ไบโอดีเซลจากทรานส์เอสเทอริฟีเคชันเร่งปฏิกิริยาด้วยเบสของน้ำมันไก่

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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BIODIESEL FROM BASE-CATALYZED TRANSESTERIFICATION OF CHICKEN OIL



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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science Program in Petrochemistry and Polymer Science Faculty of Science Chulalongkorn University Academic Year 2008 Copyright of Chulalongkorn University

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The objectives of this study, is to study biodiesel production from a by-products of chicken essences soup manufacturing via alkaline-catalyzed transesterification using sodium hydroxide, potassium hydroxide and potassium carbonate as catalyst. To optimize the reaction condition, the amount of catalyst, molar ratio of methanol to chicken oil, reaction temperature and reaction time were investigated. The chemical and physical properties of biodiesel produced from the transesterification, such as density, flash point, cloud point, pour point, kinematic viscosity, cetane number, cetane index, %sulphur, ester content, and mono-, di-, triglyceride content were measured. The results showed that KOH and NaOH are suitable catalyst for biodiesel production and the biodiesel with best product yield and quality was produced at a 10:1 molar ratio of methanol to chicken oil, 1.0% of potassium hydroxide catalyst; reaction temperature 65°C and reaction time 50 minutes. The product yield of the biodiesel produced under optimal condition was 99.02% with 98.27% of fatty acid methyl ester (FAME).

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LIST OF ABBREVIATIONS

° C	=	Degree Celsius
ASTM	=	American Society for Testing and Materials
		Methods of Analysis of AOAC
FAME	=	Fatty acid methyl ester
EN	=	European Standards
% wt	=	Percent by weight
wt	=	Weight
h 🛁	=	Hour
КОН	=	Potassium hydroxide
NaOH	=	Sodium hydroxide
K ₂ CO ₃	=	Potassium carbonate
TLC	= 2	Thin Layer Chromatography
% product yield	= 9.	Percentage of product yield
% conversion	=	Percentage of conversion
¹ NMR	=	Proton Nuclear Magnetic Resonance
α	7.44	Alpha

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CHAPTER I INTRODUCTION

Energy consumption in developing countries has increased more than fourfold over the past three decades and is expected to continue increasing rapidly. For many developing countries, imported petroleum will be the source of this energy. Petroleum engines are widely used as sources of power in developing areas in tractors, irrigation pumps, village generators and trucks. Increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO₂.

Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns there has been focusing on a renewable sources such as vegetable oils and animal fats to make biodiesel fuels. (Ma, F. et al., 1999)

Fatty acid methyl esters, known as biodiesel, including derived from triglycerides by transesterification with methanol have received the most attention. The main advantages of using biodiesel are its renewability, better-quality exhaust gas emissions, its biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect. (Srivastava, A. et al., 2000)

There are four primary ways to make biodiesel, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification as the biodiesel from transesterification can be used directly or as blends with diesel fuel in diesel engine. (Ma, F. et al., 1999) The fatty acid methyl ester are attractive as alternative diesel fuels. Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than an alcohol is used instead of water. This process has been widely used to reduce the viscosity of triglycerides. (Srivastava, A. et al., 2000)

Alkaline-catalyzed transesterification method is normally adopted for biodiesel production. However, the biodiesel produced from oils, no matter if it is neat vegetable oil or animal fat, is usually more expensive than petroleum-base diesel fuel from 10% to 50%. Therefore, the high cost of biodiesel is the major obstacle for its commercialization. It is reported that approximately 70-95% of the total cost of biodiesel production arises from the cost of raw materials, that is, vegetable oils or

animal fats. Many researchs found that biodiesel can be produced from waste oils such as used frying oil. However, used frying oils from restaurant and food industries have a variety of qualities, and process properties different from neat vegetable oils in biodiesel production. (Dyal, S. D. et al., 2005)

Thailand is the centre of chicken essence soup production. The maximum of chicken meat to used produced chicken essence soup about 25 ton/day. In chicken essence soup production process have separated oil or chicken oil from chicken essence soup estimate about 1.5 ton/day.

Therefore, biodiesel can be produced from by product of chicken essence soup manufacturing offer a significant as an alternative low-cost biodiesel feedstock

1.1 Objective of the research

- To study the physical and chemical properties of chicken oil
- To study biodiesel production from chicken oil by used base-catalyst
- To study the physical and chemical properties of biodiesel from chicken oil



CHAPTER II THEORY AND LITERATURE REVIEWS

2.1 Biodiesel

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic which has low emission profiles and so is environmentally beneficial. Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as vegetable oils or animal fats, for use in compression-ignition (diesel) engines. The biodiesel that is considered as a possible substitute or extender of conventional diesel fuel is commonly composed of fatty acid methyl esters that are prepared from the triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Biodiesel is compatible with conventional diesel and both can be blended in any proportion. A number of plants are manufacturing biodiesel worldwide. These units are using sunflower oil, used-frying oil, jatropha oil, etc. as a source of triglycerides. (Ma, F. et al., 1999)

2.1.1 Biological of biodiesel sources, vegetable oils or fats, and alcohol were use as feedstocks for the biodiesel production. Commonly used feedstocks are shown in Table 2.1.

 Table 2.1 Feedstocks used for biodiesel manufacture vegetable oils animal fats other sources (Strong, C. et al., 2004)

Vegetable Oils	Animal Fats	Other Source
Soybeans	Lard	Recycled Restaurant
Rapeseed	Tallow	Cooking Oil
Canola Oil (a modified version of	Poultry Fat	
rapeseed)		
Safflower Oil		
Sunflower Seeds		
Yellow Mustard Seed		

Vegetable oils are primarily water-insoluble hydrophobic substances that are made of one mole glycerol and three moles of fatty acids and are commonly called triglycerides. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The fatty acids found in vegetable oils and typical fatty acid compositions of common oil sources are summarized in Table 2.2.

Vegetable oil		Fatty acid composition, % by weight							
	16:0	18:0	20:0	22:0	24:0	18:1	18:2	18:3	22:1
Corn	12	2	1	0	0	25	61	1	0
Cottonseed	28	1	0	0	0	13	58	0	0
Rapeseed	4	1	0	0	0	64	22	8	0
Soybean	12	3	0	0	0	23	56	7	0
Sunflower seed	6	3	0	0	0	17	74	0	0
Canola oil	6	2	1	1	0	55	24	9	1
Palm	44	4	1	0	0	40	10	0	0
Butter	30	30	2	1	0	30	3	0	2
Peanut	6	6	10	10	0	66	38	0	0
Linseed	9	1	0	0	0	9	8	45	0
								•	

Table 2.2 Percentage of fatty acid type for different oils. (Strong, C. et al., 2004)

ศูนย์วิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย The fatty acids were also found in microorganisms, such as algae, fungus etc. Table 2.3 showed the fatty acids compositions of microorganism oil and Table 2.4 showed the names, of formats, of common fatty acids.

microorganism oil	Fatty acid composition								
	14:0	16:0	<u>18:0</u>	18:1	18:2	18:3	20:4	20:5	22:1
Algae	-	1	/	1	/	/	-	-	-
Yeast	/	/	/	1	/	/	/	-	-
Fungus	/	1	1-	/	/	/	/	/	-

Table 2.3 Fatty acids compositions of microorganism oil (Harris, R. et al., 1965)

Remark ; / = the fatty acids were also found in microorganism.

- = not appeared

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No. of C:No.	Molecular	Molecular mass	Systematic name	Other names
of double	formular			
bound				
C12:0	C ₁₂ H ₂₄ O ₂	200.32	Dodecanoic acid	Lauric acid,
				n-Dodecanoic acid
	1	- Milling	1	0
	\sim		\sim \sim	
		\checkmark \checkmark	\sim \sim	ОН
C14:0	$C_{14}H_{28}O_2$	228.38	Tetradecanoic acid	Myristic acid
				0
	~		<u> </u>	
	\checkmark			ОН
C16:0	$C_{16}H_{32}O_2$	256.43	Dexadecanoeic acid	Palmitic acid,
		3. 4th Ours		Hexadecylic acid,
		Real		Cetylic acid
			2	0
	\sim	\sim	\sim \sim \sim	
		\checkmark \checkmark	\sim \sim	ОН
C16:1	$C_{16}H_{30}O_2$	254.41	9-hexadecanoic acid	Palmitoleic acid
				0
	\sim \land		\sim \sim \sim	R
			\sim \sim	~ `0'

Table 2.4 Names and structures of the most common fatty acids [9]

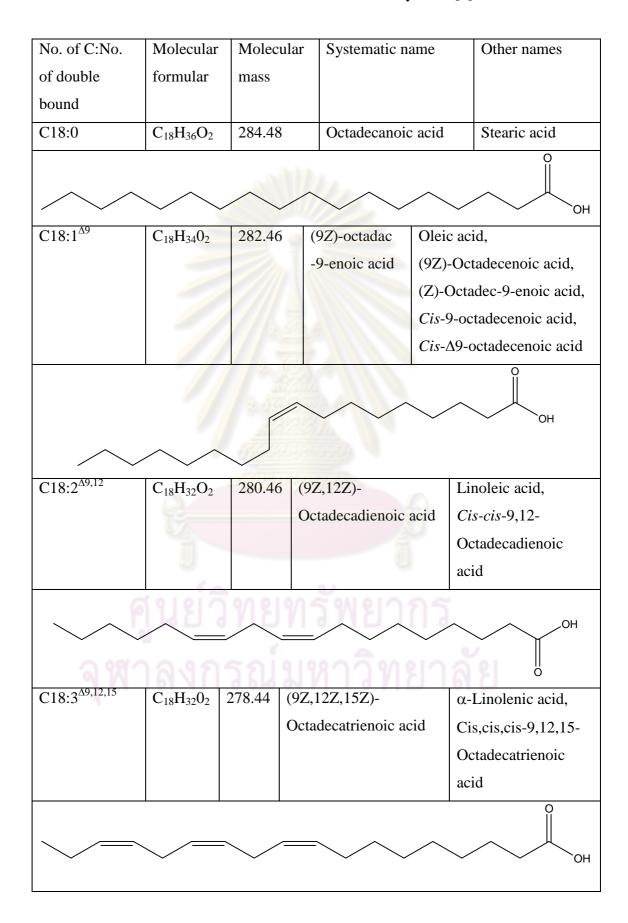


Table 2.4 Names and structures of the most common fatty acids [9]

 Table 2.4 Names and structures of the most common fatty acids [9]

No. of C:No.	Molecular	Molecular	Systematic name	Other names
of double	formular	mass		
	Torritural	111855		
bound				
C20:0	$C_{20}H_{40}O_2$	312.54	Icosanoic acid	Arachidic acid,
		s and a		Arachic acid
			120	Eicosanoic acid,
	- 2			<i>n</i> -eicosanoic acid
			ОН	
			0	
C22:0	$C_{22}H_{44}0_2$	340.60	Docosanoic acid	Behenic acid
		ALA A	4	I
		$ \land \land $	$\wedge \wedge \wedge$	ОН
	Ŷ Ŷ			
C22:1	$C_{22}H_{42}O_2$	338.58	Z-13-Docosenoic	Erucic acid
	Ū.			Cis-13-Docosenoic
	100			0
	\sim	\sim	$\sim \sim \sim$	
	\sim			ОН
	\sim	$\sim \sim$		Š al
				3 8
C24:0	$C_{22}H_{48}O_3$	368.63	Tetracosanoic acid	Lignoceric acid
	\checkmark	\sim	\sim	OH
				5

Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats as well as their methyl esters are listed in Table 2.5

Table 2.5 Selected properties of some common fatty acids and ester (Veljkovic, V. B.et al., 2006)

Trivial (Systematic) name: Acronym	Mol. wt.	m.p. (C)	b.p. (C)	Cetane No.	Heat of Combustion (kg-cal/mole)
Caprylic acid (Octanoic acid); 8:0	144.22	16.5	239.3	-	-
Capric acid (Decanoic acid); 10:0	172.27	31.5	270	47.6	1435.07
Lauric acid (Dodecanoic acid); 12:0	200.32	44	131	-	1763.25
Myristic acid (Tetradecanoic acid); 14:0	228.38	58	250.5	-	2073.91
Palmitic acid (Hexadecanoic acid); 16:0	256.43	63	350	-	2384.76
Steric acid (Octadecanoic acid); 18:0	284.48	71	360	-	2696.12
Oleic acid (9Z-Octadecenoic acid); 18:1	282.47	16	286	_	2657.4
Linoleic acid (9Z,12Z-Octadecadienoic acid) ; 18:2	280.45	-5	229	ลัย	-
Linolenic acid (9Z,12Z,15Z- Octadecatrienoic acid); 18:3	278.44	-11	230	-	-
Erucic acid (13Z-Docosenoic acid); 22:1	338.58	33	265	-	-
Methyl caprylate (Methyl octanoate)	158.24	-	193	33.6	1313

Trivial (Systematic) name: Acronym	Mol. wt.	m.p. (C)	b.p. (C)	Cetane No.	Heat of Combustion (kg-cal/mole)
Methyl caprate (Metyl decanoate)	186.30	-	224	47.7	1625
Methyl laurate (Methyl dodecanoate)	214.35	5	266	61.4	1940
Methyl myristate (Methyl tetradecanoate)	242.21	18.5	295	66.2	2254
Methyl palmitate (Methyl hexadecanoate)	270.46	30.5	415	74.5	2550
Methyl stearate (Methyl octadecanoate)	298.51	39.1	442	86.9	2859
Methyl oleate (Methyl 9Z-octadecenoate)	296.49	-20	218.5	47.2	2828
Methyl linoleate (Methyl 9Z,12Z- octadecadienoate)	294.48	-35	215	28.5	2794
Methyl linolenate (Methyl 9Z,12Z,15Z- octadecatrienoate)	292.46	-57	109	20.6	2750
Methyl erucate (Methyl 13Z-docosenoate)	352.60	เวิ่ม	221	76.0	3454

Table 2.5 Selected properties of some common fatty acids and ester (Veljkovic, V. B.et al., 2006)

2.1.2 Biodiesel production (Gerpen, J. V. et al., 2005)

The major steps required to synthesize biodiesel are as follows:

1. Purification

If waste vegetable oil is used, it is filtered to remove dirt, charred food, and other non-oil materials often found. Water is removed because its presence causes hydrolysis of triglyceride to give salts of the fatty acids instead of undergoing transesterification to give biodiesel. At home, this is often accomplished by heating the filtered oil to approximately 120°C. At this point, dissolved or suspended water will boil off. When the water boils, it spatters (chemists refer to it as "bumping"). To prevent injury, this operation should be done in a sufficiently large container (at most two thirds full) which is closed but not sealed.

