การสังเคราะห์ไบโอดีเซลโดยตรงจากเมล็ดมะเขือเทศ

Lycopersicon esculentum Mill.

นางสาวโชติกา ลักษณะ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
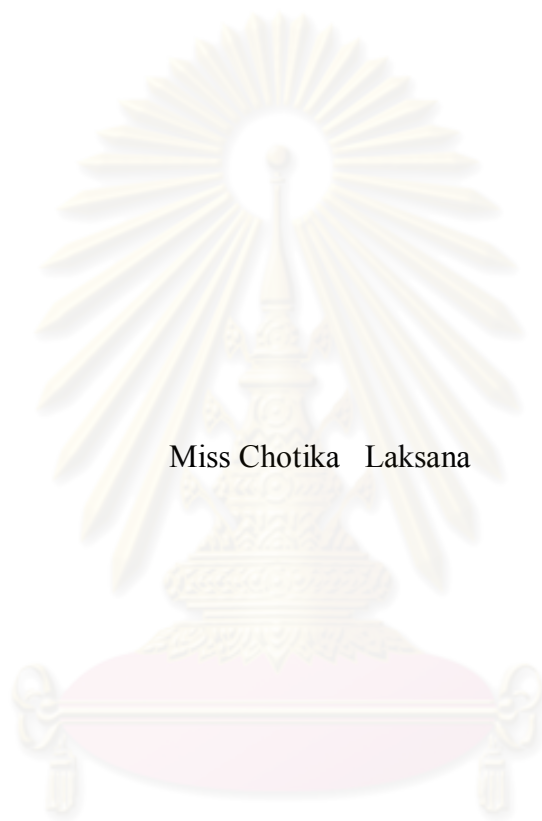
ปีการศึกษา 2553

DIRECT SYNTHESIS OF BIODIESEL FROM TOMATO
Lycopersicon esculentum Mill. SEEDS

Miss Chotika   Laksana

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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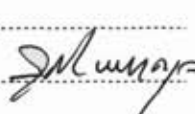Chulalongkorn University
Academic Year 2010

Thesis Title	DIRECT SYNTHESIS OF BIODIESEL FROM TOMATO
	Lycopersicon esculentum Mill. SEEDS
By	Miss Chotika Laksana
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Surachai Pornpakakul. Ph.D.

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โชติกา ลักษณะ : การสังเคราะห์ไบโอดีเซลโดยตรงจากเมล็ดมะเขือเทศ *Lycopersicon esculentum* Mill. (DIRECT SYNTHESIS OF BIODIESEL FROM TOMATO *Lycopersicon esculentum* Mill. SEEDS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.สุรชัย พรภคกุล, 86 หน้า.

วัตถุประสงค์ของงานวิจัยนี้เพื่อศึกษาการผลิตไบโอดีเซลจากน้ำมันเมล็ดมะเขือเทศ โดยใช้กรด ซัลฟิวริกเข้มข้นเป็นตัวเร่งปฏิกิริยาแบบเอกพันธุ์ชนิดกรด ในการศึกษานี้มีการเก็บเมล็ดมะเขือเทศจาก โรงงานผลิตซอสมะเขือเทศ ในเดือนมีนาคม (2553) และเดือนมกราคม (2554) กระบวนการสกัดน้ำมันเมล็ด มะเขือเทศดำเนินการภายใต้การรีฟลักซ์ในตัวทำละลายเฮกเซนและเมทานอล โดยใช้การสกัดแบบธรรมดาและ ใช้อุปกรณ์ซ็อกเล็ต (soxhlet apparatus) การสกัดในตัวทำละลายเมทานอลและเฮกเซนโดยใช้อุปกรณ์การสกัด แบบธรรมดาจะให้ปริมาณน้ำมัน 25 เปอร์เซ็นต์และ 32 เปอร์เซ็นต์ ตามลำดับ ขณะที่การสกัดโดยใช้อุปกรณ์ซ็ อกเล็ตโดยใช้เมทานอลและเฮกเซนเป็นตัวทำละลาย จะให้ปริมาณน้ำมัน 24 เปอร์เซ็นต์ และ 31 เปอร์เซ็นต์ ตามลำดับ ปริมาณกรดไขมันอิสระของน้ำมันเมล็ดมะเขือเทศที่ได้จากเมล็ดมะเขือเทศในเดือนมีนาคม 2553 ที่ สกัดด้วยตัวทำละลายเฮกเซน มีปริมาณกรดไขมันอิสระ 40 เปอร์เซ็นต์ และที่สกัดด้วยเมทานอลจะมีปริมาณ กรดไขมันอิสระ 60 เปอร์เซ็นต์ ซึ่งมากกว่ากรดไขมันอิสระในน้ำมันเมล็ดมะเขือเทศในเดือนมกราคม 2554 (17 เปอร์เซ็นต์ จากการสกัดด้วยเฮกเซน และ 26 เปอร์เซ็นต์ จากการสกัดด้วยเมทานอล) การผลิตไบโอดีเซล โดยตรงในระหว่างการสกัดโดยใช้อุปกรณ์ซ็อกเล็ตเป็นเวลา 10 ชั่วโมง จะให้เปอร์เซ็นต์การเปลี่ยนแปลงเป็น เมทิลเอสเทอร์ 99.5 เปอร์เซ็นต์และปริมาณเมทิลเอสเทอร์คิดเป็น 24.25 เปอร์เซ็นต์ของน้ำหนักเมล็ดมะเขือเทศ ขณะที่การผลิตไบโอดีเซลจากน้ำมันเมล็ดมะเขือเทศ ให้เปอร์เซ็นต์การเปลี่ยนแปลงเป็นไบโอดีเซล 96.21 เปอร์เซ็นต์

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต โชติกา ลักษณะ

ปีการศึกษา   2553   ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

v

5172267623 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : DIRECT BIODIESEL / ESTERIFICATION

CHOTIKA LAKSANA : DIRECT SYNTHESIS OF BIODIESEL FROM TOMATO *Lycopersicon esculentum* Mill. SEEDS ADVISOR : ASSOC. PROF. SURACHAI PORNPAKAKUL, Ph.D., 86 pp.

The objective of this research is to study biodiesel production from tomato seed oil using conc. H_2SO_4 as a homogeneous acid catalyst. Throughout this study tomato seeds were obtained from tomato sauce manufacturing in March (2010) and January (2011). Extraction process of tomato seed oil was carried out under refluxing in solvents (hexane and methanol) with and without soxhlet apparatus. Under refluxing in methanol and hexane without soxhlet apparatus, it gave oil product 25% w/w and 32% w/w, respectively. While refluxing in methanol and hexane with soxhlet apparatus, it gave oil product 24% w/w and 31% w/w, respectively. Free fatty acid content of tomato seed oil obtained from seeds in March 2010 was 40% (extracted with hexane) and 60% (extracted with MeOH) which was higher than the oil obtained from seed in January (2011) (17% from extraction with hexane and 26% from extraction with MeOH). Biodiesel production was carried out directly during extraction using soxhlet for 10 hours to give 99.5% conversion and 24.25 % weight of methyl ester/weight of seeds while biodiesel production from tomato seed oil gave 96.21% conversion.

Field of Study : Petrochemistry and Polymer Science   Student's Signature *Chotika Laksana*

Academic Year : 2010   Advisor's Signature *S. Pornpakakul*

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LIST OF ABBREVIATIONS

CO_2	=	Carbon dioxide
ºC	=	Degree Celsius
ASTM	=	American Society for Testing and Materials Methods of Analysis of AOAC
FAME	=	Fatty acid methyl ester
NO_x	=	Nitrogen oxides
SO_2		Sulphur dioxide
h	=	Hour
TLC	=	Thin Layer Chromatography
% yield	=	Percent yield
% conversion	=	Percent conversion
^{1}H-NMR	=	Proton Nuclear Magnetic Resonance

CHAPTER I

INTRODUCTION

Energy is a basic requirement for every sector of economic development in a country. As a result, energy demands have been steadily increasing along with the growth of human population and industrialization. Common sources of energy are petroleum, natural gas and coal from fossil fuels. This growing consumption of energy has rapidly depleted non-renewable sources of energy. Rising price of fossil-based fuels and potential shortage in the future have led to a major concern about the energy security in every country. Moreover, there are many disadvantages of using fossil-based fuels, such as atmospheric pollution and environmental issues. Fossil fuels emissions are major contributors of greenhouse gases which may lead to global warming. Combustion from fossil fuels is major source of air pollutants, which consist of CO, NO_x, SO_x, hydrocarbons, particulates and carcinogenic compounds. The disadvantages and shortages of fossil fuels have motivated many researchers to find an alternative source of renewableenergy (Ching Juan, J. et al., 2010).

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 atmpsphere and consequently to the greenhouse effect (Srivastava, A. et al., 2000).

There are four primary ways to produce biodiesel, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterifications. The most commonly used method is transesterification in which oil or fat is reacted with a monohydric alcohol in presence of catalyst. The chemical process for biodiesel production, alkali or acid is usually adopted as a catalyst. Alkali-catalyzed process has been established that gives high conversion levels of oils to methyl esters. However, it

has several drawbacks, including difficulty of recycling glycerol and the need for either removal of catalyst or the wastewater treatment.

Most of biodiesel currently being produced is mainly dependent on edible oil sources (e.g. Soybean oil, Palm oil). Other sources were researched in order to find alternative raw material for the process but most of which cannot compete with the ready availability of large stocks of edible oils. Despite the fact, nonedible oils cover a wide range of low cost, underutilized feedstock with potential in large production level. One of the problems associated with crude nonedible oils and fats is the high free fatty acid content. Also acid-catalyzed esterification of high FFA content vegetable oils is a typical method of biodiesel production due to high reaction speed and high yield (Gerpen, V. et al., 1999).

Vegetable oils are renewable fuels extracted from the seeds of several plants like corn, cotton, soya, sunflower and tobacco. The prospect of using food processing by-products and wastes as a source of seeds, affected by a number of factors including the physical and chemical characteristics of these byproducts, the quantity produced and other market and technical considerations.

Tomato seed is the major by-product of the tomato paste manufacturing industry and is a potential raw material for producing alternative fuels. There are about 18 tomato sauce manufacturing plants, five large plants and thirteen small plants in the north and northeast of Thailand. For large plant, tomato for production of tomato sauce was about 6000 ton/day. Each day tomato paste manufacturing units generate 7.0-7.5% solid waste and 71-72% of the solid waste is pomace. Tomato pomace primarily consists of seeds and skin. Tomato seeds can be separated from pulp and skin by a sedimentation system. Dried tomato seed was used for oil extraction. The new products coming from tomato paste industry wastes, would be value added to tomatoes paste and support to the agricultural economy.

This research focuses on biodiesel production from by-product of tomato paste industry wastes using homogeneous acid catalyst.

1.1 Objectives of the research

- To produce direct biodiesel from tomato seeds using homogeneous acid catalyst.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Biodiesel

Biodiesel (BD) as an alternative fuel for diesel engines is receiving increased attention. BD, which is a relatively clean-burning, renewable fuel produced from new and used animal and vegetable oil, could be used to replace diesel fuel. BD has three large advantages over regular petroleum diesel. First, it is not a petroleum-based fuel, which means that using biodiesel would reduce our dependency on foreign oil. Second, BD is produced domestically, which means that using biodiesel will create jobs and contribute to local economies. The third major advantage of biodiesel is that it is cleaner than conventional diesel; biodiesel produces significantly less harmful emissions than regular petroleum diesel when burned in a combustion engine. BD produces significantly less harmful emissions than regular petroleum diesel when burned in a combustion engine. The source of BD usually depends on the crops amenable to the regional climate. Vegetable oils are renewable fuels extracted from the seed of several plants like corn, cotton, soya, sunflower and tobacco. The prospect of using food processing by products and wastes as a source of seeds. (Ma, F. et.al., 1999)

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

Biodiesel can be considered a new technology, taking into account all the years consumers have had to settle for traditional diesel. Using biodiesel has many advantages.

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.

2.1.2 Biological of biodiesel sources

Vegetable oils or fats, and alcohol were used 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 rapeseed)	Poultry	
Safflower Oil		
Sunflower Seeds		
Yellow Mustard Seed		

Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979). Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The fatty acids found in vegetable oils are summarized in Table 2.2.

Table 2.2 Chemical properties of vegetable oil (Lam, M. et al., 2010)

Vegetable oil	Fatty acid composition, % by weight									Acid value[a]
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3	
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48	0.11
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00	0.07
Crambe	2.07	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85	0.36
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93	0.20
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.40	0.00	22.30	8.23	1.14
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31	0.20
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00	0.15

[a] Acid values are milligrams of KOH necessary to neutralize the FFA in 1 g of oil sample.

2.1.3 Free fatty acids on biodiesel production

Biodiesel is an alternative fuel for diesel engines consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost–effective fuel very challenging. However there are large amounts of low–cost oils and fats such as restaurant waste and animal fats (Table 2.3) that could be converted to biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be converted to biodiesel using an alkaline catalyst (Canakci, M. et al., 2001).

Table 2.3 Examples of feedstocks with high in free fatty acids (FFA) (Moser, B., 2009)

Feedstock	FFA(wt %)	Ref
Pongamia pinnata	Up to 20	Naik et al. 2008
Moringa oleifera	2.9	Rashid et al. 2008
Jatropha curcas	14	Kumartiwari et al. 2007
Madhuca indica	20	Kumari et al. 2007
Nicotiana tabacum	35	Veljkovic et al. 2006
Calophyllum inophyllum	22	Sahoo et al. 2007
Zanthoxylum bungeanum	45.5	Zhang and Jiang 2008
Hevea brasiliensis	17	Ramadhas et al. 2005
Heterotrophic microalgal	8.97	Miao and Wu 2006
Acid oil	59.3	Haas et al. 2003
Fat from meat and bone meal	11	Nebel and Mittelbach 2006

Brown grease	40	Ngo et al. 2008
Waste cooking oil	7.25	Meng et al. 2008
Waste fryer grease	5.6	Issariyakul et al. 2007
Tung oil	9.55	Park et al. 2008
Tall oil	100	Demirbas 2008
Sorghum bug oil	10.5	Mariod et al. 2006

2.1.4 The chemical composition of biodiesel

The fatty acid composition of the source oil or fat is important in biodiesel because, in the winter, oil containing more saturated fatty acids than unsaturated fatty acids may solidify and clog the fuel lines. The fatty acid found in vegetable oils and typical fatty acid composition of common oil sources was summarized in Table 2.4 and Table 2.5 respectively. Table 2.6 showed the names, in a variety of formats, of common fatty acid.

Table 2.4 Typical fatty acid composition (wt. %) of a number of common feedstock oils[a] and fats that may be used for biodiesel production (Moser, B., 2009)

Fatty acid	CO	PO	SBO	SFO	COO	CSO	CCO	CF	BT
C6:0							1		
C8:0							7		
C10:0							7		
C12:0							47		1
C14:0		1				1	18	1	4
C16:0	4	45	11	6	11	23	9	25	26
C18:0	2	4	4	5	2	2	3	6	20
C20:0									
C22:0				1					
C16:1						1		8	4
C18:1	61	39	23	29	28	17	6	41	28
C18:2	22	11	54	58	58	56	2	18	3
C18:3	10		8	1	1			1	
C20:1	1								
Other									14
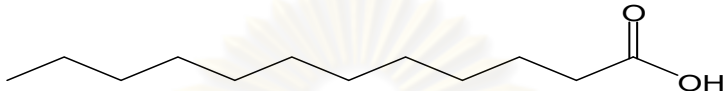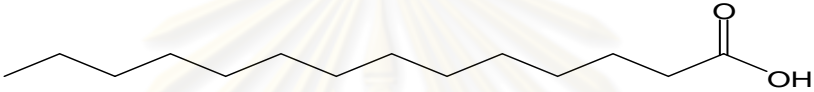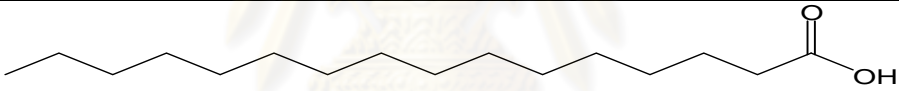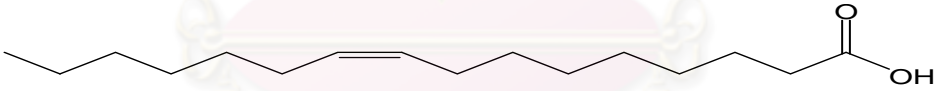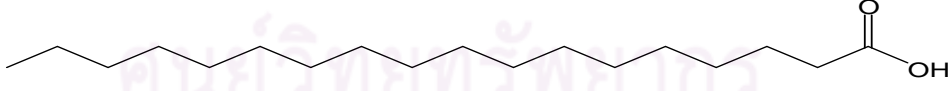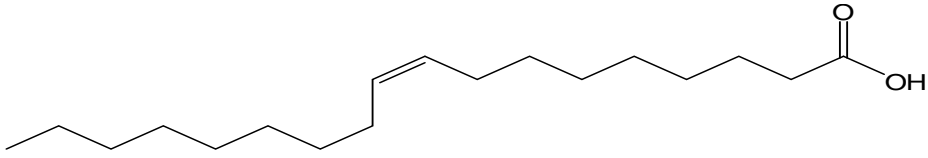
[a] CO canola (low erucic acid rapeseed oil) oil, PO palm oil, SBO soybean oil, SFO sunflower oil, COO corn oil (maize), CSO cottonseed oil, CCO coconut oil, CF chicken fat, BT beef tallow
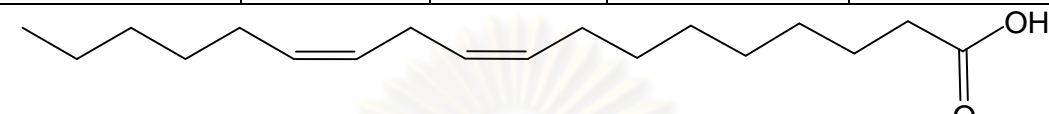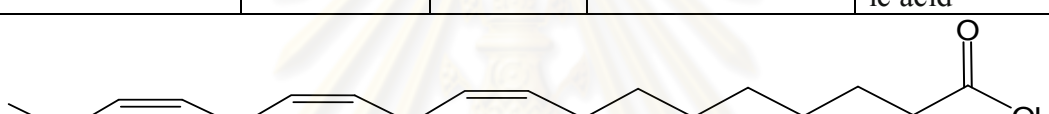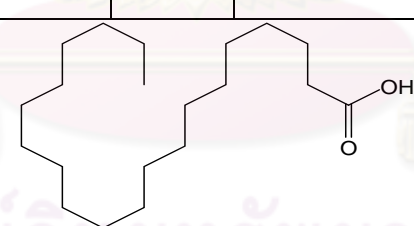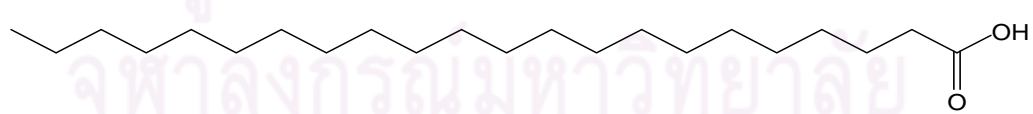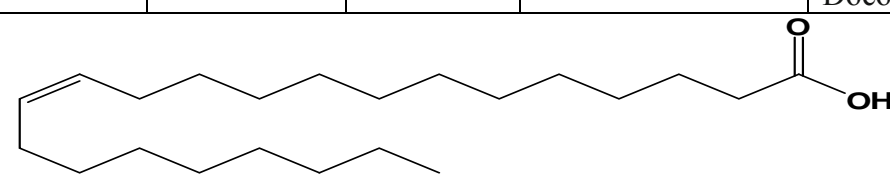
Table 2.5 Typical fatty acid composition-common oil sources
(Marchetti, J.M. et al., 2005)
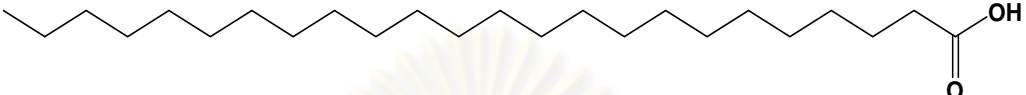
Fatty acid	Soybean	Cotton	Palm	Lard	Tallow	Coconut seed
Lauric, C12:0	0.1	0.1	0.1	0.1	0.1	46.5
Myristic, C14:0	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic, C16:0	10.2	20.1	42.8	23.6	23.3	9.8
Stearic, C18:0	3.7	2.6	4.5	14.2	19.4	3.0
Oleic, C18:1	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic, C18:2	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic, C18:3	8.6	0.6	0.2	0.4	0.9	0.0

Table 2.6 Names and structures of the most common fatty acids
(http://www.eppo.go.th,INTERNET)

No. of C:No. Of double bound	Molecular formular	Molecular mass	Systematic name	Other names
C12:0	$C_{12}H_{24}O_2$	200.32	Dodecanoic acid	Lauric acid, n-Dodecanoic acid
C14:0	$C_{14}H_{28}O_2$	228.38	Tetradecanoic acid	Myristic acid
C16:0	$C_{16}H_{32}O_2$	256.43	Dexadecanoic acid	Palmitic acid, Hexadecylic acid, Cetylic acid
C16:1	$C_{16}H_{30}O_2$	254.41	9-hexadecanoic acid	Palmitoleic acid
C18:0	$C_{18}H_{36}O_2$	284.48	Octadecanoic acid	Stearic acid
C18:1$^{\Delta 9}$	$C_{18}H_{34}O_2$	282.46	(9Z)-octadac -9-enoic acid	Oleic acid, (9Z)-Octadecenoic acid, (Z)-Octadec-9-enoic acid, Cis-9-octadecenoic acid, Cis-Δ9-octadecenoic acid

No. of C:No. Of double bound	Molecular formular	Molecular mass	Systematic name	Other names
C18:2 $^{\Delta 9,12}$	$C_{18}H_{32}O_2$	280.46	(9Z,12Z)-Octadecadienoic acid	Linoleic acid, *Cis-cis*-9,12-Octadecadienoic acid
C18:3 $^{\Delta 9,12,15}$	$C_{18}H_{30}O_2$	278.44	(9Z,12Z,15Z)-Octadecatrienoic acid	α –Linolenic acid, *Cis,cis,cis*-9,12,15-Octadecatrienoic acid
C20:0	$C_{20}H_{40}O_2$	312.54	Icosanoic acid	Arachidic acid,Arachic acid, Eicosanoic acid,n-eicosanoic acid
C22:0	$C_{22}H_{44}O_2$	340.60	Docosanoic acid	Behenic acid
C22:1	$C_{22}H_{42}O_2$	338.58	Z-13-Docosenoic	Erucic acid *Cis*-13-Docosenoic

No. of C: No. Of double bound	Molecular formular	Molecular mass	Systematic name	Other names
C24:0	$C_{24}H_{48}O_2$	368.63	Tetracosanoic acid	Lignoceric acid

The boiling points and melting points of the fatty acids, methyl esters, mono-, di- and triglycerides increase as the number of carbon atoms in the carbon chain increase, but decrease with increases in the number of double bonds. The melting points increase in the order of tri-, di- and monoglycerides due to the polarity of the molecules and hydrogen bonding. The physical properties of the primary chemical products of transesterification are summarized in Tables 2.7 and 2.8.

Table 2.7 Physical properties of chemicals related to transesterification
        (Zhang, J. et al., 2008)

Name	Specific gravity, g/ml (°C)	Melting point (°C)	Boiling point (°C)	Solubility (>10%)
Methyl Myristate	0.875 (75)	18.8	-	-
Methyl Palmitate	0.825 (75)	30.6	196.0	Acids, benzene, EtOH, Et_2O
Methyl Stearate	0.850	38.0	215.0	Et_2O, chloroform
Methyl Oleate	0.875	-19.8	190.0	EtOH, Et2O
Methanol	0.792	- 97.0	64.7	H_2O, Et_2O, EtOH
Ethanol	0.789	- 112.0	78.4	H_2O, ether
Glycerol	1.260	17.9	290.0	H_2O, EtOH

Table 2.8 Melting points of fatty acids, methyl esters and mono-, di-, and triglyceride
(Zhang, J. et al., 2008)

Fatty acid		Melting point (°C)				
Name	Carbons	Acid	Methyl	1-Monoglyceride	1,3-Diglyceride	Triglyceride
Myristic	14	54.4	18.8	70.5	66.8	57.0
Palmitic	16	62.9	30.6	77.0	76.3	63.5
Stearic	18	69.6	39.1	81.5	79.4	73.1
Oleic	18:1	16.3	- 19.8	35.2	21.5	5.5
Linoleic	18:2	-6.5	-35.0	12.3	-2.6	- 13.1

2.2 Oil Extraction (www.oilgae.com)

2.2.1 Mechanical methods

2.2.1.1 Expression/expeller press

Expeller pressing (also called oil pressing) is a mechanical method for extracting oil from raw materials such as nut, seeds and algae. An expeller press is a screw-type machine that presses oil seeds through a caged barrel-like cavity. Raw materials enter one side of the press and waste products exit the other side. The machine uses friction and continuous pressure from the screw drives to move and compress the seed material. The oil seeps through small openings that do not allow seed fiber solids to pass through. Afterward, the pressed seeds are formed into a hardened cake, which is removed from the machine. Pressure involved in expeller pressing creates heat in the range of 140-210ºF (60-99ºC). Some companies claim that they use a cooling apparatus to reduce this temperature to protect certain properties of the oils being extracted.

2.2.1.2 Ultrasonic-assisted extraction

Ultrasonic extraction, a branch of sonochemistry, can greatly accelerate extraction processes. Using an ultrasonic reactor, ultrasonic waves are used to create cavitation bubbles in a solvent material, when these bubbles collapse near the cell walls, it creates shock waves and liquid jets that causes those cells walls to break and release their contents into the solvent.

2.2.2 Chemical methods

2.2.2.1 Hexane solvent method

Solvent extraction is a process which involves extracting oil from oil-bearing materials by treating it with a low boiler solvent as opposed to extracting the oils by mechanical pressing methods (such as expellers, hydraulic presses, etc.). The solvent extraction method can be applied directly to any low oil content raw materials. It can also be used to extract pre-pressed oil cakes obtained from high oil content materials. Because of the high percentage of recovered oil, solvent extraction has become the most popular method of extraction of oils and fats. Today large quantities of oil cakes such as peanut, cottonseed, linseed, kardiseed, neem, castor, mowha, copra, sunflower, etc. are extracted. Direct extraction of rice bran, salseed and soybean is also used. Solvent Extraction is basically a process of diffusion of a solvent into oil-bearing cells of the raw material resulting in a solution of the oil in solvent. Various solvents can be used for extraction. However, after extensive research and consideration of various factors, such as commercial economics, edibility of the various products obtained from extraction, physical properties of the solvent especially its low boiling point etc. Hexane is considered to be the best and it is exclusively used for the purpose. In a nutshell, the extraction process consists of treating the raw material with hexane and recovering the oil by distillation. The hexane thus recovered is reused for extraction. The low boiling point of hexane (67°C / 152°F) and the high solubility of oils and fats in it are the properties exploited in the solvent extraction process.

2.2.2.2 Soxhlet extraction

A Soxhlet extractor is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet. It was originally designed for the extraction of a lipid from a solid material. Normally a solid material containing some of the desired compound is placed inside a thimble made from thick filter paper, which is loaded into the main chamber of the soxhlet extractor. The Soxhlet extractor is placed onto a flask containing the extraction solvent. The soxhlet is then equipped with a condenser. The solvent is heated to reflux. The solvent vapour travels up a distillation arm and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid

material. The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound will then dissolve in the warm solvent. When the Soxhlet chamber is almost full, the chamber is automatically emptied by a siphon side arm, with the solvent running back down to the distillation flask. This cycle may be allowed to repeat many times, over hours or days. During each cycle, a portion of the non-volatile compound dissolves in the solvent. After many cycles the desired compound is concentrated in the distillation flask.

The advantage of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled. After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound. The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded.

