THESIS

BIODIESEL PRODUCTION FROM CRUDE PALM OIL USING K_2CO_3/CaO AS HETEROGENEOUS CATALYST

MAYTHINEE SIRIKULBODEE

GRADUATE SCHOOL, KASETSART UNIVERSITY
2007

THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Chemical Engineering)
DEGREE

Chemical Engineering	Chemical Engineering
FIELD	**DEPARTMENT**

TITLE: Biodiesel Production from Crude Palm Oil using K_2CO_3/CaO as Heterogeneous Catalyst

NAME: Ms. Maythinee Sirikulbodee

THIS THESIS HAS BEEN ACCEPTED BY

THESIS ADVISOR
(Assistant Professor Kandis Sudsakorn, Ph.D.)

DEPARTMENT HEAD
(Associate Professor Paisan Kongkachuichay, Ph.D.)

APPROVED BY THE GRADUATE SCHOOL ON 9/11/07

DEAN
(Associate Professor Vinai Artkongharn, M.A.)

THESIS

BIODIESEL PRODUCTION FROM CRUDE PALM OIL USING K_2CO_3/CaO AS HETEROGENEOUS CATALYST

MAYTHINEE SIRIKULBODEE

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Chemical Engineering)
Graduate School, Kasetsart University
2007

Maythinee Sirikulbodee 2007: Biodiesel Production from Crude Palm Oil using K_2CO_3/CaO as Heterogeneous Catalyst. Master of Engineering (Chemical Engineering), Major Field: Chemical Engineering, Department of Chemical Engineering. Thesis Advisor: Assistant Professor Kandis Sudsakorn, Ph.D. 87 pages.

At present, alternative fuels for diesel engines are becoming more important due to limited resource of fossil fuel, increasing price of crude oil and also environmental concerns. Biodiesel can be a substitute for conventional diesel due to its comparable fuel properties and cleaner emission. In this study, transesterification of crude palm oil with methanol was catalyzed by heterogeneous catalyst, K_2CO_3/CaO and the optimum condition for biodiesel production was investigated. The catalyst was prepared by incipient wetness impregnation having different loadings of K_2CO_3 (5, 15, 25 and 35 wt%) and used without calcination. The catalysts were characterized by XRD, XRF, N_2 Physisorption and DTA/TGA. Transesterification was studied 6:1, 12:1, 18:1, 26:1 and 33:1 methanol to oil molar ratio, reaction time of 2, 3 and 5 h and catalyst amount of 2, 4, 6 and 9 wt%. The highest of methyl ester content and yield were obtained as 96 and 81 %, respectively, with the 35 wt% K_2CO_3/CaO catalyst. The optimum condition was found to be 60 ^{O}C, 3h, 26:1 methanol to oil molar ratio, 6 wt% catalyst amount, 20 wt% THF and 300 rpm stirring speed. The methyl ester properties including flash point, pour point, cloud point, viscosity and density were determined and found to be comparable to the standard values. Furthermore, a comparison of catalytic activities of K_2CO_3/CaO and others including K_2CO_3/Al_2O_3 and KNO_3/ Al_2O_3 confirmed that K_2CO_3/CaO show to be most active due to the highest basicity of K_2CO_3 and higher transesterification activity of CaO compared to Al_2O_3. Finally K_2CO_3/CaO without calcination was shown to behave partly like a homogeneous catalyst. However, it could be completely regenerated to have activity similar to a fresh catalyst without calcination- a step where a large amount of energy was consumed.

ythinee Sirikulbodee — 28 / 10 / 07

Student's signature — Thesis Advisor's signature

ACKNOWLEDGMENT

I would like to dedicate my sincere thank to people who have contributed either directly or indirectly to this thesis. First, I would like to thank Asst.Prof.Dr. Kandis Sudsakorn, my thesis advisor, for the guidance throughout the course of this work. I would like to thank Assoc.Prof.Dr.Paisan Kongkachuichay, the thesis committee who gave me ideas and suggestions for my work.

In addition, I would like to thank Kasetsart University Research and Development Institute (KURDI) for the financial support and the Siam oil and Fat Co., Ltd. for crude palm oil supply.

Finally, I would like to thank my family, my mother and father who support and help me every time.

Maythinee Sirikulbodee
March 2007

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

Figures **Page**

LIST OF APPENDIX FIGURES

Figures **Page**

LIST OF APPENDIX TABLES

LIST OF ABBREVIATIONS

ASTM = The American society for testing and materials
BET = Brunuer-Emmett-Teller
^{o}C = Degree celsius
cSt. = Centistokes
CaO = Calcium oxide
$CaCO_3$ = Calcium carbonate
$Ca(HO)_2$ = Calcium hydroxide
Cu = Copper
D = Density
DTA/TGA = Differential thermal analysis/Thermogravimetric analysis
^{o}F = Degree Fahrenheit
GC = Gas chromatography
g/l = Gram per liters
g/ml = Gram per milliliters
h = Hour
H_2O = Water
H_2SO_4 = Sulfuric acid
K_2CO_3 = Potassium carbonate
K_2CO_3/Al_2O_3 = Potassium carbonate alumina
K_2CO_3/CaO = Potassium carbonate on calcium oxide
KNO_3 = Potassium nitrate
KNO_3/Al_2O_3 = Potassium nitrate on alumina
lb/gal = Pound per gallon
M = Mole
MEOH = Methanol
min = Minute
NaCl = Sodium chloride
$NaOCH_3$ = Sodium methoxide
NaOH = Sodium hydroxide

rpm = Revolution per minute
s = Second
SEM = Scanning electron
THF = Tetrahydrofuran
wt % = Percentage by weight
Xe = Xenon
XRD = X-Ray Diffraction spectrometer
XRF = X-Ray Fluorescence spectroscopy

BIODIESEL PRODUCTION FROM CRUDE PALM OIL USING K_2CO_3/CaO AS HETEROGENEOUS CATALYST

INTRODUCTION

At present, the demand for fossil fuels has continuously been increasing especially for diesel. Unfortunately, there are limited resources of fossil fuel, which will be used up within 50 years at this rate of consumption. As a result, the price of diesel fuel has been sharply increasing from 7-8 baht/liter at the end of 2005 to 30.39 baht/liter in the middle of 2007. Consequently it has a direct impact on the cost of living due to higher production costs of consumer products. One of the approaches in dealing with the fossil fuel shortage is producing and using renewable energy. Thailand started the renewable energy project in 2001 that focused on various alternatives including solar energy, biomass, biogas and especially biodiesel - a substitute to diesel that has recently gained lots of interest from government and the public.

Biodiesel is renewable diesel fuel which is considered a clean environmentally - friendly energy. Its emission has a lower content of CO by 10 %, particulates by 15 %, hydrocarbons by 10 %, and sulfates by 20 % compared to that of conventional diesel. Biodiesel can be produced from vegetable oils or animal fats by transesterification with methanol or ethanol. A catalyst such as alkali, acid or heterogeneous catalyst is required for the reaction. The products of this reaction are the desirable alkyl esters (biodiesel) and the by-product glycerol. The raw materials for producing biodiesel come from renewable natural resources such as oil plants i.e., palm , rapeseed, soybean, sunflower, cotton seed, coconut, canola, Jatropha, and animal fats, i.e., beef tallow and pork lard. Used cooking oil from restaurants can also be converted into biodiesel.

Transesterification reaction can reduce the molecular weight of triglyceride in vegetable oils and their viscosities and increase the oxygen content by 10 to 11 wt%. The higher oxygen content of biodiesel allows more complete combustion in diesel engines than the conventional diesel. The cetane numbers of biodiesel range between 49 to 62 which are acceptable and comparable to the conventional diesel. The cloud point and pour point of biodiesel are ranged 15 to 25 ^{O}C. Although they are higher than those of the conventional diesel, they are still acceptable.

The choice of vegetable oil for biodiesel production depends on climates and soil conditions. Therefore, each country may have different choices, for example, soybean oil in the United states , rapeseed oil and sunflower oil in Europe, coconut oil in Philippines, and palm oil in Southeast Asia (Malaysia and Indonesia). Thailand is the fourth largest palm oil manufacturer in the world. This thesis, is therefore focusing on using crude palm oil as raw material due to its easy availability in the country and low cost. Crude palm oil is a semi-solid material at room temperature with a melting point of 36 °C. The compositions of crude palm oil are 90 % triglycerides, 2–7 % diglycerides, 1 % monoglycerides and 3–5 % free fatty acids.

The conventional method for biodiesel production relies on using one of various acids or alkalis as a homogeneous catalyst which causes a difficulty in catalyst separating from the products. This separation is normally done by washing with water which generates a lot of waste water in downstream process. This is, however, not the case when using a heterogeneous catalyst which can be easily removed from the products by filtration and reused.

However, there are a number of problems in biodiesel production with heterogeneous catalysts. For example, it gives lower yield and requires more time to complete the reaction compared to the conventional process. Therefore, this thesis proposes to resolve these problems by developing a better heterogeneous catalysts and finding the optimum condition to obtain the highest yield of methyl ester. Also, the quality of the biodiesel produced will be investigated and compared to the standard values.

OBJECTIVES

1. To develop a better heterogeneous catalyst for the production of biodiesel from crude palm oil by transesterification reaction.
2 To determine the optimum condition to obtain maximum yield of biodiesel
3. To investigate the possibilities of reuses and regeneration of the after multiple uses.
4. To analyze the quality of biodiesel product compared to that of conventional diesel.

Scopes of thesis

1. The reaction was done in a batch glass reactor with hot plate magnetic stirrer (30-1000^{O}C and 1-200 rpm), 250ml two necked glass flask, 2000 ml beaker, condenser and thermometer (0-100 ^{O}C).
2. Factors to be studied are type of catalysts (CaO, K_2CO_3/CaO, K_2CO_3/Al_2O_3, KNO_3/Al_2O_3), calcination temperature, catalyst loading, methanol to oil molar ratio, amount of catalyst and reaction time.
3. All of catalysts were characterized by XRD, XRF, SEM, N_2 physisorption and DTA/TGA. Then, the catalysts were calcined at 300, 500 and 800 ^{O} C and the catalyst loading was 5, 15, 25 and 35 wt%. The methanol to oil molar ratio was varied at 6:1, 12:1, 26:1, and 33:1. The amount of catalysts was 1, 3, 6 and 9 wt %. The reaction time was 1, 2, 3 and 5 hr.
4. Several fuel properties of biodiesel product are of interest including viscosity, pour point, cloud point, flash point and density. These properties will be tested and compared to the B100 standard.

Thesis contributions

1. A highly efficient heterogeneous catalyst for biodiesel production from crude palm.
2. Biodiesel from crude palm oil having fuel properties meeting the B100 standard set by the department of energy business
3. Reduction of polluted emission due to cleaner combustion of biodiesel.
4. Reduction of crude petroleum imports promoting a self-reliability and sustainability in energy production and consumption.

LITERATURE REVIEW

Furuta *et al.* (2006) studied about transesterification of soybean oil using various solid catalysts with methanol. They studied several solid catalysts including tungstated zirconia-alumina (WZA), sulfated tin oxide (SO_4^{2-}/SnO_2 or STO) and sulfated zirconia-alumina (SZA). The effects of reaction temperature and acid strength were investigated at conditions of 573-673 K, 4h, 4 wt% catalyst amount and 10 wt% THF. The results showed that all catalysts gave the conversion closed to 100 % at 548 K. WZA showed the highest catalytic activity 100 % conversion. Although the acid strength of STO is higher than those of SZA and WZA, WZA showed the highest catalytic activity. Therefore, the acid strength did not affect the transesterification of soybean oil with methanol.

Lopez *et al.* (2007) studied transesterification of triacetin with methanol using solid acid and base catalysts. The purpose of this research was to find catalyst characteristics that would be suitable for biodiesel production. The catalytic activities of solid catalysts were compared by triacetin conversion. The solid acid catalysts studied were tungstated zirconia (WZ), sulfated zirconia (SZ), Amberlyst-15, Nafion NR50, supported phosphoric acid (SPA), $H\beta$ zeolite and ETS-10 (H). The solid base catalysts studied were MgO, and ETS-10 (Na, K). The methyl esters were analyzed by Gas chromatography (GC). All solid catalysts were pretreated for 3 h with UHP air before calcination with desired temperature, except Nafion NR50 was not calcined because it is resin catalyst. The effect of reaction temperature, reaction time and deactivation of catalysts were investigated. For solid base catalysts, the results showed that ETS-10(Na, K) have higher conversion than MgO of 99 % and 30 %, respectively at the condition 60 ^{O}C, 4 h and 6:1methanol to oil molar ratio. For the solid acid catalysts, the order of catalytic activities was: Amberlyst-15 > SZ >Nafion NR50 > WZ > SPA > $H\beta$ zeolite > ETS-10 (H) and the conversion was 79 %, 57 %, 33 %, 15 %, 10 % and 5 %, respectively, for the same reaction condition. Furthermore, deactivation studies were carried out for the most active solid catalysts: ETS-10 (Na, K), Amberlyst-15, SZ, WZ, and Nafion NR50. The results showed that

ETS-10(Na, K) have less deactivation than other catalysts and, therefore, was a suitable catalyst for the biodiesel production from triacetin.

Suppes *et al.* (2004) studied biodiesel production from soybean oil using ETS-10 zeolite and a series of NaX faujasite zeolite as catalysts. ETS-10 showed a very high cation – exchange capacity, large pore structure, and strong basicity. NaX was occluded with amount of 0.25, 1, 3, 4 wt% sodium oxide (NaO_x/NaX) by impregnation method. All catalysts were calcined at 723 K for 10 h to removal water and carbon dioxide from the surface of catalyst. Transesterification of soybean oil was studied with reaction temperature from 333 K to 423 K, 24 h, 6:1 methanol to oil molar ratio. The result showed that calcined catalysts gave higher conversion of soybean oil than those without calcination. The conversion of soybean oil was increased with increasing temperature (333, 393, and 423 K). At 423 K, ETS-10 gave higher conversion of soybean oil than $4NaO_x$/NaX catalysts that were 95.8 % and 94.5 %, respectively.

Jitputti *et al.* (2006) studied biodiesel production from crude palm kernel oil (PKO) and crude palm coconut oil (CCO) by using solid and zeolite catalysts. The catalyst studied were zinc oxide (ZnO), sulphated zirconia (SO_4^{2-}/ZrO_2), sulphated stannous oxide (SO_4^{2-}/SnO_2), KNO_3/KL zeolite and zirconia-supported potassium nitrate (KNO_3/ZrO_2). All catalysts were calcined at desired temperatures. Transesterification reaction was used for reducing the viscosity of vegetable oil by using Parr series reactor. The conditions for experiment were at 473 K, 4 h and 6:1 methanol to oil molar ratio. For PKO, all catalysts showed the high activity for transesterification of PKO with methanol. Moreover, soap information was not observed when these catalysts were used. The yield of methyl esters from solid and zeolite catalysts were followed by this order: (SO_4^{2-}/ZrO_2) and (SO_4^{2-}/SnO_2) >ZnO > KNO_3/ZrO_2 > KNO_3/KL zeolite with methyl esters yields of 90.3 %, 90.3 %, 86.1 %, 71.4 % and 64.5 %, respectively. For CCO, SO_4^{2-}/ZrO_2 gave the highest methyl ester yield (86.3 %), followed by SO_4^{2-}/SnO_2 , ZnO, KNO_3/KL zeolite and KNO_3/ZrO_2 with methyl esters yields of 86.3 %, 80.6 %, 77.5 %, 77.2 % and 65.5 %, respectively. The methyl esters yield that produced from PKO is higher than that from CCO. This may be due to the higher amount of free fatty acid and water content of CCO which have an effect on the reaction.

Xie *et al.* (2007) investigated many heterogeneous catalysts such as modified zeolites, ETS-10, CaO, tungstated zirconia (WZ), sulfated zirconia (SO_4^{2-}/ZrO_2 or SZ). However, these catalysts were expensive or sensitive to water and acid. Therefore, they needed to find more efficient and cheap catalysts for transesterification of soybean oil with methanol. KF/ZnO was selected as a heterogeneous catalyst due to novelty for use in transesterification, low cost and easy preparation. The effects of calcination temperature, molar ratio of methanol to oil, catalyst amount and reaction time were investigated. The results showed the conversion of soybean oil was increased with increasing the basic strength, molar ratio methanol to oil, catalyst amount and reaction time. But, the conversion of soybean oil was decreased when the calcination temperature was higher than 887 K and when the catalyst amount was higher than 3 wt%. Calcination at 973 K or higher temperature led to loss in catalytic activity may be resulted from the loss of potassium species. When increasing the amount of catalyst beyond 3 wt% the conversion of soybean oil was decreased because of the mixing problem. Therefore, well - dispersed mixing was essential to reach the maximum conversion. It was found that the optimum condition for transesterification of soy bean oil with methanol was at 9 h, 10:1 methanol to oil molar ratio and 3 wt% catalyst amount calcined at 873 K. At this condition, the conversion of soy bean oil was 87 %.

Xie *et al.* (2006) studied transesterification of soy bean oil using potassium iodide (KI) loaded onto alumina (Al_2O_3) as a solid catalyst. The effects of KI loadings, molar ratio of methanol to oil, catalyst amount and reaction time were investigated. The catalyst was prepared by impregnation method followed by calcination at 773 K for 3 h. The results showed, the conversion of soybean oil was increase with increasing the KI loadings (up to 35 wt%), molar ratio of methanol to oil, catalyst amount and reaction time. However, when the KI loading was more than 35 wt% the conversion decreased due to the excess KI could cover the basic sites on the surface of catalyst. Moreover, the conversion of soybean oil was decreased when the calcination temperature was higher than 773 K and the catalyst amount was higher than 2.5 wt% similarly due to the loss of K and poor catalyst dispersion best KI loading was of 35 wt% for this catalyst. And when it was used at 783 K, 8 h, 15:1 methanol to oil molar ratio, and 2.5 wt% catalyst amount, the highest conversion of soy bean oil of 96 % was obtain.

Xie *et al.* (2005) studied biodiesel production from soybean oil with methanol using potassium nitrate (KNO_3) loaded on alumina (Al_2O_3). The catalytic activity of the solid catalyst was also investigated to determine the optimal condition. The effects of KNO_3 loading, calcination temperature, methanol to oil molar ratio, catalyst amount and reaction time were investigated. The alumina had a surface area of 126 m^2/g. Potassium nitrate was loaded on to alumina by impregnation method from aqueous solution, followed by drying at 393 K for 16 h. The catalyst was calcined at 773 K for 5 h. The results showed that the conversion of soybean oil increase with increasing the KNO_3 loading, molar ratio methanol to oil, catalyst amount and reaction time. However, excess KNO_3 loading decreased the conversion of soybean oil because the dispersion limitation. The conversion of soybean oil was decreased when the calcination temperature was higher than 773 K and that possibly because of the loss of K. When the reaction was carried out at reflux of methanol, with molar ratio of methanol to oil of 15:1, a reaction time 7 h and a catalyst amount of 6.5 wt%, the highest conversion was reached 87 %.

Theory

1. Palm oil

Palm is a plant that gives a large amounts of oil compared to other crops. As shown in Table 1 palm contains 5000 kg oil/ha which is the third highest rank among all crops. Fresh fruits of palm are reddish in color having a shape as shown in Fig 1. The size of the fruit is about that of a large plum. It grows in large bunches and matures after 5-7 years with a harvesting age up to 25 years. The weight of a fruit bunch is between 10 to 40 kilograms. Each fruit contains a single seed (containing palm kernel oil) coated by a soft oily pulp. Oil can be extracted from both the pulp of the fruit (crude palm oil for edible oil production) and the kernel (crude palm kernel oil, used for soap manufacturing). The general unit of palm oil processing is shown in Figure 2. Every 100 kilograms of fruit bunches can be extracted to about 22 kilograms of palm oil and 1.6 kilograms of palm kernel oil. After extraction, crude palm oil contains contaminates and impurities as shown in Table 2.

Table 1 Oil production per area of various Crops

Crops	kg oil/ha	liters oil/ha	lbs oil/acre	US gal/acre
Algae	79832	95,000	-	10,000
Chinese tallow	5500	6545	4912	699
Palm oil	5000	5950	4465	635
Coconut	2260	2689	2018	287
Avocado	2217	2638	1980	282
Brazil nuts	2010	2392	1795	255
Macadamia nuts	1887	2246	1685	240
Jatropha	1590	1892	1420	202
Jojoba	1528	1818	1365	194
Pecan nuts	1505	1791	1344	191
Castor beans	1188	1413	1061	151
Olives	1019	1212	910	129
Rapeseed	1000	1190	893	127
Opium poppy	978	1163	873	124
Peanuts	890	1059	795	113
Cocoa (cacao)	863	1026	771	110
Sunflowers	800	952	714	102
Tung oil tree	790	940	705	100
Rice	696	828	622	88

Table 1 (Continued)

Crops	kg oil/ha	liters oil/ha	lbs oil/acre	US gal/acre
Safflower	655	779	585	83
Sesame	585	696	522	74
Camelina	490	583	438	62
Mustard seed	481	572	430	61
Coriander	450	536	402	57
Pumpkin seed	449	534	401	57
Hazelnuts	405	482	362	51
Linseed (flax)	402	478	359	51
Coffee	386	459	345	49
Soybean	375	446	335	48
Hemp	305	363	272	39
Cotton	273	325	244	35
Oats	183	217	163	23
Cashew nut	148	176	132	19
Corn (maize)	145	172	129	18

Note: Chinese tallow (Triadica Sebifera or Sapium sebiferum) is also known as the "Popcorn Tree" or Florida Aspen.