In the laboratory, the crude oil may be stirred with a drying agent such as magnesium sulfate to remove the water in the form of water of crystallization. The drying agent can be separated by decanting or by filtration. However, the viscosity of the oil may not allow the drying agent to mix thoroughly.

2. Neutralization of free fatty acids

A sample of the cleaned oil is <u>titrated</u> against a standard solution of base in order to determine the concentration of free fatty acids (RCOOH) present in the waste vegetable oil sample. The quantity (in <u>moles</u>) of base required to neutralize the acid is then calculated.

3. Transesterification

While adding the base, a slight excess is factored in to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide) is added slowly to the alcohol and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess is added to drive the reaction to completion. The solution of sodium hydroxide in the alcohol is then added to a warm solution of the waste oil, and the mixture is heated (typically 50°C) for several hours (4 to 8 typically) to allow the transesterification to proceed. A condenser may be used to prevent the evaporative losses of the alcohol. Care must be taken not to create a closed system which can explode.

4. Workup

Once the reaction is complete, the glycerol should sink. When ethanol is used, it is reported that an emulsion often forms. This emulsion can be broken by standing, centrifugation, or the addition of a low boiling (easily removed) nonpolar solvent, decanting, and distilling. The top layer, a mixture of biodiesel and alcohol, is decanted. The excess alcohol can be distilled off, or it can be extracted with water. If the latter, the biodiesel should be dried by distillation or with a drying agent.

2.1.3 Biodiesel properties (Tyson, K. S. et al., 2001)

Biodiesel is made up of fourteen different types of fatty acids of triglycerides which are transformed into fatty acid methyl esters (FAME) by transesterification. Different fractions of each type of FAME present in various feedstocks influence some properties of fuels. Table 2.6 shows some of the properties defined in the ASTM standards for diesel and biodiesel. These properties are described in the remainder of this section, and will be referred to later in this report.



Fuel Property	Diesel	Biodiesel
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower Heating Value, Btu/gal	131,295	117,093
Viscosity, @ 40° C	1.3-4.1	1.9-6.0
Specific Gravity kg/l @ 60° F	0.85	0.88
Density, lb/gal @ 15° C	7.079	7.328
Water, ppm by wt	161	0.05% max
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. wt %	0	11
Sulfur, wt %	.0 <mark>5</mark> max	0.0 - 0.0024
Boiling Point (°C)	188-343	182-338
Flash Point (°C)	60-80	100-170
Cloud Point (°C)	-15 to 5	-3 to 12
Pour Point (°C)	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Stoichiometric Air/Fuel Ratio wt./wt.	15	13.8
BOCLE Scuff, grams	3,600	>7,000

Table 2.6: Comparison of fuel properties between Diesel and Biodiesel (Tyson, K. S.et al., 2001)

2.1.4 Advantages of biodiesel (Schuchardf, U. et al., 1998)

1. Conventional diesel engines can be operated without much, if any, modification on biodiesel.

2. Biodiesel can be used pure or in a mixture with hydrocarbon-based diesel fuels.

3. Biodiesel is nontoxic, safe to handle and biodegradable.

4. No evaporation of low-boiling components takes place.

5. Exhaust gas is free of SO_2 and halogens.

6. There is substantial reduction of soot, unburnt hydrocarbons, and also of carbon monoxide (when an oxidation catalyst is used) in the exhaust gases.

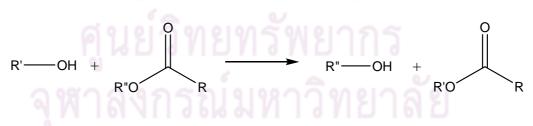
7. NO_X emissions increase slightly if there are no changes in the engine setting.

8. Good performance in auto-ignition of fatty esters results in a smooth running diesel engine.

9. Biodiesel consumption is similar to hydrocarbon-based diesel fuels.

2.2 Transesterification

In organic chemistry, transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. These reactions are often catalyzed by the addition of an acid or base.



Transesterification: $alcohol + ester \rightarrow different alcohol + different ester$

Figure 2.1 Transesterification reaction

Acids can catalyze the reaction by donating a proton to the carbonyl group, thus making it more reactive, while bases can catalyze the reaction by removing a proton from the alcohol, thus making it more reactive.

Transesterification is used in the synthesis of polyester, in which diesters undergo transesterification with diols to form macromolecules. For example, dimethyl terephthalate and ethylene glycol react to form polyethylene terephthalate and methanol, which is evaporated to drive the reaction forward. The reverse reaction (methanolysis) is also an example of transesterification, and has been used to recycle polyesters into individual monomers.

One of the first uses of transesterified vegetable oil (biodiesel) was to power heavy-duty vehicles in South Africa before World War II. The name "biodiesel" has been given to transesterified vegetable oil to describe its use as a diesel fuel.

Biodiesel is produced from vegetable oils by converting the triglyceride oils to methyl (or ethyl) esters with a process known as transesterification. In the transesterification process alcohol reacts with the oil to release three "ester chains" from the glycerin backbone of each triglyceride. The reaction requires heat and a strong base catalyst (e.g., hydroxide or lye), to achieve complete conversion of the vegetable oil into the separated esters and glycerin. The glycerin can be further purified for sale to the pharmaceutical and cosmetic industries. The mono-alkyl esters become the biodiesel, with one-eighth the viscosity of the original vegetable oil. Each ester chain, usually 18 carbons in length for soy esters, retains two oxygen atoms forming the "ester" and giving the product its unique combustion qualities as an oxygenated vegetable based fuel. Biodiesel is nearly 10% oxygen by weight. (Fukuda,

H. et al.,2001)

- 2.2.1 Type of transesterification (Ma, F. et al., 1998)
 - 1. Acid-catalyzed processes

The processes are catalyzed by Bronsted acids, preferably by sulfonic acids, sulfuric acid and hydrochloric acid. These catalysts give very high yields in alkyl esters but the reactions are slow and requiring temperature above 100°C and more than 3 h to reach the complete conversion. Transesterification process under acid-catalyzed condition needs to be done in absences of water because the water reduces the yield alkyl ester. The alcohol/oil molar ratio is one of the main factors that influence the transesterification. An excess alcohol favors the formation of products. On the other hand, an excessive amount of alcohol makes the recovery of glycerol difficult.

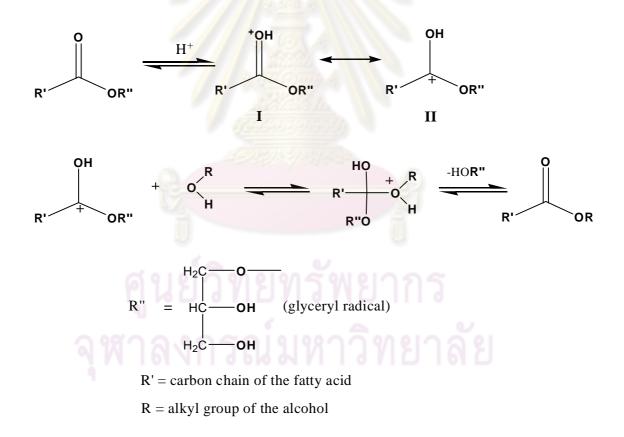


Figure 2.2 Mechanism of the acid catalyst transesterification (Ma, F. et al., 1998)

2. Base-catalysed processe

This reaction is catalyzed by base. Any strong base will do, e.g. NaOH, KOH, sodium methoxide etc. Commonly the base (KOH and NaOH) is dissolved in the alcohol to make a convenient method of dispersing the otherwise solid catalyst into the oil. The ROH needs to be very dry. Any water in the process promotes the saponification reaction and inhibits the transesterification reaction.

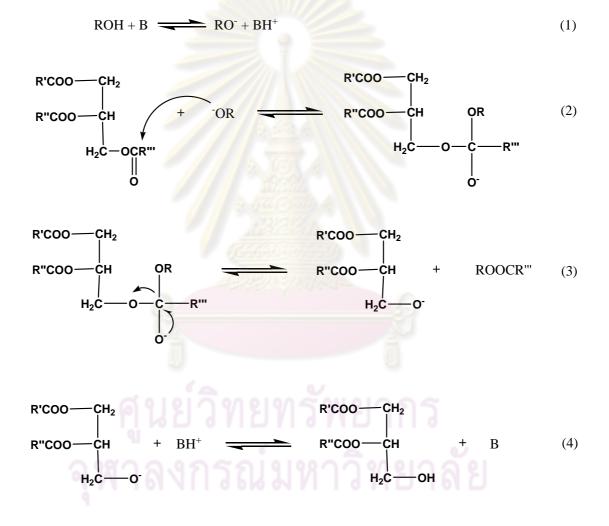


Figure 2.3 Mechanism of the base catalyst transesterification (Ma, F. et al., 1998)

3. Lipase-catalyzed process

Although chemical transesterification using an alkali-catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline wastewater requires treatment, and free fatty acids and water interfere with the reaction. The example of lipase catalysts includes PS 30, Novozyme 435-catalyzed. Recent studies have indicated the use of biocatalyst on the production of biodiesel. The use of whole cell biocatalyst immobilized within biomass support particle, like lipase is of advantage to the biodiesel industry. Immobilized *Pseudomonas fluorescence* lipases is very popular as a biocatalyst relative to mobilized biocatalyst as its activity is more effective and it can be repeatedly used without any decrease activity. Further studies to genetically engineer of this product are being are being done.

4. Non-ionic base-catalyzed process

A great number of organic bases has been developed and used as catalyst or reactant for organic synthesis. These provide for a mild reaction condition to simplify manipulation of the factors involved in increasing the yield of the alkly ester. Bases were used in this process including amines such as triethylamine, piperidine, amidines such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), guanidines such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,1,3,3-tetramethylguanidine (TMG) and amino- and nitroguanidines such as tris(dimethylamino)methyliminophosphorane (Me₇P).



Figure 2.4 Samples of non-ionic base-catalysts

5. Heterogeneously catalyzed processes (Ramadhas, A. S. et al., 2005)

Although transesterification using a conventional base-catalyzed process gives high conversion levels of triglycerides to their corresponding alkyl ester in short times, the reaction has several drawback: it is energy intensive; recovery of glycerine is difficult; the catalyst has to be removed from the product; alkaline wastewater requires treatment and FFAs and water interfere with reaction. In order to minimize problems, attempts to use heterogeneous catalyst system in alcoholysis of triglycerides have been made. They can be easily separated from the system at the end of the reaction and could also be reused even they could not be for a long duration of time as they leach out and the reaction is incomplete and the phases are difficult to separate.

6. Noncatalytic transesterification process (Ramadhas, A. S. et al., 2005)

With the aim of developing a novel methanolysis process for oil without using any catalyst, made a fundamental study of biodiesel production in supercritical methanol. They demonstrated that preheating to a temperature of 350°C and treatment for 240 s in supercritical methanol were sufficient to convert oil to methyl ester. Moreover, while the methyl esters produced were basically the same as those obtained in the conventional method with a basic catalyst, the methyl ester yield of the supercritical methanol method was higher. Kinetic analyses of the reactions in subcritical and supercritical methanol revealed that the rate of oil conversion to methyl esters increased dramatically in the supercritical state. A reaction temperature of 350°C and a molar ratio of methanol to oil of 42 to 1 were considered to be the best conditions.

The preparation of biodiesel according to used process, was summarized in Table 2.7.

 Table 2.7 Classification of processes use different catalysts for the preparation of biodiesel

Homogeneous processes	Heterogeneous processes
Acid-catalyzed process	Immobilized lipase-catalyzed process
Base-catalyzed process	Heterogeneous process
Non-ionic base-catalyzed process	
Noncatalytic process	

Normally, transesterification of vegetable oils is the base-catalyzed processes because this process give a very high yields and very active. After transesterification of vegetable oils, the product is a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglyceride. There, it is not easy to gain pure ester without impurities such as di- and monoglycerides. (Veljkovic, V. B. et al., 2006)



2.3. Technical Consideration (R&D Division Royal Thai Naval Dockyard., 2005)

To ensure that the biodiesel quality reaches decent standard and not causing harmful impacts on diesel engines, the biodiesel has been tested on several types of engines e.g.trucks, vans, pick-up trucks, buses and marine diesel engines etc. both short term and long term effects. Then the test results can be further reveal to the public.

2.3.1 Install capacity

The size of biodiesel plant can be varied according to the requirement of users. At the beginning of this research, the 2,000 litres capacity plant was constructed and it was found to be appropriate size for chicken oil is by product from chicken essence soup manufacturing in Thailand.

2.3.2 Technical Design

The 2,000 litres capacity plant is semi-continuous batch type. This plant is very simple to construct and the process in making biodiesel is very straightforward.

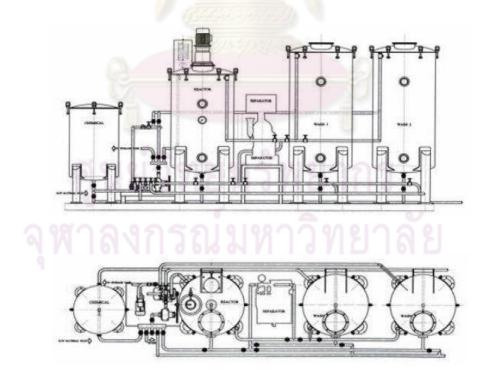


Figure 2.5 The prototype of biodiesel plant

The necessary equipment for plant system are as following;

- Chemical Mixing Tank
- Reactor Tank ; a 400 litres capacity and made of stainless steel.
- Separator ; Centrifugal type
- Washing Tank no.1; a 800 litres capacity made of stainless steel.
- Washing Tank no.2; a 800 litres capacity made of stainless steel.
- Storage Tanks; can store up to 1,000 litres of biodiesel oil.
- Temperature Sensors
- Pumps ; Centrifugal pump
- Etc.



2.4 Literature reviews

2.4.1 Biodiesel production

According to Ramadhas and Jayaraj (2004), studied production of fuelquality biodiesel from high FFA. It is found that the feedstocks with high FFAs could be transesterified with the commercially available alkaline catalyst not transesterification process. A two-step transesterification process is developed to convert the high FFA oils to its esters. The first step (acid catalyzed esterification via H₂SO₄ 1%w/w) reduces the FFA content of the oil to less than 2%. The alkaline catalyst transesterification process converts the products of the first step to its monoesters and glycerol. Excess addition of sulphuric acid darkens the product. It has been also found that the conversion efficiency is strongly affected by molar ratio of alcohol to oil. The molar ratio of 6:1 favors the completion of alkaline catalyzed esterification process with in half an hour. The maximum ester conversion is achieved at the reaction temperature of 45-50 °C. The viscosity of biodiesel is nearer to that diesel. The flash point of biodiesel (about 130 °C) is greater than that of diesel and the calorific value is slightly lower than that of diesel. This two-step esterification method reduces the overall production cost of the biodiesel, as it uses low cost unrefined nonedible oils.