2.2.2.3 Supercritical fluid extraction

Supercritical Fluid Extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids as the extracting solvent. Extraction is usually from a solid matrix, but can also be from liquids. Carbon dioxide (CO_2) is the most used supercritical fluid, sometimes modified by co-solvents such as ethanol or methanol. Extraction conditions for supercritical CO_2 are above the critical temperature of 31°C and critical pressure of 74 bar Addition of modifiers may slightly alter this. The discussion below will mainly refer to extraction with CO_2, except where specified

Each of these methods has drawbacks:

1. The mechanical press generally requires drying the sample, which is energy intensive.
2. The use of chemical solvents present safety and health issues.
3. Supercritical extraction requires high pressure equipment that is both expensive and energy intensive.

Many manufacturers use a combination of mechanical pressing and chemical solvents in extracting oil.

2.3 Process technologies for biodiesel production

2.3.1 Chemical Principles

Chemically, biodiesel is equivalent to fatty acid methyl esters or ethyl esters, produced out of triacylglycerols via transesterification or out of fatty acids via esterification. In figure 2.1 the formula scheme for the production of fatty acid methyl esters (FAME) out of triacylglycerols is shown. Fatty acid methyl esters today are the most commonly used biodiesel species, whereas fatty acid ethyl esters (FAEE) so far have been only produced in laboratory or pilot scale.(Bacovsky, D. et al., 2007)

$$H_2C-O-COR$$
$$HC-O-COR \quad + \quad 3\,CH_3OH \quad \rightleftharpoons \quad HC-OH \quad + \quad 3\,R-COOCH_3$$
$$H_2C-O-COR \qquad\qquad\qquad\qquad H_2C-OH$$

triacylglycerol   methanol   glycerol   (FAME)

R = fatty acid chain
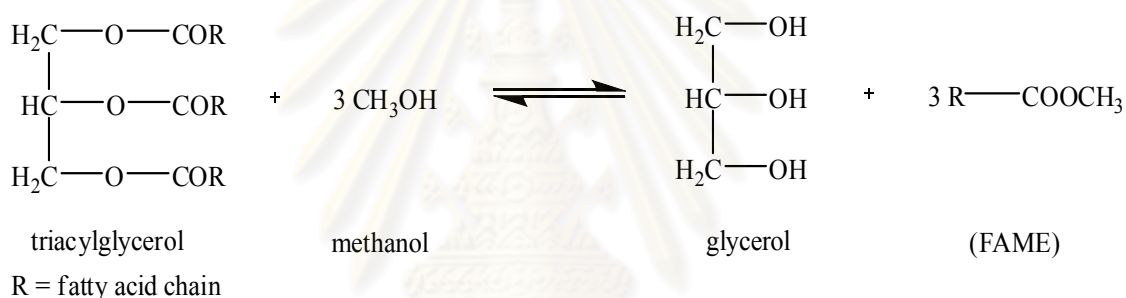
Figure2.1 Production of fatty acid methyl esters via transesterification

(Bacovsky, D. et al., 2007)

$$R\text{-}COOH \quad + \quad CH_3OH \quad \rightleftharpoons \quad R\text{-}COOCH_3 \quad + \quad H_2O$$

fatty acid   methanol   FAME   water

R = fatty acid chain

Figure2.2 Production of fatty acid methyl esters via esterification

(Bacovsky, D. et al., 2007)

Figure 2.1 shows the chemical equations for a transesterification and Figure 2.2 for an esterification reaction. As vegetable oils or animal fats mainly consist of triacylglycerols (triglycerides) the main reaction for the production of biodiesel is the transesterification or alcoholysis reaction. In a transesterification or alcoholysis

reaction one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid alkyl ester. The process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol. In order to shift the equilibrium to the right, methanol is added in an excess over the stoichiometric amount in most commercial biodiesel production plants. This process removes glycerol from the reaction mixture and enables high conversion (Srivastava, A. et al., 2000). Finally, regardless of the type of alcohol used, some form of catalyst has to be present to achieve high ester yields under comparatively mild reaction conditions.

The esterification reaction according to Figure 2.6 is a typical equilibrium reaction, thus, in order to increase the yield of fatty acid alkyl esters it is necessary to use an excess of alcohol or to remove one of the end products out of the equilibrium, e.g. the water by distillation or by the use of concentrated sulfuric acid. In order to increase the reaction rate of both transesterification and esterification reactions, in most cases catalysts are use (Bacovsky, D. et al., 2007).

2.4 Catalysts for transesterification and esterification reactions
(Bacovsky, D. et al., 2007)

2.4.1 Homogeneous catalysts for transesterification and esterification reactions
2.4.1.1 Alkaline catalysis

Alkaline or basic catalysis is by far the most commonly used reaction type for biodiesel production. The main advantage of this form of catalysis over acid catalyzed transesterifications is high conversion under mild conditions in comparatively short reaction time. It was estimated that under the same temperature conditions and catalyst concentrations methanolysis might proceed about 4000 times faster in the presence of an alkaline catalyst than in the presence of the same amount of an acidic equivalent. Moreover, alkaline catalysts are less corrosive to industrial equipment, and thus enable the use of less expensive carbon-steel reactor material. The main drawback of the technology is the sensitivity of alkaline catalysts to free fatty acids contained in the feedstock material. Therefore alkali-catalyzed transesterifications optimally work with high-quality, low-acidic vegetable oils, which

are however more expensive than waste oils. If low-cost materials, such as waste fats with a high amount of free fatty acids, are to be processed by alkaline catalysis, deacidification or pre-esterification steps are required.

Today most of the commercial biodiesel production plants are utilizing homogeneous, alkaline catalysts. Traditionally the alkoxide anion required for the reaction is produced either by using directly sodium or potassium methoxide or by dissolving sodium or potassium hydroxide in methanol. The amount of alkaline catalyst depends on the quality of the oil, especially on the content of free fatty acids. Under alkaline catalysis free fatty acids are immediately converted into soaps, which can prevent the separation of glycerol and finally can lead to total saponification of all fatty acid material. So the alkaline catalysis is limited to feedstock up to a content of approx. 3 % of fatty acids.

Table 2.9 Overview of homogenous alkaline catalysts

Type of Catalyst	Comments
Sodium hydroxide	Cheap, disposal of residual salts necessary
Potassium hydroxide	Reuse as fertilizer possible, fast reaction rate, better separation of glycerol
Sodium methoxide	No dissolution of catalyst necessary, disposal of salts necessary
Potassium methoxide	No dissolution of catalyst necessary, use as fertilizer possible, better separation of glycerol, higher price

(1) ROH + B ⇌ RO⁻ + B⁺

(2)

(3)

(4)
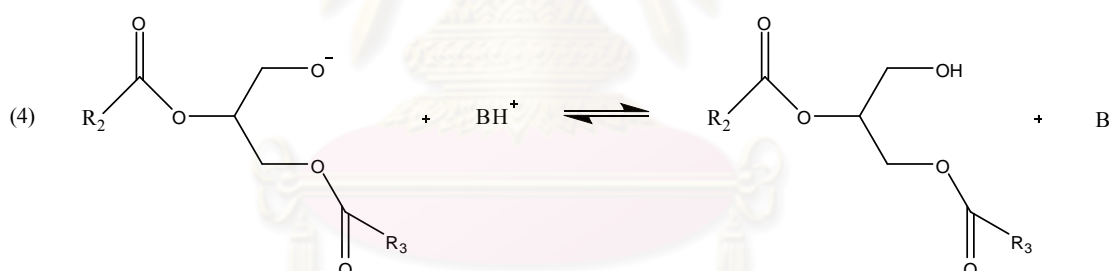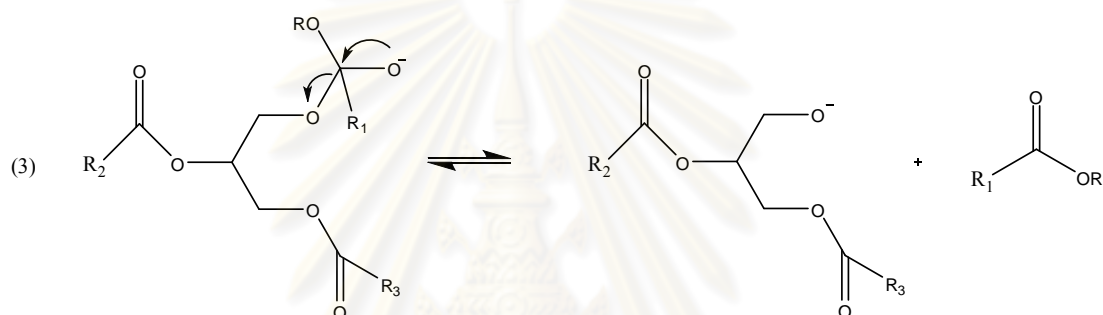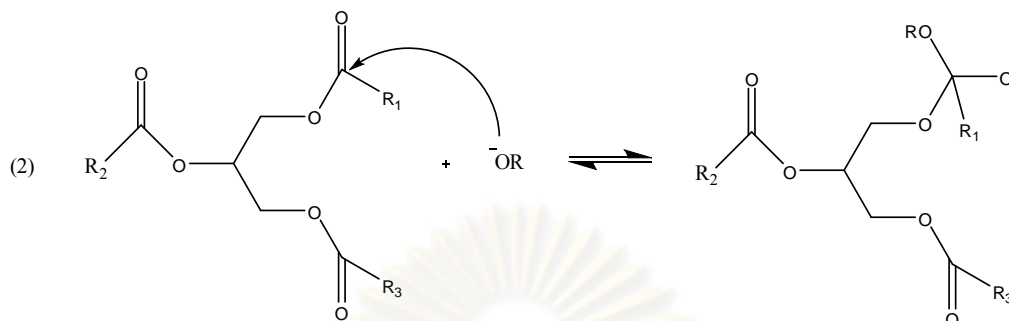
B : base catalyst
R₁,R₂,R₃ : carbon chain of the fatty acids
R : akyl group of the alcohol

Figure 2.3 Mechanism of homogeneous base-catalyzed reaction for transesterification
of TG (Lotero, E. et al., 2005)

2.4.1.2 Acid catalysis

Acid catalysis offers the advantage of also esterifying free fatty
acids contained in the fats and oils and is therefore especially suited for the
transesterification of highly acidic fatty materials. However, acid-catalyzed
transesterifications are usually far slower than alkalicatalyzed reactions and require
higher temperatures and pressures as well as higher amounts of alcohol. The typical

reaction conditions for homogeneous acid-catalyzed methanolysis are temperatures of up to 100°C and pressures of up to 5 bars in order to keep the alcohol liquid. A further disadvantage of acid catalysis – probably prompted by the higher reaction temperatures – is an increased formation of unwanted secondary products, such as dialkylethers or glycerol ethers. Because of the slow reaction rates and high temperatures needed for transesterification, acid catalysts are only used for esterification reactions. For vegetable oils or animal fats with an amount of free fatty acids larger than approx. 3 % two strategies are possible. The free fatty acids can either be removed by alkaline treatment, or they can be esterified under acidic conditions prior to the alkaline catalyzed transesterification reaction. This so-called preesterification has the advantage that prior to the transesterification most of the free fatty acids are already converted into FAME, thus the overall yield is very high. The cheapest and best known catalyst for esterification reactions is concentrated sulfuric acid. The main disadvantage of this catalyst is the possibility of the formation of side products like dark colored oxidized or other decomposition products. The organic compound, p-toluene sulphonic acid, can also be used. However the high price of the compound so far prevented broader application. As heterogeneous catalyst also cationic ion exchange resins can be used in continuous reaction columns, however, this approach has only be used so far in pilot plants.

Table 2.10 Overview of acidic catalysts

Type of Catalyst	Comments
Conc. sulphuric acid	Cheap, decomposition products, corrosion
p-Toluene-sulphonic acid	High price, recycling necessary
Acidic ion exchange resins	High price, continuous reaction possible, low stability
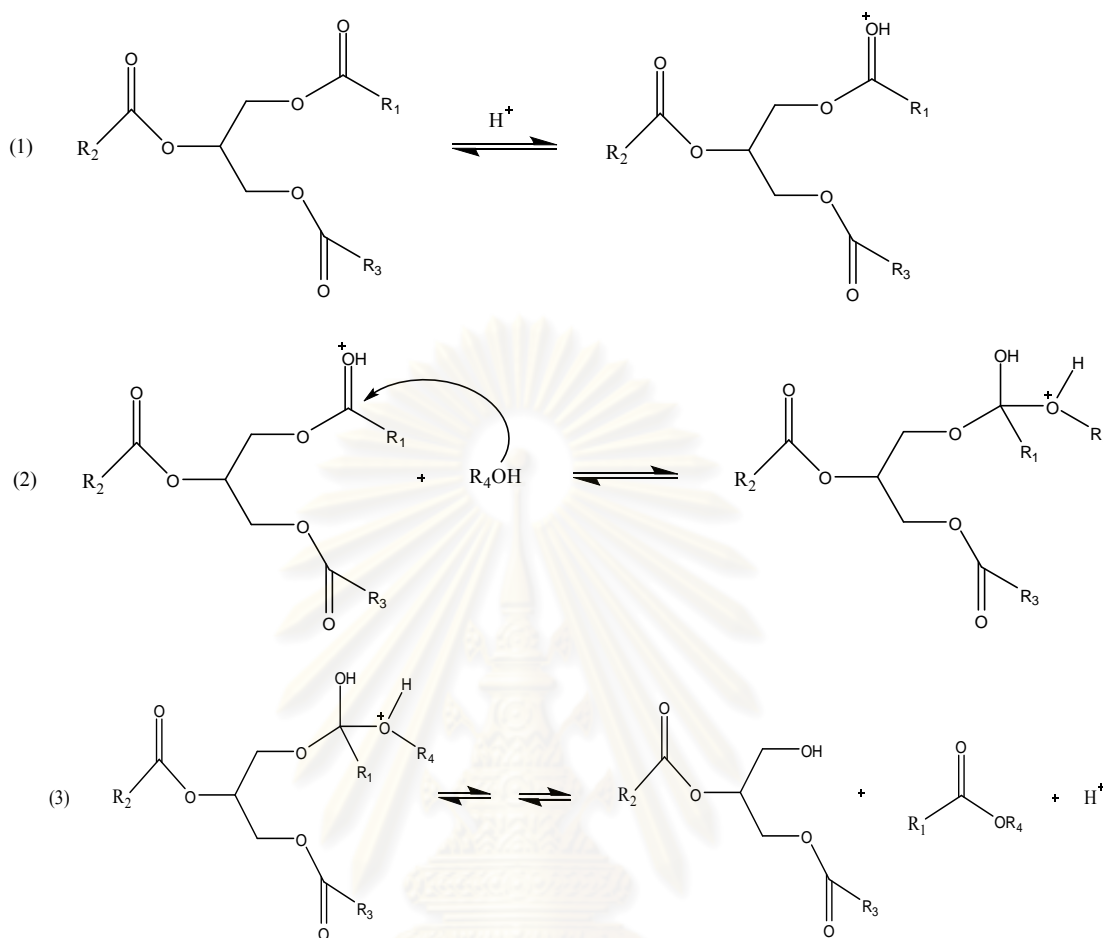
Figure 2.4 Mechanism of homogeneous acid-catalyzed reaction for transesterification of triglycerides (Lotero, E. et al., 2005)

2.4.2 Heterogeneous catalysis

Whereas traditional homogeneous catalysis offers a series of advantages, its major disadvantage is the fact that homogenous catalysts cannot be reused. Moreover, catalyst residues have to be removed from the ester product, usually necessitating several washing steps, which increases production costs. Thus there have been various attempts at simplifying product purification by applying heterogeneous catalysts, which can be recovered by decantation or filtration or are alternatively used in a fixed-bed catalyst arrangement. The most frequently cited heterogeneous alkaline catalysts are alkali metal- and alkaline earth metal carbonates and oxides (confer table 2.11).

Among the catalysts listed in table 2.11, the application of calcium carbonate may seem particularly promising, as it is a readily available, low-cost

substance. Moreover, the catalyst showed no decrease in activity even after several weeks of utilization (Marchetti, J.M., et.al). However, the high reaction temperatures and pressures and the high alcohol volumes required in this technology are likely to prevent its commercial application.

Table 2.11 Overview on heterogeneous catalysts (www.eppo.go.th)

Catalyst type	Examples
Alkali metal carbonates and hydrogen carbonates	Na_2CO_3, $NaHCO_3$ K_2CO_3, $KHCO_3$
Alkali metal oxides	K_2O (produced by burning oil crop waste)
Alkali metal salts of carboxylic acids	Cs-laurate
Alkaline earth metal alcoholates	Mixtures of alkali/alkaline earth metal oxides and alcoholates
Alkaline earth metal carbonates	$CaCO_3$
Alkaline earth metal oxides	CaO, SrO, BaO
Alkaline earth metal hydroxides	$Ba(OH)_2$
Alkaline earth metal salts of carboxylic acids	Ca- and Ba- acetate
Strong anion exchange resins	Amberlyst A 26, A 27
Zink oxides/ aluminates	
Metal phosphates	ortho-phosphates of aluminum, gallium or iron (III)
Transition metal oxides, hydroxides and carbonates	Fe_2O_3 ($+ Al_2O_3$), Fe_2O_3, Fe_3O_4, FeOOH, NiO, Ni_2O_3,$NiCO_3$, $Ni(OH)_2$ Al_2O_3
Transition metal salts of amino acids	Zn- and Cd-arginate
Transition metal salts of fatty acids	Zn- and Mn-palmitates and stearates
Silicates and layered clay minerals	Na-/K-silicate Zn-, Ti- or Sn- silicates and aluminates
Zeolite catalysts	Titanium-based zeolites, faujasites

2.4.3 Enzymes as catalysts

In addition to the inorganic or metallo-organic catalysts presented so far, also the use of lipases from various microorganisms has become a topic in biodiesel production. Lipases are enzymes which catalyze both the hydrolytic cleavage and the synthesis of ester bonds in glycerol esters. As compared to other catalyst types, biocatalysts have several advantages. They enable conversion under mild temperature-, pressure- and pH-conditions. Neither the ester product nor the glycerol phase has to be purified from basic catalyst residues or soaps. Therefore phase separation is easier, high-quality glycerol can be sold as a by-product, and environmental problems due to alkaline wastewater are eliminated. Moreover, both the transesterification of triglycerides and the esterification of free fatty acids occur in one process step. As a consequence, also highly acidic fatty materials, such as palm oil or waste oils, can be used without pre-treatment. Finally, many lipases show considerable activity in catalyzing transesterifications with long or branchedchain alcohols, which can hardly be converted to fatty acid esters in the presence of conventional alkaline catalysts. However, lipase-catalyzed transesterifications also entail a series of drawbacks. As compared to conventional alkaline catalysis, reaction efficiency tends to be poor, so that biocatalysis usually necessitates far longer reaction times and higher catalyst concentrations. The main hurdle to the application of lipases in industrial biodiesel production is their high price, especially if they are used in the form of highly-purified, extra cellular enzyme preparations, which cannot be recovered from the reaction products. One strategy to overcome this difficulty is the immobilization of lipases on a carrier, enabling the removal of the enzymes

from the reaction mixture and their reuse for subsequent transesterifications. Immobilization could furthermore be advantageous inasmuch fixed lipases tend to be more active and stable than free enzymes. Traditional carrier materials (such as anion exchange resins or polyethylene) can be replaced by renewable, readily available substances like corn cob granulate.

2.4.4 Transesterification without catalysts

Basically, transesterification of triglycerides with lower alcohols also proceeds in the absence of a catalyst, provided reaction temperatures and pressures

are high enough. Ester conversion surpassed 85% (m/m) after ten hours of reaction for non-catalytic methanolysis of soybean oil at 235°C and 62 bars. The advantages of not using a catalyst for transesterification are that high-purity esters and soap-free glycerol are produced. Especially in the last years reactions using supercritical methanol without any catalyst have been reported, however, the reaction conditions are very drastic. The high excess of methanol which has to be used during supercritical transesterification seems to make the process not economically feasible, however, a two-step process has been described, which in the first step hydrolyzes the glycerides into fatty acid with an excess of water, and in the second step esterification takes place, which requires lower amounts of methanol.

Table 2.12 Comparison of the different technologies to produce biodiesel
(Zhang, J.et al., 2008)

Variable	Base catalyst	Acid catalyst	Lipase catalyst	Supercritical alcohol	Heterogeneous catalyst
Reaction temperature (°C)	60-70	55-80	30-40	239-385	180-220
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters	Not sensitive
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence	-	Not sensitive
Yields of methyl esters	Normal	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Difficult	Easy	-	Easy
Purification of methyl esters	Repeated washing	Repeated washing	None	-	Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially cheaper

Table 2.13 Advantages and disadvantages at different types of catalysts used in the biodiesel production. (Leung, Y.C. et al., 2010)

Type	Example	Advantages	Disadvantages
Alkali Homogeneous	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest operation conditions	Low FFA requirement,anhydrous conditions,saponification, emulsion formation,more wastewater from purification, disposable
Heterogeneous	CaO, CaTiO$_3$, CaZrO$_3$, CaO–CeO$_2$, CaMnO$_3$, Ca$_2$Fe$_2$O$_5$, KOH/Al$_2$O$_3$, KOH/NaY, Al$_2$O$_3$/KI, ETS-10 zeolite, alumina/silica supported K$_2$CO$_3$	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost
Acid Homogeneous	Concentrated sulphuric acid	Catalyze esterification and transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity
Heterogeneous	ZnO/I$_2$, ZrO$_2$=SO$_{24}$, TiO$_2$=SO$_{24}$, carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, Nafion-NR50	Catalyze esterification and transesterification simultaneously, recyclable, eco-friendly	Low acid site concentrations, low microporosity, diffusion limitations, high cost
Enzymes	*Candida antarctica* fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, nonpolluting, easier purification	Expensive, denaturation

2.5 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 2.13 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.

Table 2.14 Comparison of fuel properties between diesel and biodiesel
(Tyson, K. S.et al., 2001)

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%	0.05 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

2.7 Literature reviews

2.7.1 Biodiesel production

Zhang and Jiang (2008), studied method for the production of biodiesel from *Zanthoxylum bungeanum* seed oil (ZSO). ZSO is widely used for its medicinal and flavor characteristics. It is especially used as a spice in indigenous kitchens in China. *Zanthoxylum bungeanum* seed has an estimated annual production potential of one million metric tons in China and it contains 27%–31% oil. Unfortunately, ZSO contains about 25% free fatty acids (FFA). This paper focused on the reaction parameters that affected the conversion of FFA in crude ZSO by means of acid-catalyzed esterification with methanol. It was found that the acid value of ZSO with high FFA would be reduced to less than 2 mg KOH/g in only one-step pretreatment of esterification using H_2SO_4 as catalyst. The combination of methanol-to-oil molar ratio 24:1, sulfuric acid 2%, temperature 60 ºC and reaction time 80 min, which reduced the acid value from 45.51 to less than 2 mg KOH/g, was selected as optimum for the acid-catalyzed esterification. The pretreated ZSO was used for alkali-catalyzed transesterification, and such process gave a yield of above 98% ZSO biodiesel. This one-step pretreatment reduced the production cost of the ZSO biodiesel.

Nakpong and Wootthikanokkhan (2010), studied production of biodiesel from high free fatty acid coconut oil. It was found that the FFA content in coconut oil was reduced from the initial value of 12.8 to 0.6% by acid-catalyzed esterification. The optimum condition of this step was methanol-to-oil ratio of 0.35 v/v catalyst concentration of 0.7% v/v of oil, reaction temperature of 60 ºC, and reaction time of 60 min. After that, the 0.6% FFA oil was transesterified with methanol using an alkaline catalyst. The optimum condition for this step was methanol-to-oil ratio of 0.4 v/v, catalyst (sulfuric acid)concentration of 1.5% w/v of oil, reaction temperature of 60 ºC, and reaction time of 60 min. The methyl ester content of the coconut biodiesel product was achieved at 98.4% w. From all of these results, therefore, the low cost coconut oil having 12.8% FFA has a high potential as a feedstock for biodiesel production. It can be recommended as supplementary oil feedstock for biodiesel production in Thailand if engine performance tests provide satisfactory results.

Naik, Meher and Das (2008), studied production of biodiesel from high free fatty acid Karanja (Pongamia pinnata) oil. Karanja oil is one of the potential oils with yearly production of 200 t (metric ton), out of which 6% is being presently utilized. The main production area for the Karanja oil is in the village level and villagers use this oil in some of their daily activities. This paper highlights the efforts made to develop biodiesel from Karanja oil, which is availablein rural India. The high FFA makes transesterification reaction difficult because of the formation of soap with alkaline catalyst. The alternative route of using acid catalyst was adopted for biodiesel production from Karanja oil. Mechanism of a dual process adopted for the production of biodiesel from Karanja oil containing FFA up to 20%. The first step is acid-catalyzed esterification by using 0.5% H_2SO_4, alcohol 6:1 molar ratio with respect to the high FFA Karanja oil to produce methyl ester by lowering the acid value, and the next step is alkali-catalyzed transesterification. The yield of biodiesel from high FFA Karanja oil by dual step process has been observed to be 96.6–97%.

Hayyan et al. (2011), studied the reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production. The optimum condition for reducing the free fatty acids (FFA) content from high content FFA (N23%) of sludge palm oil (SPO) to a minimum level for biodiesel production (N2%) are using 0.75% wt/wt of sulphuric acid with the molar ratio of methanol to oil of 8:1 for 60 min reaction time at 60 °C. The results showed that the FFA of SPO was reduced from 23.2% to less than 2%FFA. For transesterification with esterified SPO showedthe yield (ester) of biodiesel was 83.72% with the process conditions of molar ratio of methanol to SPO 10:1, reaction temperature 60 °C, reaction time 60 min, stirrer speed 400 rpm and KOH 1% (wt/wt).

Marchetti and Errazu (2008), studied biodiesel production by direct esterification reaction of triglycerides using model acid oil. The model acid oil was produced by mixing pure oleic acid with refined sunflower oil. Ethanol was used in the experiments instead of methanol since it is less toxic and safer to handle. Sulfuric acid was employed as catalyst because of its advantages compared with conventional homogeneous catalysts (NaOH). It found that, sulfuric acid is an attractive alternative

to produce biodiesel by direct esterification of a spent oil with high amounts of FFA compared with conventional technology using KOH as catalyst. The esterification process that has been studied shows that the amount of FFA was reduced from 10.684% to values around 0.54% w/w and the best operational conditions, are amount of catalyst = 2.261%, FFA = 10.684%, ratio of alcohol to acid oil = 6.126, Temperature= 55 1C, reaching a final conversion of 96%.

2.7.2 Biodiesel from waste oil

Bhatti et al. (2008), studied biodiesel production from waste chicken and mutton tallow. Waste tallow is a low cost sustainable potential feed stock for biodiesel production. Effect of various process parameters such as amount of catalyst, temperature and time on biodiesel production was investigated. Biodiesel produced from chicken and mutton fats using acid catalysis resulted in higher yield in comparison to base catalysis. Optimum amount of H_2SO_4, temperature and time were 1.25 g (on fat weight basis), 50 $^{\circ}$C and 24 hours for chicken fat, and 2.5 g (on fat weight basis), 60°C and 24 h for mutton fat. The evaluation of transesterification process was followed by gas chromatographic analysis of tallow fatty acid esters. A total of 98.29% and 97.25% fatty acids were identified in chicken and mutton fats, respectively. Both fats were found highly suitable to produce biodiesel with recommended fuel properties. Results of present study clearly demonstrated that the use of chicken and mutton fats is very suitable as low cost feed stocks for biodiesel production.

Farag et al. (2011), studied factors affecting esterification of mixed oil with high percentage of free fatty acid. The oils contain high levels of FFAs, it cannot be directly used with the base catalysts currently employed. Acid esterification reduces the FFAs content to the desirable level. The major factors that affected the conversion efficiency of the process are molar ratio of alcohol/oil, amount of catalyst, reaction temperature, catalyst type and stirring speed according to reaction duration and used a model acid produced by mixing pure oleic acid with mixed oil (50% sunflower+50% soybean oil). Methanol was used in the experiments due to its low cost. The best

conversion efficiency obtained was 96.6% for a molar ratio of 6:1 at a temperature of 60 °C, 2.5% H_2SO_4 and stirring speed of 300 rpm.

