ทรานซ์เอสเทอริฟิเคชันที่ใช้เบสเป็นตัวเร่งปฏิกิริยาของน้ำมันพืชใช้แล้วโดยใช้ตัวทำละลายร่วม

นางสาวเทพญาณี หลอดคำ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
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ปีการศึกษา 2552

ALKALI-CATALYZED TRANSESTERIFICATION OF WASTE COOKING OIL WITH COSOLVENT

Miss Thepyanee Lodcam

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2009

Thesis Title	ALKALI-CATALYZED TRANSESTERIFICATION OF WASTE COOKING OIL WITH COSOLVENT
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Field of Study	Chemical Engineering
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เทพญาณี หลอดคำ : ทรานซ์เอสเทอริฟิเคชันที่ใช้เบสเป็นตัวเร่งปฏิกิริยาของน้ำมันพืชใช้แล้วโดยใช้ตัวทำละลายร่วม. (ALKALI-CATALYZED TRANSESTERIFICATION OF WASTE COOKING OIL WITH COSOLVENT) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร. มนตรี วงศ์ศรี, 88 หน้า.

งานวิจัยนี้ศึกษาปัจจัยที่มีผลต่อกระบวนการสังเคราะห์ไบโอดีเซลจากน้ำมันพืชใช้แล้วจากการทอดอาหารโดยใช้ปฏิกิริยาทรานส์เอสเทอริฟิเคชัน ทำการทดลองที่สภาวะของโพแทสเซียมไฮดรอกไซด์ร้อยละ 2.6, 2.9 และ 3.1 โดยน้ำหนักน้ำมันพืชใช้แล้ว ใช้เวลาในการทำปฏิกิริยา 10, 15 และ 30 นาที อัตราส่วนโดยโมลของน้ำมันพืชใช้แล้วต่อเมทานอลคือ 1:9 รวมถึงการศึกษาการใช้ตัวทำละลายร่วมในการสังเคราะห์เพื่อเร่งอัตราการเกิดปฏิกิริยาโดยการปรับปรุงความสามารถในการละลายเข้าด้วยกันของเมทานอลและน้ำมันพืชโดยใช้ตัวทำละลายร่วม เตตระไฮโดรฟูแรน MTBE และไดเอทิลอีเทอร์ ถูกใช้เป็นตัวทำละลายร่วมเนื่องจากสามารถละลายได้ทั้งในเมทานอลและน้ำมันพืช มีราคาถูก ไม่เป็นพิษ ไม่มีผลต่อปฏิกิริยาและสามารถแยกออกจากผลิตภัณฑ์ได้ง่ายเนื่องจากมีจุดเดือดที่ใกล้เคียงกับเมทานอล การทดลองทำโดยใช้อัตราส่วนโดยโมลของเมทานอลต่อตัวทำละลายร่วม ที่ 1:0.2 จากการทดลองพบว่าร้อยละของโพแทสเซียมไฮดรอกไซด์ที่เหมาะในการทำปฏิกิริยาคือ ร้อยละ 2.6 ต่อน้ำหนักน้ำมัน และเมื่อทำการทดลองที่รอบกวน 400 รอบต่อนาที พบว่า ปริมาณเมทิลเอสเทอร์สูงสุดที่อุณหภูมิ 60 องศาเซลเซียส 30 นาที สำหรับการทดลองที่ไม่ใช้ตัวทำละลายร่วมจะได้ร้อยละเมทิลเอสเทอร์ 92.8 ในขณะที่การใช้ THF, MTBE และ DEE เป็นตัวทำละลายร่วม จะทำให้ได้ร้อยละเมทิลเอสเทอร์สูงถึง 95.8, 93.8 และ 94.0 ตามลำดับ

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ปีการศึกษา 2552

4971495621 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : METHYL ESTER / BIODIESEL / WASTE COOKING OIL / COSOLVENT

THEPYANEE LODCAM: PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL. THESIS ADVISOR: ASST. PROF. MONTREE WONGSRI, D.Sc., 88 pp.

The objective of this research was to study the effect factors of biodiesel synthesis from waste cooking oil (WCO) used in food frying using transesterification reaction. The series of experiment were carried out by using potassium hydroxide with 2.6, 2.9 and 3.1 wt% potassium hydroxide to WCO between 10, 15 and 30 minutes and WCO to methanol molar ratio 1:9. In addition, the thesis also investigated cosolvent of biodiesel synthesis in order to accelerate the reaction rate by improving the miscibility of methanol and WCO by the cosolvent. Tetrahydrofuran (THF), Methyl Tertiary Butyl Ether (MTBE) and diethyl ether (DEE) was used as a cosolvent due to they are miscible in both methanol and WCO, cheap price, non-toxic, inert to the reaction and easy to remove from the product due to their boiling point are close to methanol. The experiments were carried out by using methanol to cosolvent 1:0.2 by mole. The experiment result showed that potassium hydroxide 2.6 wt% is suitable for the reaction. From the experiments at 400 rpm found that the maximum methyl ester contents obtained from the reaction at 60 degree Celsius, 30 minutes were 92.8% for the reaction without cosolvent. While methyl ester contents from the reaction with THF, MTBE and DEE cosolvent at the same condition are 95.8%, 93.8% and 94.0% respectively.

Department : Chemical Engineering
Field of Study : Chemical Engineering
Academic Year : 2009
Student's Signature
Advisor's Signature

ACKNOWLEDGEMENTS

I would like to acknowledge Ass. Prof. Dr. Montri Wongsri for his guidance and support throughout the course of my graduate studies and research.

Many thanks are also extended to KFC (Siam Paragon Brach) provide assistance on the provision of feedstock. Also, I am thankful to Scientific and Technology Research Center of Chulalongkorn University for assistance in the provision of experimental instrument.

Also, I am thankful to the advisory committee members, Prof. Dr. Piyasarn Praserthdam, Dr. Surathep Kheowhom and Dr. Prakorn Ramakul to their time spending for many useful advices and suggestions.

