 Raw data of CaO based catalysts with strong based compounds for transesterification reaction.

Reaction time (h)	Conversion of oil (%)					
	CaO*	[H ₂ O/CaO]*	[0.5 M NaOH/CaO]*	[1 M NaOH/CaO]*	[0.5 M KOH/CaO]*	[1 M KOH/CaO]*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	4.5	4.5	0.5	0.8	0.0	0.3
4	6.4	10.1	1.0	1.1	0.6	1.2
6	7.6	26.4	1.5	1.9	1.2	2.0
8	7.9	54.1	2.2	2.5	1.9	3.2
10	9.3	68.5	2.7	2.9	2.2	3.7

Table A.3 Raw data of heterogeneous reused catalysts for transesterification reaction.

Conversion of oil (%)						
No.	CaO*	[H ₂ O/CaO]*	[0.5M NH ₄ OH/caO]*	[1M NH ₄ OH/CaO]*	[0.4M Ca(OH) ₂ /CaO]*	[1M Ca(OH) ₂ /CaO]*
#1	10.9	68.9	83.5	82.9	93.2	89.4
#2	11.7	66.6	80.0	79.2	88.8	85.5
#3	11.7	62.8	82.8	81.6	90.5	87.0
#4	12.3	65.8	85.5	84.0	92.2	88.4

VITA

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Publications

“Calcium oxide based catalysts for ethanolysis of soybean oil,” Songklanakarin Journal of Science and Technology, 32(6) (2010): 627-634

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