Source: The Global Petroleum Club (2007)

Figure 1 Fresh fruit of palm oil

Source: Malaysian Palm Oil Promotion Council (2000)

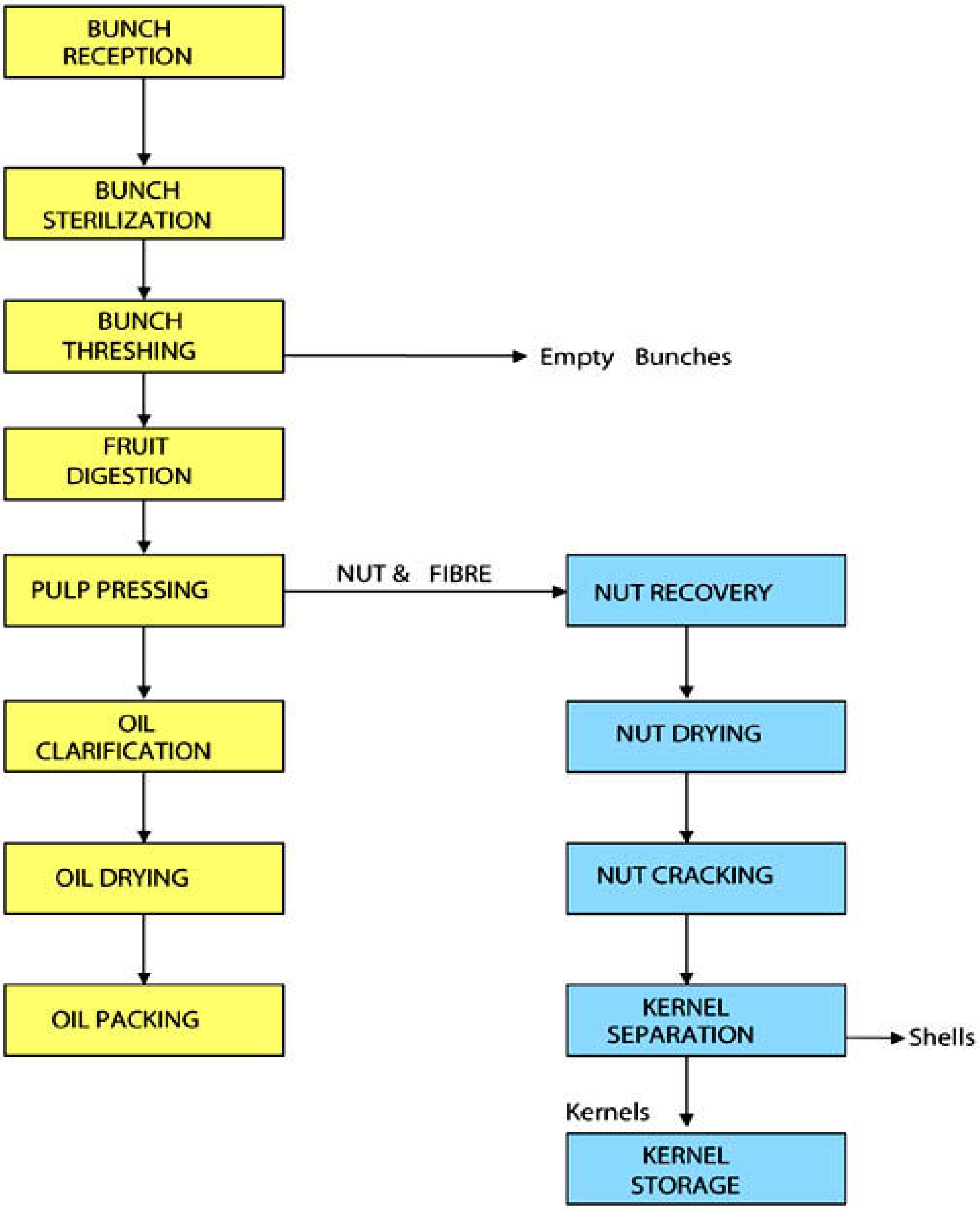


Figure 2 Palm oil processing unit operation

Source: Agriculture department

Table 2 Composition of crude palm oil

Substances	Contents
Free Fatty Acid (FFA)	3 – 5 %
Gums (phospholipids, phosphotides)	300 ppm
Dirt	0.01 %
Shell	Trace
Moisture and Impurities	0.15 %
Trace metal	0.50 %
Oxidation Products	Trace
Total Carotenoids	500 - 1000 mg/kg

Source: Biodiesel fuel production by transesterification of oils (2001).

1.1 Crude palm oil composition

Crude palm oil is composed of 95 % glyceride, 3-5 % free fatty acid and 1 % minor and trace component. Crude palm oil and palm kernel oil are composed of fatty acids. Both are high in saturated fatty acids, about 50 % and 80 %, respectively. The palm oil has the 16 carbon saturated fatty acids in which palmitic acid and monounsaturated oleic acid are also constituent of palm oil while palm kernel oil contains mainly lauric acid. The compositions of fatty acids in palm oil and palm kernel oil are shown in Table 3. Palm oil is the largest natural source of tocotrienol, part of the vitamin E family. It also contains high vitamin K, dietary magnesium, and a large amount of carotenoids.

Table 3 Fatty acid compositions of palm oil and palm kernel oil

Fatty acid composition of palm oil		Fatty acid composition of palm kernel oil	
Saturated (total: 49.9%)		Saturated (total: 82%)	
Palmitic acid C16:0	44.3%	Lauric C12:0	48.2%

Table 3 (Continued)

Fatty acid composition of palm oil		Fatty acid composition of palm kernel oil	
Stearic C18:0	4.6 %	MyristicC14:0	16.2 %
Myristic C14:0	1.0 %	Palmitic acid C16:0	8.4 %
		Capric C10:0	3.4 %
		Caprylic C8:0	3.3 %
		Stearic C18:0	2.5 %
Monounsaturated		Monounsaturated	
Oleic C18:1	38.7 %	Oleic C18:1	15.3 %
Polyunsaturated		Polyunsaturated	
Linoleic C18:2	10.5 %	Linoleic C18:2	2.3 %

Source: Dietary lipid and palm oil source affects growth, fatty acid composition and muscle α-tocopherol concentration of African catfish, Clarias gariepinus (2003)

1.2 Potential of crude palm oil as raw material for biodiesel production

In Thailand about 90 % of the palm oil is used for the food industry and 10 % is used for others such as cosmetics. Moreover, palm oil has a high potential to produce biodiesel that can be used to replace conventional diesel. Stocks of CPO at the end of year 2006 and 2007 as shown in Table 4 are 164,521 and 301,812 tons, respectively.

Table 4 A balance sheet of crude palm oil in 1998-2007

Years	Stock at the begin of the year (tons)	Production (tons)	Import (tons)	Total (tons)	Export (tons)	Domestic used (tons)	Stock at the end of the year (tons)
1998	70,181	352,118	11,373	422,672	23,483	384,490	25,699
1999	25,699	707,951	-	733,650	16,967	536,106	180,577
2001	157,388	780,389	-	937,777	160,810	688,083	108,884
2003	59,995	863,835	-	923,830	76,667	732,210	114,953
2004	114,953	820,841	-	935,794	3,036	781,636	151,122
2005	151,122	783,953	-	935,075	-	821,406	113,669
2006	113,669	1,167,126	-	1,280,795	199,957	916,317	164,521
2007	164,521	1,289,750	-	1,454,271	-	980,459	301,812

Source: Biodiesel fuel production by transesterification of oils (2001).

Source: Bangkok renewable energy Co., Ltd (2007)

The stock of CPO in Thailand has increased continuously from 1998 to 2007 due to the expanding of the palm-growing area. The major growing areas are Krabi, Surathanee, Chumporn, Trung and Satool. There are 23 large palm oil extraction plants and 22 small palm oil extraction plants in Thailand which have the capacities about 7.78 and 4.50 million tons of bunches/years. These capacities can sufficiently serve for biodiesel production in a commercial scale. Moreover, the price of CPO is cheaper than refined palm oil. Therefore, in this thesis, CPO was selected as raw material for biodiesel production. The properties of palm oil are shown in Table 5.

Table 5 Properties of palm oil

Property	Range
Kinematics viscosity at 38 ^{0}C (mm^2/s)	39.6
Cetane number	42.0
Heating value	-
Cloud point (^{0}C)	31.0
Pour point (^{0}C)	-
Flash point (^{0}C)	267
Density (kg/l)	0.9180
Carbon residue (wt%)	-
Ash (wt%)	-
Sulphur (wt%)	-

Source: Biodiesel fuel production by transesterification of oils (2001).

Some properties are higher than those of conventional diesel. However, after the conversion of palm oil into biodiesel, the properties are changed significantly as shown in Table 6.

Table 6 Properties of Biodiesel from palm oil .

Property	Range
Kinematics viscosity at 37.8 ^{0}C (mm^2/s)	5.7
Cetane number	62.0
Lower heating value (MJ/l)	33.5
Cloud point (^{0}C)	13.0
Pour point (^{0}C)	-
Flash point (^{0}C)	164
Density (g/ml)	0.880
Carbon residue (wt%)	-

Source: Biodiesel fuel production by transesterification of oils (2001).

There are many properties of biodiesel that affect on diesel engine such as viscosity, flash point and density. The high viscosity will result in bigger size droplets out of the injection nozzle causing incomplete combustion. The density of biodiesel should be nearly that of diesel for good mixing when blending with the diesel. Too low a flash point will cause injector failure, fires, or even explosions, therefore the final biodiesel product must be methanol free. Table 7 shows the standard of biodiesel (B100) set by the Department of Energy to avoid engine problems. When comparing the properties of biodiesel from palm oil (Table 7) with the standard, it shows quite similar properties. This confirms that palm oil have high potential to be used as raw material for biodiesel production.

Table 7 Specification from the department of energy business for biodiesel (B100)

Item	Description	Standard requested by department of energy business	Unit	Test
1	Density @ 15 ^{O} C	not less than 860 and not more than 900	kg/m^3	ASTM D1298
2	Kinematics viscosity @ 40 ^{O} C	not less than 3.5 and not more than 5.0	cSt	ASTM D 445
3	Flash point	not less than 120	^{O} C	ASTM D 93
4	Sulfur	not more than 10	mg/kg	ASTM D 2622
5	Sulfated ash content	not more than 0.30	% wt	ASTM D 874
6	Water content	not more than 0.05	% wt	EN ISO12937
7	Total contaminate	not more than 0.0024	% wt	EN 12662

Table 7 (Continued)

Item	Description	Standard requested by department of energy business	Unit	Test
8	Copper strip corrosion (3 hrs@50 ^{O} C)	not more than "Standard No. 1"	Rating	ASTM D 130
9	Oxidation stability @ 110 ^{O} C	not less than 6	hours	EN 14112
10	Cetane number	not less than 51	-	ASTM D 613
11	Carbon residue (10% distillation residue)	not more than 0.30	% wt	ASTM D 4530
12	Acid value	not more than 0.50	mgKOH/g	ASTM D 664
13	Iodine value	not more than 120	g l/100 g	EN 1411
14	Methyl ester	not less than 96.5	% wt	EN 14103
15	Linolenic acid methyl ester	not more than 12.0	% wt	EN14103
16	Methanol	not more than 0.20	% wt	EN 14110
17	Monoglycerides	not more than 0.80	% wt	EN14105
18	Diglycerides	not more than 0.20	% wt	EN14105
19	Triglycerides	not more than 0.20	% wt	EN14105
20	Free glycerin	not more than 0.02	% wt	EN14105
21	Total glycerin	not more than 0.25	% wt	EN14105
22	Phosphorous	not more than 0.0010	mg/kg	ASTM D 4951

Table 7 (Continued)

Item	Description	Standard requested by department of energy business	Unit	Test
23	Group I metals (Na+K)	not more than 5.0	mg/kg	EN 14108 and EN14109
24	Group II metals (Ca+Mg)	not more than 5.0	mg/kg	EN 14538

Source: The Department of Energy Business (2007)

2. Biodiesel

Biodiesel is an alternative fuel for diesel engine. Moreover, biodiesel is a renewable energy which is biodegradable, friendly environmentally and nontoxic. Using biodiesel can reduce air pollutants, such as particulates, carbon monoxide and hydrocarbons. Biodiesel derived from vegetable oils or animal fats has shown potential as a substitute for conventional diesel fuels. For example, it has a viscosity close to conventional diesel fuels, its volumetric heating values are a little lower but it has high cetane and flash point. These comparable properties allow, it being used in a diesel engine directly without engine modifications. Recently, the government has made a new plan for biodiesel production. The future plan expects a consumption of biodiesel about 4 million L/day (B5, a mixture of 5 % biodiesel and 95 % petroleum diesel) in 2010 for reducing pollutions and supporting local economy. After 2010, the biodiesel blend will increase to B10 (a mixture of 10 % biodiesel and 90 % petroleum diesel) as shown in Table 8.

Table 8 New government plan for future biodiesel consumption 2005-2020

Years	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20
Palm stearin (millions liters/ days)							production 0.5									
Growing palm trees (million ha/yrs)	-	-	0.3	0.3	0.3	0.3	0.3		total palm tree in 2010 are 1.5 million ha/yrs							
Using B100 (millions liters/ days)		in 2010 will used 4 millions L/days (B 5)						supported B 10 after 2010								
Imports (millions liters/ days)							no support									

Source: Ministry of Energy Thailand (2007)

As a result, biodiesel production is of interest for Thailand because it helps reducing petroleum diesel imports and improving the local economy. Biodiesel in Europe and in the United States is utilized by blending with diesel fuel or using as pure biodiesel. The most common mixture is B20 that is a mixture of 20 % biodiesel and 80 % petroleum diesel. B100, or 100 % biodiesel, which is called “neat biodiesel” is still not widely used because of its effects on engine and its high cost.

Biodiesel can be produced by different methods such as pyrolysis, microemulsification, dilution and transesterification. In transesterification triglyceride is reacted with methanol or ethanol in the presence of a catalyst such as one of alkalis, acids or enzymes or without any catalyst such as reaction in a supercritical media. The products are biodiesel (methyl ester) and glycerol. The raw materials for producing biodiesel come from various vegetable oils such as soybean, palm, canola , sunflower, etc. and even animal fats.

2.1 Methods to produce biodiesel from vegetable oils

Properties of crude palm oil are not suitable for use in a diesel engine. Many properties such as viscosity, flash point and density could be improved to be close those of conventional diesel. This can be done with different methods, for example:

- Pyrolysis
- Microemulsification
- Esterification
- Transesterification

a) Pyrolysis

Pyrolysis is a process of heating to high temperature under an oxygen free environment which is commonly done in a nitrogen atmosphere. This process can change triglycerides to biodiesel by using thermal energy. Many researchers have studied the pyrolysis of triglyceride to produce a diesel substitutes. Biodiesel from pyrolysis has low viscosity and high cetane number. Although, the amount of sulfur from pyrolysed vegetable oil is acceptable, the amount of ashes and carbon residues are not.

b) Microemulsification

Microemulsification uses either vegetable oil with ester and dispersant (co-solvent) or vegetable oil with alcohol and surfactant. The products from both method can be blended with or without conventional diesel. The viscosity of the products was reduced. However, there are still some carbons accumulated around the injector nozzles during combustion of this microemulsified biodiesel.

c) Esterification

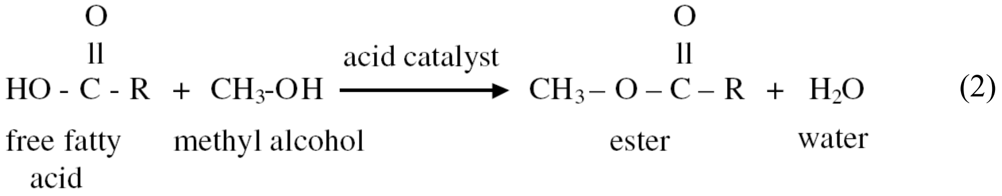
Biodiesel production normally uses alkali catalysts because they give high yields. However, the main problem is residual catalysts in biodiesel and soap formation from free fatty acids (FFAs) in feedstock. Feedstocks that have high FFAs are such as crude palm oil (2-10 %), crude corn oil (3-5 %) and rubber seed oil (4-9 %). When FFA in feedstocks react with alkali catalysts during transesterification, will the presence of water as a catalyst it will form soap. This reaction is known as saponification reaction reacting between a free fatty acid and an alkali either sodium or magnesium to produce soap plus a molecule of water:

$$RCOOH + NaOH \Rightarrow RCOONa + H_2O \qquad (1)$$

Soaps are implicated in 3 reactions; first they are a necessary component in the hydrolysis reaction by acting as an emulsifier which allows water to more easily react with the oil. Second they can reduce the surface tension of the oil which allows oxygen to more easily attack the oil in the oxidation reaction. Finally, again acting as an emulsifier at the oil and “free water” interface at the bottom of storage tanks, they can promote bacteriological growth. The maximum amount of free fatty acid in alkali catalyzed systems is less than 0.5 %. If the feedstock has FFA level higher more than 0.5 % it must undergo esterification process to convert FFA to methyl ester before transesterification. In this thesis, several solid the alkali catalysts were used in transesterification and the FFA of CPO is higher than 0.5 % in which esterification reaction (Eq.2) is required.

Esterification normally uses acid catalyst such as sulfuric acid or phosphoric acid. This method is suitable for feedstock that contains high level of FFA such as crude palm oil, crude rice bran oil rubber seed oil and tallow.

In addition, acid-catalyzed esterification of free fatty acid is faster than acid-catalyzed transesterification reaction of triglyceride, because the molecules of FFA are smaller than the molecules of triglyceride.



$$\underset{\text{free fatty acid}}{HO-\overset{\overset{O}{\|}}{C}-R} + \underset{\text{methyl alcohol}}{CH_3\text{-}OH} \xrightarrow{\text{acid catalyst}} \underset{\text{ester}}{CH_3-O-\overset{\overset{O}{\|}}{C}-R} + \underset{\text{water}}{H_2O} \qquad (2)$$

Figure 3 Esterification of free fatty acids with alcohol using acid catalyst.

Source: Heterogeneous esterification of oil with high amount of free fatty acids (2006)

d) Transesterification

Transesterification can be used to reduce the viscosity of vegetable oils by reacting with alcohol using a catalyst. The general equation of transesterification are shown in Fig 4. Based on the stoichiometry of the transesterification reaction, it requires 3 moles of alcohol per one mole of triglyceride to yield 3 moles of fatty acid alkyl esters and 1 mole of glycerol. The first step is the conversion of triglyceride to diglyceride, following by the conversion of diglyceride to monoglyceride, and finally monoglyceride to methyl ester. The conventional catalysts for this reaction are homogeneous alkali catalysts or acid catalysts.

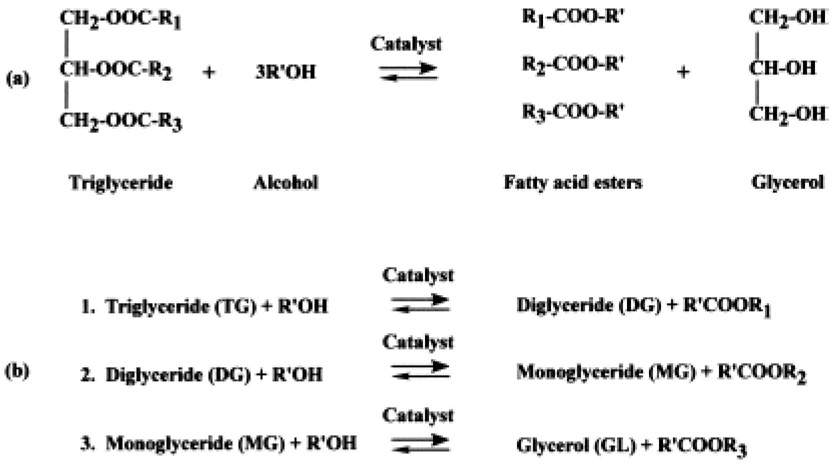


Figure 4 Transesterification of triglyceride with alcohol. (a) general equation (b) three consecutive and reversible reactions. R_1, R_2, R_3, and R' represent alkyl group

Source: Biodiesel fuel production by transesterification of oils (2001)

Catalysts for transesterification reaction

Transesterification can be catalyzed by many types of catalysts including:

1. Acidic catalysts
2. Basic catalysts
3. Solid catalysts (heterogeneous catalysts)

1. Acidic catalysts

Transesterification using acid catalysts is normally done with sulfuric, phosphoric, hydrochloric or organic sulfonic acids . In fact, transesterification using an acid catalyst is much slower than using an alkali catalyst, but it is suitable for glycerides that have high free acid contents and water. Acid catalysts can catalyze the reaction without any disturbances from those presences. Although acid catalysts can be used for transesterification they are too slow for industrial processing. Moreover, scaling up an acid-catalyzed system requires to use a corrosive resistant material which is costly.