Giannelos et al. (2005), studied physical, chemical and fuel related properties of tomato seed oil for evaluating its direct use in diesel engines. Tomato seeds by-product accounts for approximately 10% of the fruit and 60% of the total tomato industry waste, respectively. It had a low sulphur (0.004%) and low ash content (0.034%). Tomato oil exhibited poor cold flow properties (cloud point and pour point) and high density (0.9151kg/l), high iodine value (124.0) and high kinematic viscosity (28.0 mm^2/s) compared to diesel fuels. The cetane number of tomato oil was similar to the other vegetable oils(Com, Cottonseed, Peanut, Rapeseed, Sesame, Soya bean and Sunflower) used as alternative fuels and its energy content was slightly lower compared to these oils. Because of problems related to the low volatility, high viscosity and the reactivity of unsaturated fatty acid chains, engine tests should be carried out with tomato seed oil in order to evaluate the effect on the diesel engine performance and emissions.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipments

3.1.1 Chemicals

1. Methanol (MeOH); analytical grade
2. Isopropanol (IPA); analytical grade
3. Hexane; analytical grade
4. Phenolphthalein indicator solution
5. Sodium hydroxide
6. carbontetrachloride, CCl_4
7. Wijs solution (Dissolve 16.2 g iodine monochloride (ICl) in a 1 L of volumetric flask with glacial acetic acid. Store the Wijs solution in amber bottle sealed with paraffin until it is use.)
8. Potassium iodide (KI)
9. Borontrifluoride in methanol
10. conc. H_2SO_4
11. Vanillin solution (containing vanillin (1%) and conc.H_2SO_4 (4.6%) in ethanol)
12. Chloroform-d ($CDCl_3$); NMR spectroscopy grade
13. Anhydrous Na_2SO_4

3.1.2 Equipments

1. Hotplate stirrer with magnetic stirrer set
2. Thermometer
3. Vessel vial
4. Round bottom flask
5. Volumetric flask

6. Erlenmeyer flask
7. Beaker
8. Soxhlet apparatus
9. Condenser
10. Water bath
11. Filter paper
12. Centrifuge
13. Rotary evaporator
14. Buchner funnel

3.2 Extraction process

Tomato seeds (TS) were a by-product of tomato paste manufacturing industry. In this study, the tomato seeds were collected from a Srichiengmai industry which located in Nong Khai province . TS were collected for this research in March (2010) and January (2011).

Tomato seeds and pulp were separated in water. The seeds were cleaned and sun-dried for 3 days. Dried seeds were milled and dried. Effect of temperature and time on dryness of the seeds was studied and percentage of weight loss was calculated.

$$\text{Percentage of weight loss} = ((IW-AW)/IW) * 100$$

$$IW = \text{initial weight}$$

$$AW = \text{actual weight}$$

After tomato seeds were dried at temperature 40-110ºC for 10 hours, dried tomato seeds were demoisturized by silica gel in desiccator until weight was constant.

Ground dried tomato seed were extracted in solvent (MeOH and hexane). Extraction process of tomato seed oil was carried out under refluxing in solvents with and without soxhlet apparatus. The solvent was removed by rotary vacuum evaporation and tomato oil was collected. The percentage yield was calculated on a dried weight basis.

3.3 Determine properties of tomato seed oil

Fatty acid compositions was determined by gas chromatography (EN 14103) and % free fatty acid was determined by ASTM D5555 and integration of ^{1}H NMR spectrum (Jitendra, K. et al ., 2009)

3.3.1 Fatty acid compositions (EN 14103)

Fatty acid composition of tomato seed oil was determined using gas chromatography with FID detector (Varian CP3800). The sample for GC analysis was prepared by adding tomato seed oil (about 0.2 g) into a screw-capped glass tube and 1 ml of BF$_3$/methanol is added. Then heat in boiling water (or at 100°C in a sand bath) for 2 hours. After cooling, add 1 ml water and 1 ml hexane, centrifuge at low speed and collect the upper phase. The solution is ready for injection in the gas chromatograph, using helium as carrier gas. The sample (tomato seed oil, 1.0 µl) was injected in to the system at 220 °C injector temperature.

3.3.2 % free fatty acid (ASTM D5555)

Use Table 3.1 to determine the quantities to be used with various ranges of fatty acids. The sample shall be entirely liquid and well mixed before weighing. Then weigh the designated sample size into an oil-sample bottle or Erlenmeyer flask; add to that the specified amount of hot, neutralized alcohol and 2 ml of indicator (Phenolphthalein Indicator Solution). Shaking vigorously, make the titration with alkali to the appearance of the first permanent pink color of the same intensity as that of the neutralized alcohol before adding the sample. The color shall persist for 30 seconds.

TABLE 3.1 Suggested quantity of material to test

Sample, g	Isopropanol, mL	Normality of Alkali	Free Fatty Acid Range (%)
56.4 ± 0.2	50	0.1	0.0 to 0.2
28.2 ± 0.2	50	0.1	0.2 to 1.0
7.05 ± 0.05	75	0.25 or 1.0	1.0 to 30.0
7.05 ± 0.05	100	1.0	30.0 to 50.0
3.525 ± 0.001	100	1.0	50.0 to 100.0

3.3.3 % free fatty acid by integration (Jitendra, K. et al., 2009)

The area (AFFA) of the unmerged peak of the FFA triplet (appearing around 2.38 ppm. out of the ester triplet) can be determined by integration of the spectral region 2.37-2.41 ppm. The triplet appears with an intensity ratio of 1:2:1. The total area corresponding to the R-CH2 groups of the FFA, will thus, be four times the area of the single unmerged FFA peak around 2.38 ppm. The total area corresponding to R-CH2 of both FFA and ester can be determined by integrating the spectral region 2.20-2.41 ppm. The concentration of FFA (wt %) in oil or biodiesel is thus

$$\% \text{ of FFA} = 4 \times \frac{\text{Area of unmerged peak of R-CH}_2 \text{ of FFA}}{\text{Total area of R-CH}_2 \text{ of both FFA and ester}} \times 100$$

3.4 Biodiesel production

3.4.1 Direct biodiesel production

Tomato seeds (100 g) were placed in soxhlet apparatus and the soxhlet was equipped with round bottom flask and condenser. A solution of conc. H_2SO_4 in methanol (400 ml) was added to the round bottom flask and then heated at temperature 65°C for 10 hours. The reaction was monitored by TLC developed by hexane:ethylactate (90:10 v/v) and visualized by vanillin/H_2SO_4 solution. After cooling down to room temperature the reaction mixture was evaporated and transferred to separatory funnel. The product in separatory funnel was washed with hot water four times and dried over anhydrous sodium sulphate. The variables including the amount of catalyst (0.5%-4%) and reaction time (4-10 hours) were studied.

Methyl ester composition (or % FAME) of biodiesel produced from tomato seed 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 micre-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. (EN14103).

Thin layer chromatography (TLC) was also used to indicate the extent of esterification. TLC was performed on aluminium sheet coated with silica gel 60F$_{254}$ (Merck) and hexane:ethyl acetate (90:10) was used as a mobile phase.

In this study, the purity of biodiesel product from tomato seed oil was denoted by its %FAME and flash point. Percentage of product was defined as the weight percentage of the final product (esterified and purified oil) relative to the weight of oil at the start (Eq. (1)). It, in fact, indicated the final results of the competition between the main reaction (esterification) producing methyl ester and side reactions (methanol-water or saponification) influencing the ester yield.

$$\text{Percentage of product} = \frac{\text{weight of product}}{\text{weight of raw oil}} \times 100 \qquad (1)$$

3.4.1.1 Optimization of process parameter

1. Effect of sulfuric acid quantity on the esterification

The effect of sulfuric acid on biodiesel production from tomato seed oil was investigated at amount of conc.H$_2$SO$_4$ ((0.5 to 4.0 wt%) (based on the weight of tomato seed oil)). The operation condition during the whole reaction process was fixed at reaction temperature of 65°C, reaction time of 10 hours and excess methanol. Results are given in Section 4

2 Effect of reaction time

In this section, the effect of reaction time on amount of FAME and % free fatty acid of the product was investigated at reaction time varying from 4-10 hours. The operation condition during the whole reaction process were fixed at reaction temperature 65 $^{\circ}$C, methanol(400ml) and catalyst concentration 0.5-4 wt% (based on the weight of tomato seed oil). Results are given in Section4.

3.4.2 Biodiesel from tomato seed oil

The 20 g of tomato seed oil was poured into a round-bottomed flask equipped with a reflux condenser and heated to the reaction temperature (60°C). A solution of conc. H$_2$SO$_4$ in methanol was preheated at 60ºC and added to the flask. The mixture was stirred at the same speed of 600 rpm for all test runs. The reaction

was monitored by TLC developed by hexane:ethylactate (90:10 v/v) and visualized by vanillin/H_2SO_4 solution. After the reaction, the solvent was evaporated under vacuum at 50 ºC with a rotational evaporator and the mixture was allowed to settle in a separatory funnel. The product in separatory funnel was washed with hot water four times and dried over anhydrous sodium sulphate.

The variables including the amount of catalyst ((0.5%-4%)(based on the oil weight of tomato seed oil)) and reaction time (4-10 hours) and methanol-to-oil molar ratio (4:1-100:1) were studied.

The composition of methyl ester (or % FAME), thin layer chromatography (TLC), flash point and product yield were analyzed.

3.4.2.1 Optimization of process parameter

1. Effect of a molar ratio of methanol and tomato seed oil

In this section, study the effect of molar ratio on ester content and % free fatty acid of the transesterification of tomato seed oil was investigated with its molar ratio of methanol to tomato seed oil varying from 4:1 to 100:1. The operation condition during the whole reaction process was fixed at reaction temperature 60 $^\circ$C, reaction time 5 hours and catalyst concentration 2 wt% (based on the weight of tomato seed oil). Results are given in Chapter 4.

2. Effect of acid quantity of conc.H_2SO_4 on the biodiesel production

The effect of catalyst concentration on biodiesel production from tomato seed oil was investigated at concentration varying from 0.5 to 4.0 wt% (based on the weight of tomato seed oil). The operation condition during the whole reaction process was fixed at reaction temperature of 60°C, reaction time of 5 hours and molar ratio methanol to oil 4:1 to 100:1. Results are given in Chapter 4.

3. Effect of reaction time

The effect of reaction time on biodiesel production from tomato seed oil was investigated at reaction time varying from 0.5-10 hours. The operation condition during the whole reaction process was fixed at reaction temperature 60°C, molar ratio methanol to tomato seed oil 90:1 and catalyst concentration 0.5-4 wt% (based on the weight of tomato seed oil). Results are given in Chapter 4.

Figure 3.1 Soxhlet extraction

Figure 3.2 Refluxing

3.5 Direct biodiesel production in ethanol

   3.5.1 Effect of alcohol type

   Tomato seed oil with methanol and dry ethanol were conducted at 65ºC and 70ºC, respectively. Ethanol was freshy distilled from magnesium ethanolate under argon (Brian S., F. et al., 1989). The reaction mixture consisted at 400 ml of alcohol, 100g of dry tomato seed and 4% of conc.H_2SO_4 (based on tomato seed oil weight). The operation condition during the whole reaction process was fixed at reaction time 10 hours

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Extraction process

Tomato seeds collected in March (2010) and January (2011) were compared their quality and property of tomato seed oil. The seeds collected in March (2010) and January (2011) were obtained from tomatoes in varieties as shown in Table 4.1.

Table 4.1 Species of tomato seed in March (2010) and January (2011)

	Tomato seed	
	March (2010)	January (2011)
species	DELTA	DELTA
	BETA	Peto 94
	TW 4	

The seeds were cleaned and sun-dried for 3 days. After that dried seeds were milled and dried in oven. Figure 4.2 and 4.3 showed percentage of weight loss of dried tomato seeds collected in March (2010) and January (2011) respectively.
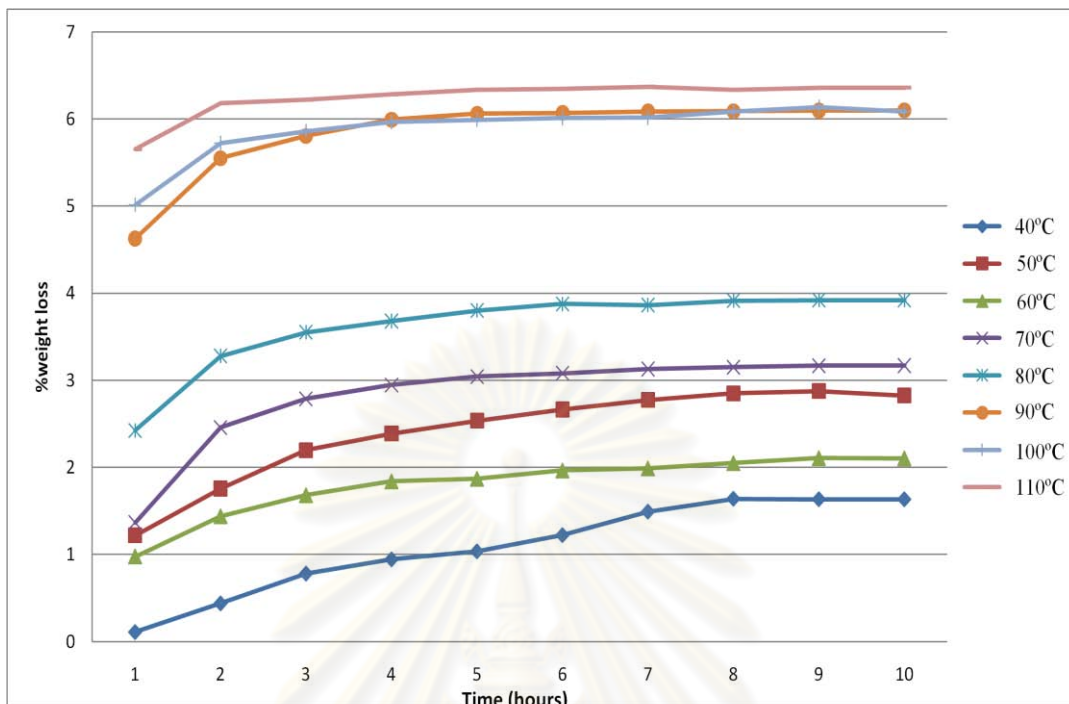
Figure 4.1 The percentage of weight loss of tomato seed in March (2010)
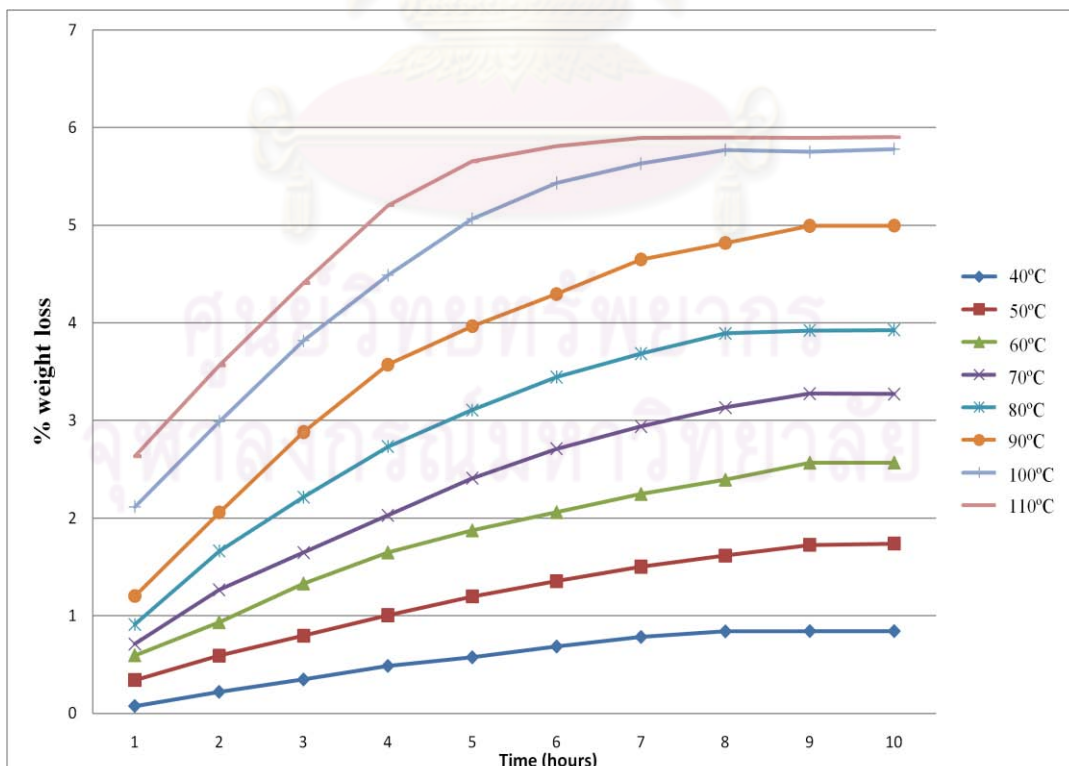

Figure 4.2 The percentage of weight loss of tomato seed in Jauary (2011)

From the Figure 4.1 and 4.2 tomato seeds (TS March and TS January) were dried at temperature 40-110ºC. The percentage of weight loss was calculated every hour. It showed that the percentage of weight loss of tomato seeds in March 2010 was increased when increasing temperature and time. When the tomato seeds were heated at temperature 40, 50, 60, 70, 80, 90, 100 and 110 ºC for 8 hours, the percentage of weight loss was relatively constant. Therefore the seeds obtained in January 2011 were dried for 8 hours before extraction for biodiesel production.

While tomato seeds in January 2011, the percentage of weight loss at temperature 40, 50, 60, 70, 80, 90, 100 and 110 ºC were relatively constant after heat for 9 hours. Therefore the seeds were dried for 9 hours before extraction for biodiesel production.

4.1.1 Effect of moisture

In extraction process, after tomato seeds were dried at temperature 40-110ºC for 8 hours (TS in March 2010) and for 9 hours (Ts in January 2011), the seeds were demoisturized by silica gel in desiccator until weight constant. The percentage of weight loss, oil content and %FFA were calculated and the results were shown in figure 4.3-4.4
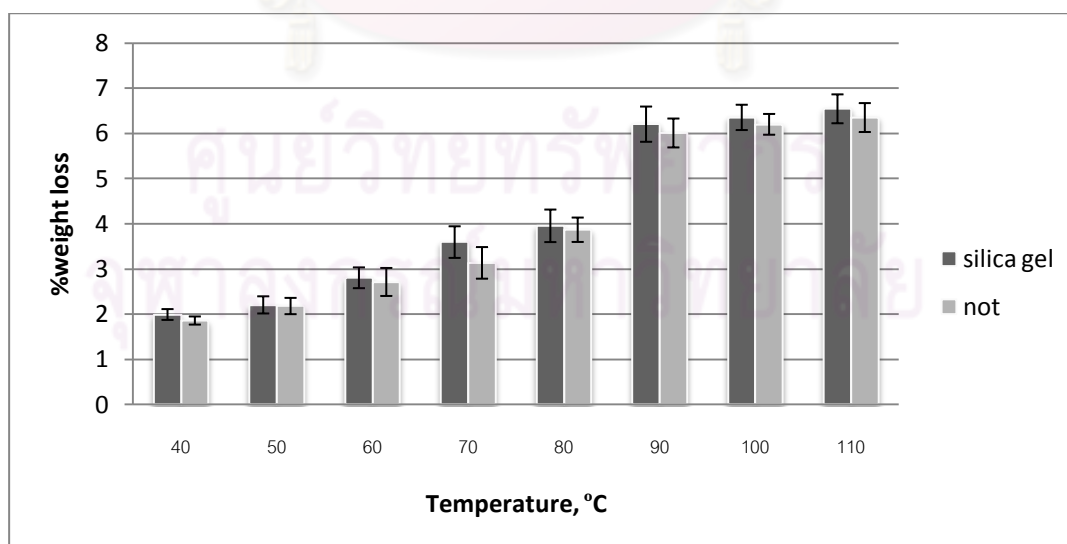

Figure 4.3 The percentage of weight loss during demoisturized with and without silica gel in desiccator (TS March 2010)
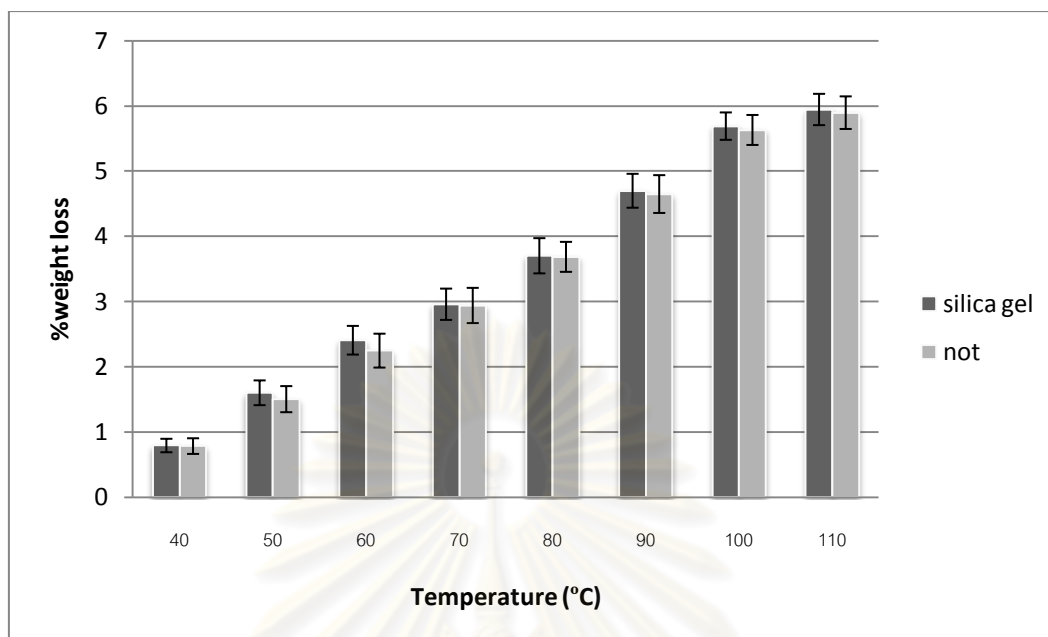
Figure 4.4 The percentage of weight loss during demoisturized with and without
silica gel in desiccator (TS January 2011)

From the Figure 4.3 and 4.4, the percentage of weight loss of dried tomato
seed kept in desicator with and without silica gel. The result showed that the
demoisturizing with silica gel in desiccator have no effect on the percentage of weight
loss of tomato seed.

4.1.1.1 Extraction with and without soxhlet apparatus in MeOH

Dried tomato seeds were extracted with and without soxhlet
apparatus in MeOH. The percentage of oil content and free fatty acid were calculated.
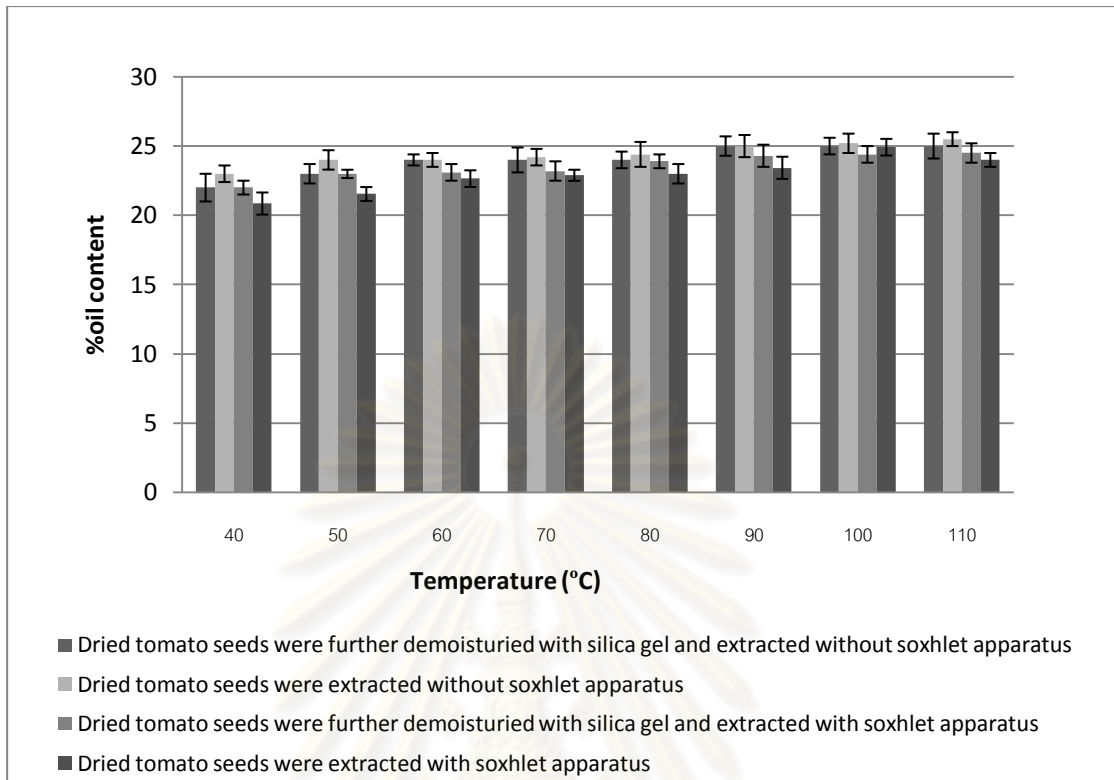
Figure 4.5 Percentage of oil content of tomato seeds (TS 2010) extracted with MeOH with and without soxhlet apparatus
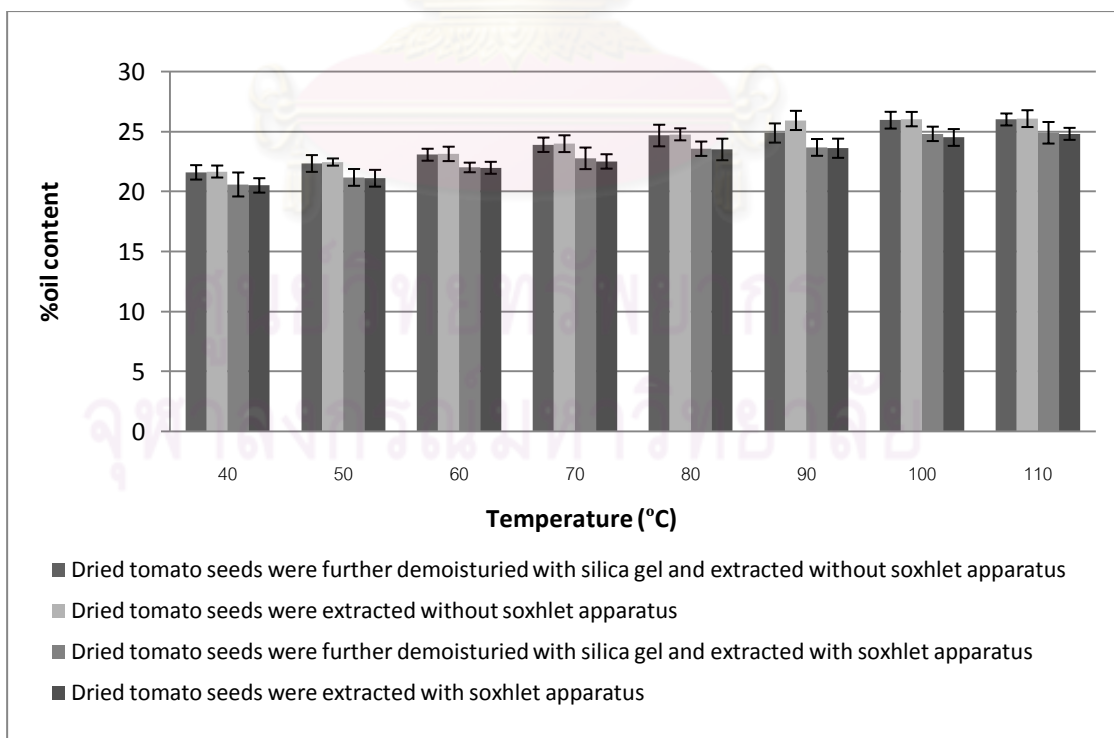