According to Miao and Wu (2005), studied method for the production of biodiesel from heterotrophic microalgal oil. Chlorella protothecoides is a microalgae that can be photoautotrophically or heterotrophically grown under different culture conditions. Heterotrophic growth of C. protothecoides resulted in the accumulation of a large amount of oil in cells. Oil content in heterotrophic cells reached as high as 55.20%. Large amount of microalgal oil was efficiently extracted from these heterotrophic cells by using n-hexane. Biodiesel comparable to conventional diesel was obtained from heterotrophic microalgal oil by acidic transesterification. Good quality of biodiesel could be obtained in the presence of 100% acid catalyst (on oil basis) at high temperature. The best combination of factors was 100% catalyst quantity (based on oil weight) with 56:1 molar ratio of methanol to oil at temperature of 30°C, which reduced product specific gravity from an initial value of 0.912 to a final value of 0.8637 in about 4 h of reaction time.

According to Veljkovic et ai. (2006), studied the production of fatty acid methyl esters (FAME) from crude tobacco seed oil (TSO) having high free fatty acids (FFA) was investigated. Due to its high FFA, the TSO was processed in two steps: the acid-catalyzed esterification (ACE) followed by the base-catalyzed methanolysis (BCM). The first step reduced the FFA level to less than 2% in 25 min for the molar ratio of 18:1. The second step converted the product of the first step into FAME and glycerol. The maximum yield of FAME was about 91% in about 30 min. The tobacco biodiesel obtained had the fuel properties within the limits prescribed by the latest American (ASTM D 6751-02) and European (DIN EN 14214) standards, except asomewhat higher acid value than that prescribed by the latter standard (<0.5). Thus, tobacco seeds (TS), as agricultural wastes, might be a valuable renewable raw material for the biodiesel production.

2.4.2 Biodiesel from waste oil

According to Leung and Guo (2006), study, the characteristics and performance of three commonly used catalysts used for alkaline-catalyzed transesterification i.e. sodium hydroxide, potassium hydroxide and sodium methoxide, were evaluated using edible Canola oil and used frying oil. The fuel properties of biodiesel produced from these catalysts, such as ester content, kinematic viscosity and acid value, were measured and compared. With intermediate catalytic activity and a much lower cost sodium hydroxide was found to be more superior than the other two catalysts. The process variables that influence the transesterification of triglycerides, such as catalyst concentration, molar ratio of methanol to raw oil, reaction time, reaction temperature, and free fatty acids content of raw oil in the reaction system, were investigated and optimized. This paper also studied the influence of the physical and chemical properties of the feedstock oils on the alkaline-catalyzed transesterification process and determined the optimal transesterification reaction conditions that produce the maximum ester content and yield. According to Wang et al. (2007), studied a two step catalyzed process for biodiesel from waste cooking oil. Acid value in oil was 75.92±0.036 mgKOH/g. The free fatty acids of WCO were esterified with methanol catalyzed by ferric sulfate in the first step, and the triglycerides (TGs) in WCO were transesterified with methanol catalyzed by potassium hydroxide in the second step. The results showed that ferric sulfate had high activity to catalyze the esterification of free fatty acids (FFA) with methanol, The conversion rate of FFA reached 97.22% when 2 wt% of ferric sulfate was added to the reaction system containing methanol to TG in10:1 (mole ratio) composition and reacted at 95°C for 4 h. The methanol was vacuum evaporated, and transesterification of the remained triglycerides was performed at 65°C for 1 h in a reaction system containing 1 wt% of potassium hydroxide and 6:1 mole ratio of methanol to TG. The final product with 97.02% of biodiesel, obtained after the two step catalyzed process, was analyzed by gas chromatography. This new process has many advantages compared with the old processes, such as no acidic waste water, high efficiency, low equipment cost and easy recovery of the catalyst.

According to Arjun et al. (2007), studied process for biodiesel from waste cooking oil collected from a local restaurant in Halifax, Nova Scotia, Canada. Ethyl alcohol with sodium hydroxide as a catalyst was used for the transesterification process. The fatty acid composition of the final biodiesel esters was determination by gas chromatography. The biodiesel was characterized by its physical and fuel properties including density, viscosity, acid value, flash point, cloud point, pour point, cetane index, water and sediment content, total and free glycerin content, diglyceride and monoglycerides, phosphorus content and sulfur content according to ASTM standards. The viscosity of the biodiesel ethyl ester was found to be 5.03 mm²/sec at 40 °C. The viscosity of waste cooking oil measured in room temperature (at 21 °C.) was 72 mm²/sec. From the tests, the flash point was found to be 164 °C., the phosphorous content was 2 ppm, those of calcium and magnesium were 1 ppm combined, water and sediment was 0%, sulfur content was 2 ppm, total acid number was 0.29 mgKOH/g, cetane index was 61, cloud point was -1 °C. and pour point was --16 °C. Production of biodiesel from waste cooking oils for diesel substitute is particularly important because of the decreasing trend of economical oil reserves,

environmental problems caused due to fossil fuel use and the high price of prtroleum products in the international market.

2.4.3 Biodiesel from by-product of manufacturing process

According to Hamed et al. (2007), studied a two step catalyzed process for biodiesel production from Salmon oil, a by-product of salmon processing, was used as a feedstock for biodiesel production via transesterification in a two-step process. Two different types of salmon oil were tested: salmon oil extracted from acidified salmon hydrolysate and salmon oil extracted from salmon by-products. Optimal amounts of chemicals required to give the highest biodiesel yield from each oil were determined using batch production procedures. It was found that due to the high acid value of salmon oil, alkaline-catalysed transesterification was not an effective method for producing biodiesel from the salmon oil. Therefore a two-step process was applied, in which a sulphuric acid-catalysed pretreatment was used in the first step to reduce the acid value from 12.0 to 3mg [KOH] g [oil⁻¹ and then, in the second step, KOH-catalysed transesterification was applied. All experiments were performed at a temperature of 5272 1C with a mixing intensity of 600 rpm. Based on the total weight of salmon oil used, the maximum biodiesel yield of 99% was achieved using a total methanol/molar ratio of 9.2% and 0.5% (w/w) KOH. Ester loss due to the formation of emulsion during the washing and drying steps was 15% maximum. This loss could be reduced in practical applications by better design of washing and drying techniques. A preliminary economic analysis showed that the cost of biodiesel production from salmon oil was almost twice that produced from soybean oil.

จุฬาลงกรณมหาวิทยาลัย

CHAPTER III EXPERIMENTAL

3.1 Materials and equipment

3.1.1 Chemical reagent

- 1. Sodium hydroxide (Na0H)
- 2. Potassium hydroxide (KOH)
- 3. Potassium carbonate (K₂CO₃)
- 4. Methanol (CH₃OH)
- 5. Methyl heptadecanoate (Internal Standard)
- 6. n-Hexane
- 7. 2-Propanol (Internal Standard)
- 8. n-Heptane
- 9. N-methyl-N-trimethysilyltrifluroacetamide (MSTFA)
- 10. Pyridine (Stored on molecular sieve; Bad for male fertility and carcinogenic)
- 11. 1,2,4-Butanetriol
- 12. 1,2,3-Tricaproylglycerol (tricaprin)
- 13. 1-monooleoylglycerol (monoolein)
- 14. 1,3-dioleoylglycerol (diolein)
- 15. 1,2,3-trioleoylglycerol (triolein)
- 16. Glycerol
- 17. Monoglycerides (Commercial mixture and should made up of monopalmitoylglycerol [monopalmitin], monostearoylglycerol [monostearin] and monooleoylglycerol [monoolein]
- 18. Paraffin oil

3.1.2 Equipment

- 1. Reflux condenser set
- 2. Hotplate with magnetic stirrer set
- 3. Separation funnel stand and clamps
- 4. Thermometer
- 5. Volumetric flask, Erlenmeyer flask and Round bottom flask
- 6. Beaker
- 7. Filter paper
- 8. Ultrasonic bath
- 9. Automatic transfer pipet
- 10. Centrifuge
- 11. Miniflash

3.2 Determine properties of chicken oil

The physical properties of chicken oil were determined according to ASTM as shown in Table 3.1. Results are given in Section 4.1.

Property	Method
% FFA	ASTM D5555
Flash point	ASTM D93
Pour point	ASTM D97
Could point	ASTM D2500
Distillation	ASTM D86
Specific gravity	ASTM D1298
Viscosity	ASTM D445
% Sulphur	ASTM D4294
Cetane Index	ASTM D976

Table 3.1 Tested method of chicken oil

The compositions of fatty acids of chicken oil were analyzed using AOAC method (AOAC 969.33). Results are given in Section 4.1



3.3 Biodiesel production

Chicken oil (50 g) was added into the round bottom flask. After preheating chicken oil to the desired temperature for transesterification, a solution of basecatalyst in methanol was added and then heated at temperature 60° C for 1 h. The reaction was monitored by TLC developed by hexane:ethylacetate (90:10 v/v) and visualized by vanillin/H₂SO₄ solution. After cooling down to room temperature the reaction mixture was transferred to separatory funnel and left overnight. The methyl ester layer and the glycerol layer were separated. The methyl ester layer (top phase) must be conducted to remove impurities by washing with hot water until washing water was neutral. The methyl ester (0.25 g) was subjected to GC-FID analysis.

The composition of methyl ester (or %FAME) in biodiesel from chicken oil was determined using a Agilent Technologies 7890A GC System and a flame ionization detector. The capillary column was a HP-INNOWax (Cross-Linked PEG) column with length of 30 m, a film thickness of 0.5 µm and an internal diameter of 0.32 mm. Helium was used as carrier gas and also as an auxiliary gas for the FID. One micro-liter of each sample was subjected to GC analysis using auto injector with Agilent Technology 7683B Series Injector. For qualitative calculation, methyl heptadecanoate was used as the internal standard. (EN 14103) see detail in Appendix A.

As a supplement to GC analysis, thin layer chromatography (TLC) was also used to indicate the extent of transesterification. TLC was performed on aluminium sheet coated with silica gel $60F_{254}$ (Merck) and hexane:ethyl acetate (90:1) was used as a mobile phase.

In this study, the purity of biodiesel product from chicken oil denoted by its %FAME, density and flash point. Product yield is defined as the weight percentage of the final product (transesterified and purified oil) relative to the weight of oil at the start (Eq. (1)). It, in fact, indicates the final results of the competition between the main reaction (transesterification) producing methyl esters and side reactions (saponification) influencing the ester yield.

Product yield =
$$\frac{\text{weight of product}}{\text{weight of raw oil}}$$
(1)

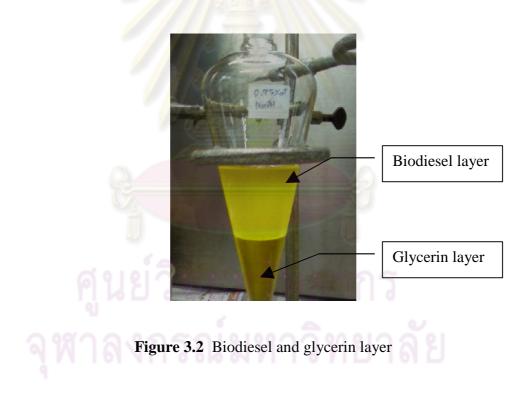
Crude methyl ester Washing and centrifugal Methyl ester Methyl ester

The flow diagram for base-catalyzed process on the laboratory scale was shown in Scheme 3.1.

Scheme 3.1 Base catalyzed transesterification



Figure 3.1 Glass reactor with heating plate and magnetic stirrer



3.4 Optimization of process parameter

3.4.1 Effect of base-catalyst concentration

The effect of NaOH and KOH concentration on the transesterification of chicken oil was investigated with its concentration varying from 0.25 to 3.0 wt% (based on the weight of chicken oil) The operation condition during the whole reaction process were fixed at reaction temperature of 65°C, reaction time of 60 minutes and molar ratio of methanol to chicken oil at 10:1. Results are given in Section 4.2.1.

The concentration of K_2CO_3 varying from 5 to 20 wt%. (based on the weight of chicken oil) The operation condition during the whole reaction process were fixed at reaction temperature of 85°C, reaction time of 180 minutes and molar ratio of methanol to chicken oil at 40:1. Results are given in Section 4.2.1.

3.4.2 Effect of molar ratio of methanol to chicken oil

In this section, study the effect of molar ratio on ester content and %product yield of the transesterification of chicken oil was investigated with its molar ratio of methanol to chicken oil varying from 3:1 to 12:1. The operation condition during the whole reaction process were fixed at reaction temperature of 65°C, reaction time of 60 minutes and molar ratio of methanol to chicken oil at 10:1. Results are given in Section 4.2.2.

The molar ratio of MeOH when used K_2CO_3 catalyst was varied from 10:1 to 80:1. The operation condition during the whole reaction process were fixed at reaction temperature of 85°C, reaction time of 180 minutes. Results are given in Section 4.2.2.

3.4.3 Effect of reaction temperature

In this section, the effect of temperature on ester content and %product yield of the transesterification of chicken oil, was investigated with its temperature varying from 45-85°C and at the optimal condition similar to that in Section 3.4.2. The operation condition during the whole reaction process were fixed at reaction time of 60 minutes. Results are given in Section 4.2.3.

When K_2CO_3 catalyst was used, the effect of temperature on ester content and %product yield of the transesterification of chicken oil, was investigated with its temperature varying from 50-130°C and at the optimal condition similar to that in Section 3.4.2. The operation condition during the whole reaction process were fixed at reaction time of 180 minutes. Results are given in Section 4.2.3.

3.4.4 Effect of reaction time

In this section, study the effect of reaction time on %FAME and %product yield of the transesterification of chicken oil, the molar ratio of methanol to chicken oil used was similar to that in Section 3.4.2, and reaction temperature used was similar to that in Section 3.4.3, sampling sample in reaction at 1, 3, 5, 10, 20, 30, 40, 50, 60 and 70 minutes. Results are given in Section 4.2.4.