2. Alkali catalysts

In transesterification with alkali catalyst, sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide can be used. Alkali catalysts in transesterification make process response faster than acidic catalysts by about 4000 times (Ma and Hanna. 1999). Therefore, the alkali catalysts are the most popular and used widely in commercial scale. An important factor in the transesterification with alkali catalysts is the moisture because it can react with the fatty acid and following the saponification reaction, produce soap. The soap consumes the catalyst, reduces the efficiency of the process, increases the viscosity and makes it difficult to separate glycerol. Hence, the free fatty acid should be reduced to lower than 0.5 % and oils should be dried to get rid of moisture.

3. Solid catalysts (Heterogeneous catalysts)

The two conventional catalysts mentioned above need to use a large amount of water during the catalyst separation and product cleaning. This process generates a large amount of waste water that requires treatment before discharging to the environment. The treatment adds an extra cost to the total production cost. Moreover, the presence of water in vegetable oils leads to the hydrolysis of ester and the result is soap. The formation of soap reduces the biodiesel yield. Therefore, heterogeneous catalysts such as Nickel, palladium, Calcium carbonate, Zinc oxide and Zinc carbonate are new 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. On the other hand, homogeneous catalysts cannot be reused because they are dissolved in methanol. 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 ester yield of 91 %. The mechanism of calcium methoxide as base heterogeneous catalyst in transesterification was shown in Fig 5.

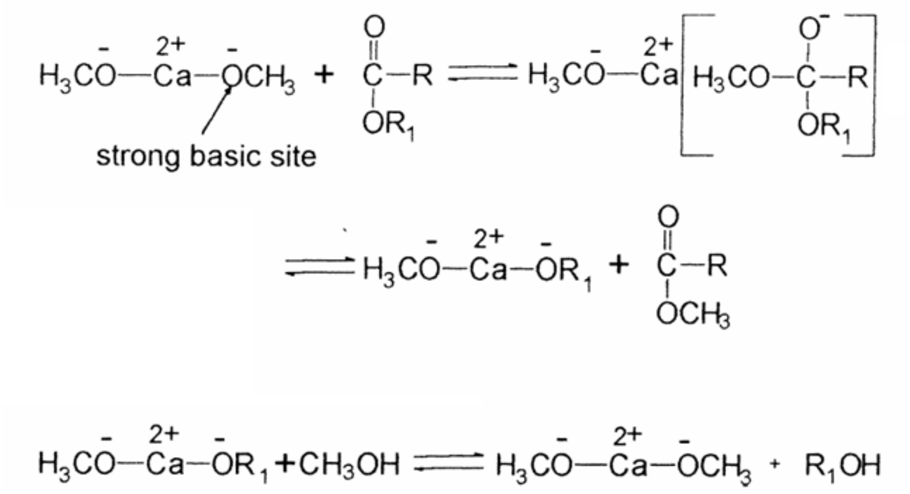


Figure 5 Transesterification mechanism proposed on calcium methoxide catalyst.

Source: Rapeseed oil methyl esters preparation using heterogeneous catalysts (1999)

Although the heterogeneous catalysts have many advantages, lower methyl ester content and yield is still a problem. For this reason, improving the methyl ester content and yield in this catalytic system is of interest. In this study, the optimum condition of methyl ester content and yield was examined. Then the catalyst was investigated for the possibilities of the recycling and regeneration.

MATERIALS AND METHODOLOGY

Materials

1. Crude palm oil MW 847.3 g/mol (Crabbe *et al.,* 2001) was supplied by Siam Oil and Fat Co., Ltd., located in Samutsakhon, Thailand, and used without degumming.

2. Methanol (Industrial grade, Asia Pacific Specialty Chemicals Ltd.) was used as a reactant.

3. Tetrahydrofuran (THF) (HPLC grade, Asia Pacific Specialty Chemicals Ltd.) was used as a co-solvent

4. Calcium oxide (CaO) (99.0 %, APS AJAX Finechem Co., Ltd.) was used as a catalyst/catalyst support.

5. Alumina (α-Al_2O_3) (95.0 %, APS AJAX Finechem Co., Ltd.) was used as a catalyst support.

6. Potassium carbonate (K_2CO_3) (99.0 %, APS AJAX Finechem Co., Ltd.) was used as a catalyst.

7. Potassium nitrate (KNO_3) (99.5 %, APS AJAX Finechem Co., Ltd.) was used as a catalyst.

8. Sulfuric acid (H_2SO_4) (99.0 %, J.T. Baker Co., Ltd.) was used as a catalyst for treating CPO with high FFA.

9. Heptane (95 %, Fluka Co., Ltd.) was used for dilution the internal standard and methyl ester before GC analysis.

10. Methyl heptadecanoate (95 %, Fluka Co., Ltd.) as internal standard was mixed with heptane and used for reducing the boiling point of product before GC analysis.

Equipment

1. A 250 ml two-necked glass flask equipped with a 30 cm socket water cooled bulb condenser (Labsystem Co., Ltd.) was used as a reactor (Fig. 6).

2. Hot plate magnetic stirrer (SCHOTT Instruments GmbH D-55122 Mainz, Scientific Promotion Co., Ltd.) was used to provide heat control the reaction temperature, and mix the reaction and catalyst (Fig. 6). It can be heated from 30-200 ^{O}C and the stirring speed can be varied from 0-1100 rpm. The power of electricity was 920 watt.

3. Gas chromatography GC 2010 (Supelco Co., Ltd.) equipped with an FID detector and a DB-5HT column was used for the analysis of methyl esters.

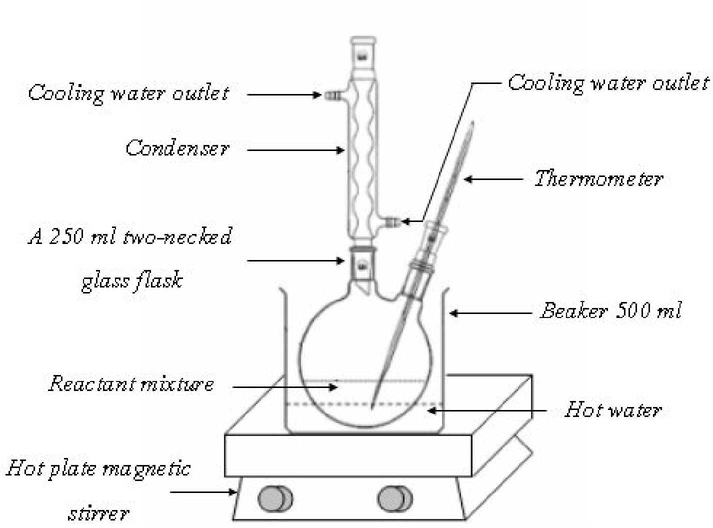


Figure 6 Experimental set up for transesterification reaction of crude palm oil.

1. Catalysts preparation

CaO, K_2CO_3/CaO, K_2CO_3/Al_2O_3 and KNO_3/Al_2O_3 were used as catalysts in this study. The performance of each catalyst in catalyzing the transesterification of crude palm oil with methanol was tested and compared. All catalysts except the CaO were prepared by incipient wetness impregnation technique using the corresponding potassium salts as precursors. The CaO and Al_2O_3 were not calcined when used as supports. After the impregnations were done to the desired concentrations, all catalysts were calcined in air, then crushed and kept in dehumidified containers. Details on the preparation of each catalyst are given as follows:

1.1 Preparation of CaO catalyst

CaO when used as a catalyst for transesterification reaction was calcined in air at the desired temperatures (500 and 900 ^{O}C) for 5 h. The calcined catalyst was kept in a dehumidified container preventing it from exposing to moisture.

1.2 Preparation of K_2CO_3/CaO, K_2CO_3/Al_2O_3, and KNO_3/Al_2O_3 catalysts

These catalysts were prepared by incipient wetness impregnation technique. First, the CaO and Al_2O_3 supports were tested for absorption capacities by measuring the volumes of distilled water that were dropped onto the supports until the supports started to form slurry. It was found that 0.9 ml of distilled water could be absorbed on 1 g of CaO, while 1.3 ml/g water was required for the Al_2O_3. Later, the K_2CO_3 and KNO_3 precursors were prepared having concentrations of 5, 15, 25 and 35 wt% based on the weight of the corresponding supports and gradually dropped onto the supports. After impregnations the catalysts were dried in oven at 120^{O}C for 12 h following by calcination in air for 5 h at various temperatures in order to study the effect of calcination temperatures (300, 500 and 800 ^{O}C). After calcination the catalysts were sieved to the size range of 5-10 μm then crushed and kept under a dehumidified condition. The sieved catalyst will increase the surface area per gram of catalyst and significantly the methyl ester content and yield. Thus, this is the important process for catalyst preparation.

2. Catalysts Characterization

2.1 DTA/TGA (Differential thermal analysis/Thermogravimetric analysis)

Thermal decomposition of all samples can be evaluated by DTA/TGA using a Shimadzu DT-40 instrument operating under a flow of air at 10 ^{O}C/min heating rate up to 1000 ^{O}C. In each analysis, a 0.2 g sample was placed in a placeholder and the weight change was recorded versus temperature over 3 h.

2.2 XRD (X-ray diffraction)

The phases of catalyst were examined using the Philips X’ pert powder X-ray diffractometer with the Cu-α radiation at 40 kV and a current of 30 mA. Data was collected over a 2θ range of 5-80 ^{O} with a step size of 0.02 ^{O}/step. The data was evaluated with the diffracplus software. The phases were detected by a proportion ZnS (Zinc sulfide) detector. A 3 g of each sample was crushed and pressed into an aluminum sample holder then put it into the X-ray diffractometer. Each sample was run for 1 h.

2.3 N_2 Physisorption

The BET surface area, pore size and pore volume were examined using Autosorb-1 AS1W in, version 1.24 (Quantachrome instruments, USA). N_2 gas was used for measuring the surface area, pore size and pore volume of sample. A 0.5 g of sample was degassed at 250 ^{O}C for 12 h under vacuum. After degassing the sample was run at -196 ^{O}C or 77 K for 6 h.

2.4 XRF (X-ray fluorescence)

The XRF spectrum was used to determine the weight fraction ratio of K to Ca in the prepared samples using the Horiba, Mesa-500 model equipped with high voltage (15/50 kV, 200/40 mA) and a high purity Si (Silicon) detector. A 5 g of catalyst sample was placed into sample cell and analyzed for 30 h.

2.5 SEM (Scanning electron microscopy)

SEM micrographs were obtained using XL30 (FEI Co., Ltd). The accelerating voltage was 12.0 kV. The catalysts ample was coated with Au (gold) for protecting the induction of electric current using Sputtering Model Scan Code (Productive vacuum technology Co., Ltd). First, a 0.1 g of catalyst powder was sprayed on a carbon tape and put it on the stub for coating. The coating was run at 0.1 mbar for 30 s. After coating, the catalyst was placed a specimens holder for 40 s.

3. Synthesis of Biodiesel

3.1 Esterification reaction

Crude palm oil (CPO) usually has high free fatty acid, therefore, it must be undergo through acid treatment or “esterification”. This reaction was catalyzed by sulfuric acid (H_2SO_4). A 20 g CPO was heated to $50^{O}C$ in a 250 ml two-necked glass flask with condenser by a hot plate magnetic stirrer. Then, a methanol-to-oil molar ratio of 12:1 was added into heated CPO following by 1wt% of sulfuric acid. The reaction was run at this temperature for 30 min.

3.2 Transesterification reaction

A 20 g of CPO/acid-treated CPO was heated to 60 ^{O}C in the reactor. The solid catalyst was mixed with methanol and then added into the oil followed by 20 wt% or 4 g of the co-solvent tetrahydrofuran (THF). Detailed calculation and formulas are presented in Appendix A. Factors affecting the methyl ester content and yield were studied including methanol-to-oil molar ratio (1:6, 1:12, 1:18, 1:26 and 1:33), reaction time (1, 2, 3 and 5 h) and temperature, catalyst loading (5, 15, 25, 35 wt%), amount of catalyst (1, 3 ,6 and 9 wt%), and catalyst calcination temperature (none, 300, 500, 800, 900 ^{O}C, based on the DTA/TGA data) . After completion of each batch, the catalyst particles were physically separated from the mixture by centrifuge. Then the methyl ester was washed with distilled water.

3.3 Washing of methyl ester

The methyl esters were put into a separating funnel. An equal amount by weight of distilled water was heated up to 50 ^{O}C and then added with a 0.1wt% sulfuric acid. This mixture was added into methyl ester to wash all other impurities.

This washing process was repeated until the color of the waste water was clear. After washing, a 0.5 g of sodium sulfate (Na_2SO_4) was added into the methyl esters to absorb the residual water and then the mixture was centrifuged to separate the solid from the methyl ester product. The product was analyzed for its compositions by gas chromatography. However, some product modification was needed to make the properties suitable for GC analysis.

3.4 Product modification for GC analysis

The boiling points of methyl ester, monoglyceride, diglyceride, triglyceride, free glycerol, total glycerol were very high. It is easier for GC detector if the boiling point of product is lower. Therefore, the product should be modified by reducing the boiling point of methyl ester with the solution of methyl heptadecanoate and heptane. Before GC analysis, 0.05g of methyl ester product was added with 1 ml of a mixture containing 10 mg methyl heptadecanoate dissolved in 1 ml heptane.

4. Determination of Biodiesel Properties

4.1 Methyl Ester Content and Yield

Identification of methyl esters species and amounts was done using GC (Shimadzu and 2010, Supelco Co., Ltd.) equipped with FID detectors, DB-5HT column and DB-wax column. The DB-wax column was used to identify methyl ester while the DB-5HT column was capable of separating monoglyceride, diglyceride, triglyceride, free glycerol and total glyceride species. The GC operating conditions of methyl ester were 210 ^{O}C while those of monoglyceride, diglyceride, triglyceride, free glycerol and total glyceride species were from 50 ^{O}C to 370 ^{O}C within 1 h. Detailed preparation of methyl ester for analyzed by GC and result of chromatogram are presented in Appendix B. Detailed calculations and formulas are presented in Appendix C.

4.2 Flash point

Flash point is the temperature at which the vapor of methyl ester can ignite in air. Pure methyl ester has flash point more than 200 ^{O}C so it is safe for transportation. The flash point of the synthesized methyl ester product was determined using Pensky-Martens equipment as shown in Fig 7. Fifty milliters of samples were used for ach analysis. While the temperature was raised, the fire was ignited on the surface of sample until the light was appeared. The method of flash point measurement was specified by ASTMD 93.

Figure 7 Pensky-Martens closed flash tester

4.3 Cloud point and pour point

Cloud point is the first point at which the crystallization occurred while reducing the temperature of fuel. Pour point is the first point at which the fuel cannot flow. The cloud point and pour point of the synthesized methyl ester product were determined using the equipment as shown in Fig 8. Ice and salt were added to the box until it was full and then the cylinder containing methyl ester was added. The cylinder was added into the hole of the box and closed with thermometer and cork. Then measured the first temperature at which the methyl esters start to crystallize as cloud point and measured until the methyl ester could not flow as the pour point. The cloud point is an important factor in cold weather. Because cold weather causes the crystallization of fuel, plugging the filter of the diesel engines. The cloud point and pour point measurements were specified by ASTM D 2500 and ASTM D 97, respectively.

Figure 8 Pour point and cloud point equipment.

4.4 Viscosity

Viscosity is the resistance of fuel flow. The viscosity of the synthesized methyl ester product was determined using viscometers as shown in Fig 9. The viscosity measurement was specified by ASTM D 445.

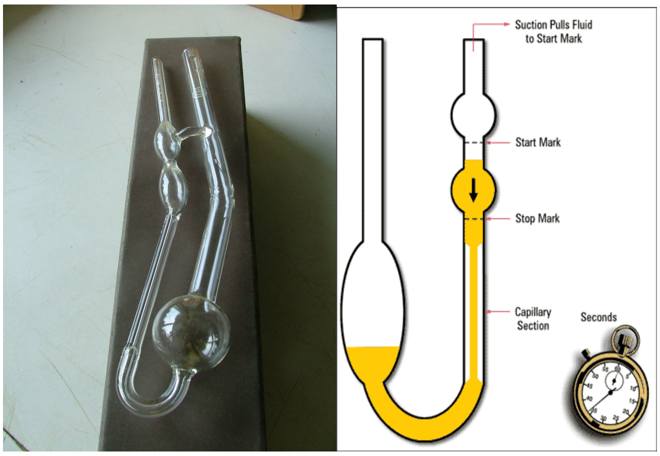


Figure 9 Viscometer testing equipment.

4.5 Density

Density is a mass per unit volume. The density of the synthesized methyl ester product was determined using Hydrometer instrument as shown in Fig 10. The hydrometer was dipped into the sample and recorded the density of the liquid fuel. The density measurement specified by ASTM D 1298.

Figure 10 Hydrometer testing equipment.

4.6 Acid value

Acid value is the quantity of base in milligrams of potassium hydroxide (KOH) per gram of sample. Normally Sodium hydroxide (NaOH) was used instead of KOH due to it has low cost. The acid value of the synthesized methyl ester product was determined using titration method. First, methyl ester 5 g was measured in flask then added 2-propanol and dropped a few phenolphthalein as an indicator into the solution. Then the mixture was titrated with NaOH solution until the color of the mixture changed to pink as the end point. The acid value measurement was specified by ASTM D 664.

RESULTS AND DISCUSSIONS

This thesis focuses on the development of heterogeneous catalysts for transesterification of crude palm oil (CPO) to methyl ester. CaO catalyst was attractive due to its performance in transesterification of palm stearin to obtain over 97.26 % methyl ester yield (Lichinda and Sudsakorn, 2006), ease of preparation, and low cost. After testing the CaO catalyst in converting CPO to biodiesel, it was found that the performance in catalyzing the reaction could still be improved. According to Huaping *et al.,* (2006), the catalytic activity of solid catalysts in transesterification could be enhanced by modifying the catalyst surface to become stronger in basicity. This could be done by dipping CaO into a 0.12 g/ml ammonium carbonate solution. The results showed that the base strength of CaO was more than 26.5 after dipping in ammonium carbonate solution.

Potassium salts including K_2CO_3 and KNO_3 have been used to prepare the K_2CO_3 /Al_2O_3 and KNO_3/Al_2O_3 catalysts and have been shown to be active for the biodiesel production from soybean oil. These enhanced activities were accounted for by the higher degree of basicity provided by the potassium salts (Xie *et al.,* 2006 and Noiroj *et al.,* 2006). Our work applied these ideas to the CaO catalyst in which its basicity was augmented by impregnating potassium precursors and calcining it to form potassium oxide (K_2O). Later on in the study, the alumina (Al_2O_3) which had much higher surface area than CaO was used as a support to increase the loading and distribution of potassium on the support surface.

The properties of the prepared catalysts, their activities in producing methyl ester (ME), the optimal condition for the maximum methyl ester yield, and finally the properties of biodiesel products were investigated and discussed. It should be noted that the CPO used in this study was grade B quality due to its low cost. This grade of CPO, extracted from its pulp and kernel, consequently had high water content. At temperatures higher than 30^{O}C, water could hydrolyze triglyceride to form diglyceride and free fatty acid (Fig 11) resulting in a high free fatty acid (FFA) CPO. The FFA in the starting CPO was determined in form of acid value (see the procedure in the experimental section 4.6 and the calculation of acid value and FFA in the appendix A) and found to be 10 mgKOH/g CPO. This value was apparently high and needed to be lowered down, when converting to biodiesel, to below 0.5 mgKOH/g ME as set standard by the Department of Energy Business.