Figure 4.6 Percentage of oil content of tomato seeds (TS 2011) extracted with MeOH with and without soxhlet apparatus
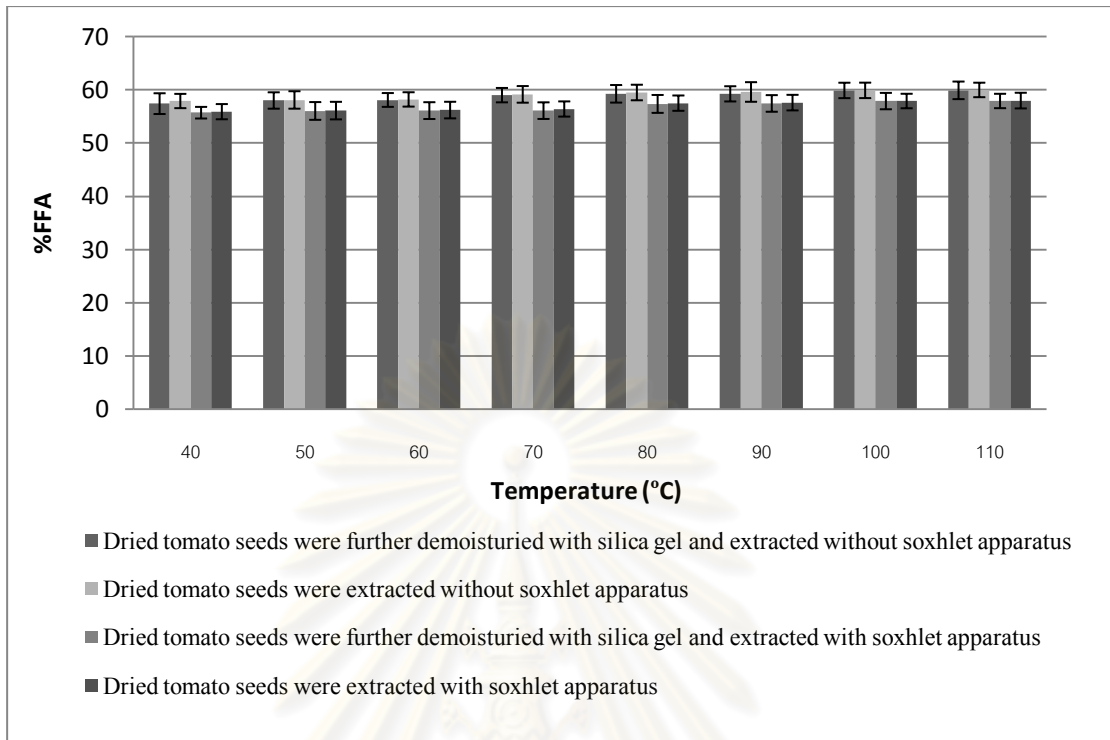
Figure 4.7 Percentage of FFA of tomato seeds (TS 2010) extracted with MeOH
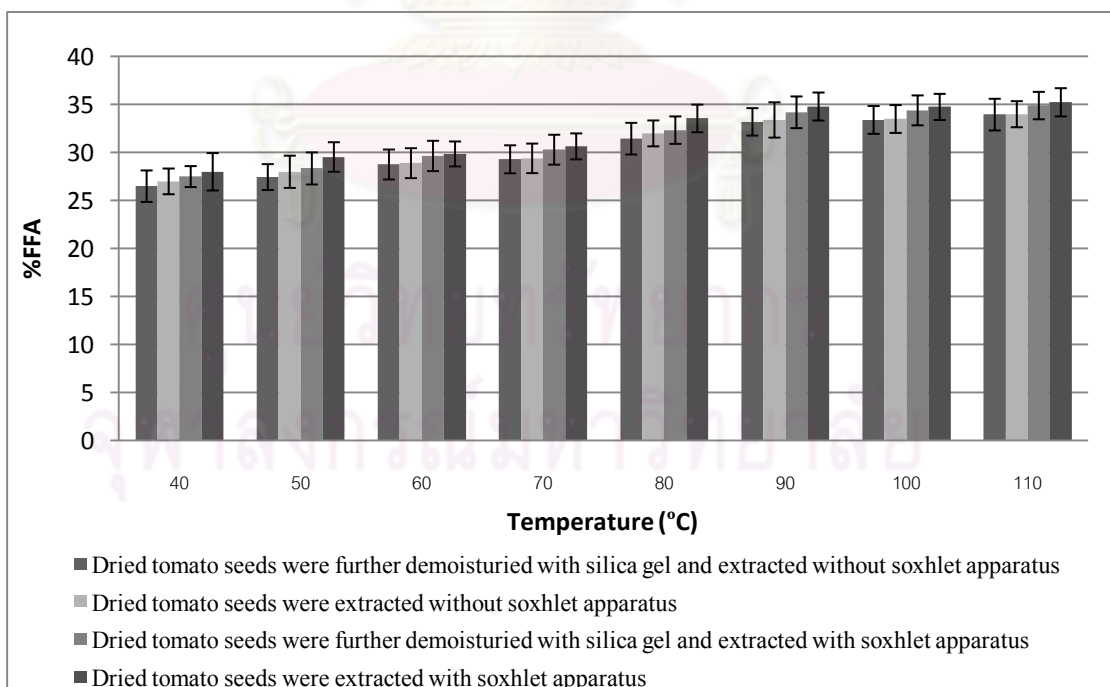
with and without soxhlet apparatus

Figure 4.8 Percentage of FFA of tomato seeds (TS 2011) extracted with MeOH

with and without soxhlet apparatus

From the Figure 4.5 and 4.6, oil content of tomato seed in March (2010) and January (2011) was calculated. The result showed that the moisture content and extraction process did not affect on oil content.

Percentage of free fatty acid was analyzed by ^{1}H-NMR shown in Figure 4.7 and 4.8. The result showed that the moisture content and extraction process did not affect on percentage of free fatty acid. Therefore, tomato seed unneeded to demoisturize with silica gel in desiccator.

4.1.1.2 Extraction with and without soxhlet apparatus in hexane

Dried tomato seeds were extracted with hexane with and without soxhlet apparatus. The percentage of oil content and free fatty acid were calculated.
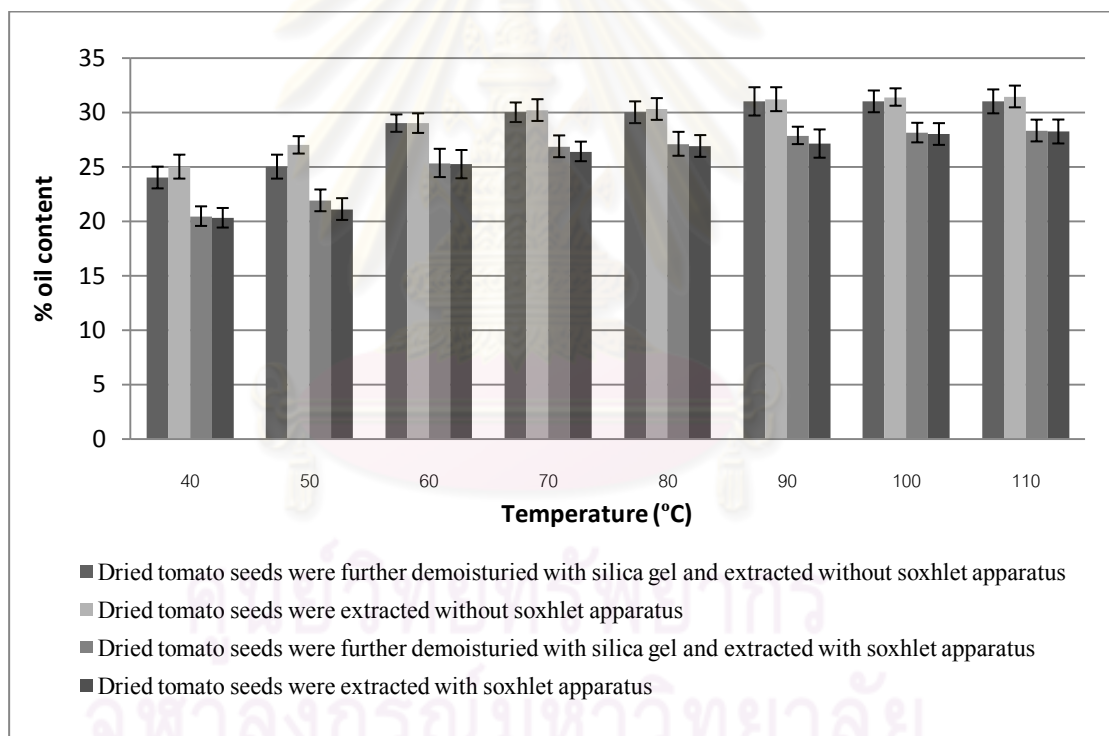

Figure 4.9 Percentage of oil content of tomato seeds (TS 2010) extracted with hexane with and without soxhlet apparatus
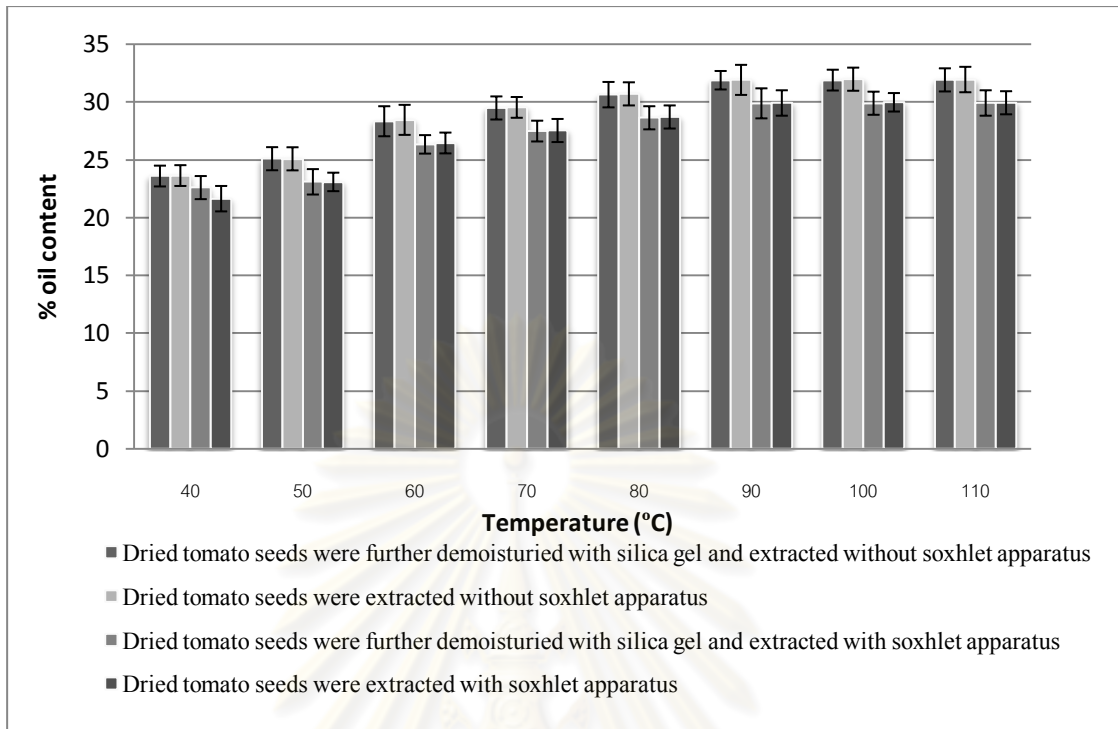
Figure 4.10 Percentage of oil content of tomato seeds (TS 2010) extracted with
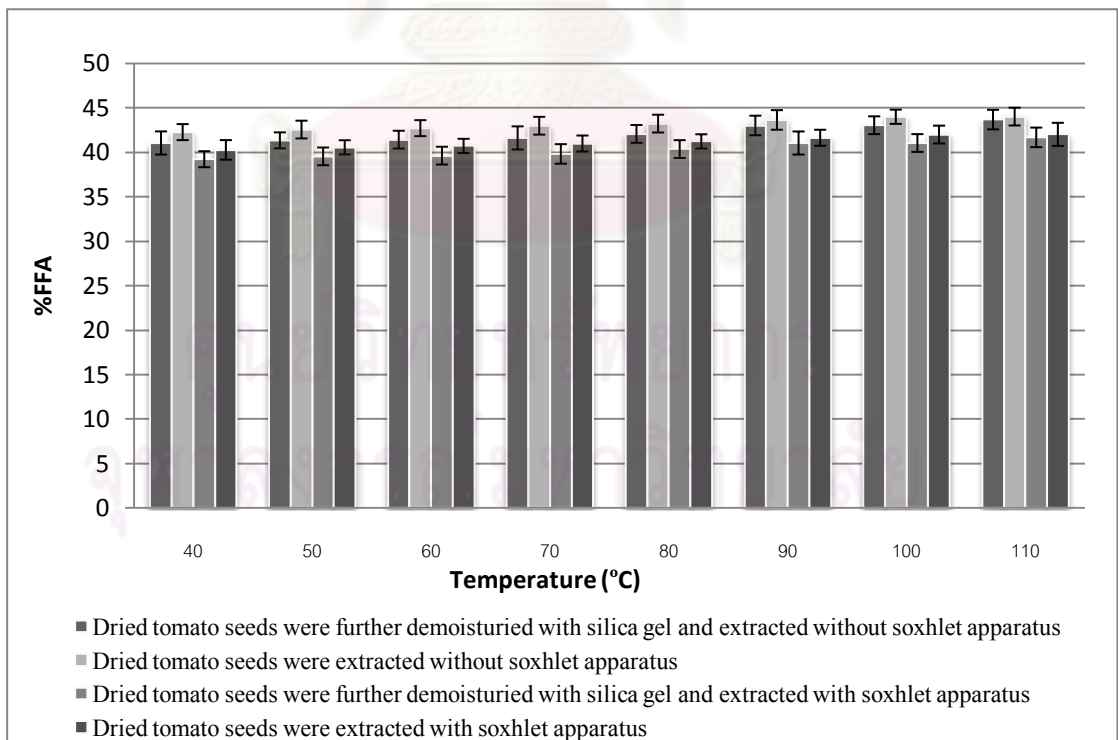hexane with and without soxhlet apparatus

Figure 4.11 Percentage of FFA of tomato seeds (TS 2010) extracted with hexane
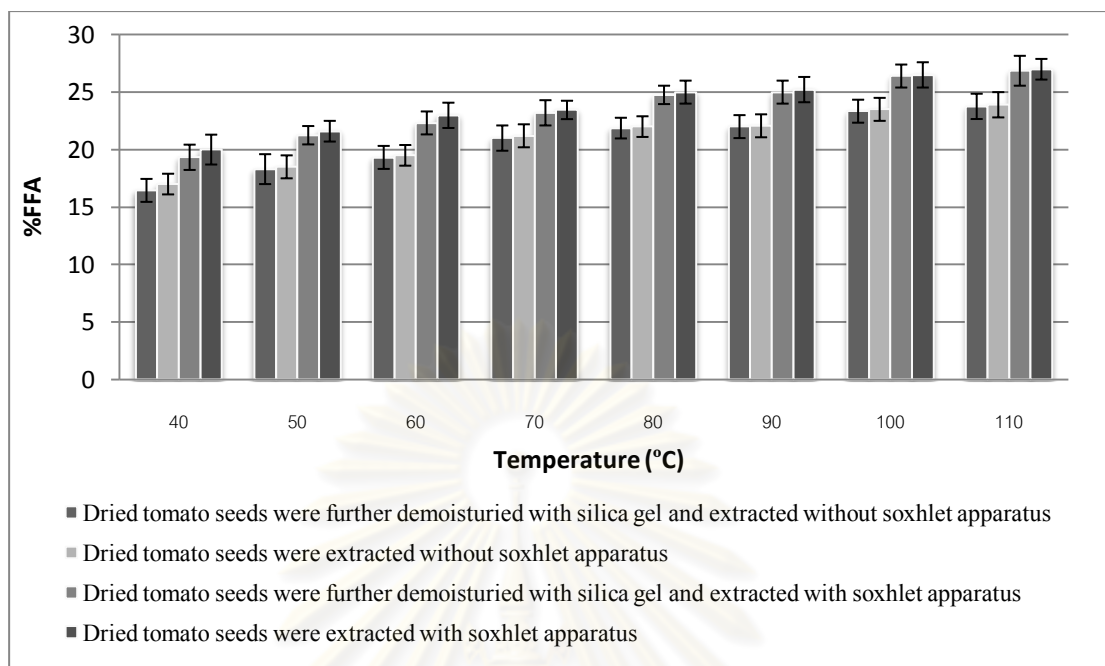with and without soxhlet apparatus

Figure 4.12 Percentage of FFA of tomato seeds (TS 2011) extracted with hexane
with and without soxhlet apparatus

Similar to extraction with MeOH with and without soxhlet apparatus, the moisture content and extraction process did not affect for oil content and percentage of free fatty acid. Therefore before extraction, tomato seed unneeded to demoisturize with silica gel in desiccator.

4.2 Compositions of tomato seed oil

The compositions of free fatty acid (FFA) of tomato seed oil were determined by EN 14103. The percentage of fatty acid and the average molecular weight of tomato seed oil (TS March 2010 and TS January 2011) that was extracted with methanol and hexane showed in table 4.2. (see detail in Appendix B)

The results (Table 4.2) indicated that oleic acid and linolenic acid were major components. The percentage of linoleic acid, oleic acid, palmitic acid, stearic acid, linolenic acid, eicosanoic acid and myristic acid were 54%, 23%, 13%, 5%, 0.14% and 0.16% respectively. The total of saturated fatty acid and unsaturated fatty acid were 80.26% and 19.74% respectively.

Table 4.2 Compositions of fatty acids in tomato seed oil

Compositions of tomato seed oil	%fatty acid (TS March,2010)		%fatty acid (TS January,2011)	
	MeOH	Hexane	MeOH	Hexane
Myristic acid	0.14	0.1489	0.1462	0.1491
Palmitic acid	13.8581	13.8907	13.7470	14.6368
Stearic acid	5.2921	4.9534	4.9881	3.3494
Oleic acid	23.6759	23.3997	23.2784	23.9559
Linoleic acid	54.1080	54.5830	54.5938	54.5247
Linolenic acid	2.3233	2.3823	2.5019	2.5594
Eicosanoic acid	0.1679	0.2777	0.3537	0.3309
M_{FFA} g/mol	283.1172	277.7010	277.8752	277.4767

*M_{FFA}: Calculated molecular weight of fatty acid

4.3 Two step extraction

Oil obtained from extraction of tomato seeds with methanol and hexane for 3 hours comprised of high amount of free fatty acid. From ^{1}H-NMR analysis, oil obtained from extraction of tomato seeds in March 2010 and January 2011 with methanol as a solvent, comprised of free fatty acid 57.5% and 33%, respectively. While extraction with hexane gave oil containing 40% and 23% of free fatty acid, respectively. Due to high FFA content of tomato seed oil, biodiesel production using basic catalyst process was disadvantageous. High FFA content will react with catalysts to produce soaps which will inhibit the tranesterification for biodiesel production and the large amount of soap can result in gel and also prevent the separation of the glycerol from the ester. Therefore reduction of free fatty acid before producing biodiesel by two step extraction process with methanol and with hexane was investigated.

Table 4.3 Two step extraction (TS 2010)

		Sucessive extraction with MeOH and hexane					
		MeOH 3h	Hexane 2h	MeOH 1h	Hexane 2h	MeOH 0.5h	Hexane 2h
TS March 2010	oil content	25.22	6.61	19.42	12.35	18.16	13.56
	%FFA	57.2	15.23	53.76	18.54	50.04	22.9
Total oil (%)		31.83		31.77		31.72	
Total FFA		72.43		72.30		72.94	

Table 4.4 Two step extraction (TS 2011)

		Sucessive extraction with MeOH and hexane					
		MeOH 3h	Hexane 2h	MeOH 1h	Hexane 2h	MeOH 0.5h	Hexane 2h
TS January 2011	oil content	19.52	12.7	15.92	16.08	13.98	18.51
	%FFA	33.27	8.95	30.03	12.5	27.53	16.06
Total oil (%)		32.22		32.00		32.49	
Total FFA		42.22		42.53		43.59	

Percentages of free fatty acid analyzed by ^{1}H-NMR and oil content were shown in Table 4.3 and Table 4.4. The results showed that extraction of tomato seeds with methanol and with hexane, respectively can reduce percentage of free fatty acid when increasing time for extraction with MeOH. Tomato seed in January 2011, %FFA was reduced from 33.27% to 8.95% after extraction with methanol 3 hours and with hexane 2 hours, respectively. It gave oil content 19.52% (extracted with MeOH 3 hours) and 12.70% (extracted with hexane 2 hours). As for tomato seed in March2011, %FFA was reduced from 57.2% to 15.23% after extraction with methanol 3 hours and with hexane 2 hours, respectively. It gave oil content 25.52% (extracted with MeOH 3 hours) and 6.61% (extracted with hexane 2 hours).

From the data, the extraction tomato seed with methanol and with hexane, respectively can reduce percentage of free fatty acid when increasing time for extraction with MeOH but it gave low oil content.

4.4 Biodiesel production

4.4.1 Direct biodiesel production of tomato seeds obtained in March 2010

4.1.1.1 Optimization of process parameter

1 Effect of catalyst concentration

In the process of biodiesel production, reaction temperature, methanol quantity and catalyst concentration were found to be significant operating parameters, which are closely associated with energy costs from an economic perspective. In the esterification reaction, biodiesel was performed at 65°C using 400 ml of methanol, tomato seeds dry 100 g and reaction time 10 hours.
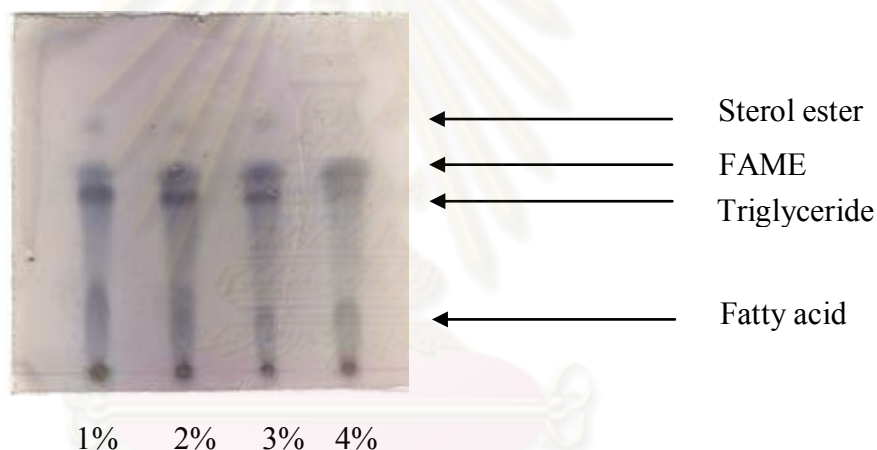

Figure 4.13 TLC chromatogram of biodiesel produced by using 1, 2, 3 and 4 % of catalyst (based on tomato seed oil weight).

The products from reaction with 1, 2, 3 and 4 % of catalyst (base on tomato seed oil weight) for 10 hours were analyzed by TLC and TLC chromatogram was shown in Figure 4.13. The changes in product compositions with reaction time and the distribution of various components in the reaction system can be clearly seen. TLC analysis and ^{1}H-NMR data of the reaction (Figure 4.13 and Figure 4.14, respectively) showed that most of free fatty acids were converted to FAME at reaction time 10 hours and the conversion was increased when increasing amount of catalyst. Using 4% sulfuric acid (based on tomato seed oil weight) as catalyst for 10 hours the highest conversion was obtained.

Percentage of FFA in biodiesel was analyzed by ^{1}H-NMR and the results were shown in Figure 4.14. After increased concentration of conc.H_2SO_4 from 1% to 4% and reaction time 10 hours, %FFA was reduced to 0.98. Therefore, the optimal reaction time was 10 hours, 4% of conc.H_2SO_4 (based on tomato seed oil weight) and 400 ml of methanol can reduce %FFA to less than 1%.
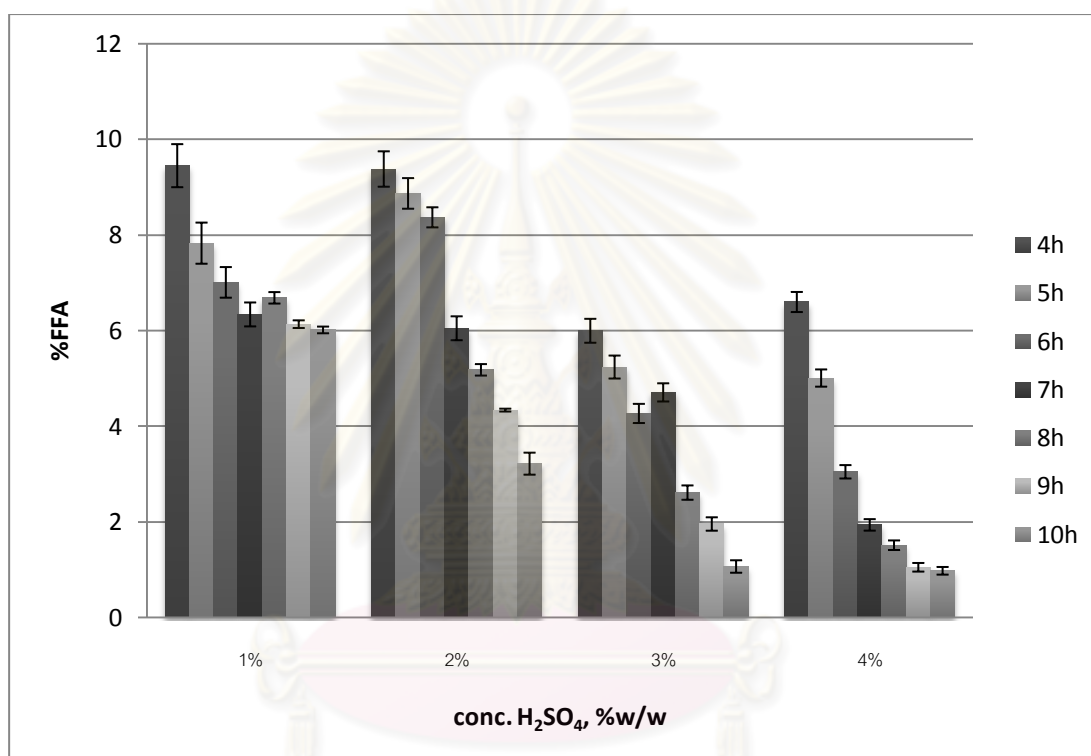

Figure 4.14 The percentage of free fatty acid in biodiesel produced from tomato seed oil at 1 - 4% sulfuric acid during reaction time 4, 5, 6, 7, 8, 9 and 10 hours using 400 ml of methanol.