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INTRODUCTION

1.1 Background

With the depletion of oil resources as well as the negative environmental impact associated with the use of fossil fuels, there is a renewed interest in alternate energy sources. As world reserves of fossil fuels and raw materials are limited, it has stimulated active research interest in nonpetroleum, renewable, and nonpolluting fuels. Biofuels are the only viable source of energy for the foreseeable future and can still form the base for sustainable development in terms of socioeconomic and environmental concerns. Biodiesel appears to be promising future energy sources. It can be produced from renewable sources such as vegetable oils or animal fats. Although this fuel has gained worldwide recognition for many years, it is not being widely commercialized mainly because it is more expensive than petroleum diesel. A cheaper feedstock, such as waste cooking oil, may be used to improve the economics of biodiesel (Issariyakul, 2007). However, due to the presence of a number of impurities, a better technology is needed if a low quality feedstock is to be used to produce biodiesel.

Alkaline catalysts such as NaOH and KOH are the most commonly used in transesterification since their reaction is much faster than an acid-catalyzed reaction. However, if high free fatty acid (FFA) feedstock such as fryer grease is used, the reaction is then partially driven to saponification which partially consumes catalysts and creates soap. Soap resulting from saponification creates difficulty in separating the by-product glycerol from biodiesel, which ultimately reduces the ester yield. Although acidcatalyzed transesterification does not encounter this problem, it requires a longer reaction time, higher reaction temperature, and a corrosion-tolerant reactor. The use of a two-step acid/alkaline catalyzed transesterification could be more suitable to produce biodiesel from high FFA feedstock such as waste cooking oil.

Alcohols used in transesterification are those of short chain carbon. The most popular one is methanol mainly because it is an economical source of alcohol. Also, the reaction can proceed faster if methanol is used due to its superior reactivity.

However, solubility of oils in methanol is low, therefore transesterification is limited by mass transfer. Ethanol, on the other hand, possesses higher solubility and reduces the effect of the mass transfer limitation. In addition, ethanol can be produced from renewable resources such as sugar crane, corn, and cassava thereby reducing dependency from petroleum sources. The disadvantage of using ethanol involves the strong emulsion formed during transesterification which causes difficulty in the glycerol separation process. However, ethanol can be used by mixing directly with gasoline for petrol fuel.

1.2 Objective of the Research

The current research work deals with the production of biodiesel from waste cooking oil using an alkaline transesterification process with a mixture of methanol and cosolvent. The objectives of this research work are

1.2.1 To produce biodiesel esters from waste cooking oil and methanol in a laboratory scale batch reactor system.

1.2.2 To study the factors affect to the transesterification reaction consisting of catalyst concentration, type of cosolvent, mixing speed, reaction time and temperature.

1.3 Scope of the Research

The research had been carried out to study the factors affect to transesterification reaction as follow:

1.3.1 Catalyst concentration varying from 2.6 to 3.1 weight percent of Potassium Hydroxide to Waste Cooking Oil (WCO).

1.3.2 Type of cosolvent consisting of tetrahydrofuran (THF), methyl tertiary butyl ether (MTBE) and diethyl ether (DEE).

1.3.3 Reaction temperature varying from 35 to 60 degree Celsius.

1.3.4 Stirring speed varying from 200 to 550 rpm.

1.3.5 Reaction time varying from 10 to 30 minutes.

1.4 Benefit of the Reseach

Process of biodiesel production from waste cooking oil with gives the highest yield of methyl ester in the short reaction time, less energy consumption and low capital cost.

1.5 Research Metodology

1.5.1 Study the previous researches and theory relevant to biodiesel production via transesterification.

1.5.2 Set up laboratory equipment and chemicals for the experiment.

1.5.3 Analyze chemical properties of raw material.

1.5.4 Carry out the experiments.

1.5.5 Analyze percentage of produced methyl ester using gas chromatograph.

1.5.6 Conclude the experimental result.

CHAPTER II

THEORY AND LITERETURE REVIEW

2.1 Biodiesel Production (Moser, 2009)

Biodiesel is defined by ASTM International as a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats. Vegetable oils and animal fats are principally composed of triacylglycerols (TAG) consisting of long chain fatty acids chemically bound to a glycerol (1,2,3-propanetriol) backbone. The chemical process by which biodiesel is prepared is known as the transesterification reaction, which involves a TAG reaction with a short-chain monohydric alcohol normally in the presence of a catalyst at elevated temperature to form fatty acid alkyl esters (FAAE) and glycerol (Figure 2.1). The conversion of TAG to biodiesel is a stepwise process whereby the alcohol initially reacts with TAG as the alkoxide anion to produce FAAE and diacylglycerols (DAG, reaction, Figure 2.1), which react further with alcohol (alkoxide) to liberate another molecule of FAAE and generate monoacylglyerols (MAG, reaction, Figure 2.1). Lastly, MAG undergo alcoholysis to yield glycerol and FAAE (reaction, Figure 2.1), with the combined FAAE collectively known as biodiesel. Three moles of biodiesel and one mole of glycerol are produced for every mole of TAG that undergoes complete conversion. The transesterification reaction is reversible, although the reverse reaction (production of MAG from FAAE and glycerol, for instance) is negligible largely because glycerol is not miscible with FAAE, especially fatty acid methyl esters (FAME) when using methanol as the alcohol component. The reaction system is biphasic at the beginning and the end of biodiesel production, as methanol and vegetable oil and glycerol and FAME are not miscible. Methanol is most commonly used in the commercial production of biodiesel, since it is generally less expensive than other alcohols, but ethanol prevails in regions such as Brazil where it is less expensive than methanol.

Other alcohols aside from methanol and ethanol are also of interest for biodiesel production because FAAE produced from higher alcohols may have different fuel properties in comparison to methyl or ethyl esters (Knothe, 2005).