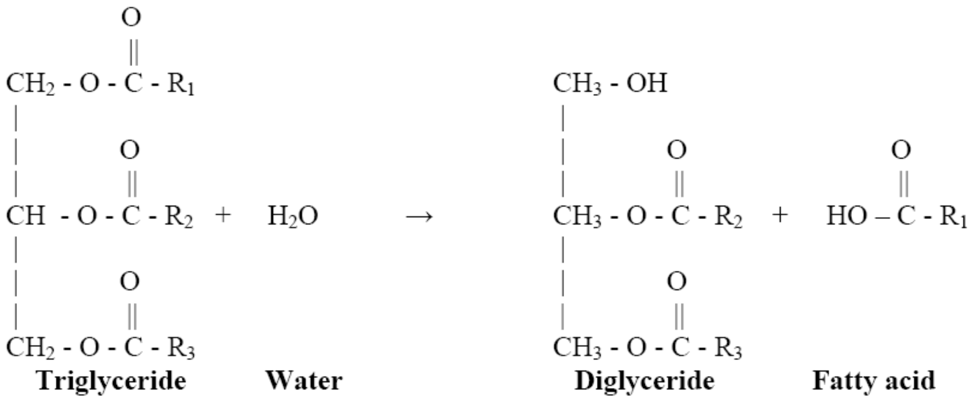


Figure 11 Hydrolysis of triglyceride to form diglyceride and free fatty acid

Source: Biodiesel production technology (2004)

Previous work with heterogeneous catalysts (Sirikulbodee and Sudsakorn, 2006) reported that the K_2CO_3/Al_2O_3 catalysts were unable to convert FFA contained in the oil and some literature found that the presence of FFA degraded the activities of base catalysts (Ramadhas *et al.,* 2004). Therefore, the FFA must be removed before transesterification not only to meet the biodiesel standard but also to improve the catalytic activity during biodiesel synthesis. This can be done by acid treatment or esterification as described in the experimental section. All of biodiesel synthesis in this study was done by esterification with sulfuric acid following by transesterification using solid catalysts.

1. Transesterification of CPO with methanol using CaO catalyst

Our previous work (Lichinda and Sudsakorn, 2006) indicated clearly by XRD that the CaO catalyst, when used as was, showed to form $Ca(OH)_2$ with moisture in air (Fig 12). This $Ca(OH)_2$ species was the cause of inactive catalyst for transesterification of palm stearin resulting in essentially zero methyl ester yield. It was also found that calcination at 550 ^{O}C was able to remove $Ca(OH)_2$ completely and the calcined catalyst showed to have high activity, yielding methyl ester content of 97 %. However, the calcined catalyst must be kept in a dehumidified condition preventing it from reacting with water to reform $Ca(OH)_2$. Therefore, it could be concluded from our previous findings that the CaO catalyst must be calcined to eliminate $Ca(OH)_2$ before use and the calcined catalyst was unstable tending to react with water in the reverse direction to form $Ca(OH)_2$ again.

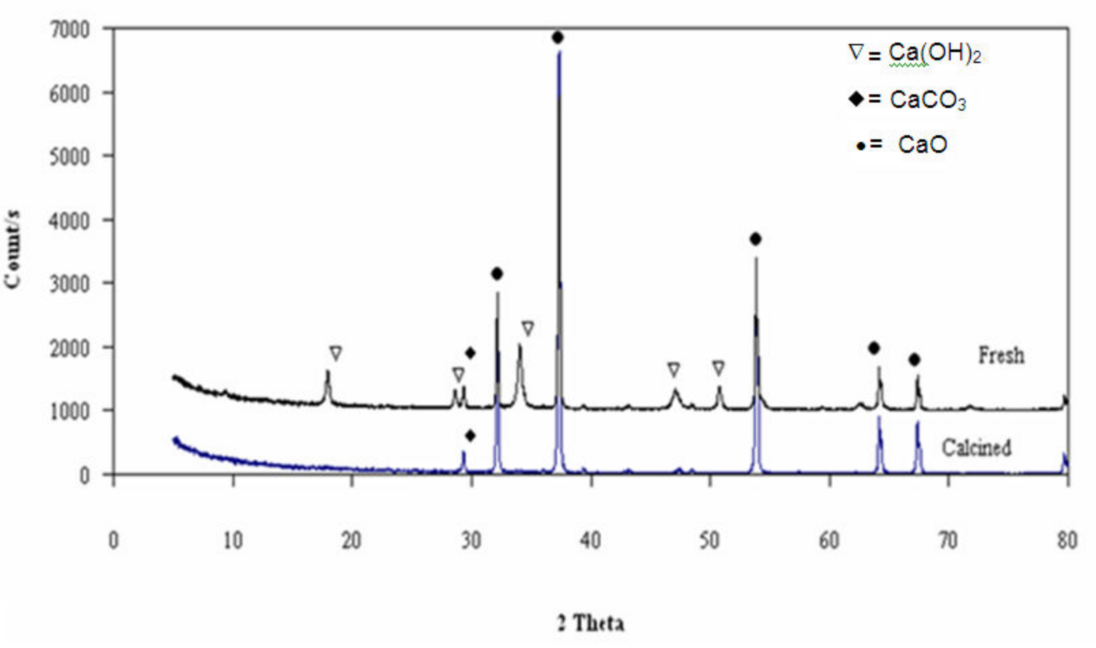


Figure 12 XRD patterns of fresh (no calcination) and calcined (500 ^{O}C) CaO catalysts

In this study, CaO catalyst was tested for transesterification of CPO. Fresh CaO catalyst was used in the reaction and found to produce infinitesimal methyl ester content. By expecting to increase the activity and stability of CaO in air, two calcination temperatures were studied which were at 500 and 900 ^{O}C. The results are plotted in Fig 13(see the preparation of methyl ester for analyzed by GC in Appendix B and see the calculations of methyl ester content and methyl ester yield in Appendix

C). It was shown that the CaO calcined at 500 ^{O}C gave both higher methyl ester content and yield (33 % and 27 %) than that calcined at 900 ^{O}C (28 % and 21 %, respectively). Furthermore, the CaO calcined at 900 ^{O}C was still susceptible to moisture exposure and became inactive similar to that calcined at 500 ^{O}C. Increasing calcination temperature not only unformed a more stable CaO catalyst by making more crystal but also worsened its activity due to decrease in surface area.

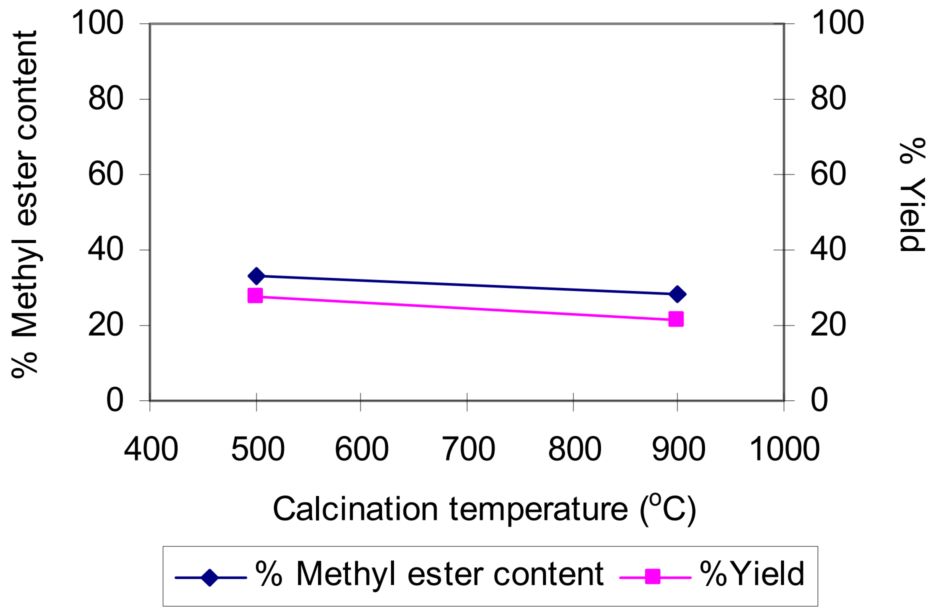


Figure 13 The effect of calcination temperatures of CaO on methyl ester content and yield carrying out at 60 ^{O}C, 3 h, methanol: oil molar ratio = 26:1, 6 wt% catalyst and 20 wt% THF.

From the results, CaO showed to have low activity in converting CPO to biodiesel. Moreover, its catalytic performance and stability in humidified condition were not able to improve by simply increasing the calcination temperature. It was reported previously that the basicity of catalyst which corresponded to the activity in transesterification, was improved by loading alkali salts (Claire *et al.,* 2007). Specifically, they improved the basicity of CaO catalyst by dipping it in ammonium carbonate solution and used in transesterification of Jatropha oil. Also, KF was loaded onto CaO and found to increase both basicity and activity in transesterification of soybean oil (Huang *et al.,* 2006). The K_2CO_3 salt has attracted our interest due to its high basicity and simply low cost. Its role in improving methyl ester content and yield will therefore be further discussed.

2. Transesterification of CPO with methanol using K_2CO_3/CaO, K_2CO_3/Al_2O_3 and KNO_3/Al_2O_3 catalyst

In this work, K_2CO_3/CaO, K_2CO_3/Al_2O_3 and KNO_3/Al_2O_3 were used as heterogeneous catalysts for maximizing methyl ester content and yield. The decomposition temperatures of all catalysts were examined using DTA/TGA (Differential temperature analysis/Thermogravimetic analysis). The DTA/TGA profiles of K_2CO_3/CaO, K_2CO_3/Al_2O_3 and KNO_3/Al_2O_3 are shown in Fig 14, 15, 16 and 17, respectively. The second mass loss at about 500 ^{O}C corresponded to the decomposition of the potassium salts to form K_2O. All of the catalysts have the same tendency which is decomposed at 500 and 800 ^{O}C. The results relate with Lehman *et al.,* (1998). They found the decomposition of K_2CO_3 which has one step at 400 ^{O}C as shown below:

$$K_2CO_3 \Leftrightarrow K_2O + CO_2 \qquad (2)$$

Xie *et al.,* (2005) reported that the decomposition of KNO_3/Al_2O_3 will be decomposed to K_2O at 500 ^{O}C. The last dropping of DTA/TGA profile may be the elimination of impurity and contaminate of the catalysts.

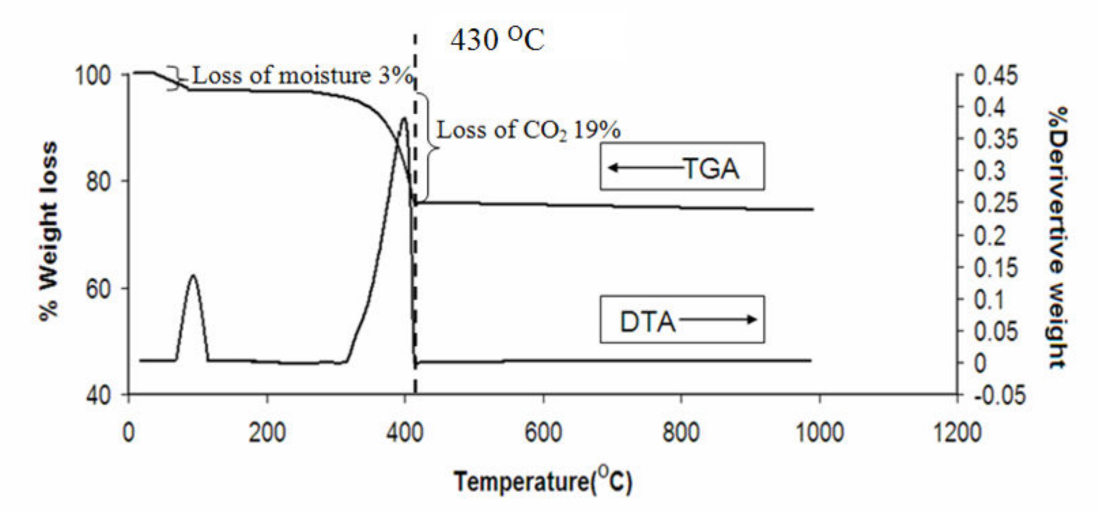
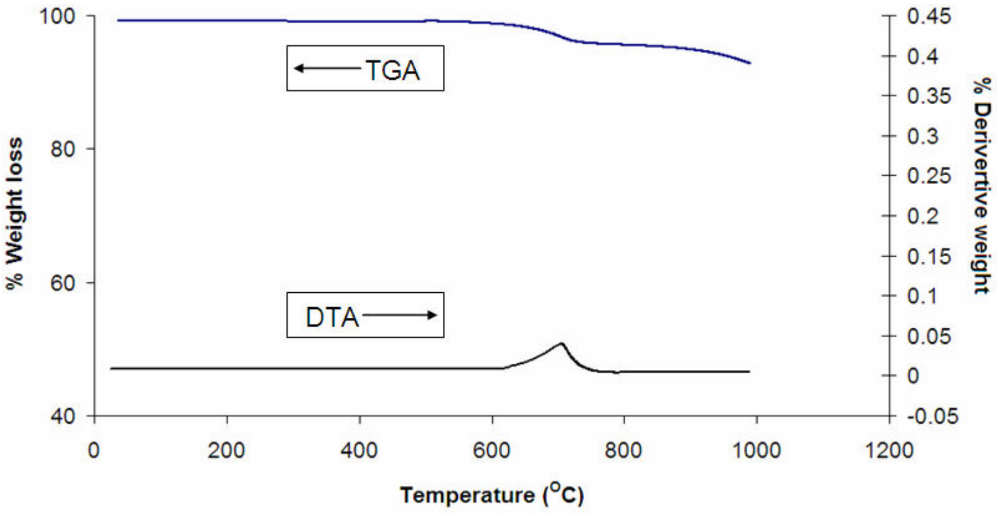


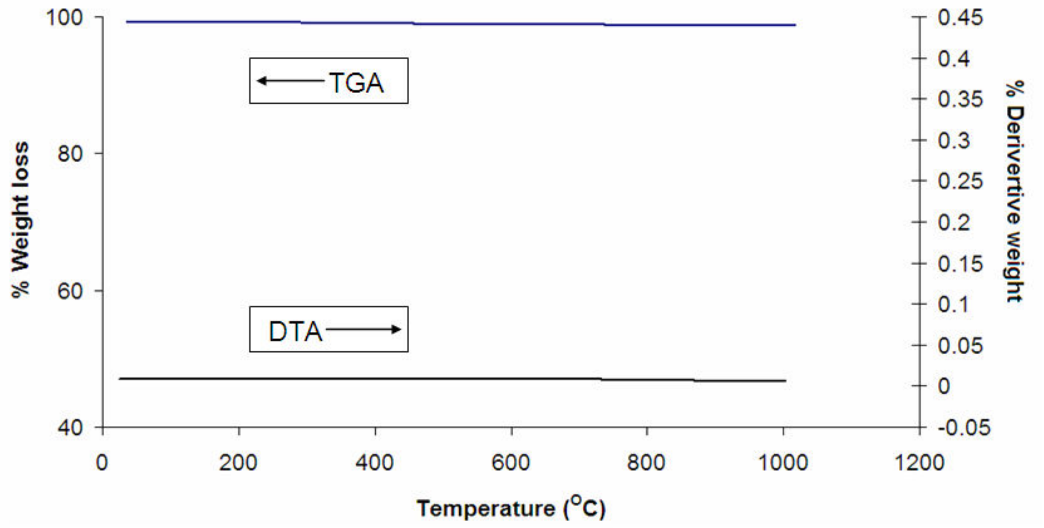
Figure 14 DTA/TGA of K_2CO_3 without calcination

The decomposition of K_2CO_3 was examined by DTA/TGA to determine the temperature that K_2CO_3 converted to K_2O. This temperature was used as a guide for finding a calcination temperature of the catalysts having a K_2CO_3 species. The DTA/TGA of pure K_2CO_3 is presented in Fig 14. The first weight loss peak at $100^{O}C$ was attributed to the removal of moisture content that was originally in the catalysts without calcination. Then, the second weight loss at $430^{O}C$ was the decomposition of K_2CO_3 to K_2O in which 41.5 % of K_2CO_3 was converted to K_2O and 38.8 % was remained unconverted (see detailed calculation in Appendix F). This unconverted K_2CO_3 species was stable and not decomposed even at much higher temperature up to 1,000 ^{O}C as observed no further significant weight loss beyond $430^{O}C$ (Fig 14). The K_2O occurred from the calcination of the catalyst over 400 ^{O}C was relatively much insoluble than K_2CO_3 and became strong basic active site for heterogeneous transesterification. However, due to the incomplete conversion to K_2O, the K_2CO_3 species remained could potentially be leached out during transesterification reaction and hence catalyzed the reaction via homogeneous mechanism (Granados *et al.,* 2007) K_2CO_3The decomposition behavior of /CaO is therefore interesting in comparing the effect with pure K_2CO_3 and these results are shown in Fig 15

a) DTA/TGA of 35 wt% K_2CO_3/CaO without calcination



b) DTA/TGA of 35 wt% K_2CO_3/CaO calcined at 500 ^{O}C



c) DTA/TGA of 35 wt% K_2CO_3/CaO calcined at 800 ^{O}C

Figure 15 DTA/TGA of 35 wt% K_2CO_3/CaO. a) DTA/TGA of 35 wt% K_2CO_3/CaO without calcination. b) DTA/TGA of 35 wt% K_2CO_3/CaO calcined at 500 ^{O}C. c) DTA/TGA of 35wt % K_2CO_3/CaO calcined at 800 ^{O}C.

The effect of the support (CaO) after loaded K_2CO_3 and the calcined temperature at 500 and 800 ^{O} C was analyzed by DTA/TGA. Fig 15a shows the DTA/TGA of 35 wt% K_2CO_3/CaO without calcination. When compared Fig 15a with Fig 14 we found that the decomposition temperature of K_2CO_3 before loaded onto CaO was 412 ^{O}C and after loaded onto CaO was 469 ^{O}C. Although, loading K_2CO_3 onto CaO the weight loss of Fig 14 and 15a has quite similar but the shift of this decomposition temperature occurred because the interaction between K_2CO_3 and CaO. The K_2CO_3/CaO without calcination will appear the weight loss of moisture evaporated of 3 % at 120 ^{O}C. The decomposition of K_2CO_3/CaO obtained weight loss of 19 % at 469 ^{O}C. The pattern of DTA/TGA of K_2CO_3/CaO is similar with Fig 14 (K_2CO_3 without calcination). From these results that can be confirmed the weight loss at 469 ^{O}C which is decomposition of K_2CO_3 to K_2O which was occurred 37.6 % of K_2O and remained 44.1 % of K_2CO_3. The last weight loss at the temperature more than 600 ^{O}C was the weight loss of $CaCO_3$ and $Ca(OH)_2$. From Fig 15b shows DTA/TGA of 35 wt% K_2CO_3/CaO calcination at 500 ^{O}C. After calcined at 500 ^{O} C can be eradicated K_2CO_3 but the $CaCO_3$ and $Ca(OH)_2$ will be remained because the calcination temperature is below than 600 ^{O}C. Therefore, the calcination temperature at 500 ^{O}C cannot see the drop of the decomposition peak. But when K_2CO_3/CaO was calcined at 800 ^{O}C (Fig 15d) which can be eliminated the impurity of CaO completely. When consider the melting point of CaO that was 2572 ^{O}C so the calcination temperature does not affect the melting of CaO.

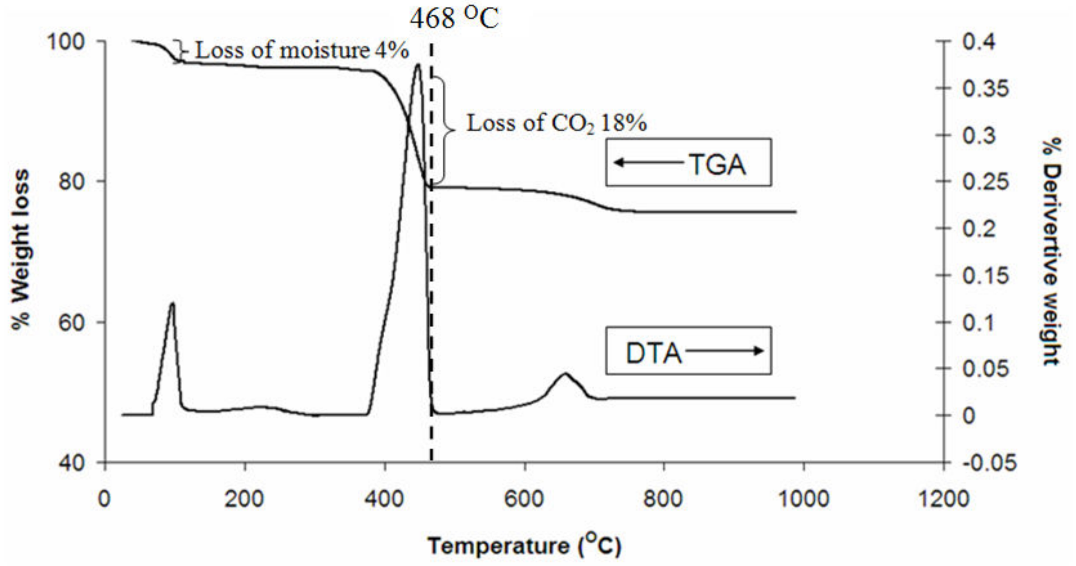


Figure 16 DTA/TGA of 35 wt% K_2CO_3/Al_2O_3

DTA/TGA of K_2CO_3/Al_2O_3 was examined for analysis the decomposition temperature of K_2CO_3. The DTA/TGA of K_2CO_3/Al_2O_3 is shown in Fig 16. The evaporation of moisture is about 4 % and the decomposition of K_2CO_3 to K_2O at 500 ^{O}C is about 18 % which was occurred 44.7 % of K_2O and remained 37.3 % of K_2CO_3. From the resulted it is confirmed that the crystallization of K_2O occurred over 500 ^{O}C. When compared the DTA/TGA pattern with Fig 14 that has similar peak of decomposition of K_2CO_3 although different precursor. The last peak may be loss of impurity of Al_2O_3 (95 % purity) such as ash, silicate and sulfate. When compared Fig 15a with Fig 16 and found that the support does not affect on the decomposition temperatures that were 469 and 468 ^{O}C, respectively.