2. Effect of reaction time

The effect of reaction time 4, 5, 6, 7, 8, 9, and 10 hours was investigated at temperature 65ºC and 1-4% of conc.H_2SO_4. The reactions were monitored by ^{1}H-NMR analysis. It was observed that the ester yield slightly increased with reaction time. Results obtained from the present experiments with tomato seed oil revealed that, about 10 hours of reaction is sufficient for biodiesel production.
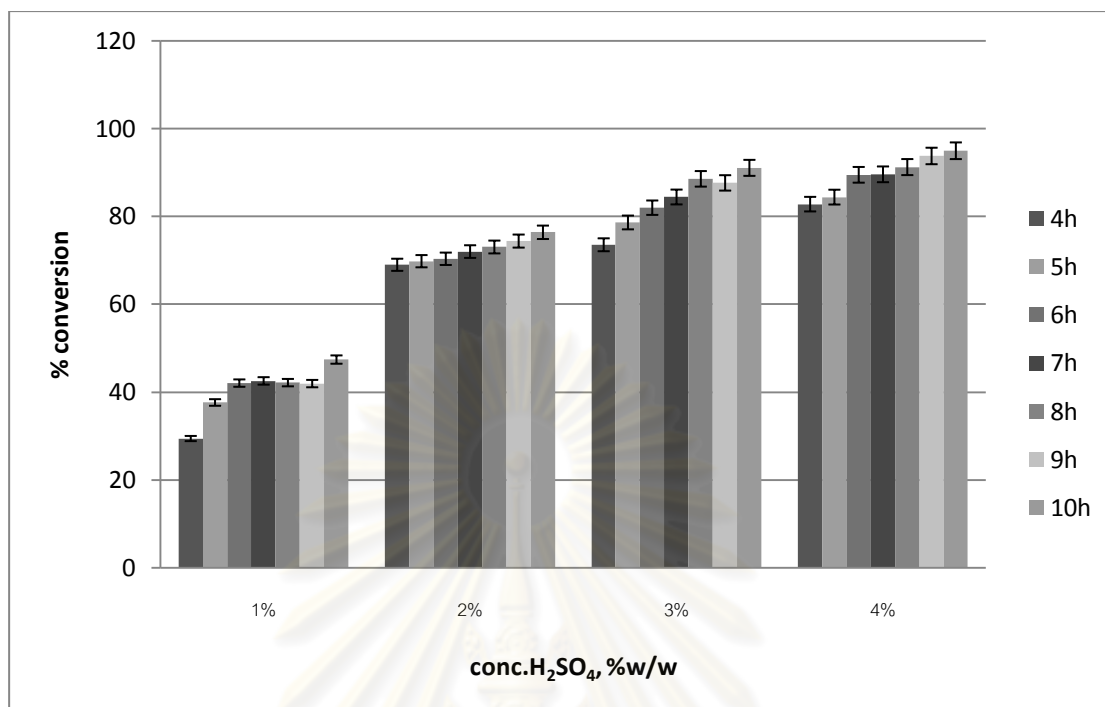
Figure 4.15 Conversion of biodiesel produced from tomato seed oil at 1 - 4%
sulfuric acid during reaction time 4, 5, 6, 7, 8, 9 and 10 hours using 400 ml of
methanol.

^{1}H-NMR analysis conversions into FAME were shown in Figure 4.15. At
difference catalyst concentration and reaction time, the highest percentage of methyl
ester (94.95%) was obtained from the reaction which using 4% of sulfuric acid and
reaction time 10 hours. Also reaction time 8 and 9 hours gave high conversion more
than 90%. The conversion was increased when increasing reaction time and catalyst
concentration. Therefore, the optimal reaction time was 10 hours.

4.4.2 Direct biodiesel production (TS January 2011)

4.4.2.1 Optimization of process parameter

1. Effect of catalyst concentration

In the process of biodiesel production, reaction temperature, methanol quantity and catalyst concentration were found to be significant operating parameters, which are closely associated with energy costs from an economic perspective. In the esterification reaction, biodiesel was performed at $65^{\circ}C$ using 400 ml of methanol, tomato seeds dry 100 g and reaction time 10 hours.
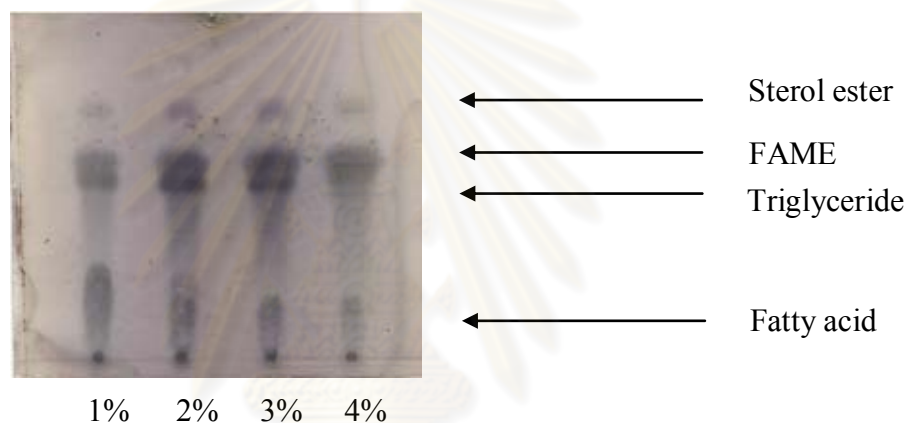

Figure 4.16 TLC chromatogram of biodiesel produced by using 1, 2, 3 and 4 % of catalyst (based on tomato seed oil weight).

The products from reaction with 1, 2, 3 and 4 % of catalyst (base on tomato seed oil weight) for 10 hours were analyzed by TLC and TLC chromatogram was shown in Figure 4.16. The changes in product compositions with reaction time and the distribution of various components in the reaction system can be clearly seen. TLC analysis and ^{1}H-NMR data of the reaction (Figure 4.18) showed that most of free fatty acids were converted to FAME at reaction time 10 hours and the conversion was increased when increasing amount of catalyst. Using 4% sulfuric acid (based on tomato seed oil weight) as catalyst for 10 hours the highest conversion was obtained.

Percentage of FFA in biodiesel was analyzed by ^{1}H-NMR and the results were shown in Figure 4.17. After increased concentration of conc.H_2SO_4 from 1% to 4% and reaction time 10 hours, %FFA was reduced to 0.54. Therefore, the optimal

reaction time was 10 hours, 4% of conc.H_2SO_4 (based on tomato seed oil weight) and 400 ml of methanol can reduce %FFA to less than 1%.
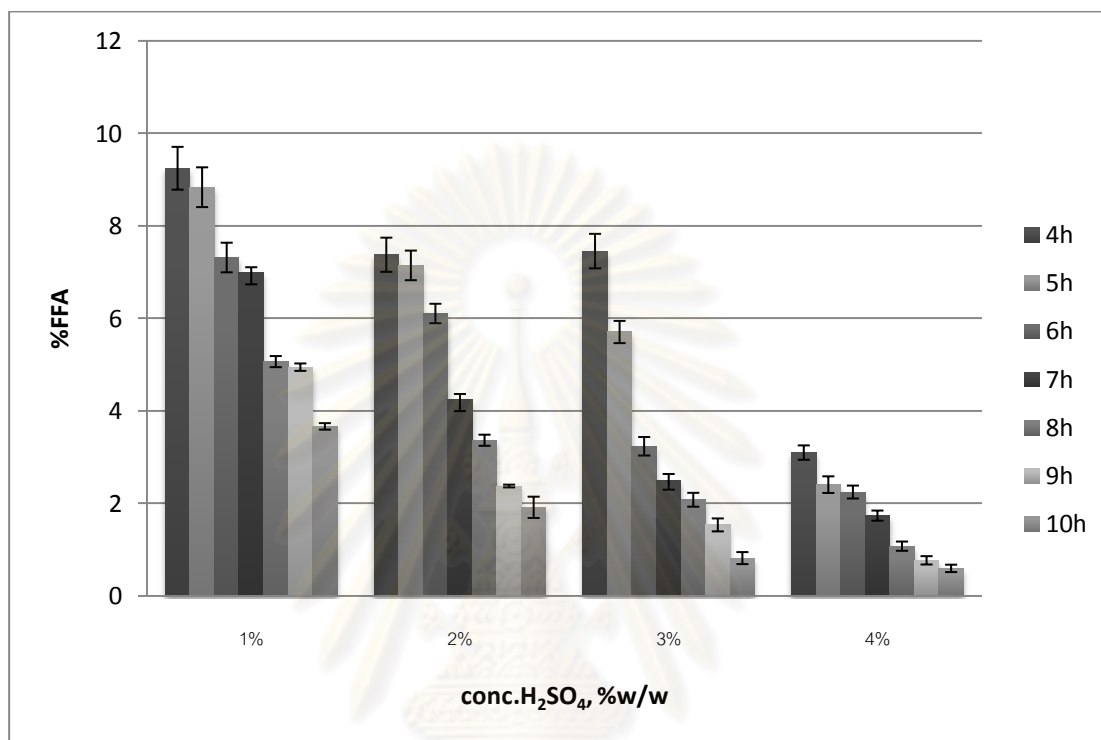

Figure 4.17 The percentage of free fatty acid in biodiesel produced from tomato seed oil at 1 - 4% sulfuric acid during reaction time 4, 5, 6, 7, 8, 9 and 10 hours using 400 ml of methanol.

2. Effect of reaction time

The effect of reaction time 4, 5, 6, 7, 8, 9, and 10 hours was investigated at temperature 65ºC and 1-4% of conc.H_2SO_4. The reactions were monitored by ^{1}H-NMR analysis. It was observed that the ester yield slightly increased with reaction time. Results obtained from the present experiments with tomato seed oil revealed that, about 10 hours of reaction is sufficient for biodiesel production.
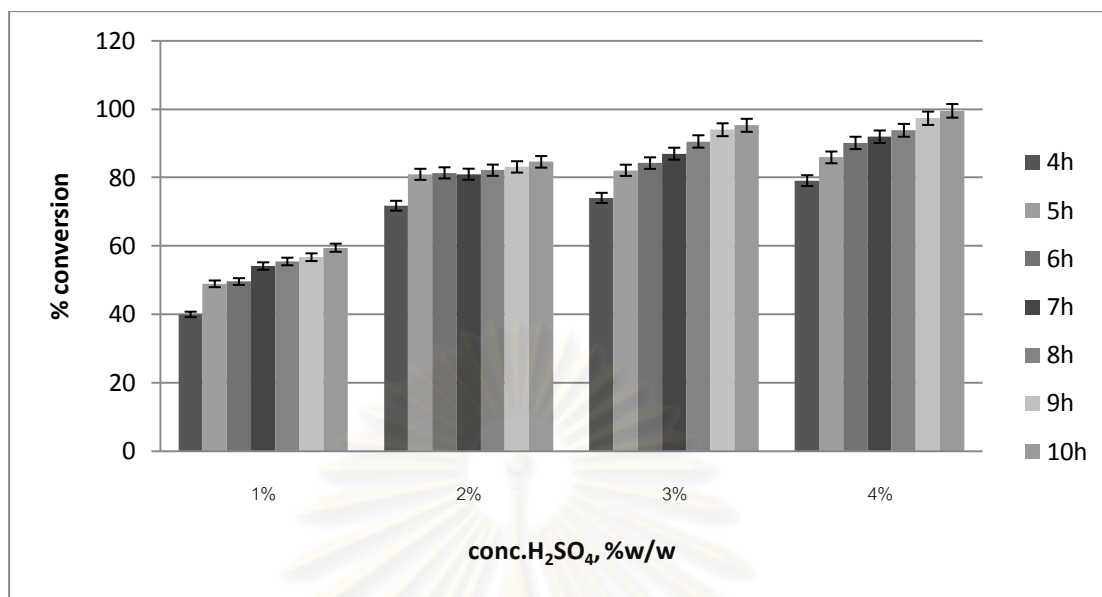
Figure 4.18 Conversion of biodiesel produced from tomato seed oil at 1 - 4% sulfuric acid during reaction time 4, 5, 6, 7, 8, 9 and 10 hours using 400 ml of methanol.

^{1}H-NMR analysis conversions into FAME were shown in Figure 4.18. At difference catalyst concentration and reaction time, the highest percentage of methyl ester (99.5%) was obtained from the reaction which using 4% of sulfuric acid and reaction time 10 hours. Also reaction time 7, 8 and 9 hours gave high conversion more than 90%. The conversion was increased when increasing reaction time and catalyst concentration. Therefore, the optimal reaction time was 10 hours.

4.4.3 Biodiesel from tomato seed oil (TS March 2010)

4.4.3.1 Optimization of process parameter

1. Effect of a molar ratio of methanol and tomato seed oil

The reaction was carried out at a constant temperature 60 $^{\circ}$C, reaction time 5 hours and 2% of conc.H_2SO_4 as catalyst. The molar ratio of methanol to oil was varied at 4:1 to 100:1. Figure 4.20 showed the percentage of conversion. It showed that % conversion increased when increasing a ratio of methanol and tomato seed oil. The high conversion was obtained at molar ratio of methanol and tomato seed oil 80:1-100:1. After 4 hours, the reaction gave >75%conversion after reaction time 5 hours.
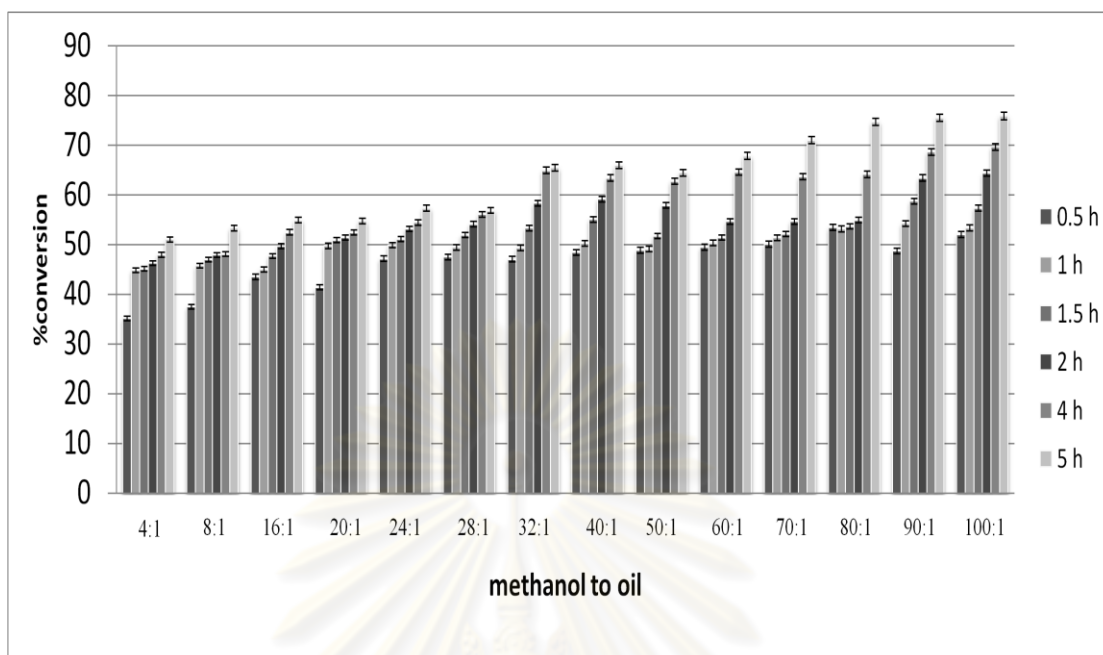
Figure 4.19 Conversion of biodiesel produced from tomato seed oil at molar ratio of methanol and tomato seed oil 4:1- 100:1and 2% of conc.H_2SO_4.
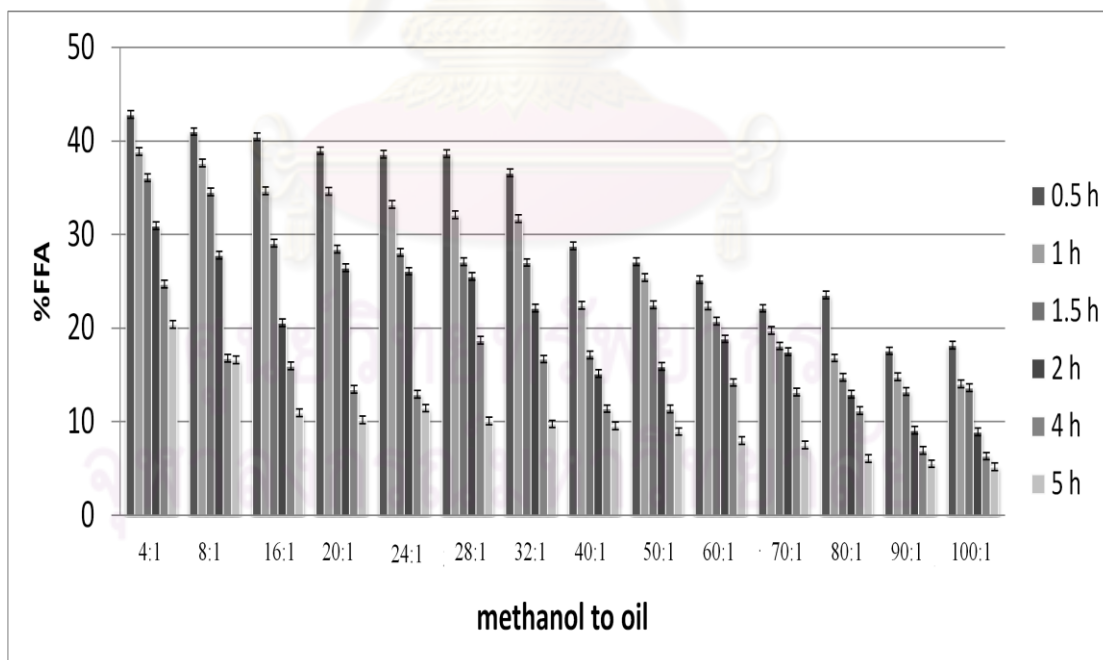

Figure 4.20 The percentage of free fatty acid in biodiesel produced from tomato seed oil at 2% sulfuric acid during reaction time 0.5- 5 hours using molar ratio of methanol to oil 4:1-100:1.

Percentage of FFA in biodiesel was analyzed by ^{1}H-NMR and the results were shown in Figure 4.20. After increased molar ratio of methanol to oil from 4:1 to 100:1 and reaction time 5 hours, %FFA was reduced to 5.20

From figure 4.20 at the same condition, molar ratio of methanol to oil 90:1 gave higher conversion (nearly molar ratio methanol to oil 100:1) than molar ratio methanol to oil 4:1 - 80:1 and could reduce percentage of free fatty acid to less than molar ratio methanol to oil 4:1 - 80:1. Therefore we used 90 M (with 75.56% of conversion and 5.54% of free fatty acid) in other experiments to reduce the cost of production.

2. Effect of catalyst concentration

In the process of biodiesel production, reaction temperature, methanol quantity and catalyst concentration were found to be significant operating parameters, which were closely associated with energy costs from an economic perspective. In the transesterification reaction, biodiesel was performed at $60^{\circ}C$ using molar ratio methanol to oil 90:1, reaction time 5 hours and catalyst concentration at 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5% and 4%.
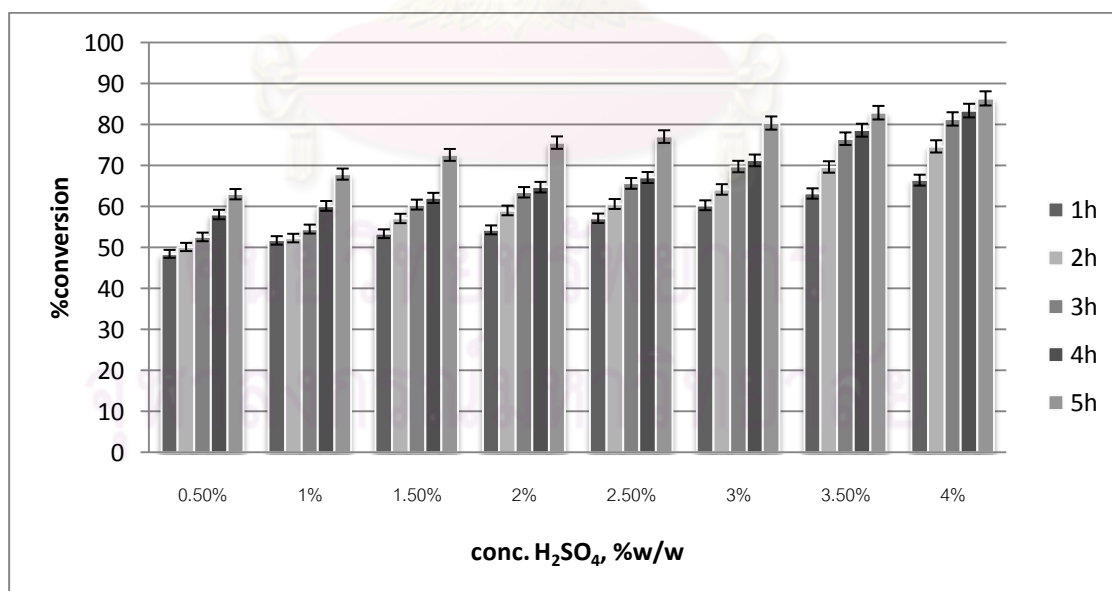

Figure 4.21 Conversion of biodiesel produced from tomato seed oil at 0.5 - 4% sulfuric acid during reaction time 1-5 hours using 90:1 of methanol to oil.

From the Figure 4.21, the percentage of FAME was 86.35±2% when 4% of catalyst was used and it was higher than 12% of FAME produced by 2% of catalyst. Thus it should by concluded that amount of catalyst resulted in increase of % methyl ester.

3. Effect of reaction time

The reaction time is an important parameter in transesterification. The ester yield slightly increased with increasing in reaction time. In the transesterification reaction, biodiesel was performed at 60°C using 2% of sulfuric acid (based on tomato seed oil weight) and reaction time 5, 6, 7, 8, 9 and 10 hours.
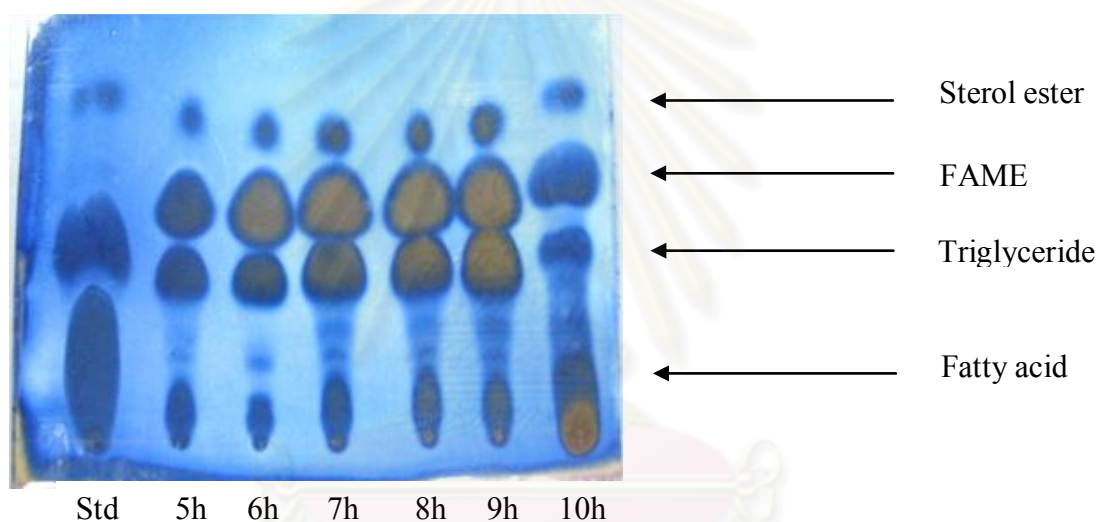

Figure 4.22 TLC chromatogram of biodiesel produced by using 90:1 molar ratio of methanol to tomato seed oil, reaction time 5, 6, 7, 8, 9 and 10 hours, 2% of conc.H_2SO_4 and reaction temperature 60°C

The products from reaction with 2% of catalyst (base on tomato seed oil weight) for 10 hours were analyzed by TLC and TLC chromatogram was shown in Figure 4.22. The changes in product compositions with reaction time and the distribution of various components in the reaction system can be clearly seen. TLC analysis and ^{1}H-NMR data of the reaction (Figure 4.22 and Figure 4.23. respectively) showed that most of free fatty acids were converted to FAME at reaction time 10 hours and the conversion was increased when increasing amount of catalyst. Using 2% sulfuric acid (based on tomato seed oil weight) as catalyst for 10 hours the high conversion was obtained.
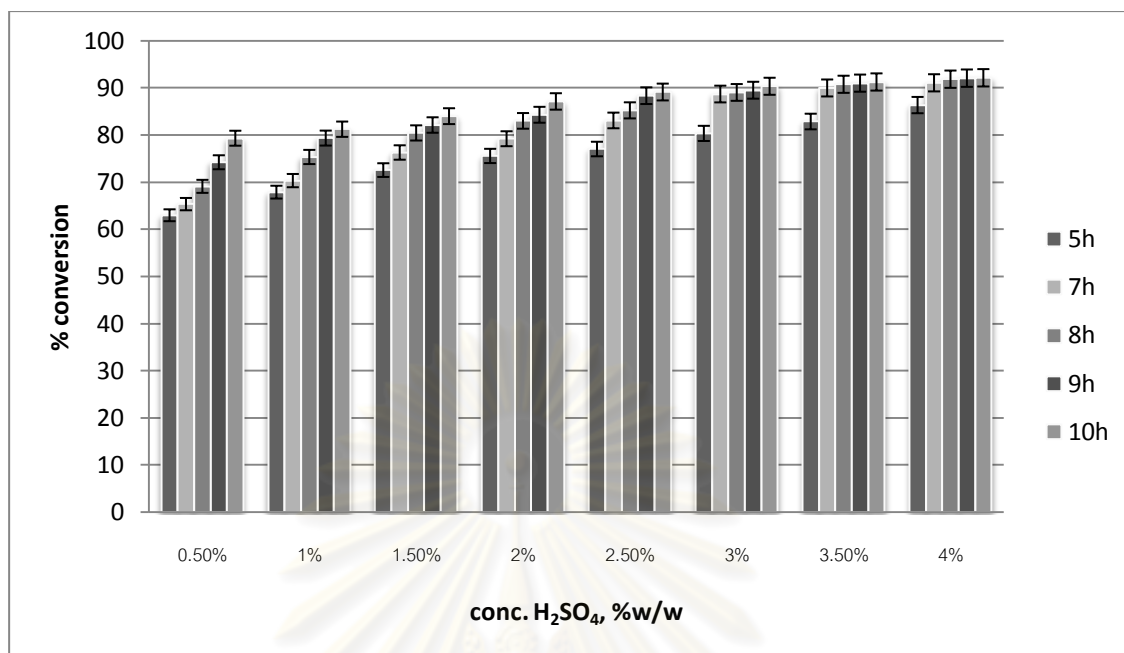
Figure 4.23 Conversion of biodiesel produced from tomato seed oil at 0.5 - 4%
sulfuric acid during reaction time 5-10 hours using 90:1 molar ratio of
methanol to oil.