The effect of reaction time when used K_2CO_3 catalyst, the molar ratio of methanol to chicken oil used was similar to that in Section 3.4.2, and reaction temperature used was similar to that in Section 3.4.3. Additionally, the reaction mixture was sampled for GC analysis at 30, 60, 90, 120, 150, 180, 210 and 240 minutes. Results are given in Section 4.2.4.

3.5 Determine properties of biodiesel from chicken oil

The physical properties of biodiesel produced from chicken oil were determined Standard methods as shown in Table 3.3. Results are given in Section 4.3.

Property	Method
Specific gravity	ASTM D1298
Flash point	ASTM D93
Pour point	ASTM D97
Could point	ASTM D2500
Distillation	ASTM D86
Viscosity	ASTM D445
% Sulphur	ASTM D4294
Cetane Index	ASTM D976
Cetane Number	ASTM D613
Fatty acid Methyl Ester content	EN 14103
Free and total glycerol and	EN 14105
mono-, di-, triglyceride content	
Methanol content	EN 14110

Table 3.2 Tested method of biodiesel from chicken oil

CHAPTER IV RESULTS AND DISCUSSION

4.1 Physical and chemical properties of chicken oil

Chicken oil (CK) was a by-product of chicken essence soup manufacturing. In this study, the chicken oil was collected from factory in local Chonburi province Figure 4.1 and 4.2.



Figure 4.1 Chicken oil (CK)



Figure 4.2 Chicken essence soup manufacturing (Cerebos in Thailand)

The physical and chemical properties of chicken oil were analyzed and the results are shown in Table 4.1.

Property	Chicken oil
% Free fatty acid	1.16
Specific gravity	0.9176
Flash point (°C)	>200
Pour point (°C)	3
Clound point (°C)	9
Distillation (°C)	IBP=209, 90% recovered =355
Viscosity (cSt at 40°C)	0.5034
Sulphur (wt%)	0.003
Cetane Index	35.78

Table 4.1 Physical and chemical properties of chicken oil

From the Table 4.1, it was found that the flash point of chicken oil is vary high about >200°C (268°C) and this is in accordance with the lower volatility of the chicken oil in comparison to diesel fuel (flash point >52°C). However, the high flash point of chicken oil is a beneficial safety feature, as this fuel can be safety stored at room temperatures. The poor volatility of chicken oil is due to their high content of unsaturated fatty acids.

The Cetane index is lower than the minimum of 47 for automotive diesel fuels in Thailand. Because it was found high specific gravity and low volatility.

The chicken oil is a mixture of triglycerides of a variety of fatty acids. Based on the GC-FID analysis, 12 types of fatty acids were identified and quality. These fatty acids vary in carbon chain length and in the number of unsaturated (double bonds) present. The fatty acid profile of chicken oil is shown in Figure 4.3.

The composition of Fatty acid of chicken oil are also analyzed using AOAC method (AOAC 969.33). The results are shown in Table 4.2.

Property	Carbon atoms	wt.%
Myristic	C14:0	0.53%
Myristoleic	C14:1	0.14%
Pentadecanoic	C15:0	0.06%
Palmitic	C16:0	22.57%
Palmiolic	C16:1	5.04%
Stearic	C18:0	4.72%
Oleic	C18:1	38.1%
Linoleic	C18:2	23.75%
Limolenic	C18:3	1.36%
cis-11,14-Eicosadienoic	C20:2	0.16%
cis-11,14,17-Eicosadienoic	C20:3	0.18%
Arachidonic	C20:4	0.3%

 Table 4.2 Fatty acid profile of chicken oil (GC-FID analysis)

It was found that the fatty acid of chicken oil mainly consisted of linoleic acid and oleic acid. The total saturated and unsaturated fatty acid composition is 27.88% and 69.03% respectively.

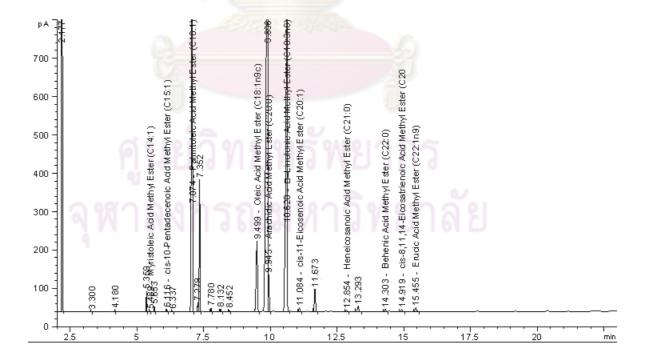


Figure 4.3 GC chromatogram of chicken oil

4.2 Biodiesel Production

4.2.1 Effect of catalyst concentration

Considering data from literature review (Gerpen, J.V. et al., 2005), the concentration of three alkaline catalysts sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium carbonate (K_2CO_3) all of which are commonly used for alkaline-catalyzed transesterification research, were selected for study. To evaluate the performance of each of these catalysts, the transesterification of the chicken oil with methanol was carried out with the use of individual catalyst under identical molar ratio of methanol to chicken oil (10:1), reaction temperature (65°C) and reaction time (60 minutes).

4.2.1.1 NaOH catalyst

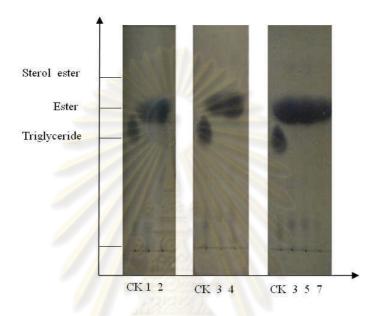
The chicken oil was used to produce biodiesel using 0.4-1.6% (%oil weight) NaOH catalyst, CK:MeOH molar ratio of 1:10, temperature of 65°C and reaction time of 60 minutes. The results are shown in Table 4.3, Figure 4.4. and Figure 4.5.

Table 4.3 The amount of NaOH converts CK as methyl ester via base-catalyzed
process Compositions of fatty acids in chicken oil
(CK:MeOH ratio 1:10, temperature of 65°C and reaction time of
60 minutes)

Amount of NaOH	%FAME	%Product	Density	Flash point
(%w/w oil)		yield	Density	(C)
0.4	95.68	79.92	0.8588	173
0.6	96.91	94.08	0.8812	162
0.8	97.95	95.84	0.8809	165
1.0	97.92	88.58	0.8790	165
1.2	97.94	76.00	0.8796	163
1.4	97.99	79.49	0.9060	153
1.6	97.86	60.56	0.8996	156

At 0.8%NaOH, the high FAME and product was obtained in a good yield with 97.95% and 95.84% respectively.

The reproductive TLC of triglyceride was converted into FAME in this Figure 4.4.



- CK : chicken oil
- 1-7 : Concentration of NaOH (1=0.4%, 2=0.6%, 3=0.8%, 4=1.0%, 5=1.2%, 6=1.4% and 7=1.6% wt)

Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v) Stationary phase : TLC aluminium sheet, silica gel 60 F_{254}

Figure 4.4 The results of TLC at different base-catalyst concentration of NaOH (CK:MeOH ratio of 1:10, temperature of 65°C and reaction time of 60 minutes)

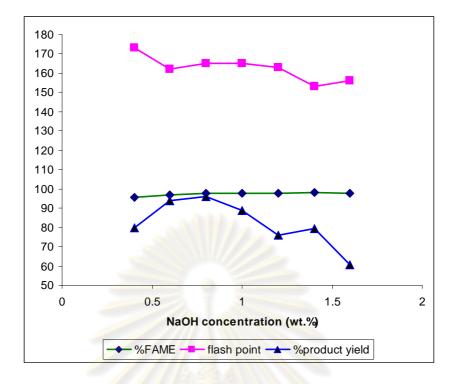


Figure 4.5 Effect of NaOH concentration on the transesterification of chicken oil

Experimental results (Figure 4.5) showed that the changes in %FAME, %product yield and flash point with catalyst concentration followed an asymptotic curve for the chicken oil. As the NaOH concentration increased, the %FAME, as well as the %product yield also increased. Insufficient amount of NaOH resulted in incomplete conversion of triglycerides into the esters as indicated from its lower %FAME. Based on this observation, the %product yield under the cases of excess NaOH concentrations (>1.0 wt.%) was examined. It can be seen from Figure 4.5 that when the NaOH concentration was increased from 1.0 wt.% to 1.6 wt.%, the %product yield of biodiesel dropped from 88.58% to 60.56% with a reduction of 20%. Large amounts of soaps were observed during the responsible for the yield reduction. This is because addition of excess alkaline catalyst (NaOH) caused more triglycerides participating in the saponification reaction with NaOH producing more soap, thereby reducing the ester yield.

4.2.1.2 KOH catalyst

The chicken oil was used to produce biodiesel using 0.4-1.6% (%oil weight) KOH catalyst, CK:MeOH ratio of 1:10, temperature of 65°C and reaction time of 60 minutes. The results are shown in Table 4.4, Figure 4.6. and Figure 4.7.

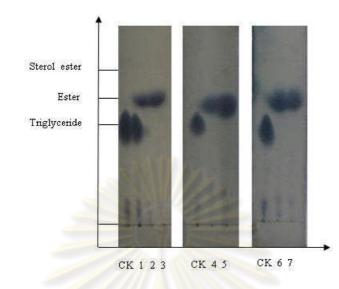
Table 4.4The amount of KOH converts CK as methyl ester via base-catalyzed
process Compositions of fatty acids in chicken oil
(CK:MeOH ratio 1:10, temperature of 65°C and reaction time of 60 minutes)

Amount of KOH (%w/w oil)	%FAME	%Product yield	Density	Flash point (C)
0.4	96.82	80.28	0.9084	173
0.6	97.90	96.88	0.9062	160
0.8	97.89	96.88	0.8796	162
1.0	97.95	97.10	0.8791	161
1.2	97.93	97.68	0.8790	162
1.4	97.94	97.74	0.8793	161
1.6	97.91	96.08	0.8790	161
1.8	97.91	81.60	0.8785	162

At 1.0% KOH, the high FAME and product was obtained in a good yield with 97.95% and 97.10% respectively.

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The reproductive TLC of triglyceride was converted into FAME in this Figure 4.6.



- CK : chicken oil
- 1-7 : Concentration of NaOH (1=0.4%, 2=0.6%, 3=0.8%, 4=1.0%, 5=1.2%, 6=1.4% and 7=1.6% wt.)
 Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v)
 Stationary phase : TLC aluminium sheet, silica gel 60 F₂₅₄

Figure 4.6 The results of TLC at different base-catalyst concentration of KOH (CK:MeOH ratio of 1:10, temperature of 65°C and reaction time of 60 minutes)

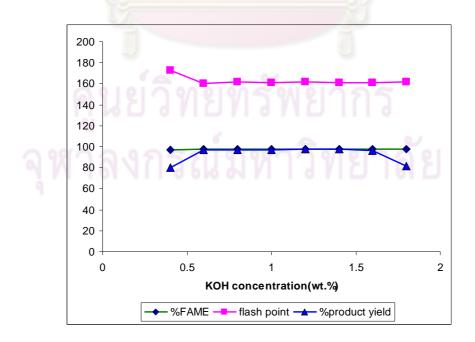


Figure 4.7 Effect of KOH concentration on the transesterification of chicken oil

Experimental result (Figure 4.7) showed that the changes in %FAME, %product yield and flash point with catalyst concentration followed an asymptotic curve for the chicken oil. As the KOH concentration increased, the %FAME, as well as the %product yield also increased. Insufficient amount of KOH resulted in incomplete conversion of triglycerides into the esters as indicated from its lower %FAME. Based on this observation, the %product yield under the cases of excess KOH concentrations (>1.6 wt.%) was examined. It can be seen from Figure. 4.7. that when the KOH concentration was increased from 1.6 wt.% to 1.8 wt.%, the %product yield of biodiesel dropped from 96.08% to 81.60%, a reduction of 10%. Large amounts of soaps were observed during the responsible for the yield reduction. This is because addition of excess alkaline catalyst (KOH) caused more triglycerides participating in the saponification reaction with KOH producing more soap, thereby reducing the ester yield.

4.2.1.3 K₂CO₃ catalyst

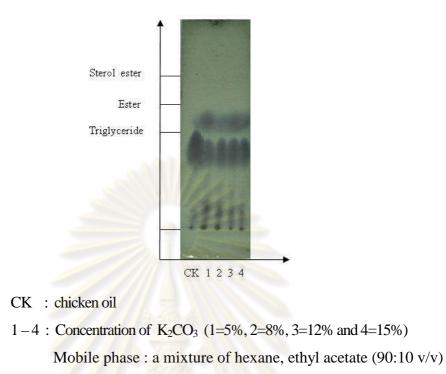
The chicken oil was used to produce biodiesel using 5-15% (%oil weight) K_2CO_3 catalyst, CK:MeOH ratio of 1:40, temperature of 85°C and reaction time of 180 minutes. The results are shown in Table 4.5, Figure 4.8. and Figure 4.9.

Table 4.5The amount of K2CO3 converts CK as methyl ester via base-catalyzed
process Compositions of fatty acids in chicken oil
(CK:MeOH ratio of 1:40, temperature of 85°C and reaction time of 180 minutes)

Amount of K ₂ CO ₃ (%w/w oil)	%FAME	%Product yield	Density	Flash point (C)
5	49.34	72.40	0.9146	167
7	71.01	72.87	0.9146	175
8	70.44	75.33	0.9030	173
9	70.68	82.84	0.9031	165
10	71.06	82.93	0.9063	159
11	72.14	76.04	0.9077	167
12	70.89	72.84	0.9104	178
15	71.45	49.62	0.9056	168

At 10%K₂CO₃, the FAME and product were obtained in a good yield with 71.06% and 82.93% respectively.

The reproductive TLC of triglyceride was converted into FAME in this Figure 4.8.