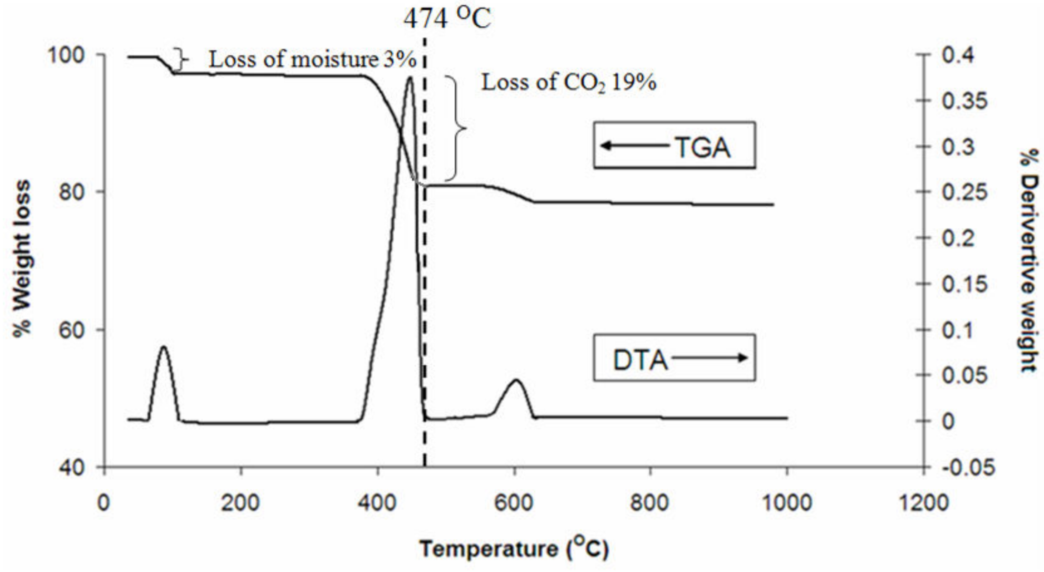


Figure 17 DTA/TGA of 35 wt% KNO_3/Al_2O_3

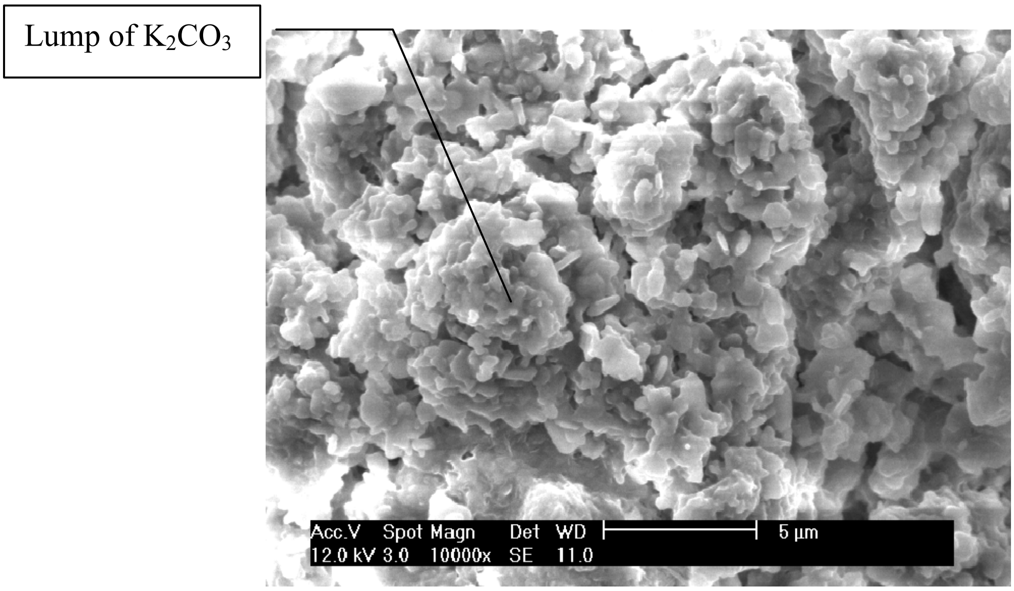
The effect of another precursor was examined by DTA/TGA. The DTA/TGA of KNO_3/Al_2O_3 is shown in Fig 17. The decomposition temperature of KNO_3 to K_2O is 500 ^{O}C and occurred K_2O about 45.2 % and remained KNO_3 about 36.4 %. The decomposition temperature of KNO_3 was nearly K_2CO_3 (Fig 14). The resulted confirmed that the crystallization of K_2O occurred over 500 ^{O}C. The last peak may be loss of impurity of Al_2O_3 (95 % purity) such as ash, silicate and sulfate. When compared the decomposition temperature of KNO_3/Al_2O_3 with K_2CO_3/Al_2O_3 that is 474, 468 ^{O}C, respectively. From the result, the various precursors does not effect on the decomposition temperature.

The surface area, pore volume and pore size of catalysts are the important factors for the catalysts in preparing the potassium salts solution. All catalysts were analyzed for physical properties which are BET surface area, pore size and pore volume by N_2 adsorption with high speed gas analyzer (Quantachrome instrument Co Ltd.,). The total surface area will be calculated automatically and the results showed in Table 9.

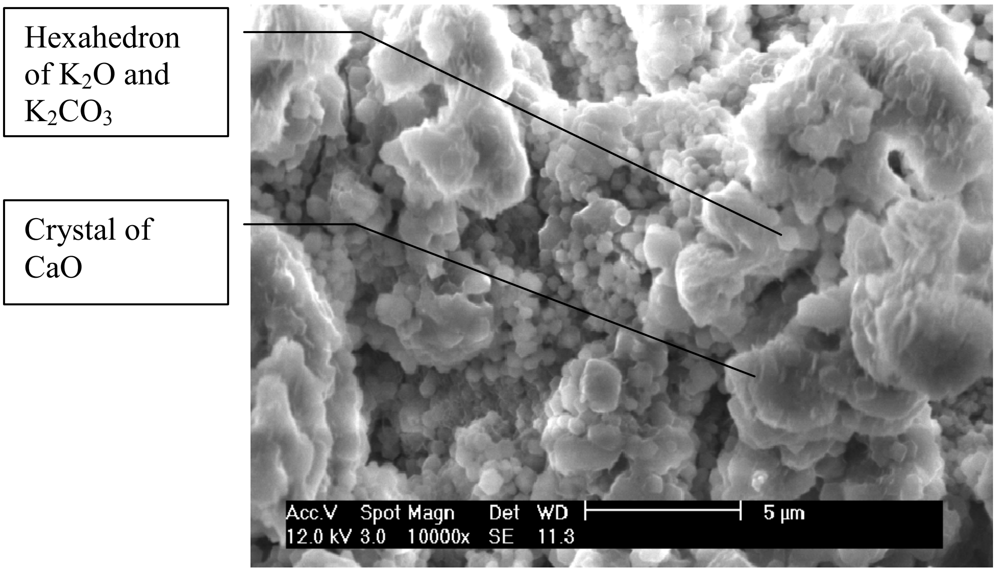
Table 9 Physical properties of catalysts without calcination

Catalysts	BET Surface Area (m^2/g)	Pore size (Å)	Pore Volume (cm^3/g)
CaO	5.0	254	4.2×10^{-2}
K_2CO_3/CaO	7.3	176	9.8×10^{-4}
Al_2O_3	112.0	130	23.0
K_2CO_3/Al_2O_3	76.0	148	171.0
KNO_3/Al_2O_3	79.0	141	181.0

From the results, loaded K_2CO_3 onto CaO increasing in BET surface area and decreased in pore size and pore volume. Mathew *et al.,* (2006), loaded Mo (molybdenum-oxo) into CaO, they found that BET surface area of CaO increased to 16 m^2/g from 8 m^2/g. These catalysts have no pore because they have no porous structure. Pore size and pore volume resulted from BET analysis belonged to the voidages between crystals. In case of CaO the crystals were well segregated and therefore the loaded K_2CO_3 could possibly be coated evenly on the outside surfaces of crystals. This could probably explain the increase in BET surface area from 5.0 to 7.3. However for Al_2O_3 the crystals were more agglomerated causing many voidages among crystals. Once potassium salt loaded on to Al_2O_3, they might coat only the outside surface of the agglomerated crystals and seal some of these voidages. The surface areas of Al_2O_3 inside the enclosed voidages would not be able to adsorb N_2, consequently resulting in the decreased BET surface areas. In transesterification, the active site has high effect on this reaction but in this case both of K_2CO_3 and CaO can be catalyzed the reaction so high surface area of Al_2O_3 does not effect on transesterification.



a) SEM of 35 wt% K_2CO_3/CaO without calcination



b) SEM of 35 wt% K_2CO_3/CaO calcined at 800 ^{O}C

Figure 18 Scanning electron microscopy (SEM) of the sample. a) 35 wt% K_2CO_3/CaO without calcination b) SEM of 35 wt% K_2CO_3/CaO calcined at 800 ^{O}C

The scanning electron microscopy (SEM) of the sample are presented in Fig 18 (magnification= 10000x). The SEMs of K_2CO_3/CaO catalyst without calcination and K_2CO_3/CaO calcined at 800 ^{O}C are shown in Fig 18a and Fig 18 b, respectively. The K_2CO_3/CaO catalyst without calcination shows the lump uniform of K_2CO_3 and the particle size of 0.3-3.3 μm. The K_2CO_3/CaO calcined at 800 ^{O}C showed a good dispersion on the surface of CaO and the particle size of 0.2-4.4 μm. Figure 8 B shows that the shape of K_2CO_3 or K_2O on CaO is nearly hexahedron. After loading K_2CO_3 on to CaO, was found highly distributed of K_2CO_3 on CaO that can be seen from this figure. Then the K_2CO_3/CaO was analyzed by XRD for verification the active site of K_2CO_3/CaO.

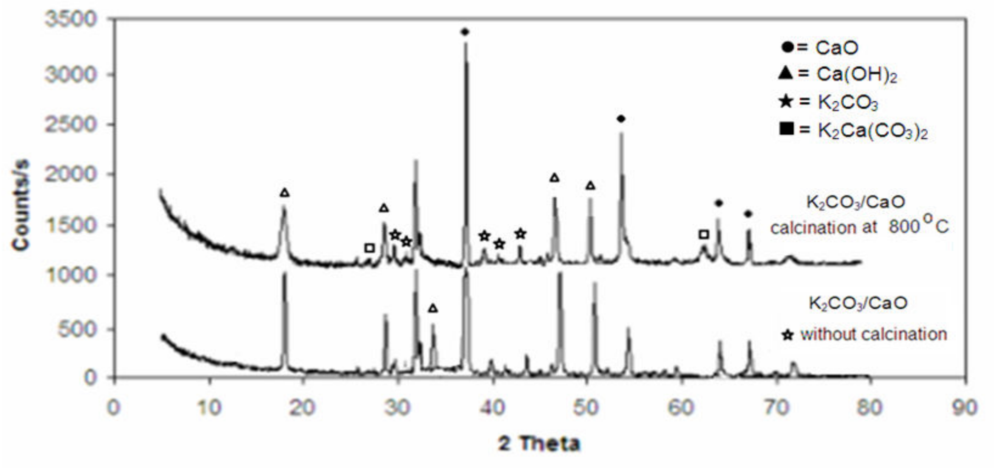


Figure 19 XRD patterns of K_2CO_3/CaO without calcination and K_2CO_3/CaO calcined at 800 ^{O}C

From XRD results as shown in Fig 19, K_2CO_3/CaO without calcination shows the peak of K_2CO_3, CaO and $Ca(OH)_2$ after calcination with air at high temperature we expected to form the K_2O peak resulting from CO_2 removal. The results correlate with DTA/TGA at 500 ^{O}C which K_2CO_3 decomposed to K_2O (The expected specie). However the K_2CO_3/CaO calcined at 800 ^{O}C shows no peak of K_2O. Therefore it was suspicious that K_2O might be well dispersed on the surface of CaO or might be formed on amorphous structure. Calcination at 800 ^{O}C did not completely change the structure of K_2CO_3 which remained significantly on the surface of CaO. CaO calcined became more crystallized as shown clearly by the XRD peaks. The more crystallized structure could result in lower BET surface area and might cause degraded catalytic activity. However it could be observed that the $Ca(OH)_2$ peaks were decreased corresponding to the dissociation of $Ca(OH)_2$. Furthermore the calcined K_2CO_3/CaO at 800 ^{O}C shows the formation of new species, $K_2Ca(CO_3)_2$ in which its role transesterification reaction was still unclear.

2.1 Influence of calcination temperature of K_2CO_3/CaO on methyl ester content and yield

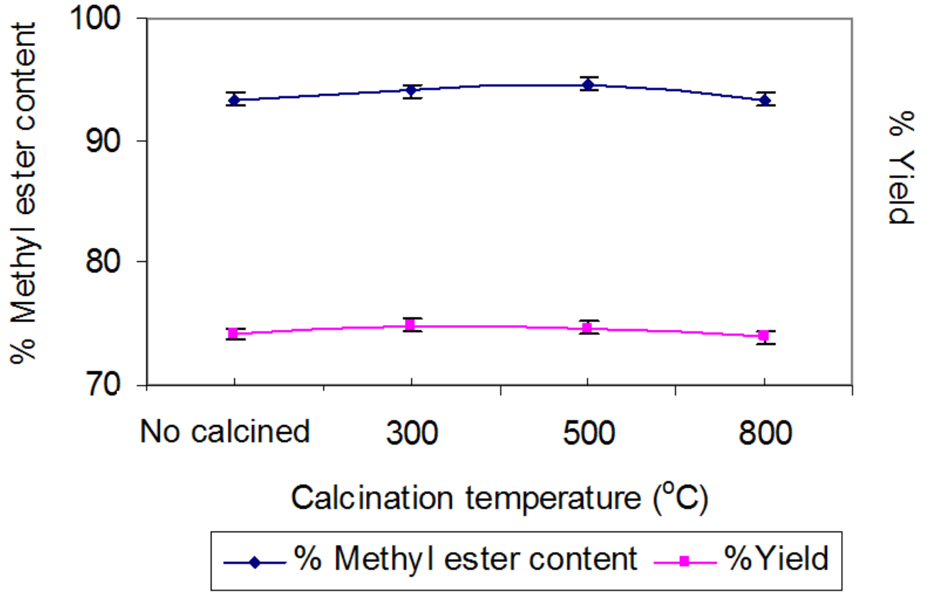


Figure 20 The effect of calcinations temperature of K_2CO_3/CaO on methyl ester content and yield carrying out at 60 ^{O}C, 2 h, methanol: oil molar ratio = 26:1, 6 wt% catalyst, 300 rpm, K_2CO_3 loading 35 wt% and 20 wt% THF.

As shown in Fig 20, the error bar in this figure is the error of GC, however, error of the whole experimental repetition would be even greater leading to the same conclusion that increasing the calcination temperature had slightly increased in methyl ester content and yield. From DTA/TGA Fig 15a when calcined K_2CO_3/CaO at 300

^{O}C that should be obtained the same amount of methyl ester content and yield because K_2CO_3/CaO will be decomposed at 469 ^{O}C and converted to K_2O as stable form. Considering, the methyl ester content and yield of K_2CO_3/CaO without calcination and calcined at 300 ^{O}C were 93, 74, 94 and 75 %, respectively. When increasing the calcination to 500 ^{O}C, the methyl ester content and yield were 95 and 76 %, respectively. Although, calcined at 800 ^{O}C can be increased in K_2O specie but the methyl ester content and yield had slightly decreased to 93 and 73 %, respectively. Due to calcined 800 ^{O}C occurred new impurity that was $K_2Ca(CO_3)_2$. Considering, the quite different of methyl ester content and yield at various calcination temperature that because the remaining amount of potassium spice after calcined at different temperature. But that not mean calcined at different temperature will obtain the different property in transesterification. The remaining K_2CO_3 at various calcination temperature will be analyzed in the further experiment. In the aspect of energy conservation, we found that no calcination would cause significantly less energy consumption during catalyst preparation. However, calcined catalyst might have benefits in reuse and regeneration. These features will therefore be tested later.

2.2 Influence of loading K_2CO_3 into CaO on methyl ester content and yield

In order to study the effect of K_2CO_3 loading amounts of catalyst on their catalytic activities, K_2CO_3/CaO sample with the loading amount of K_2CO_3 ranging from 5 to 35 wt%, were prepared and catalyzed transesterification reaction. The results are presented in Fig 21. As can be seen from this figure, the loading amount was raised from 5 to 35 wt% of K_2CO_3, the methyl ester content and yield was increased. The highest methyl ester content and yield of 93 and 74 % respectively were obtained at loading K_2CO_3 of 35 wt% on CaO.

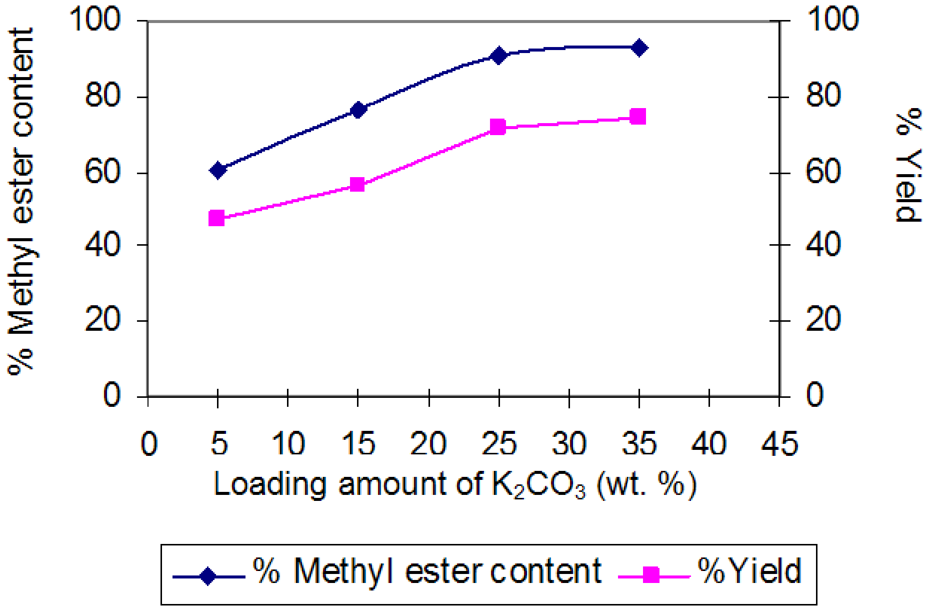


Figure 21 The effect of loading of K_2CO_3 on methyl ester content and yield carrying out at 60 ^{O}C, 2 h, methanol: oil molar ratio = 26:1, 6 wt% catalyst, 300 rpm and 20 wt% THF.

The results agree very well with the results from the literature (Xie *et al.*, 2006). They were investigated the effect of KI loading on Al_2O_3 and they found that at the loading of 35 wt% of KI on Al_2O_3 exhibited the highest conversion of 84.7 % for soybean oil. When increasing the loading amount of K_2CO_3, the methyl ester content and yield were increased because the K_2CO_3 was active site on CaO. When increasing the loading amount over 35 wt% it will not increase in methyl ester content and yield due to the agglomeration of catalyst and coverage of surface basic sites by the excessive K_2CO_3.

2.3 Influence of methanol to oil molar ratio on methyl ester content and yield

As shown in Fig 3, transesterification of triglyceride in crude palm oil with methanol requires 3 moles of methanol for each mole of triglyceride to form methyl esters and glycerol. However, in practice, higher amounts of methanol are required to drive the reversible reaction forward to produce higher yields of methyl esters. Fig 22 shows the effect of methanol to oil molar ratio on the methyl ester content and yield.