^{1}H-NMR analysis conversions into FAME were shown in Figure 4.23. At
difference catalyst concentration and reaction time, the reaction was carried out at
60°C and 90:1 molar ratio of methanol to oil. The highest percentage of methyl ester
(92.14±2%) was obtained from the reaction which using 4% of sulfuric acid and
reaction time 10 hours. The conversion was increased when increasing reaction time
and catalyst concentration. Therefore, the optimal reaction time was 10 hours.
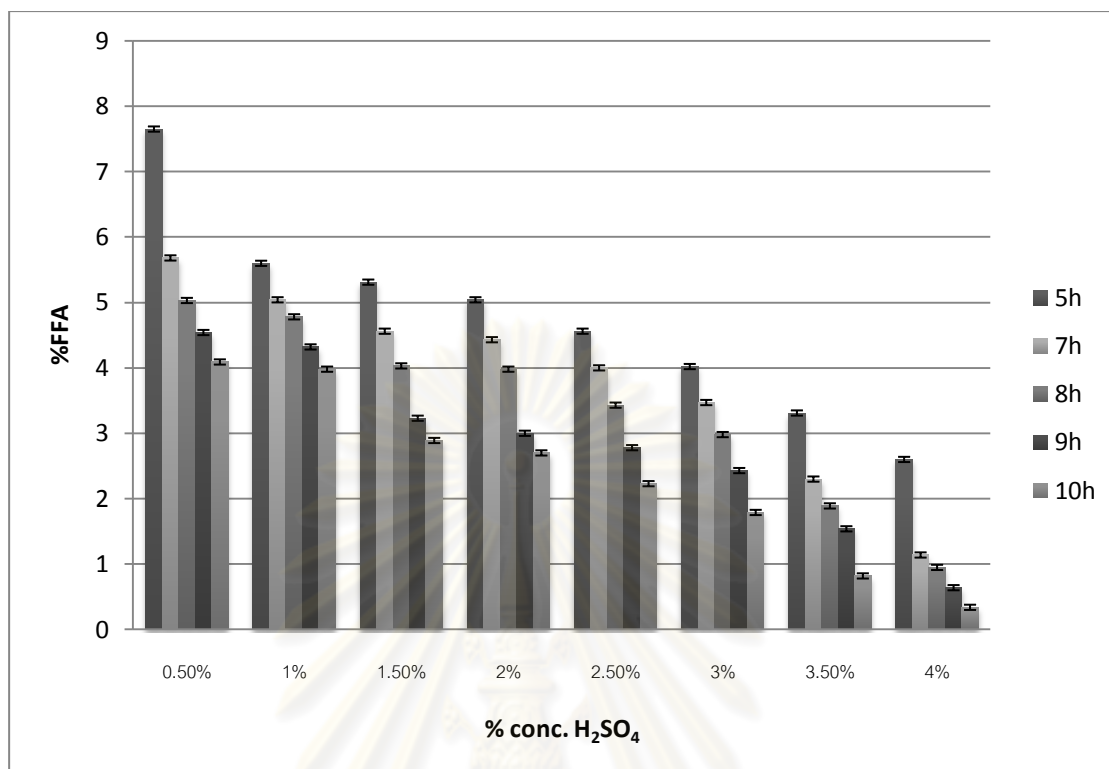
Figure 4.24 The percentage of free fatty acid in biodiesel produced from tomato seed
oil at 1 - 4% sulfuric acid during reaction time 5-10 hours using 90:1
molar ratio of methanol to oil.

Percentage of FFA in biodiesel was analyzed by ^{1}H-NMR and the results were
shown in Figure 4.24. After increased concentration of conc.H_2SO_4 from 0.5% to 4%
and reaction time 10 hours, %FFA was reduced to 0.34. Therefore, the optimal
reaction time was 10 hours, 4% of conc.H_2SO_4 (based on tomato seed oil weight) and
using 90:1 molar ratio of methanol to oil can reduce %FFA to less than 1%.

4.4.4 Biodiesel from tomato seed oil (TS January 2011)

4.4.4.1 Optimization of process parameter

1. Effect of a molar ratio of methanol and tomato seed oil

The reaction was carried out at a constant temperature 60 $^\circ$C, reaction
time 5 hours and 2% of conc.H_2SO_4 as catalyst. The molar ratio of methanol to oil
was varied at 4:1 to 100:1. Figure 4.25 showed the percentage of conversion. It
showed that % conversion increased when increasing a ratio of methanol and tomato

seed oil. The high conversion was obtained at molar ratio of methanol and tomato seed oil 80:1-100:1. After 4 hours, the reaction gave >75%conversion after reaction time 5 hours.
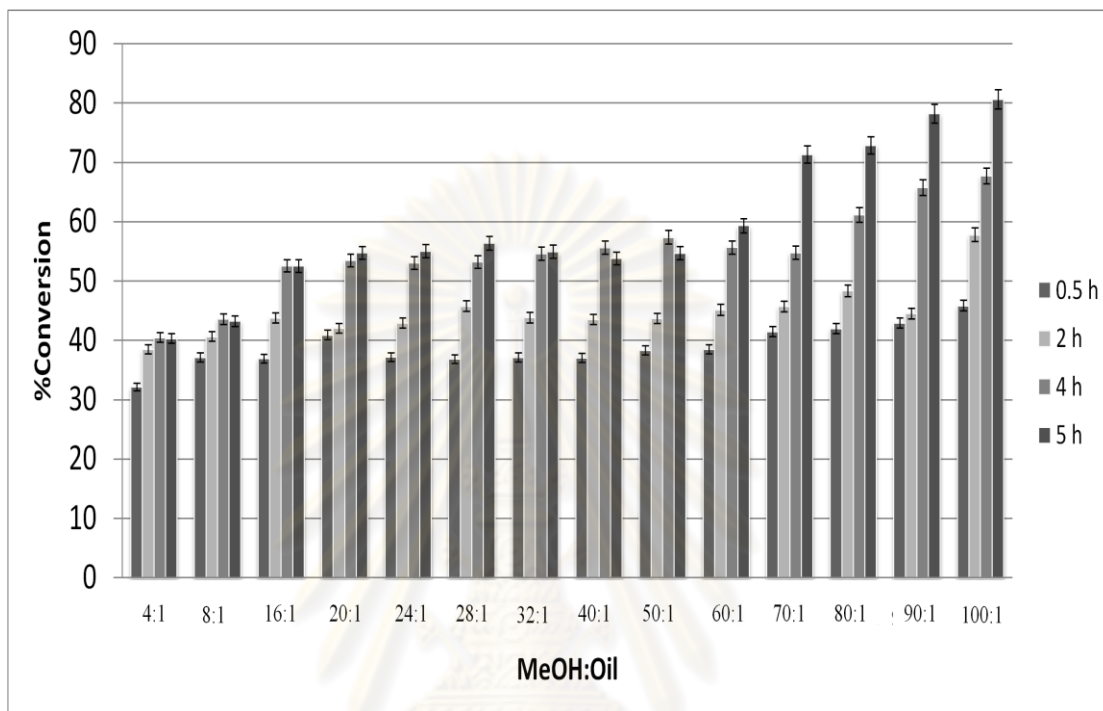

Figure 4.25 Conversion of biodiesel produced from tomato seed oil at molar ratio of methanol and tomato seed oil 4:1- 100:1and 2% of conc.H_2SO_4.
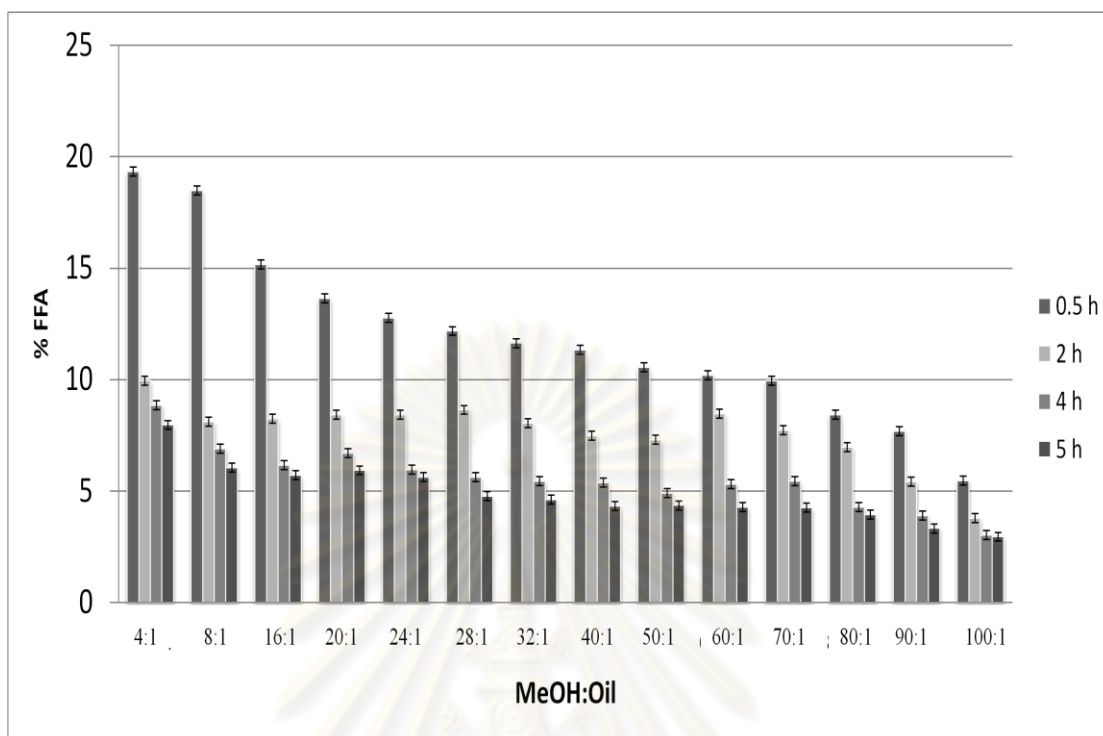
Figure 4.26 The percentage of free fatty acid in biodiesel produced from tomato seed
oil at 2% sulfuric acid during reaction time 0.5- 5 hours using molar
ratio of methanol to oil 4:1-100:1.

Percentage of FFA in biodiesel was analyzed by ^{1}H-NMR and the results were
shown in Figure 4.26. After increased molar ratio of methanol to oil from 4:1 to 100:1
and reaction time 5 hours, %FFA was reduced to 2.95

From figure 4.25 at the same condition, molar ratio of methanol to oil 90:1
gave higher conversion (nearly molar ratio methanol to oil 100:1) than molar ratio
methanol to oil 4:1 - 80:1 and could reduce percentage of free fatty acid to less than
molar ratio methanol to oil 4:1 - 80:1. Therefore we used 90 M (with 78.25% of
conversion and 2.95% of free fatty acid) in other experiments to reduce the cost of
production.

2. Effect of catalyst concentration

In the process of biodiesel production, reaction temperature, methanol quantity and catalyst concentration were found to be significant operating parameters, which were closely associated with energy costs from an economic perspective. In the transesterification reaction, biodiesel was performed at $60^{\circ}C$ using molar ratio methanol to oil 90:1, reaction time 5 hours and catalyst concentration at 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5% and 4%.

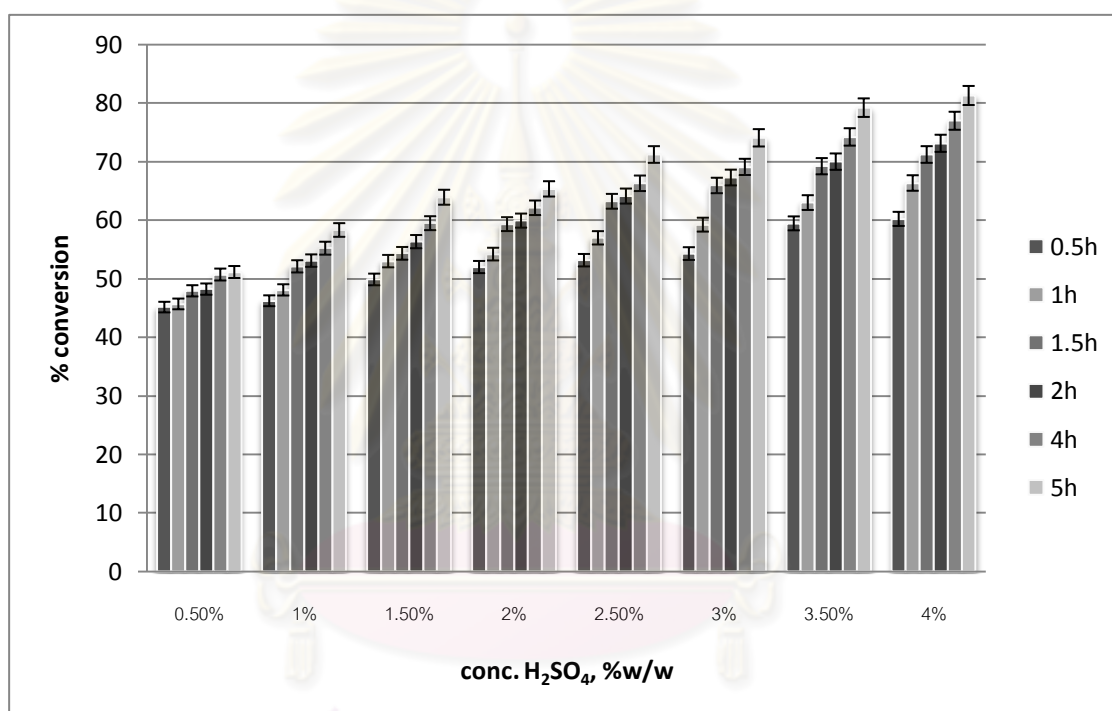**Figure 4.27** Conversion of biodiesel produced from tomato seed oil at 0.5 - 4% sulfuric acid during reaction time 1-5 hours using 90:1 of methanol to oil.

From the Figure 4.27, the percentage of FAME was 81.29±2% when 4% of catalyst was used and it was higher than 16% of FAME produced by 2% of catalyst. Thus it should by concluded that amount of catalyst resulted in increase of % methyl ester.

3. Effect of reaction time

      The reaction time is an important parameter in transesterification. The ester yield slightly increased with increasing in reaction time. In the transesterification reaction, biodiesel was performed at 60°C using 2% of sulfuric acid (based on tomato seed oil weight) and reaction time 5, 6, 7, 8, 9 and 10 hours.
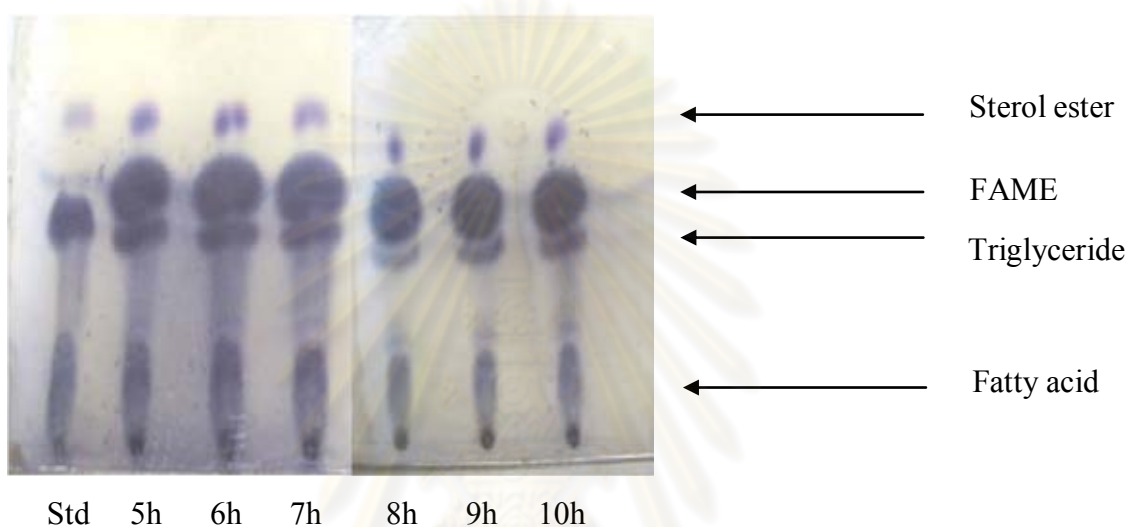

Std 5h 6h 7h 8h 9h 10h

Figure 4.28 TLC chromatogram of biodiesel produced by using 90:1 molar ratio of methanol to tomato seed oil, reaction time 5, 6, 7, 8, 9 and 10 hours, 2% of conc.H_2SO_4 and reaction temperature 60°C

      The products from reaction with 2% of catalyst (base on tomato seed oil weight) for 10 hours were analyzed by TLC and TLC chromatogram was shown in Figure 4.28. The changes in product compositions with reaction time and the distribution of various components in the reaction system can be clearly seen. TLC analysis and ^{1}H-NMR data of the reaction (Figure 4.28 and Figure 4.29. respectively) showed that most of free fatty acids were converted to FAME at reaction time 10 hours and the conversion was increased when increasing amount of catalyst. Using 2% sulfuric acid (based on tomato seed oil weight) as catalyst for 10 hours the high conversion was obtained.
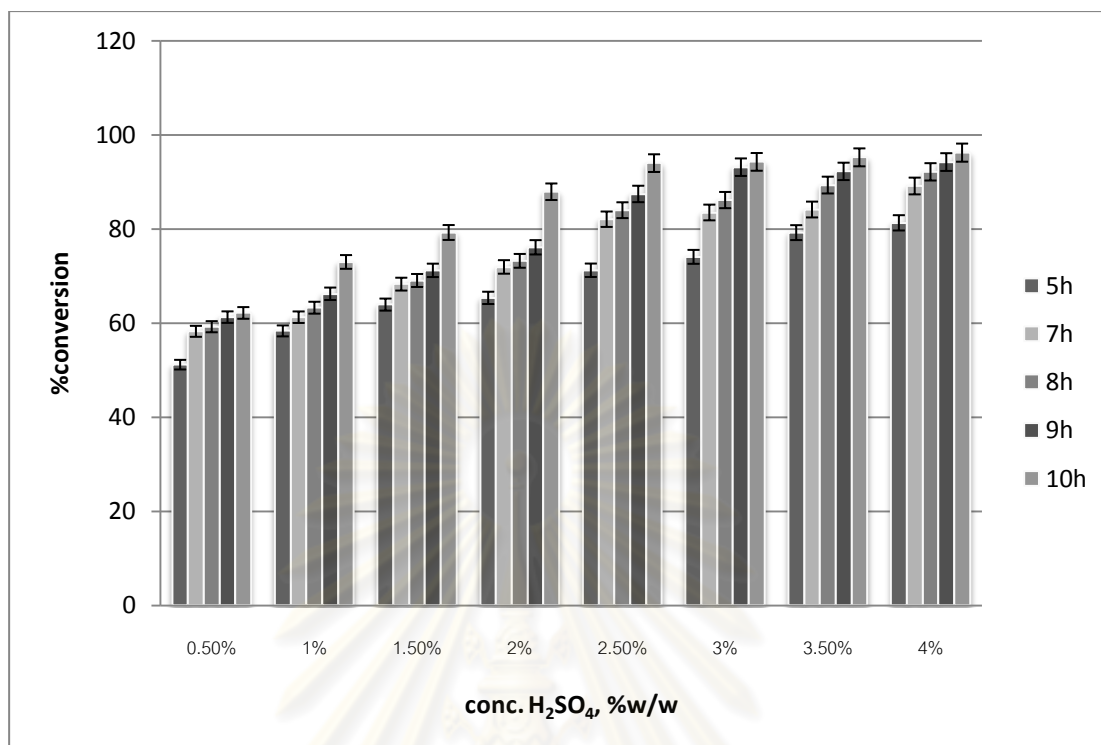
Figure 4.29 Conversion of biodiesel produced from tomato seed oil at 0.5 - 4%
sulfuric acid during reaction time 5-10 hours using 90:1 molar ratio of
methanol to oil.

^{1}H-NMR analysis conversions into FAME were shown in Figure 4.29. At
difference catalyst concentration and reaction time, the reaction was carried out at
60°C and 90:1 molar ratio of methanol to oil. The highest percentage of methyl ester
(96.21±2%) was obtained from the reaction which using 4% of sulfuric acid and
reaction time 10 hours. The conversion was increased when increasing reaction time
and catalyst concentration. Therefore, the optimal reaction time was 10 hours.
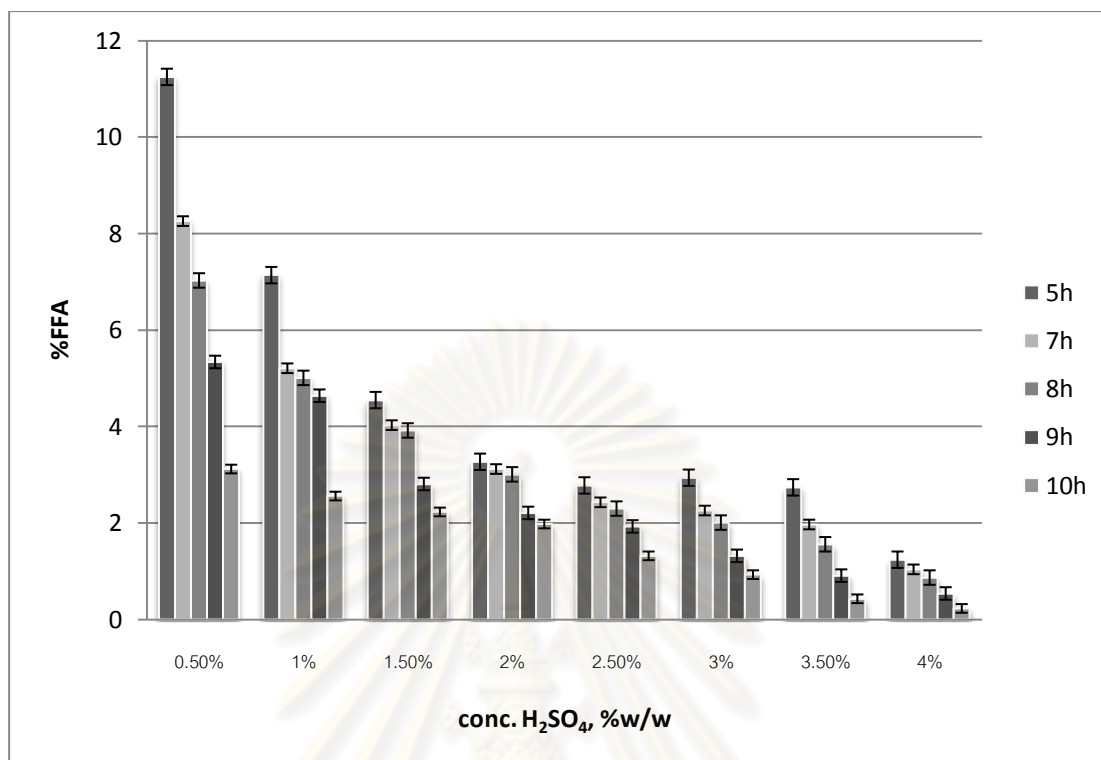
Figure 4.30 The percentage of free fatty acid in biodiesel produced from tomato seed
oil at 1 - 4% sulfuric acid during reaction time 5-10 hours using 90:1
molar ratio of methanol to oil.

Percentage of FFA in biodiesel was analyzed by ^{1}H-NMR and the results were
shown in Figure 4.30. After increased concentration of conc.H_2SO_4 from 0.5% to 4%
and reaction time 10 hours, %FFA was reduced to 0.23. Therefore, the optimal
reaction time was 10 hours, 4% of conc.H_2SO_4 (based on tomato seed oil weight) and
using 90:1 molar ratio of methanol to oil can reduce %FFA to less than 1%.

4.5 Direct biodiesel production in ethanol

To determine the effect of alcohol type on esters formation, the esterification reaction using ethanol was carried out under the optimal conditions using methanol in the previous section [i.e. 4% of conc.H_2SO_4 (based on tomato seed oil), 400ml of dry ethanol and 100g of dry tomato seed]. The reaction was conducted at 70 ℃. Percentage of conversion and free fatty acid were analyzed by ^{1}H-NMR and the results were shown in Table 4.5(see detail in appendix A).

Table 4.5 Comparision the product of biodiesel in organic solvent

	TS March 2010		TS January 2011	
	MeOH	EtOH	MeOH	EtOH
%conversion	95.5%	84.86%	99.50%	91.48%
%FFA	0.98%	6.52%	0.60%	4.84%

From the Table 4.5, the results showed that esterification of methanol and fatty acid of tomato seed oil in March 2010 and January 2011 gave higher percentage of conversion than esterification by using ethanol as a solvent. While the percentage of free fatty acid of ethyl ester higher than methyl ester. The percentage of free fatty acid were 6.52(TS March 2010) and 4.84 (TS January 2011), respectively.

From the data indicated that direct biodiesel production from tomato seed in March 2010 and January 2011 by using methanol as a solvent gave the best product yield and quality.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

Biodiesel production from by-product of tomato paste manufacturing industry via direct biodiesel production in methanol using soxhlet apparatus and biodiesel production with reflux by using homogeneous acid catalyst (sulfuric acid) were studied. Tomato seeds were collected in March (2010) and January (2011) for comparing the quality and property of tomato seed oil. To optimize the reaction condition for direct biodiesel production in methanol using soxhlet apparatus, the amount of catalyst and reaction time were investigated. While biodiesel production from tomato seed oil, amount of catalyst, molar ratio of methanol to tomato seed oil and reaction time were investigated

Tomato seeds were collected in January 2011 gave the best product yield of FAME. In direct biodiesel production in methanol using soxhlet apparatus, the good product yield of FAME was produced at 400 ml of methanol, 4.0% of conc.H_2SO_4 (base on tomato seed oil weight), reaction temperature $65^{\circ}C$ and reaction time 10 hours. The product conversion under optimal condition was 99.5% and %FFA was 0.54.

For biodiesel production of tomato seed oil using homogeneous acid catalyst (sulfuric acid), the best product yield and quality was produced at a 90:1 molar ratio of methanol to tomato seed oil, 4.0% of conc.H_2SO_4, reaction time 10 hours and reaction temperature $60^{\circ}C$. The product conversion under optimal condition was 96.21% and %FFA was 0.28.