Stationary phase : TLC aluminium sheet, silica gel 60 F_{254}

Figure 4.8 The result of TLC at different base-catalyst concentration of K_2CO_3 (CK:MeOH ratio of 1:40, temperature of 65°C and reaction time of 180 minutes)

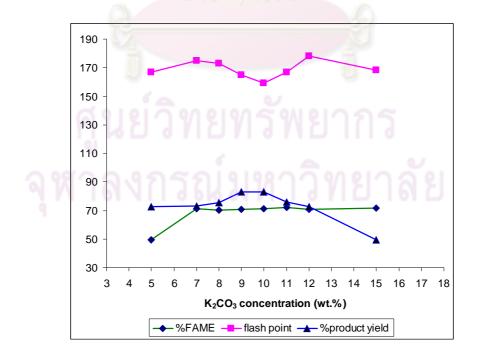


Figure 4.9 Effect of K₂CO₃ concentration on the transesterification of chicken oil

Experimental result (Figure 4.9) showed that the changes in %FAME, %product yield and flash point with catalyst concentration followed an asymptotic curve for the chicken oil. As the K_2CO_3 concentration increased, the %FAME, as well as the %product yield also increased. Insufficient amount of K_2CO_3 resulted in incomplete conversion of triglycerides into the esters as indicated from its lower %FAME. Based on this observation, the %product yield under the cases of excess K_2CO_3 concentrations (>11.0 wt.%) was examined. It can be seen from Figure 4.9 that when the K_2CO_3 concentration was increased from 11.0 wt.% to 15.0 wt.%, the %product yield of biodiesel dropped from 76.04% to 49.62%, a reduction of 20%. Large amounts of soaps were observed during the responsible for the yield reduction. This is because addition of excess alkaline catalyst (K_2CO_3) caused more triglycerides participating in the saponification reaction with K_2CO_3 producing more soap, thereby reducing the ester yield.



4.2.2 The Effect of molar ratio of methanol to oil

In order to study the effect of molar ratio on %FAME and %product yield of the transesterification, experiments were conducted with various molar ratios of methanol to oil in the range of 5:1 to 16:1. The optimized catalyst concentration and reaction times as obtained in the previous sections were adopted.

4.2.2.1 NaOH catalyst

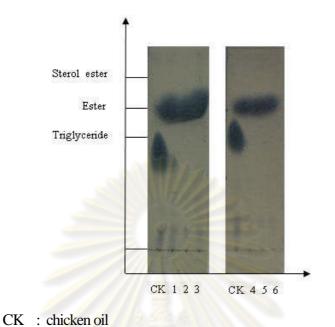
The CK:MeOH ratio of the NaOH are shown in Table 4.6.

Table 4.6The amount of MeOH converts CK as methyl ester via base-catalyzed
process Compositions of fatty acids in chicken oil
(NaOH 0.8% wt., temperature of 65 °C and reaction time of 60 minutes)

Molar ratio (MeOH: CK)	%FAME	%Product yield	Density	Flash point (C)
4	<mark>91.77</mark>	76.32	0.8893	163
6	9 5 .07	89.74	0.8833	165
8	95.12	93.22	0.8821	165
10	97.95	95.84	0.8809	165
12	97.14	91.14	0.8969	167
14	97.94	96.24	0.8794	162
16	88.96	75.60	0.8564	172

From the Table 4.6, The high %FAME and %product yield was obtained with 10:1 of MeOH:chicken oil as 97.95 %FAME and 95.84 %product yield

The reproductive TLC of triglyceride was converted into FAME in this Figure 4.10.



1-6 : CK:MeOH ratio (1=6:1, 2=8:1, 3=10:1, 4=12:1, 5=14:1 and 6=16:1) Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v) Stationary phase : TLC aluminium sheet, silica gel 60 F_{254}

Figure 4.10 The result of TLC at different CK:MeOH ratio of NaOH (NaOH 0.8% wt.,

temperature of 65°C and reaction time of 60 minutes)

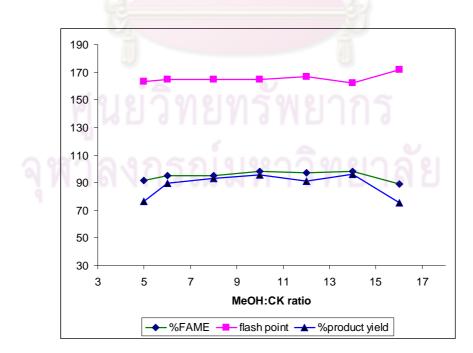




Figure 4.11 showed the results of these experiments, which exhibited an asymptotic trend for the %FAME and %product yield. For the stoichiometric transesterification reaction, three moles of methanol per a mole of triglyceride were required to yield three moles of fatty methyl esters and one mole of glycerol. The theoretical molar ratio of methanol to triglyceride should therefore be 3:1. However, as shown in Figure 4.11, maximum ester yield was obtained at a molar ratio of 10:1 for chicken oil. This higher molar ratio than the stoichiometric value resulted in a greater ester conversion and could ensure complete reaction. When the ratio was increased from 5:1 to 10:1, the %FAME raised from 91.77% to 97.95%, while the yield rose from 76.32% to 95.84%. Therefore, the reaction was incomplete for a molar ratio less than 16:1.

On the other hand, there is very little effect on the biodiesel yield and purity for molar ratio beyond 10:1. Moreover, it was observed that for high molar ratio a longer time was required for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier that enhances emulsion. Therefore, increasing the molar ratio of methanol/oil beyond 10:1 did not increase the product yield as well as the ester content, but complicated the ester recovery process and raised the cost for methanol recovery. The results showed that the molar ratio of alcohol to oil is another important parameter affecting the biodiesel yield and biodiesel purity, apart from catalyst concentration and reaction time.

4.2.2.2 KOH catalyst

The CK:MeOH ratio of the KOH are shown in Table 4.7.

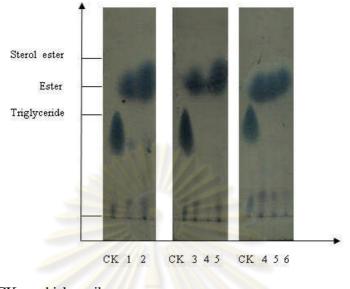
Molar ratio (MeOH:CK)	%FAME	%Product yield	Density	Flash point (C)
4	70.79	80.28	0.9137	168
6	95.32	83.58	0.9119	169
8	95.04	95.74	0.8889	164
10	97.95	97.10	0.8791	161
12	95.12	94.24	0.8954	168
14	95.03	95.72	0.8833	170
16	95.11	94.84	0.8921	165

Table 4.7 The amount of MeOH converts CK as methyl ester via base-catalyzed process.(KOH 1.0% wt., temperature of 65°C and reaction time of 60 minutes)

From the table 4.7, the high product yield and the high %FAME was obtained with 10:1 of MeOH:chicken oil as 97.95 %FAME and 97.10 %product yield.



The reproductive TLC of triglyceride was converted into FAME in this Figure 4.12.



- CK : chicken oil
- 1-6 : CK:MeOH ratio (1=6:1, 2=8:1, 3=10:1, 4=12:1, 5=14:1 and 6=16:1) Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v) Stationary phase : TLC aluminium sheet, silica gel 60 F₂₅₄

Figure 4.12 TLC result of product composition at different CK:MeOH ratio (KOH 1.0% wt., temperature of 65°C and reaction time of 60 minutes)

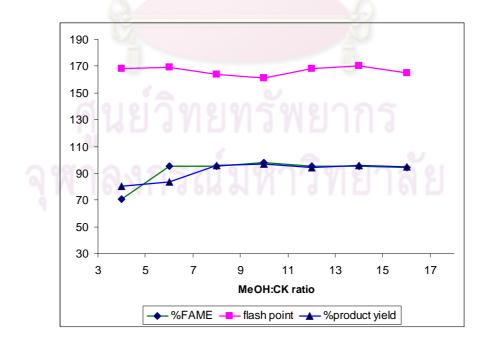


Figure 4.13 Effect of MeOH:CK ratio of KOH on the transesterification of chicken oil

Figure 4.13, showed the results of these experiments, which exhibited an asymptotic trend for the %FAME and %product yield. For the stoichiometric transesterification reaction, three moles of methanol are required per mole of triglyceride to yield three moles of fatty methyl esters and one mole of glycerol. The theoretical molar ratio of methanol to triglyceride should therefore be 3:1. However, as shown in Figure 4.13, maximum ester yield was obtained at a molar ratio of 10:1 for chicken oil. This higher molar ratio than the stoichiometric value resulted in a greater ester conversion and could ensure complete reaction. When the ratio was increased from 5:1 to 10:1, the %FAME raised from 70.79% to 97.95%, while the yield rose from 80.28% to 97.10%. Therefore, the reaction was incomplete for a molar ratio less than 14:1.

On the other hand, there is very little effect on the biodiesel yield and purity for molar ratio beyond 10:1. Moreover, it was observed that for high molar ratio a longer time was required for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier that enhances emulsion. Therefore, increasing the molar ratio of methanol/oil beyond 10:1 did not increase the product yield as well as the ester content, but complicated the ester recovery process and raised the cost for methanol recovery. The results showed that the molar ratio of alcohol to oil is another important parameter affecting the biodiesel yield and biodiesel purity, apart from catalyst concentration and reaction time.

4.2.2.1 K₂CO₃ catalyst

The CK:MeOH ratio of the K_2CO_3 are shown in Table 4.8.

Molar ratio (Oil : CH ₃ OH)	%FAME	%Product yield	Density	Flash point (C)
10	0.00	77.60	0.9038	175
20	71.51	81.40	0.9016	168
30	71.51	80.80	0.9183	162
40	89.51	70.10	0.8956	169
50	94.71	73.70	0.9027	177
60	94.16	78.37	0.9063	188
70	94.66	76.40	0.8923	186
80	94.69	74.82	0.8839	176

Table 4.8 The amount of MeOH converts CK to methyl ester via base-catalyzed process.(K2CO3 10% wt., temperature of 85 °C and reaction time of 180 minutes)

From the table 4.8, the product yield and the FAME was obtained with 1:20 of CK:methanol as 71.51 %FAME and 81.40 %product yield



The reproductive TLC of triglyceride was converted into FAME in this Figure 4.14.

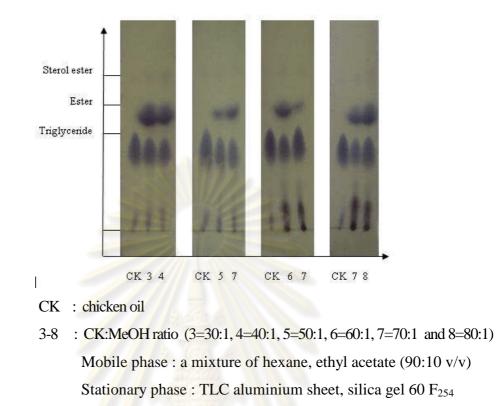


Figure 4.14 TLC result of product composition at different CK:MeOH ratio (K₂CO₃ 10% wt., temperature of 90 °C and reaction time of 180 minutes)

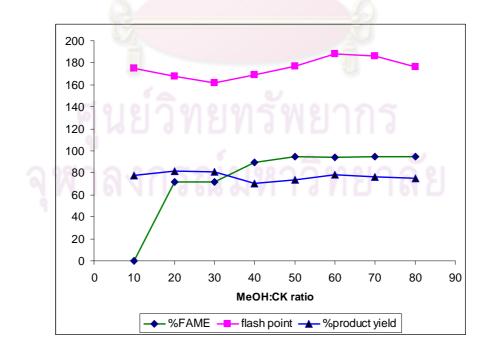


Figure 4.15 Effect of MeOH:CK ratio of K₂CO₃ on the transesterification of chicken oil

Figure 4.15, showed the results of these experiments, which exhibited an asymptotic trend for the %FAME and %product yield. For the stoichiometric transesterification reaction, three moles of methanol are required per mole of triglyceride to yield three moles of fatty methyl esters and one mole of glycerol. The theoretical molar ratio of methanol to triglyceride should therefore be 3:1. However, as shown in Figure 4.15, maximum ester yield was obtained at a molar ratio of 20:1 for chicken oil. This higher molar ratio than the stoichiometric value resulted in a greater ester conversion and could ensure complete reaction. When the ratio was increased from 10:1 to 20:1, the %FAME raised from 0.0% to 71.51%, while the yield rose from 77.60% to 81.40%. Therefore, the reaction was incomplete for a molar ratio less than 80:1.

On the other hand, there is very little effect on the biodiesel yield and purity for molar ratio beyond 20:1. Moreover, it was observed that for high molar ratio a longer time was required for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier that enhances emulsion. Therefore, increasing the molar ratio of methanol/oil beyond 20:1 did not increase the product yield as well as the ester content, but complicated the ester recovery process and raised the cost for methanol recovery. The results showed that the molar ratio of alcohol to oil is another important parameter affecting the biodiesel yield and biodiesel purity, apart from catalyst concentration and reaction time.

4.2.3 The Effect of reaction temperature

Reaction temperature of NaOH catalyst

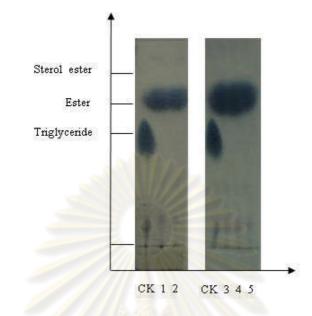
To determine the effect of reaction temperature on methyl esters formation, the transesterification reaction was carried out under the optimal conditions obtained in the previous section (i.e. KOH 0.8% weight by weight of chicken oil, a 10:1 of methanol/oil molar ratio and reaction time of 60 min). The experiments were conducted at temperatures ranging from 45°C to 85°C. The effect of reaction temperature on the product yield and reaction time was presented in Table 4.9 and Figure 4.10

 Table 4.9
 The amount of temperature converts CK to methyl ester via base-catalyzed process. (NaOH 0.8%wt., CK:MeOH ratio of 1:10 and reaction time of 60 minutes)

Temperature(°C)	%FAME	%Product yield	Density	Flash point (C)
45	75.54	89.14	0.8563	168
55	98.15	95.88	0.8566	167
65	97.95	95.84	0.8554	165
75	97.68	95.76	0.8565	168
85	97.65	93.96	0.8563	166

From the table 4.9, the high product yield and the high FAME was obtained with 55°C as 98.15 % FAME and 95.88 % product yield

The reproductive TLC of triglyceride was converted into FAME in this Figure 4.16.



CK : chicken oil

1-5 : Temperature of reaction (1=45, 2=55, 3=65, 4=75 and 5=85°C)
 Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v)
 Stationary phase : TLC aluminium sheet, silica gel 60 F₂₅₄

Figure 4.16 TLC result of product composition at different temperature (°C) (NaOH 0.8% wt., CK:MeOH ratio of 1:10 and reaction time of 60 minutes)

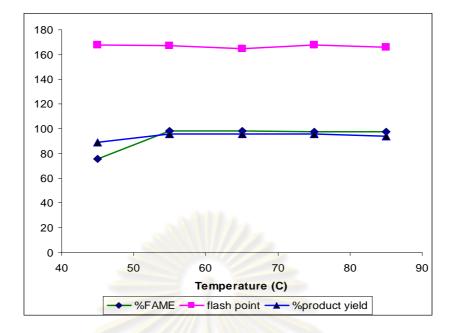


Figure 4.17 The Effect of temperature on %FAME, %Product yield, density and flash point of biodiesel from chicken oil

Experimental results showed that the transesterification reaction could proceed within the reaction temperature range studied but the reaction time to complete the reaction varied significantly with reaction temperature. It can be seen that a high product yield could be achieved even at room temperature but the reaction time would be substantially increased. It was also observed that for neat oil the maximum yield occurred at a lower temperature range between 55°C and 65°C. When temperature was reduced from 75°C to 45°C, the product yield can be increased from 89.14% to 95.76%. This significant increase in ester yield at a lower temperature indicated that higher temperature had a negative impact.