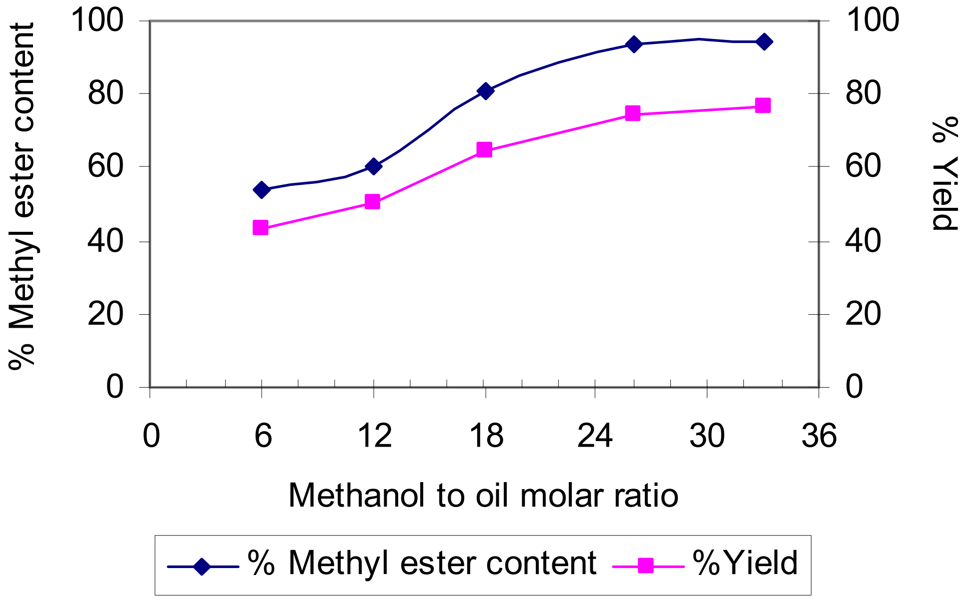


Figure 22 The effect of methanol to oil molar ratio on methyl ester content and yield carrying out at 60 ^{O}C, 2 h, 6 wt% catalyst, 300 rpm, K_2CO_3 loading 35 wt% and 20 wt% THF.

It was found that the methyl ester content and yield increased with increasing amounts of methanol/oil ratio. This is due to the excess methanol that favored the transesterification in forward direction. From many literature review such as Xie *et al.,* (2006) and Jitputti *et al.,* (2005) found that the transesterification of heterogeneous catalyst required high amount of methanol because the solid catalyst did not well disperse in the mixture. However, the excess methanol can be recovery and reuse again. In this experiment, at beyond 26:1 methanol to oil molar ratio, the percentages were leveled off at maximum values of methyl ester content and yield of 93 and 74 %, respectively. This was the evidence that the reaction has reached equilibrium. Addition of more methanol would cause no further increase in methyl ester content and yield. Therefore, the optimum molar ratio of methanol/oil to produce methyl ester is 26:1. This increasing and leveling off of methyl ester content and yield with increasing methanol to oil molar ratio was common and has also been reported previously in the literature (Dora *et al.,* 2005) . From the literature, we found that transesterification without using THF can complete the reaction but it used more methanol than the reaction with THF. So, we examined that in the next experiment.

2.4 Influence of methanol to oil molar ratio on methyl ester content and yield without THF

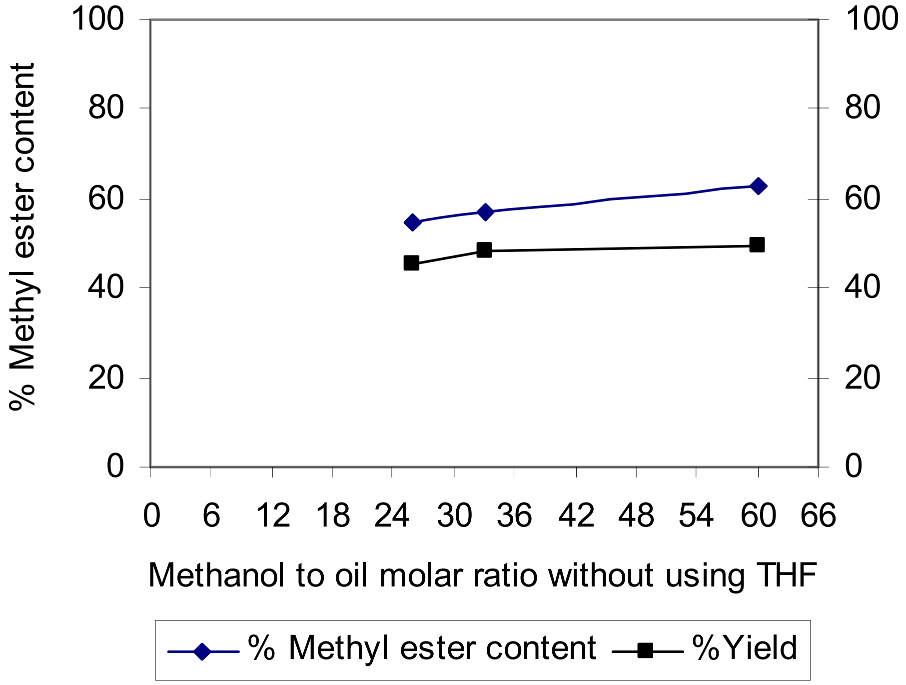


Figure 23 The effect of methanol to oil molar ratio without THF on methyl ester content and yield carrying out at 60 ^{O}C, 2 h, 6 wt% catalyst, 300 rpm.

This is the heterogeneous reaction in which the mixture was separated into three phases (oil, methanol, catalyst). A co-solvent like THF can produce an oil dominant one phase system which obtained the higher methyl ester content and yield due to methanolysis speeding up. In the absence of THF, the reaction will occur but results in lower methyl ester content and yield than using THF due to the slow dissolution of oil in methanol and this is also in an initial lag phase (Freedman *et al.,* 1986). As shown in Fig 23, with increased methanol to oil molar ratio, the methyl ester content and yield were increased. The maximum methyl ester content and yield were obtained when the molar ratio of methanol to oil was 60:1. The optimal methyl ester content and yield were 63 and 49 %, respectively. The transesterification without THF obtain lower contact between the methanol and oil. However, the methyl ester content and yield can be increased via added the amount of methanol or increased the reaction time for longer contact between methanol and oil but this methods are not economic. From this reasons, we desired to use THF in the transesterification via K_2CO_3/CaO as heterogeneous catalyst.

2.5 Influence of reaction time on methyl ester content and yield

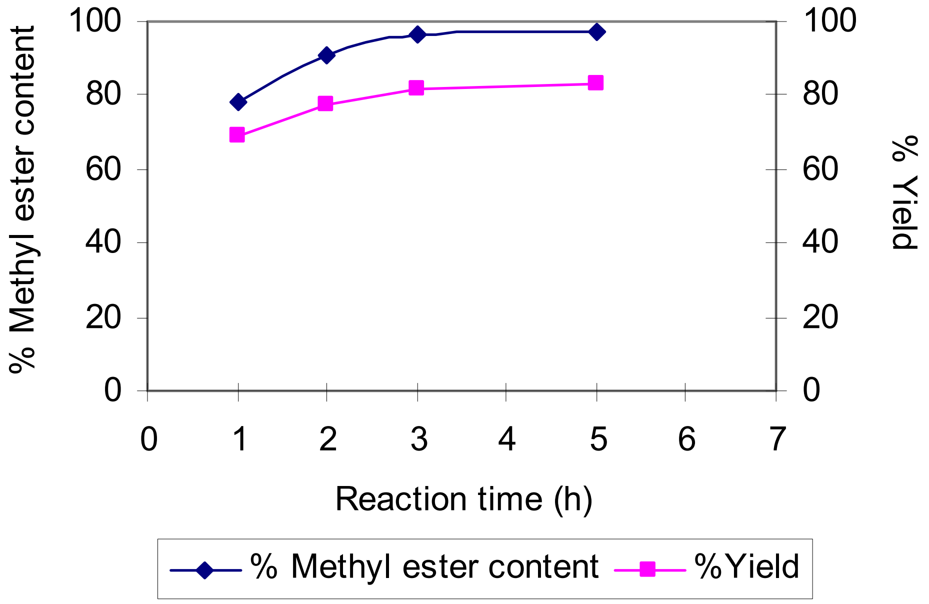


Figure 24 The effect of reaction time on methyl ester content and yield carrying out at 60 ^{O}C, methanol: oil molar ratio = 26:1, 6 wt% catalyst, 300 rpm, K_2CO_3 loading 35 wt% and 20 wt% THF.

The effect of reaction time on the methyl ester content and yield are illustrated in Fig 24. The methyl ester content and yield were increased with increasing the reaction time and eventually reached the optimum value after 3 h. The methyl ester content was also found to follow the same tendency, showing the maximum value at 96 and 81 %, respectively. Further increase in reaction time beyond 3 h had no significant impact on the methyl ester content and yield because the reaction had approached equilibrium. Therefore, the optimum reaction time for biodiesel production from crude palm oil over the K_2CO_3/CaO catalyst was 3 h and the results related very well with Huaping *et al.,* (2006).

2.6 Influence of catalyst amount on methyl ester content and yield

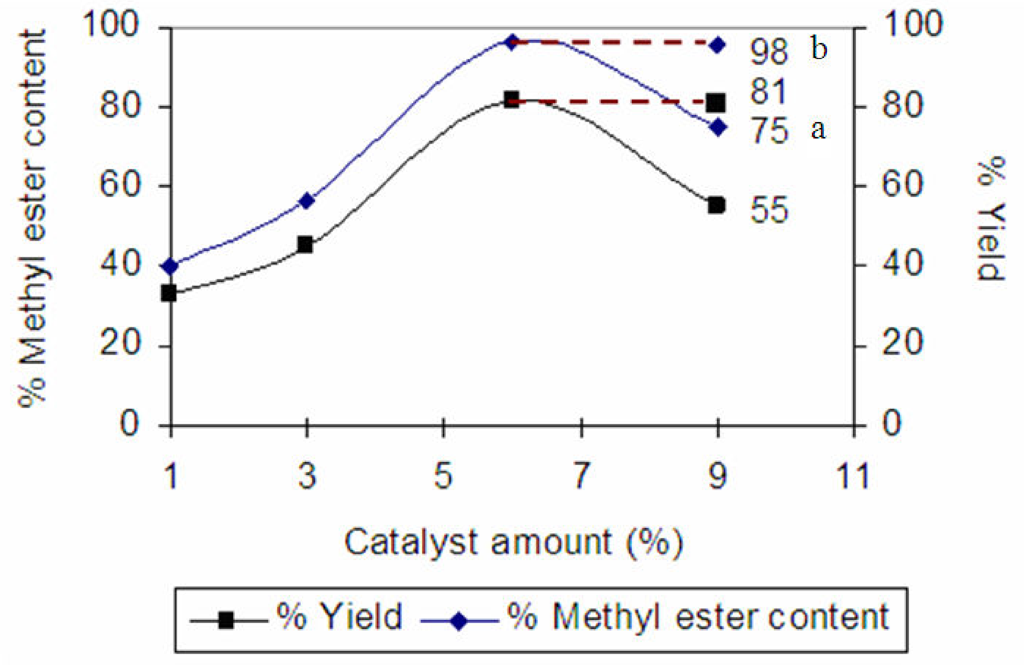


Figure 25 The effect of catalyst amount on methyl ester content and yield carrying out at 60 ^{O}C, 2 h, methanol: oil molar ratio = 26:1, K_2CO_3 loading, 35wt% and 20 wt% THF.

[a] Corresponding reaction at 300 rpm.

[b] Corresponding reaction at 600 rpm.

The effect of catalyst amounts on the methyl ester content is presented in Fig 25. The catalyst amount was varied in the range between 1 wt% and 9 wt%. When the catalyst amount increased, the methyl ester content and yield increased because increasing the active site. The optimum catalyst amount of 6 wt% was found to produce the highest methyl esters content and yield of 96 and 81%, respectively. Increasing catalyst amounts initially increased the active sites for the transesterification. However, further addition of the catalyst beyond 6 wt% resulted decreased methyl ester content and yield due to deteriorated mixing, poorer catalyst dispersion and consequently poorer adsorption of reactants on catalyst surface. The effect of mixing of 9 wt% catalyst amount was also determined.

To determine the effect of mixing, the transesterification reaction of 9 wt% of K_2CO_3/CaO was carried out under stirring speeds of 600 rpm. At lower stirring speed (300 rpm) as shown in Fig 25, the methyl ester content and yield were 75 and 55 %, respectively. At 600 rpm the methyl ester content and yield reached to 98 and 81 %, respectively. When increasing the speed of the stirrer from 300 rpm to 600 rpm, the result showed that the mixing of reagents was efficient due to reaching a high methyl ester content and yield. The result related with literature (Xie *et al.,* 2006). They found that at two randomly chosen stirring speeds (200 and 800 rpm) the conversion reached 68 % after 8 h of reaction, whereas at 800 rpm the oil conversion reached 85 %. The result showed that an efficient mixing of the reagents was essential to reach a high conversion of the oil. From the results, increasing the amount of catalyst and stirring speeds to 9 wt % and 600 rpm from 6 wt % and 300 rpm, respectively led to a slight increase in methyl ester content and yield from 96 to 98 %. Therefore, we were interested in the previous optimal condition and the effect of deactivation will be further discussed.

2.7 Influence of Deactivation of catalysts on methyl ester content

Heterogeneous catalysts have the potential to be recovered, regenerated and reused. Deactivation studies were carried out with K_2CO_3/CaO calcined at 800 ^OC, 500 ^OC and no calcined as shown in Fig 26.

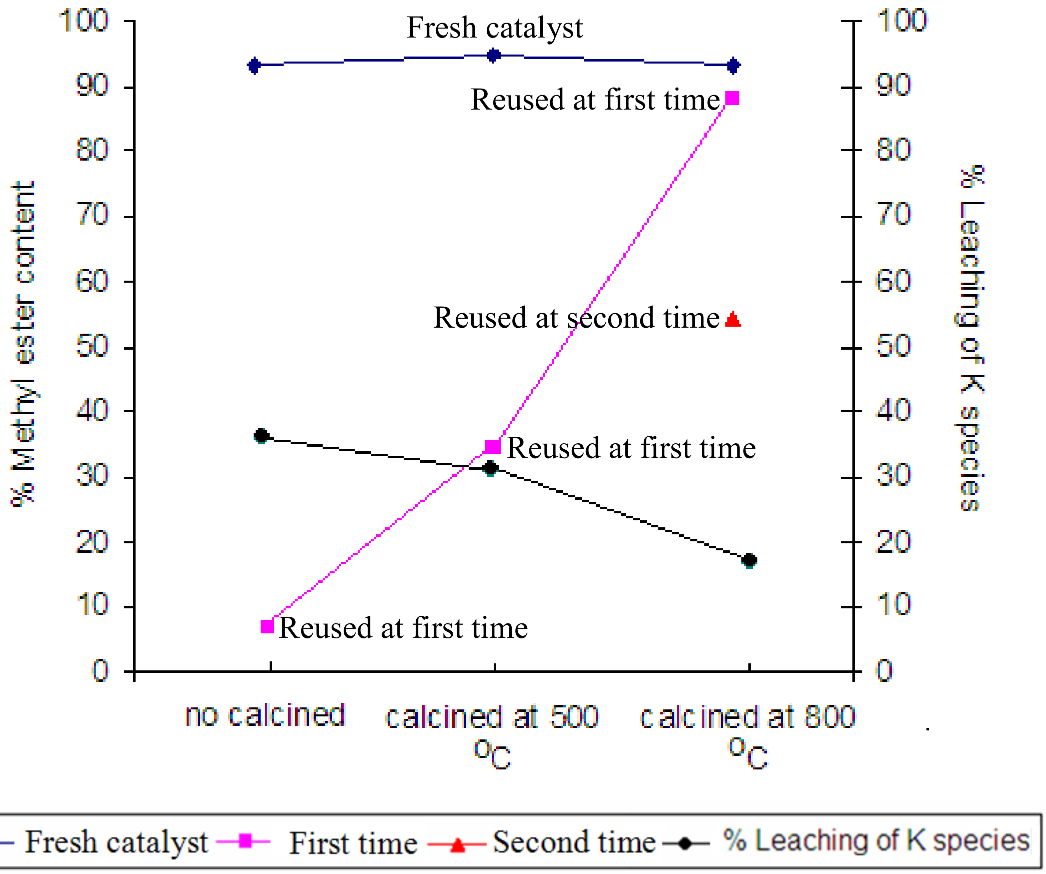


Figure 26 The effect of reused catalyst of various calcination temperatures on methyl ester content comparing with % leaching of K species carrying out at 60 ^{O}C, 2 h, methanol: oil molar ratio = 26:1, 6 wt% catalyst, K_2CO_3 loading, 35 wt%, 300 rpm and 20 wt% THF.

After the reaction cycle, the catalyst was washed with hexane and dried at 120 ^{O}C for 12 h. Fresh catalyst, the methyl ester content of without calcination, calcined at 500 ^{O}C and 800 ^{O}C were 93, 94 and 93 %, respectively. When reusing all of catalysts in the first time, the activity of the catalyst followed the order by calcination temperature: 800 ^{O}C > 500 ^{O}C > no calcined. All catalysts exhibited decreases in methyl ester content of 7, 34 and 88 %, respectively. The second time of reused K_2CO_3/CaO calcined at 800 ^{O}C was analyzed and it obtained the methyl ester of 54 %. The catalyst has lower activity due to loss of potassium specie. Regarding on this issue, three samples of catalyst contain with K_2CO_3/CaO without calcination reused at the first time, K_2CO_3/CaO calcined at 500 ^{O}C reused at the first time and K_2CO_3/CaO calcined at 800 ^{O}C reused at the second time were analyzed by XRF (X-Ray Fluorescence spectroscopy) as shown in Table 10 and detail of calculation can be found in Appendix E. The results from XRF related with the assumption that are the used catalysts will loss of potassium due to loss of potassium specie. From the previously, the different calculation temperature obtained similar methyl ester content and yield in the transesterification. From the previously experiment, the different calculation temperature has no affected on methyl ester content and yield in transesterification but from Fig 26 when reused K_2CO_3/CaO without calcination will obtained the lower activity due to K_2CO_3 form can be diluted in methanol more than K_2CO_3/CaO calcined at 500 and 800 ^{O}C. Influence of calcination temperature has significant affected on K_2CO_3 species that make K_2CO_3 stable and hard to dissolve in methanol. Therefore, the activity of catalyst in transesterification depends on the remaining of potassium content on the catalyst. However, the advantage of catalyst without calcination is consuming less of energy, ease of preparation and regeneration. Among these catalysts, the non-calcined catalyst showed the lowest activity due to the leaching of potassium from CaO reaching about 38 % and the results are presented in Table 10 (X-Ray fluorescence analysis). It was found that the calcination temperature has a significant impact on potassium leaching. When the calcination temperature is higher than 500 ^{O}C the K_2CO_3 can also be converted to K_2O by thermal decomposition of the carbonates as described previously. Therefore, the K_2O species derived from decomposition process is possibly being the main active species which is a stable and high basicity catalyst. So, the leaching of potassium at 500 ^{O}C and 800 ^{O}C were 30 and 17 %, respectively.

Table 10 The Leaching of potassium species of the reused catalysts by XRF (X-Ray fluorescence spectroscopy) analysis

Calcination Temperature	Leaching of potassium species
No calcined	38 %
500 ^{O}C	30 %
800 ^{O}C	17 %

2.8 Comparison between regeneration of no calcined catalyst and reused of calcined catalyst at 800 ^{O}C

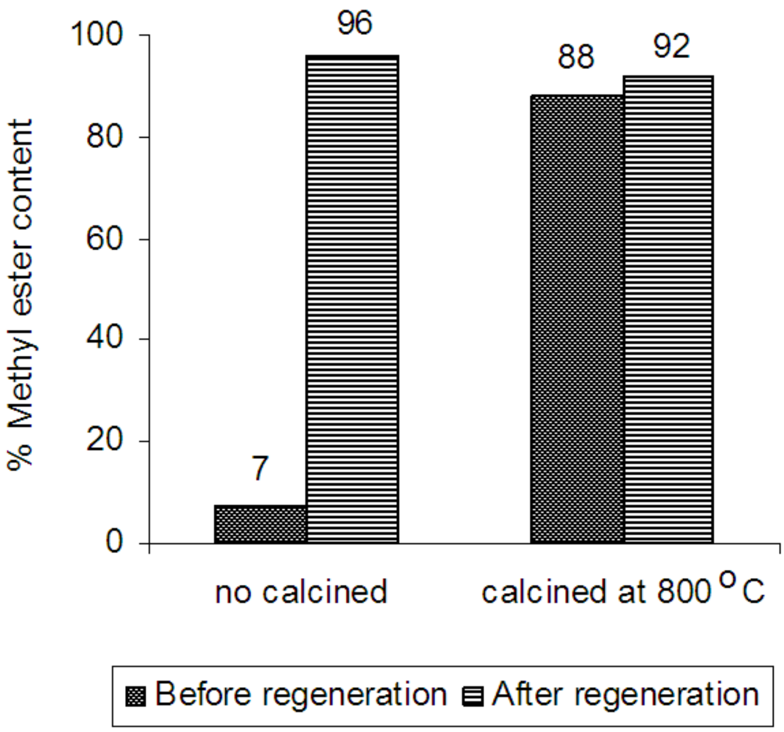


Figure 27 The effect of catalyst regeneration at various calcination temperatures on methyl ester content and yield carrying out at 60 ^{O}C, 3 h, methanol: oil molar ratio = 26:1, 6 wt% catalyst, K_2CO_3 loading, 35 wt%, 300 rpm and 20 wt% THF.