5.2 Suggestion

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

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APPENDICES

APPENDIX A

CALCULATIONS

1. Composition of fatty acid in tomato seed oil

Table A-1 Molecular weight of tomato seed oil

	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	M_{FFA}, g/mol
TS 2010 extracted with MeOH	0.1400	13.8581	5.2921	23.6759	54.1080	2.3233	0.1679	283.1172
TS 2010 extracted with hexane	0.1489	13.8907	4.9534	23.3997	54.5830	2.3823	0.2777	277.7010
TS 2011 extracted with MeOH	0.1462	13.7470	4.9881	23.2784	54.5938	2.5019	0.3537	277.8752
TS 2010 extracted with hexane	0.1491	14.6368	3.3494	23.9559	54.5247	2.5594	0.3309	277.4767

Where

$$M_{FFA} = \frac{\Sigma \,[(\text{MW of fatty acid} \times \% \text{ fatty acids})]}{\text{Total of fatty acid (only fatty acid)}}$$

So,

$$M_{FFA} = \frac{[(200.32 \times 0.1491) + (256.43 \times 14.6368) + (284.48 \times 3.3494) + \ldots]}{99.5062}$$

$$= 277.47 \text{ g/mol}$$

2. Calculation of % conversion of biodiesel

2.1 direct biodiesel from tomato seed oil in methanol (TS March 2010)
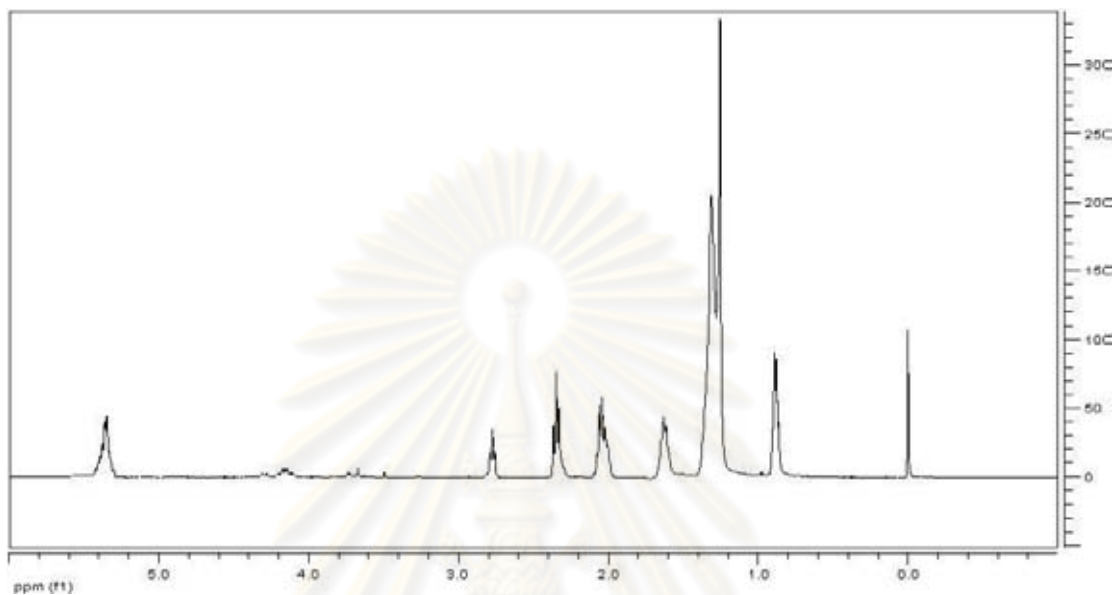

Figure A-1 ^{1}H NMR spectrum of tomato seed oil (TS March 2010)

$$\% \text{ conversion} = \frac{\text{integration of methoxy group per one mole equivalent}}{\text{integration of methylene group per one mole equivalent}}$$
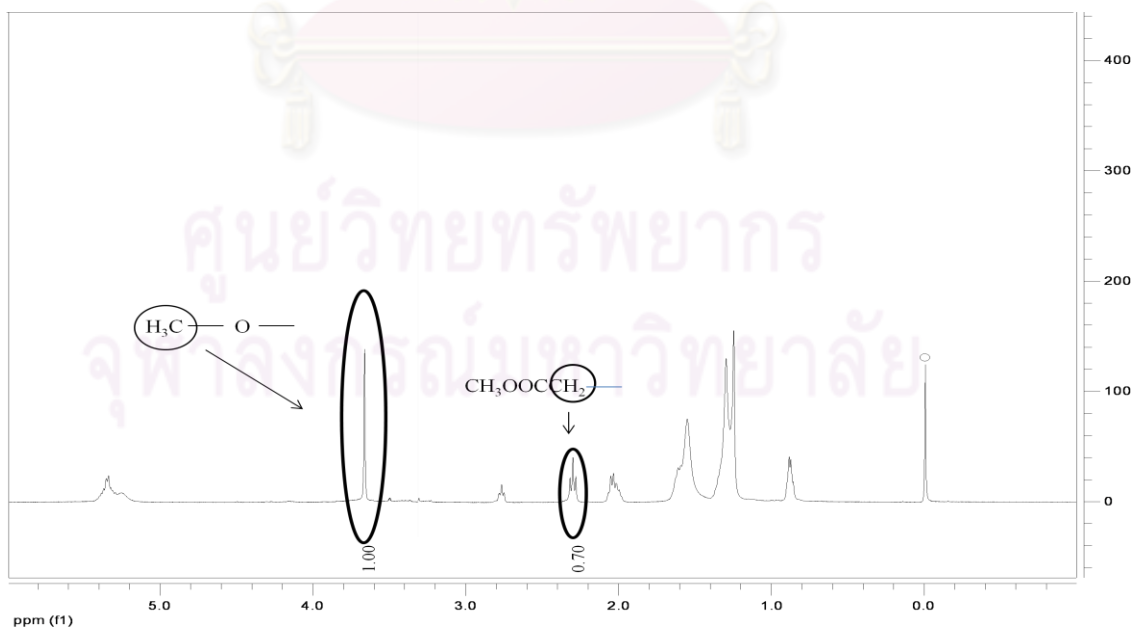

Figure A-2 ^{1}H NMR spectrum of direct biodiesel from tomato seed oil

(TS March 2010)

% conversion = (1/3)/(0.70/2)×100 = 94.95%

2.1 direct biodiesel from tomato seed oil in ethanol (TS March 2010)
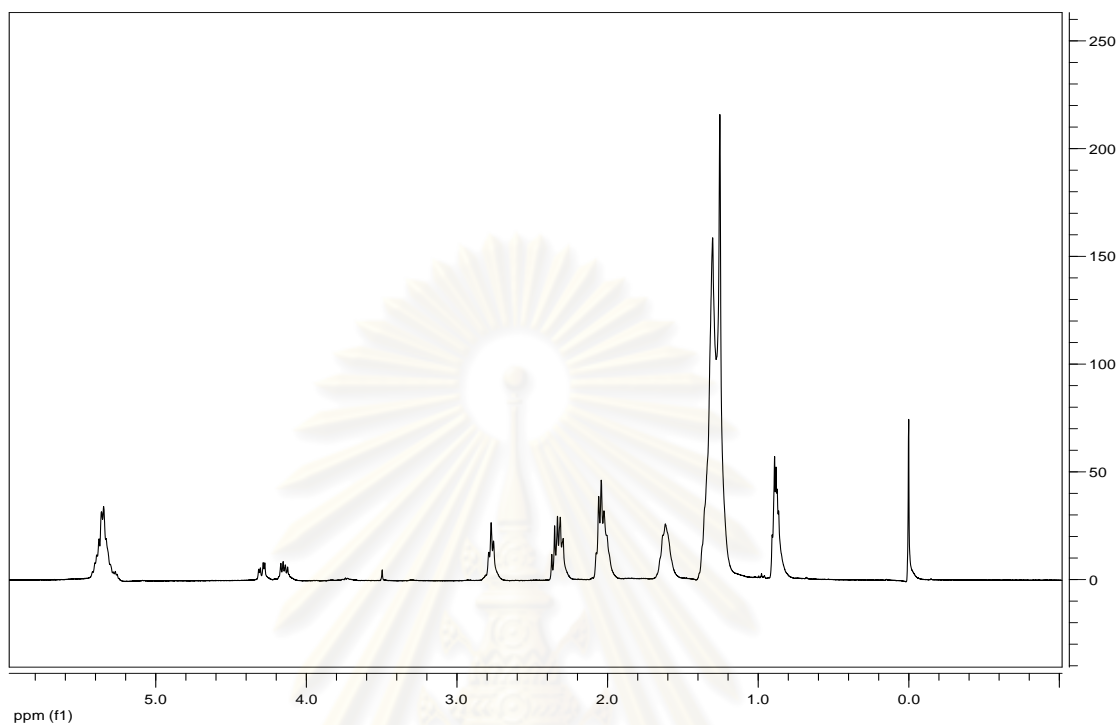

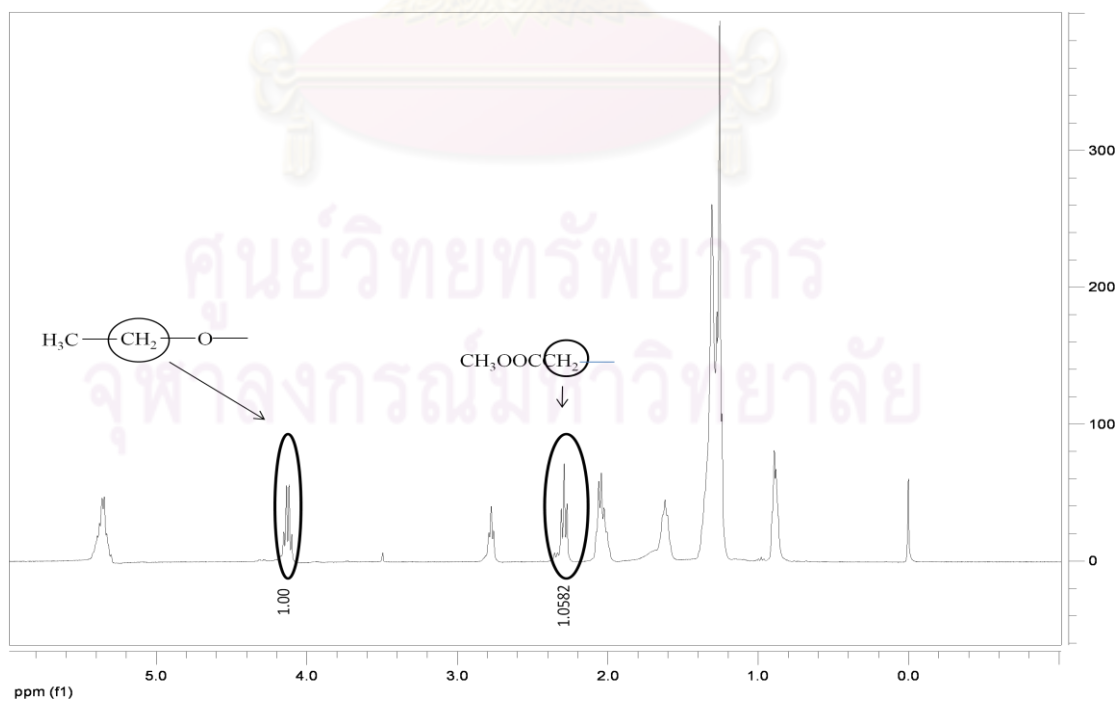**Figure A-3** ^{1}H NMR spectrum of tomato seed oil extracted with ethanol
(TS March 2010)

Figure A-4 ^{1}H NMR spectrum of ethyl ester (TS March 2010)

% conversion = (1/1.1784)×100 = 84.86%

2.2 direct biodiesel from tomato seed oil in methanol (TS January 2011)
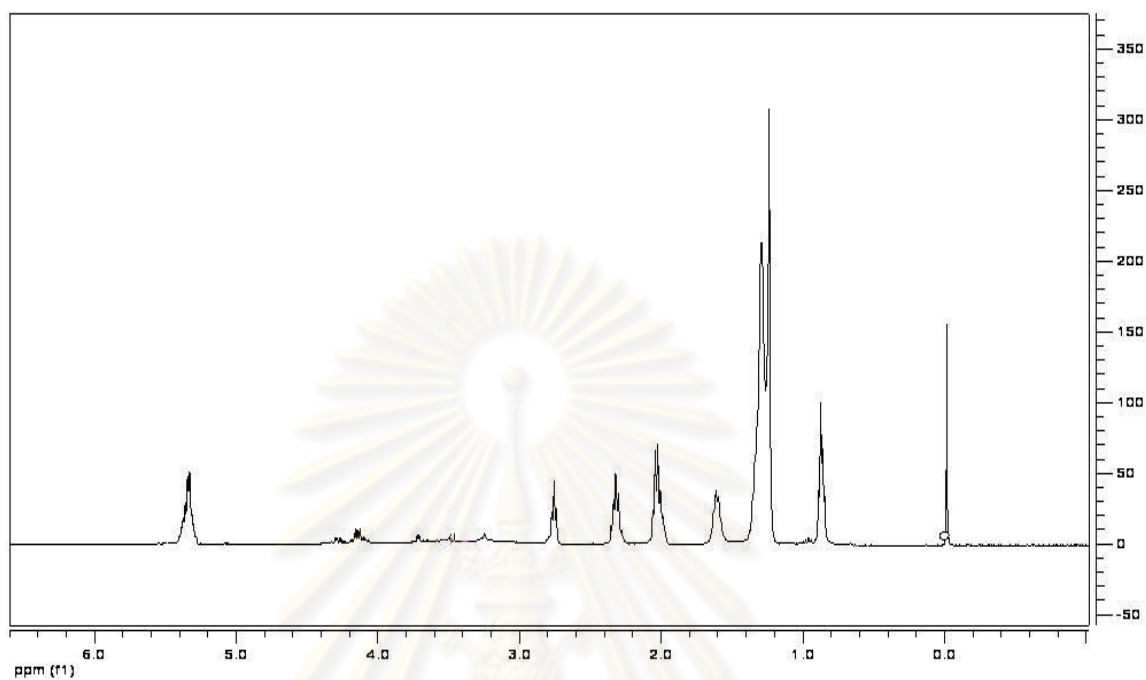

Figure A-5 ^{1}H NMR spectrum of tomato seed oil (TS January 2011)
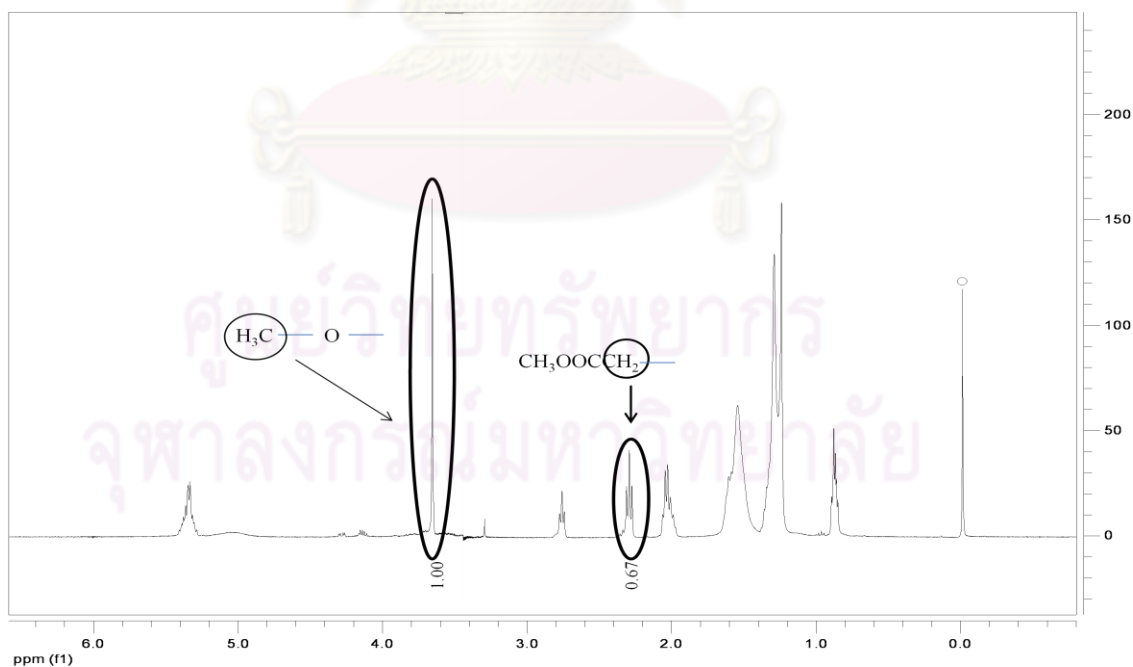

Figure A-6 ^{1}H NMR spectrum of direct biodiesel from tomato seed oil

(TS January 2011)

% conversion = $(1/3)/(0.67/2)\times100 = 99.50\%$

2.1 direct biodiesel from tomato seed oil in ethanol (TS January 2011)

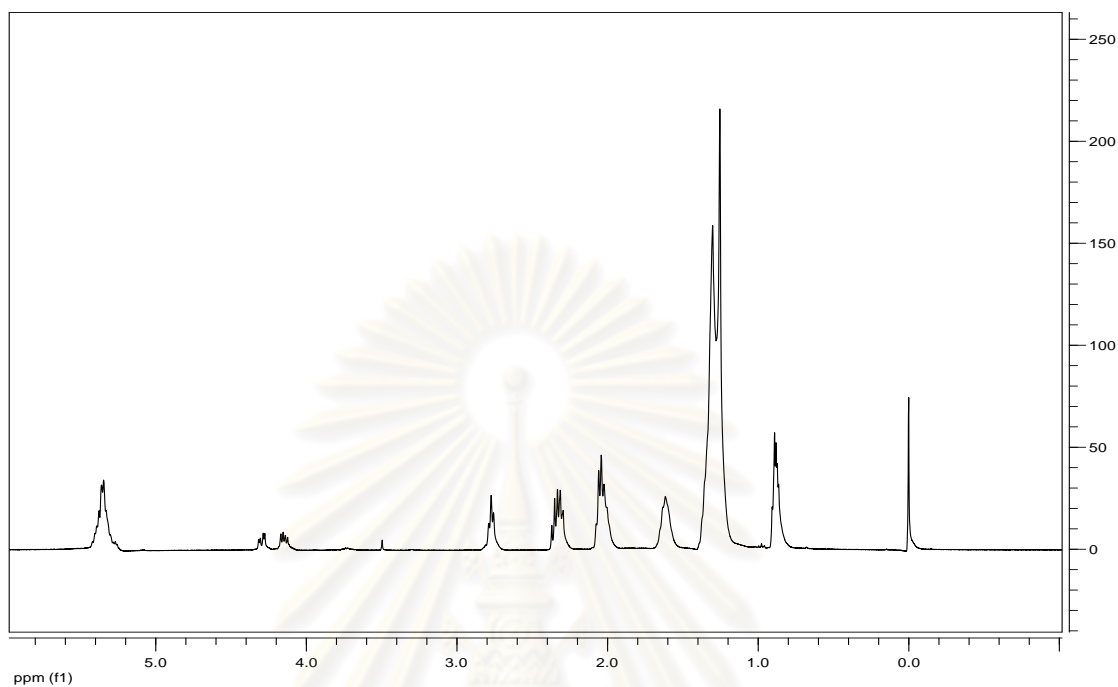**Figure A-7** ^{1}H NMR spectrum of tomato seed oil extracted with ethanol
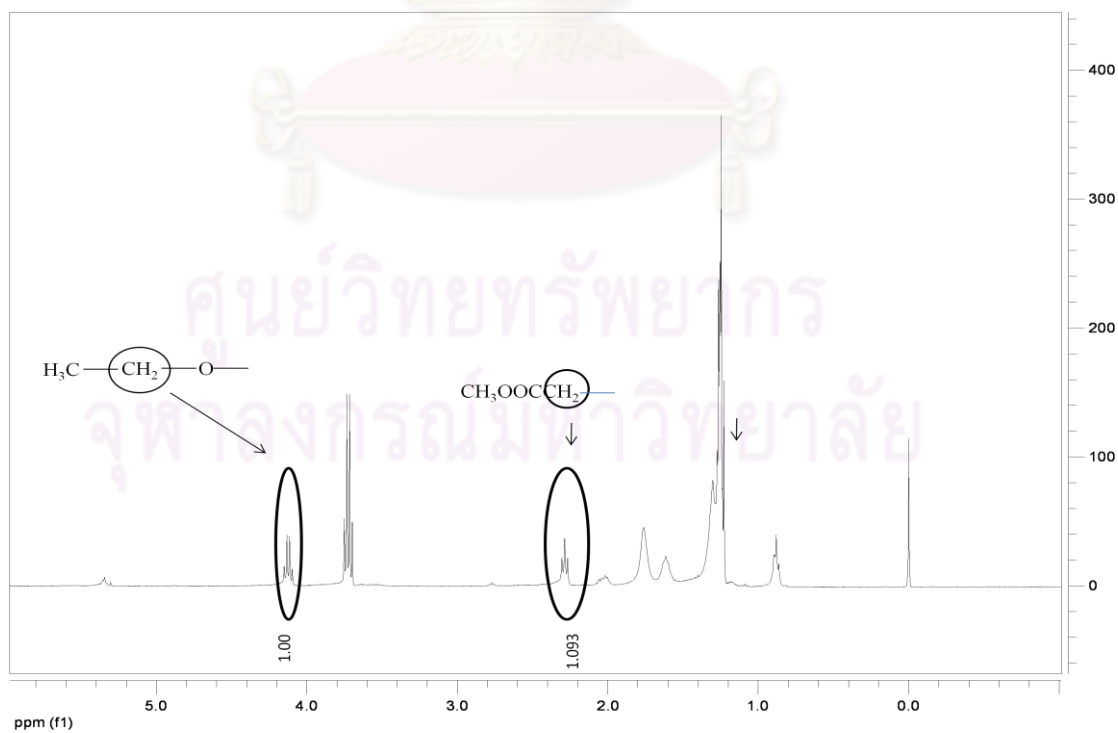(TS January 2011)

Figure A-8 ^{1}H NMR spectrum of ethyl ester (TS January 2011)

% conversion = $(1/1.093) \times 100 = 91.48\%$

2.3 Biodiesel production from tomato seed oil (TS March 2010)

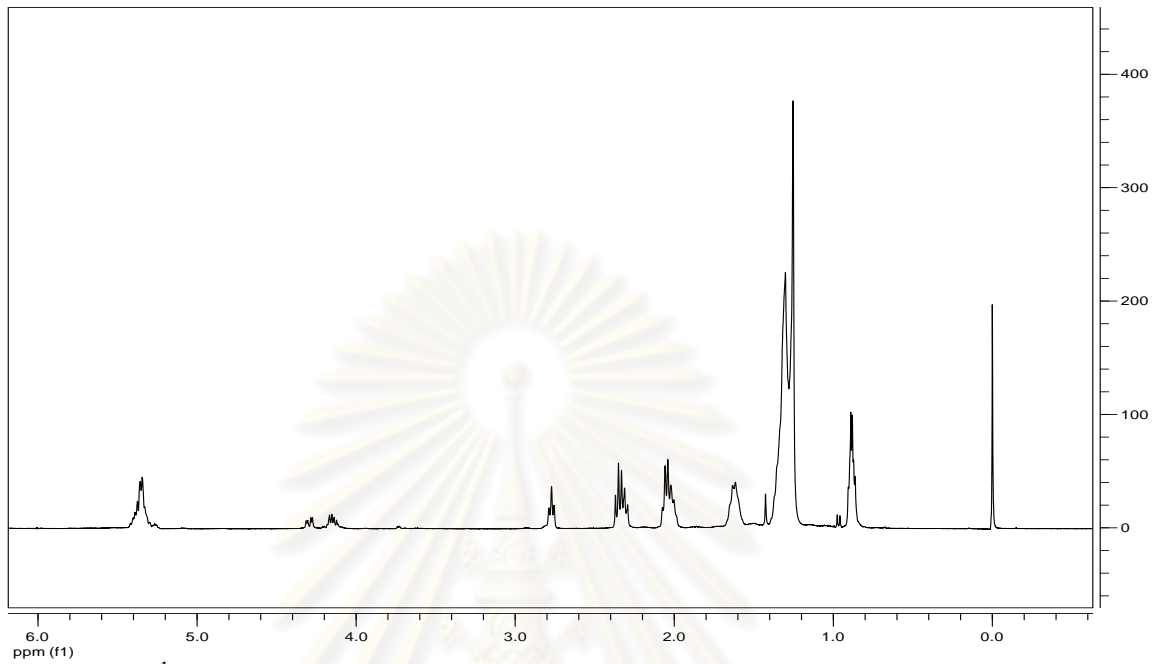**Figure A-9** ^{1}H NMR spectrum of tomato seed oil (extracted by hexane)

Figure A-10 ^{1}H NMR spectrum of biodiesel production from tomato seed oil

(TS March 2010)

% conversion = (1/3)/(0.72/2)×100 = 92.14%

2.4 Biodiesel production from tomato seed oil (TS January 2011)
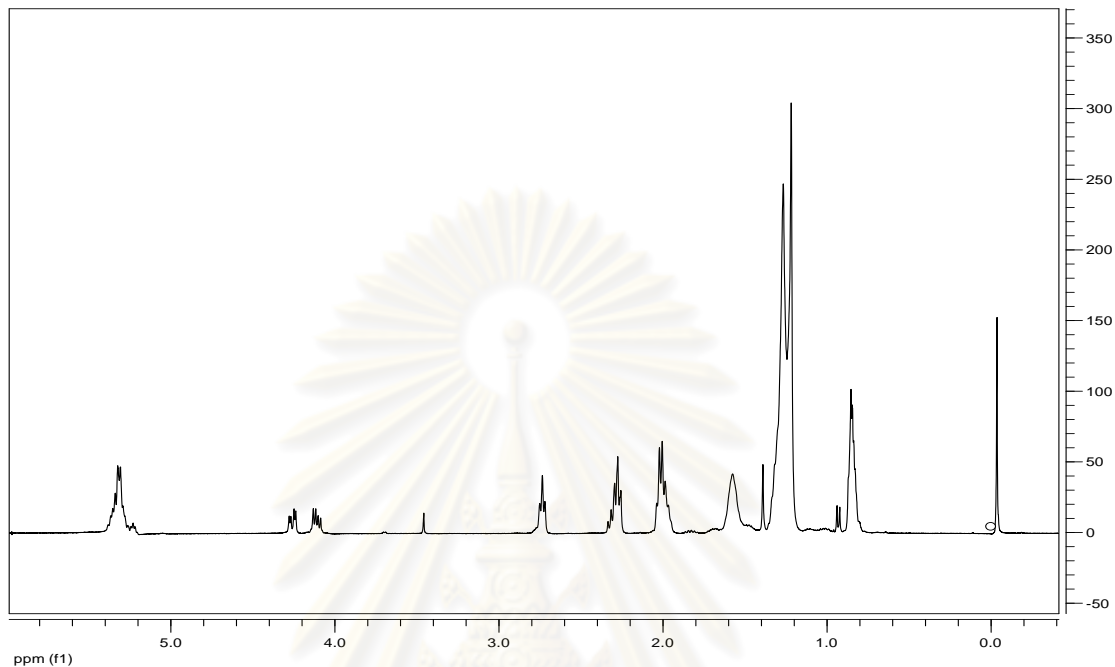
Figure A-11 ^{1}H NMR spectrum of tomato seed oil (extracted by hexane)
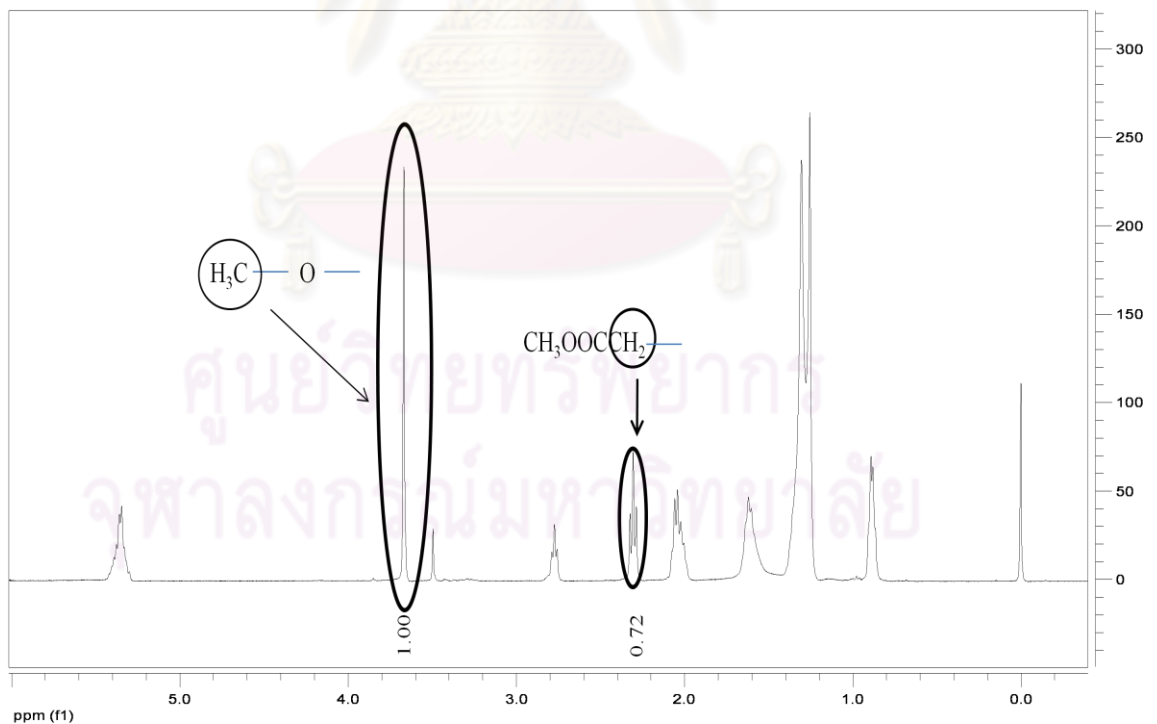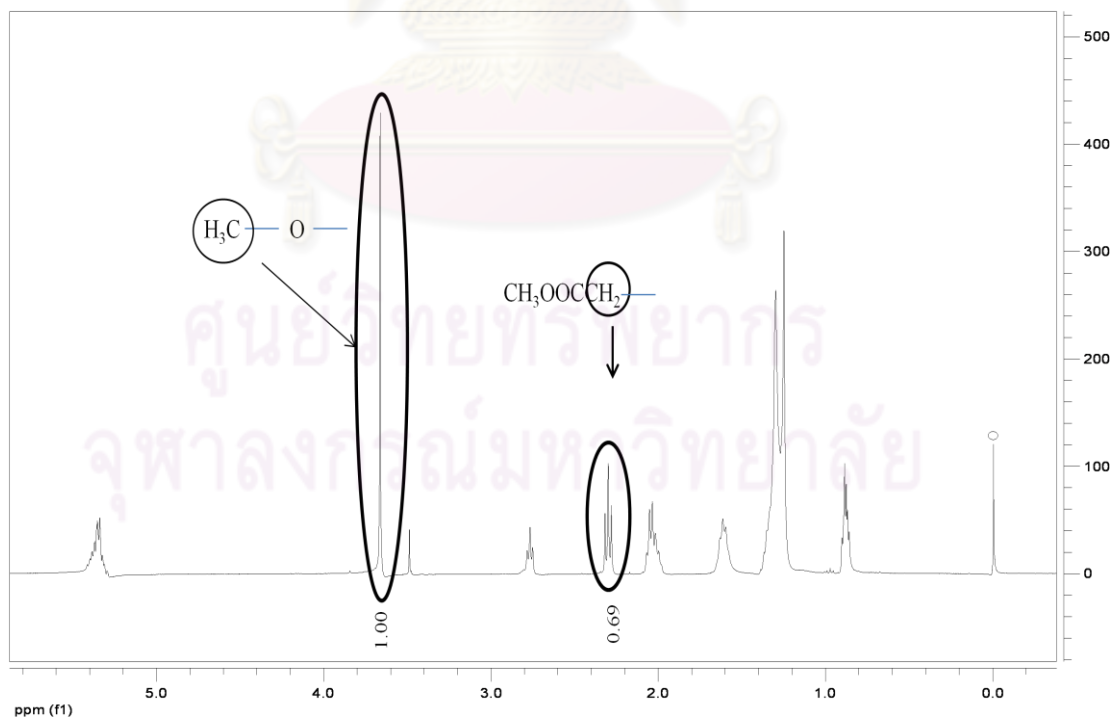