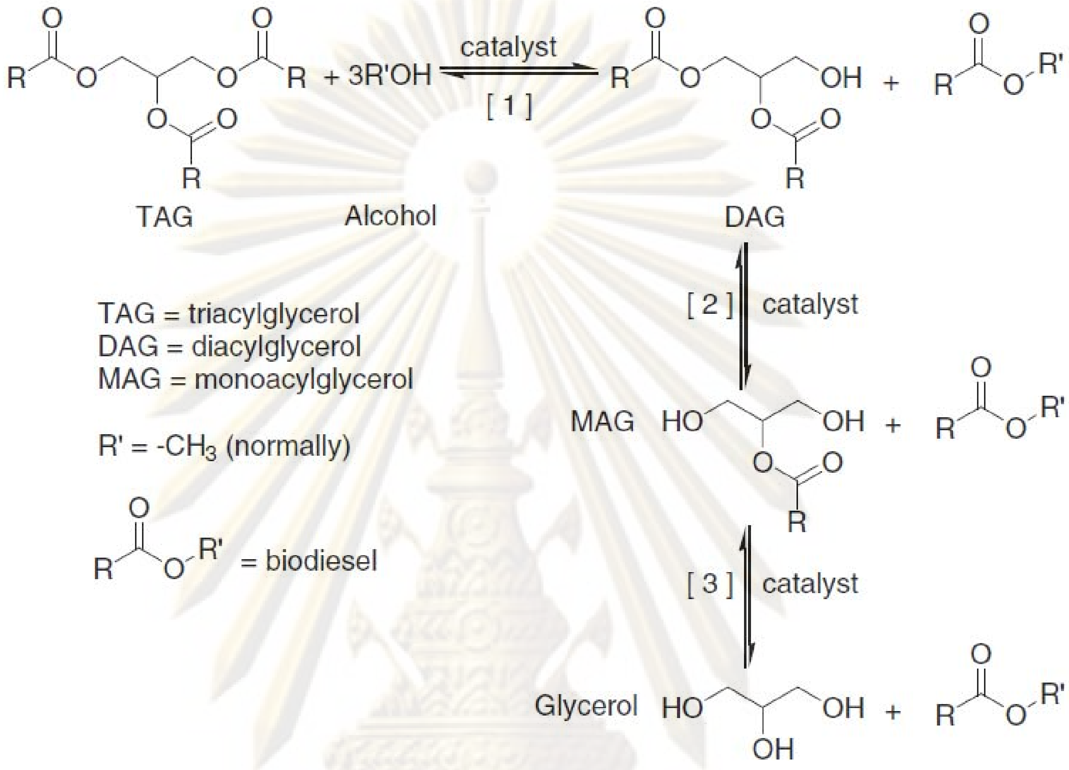
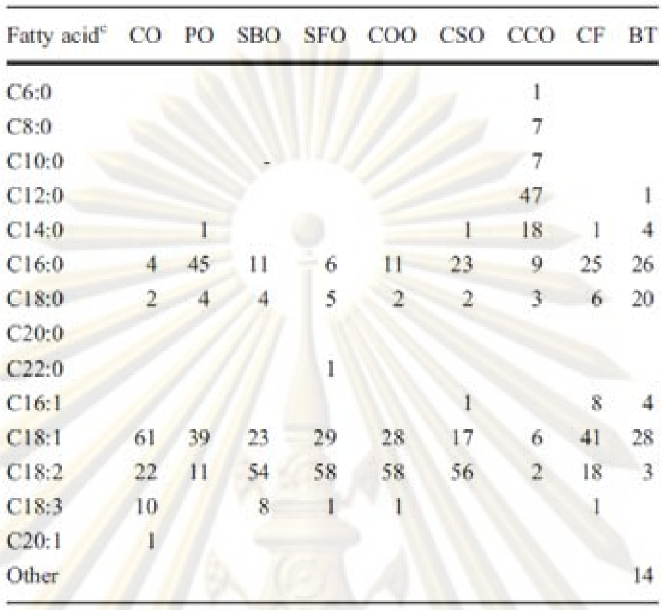


Figure 2.1 Transesterification of triacylglycerols to yield fatty acid alkyl esters (biodiesel).

Inexpensive homogenous base catalysts such as sodium or potassium hydroxide or methoxide are typically used in the commercial preparation of biodiesel from refined or treated oils. The classic alcoholysis conditions described by Freedman et al. (1984) include a TAG reaction with an excess of six molar equivalents of methanol (with respect to TAG) and 0.5 weight percent (wt.%) alkali catalyst (with respect to TAG) at 60°C for 1 h to produce fatty acid methyl esters (FAME, biodiesel) and glycerol. The chemical composition of biodiesel is dependent upon the feedstock from which it is produced, as vegetable oils and animal fats of differing origin have dissimilar fatty acid compositions (Table 2.1). The fatty ester composition of biodiesel is identical to that of the parent oil or fat from which it was produced.

A recent report from International Grains Council in 2008 indicated that rapeseed oil was the predominant feedstock for worldwide biodiesel production in 2007 (48%, 4.6 million metric tons, MMT). The remaining oils included soybean (22%, 2.1 MMT) and palm (11%, 1.0 MMT), with the rest (19%, 1.8 MMT) distributed among other unspecified vegetable oils and animal fats. The leading vegetable oils produced worldwide during the 2008 fiscal year (October 1, 2008 to September 30, 2009) are palm (43.20 MMT), soybean (37.81 MMT), rapeseed (19.38 MMT), and sunflower (11.68 MMT) oils. Not surprisingly, vegetable oil production and biodiesel feedstock usage are intimately related. Feedstocks for biodiesel production vary with location according to climate and availability. Generally, the most abundant commodity oils or fats in a particular region are the most common feedstocks. Thus, rapeseed and sunflower oils are principally used in Europe for biodiesel production, palm oil predominates in tropical countries, and soybean oil and animal fats are most common in the USA (Demirbas 2006). However, even combining these feedstocks do not suffice to fully replace the volume of conventional petroleum diesel fuel (petrodiesel). Therefore, exploration of additional feedstocks for biodiesel production has been continuously gaining significance.