In this case, solid catalysts can be easily regenerated by adding the amount of catalyst onto the support by considering the percentage of leaching potassium then dried at 120 ^{O}C for 12 h for no calcined catalyst and for calcination catalyst calcined at 800 ^{O}C for 5 hr. After using in transesterification reaction, K_2CO_3/CaO without calcination and K_2CO_3/CaO calcination at 800 ^{O}C were loaded amount of K_2CO_3 where leached from the surface area of support from Table 10. From Fig 27, it was found that the regeneration of non-calcined catalyst obtained high methyl ester content of 96 %, when compared with regeneration catalyst at 800 ^{O}C which obtained lower methyl ester content 93 %, respectively. We found that regeneration of non-calcined is worth than reused of 800 ^{O}C without regeneration due to the advantage of non-calcined catalyst after regenerated obtained the high activity and ease of regeneration. Moreover, the leaching species of potassium has no affected in soap formation. The disadvantage of non-calcined catalyst is must be regenerated all time after using. When calcination catalyst at high temperature it make stable form of catalyst and obtained high methyl ester content and yield after reused but it consumed a high amount of energy. Therefore, all of experiment non-calcined catalyst was analyzed. Then the properties (density, viscosity, cloud point, pour point and flash point) of non-calcination and of the calcined catalyst at 800 ^{O}C were further investigated.

2.9 The properties of biodiesel from crude palm oil via K_2CO_3/CaO compared with the standard from department of energy business

Table 11 Biodiesel properties using K_2CO_3/CaO without calcination

Properties	B100 [a]	B100 [b]	B100 [c]	Standard
Density, lb/gal at 15 ^{O}C	8.68	8.73	8.93	8.60-9.00
viscosity, mm^2/s at 40 ^{O}C	4.9	5.0	5.1	3.5-5.0
Cloud point ^{O}C	23	23	24	-
Pour point ^{O}C	18	18	19	-
Flash point ^{O}C	210	212	213	Not less than 120
% Methyl ester content	96.3	96.2	89.6	>96.5

Source: Standard by department of energy business

[a] corresponding methyl ester via catalyst absence calcination used at the first time

[b] corresponding methyl ester via catalyst absence calcination and regeneration after using the second time

[c] corresponding methyl ester via reused catalyst calcination at 800 ^{O}C using the second time

In biodiesel production it is important that the properties should comply with the standards of the department of energy business (Table 7). Table 11 presents the properties of B100 via K_2CO_3/CaO (no calcined), regenerated K_2CO_3/CaO (no calcined) and reused K_2CO_3/CaO (calcined at 800 ^OC). Notice that almost all of the properties were acceptable when compared with the standard, excepting some properties such as % methyl ester content of all catalyst and the viscosity of reused K_2CO_3/CaO (calcined at 800 ^OC) was slightly higher than the standard. As a result, we can conclude that reused and regenerated K_2CO_3/CaO catalyst obtained the same properties of biodiesel when compared with biodiesel from fresh catalyst. Cloud point and pour point are very high but are suitable for the weather in Thailand. However, in Europe they very concerned about cloud point and pour point in winter. Winterization has also been employed to reduce the pour point and cloud point of biodiesel by lowering its saturated methyl ester component then separating them (RO *et al.,* 2002). Dunn *et al.,* 1996 tried to improve cloud point and pour point by using commercial additive including: 409 Flowmaster, 8500 winterflow, DFI-100 and DFI-200. The lowest pour point was -8 ^OC for biodiesel from soybean oil.

2.10 Influence of other catalysts on methyl ester content and yield

From the previous result, the optimum condition of K_2CO_3/CaO was 6 wt. % of catalyst amount, 3 h, 60^OC, 26:1 methanol to oil molar ratio, 20 wt % THF and 300 rpm. At the optimal condition, K_2CO_3/Al_2O_3 and KNO_3/Al_2O_3 were examined for comparing the catalytic activity with K_2CO_3/CaO as shown in Fig 28.

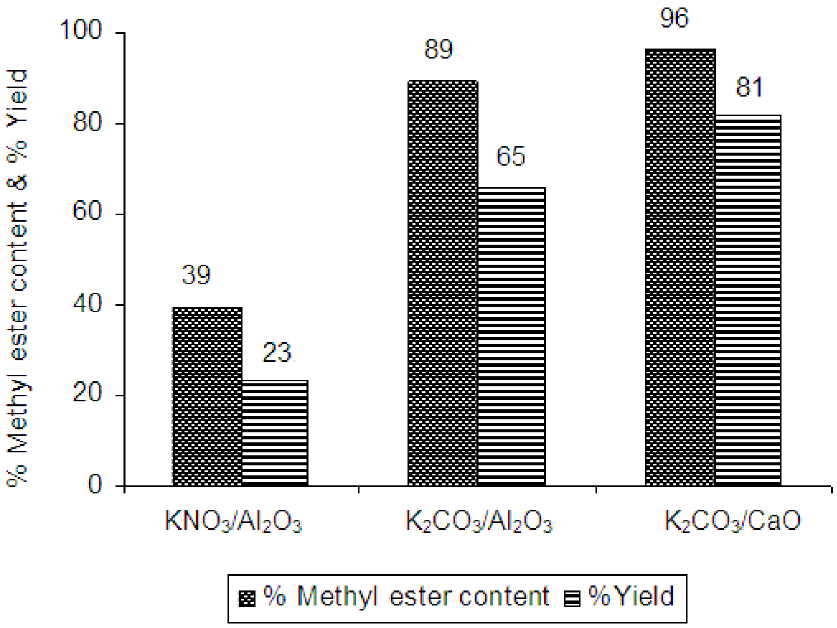


Figure 28 The effect of other catalysts on methyl ester content and yield carrying out at 60 ^{O}C, 3 h, methanol: oil molar ratio = 26:1, 6 wt% catalyst, 300 rpm and 20 wt% THF.

The catalytic activity over the catalyst is in the following order: K_2CO_3/CaO > K_2CO_3/Al_2O_3 > KNO_3/Al_2O_3 due to K_2CO_3/CaO having the highest basicity. Although, Al_2O_3 has higher BET surface area than CaO but Al_2O_3 cannot catalyze the reaction while CaO can catalyze the reaction. So, K_2CO_3/CaO shows the highest catalytic activity which obtained the highest yield and methyl ester content.

CONCLUSIONS

The K_2CO_3 loaded on CaO was shown to be an active catalyst for transesterification of crude palm oil with methanol. Effects of loading amount of catalyst, methanol to oil molar ratio, catalyst amount, and reaction time were studied and found to have significant impacts on the methyl ester content. The maximum attainable methyl ester content and yield was found to be 96 and 81%, respectively, at loading amount K_2CO_3 of 35 wt% on CaO, a molar ratio of methanol to crude palm oil of 26:1, amount of K_2CO_3/CaO of 6 wt%, , and 3 h reaction time.

K_2CO_3/CaO shows the highest activity when compared with K_2CO_3/ Al_2O_3 and KNO_3/Al_2O_3 due to the highest basicity. Although Alumina has high surface area, it can not catalyze the transesterification while CaO can catalyze the reaction. Therefore, the active support (CaO) promised a higher methyl ester content and yield than non active support (Al_2O_3). When K_2CO_3/CaO without calcination was regenerated by loading the K_2CO_3 onto CaO, the methyl ester content and yield obtained was 96 and 80%, respectively and the properties (flash point, pour point, cloud point, density and viscosity) meet the standard from the Department of energy business. Therefore, the catalysts without calcination can be easily regenerated, ease of preparation and shows high performance for biodiesel production from CPO. Moreover, this catalyst can be used without calcination so it reduces the energy consumption.

The K_2CO_3/CaO was shown to be an interesting choice of catalysts due to its reasonably high activity, ease of preparation, simple separation and low cost. Together, features can make biodiesel production from crude palm oil become more economically feasible.

LITERATURE CITED

Arzamendi G., I. Campo, E. Arguiarena, M. Sanchez, M. Montes and L.M. Gandia. 2007. Esterification and transesterification on tungstated zirconia: Effect of calcination temperature. **Journal of Catalysis.** 247: 43-50.

Chen G., 2007. Sintering, crystallization, and properties of CaO doped cordierite-based glass–ceramics. **Journal of Alloys and Compounds.** In Press.

Crabbe E., C. Hipolito, G. Kobayashi, K. Sonomoto and A. Ishizaki. 2001. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. **Process Biochemistry**. 37: 65-71.

Claire S. M., A. P. Harvey, A. F. Lee and K. Wilson. 2007. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production **Chemical Engineering Journal**. In Press.

Dora E. Lopez, K. Suwannakarn, D. A. Bruce and J. G. Goodwin. 2007. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: Comparison with homogeneous NaOH. **Chemical Engineering Journal**. In Press.

Dora E. Lopez, J. G. Goodwin and David A. 2007. Transesterification of triacetin with methanol on Nafion acid resins. **Journal of Catalysis**. 245: 381-391.

Dunn T., C. Chiu, G. Schumacher and J. Suppes. 1996. Impact of cold flow improvers on soybean biodiesel blend. **Biomass and Bioenergy**. 27: 485-491

Ebiura T., T. Echizen, A. Ishikawa, K. Murai and T. Baba. 2005. Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina load with alkali metal salt as a solid-base catalyst. **Applied Catalyst A.** 283: 111-116.

Fukuda H., A. Kondo, and H. Noda. 2001. Biodiesel fuel production by tranesterification of oils. **Bioscience Bioengineering.** 92: 405-416.

Furuta S., H. Matsuhashi and K. Arata. 2006. Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor. **Biomass and Bioenergy.** 30: 870-873.

Gerpen J., B. Shanks and R. Pruszko. 2004. Biodiesel production technology. **Renewable Product Development Laboratory.** 43: 233-245

Granados M. Lopez, M.D. Zafra Poves, D. Martin Alonso, R. Mariscal, F. Cabello Galisteo, R. Moreno-Tost, J. Santamaria and J.L.G. Fierro. 2007. Biodiesel from sunflower oil by using activated calcium oxide. **Applied Catalysis B**: **Environmental**, In Press.

Galen J.S., A.D. Mohanprasad, E.J. Doskocil, P.J. Mankidy and M.J. Goff. 2004. Tranesterification of soybean oil with zeolite and metal catalysts. **Applied Catalysis.** 257: 213-223.

Gauglitz E.,F and L.W. Lehman. 1963. The preparation of alkyl ester from highly unsaturated triglycerides. **Journal of the American Oil Chemists' Society.** 40: 197-201.

Gryglewicz S. 1999. Rapeseed oil methyl esters preparation using heterogeneous catalysts. **Bioresource Technology.** 70: 249-253.

Huaping Z., W. Zongbin , C. Yuanxiong, Z. Ping, D. Shijie, L. Xiaohua. 2006. Preparation of Biodiesel Catalyzed by Solid Super Base of Calcium Oxide and Its Refining Process. **Chin J Catalysis.** 27: 391–396.

Huang W., B. Liu, F. Sun, Z. Zhang and X. Bao. 2006. Synthesis and characterization of thermally stable MCM-41/γ-Al_2O_3 composite materials, **Microporous and Mesoporous Materials.** 94: 254-260.

Jamna T. 2002. Development of jatropha based biodiesel in Transesterification Process. **Bioresource Technology.** 85: 261-266.

Jitputti J., B. Kitiyanan, P. Rangsunvigit and K. Bunyakiat. 2006. Transesterification of crude palm oil and crude coconut oil by different solid catalyst. **Chemical Engineering Journal.** 116: 61-66

Marchetti J.M., V.U. Miguel and A.F. Errazu. 2007. Heterogeneous esterification of oil with high amount of free fatty acids. **Applied Catalysis.** 86: 906-910.

Kim H.J., B.S. Kang, M.J. Kim, Y.M. Park and D.K. Kim. 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. **Catalysis Today.** 93: 315-320.

Krawczyk T. 1996. Biodiesel alternative fuel makes inroads but hurdles remain. **Inform.** 7: 801-829.

Lichinda N. and Sudsakorn K. 2006. Biodiesel production from palm stearin using heterogeneous catalyst.

Liu X., H. Huayang, W. Yujun and Z. Shenlin. 2006. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. **Bioresource Technology**. In Press.

Marchetti J.M., V.U. Miguel and A.F. Errazu. 2006. Heterogeneous esterification of oil with high amount of free fatty acids**. Journal of Catalysis**. In Press.

Ma F., and M.A. Hanna. 1999. Biodiesel production : a review. **Bioresource Technology.** 70: 1-15.

Mathew S., C. Shiva Kumara and N. Nagaraju. 2006. Influence of nature of support on the catalytic activity of supported molybdenum-oxo species in benzyl alcohol conversion. **Journal of Molecular Catalysis A: Chemical**. 255: 243-248

Noiroj K., A. Luengnaruenmitchai and S. Jaiin. 2006. Potassium hydroxide on alumina support for biodiesel production via transesterification from crude palm oil. **The 16 th Thai Chemical Engineering and Applied Chemistry Conference.**

Nestor U. and M. Matsumuraa. 2005. Ozonized vegetable oil as pour point depressant for neat biodiesel. **Fuel**. 85: 25–31

Ramadhas A.S., S. Jayaraj and C. Muraleedharan. 2004. Biodiesel production from high FFA rubber seed oil. **Fuel**. 84: 335-340.

Ro P., D. Kim, J. Lee, S. Park, Y. Kim and J. Lee. 2002. Blending effects of biodiesels on oxidation stability and low temperature flow properties **Bioresource Technology.** In Press

Sirikulbodee M. and K. Sudsakorn. 2006. Biodiesel production from crude palm oil using heterogeneous catalyst. **The 16 th Thai Chemical Engineering and Applied Chemistry Conference.**

Wing K. Ng., P.K. Lim and P.L. Boey. 2003. Dietary lipid and palm oil source affects growth, fatty acid composition and muscle α-tocopherol concentration of African catfish. **Aquaculture**. 215: 229-243

Xie W., X. Huang and H. Li. 2007. Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. **Bioresource Technology**. 98: 936-939

Xie W, X. Huang and H. Li. 2005. Tranesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. **Applied Catalysis A: General**. 300: 67-74.

Xie W. and Li H. 2006. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. **Journal of Molecular Catalysis A: Chemical**. 255: 1-9

Xie W. and Z. Yang. 2007. Soybean oil transesterification over zinc oxide modified with alkali earth metals. **Fuel Processing Technology**. In Press.

Bangkok renewable energy Co., Ltd. 2007. www.bkkre.com

Ministry of Energy Thailand. 2007. www.energy.go.th/th/knowledge.asp

Palm oil production. 2007. http://www.fao.org/DOCREP/005/Y4355E/y4355e04.htm

The department of energy business. 2007. www.ore.go.th

The global petroleum club. 2007. http://www.globalpetroleumclub.com

APPENDIX

Appendix A

1. Determination of raw materials

Molecular weight of CPO is 847.3 (Crabbe et al., 2001)

Molecular weight of methanol (CH_3OH) is 32.04

Measuring CPO for 20 g

Calculation of methanol amount

Changing CPO into mol 20/847.3 = 0.0236 mol

Molar ratio of methanol to oil is 26:1, the amount of methanol

= 26*0.112

= 0.6137 mol

Changing in to gram 0.6317*32.04 = 19.663 g.

Changing in to volume 19.663/0.792 = 24.827 ml.

Co-solvent THF 20wt%

Measuring THF for 4 g

Specific gravity of THF = 0.89

Changing in to volume 4/0.89 = 4.494 ml.

2. Determination of acid value and free fatty acid

$$\text{Acid value (AV)} = \frac{(56.1)AN}{w}$$

Where

A = volume of potassium hydroxide solution used (ml)

N = concentration of potassium hydroxide solution (mol)

w = sample weight (g)

Free fatty acid (FFA) $= \frac{AV}{2.19}$

Where

AV = Acid value (mg KOH/g)

Calculation of Acid value and free fatty acid of crude palm oil

A = 9 ml
N = 0.1 mol
w = 5 g

Therefore

Acid value $= \frac{(56.1) \times 9 \times 0.1}{5}$

$= 10$

AV = 10 mgKOH/g

Therefore

Free fatty acid $= \frac{10}{2.19}$

$= 4.56$

FFA = 4.56 %

Appendix B

1. Preparation of methyl ester for analyzed by Gas chromatography

1. Methyl ester was weighted about 50 milligram in to vial.
2. Methyl heptadecanoate was mixed with heptane (10 mg/ml).
3. One milliliters of methyl heptadecanoate solution was added into methyl ester.

2. The result of chromatogram

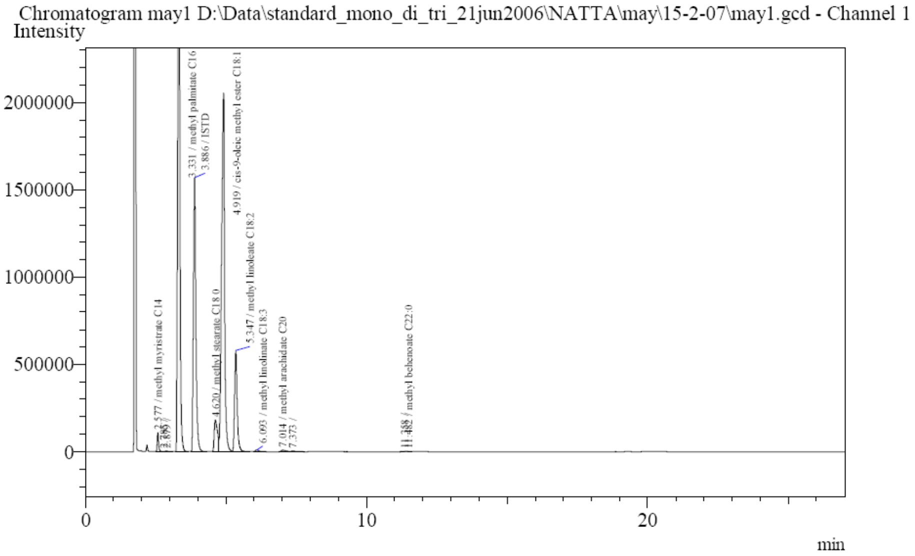
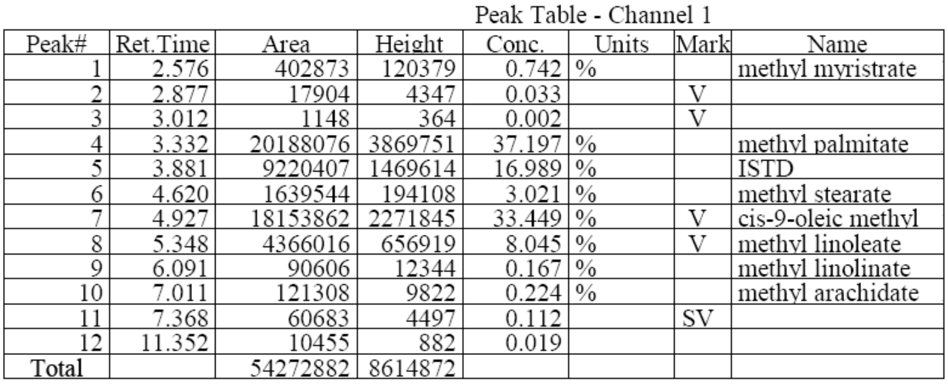


Figure B.1 Chromatogram of a crude palm oil FAME sample

Table B.1 Peak area and retention time of crude palm oil FAME sample



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Units	Mark	Name
1	2.576	402873	120379	0.742	%		methyl myristrate
2	2.877	17904	4347	0.033		V	
3	3.012	1148	364	0.002		V	
4	3.332	20188076	3869751	37.197	%		methyl palmitate
5	3.881	9220407	1469614	16.989	%		ISTD
6	4.620	1639544	194108	3.021	%		methyl stearate
7	4.927	18153862	2271845	33.449	%	V	cis-9-oleic methyl
8	5.348	4366016	656919	8.045	%	V	methyl linoleate
9	6.091	90606	12344	0.167	%		methyl linolinate
10	7.011	121308	9822	0.224	%		methyl arachidate
11	7.368	60683	4497	0.112		SV	
12	11.352	10455	882	0.019			
Total		54272882	8614872				

Appendix C

1. Determination of methyl ester content

The Methyl ester content, expressed as a mass fraction in percentage, is calculated using the following formula refer to EN 14124:

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

Where

$\sum A$ is the total peak area from the methyl ester in C14 to that in C24:1

A_{EI} is the peak area corresponding to methyl heptadecanoate

C_{EI} is the concentration, in milligram per milliliter, of methyl heptadecanoate solution