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Reaction temperature of KOH catalyst

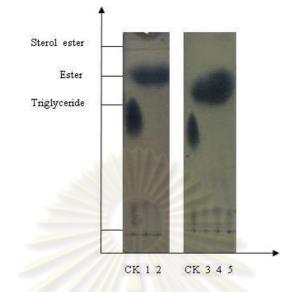
To determine the effect of reaction temperature on methyl esters formation, the transesterification reaction was carried out under the optimal conditions obtained in the previous section (i.e. KOH 1.0% weight by weight of chicken oil, a 10:1 of methanol/oil molar ratio and reaction time of 60 min). The experiments were conducted at temperatures ranging from 45°C to 85°C. The effect of reaction temperature on the product yield and reaction time was presented in Table 4.10 and Figure 4.19.

Table 4.10The amount of temperature converts CK as methyl ester via
base-catalyzed process Compositions of fatty acids in chicken oil
(KOH 1.0%wt., CK:MeOH ratio of 1:6 and reaction time of 60 minutes)

Temperature(°C)	%FAME	%Product yield	Density	Flash point (C)
45	97.74	97.36	0.8566	163
55	97.65	97.38	0.8554	162
65	97.95	97.10	0.8569	161
75	97.68	97.08	0.8564	162
85	97.09	97.02	0.8594	165

From the table 4.10, The high product yield and the high FAME was obtained with 65°C as 97.95 % FAME and 97.10 % product yield

The reproductive TLC of triglyceride was converted into FAME in this Figure 4.18.



- CK : chicken oil
- 1-5 : Temperature of reaction (1=45, 2=55, 3=65, 4=75 and 5=85°C)
 Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v)
 Stationary phase : TLC aluminium sheet, silica gel 60 F₂₅₄

Figure 4.18 TLC result of product composition at different temperature (°C) (KOH 1.0% wt., CK:MeOH ratio of 1:10 and reaction time of 60 minutes)

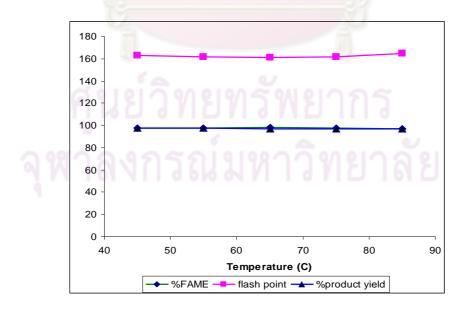


Figure 4.19 Effect of temperature on %FAME, %product yield, density and flash point of biodiesel from chicken oil

Experimental results showed that the transesterification reaction could proceed within the reaction temperature range studied but the reaction time to complete the reaction significantly with reaction temperature. It can be seen that a high product yield could be achieved even at room temperature but the reaction time would be substantially increased. It was also observed that for neat oil the maximum yield occurred at a lower temperature range between 55°C and 65°C. When temperature was reduced from 75°C to 45°C, the product yield can be increased from 89.14% to 95.76%. This significant increase in ester yield at a lower temperature indicated that higher temperature had a negative impact.



Reaction temperature of K₂CO₃ catalyst

To determine the effect of reaction temperature on methyl esters formation, the transesterification reaction was carried out under the optimal conditions obtained in the previous section (i.e. K_2CO_3 10% weight by weight of chicken oil, a 20:1 of methanol/oil molar ratio and reaction time of 180 min). The experiments were conducted at temperatures ranging from 40°C to 135°C. The effect of reaction temperature on the product yield and reaction time was presented in Table 4.11 and Figure 4.21.

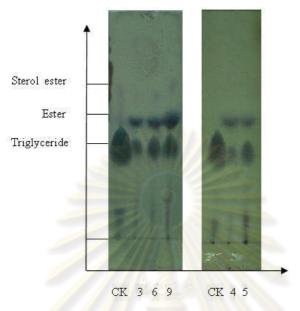
Table 4.11The amount of temperature converts CK as methyl ester via
base-catalyzed process Compositions of fatty acids in chicken oil
(K2CO3 10% wt., CK:MeOH ratio of 1:20 and reaction time of 180 minutes)

Temperature(°C)	%FAME	%Product yield	Density	Flash point (C)
40	89.07	76.60	0.8946	183
60	88.97	76.23	0.8879	176
70	89.03	79.40	0.8800	168
75	<mark>89.15</mark>	80.00	0.8871	167
80	89.97	79.20	0.9063	169
90	89.24	81.90	0.9153	171
100	89.15	82.52	0.9099	172
120	89.19	72.63	0.9026	151
135	72.04	68.49	0.9026	157

From the table 4.11, The high product yield and the high FAME was obtained with 90°C as 89.24 %FAME and 81.9 %product yield

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The reproductive TLC of triglyceride was converted into FAME in this Figure 4.20.



- CK : chicken oil
- 3-9 : Temperature of reaction (3=70, 4=75, 5=80, 6=90 and 9=135°C)
 Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v)
 Stationary phase : TLC aluminium sheet, silica gel 60 F₂₅₄

Figure 4.20 TLC result of product composition at different temperature (°C) (K₂CO₃ 10% wt., CK:MeOH ratio of 1:20 and reaction time of 180 minutes)

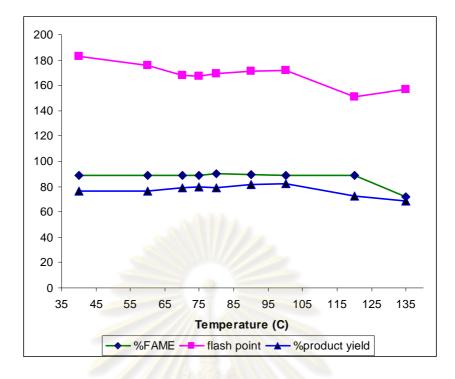


Figure 4.21 Effect of temperature on %FAME, %Product yield and flash point of biodiesel from chicken oil

The results showed that %FAME was significantly constant at the temperature from 40-120°C, while, there was a slight reduction in the %FAME at the reaction temperature of 135°C. This may be caused by enhancement of both transesterification and saponification at high temperature. (Leung, D.Y.C. et al., 2006)

4.2.4 The Effect of reaction time

Effect of reaction time for NaOH catalyst

In the order to study indicated that the reaction time required for the completion of the alkaline-catalyzed transesterification reaction depends not only on the reaction temperature, but also on the degree of mixing in the process. The reaction rate of transesterification increases with increasing temperature and mixing degree. The reaction time of the transesterification reaction conducted at 65°C was optimized with the highest achievable mixing degree and an excess molar ratio of methanol to oil (10:1) with the optimal NaOH concentration at 0.8 % weight by weight of chicken oil.

The result analyzed from %FAME by GC-FID for chicken oil was shown in Table 4.12 and Figure 4.22.

Table 4.12The amount of reaction time converts CK as methyl ester via
base-catalyzed process Compositions of fatty acids in chicken oil
(NaOH 0.8% wt., CK:MeOH ratio of 1:10 and temperature of 55°C)

		I
Time (min)	%FAME	
1	24.72	
3	39.78	
5	46.71	
10	76.74	
15	82.24	
20	88.82	
30	90.44	
40	91.46	Ň
50	91.45	ละ
60	91.43	
70	91.72	

From the table 4.12, The high FAME was obtained with 40 minutes as 91.46 %FAME

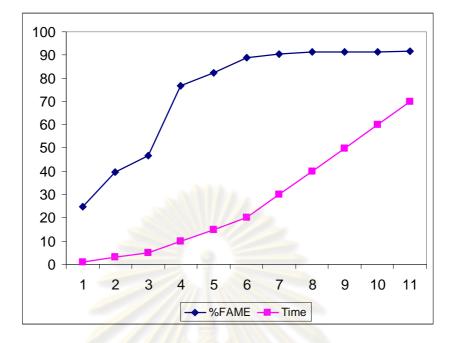


Figure 4.22 %FAME in biodiesel from chicken oil and NaOH 0.8%wt., CK:MeOH ratio of 1:10 and temperature 55°C (Reaction time at 1, 3, 5, 10, 20, 30, 40, 50, 60, and 70 minutes)

Figure 4.13 showed a plot of %FAME vs. reaction time for chicken oil. The results showed that the reaction was very fast in the first few minutes, a product of more than 76.74%FAME was formed within the first 10 min. After that, the reaction slowed down and entered a slow rate stage untill the reaction equilibrium was reached eventually.

The Effect of reaction time for KOH catalyst

In the order to study indicated that the reaction time required for the completion of the KOH-catalyzed transesterification reaction depends not only on the reaction temperature, but also on the degree of mixing in the process. The reaction rate of transesterification increases with increasing temperature and mixing degree. The reaction time of the transesterification reaction conducted at 65°C was optimized with the highest achievable mixing degree and an excess molar ratio of methanol to oil (10:1) with the optimal KOH concentration at 1.0 % weight by weight of chicken oil.

The result analyzed from %FAME by GC-FID for chicken oil were shown in Table 4.13 and Figure 4.17

Table 4.13 The amount of reaction time converts CK as methyl ester via base-catalyzed process Compositions of fatty acids in chicken oil (KOH 1.0% wt., CK:MeOH ratio of 1:10 and temperature of 65°C)

	Time (min)	%FAME
	1	29.88
-	3	42.23
-	5	44.45
0	10	76.74
CA.	20	81.89
	30	91.98
~ ~ ~ ~ ~	40	92.01
คนย	50	92.01
91	60	92.01
หาลง	70	92.01

From the table 4.13, the high FAME was obtained with 50 minutes as 92.01 %FAME

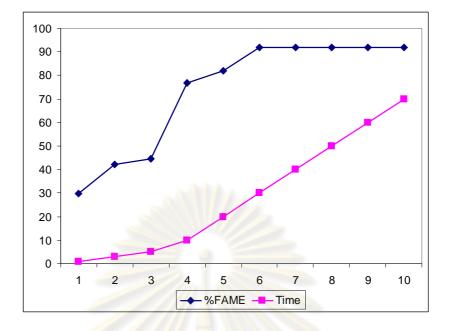


Figure 4.23 %FAME in biodiesel from chicken oil and KOH 1.0%wt.,CK:MeOH ratio of 1:10 and temperature of 65°C (Reaction time at 1, 3, 5, 10, 20, 30, 40, 50, 60, and 70 minutes)

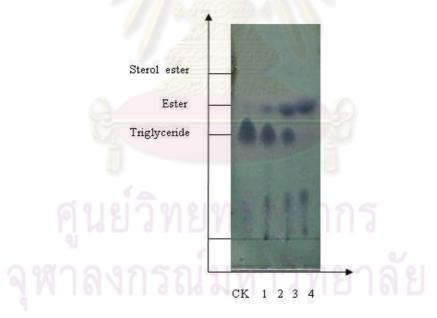
Figure 4.23 showed a plot of %FAME vs. reaction time for chicken oil. The results showed that the reaction was very fast in the first few minutes, a product of more than 76.74%FAME was formed within the first 10 min. After that, the reaction slowed down and entered a slow rate stage until the reaction equilibrium was reached eventually.

Table 4.14The amount of reaction time converts CK to methyl ester via
base-catalyzed process.(K2CO3 10% wt., CK:MeOH ratio of 1:20 and
temperature of 90°C)

Time (min)	%FAME	%Product yield	Density	Flash Point
30	-	-	0.9149	268
60	-	-	0.9134	193
120	89.59	71.40	0.9074	188
180	89.51	73.56	0.9006	176
240	93.80	82.52	0.8955	168
300	88.67	74.50	0.9136	171

From the table 4.14, the high product yield and the high FAME was obtained with 240 minute as 93.80 %FAME and 82.52%product yield.

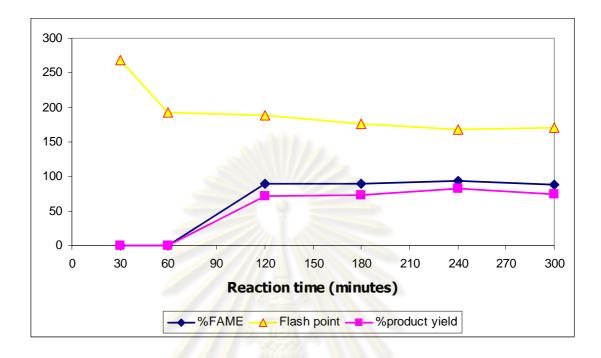
The reproductive TLC of triglyceride was converted into FAME in this Figure 4.24.



CK : chicken oil

1-4 : Reaction time (minute) 1=60, 2=120, 3=180 and 4=240
Mobile phase : a mixture of hexane, ethyl acetate (90:10 v/v)
Stationary phase : TLC aluminium sheet, silica gel 60 F₂₅₄

Figure 4.24 TLC result of product composition at different reaction time (minute) (K₂CO₃ 10%wt., CK:MeOH ratio of 1:20 and temperature of 90°C)



From the table 4.14, relative reaction time with flash point value is shown in figure 4.19.

Figure 4.25 Flash Point value in biodiesel from chicken oil at different reaction time (minute) (Reaction time at 30, 60, 120, 180, 240 and 300 minute)

Figure 4.19 showed a plot of %FAME, reaction time and flash point for chicken oil. The results showed that the reaction was fast in 120 minutes, a product of more than 89.59%FAME was formed within the 120 min. After that, the reaction slowed down and entered a slow rate stage till the reaction equilibrium was reached eventually.

As can be observed, the flash point was very high about 268°C at a reaction time of 30 min. However, the flash point reduced to 168°C at a reaction time of 240 min. The reason for this is that of transesterification was completed at long duration time of the reaction.

4.3 Physical and chemical properties of biodiesel from chicken oil

The optimal values of these parameters for achieving maximum conversions of triglycerides to esters depended on the chemical and physical properties of the biodiesel from chicken oil.