Table 2.1. Typical fatty acid composition (wt.%)[a] of a number of common feedstock oils[b] and fats that may be used for biodiesel production (Moser et al., 2009)



Fatty acid[c]	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] From Gunstone and Harwood (2007); trace amounts (<1%) of other constituents may also be present

[b] 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

[c] C6:0 methyl caproate, C8:0 methyl caprylate, C10:0 methyl caprate, C12:0 methyl laurate, C14:0 methyl myristrate, C16:0 meythyl palmitate, C18:0 methyl stearate, C20:0 methyl arachidate, C22:0 methyl behenate, C16:1 methyl palmitoleate, C18:1 methyl oleate, C18:2 methyl linoleate, C18:3 methyl linolenate, C20:1 methyl Eicosenoate

2.2 Advantages and Disadvantages of Biodiesel (Moser, 2009)

Biodiesel has attracted considerable interest as an alternative fuel or extender for petrodiesel for combustion in compression–ignition (diesel) engines. Biodiesel is miscible with petrodiesel in any proportion and possesses several technical advantages over ultra-low sulfur diesel fuel (ULSD, <15 ppm S), such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content, and lower overall exhaust emissions. Important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability versus petrodiesel, and in some cases, higher NO_x exhaust emissions (Knothe et al., 2008). However, feedstock acquisition currently accounts for over 80% of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry. One potential solution to this problem is employment of alternative feedstocks of varying type, quality, and cost. These feedstocks may include soapstocks, acid oils, tall oils, waste cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. However, many of these alternative feedstocks may contain high levels of free fatty acids (FFA), water, or insoluble matter, which affect biodiesel production.

2.3 Influence of Free Fatty Acids on Biodiesel Production (Moser, 2009)

Feedstock quality in large part dictates what type of catalyst or process is needed to produce FAAE that satisfies relevant biodiesel fuel standards. If the feedstock contains a significant percentage of FFA (>3 wt.%), typical homogenous base catalysts such as sodium or potassium hydroxide or methoxide will not be effective as a result of an unwanted side reaction (reaction [1], Fig. 2.2) in which the catalyst will react with FFA to form soap (sodium salt of fatty acid) and water (or methanol in the case of sodium methoxide), thus irreversibly quenching the catalyst and resulting in an undesirable mixture of FFA, unreacted TAG, soap, DAG, MAG, biodiesel, glycerol, water, and/or methanol (Lotero et al. 2005). In fact, the base-catalyzed transesterification reaction will not occur or will be significantly retarded if the FFA content of the feedstock is 3 wt.% or greater (Canakci and Van Gerpen, 1999, 2001). For instance, nearly quantitative yields of biodiesel are achieved with homogenous base catalysts in cases where the FFA content of the feedstock is 0.5 wt.% or less (Naik et al., 2008). However, the yield of biodiesel plummets to 6% with an increase in FFA content to 5.3 wt.% (Naik et al., 2008). A further complicating factor of high FFA content is the production of water upon reaction with homogenous base catalysts (reaction [1], Fig. 2.2). Water is particularly problematic because, in the presence of any remaining catalyst, it can participate in hydrolysis with biodiesel to produce additional FFA and methanol (reaction, Fig. 2.2).

A common approach in cases where the FFA content of a feedstock is in excess of 1.0 wt.% (Freedman et al., 1984; Zhang et al., 2003) is a two-step process in which acid pretreatment of the feedstock to lower its FFA content is followed by transesterification with homogenous base catalysts to produce biodiesel. In a typical acid pretreatment procedure, FFA are esterified to the corresponding FAME in the presence of heat, excess methanol, and acid catalyst, normally sulfuric acid (Issariyakul et al., 2007; Kumartiwari et al., 2007; Meng et al. 2008; Naik et al., 2008; Rashid et al. 2008). The two-step procedure readily accommodates high FFA-containing low-cost feedstocks for the preparation of biodiesel (Canakci and Van Gerpen 1999, 2001, 2003).