V_{EI} is the volume, in milliliters, of the methyl heptadecanoate solution

W is the mass, in milligrams, of sample

$$\text{Yield } (\%) = (W_i / W_0) \times 100\%$$

Where

W_i is the weight of biodiesel (g)

W_0 is the weight of crude palm oil (g)

Calculation of Methyl ester content and yield of no calcined catalyst

1. Methanol oil molar ratio = 26 : 1
2. Reaction time = 2 h
3. Reaction temperature 60 ^{O}C
4 Stirrer speeds = 300 rpm

Determination of methyl ester content from Table B.1

$\sum A$ = 402873+9220407+20188076+1629544+18153862+4366016 +90606+121308

= 54063692

A_{EI} = 9220407

C_{EI} = 10 mg/ml

V_{EI} = 1 ml

W = 52.11 mg

Therefore

$$C = \frac{(5406392 - 9220407) \times 10 \times 1}{9220407 \times 52.11} \times 100\%$$

= 93.32 %

Determination of yield

W_i = 14.844 g

W_0 = 20 g

Therefore

Yield (%) = (14.844 x 100)/20

= 74.22 %

Appendix D

Nitrogen adsorption analysis of CaO

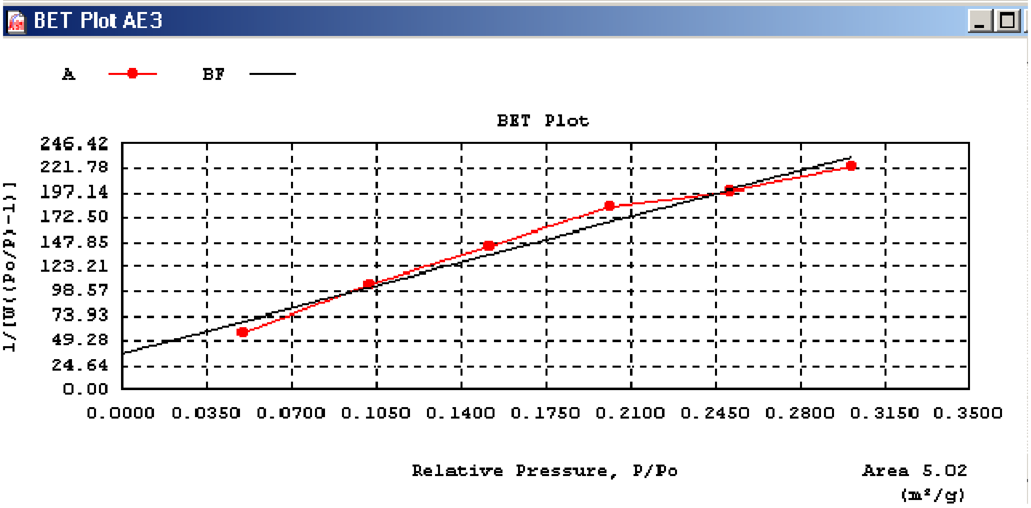
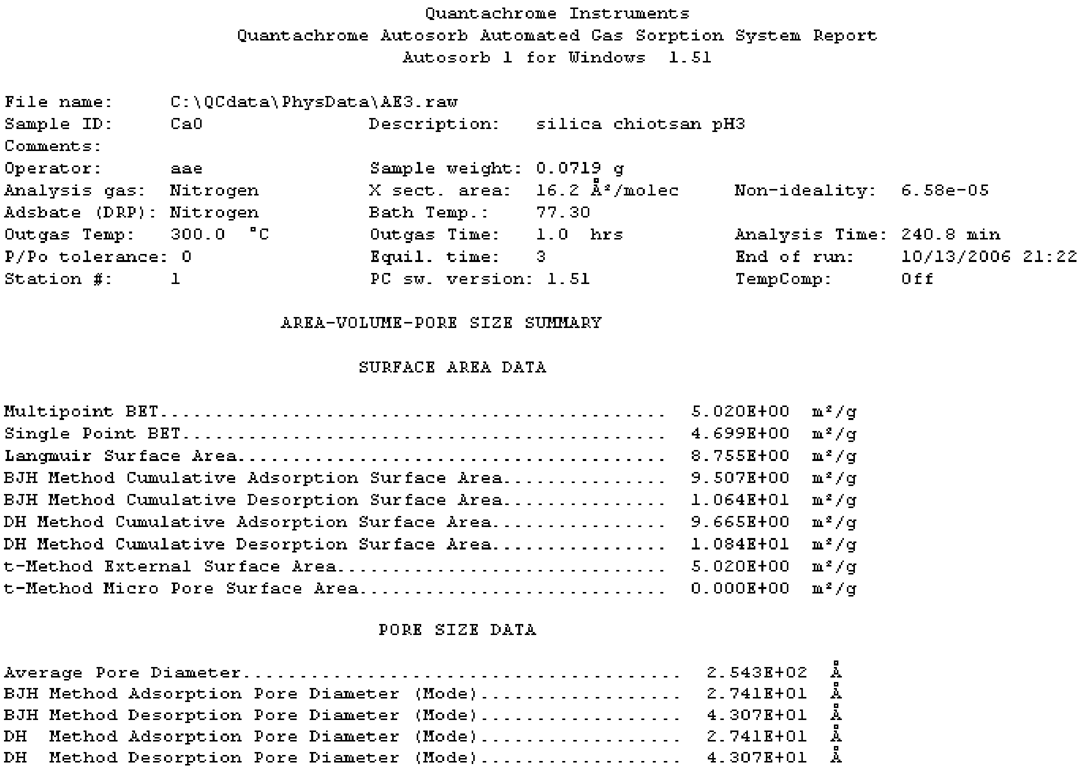


Figure D.1 BET plot of CaO

Table D.1 Data of BET surface area of CaO

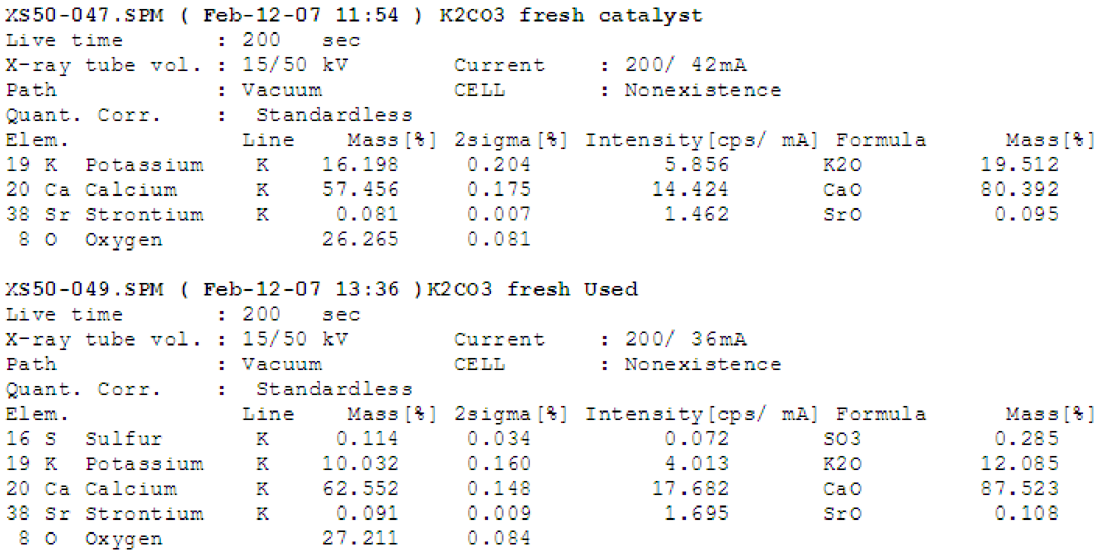


```
                              Quantachrome Instruments
                 Quantachrome Autosorb Automated Gas Sorption System Report
                              Autosorb 1 for Windows  1.51

File name:      C:\QCdata\PhysData\AE3.raw
Sample ID:      CaO                Description:    silica chiotsan pH3
Comments:
Operator:       aae                Sample weight:  0.0719 g
Analysis gas:   Nitrogen           X sect. area:   16.2 Å²/molec      Non-ideality:   6.58e-05
Adsbate (DRP):  Nitrogen           Bath Temp.:     77.30
Outgas Temp:    300.0  °C          Outgas Time:    1.0  hrs           Analysis Time:  240.8 min
P/Po tolerance: 0                  Equil. time:    3                  End of run:     10/13/2006 21:22
Station #:      1                  PC sw. version: 1.51               TempComp:       Off

                         AREA-VOLUME-PORE SIZE SUMMARY

                                SURFACE AREA DATA

Multipoint BET............................................  5.020E+00  m²/g
Single Point BET..........................................  4.699E+00  m²/g
Langmuir Surface Area.....................................  8.755E+00  m²/g
BJH Method Cumulative Adsorption Surface Area.............  9.507E+00  m²/g
BJH Method Cumulative Desorption Surface Area.............  1.064E+01  m²/g
DH Method Cumulative Adsorption Surface Area..............  9.665E+00  m²/g
DH Method Cumulative Desorption Surface Area..............  1.084E+01  m²/g
t-Method External Surface Area............................  5.020E+00  m²/g
t-Method Micro Pore Surface Area..........................  0.000E+00  m²/g

                                 PORE SIZE DATA

Average Pore Diameter.......................................  2.543E+02  Å
BJH Method Adsorption Pore Diameter (Mode)..................  2.741E+01  Å
BJH Method Desorption Pore Diameter (Mode)..................  4.307E+01  Å
DH  Method Adsorption Pore Diameter (Mode)..................  2.741E+01  Å
DH  Method Desorption Pore Diameter (Mode)..................  4.307E+01  Å
```

Appendix E

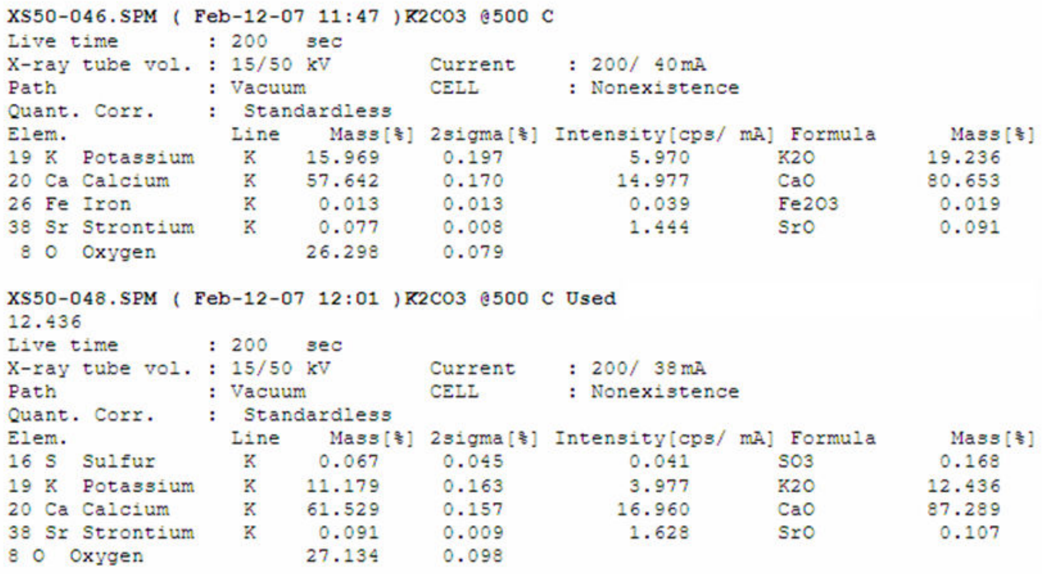
X-Ray fluorescence spectroscopy analysis

Table E.1 XRF data of K_2CO_3/CaO without calcination of fresh catalyst and reused at first time



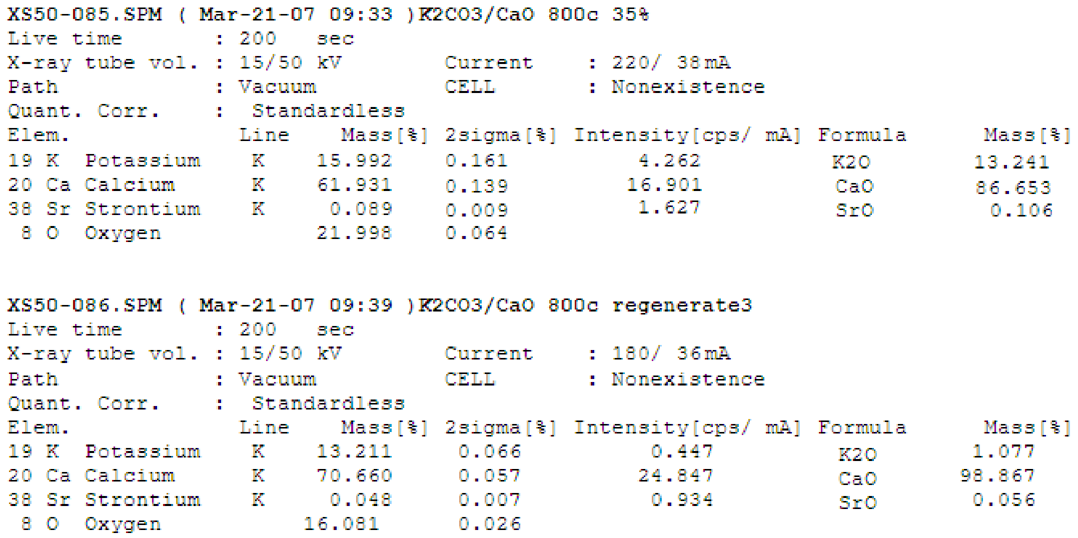
```
XS50-047.SPM ( Feb-12-07 11:54 ) K2CO3 fresh catalyst
Live time        : 200   sec
X-ray tube vol. : 15/50 kV        Current    : 200/ 42mA
Path             : Vacuum         CELL       : Nonexistence
Quant. Corr.     :  Standardless
Elem.              Line    Mass[%] 2sigma[%] Intensity[cps/ mA] Formula      Mass[%]
19 K  Potassium     K    16.198     0.204          5.856       K2O        19.512
20 Ca Calcium       K    57.456     0.175         14.424       CaO        80.392
38 Sr Strontium     K     0.081     0.007          1.462       SrO         0.095
 8 O  Oxygen             26.265     0.081

XS50-049.SPM ( Feb-12-07 13:36 )K2CO3 fresh Used
Live time        : 200   sec
X-ray tube vol. : 15/50 kV        Current    : 200/ 36mA
Path             : Vacuum         CELL       : Nonexistence
Quant. Corr.     :  Standardless
Elem.              Line    Mass[%] 2sigma[%] Intensity[cps/ mA] Formula      Mass[%]
16 S  Sulfur        K     0.114     0.034          0.072       SO3         0.285
19 K  Potassium     K    10.032     0.160          4.013       K2O        12.085
20 Ca Calcium       K    62.552     0.148         17.682       CaO        87.523
38 Sr Strontium     K     0.091     0.009          1.695       SrO         0.108
 8 O  Oxygen             27.211     0.084
```

Table E.2 XRF of K_2CO_3/CaO calcined at 500 ^{O}C of fresh catalyst and reused at the first time



```
XS50-046.SPM ( Feb-12-07 11:47 )K2CO3 @500 C
Live time        : 200   sec
X-ray tube vol. : 15/50 kV        Current    : 200/ 40mA
Path             : Vacuum         CELL       : Nonexistence
Quant. Corr.     :  Standardless
Elem.              Line    Mass[%] 2sigma[%] Intensity[cps/ mA] Formula      Mass[%]
19 K  Potassium     K    15.969     0.197          5.970       K2O        19.236
20 Ca Calcium       K    57.642     0.170         14.977       CaO        80.653
26 Fe Iron          K     0.013     0.013          0.039       Fe2O3       0.019
38 Sr Strontium     K     0.077     0.008          1.444       SrO         0.091
 8 O  Oxygen             26.298     0.079

XS50-048.SPM ( Feb-12-07 12:01 )K2CO3 @500 C Used
12.436
Live time        : 200   sec
X-ray tube vol. : 15/50 kV        Current    : 200/ 38mA
Path             : Vacuum         CELL       : Nonexistence
Quant. Corr.     :  Standardless
Elem.              Line    Mass[%] 2sigma[%] Intensity[cps/ mA] Formula      Mass[%]
16 S  Sulfur        K     0.067     0.045          0.041       SO3         0.168
19 K  Potassium     K    11.179     0.163          3.977       K2O        12.436
20 Ca Calcium       K    61.529     0.157         16.960       CaO        87.289
38 Sr Strontium     K     0.091     0.009          1.628       SrO         0.107
8 O  Oxygen              27.134     0.098
```

Table E.3 XRF of K_2CO_3/CaO calcined at 800 ^{O}C of fresh catalyst and reused at the second time



```
XS50-085.SPM ( Mar-21-07 09:33 )K2CO3/CaO 800c 35%
Live time        : 200   sec
X-ray tube vol. : 15/50 kV         Current     : 220/ 38mA
Path             : Vacuum          CELL        : Nonexistence
Quant. Corr.     :  Standardless
Elem.              Line     Mass[%] 2sigma[%] Intensity[cps/ mA] Formula      Mass[%]
19 K  Potassium     K     15.992    0.161       4.262           K2O        13.241
20 Ca Calcium       K     61.931    0.139      16.901           CaO        86.653
38 Sr Strontium     K      0.089    0.009       1.627           SrO         0.106
 8 O  Oxygen              21.998    0.064

XS50-086.SPM ( Mar-21-07 09:39 )K2CO3/CaO 800c regenerate3
Live time        : 200   sec
X-ray tube vol. : 15/50 kV         Current     : 180/ 36mA
Path             : Vacuum          CELL        : Nonexistence
Quant. Corr.     :  Standardless
Elem.              Line     Mass[%] 2sigma[%] Intensity[cps/ mA] Formula      Mass[%]
19 K  Potassium     K     13.211     0.066        0.447          K2O        1.077
20 Ca Calcium       K     70.660     0.057       24.847          CaO       98.867
38 Sr Strontium     K      0.048     0.007        0.934          SrO        0.056
 8 O  Oxygen             16.081      0.026
```

Table E.4 Conclusion of XRF for calculation the leaching of potassium specie

Types of Catalyst	Calcination temperature (^{O} C)	Number of used	Mass of Potassium specie (%)
K_2CO_3/CaO	non-calcined	1	16.198
K_2CO_3/CaO	non-calcined	2	10.032
K_2CO_3/CaO	500	1	15.969
K_2CO_3/CaO	500	2	11.179
K_2CO_3/CaO	800	1	15.992
K_2CO_3/CaO	800	3	13.211

Example calculation the leaching of potassium specie of non-calcined catalyst

$$\text{\% Leaching of potassium specie} = ((M_{fresh} - M_{reused})/M_{fresh})*100$$

Where

M_{fresh} = Mass of potassium species of fresh catalyst

M_{reused} = Mass of potassium species of reused catalyst

Determination of % Leaching of potassium specie from Table E.4

M_{fresh} = 16.198

M_{reused} = 10.032

Therefore

% Leaching of potassium specie = ((16.198-10.032)/16.198)*100

= 38 %

Appendix F

Calculation of K_2CO_3, K_2O and CO_2 of K_2CO_3 without calcination in DTA/TGA

Weight of K_2CO_3 = 0.2 g

Molecular weight of K_2CO_3 = 138 g/mol

Converting to mol = 0.2/138

= 0.0014 mol

Weight loss of CO_2 about 19%

Actual weight of CO_2 = 0.2*0.19

= 0.38 g

Molecular weight of CO_2 = 44 g/mol

Converting to mol

= 0.38/44

= 0.00086 mol

From mol balance

The weight of K_2CO_3 remaining = mol of K_2CO_3 - mol of CO_2

= 0.0014-0.00086

= 0.00054 mol

Converting to mass = 0.00054*138

= 0.075 g

The weight of K_2O occurring = 0.00086 mol

Molecular weight = 94 g/mol

Converting to mass = 0.00086*94

= 0.08 g

The weight of CO_2 occurring = 0.00086 mol

Converting to mass = 0.00086*44

= 0.038 g

Total mass = 0.075+0.08+0.038

= 0.193 g

The percentage of K_2CO_3 remaining = (0.075/0.193)*100

= 38.8 %

The percentage of K_2O occurring = (0.08/0.193)*100

= 41.5%

The percentage of CO_2 occurring = (0.038/0.193)*100

= 19.7%

CURRICULUM VITAE

NAME : Ms. Maythinee SIRIKULBODEE

BIRTH DATE : September 12, 1982

BIRTH PLACE : Bangkok, Thailand

EDUCATION :

YEAR	INSTITUTION	DEGREE/DIPLOMA
2005	Kasetsart Univ.	B.Eng. (Chemical)