Additionally, the methyl ester was confirmed by analysis of 1 H NMR was 99.59% conversion when used KOH as shown in Figures 4.20

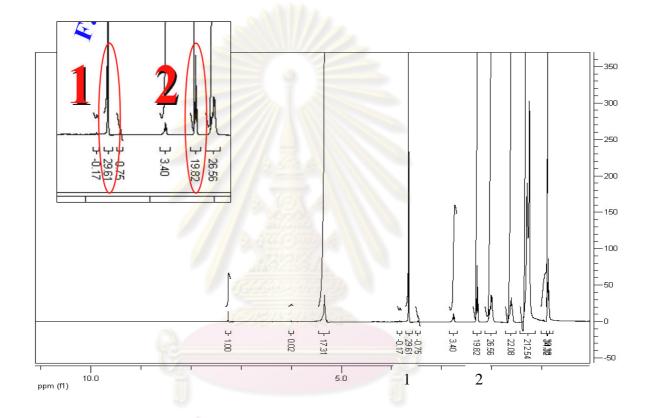


Figure 4.26 ¹H NMR spectrum of biodiesel from chicken oil (KOH 1.0% wt, CK:MeOH ratio of 1:10, temperature of 65°C and reaction time of 50 minutes)

% conversion =
$$\frac{29.61 \text{ x } 2}{19.82 \text{ x } 3}$$
 (1)

$$\% \text{ conversion} = 99.59$$
 (2)

The physical properties of biodiesel were determined as shown in Table 4.15.

Table 4.15 The physical properties of CK and the base-catalyst of biodieselproduction (NaOH, KOH and K_2CO_3 catalyst).

Property	СК	NaOH	КОН	K ₂ CO ₃
Flash point (C)	>200 (268)	165	162	168
Pour point (C)	3	3	3	3
Cloud point (C)	9	6	6	9
Specific gravity	0.9340	0.8456	0.8447	0.8955
Viscosity (cSt at 40C)	5.0340	4.5650	4.5787	4.5882
Distillation (C)	IBP = 230,	IBP = 189,	IBP = 178,	IBP = 200,
	50% = 338	50% = 331	50% = 334	50% = 352
Sulphur (wt%)	0.003	0.000	0.000	0.000
Cetane Index	35.78	54.8	52.4	48.2
Cetane Number	RAZIA	54.8	52.6	49.4
Fatty acid Methyl Ester content (%wt)		98.35	98.27	93.80
Free glycerol content (%wt)	eeee y saa	0.047	0.005	0.002
Total glycerol content (%wt)	-	0.066	0.059	0.011
Monoglyceride content (%wt)	-	0.022	0.198	0.311
Diglyceride content (%wt)	-	0.080	0.004	1.053
Triglyceride content (%wt)	เยทรัง	0.00	0.024	1.476
Methanol content (%wt)		0.01	0.00	0.00
% Product yield	อโจวจรา	93.58	99.02	82.52
% Conversion	DK PL L	98.74	99.59	97.47

Using KOH as catalyst, the product yield, FAME and conversion was obtained in the highest percentage with 98.27%, 99.02% and 99.59%, respectively.

The cetane number ratings of biodiesel from chicken oil was higher than the minimum of 51 for automotive diesel fuels in Thailand. (Diesel and biodiesel specification of Thailand shown in Appendix C) Cetane number increases with chain length, decreases with number of double bonds, and decreases as double bounds and carbonyl groups move toward the center of the chain.

Distillation of biodiesel from chicken oil is shown in Figure 4.18. The initial boiling point of the biodiesel (IBP) from NaOH catalyst was 189°C, KOH catalyst was 170°C, K₂CO₃ catalyst was 200°C and diesel B5 was 192°C.

The 50% recovery of biodiesel from chicken oil was higher than diesel B5 because the double bond of unsaturated of alkyl chains could polymerized at high temperatures. And data distillation of biodiesel from chicken oil is shown in Figures 4.27.

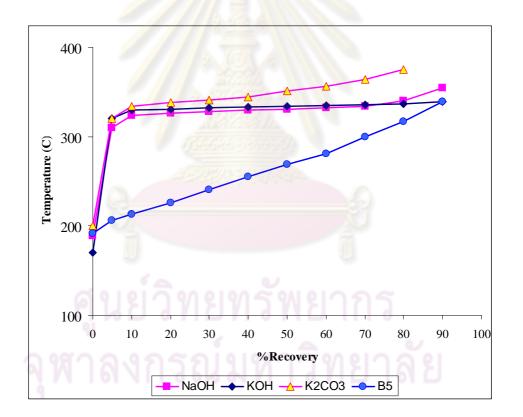
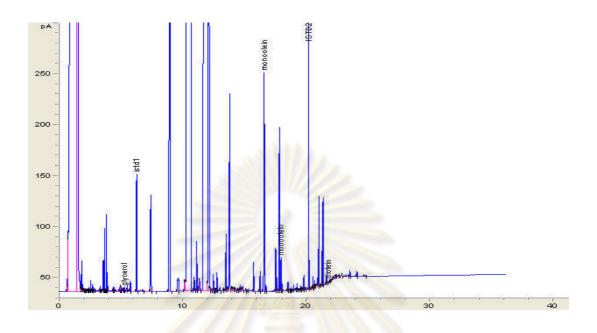
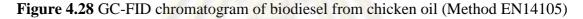


Figure 4.27 Distillation of biodiesel from chicken oil and diesel B5

Free and Total glycerol content (%wt) and mono-, di-, triglyceride content (%wt) determined by GC-FID (EN14105) is shown in Figure 4.28.





Methanol content (%wt) determined by GC-FID (EN14110) is shown in Figure 4.29.

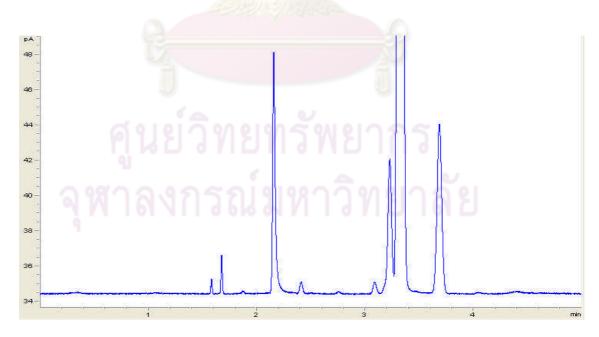


Figure 4.29 GC-FID chromatogram of biodiesel from chicken oil (Method EN14110)

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

Biodiesel production from a by-products of chicken essence soup manufacturing via alkaline-catalyzed transesterification using sodium hydroxide, potassium hydroxide and potassium carbonate as catalyst. To optimize the reaction condition, the amount of catalyst, molar ratio of methanol to chicken oil, reaction temperature and reaction time were investigated. The chemical and physical properties of biodiesel produced from the transesterification, such as density, flash point, cloud point, pour point, kinematic viscosity, cetane number, cetane index, %sulphur, ester content, and mono-, di-, triglyceride content were measured. The results showed that KOH and NaOH are suitable catalyst for biodiesel production and the biodiesel with best product yield and quality was produced at a 10:1 molar ratio of methanol to chicken oil, 1.0% of potassium hydroxide catalyst; reaction temperature 65°C and reaction time 50 minutes. The product yield of the biodiesel produced under optimal condition was 99.02% with 98.27% of fatty acid methyl ester (FAME).

Results of present study clearly demonstrated that the use of chicken oil is very suitable as low cost feed stocks for biodisel production.

5.2 Suggestion

However, further research and development on additional fuel property measures, long-term run and wear analysis of biodiesel-fueled engine is also necessary.

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APPENDIX A

CALCULATIONS

1. Molecular weight of chicken oil can be calculated in following:

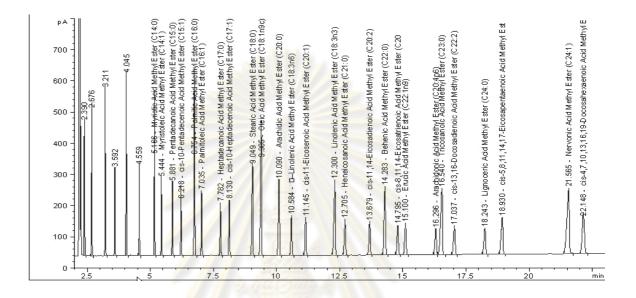


Figure A.1 GC chromatogram of Mix SupelcoTM 37 Component FAME Mix C4-C24

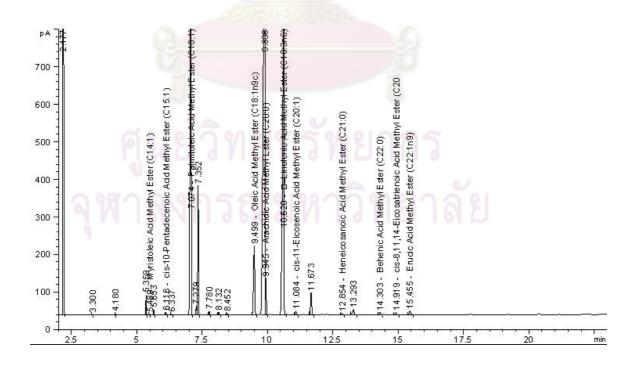
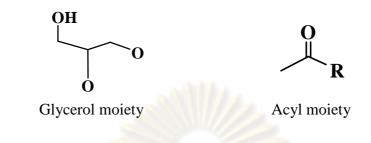


Figure A.2 GC chromatogram of biodiesel from chicken oil

$$\begin{split} & \text{Molecular weight (approx.) of crude oil} = M_G + 3M_{Ac} \\ & \text{where } M_G: \text{Molecular weight of glycerol moiety} = C_3H_5O_3 = 89.07 \text{ g/mol} \\ & M_{Ac}: \text{Molecular weight of acyl moiety of fatty acid} \\ & M_{FFA}: \text{Molecular weight of fatty acid} \end{split}$$



where;

$$M_{FFA} = [(\Sigma\% \text{ Area from GC} \times \text{MW of fatty acids})]$$

Total % Area from GC

So,
$$M_{FFA} = [(0.25 \times 228.38) + (22.3452 \times 256.43) + (0.2507 \times 254.41) +....]$$

100.0001
= 266.54 g/mol

and M_{Ac} = molecular weight (approx.) of fatty acid – weight of -OH

= 266.54 - 17.01

= 249.53 g/mol

 \therefore Molecular weight (approx.) of chicken oil = 249.53 × 3

● = 748.59 g/mol

The molecular weight of oil methyl ester has been calculated from the molecular weight (approx.) of acyl moiety of fatty acid, that is

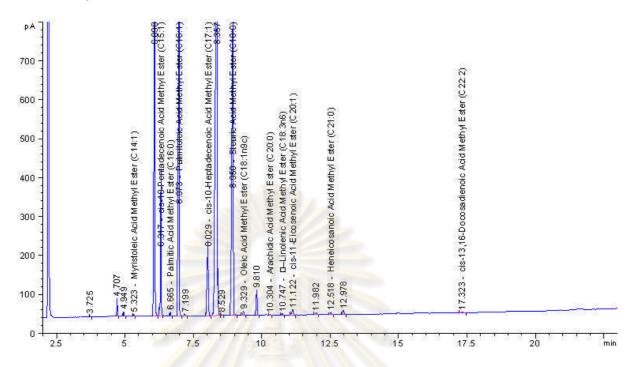
MW of methyl ester = M_{Ac} + molecular weight of acyl moiety of fatty acid

$$= 748.59 + 89.07$$

So, Molecular weight of methyl ester of chicken oil

= 837.66 g/mol

2. %Methyl ester content from GC (EN 14103)



Condition KOH1.0% wt, MeOH:CK ratio = 10:1, Temp. 65°C and Reaction time 60 min

Figure A.3 GC chromatogram of biodiesel from chicken oil

% Methyl ester content from GC can be calculated this equation

$$\underbrace{\sum A - Ai}_{Ai} \times \underbrace{C \times V}_{m} \times 100;$$

$$C = Concentration of standard$$

$$V = Volume of standard$$

$$m = Amount of sample$$

$$Ai = Peak area of Internal standard$$

$$\sum A = Total peak area$$

$$= \underbrace{15769.77 - 2475.10}_{2475.10} \times \underbrace{500.29}_{50} \times \underbrace{4.5 \times 100}_{252.51} = 97.75\%$$

3. Cetane Index (ASTM D613)

can be calculated this equation

CI =
$$454.74 - 1641.416 \text{ D} + 774.74 \text{ D}^2 - 0.554 \text{ B} + 97.803 (\log \text{ B})^2$$
;

 $D = \text{density at } 15^{\circ}\text{C}, \text{ g/mL}, \text{determined by}$

Test Method D1298

- B = mid-boiling temperature[•]C determined by Test Method D86
- CI = 454.74 1641.416 (0.9335) + 774.74 (0.9335²) 0.554 238 + 97.803 (log238)²
- CI = 454.74 1532.26 + 675.13 121.85 + 552.40

CI = 28.16

4. °API (ASTM D1298)

can be calculated this equation

$$^{\circ}API = \frac{141.5}{\text{Sp gr 60/60°F}} -131.5$$
$$^{\circ}API = \frac{141.5}{0.9176} -131.5$$
$$^{\circ}API = 154.2 -131.5$$
$$^{\circ}API = 22.70$$

5. %Conversion

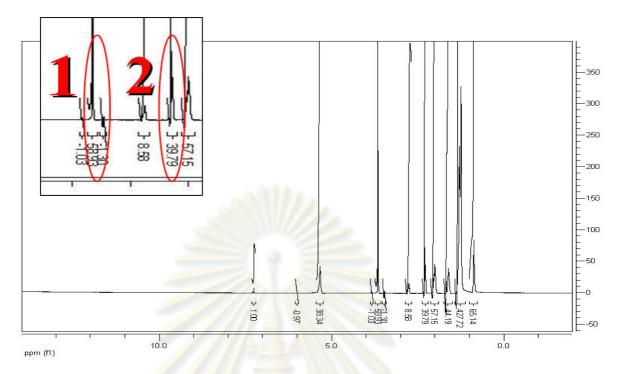
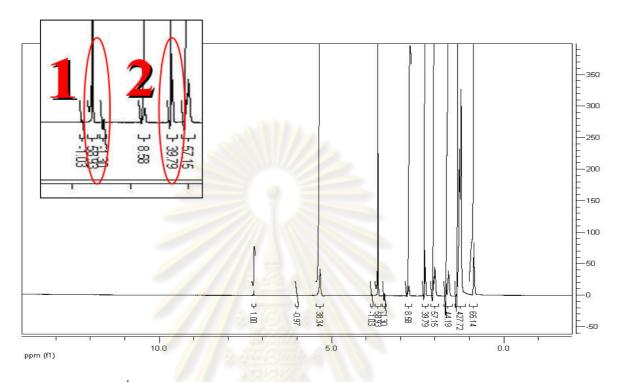