Figure A-12 ^{1}H NMR spectrum of biodiesel production from tomato seed oil

(TS January 2011)

% conversion = $(1/3)/(0.69/2)\times100 = 96.12\%$

3. Calculation of % free fatty acid

$$\% \text{ of FFA} = 4 \times \frac{\text{Area of unmerged peak of R-CH2 of FFA}}{\text{Total area of R-CH2 of both FFA and ester}} \times 100$$

3.1 Direct biodiesel from tomato seed oil (TS March 2010)

Figure A-13 Percentage of FFA in direct biodiesel production from tomato seed oil
(TS March 2010)

$$\% \text{ of FFA} = 4\frac{(0.0016)}{0.70} \times 100 = 0.97\%$$

3.2 Direct biodiesel from tomato seed oil (TS January2011)

Figure A-14 Percentage of FFA in direct biodiesel production from tomato seed oil
(TS March 2011)

$$\% \text{ of FFA} = 4\frac{(0.0013)}{0.67} \times 100 = 0.82\%$$

3.3 Biodiesel production from tomato seed oil (TS March 2010)

Figure A-15 Percentage of FFA in biodiesel production from tomato seed oil
(TS March 2010)

$$\% \text{ of FFA} = \frac{4(0.0011)}{0.72} \times 100 = 0.61\%$$

3.4 Biodiesel production from tomato seed oil (TS January 2011)
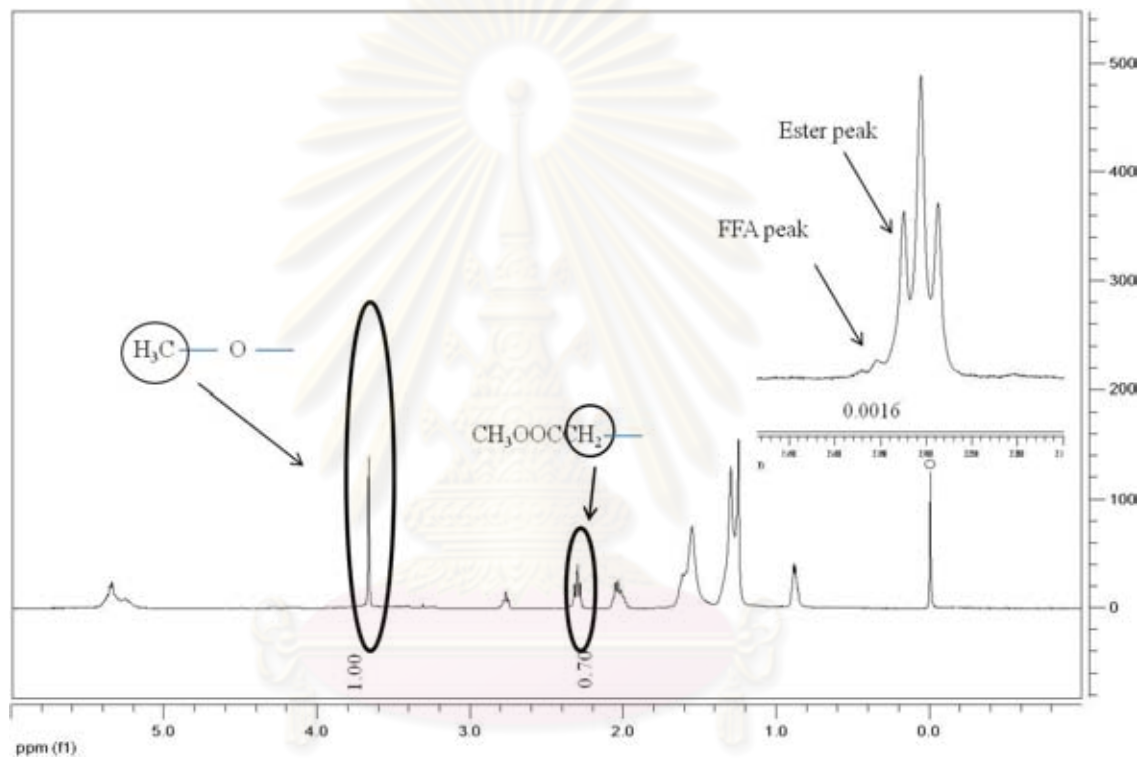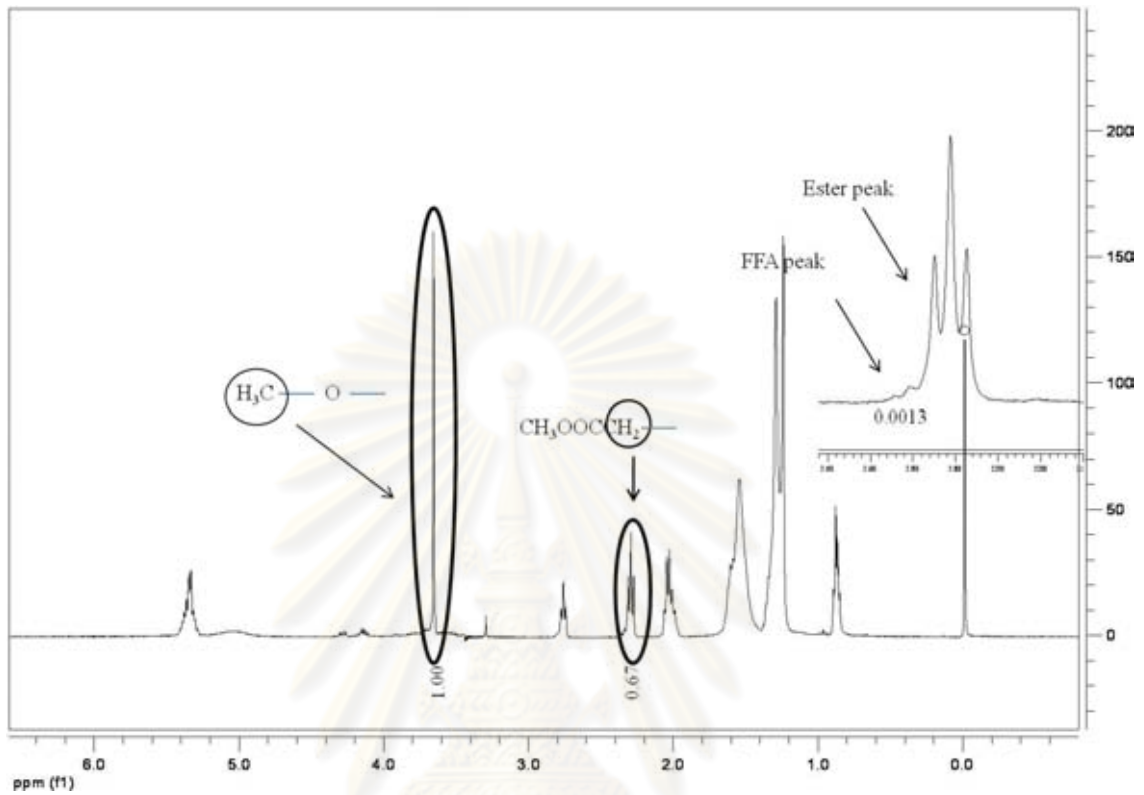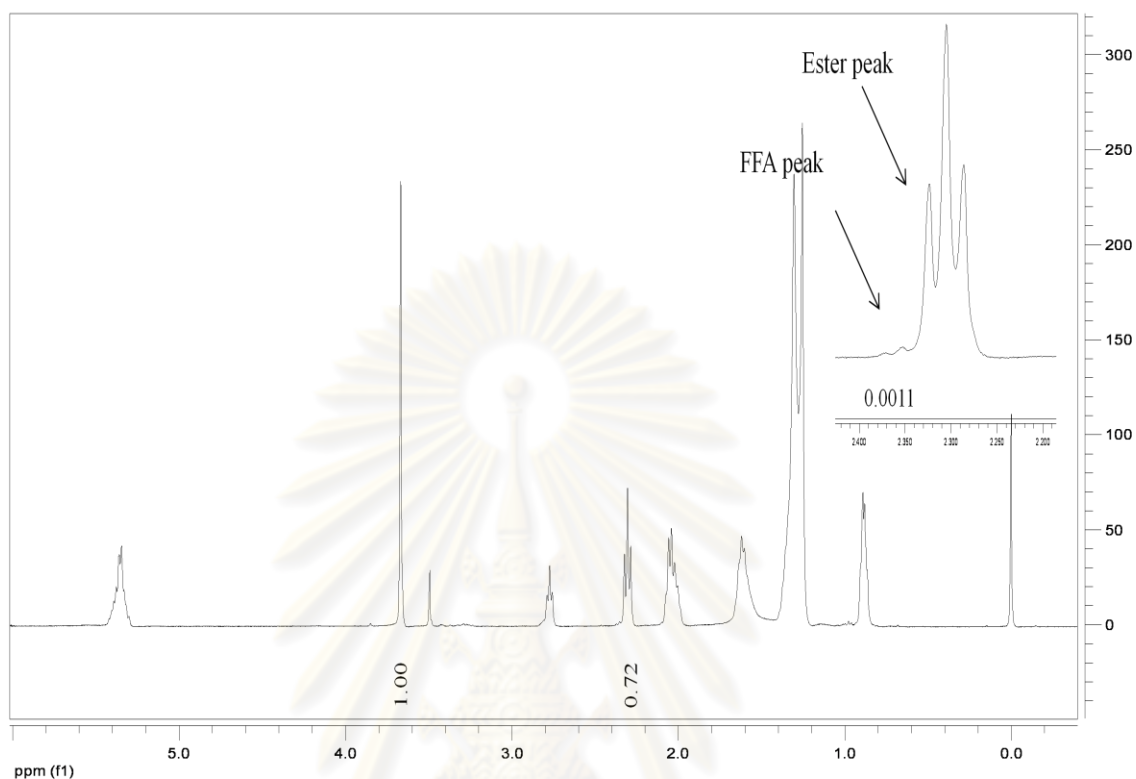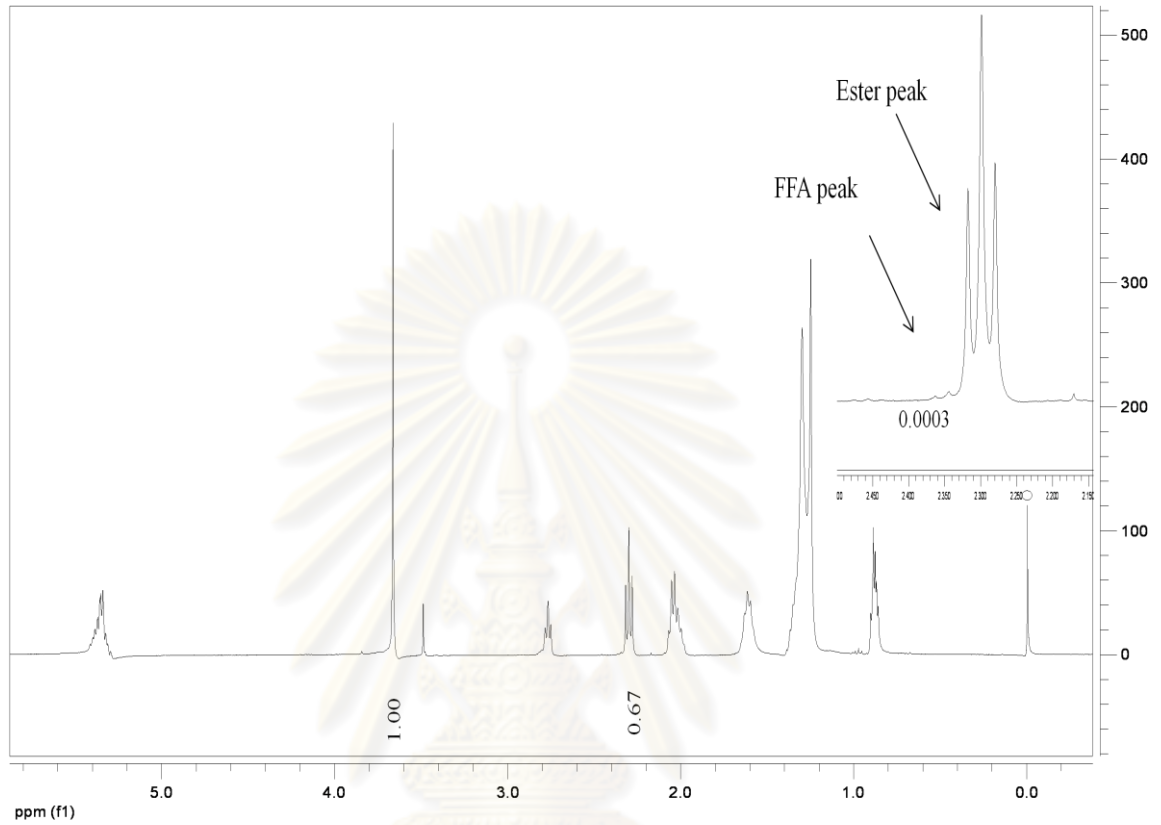

Figure A-16 Percentage of FFA in biodiesel production from tomato seed oil
(TS March 2011)

$$\% \text{ of FFA} = 4\frac{(0.0003)}{0.6} \times 100 = 0.22\%$$

ศูนย์วิทยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX B

Chromatogram of GC

Environmental Science,Chulalongkorn U.

Data File:	c:\star\joe\011010meoh3h 2;08;31	
Channel:	Front = FID RESULTS	
Sample ID:	011010MeOH3h	
Operator (Inj):	new	
Injection Date:	25/11/2010 14:08:31	
Injection Method:	c:\labchem07\new method jo-1.2.mth	
Run Time (min):	59.440	
Workstation:		
Instrument (Inj):	gc	

Operator (Calc):	new
Calc Date:	25/11/2010 15:15:06
Times Calculated:	6
Calculation Method:	011010meoh3h 2;08;31 pm-front.mth
Instrument (Calc):	gc
Run Mode:	Analysis
Peak Measurement:	Peak Area
Calculation Type:	Percent
Calibration Level:	N/A
Verification Tolerance:	N/A
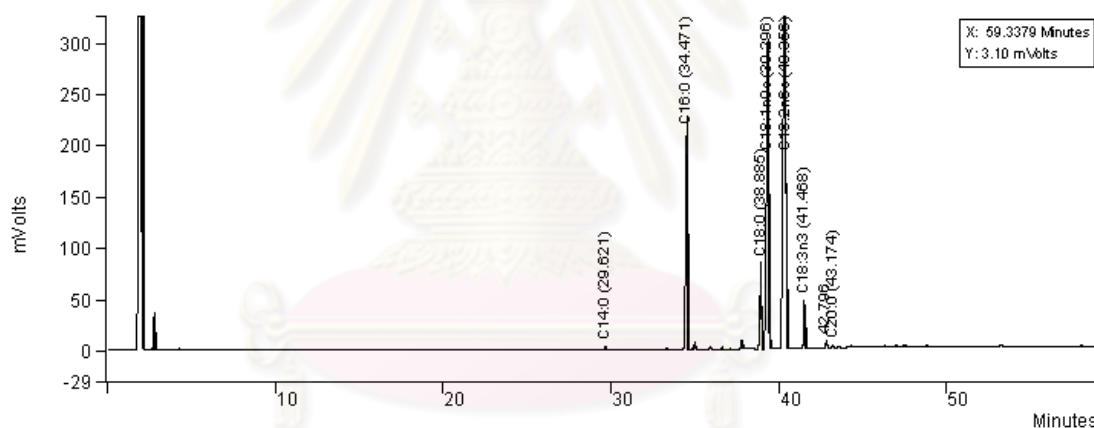
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C14:0	0.1452	29.621	-0.224	14141	0.00	BB	4.0		0
2	C16:0	13.8581	34.471	-0.210	1349874	0.00	BB	5.7		0
3	C18:0	5.2921	38.885	-0.208	515486	0.00	BP	5.7		0
4	C18:1n9c	23.6759	39.296	-0.000	2306185	0.00	GR	0.0		0
5	C18:2n6c	54.1080	40.356	-0.044	5270482	0.00	BB	9.0		0
6	C18:3n3	2.3233	41.468	-0.163	226308	0.00	VB	4.5		0
7		0.4295	42.796	0.000	41837	0.00	BV	4.8		0
8	C20:0	0.1679	43.174	-0.000	16350	0.00	VB	7.7		0
	Totals	100.0000		-0.849	9740663					

Figure B-1 GC Chromatogram of tomato seed oil (TS March 2010)

Extracted with MeOH

Environmental Science,Chulalongkorn U.

| Data File: | c:\star\joe\061010meoh30min 4;47;53 | Operator (Calc): | new |
Channel:	Front = FID RESULTS	Calc Date:	24/11/2010 18:36:31
Sample ID:	061010MeOH30min	Times Calculated:	3
Operator (Inj):	new	Calculation Method:	061010meoh30min 4;47;53
Injection Date:	24/11/2010 16:47:53	Instrument (Calc):	gc
Injection Method:	c:\labchem07\new method jo-1.2.mth	Run Mode:	Analysis
Run Time (min):	59.440	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A
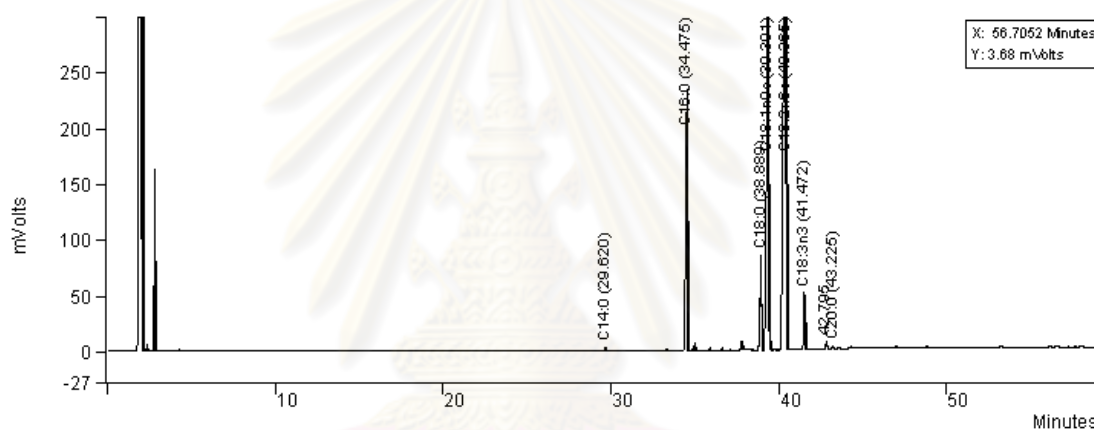
Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C14:0	0.1489	29.620	-0.225	15362	0.00	BB	4.1		0
2	C16:0	13.8907	34.475	-0.206	1433149	0.00	BB	5.8		0
3	C18:0	4.9534	38.889	-0.204	511058	0.00	BP	5.5		0
4	C18:1n9c	23.3997	39.301	-0.193	2414215	0.00	GR	0.0		0
5	C18:2n6c	54.5830	40.365	-0.035	5631495	0.00	BB	9.2		0
6	C18:3n3	2.3823	41.472	-0.160	245785	0.00	VB	4.5		0
7		0.3644	42.795	0.000	37595	0.00	BV	4.7		0
8	C20:0	0.2777	43.225	0.051	28652	0.00	GR	0.0		0
	Totals	100.0001		-0.972	10317311					

Figure B-2 GC Chromatogram of tomato seed oil (TS March 2010)

Extracted with hexane

Environmental Science,Chulalongkorn U.

Data File: c:\star\joe\011010meoh1h 2;38;56
Channel: Front = FID RESULTS
Sample ID: 011010MeOH1h
Operator (Inj): new
Injection Date: 24/11/2010 14:38:56
Injection Method: c:\labchem07\new method jo-1.2.mth
Run Time (min): 59.440
Workstation:
Instrument (Inj): gc

Operator (Calc): new
Calc Date: 24/11/2010 16:34:44
Times Calculated: 4
Calculation Method: 011010meoh1h 2;38;56 pm-front.mth
Instrument (Calc): gc
Run Mode: Analysis
Peak Measurement: Peak Area
Calculation Type: Percent
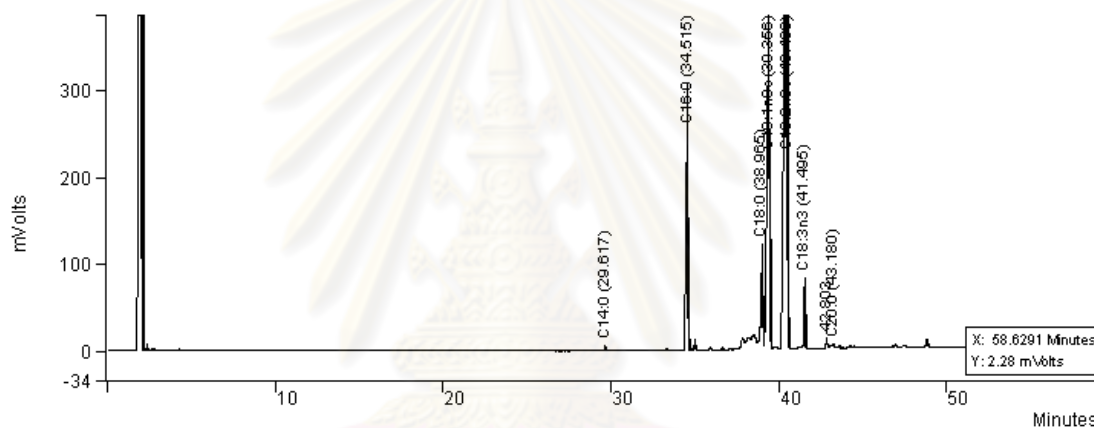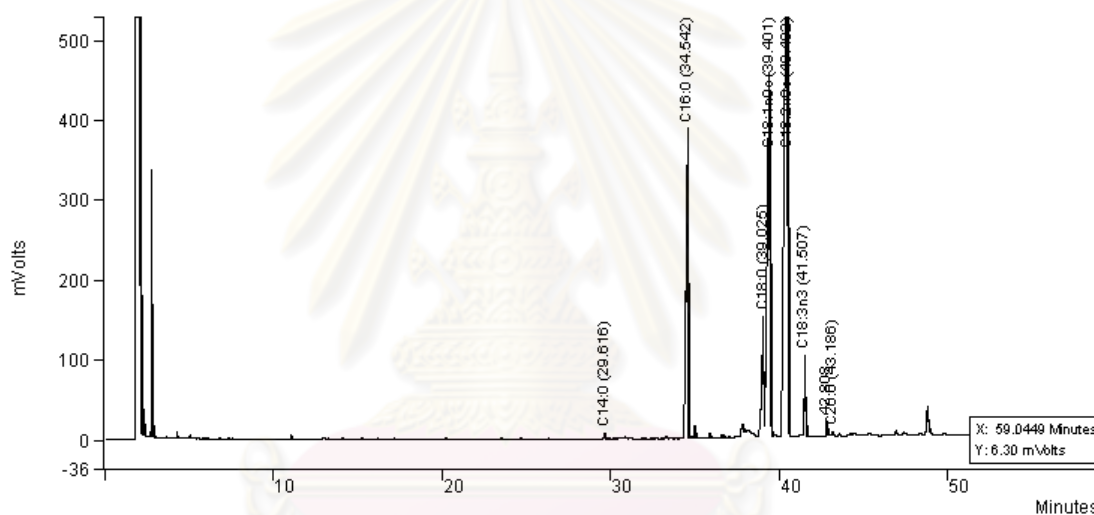Calibration Level: N/A
Verification Tolerance: N/A

Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C14:0	0.1462	29.617	-0.228	23776	0.00	BB	4.1		0
2	C16:0	13.7470	34.515	-0.166	2235340	0.00	BB	6.9		0
3	C18:0	4.9881	38.965	-0.127	811095	0.00	BP	6.1		0
4	C18:1n9c	23.2784	39.356	-0.138	3785207	0.00	PP	9.4		0
5	C18:2n6c	54.5938	40.438	0.038	8877279	0.00	PP	11.2		0
6	C18:3n3	2.5019	41.495	-0.136	406820	0.00	VB	4.3		0
7		0.3910	42.803	0.000	63581	0.00	BV	4.8		0
8	C20:0	0.3537	43.180	0.006	57517	0.00	VB	11.4		0
	Totals	100.0001		-0.751	16260615					

Figure B-3 GC Chromatogram of tomato seed oil (TS January 2011)

Extracted with MeOH

Environmental Science,Chulalongkorn U.

Data File:	c:\star\joe\011010hex2h 12;26;05	Operator (Calc):	new
Channel:	Front = FID RESULTS	Calc Date:	24/11/2010 13:49:17
Sample ID:	011010hex2h	Times Calculated:	10
Operator (Inj):	new	Calculation Method:	011010hex2h 12;26;05 pm-front.mth
Injection Date:	24/11/2010 12:26:05	Instrument (Calc):	gc
Injection Method:	c:\labchem07\new method jo-1.2.mth	Run Mode:	Analysis
Run Time (min):	59.440	Peak Measurement:	Peak Area
Workstation:		Calculation Type:	Percent
Instrument (Inj):	gc	Calibration Level:	N/A
		Verification Tolerance:	N/A

Peak No	Peak Name	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	C14:0	0.1491	29.616	-0.229	31247	0.00	BB	4.0		0
2	C16:0	14.6368	34.542	-0.139	3067787	0.00	BB	7.6		0
3	C18:0	3.3494	39.025	-0.068	702020	0.00	BP	6.7		0
4	C18:1n9c	23.9559	39.401	-0.093	5021014	0.00	PP	10.4		0
5	C18:2n6c	54.5247	40.492	0.092	11428056	0.00	PB	20.2		0
6	C18:3n3	2.5594	41.507	-0.124	536425	0.00	BB	4.6		0
7		0.4937	42.808	0.000	103486	0.00	BV	4.9		0
8	C20:0	0.3309	43.186	0.012	69363	0.00	VV	9.7		0
	Totals	99.9999		-0.549	20959396					

Figure B-4 GC Chromatogram of tomato seed oil (TS January 2011)

Extracted with hexane

VITA

Miss Chotika Laksana was born on May, 1985 in Phattalung province, Thailand. She got a Bachelor's Degree of chemistry in Faculty of Science at Prince of Songkhla University, Songkhla in 2007. After that, she was admitted into a Master Degree program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok in 2007 and completed the program in 2010.

Poster presentation for Pure and Applied Chemistry International Conference (PACCON2011) which organized by Department of Chemistry, Faculty of Science, Srinakharinwirot University and Chemical Society of Thailand in the topic of "Extraction process of tomato seed oil for producing biodiesel" on 5-7 January 2011at The Miracle Grand Hotel, Bangkok, Thailand.