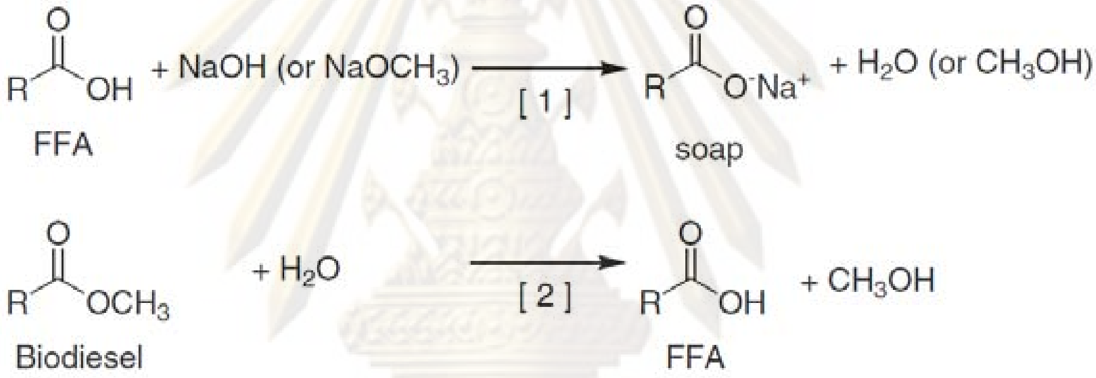
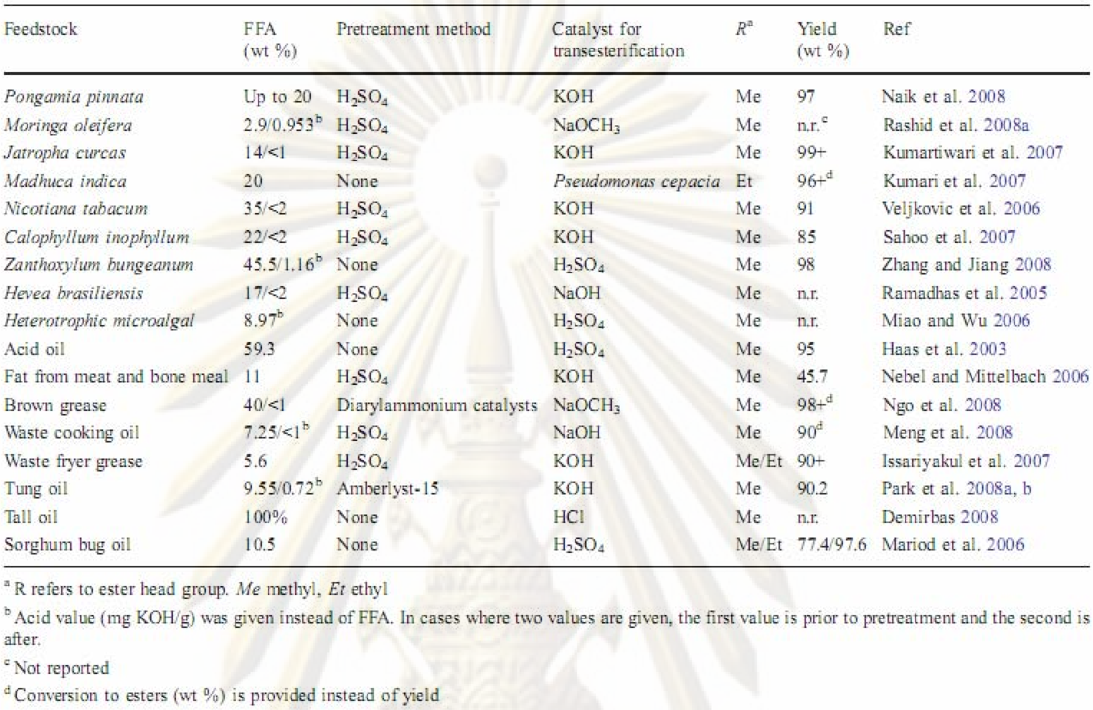


Figure 2.2 Formation of soap from reaction of free fatty acids (FFA) with catalyst and hydrolysis of biodiesel to yield FFA and methanol.

Despite the added capital costs associated with production, the integrated two-step process is being increasingly applied to prepare biodiesel from low-cost feedstock containing high numbers of FFA with good results (Lotero et al. 2005). Table 2.2 lists a number of recent examples of biodiesel prepared from feedstocks with high FFA content. Other potential strategies for the production of biodiesel from feedstocks with high FFA content include feedstock purification such as refining, bleaching, and deodorization to remove FFA content and other undesirable materials, if present. However, feedstock refining further increases production costs as a result of the additional equipment, time, and manpower that are required.

Lastly, the employment of catalysts that are not destroyed by FAA in the production of biodiesel is another alternative to the methods listed above.

Table 2.2 Examples of biodiesel production from feedstocks high in free fatty acids (FFA) (Moser, 2009)



Feedstock	FFA (wt %)	Pretreatment method	Catalyst for transesterification	R[a]	Yield (wt %)	Ref
Pongamia pinnata	Up to 20	H_2SO_4	KOH	Me	97	Naik et al. 2008
Moringa oleifera	2.9/0.953[b]	H_2SO_4	$NaOCH_3$	Me	n.r.[c]	Rashid et al. 2008a
Jatropha curcas	14/<1	H_2SO_4	KOH	Me	99+	Kumartiwari et al. 2007
Madhuca indica	20	None	*Pseudomonas cepacia*	Et	96+[d]	Kumari et al. 2007
Nicotiana tabacum	35/<2	H_2SO_4	KOH	Me	91	Veljkovic et al. 2006
Calophyllum inophyllum	22/<2	H_2SO_4	KOH	Me	85	Sahoo et al. 2007
Zanthoxylum bungeanum	45.5/1.16[b]	None	H_2SO_4	Me	98	Zhang and Jiang 2008
Hevea brasiliensis	17/<2	H_2SO_4	NaOH	Me	n.r.	Ramadhas et al. 2005
Heterotrophic microalgal	8.97[b]	None	H_2SO_4	Me	n.r.	Miao and Wu 2006
Acid oil	59.3	None	H_2SO_4	Me	95	Haas et al. 2003
Fat from meat and bone meal	11	H_2SO_4	KOH	Me	45.7	Nebel and Mittelbach 2006
Brown grease	40/<1	Diarylammonium catalysts	$NaOCH_3$	Me	98+[d]	Ngo et al. 2008
Waste cooking oil	7.25/<1[b]	H_2SO_4	NaOH	Me	90[d]	Meng et al. 2008
Waste fryer grease	5.6	H_2SO_4	KOH	Me/Et	90+	Issariyakul et al. 2007
Tung oil	9.55/0.72[b]	Amberlyst-15	KOH	Me	90.2	Park et al. 2008a, b
Tall oil	100%	None	HCl	Me	n.r.	Demirbas 2008
Sorghum bug oil	10.5	None	H_2SO_4	Me/Et	77.4/97.6	Mariod et al. 2006

[a] R refers to ester head group. *Me* methyl, *Et* ethyl

[b] Acid value (mg KOH/g) was given instead of FFA. In cases where two values are given, the first value is prior to pretreatment and the second is after.