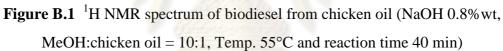
Figure A.4. ¹H NMR spectrum of biodiesel from chicken oil (NaOH 0.8% wt, MeOH:chicken oil = 10:1, Temp. 55°C and reaction time 40 min)

% conversion =
$$\frac{58.93 \times 2}{39.79 \times 3}$$
 (1)
% conversion = 98.74 (2)

APPENDIX B

Chromatogram of NMR





% conversion =
$$\frac{58.93 \times 2}{39.79 \times 3}$$
 (1)
% conversion = 98.74 (2)

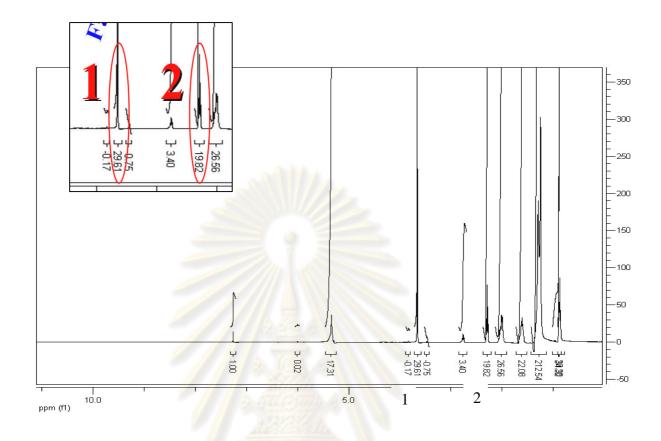


Figure B.2 ¹H NMR spectrum of biodiesel from chicken oil (NaOH 0.8% wt, MeOH:chicken oil = 10:1, Temp. 55°C and reaction time 50 min)

% conversion =
$$\frac{29.61 \text{ x } 2}{19.82 \text{ x } 3}$$
 (1)
% conversion = 99.59 (2)

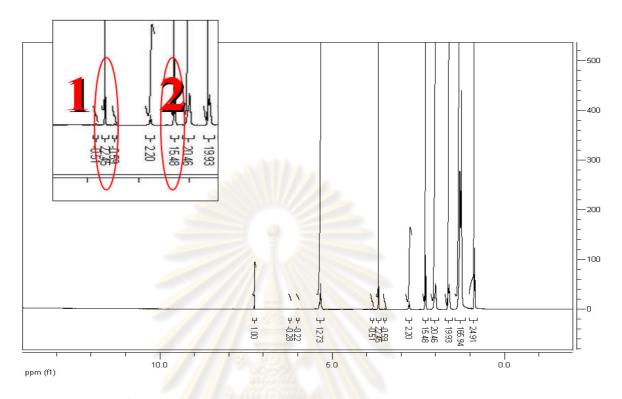


Figure B.3 ¹H NMR spectrum of biodiesel from chicken oil (K_2CO_3 10% wt, MeOH:chicken oil = 20:1, Temp. 90°C and reaction time 240 min)

% conversion =
$$\frac{22.45 \times 2}{15.48 \times 3}$$
 (1)
% conversion = 97.07 (2)

APPENDIX C

Chromatogram of GC





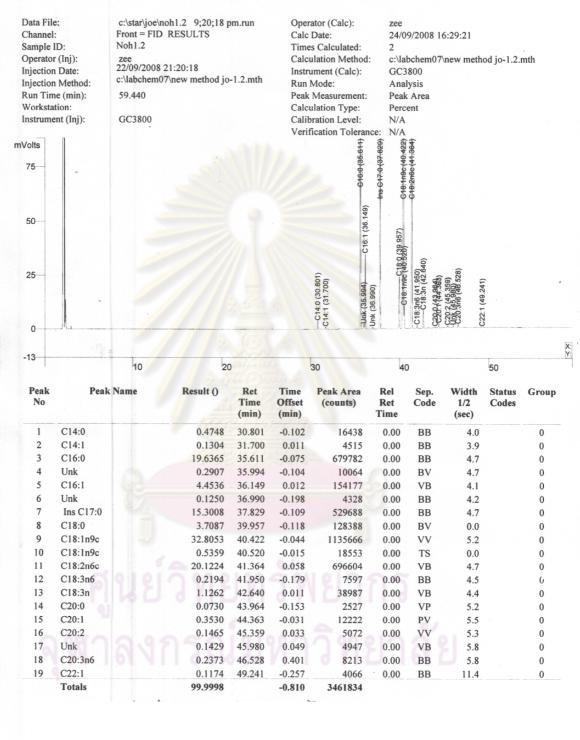


Figure C1 GC Chromatogram of biodiesel from chicken oil (KOH 1.0% wt., MeOH:CK ratio of 10:1, temperature of 65°C and reaction time of 50 minutes)

Environmental Science, Chulalongkorn U.

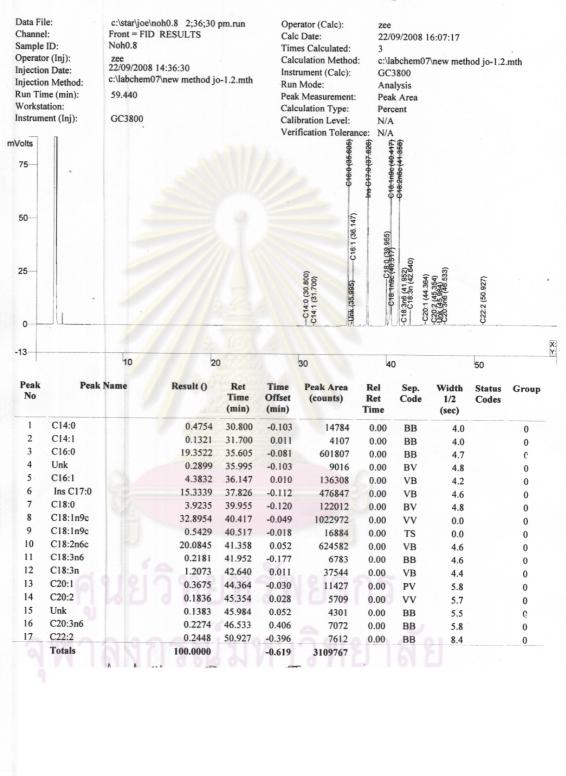


Figure C2 GC Chromatogram of biodiesel from chicken oil

(NaOH 0.8% wt., MeOH:CK ratio of 10:1, temperature of 55°C and reaction time of 40 minutes)

Environmental Science, Chulalongkorn U.

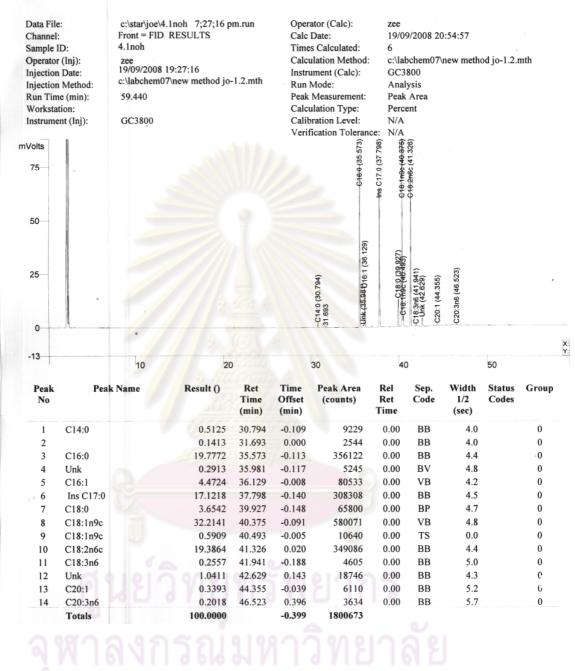


Figure C3 GC Chromatogram of biodiesel from chicken oil (K₂CO₃ 10.0% wt., MeOH:CK ratio of 20:1, temperature of 90°C and reaction time of 240 minutes)

APPENDIX D

Biodiesel specification in Thailand



รายละเอียดแนบท้ายประกาศกรมธุรกิจพลังงาน

เรื่อง กำหนดลักษณะและคุณภาพของไบโอดีเซลประเภทเมทิลเอสเตอร์ของกรดไขมัน

พ.ศ. 2550

รายการ	ข้อกำหน	อัตรา	อัตราสูงต่ำ		
1	เมทิลเอสเตอร์ (Methyl Ester,	ร้อยละโดยน้ำหนัก % wt.)	ไม่ต่ำกว่า	96.5	EN 14103
2	ความหนาแน่น ณ อุณหภูมิ 15 °ฃ (Density at 15 °C,	กิโลกรัม/ลูกบาศก์เมตร kg/m ³)	ไม่ต่ำกว่า และ	860	ASTM D 1298
	(Density at 15 C,	Kg/m)	ไม่สูงกว่า	900	
3	ความหนึด ณ อุณหภูมิ 40 °ซ	เซนติสโตกส์	ไม่ต่ำกว่า	3.5	ASTM D 445
	(Viscosity at 40 °C,	cSt)	และ ไม่สูงกว่า	5.0	
4	จุดวาบไฟ	องศาเซลเซียส	ไม่ต่ำกว่า	120	ASTM D 93
57° -	(Flash Point,	°C)			
5	กำมะถัน (Sulphur,	ร้อยละโดยน้ำหนัก %wt.)	ไม่สูงกว่า	0.0010	ASTM D 2622
6	กากถ่าน (ร้อยละ 10 ของกากที่เหลือจากการก	ร้อยละโดยน้ำหนัก เลั่น)	ไม่สูงกว่า	0.30	ASTM D 4530
	(Carbon Residue , on 10 % distil	lation residue, %wt)			
7	จำนวนซีเทน		ไม่ต่ำกว่า	51	ASTM D 613
	(Cetane Number)				
8	เถ้าขัลเฟต (Sulphated Ash,	ร้อยละโดยน้ำหนัก %wt.)	ไม่สูงกว่า	0.02	ASTM D 874
9	น้ำ (Water,	ร้อยละโดยน้ำหนัก wt.)	ไม่สูงกว่า	0.050	EN ISO 12937
10	สิ่งปนเปื้อนทั้งหมด (Total Contaminate,	ร้อยละโดยน้ำหนัก %wt.)	ไม่สูงกว่า	0.0024	EN 12662
11	การกัดกร่อนแผ่นทองแดง (Copper Strip Corrosion)		ไม่สูงกว่า	หมายเลข 1	ASTM D 130
12	เสถียรภาพต่อการเกิดปฏิกิริยา ออกซิเดชั่น ณ อุณหภูมิ110 องศาเข (Oxidation Stability at 100 °C,	ชั่วโมง ชลเซียส hours)	ไม่ต่ำกว่า	6	EN 14112

รายการ	ข้อกำหนด		อัตราสูงต่ำ		วิธีทดสอบ ^บ
13	ค่าความเป็นกรด มิลลิกรับโร	lตัสเซียมไฮครอกไซค์/กรัม	ไม่สูงกว่า	0.50	ASTM D 664
	(Acid Value , mg KOF	√g)			
14	ค่าไอโอดีน	กรัมไอโอดีน/ 100 กรัม	ไม่เสูงกว่า	120	EN 14111
	(Iodine Value ,	g lodine / 100 g)			
15	กรดลิโนเลนิกเมทิลเอสเตอร์	ร้อยละโดยน้ำหนัก	ไม่สูงกว่า	12.0	EN 14103
	(Linolenic Acid Methyl Ester,	%wt.)			
16	เมทานอล	ร้อยละโคยน้ำหนัก	ไม่สูงกว่า	0.20	EN 14110
	(Methanol,	%wt.)			
17	โมโนกลีเซอไรด์	ร้อยละโคยน้ำหนัก	ไม่สูงกว่า	0.80	EN 14105
	(Monoglyceride	%wt.)			
18	ไดกลีเซอไรด์	ร้อยละโดยน้ำหนัก	ไม่สูงกว่า	0.20	EN 14105
	(Diglyceride,	%wt)			
19	ไตรกลีเซอไรด์	ร้อยละโดยน้ำหนัก	ไม่สูงกว่า	0.20	EN 14105
	(Triglyceride,	%wt)			
20	กลีเขอรีนอิสระ	ร้อยละโคยน้ำหนัก	ไม่สูงกว่า	0.02	EN 14105
	(Free glycerin ,	%wt.)	0.1498		
21	กลีเซอรีนทั้งหมด	ร้อยละโดยน้ำหนัก	ไม่สูงกว่า	0.25	EN 14105
	(Total glycerin,	%wt.)			
22	โลหะกลุ่ม 1 (โซเดียมและโปแตสเซียม)	มิลลิกรัม/กิโลกรัม	ไม่สูงกว่า	5.0	EN 14108 และ
	(Group metals (Na+K),	mg/kg)			EN 14109
	โลหะกลุ่ม 2 (แคลเซียมและแมกนีเซียม)	มิลลิกรัม/กิโลกรัม	ไม่สูงกว่า	5.0	pr EN 14538
	(Group II metals (Ca+Mg),	mg/kg)	5171		
23	พ่อสฟอรัส	ร้อยละโดยน้ำหนัก	ไม่สูงกว่า	0.0010	ASTM D 4951
1	(Phosphorus,	%wt.)	ุกยา		
24	สารเติมแต่ง (ถ้ำมี)		ให้เป็นไปตา:	มที่ได้รับความ	มเห็นชอบจากอธิบเ
	(Additive)			กรมธุรกิจพ	ลังงาน

<u>หมายเหตุ 1/</u> วิธีทดสอบอาจใช้วิธีอื่นที่เทียบเท่าก็ได้ แต่ในกรณีที่มีข้อโต้แย้งให้ใช้วิธีที่กำหนดในรายละเอียดแนบท้ายนี้

VITA

Mr. Yoottana Jampahom was born on September 22, 1976 in Bangkok, Thailand. He graduated at Matthayom Watboengthonglang School in 1992. He received the Bachelor Degree of Chemistry, Rajapath Chantakaseam University in 1996. He worked at Beger Paint (Thailand) Co.Ltd. in 1996 for 1 years until he worked at Ministry of commercial in 1997 for 6 years. Now, he worked at Ministry of Energy. He continued his Master study in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2005 and completed the program in 2008.

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