[c] Not reported

[d] Conversion to esters (wt %) is provided instead of yield

2.4 Catalysts for Biodiesel Production (Moser, 2009)

Biodiesel is produced commercially using homogenous basic catalysts such as sodium (or potassium) hydroxide or methoxide because the transesterification reaction is generally faster, less expensive, and more complete with these materials than with acid catalysts (Boocock et al., 1996). The biodiesel industry currently uses sodium methoxide, since methoxide cannot form water upon reaction with alcohol such as with hydroxides (see Fig. 2.2; Zhou and Boocock, 2006a). Other alkoxides, such as calcium ethoxide, have also effectively catalyzed biodiesel production, albeit with higher methanol and catalyst requirements (Liu et al., 2008). The homogenous base-catalyzed transesterification reaction is about 4,000 times faster than the corresponding acid-catalyzed process (Srivastava and Prasad, 2000). Furthermore, base-catalyzed reactions are performed at generally lower temperatures, pressures, and reaction times and are less corrosive to industrial equipment than acid-catalyzed methods. Therefore, fewer capital and operating costs are incurred by biodiesel production facilities in the case of the base-catalyzed transesterification method (Freedman et al., 1986; Demirbas, 2008). However, the homogenous acid-catalyzed reaction holds an important advantage over the base-catalyzed method in that the performance of acid catalysts is not adversely influenced by the presence of FFA. In fact, acids can simultaneously catalyze both esterification and transesterification. For instance, FAME were prepared from acid oil, which consisted of 59.3 wt.% FFA, by acid-catalyzed transesterification at 65°C for 26 h with H2SO4 (1.5:1 molar ratio of catalyst to oil) and methanol (15:1 molar ratio of methanol to oil) in 95 wt.% purity. The remaining products consisted of FFA (3.2 wt.%), TAG (1.3 wt.%), and DAG (0.2 wt.%) (Haas et al., 2003).

A wide range of catalysts may be used for biodiesel production, such as homogenous and heterogeneous acids and bases, sugars, lipases, ion exchange resins, zeolites, and other heterogeneous materials. In general, acids are more appropriate for feedstocks high in FFA content. Homogenously catalyzed reactions generally require less alcohol, shorter reaction times, and more complicated purification procedures than heterogeneously catalyzed transesterification reactions. Heterogeneous lipases are generally not tolerant of methanol, so production of ethyl or higher esters is more common with enzymatic methods.

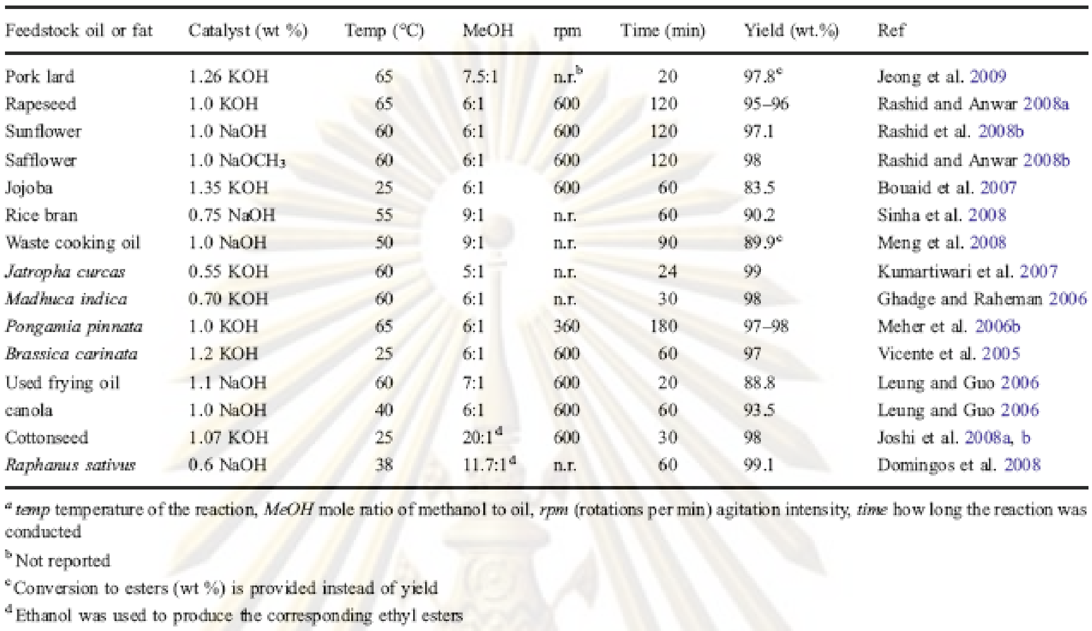
Noncatalytic transesterification of biodiesel may be accomplished in supercritical fluids such as methanol, but a very high pressure (45–65 bar), temperature (350°C), and amount of alcohol (42:1 molar ratio) are required (Saka and Kusdiana, 2001; Demirbas, 2003, 2005, 2006; Kusdiana and Saka, 2004). Advantages of supercritical transesterification versus various catalytic methods are that only very short reaction times (4 min, for instance) are needed, and product purification is simplified because there is no need to remove a catalyst. Disadvantages of this approach include limitation to a batch-wise process, elevated energy and alcohol requirements during production, and increased capital expenses and maintenance associated with pressurized reaction vessels (Saka and Kusdiana, 2001; Demirbas, 2003, 2005, 2006; Kusdiana and Saka, 2004).

2.5 Alcohols Used in the Production of Biodiesel (Moser, 2009)

As previously mentioned, methanol is the most common alcohol used in the production of biodiesel. Other alcohols may also be used in the preparation of biodiesel, such as ethanol, propanol, iso-propanol, and butanol (Freedman et al., 1984, 1986; Zhou et al., 2003; Issariyakul et al., 2007; Stavarache et al., 2008). Ethanol is of particular interest primarily because it is less expensive than methanol in some regions of the world, and biodiesel prepared from bio-ethanol is completely bio-based. Butanol may also be obtained from biological materials, thus yielding completely bio-based biodiesel as well. Methanol, propanol, and iso-propanol are normally produced from petrochemical materials such as methane obtained from natural gas in the case of methanol.

Methanolysis. The classic reaction conditions for the methanolysis of vegetable oils or animal fats are 6:1 molar ratio of methanol to oil, 0.5 wt.% alkali catalyst (with respect to TAG), 600+ rpm, 60°C reaction temperature, and 1 h reaction time to produce FAME and glycerol (Freedman et al. 1984). A number of recent studies have describedoptimal reaction conditions for biodiesel production from various feedstocks using response surface methodology (RSM). Parameters that are normally optimized to produce the most biodiesel include catalyst type and amount, reaction time and temperature, amount of alcohol, and/or agitation intensity. Please refer to Table 2.3 for a summary of recent examples of biodiesel process optimization employing RSM. In addition to the studies listed in Table 2.3 are the following: Park et al. (2008), Rashid and Anwar (2008), Wang et al. (2008), Cetinkaya and Karaosmanoglu (2004). A representa- tive example of reaction conditions optimized by RSM is the work of Kumartiwari et al. (2007) in which Jatropha curcas oil methyl esters were produced (after acid pretreatment) using 0.55 wt.% KOH, 60°C reaction temperature, 5:1 molar ratio of methanol to oil, and 24 min reaction time to provide biodiesel in 99% yield. The reaction parameters do not vary by a significant amount, as seen by comparison of the classic reaction conditions to that of Kumartiwari et al. (2007) and others listed in Table 2.3, as discussed by Freedman et al. 1984.

Table 2.3 Recent examples of optimization of reaction conditions for production of biodiesel from various feedstocks using response surface methodology



Feedstock oil or fat	Catalyst (wt %)	Temp (°C)	MeOH	rpm	Time (min)	Yield (wt.%)	Ref
Pork lard	1.26 KOH	65	7.5:1	n.r.[b]	20	97.8[c]	Jeong et al. 2009
Rapeseed	1.0 KOH	65	6:1	600	120	95–96	Rashid and Anwar 2008a
Sunflower	1.0 NaOH	60	6:1	600	120	97.1	Rashid et al. 2008b
Safflower	1.0 $NaOCH_3$	60	6:1	600	120	98	Rashid and Anwar 2008b
Jojoba	1.35 KOH	25	6:1	600	60	83.5	Bouaid et al. 2007
Rice bran	0.75 NaOH	55	9:1	n.r.	60	90.2	Sinha et al. 2008
Waste cooking oil	1.0 NaOH	50	9:1	n.r.	90	89.9[c]	Meng et al. 2008
Jatropha curcas	0.55 KOH	60	5:1	n.r.	24	99	Kumartiwari et al. 2007
Madhuca indica	0.70 KOH	60	6:1	n.r.	30	98	Ghadge and Raheman 2006
Pongamia pinnata	1.0 KOH	65	6:1	360	180	97–98	Meher et al. 2006b
Brassica carinata	1.2 KOH	25	6:1	600	60	97	Vicente et al. 2005
Used frying oil	1.1 NaOH	60	7:1	600	20	88.8	Leung and Guo 2006
canola	1.0 NaOH	40	6:1	600	60	93.5	Leung and Guo 2006
Cottonseed	1.07 KOH	25	20:1[d]	600	30	98	Joshi et al. 2008a, b
Raphanus sativus	0.6 NaOH	38	11.7:1[d]	n.r.	60	99.1	Domingos et al. 2008

[a] *temp* temperature of the reaction, *MeOH* mole ratio of methanol to oil, *rpm* (rotations per min) agitation intensity, *time* how long the reaction was conducted

[b] Not reported

[c] Conversion to esters (wt %) is provided instead of yield

[d] Ethanol was used to produce the corresponding ethyl esters

The transesterification reaction employing methanol commences as two immiscible phases as a result of the very low solubility of TAG in methanol. Illustrative of this point is the fact that only 7.5 g of soybean oil is soluble in 1 L of methanol at 30°C (Boocock et al., 1996). The polar homogenous alkali catalyst is essentially exclusively dissolved in the polar methanol phase at the beginning of the reaction and does not come into contact with the TAG phase unless sufficient agitation is introduced. Stirring of sufficient magnitude causes TAG transport into the methanol phase where it is rapidly converted into FAME and glycerol, as depicted in Fig. 2.1. The rate at which FAME are produced during the transesterification reaction is thus controlled by mass-transfer limitations, which results in a lag time before conversion to FAME begins.

Once DAG and MAG intermediates are formed in sufficient quantity during the transesterification reaction, they serve as surfactants that improve mass transfer of TAG into the methanol phase. The reaction eventually transforms into another biphasic system that consists of ester-rich (FAME) and glycerol-rich phases. The alkali catalyst is preferentially soluble in the more polar glycerol-rich phase, which may result in a retardation of the rate of reaction (Mao et al., 2004). The glycerol-rich phase settles to the bottom of the reaction vessel when agitation is ceased, which facilitates purification of FAME.

As a result of the biphasic nature of the reaction mixture, there is a lag time at the beginning of the methanolysis reaction before FAME begins to form, after which the reaction speeds up, but then quickly decelerates (Freedman et al., 1984; Darnoko and Cheryan, 2000). The addition of co-solvents such as tetrahydrofuran (THF) to the methanolysis reaction significantly accelerates the production of FAME as a result of the formation of a monophasic as opposed to a biphasic reaction mixture (Mahajan et al., 2006). However, the molar ratio of methanol to oil must be increased to at least 25:1, which results in additional solvent that must be removed and recovered during purification. Other possibilities for accelerating the methanolysis reaction are micro- wave or ultrasonic (Stavarache et al., 2008) irradiation.

Ethanolysis. The classic conditions for ethanolysis of vegetable oils or animal fats are 6:1 molar ratio of ethanol to oil, 0.5 wt.% catalyst (with respect to TAG), 600+ rpm, 75°C reaction temperature, and 1 h reaction time to produce fatty acid ethyl esters (FAEE) and glycerol (Freedman et al. 1984). Ethyl esters have been prepared from a number of feedstocks for use or evaluation as potential biodiesel fuels (Issariyakul et al., 2007; Stavarache et al., 2008). In addition, mixtures of methyl and ethyl ester shave been reported whereby the transesterification reaction was conducted with both methanol and ethanol (Issariyakul et al., 2007). As in the case of methanolysis, the ethanolysis reaction has been optimized using RSM (Kucek et al., 2007)). Please refer to Table 6 for two recent examples from the literature. A representative example is that of the ethanolysis of crude Raphanus sativus oil (Domingos et al., 2008) in which 0.60 wt.% NaOH, 11.7:1 molar ratio of ethanol to oil, 38°C reaction temperature, and a 1-h reaction time afforded the corresponding ethyl esters in 99.1% yield. The reaction temperature and amount of ethanol in this case varied considerably from the conditions initially reported by Freedman et al. (1984).

Ethanolysis proceeds at a slower rate than methanolysis because of the higher reactivity of the methoxide anion in comparison to ethoxide. As the length of the carbon chain of the alkoxide anion increases, a corresponding decrease in nucleophilicity occurs, resulting in a reduction in the reactivity of ethoxide in comparison to methoxide. An example of this phenomenon is the transesterification (at 25°C) of canola oil with a 1:1 mixture of ethanol and methanol (to provide an overall molar ratio of alcohol to oil of 6:1) that results in 50% more methyl than ethyl esters (Kulkarni et al., 2007).

Another example is the transesterification of canola oil at 25°C with a 1:1 mixture of ethanol and methanol that results in methyl to ethyl ester ratios of 2.7:1 and at 75°C with a 1:1 mixture of ethanol and methanol that results in methyl to ethyl ester ratios of 1.3:1. These results indicate that methyl esters are preferentially formed at both ambient and elevated reaction temperatures but at elevated temperatures, the preference is diminished. Even though the formation of ethyl esters is comparatively slow, the overall rate of formation of esters is faster than with methanol alone due to the better solubility of TAG in a mixture of methanol and ethanol, which results in a reduction of mass transfer limitations (Kulkarni et al., 2007). For example, ultrasonically assisted transesterification of Melia azedarach (syringa) oil with methanol is complete after 40 min and with ethanol is complete after 20 min, respectively (Stavarache et al., 2008).

The base-catalyzed formation of fatty acid ethyl esters (FAEE) is more complicated than the production of FAME. Specifically, the formation of stable emulsions during ethanolysis is problematic during subsequent purification (Zhou et al., 2003; Zhou and Boocock, 2006a). In the case of methanolysis, these emulsions quickly and easily separate to form a lower glycerol-rich and an upper FAME-rich phase after agitation of the reaction has ceased. In ethanolysis, these emulsions are much more stable and severely complicate separation and purification of biodiesel (Zhou et al., 2003; Zhou and Boocock, 2006a). Ethanol is less polar than methanol, so it is slightlymoremiscible with TAG at ambient temperature than methanol, but mechanical agitation during the transesterification reaction is once again required to facilitate sufficient mass transfer between phases (Kulkarni et al., 2007).

Butanolysis. The classic conditions for butanolysis of vegetable oils or animal fats are 6:1 molar ratio of butanol to oil, 0.5 wt.% catalyst (with respect to TAG), 600+ rpm, 114°C reaction temperature, and 1 h reaction time to produce fatty acid butyl esters and glycerol (Freedman et al., 1984). Butyl esters have been prepared from a variety of feedstocks for use or evaluation as potential biodiesel fuels (Freedman et al., 1986; Schwab et al., 1987; Zhou and Boocock, 2006a, b). To date, the butanolysis reaction has not yet been optimized by RSM.

Butanol is completely miscible with vegetable oils and animal fats because it is significantly less polar than methanol and ethanol (Boocock et al., 1996). Consequently, transesterification reactions employing butanol are monophasic throughout (Zhou and Boocock, 2006a, b). The monophasic nature of butanolysis reactions influences the rate and extent of the reaction. There are no mass transfer limitations in the case of butanolysis, since all reactants and catalysts are contained in a single phase. As a result, the initial rate of butanolysis is considerably faster than that of methanolysis. For example, the yield of esters after 1 min is 88 wt.% in the case of butanolysis (114°C reaction temperature) but only 78 wt.% for methanolysis (60°C; Schwab et al., 1987). Another study found that butanolysis (30°C) was 50% complete after only 15 s of reaction time, and 60% and 63.5% complete after 90 and 150 s, respectively. However, methanolysis (40°C) was only 55% complete after 10 min (Freedman et al., 1986). In a more recent example, 15.4 wt.% of TAG remained after 3 min of butanolysis as opposed to 84.4 wt.% in the case of methanolysis (Zhou and Boocock, 2006a). At up to 40% conversion to alkyl esters, methanolysis is 12–16 times slower than butanolysis if lag time in the case of methanolysis is ignored and even slower if it is not ignored (Boocock et al., 1996; Freedman et al., 1986). The difference in reactivity would be even more striking had the reactions in the above example been performed at similar temperatures (methanolysis was conducted at 40°C as opposed to 30°C for butanolysis). Because the reactions depicted in Fig. 1 for the conversion of TAG into alkyl esters are reversible, the monophasic nature of butanolysis affects the extent of reaction. In the case of methanolysis, glycerol separation from FAME severely curtails the unwanted reverse reactions.

In the case of butanolysis, the reverse reactions are more likely to occur because all materials are in contact throughout the reaction. The monophasic nature of butanolysis reactions also complicates purification of the resultant butyl esters, as gravity separation of glycerol at the conclusion of the reaction is not possible. The weaker nucleophilicity of butoxide versus methoxide is another factor that affects the extent of reaction. Although butanolysis proceeds at a faster initial rate than methanolysis, the final conversion to products after 1 h reaction (114°C and 60°C reaction temperatures, respectively) is 96 wt.% versus 98 wt.% for methanolysis (Schwab et al., 1987). In addition, after 1 h (at 23°C), 14.4 wt.% of bound glycerol (TAG + DAG + MAG) remained, whereas only 11.7 and 7.2 wt.% remained in the cases of methanolysis and ethanolysis, respectively (Zhou and Boocock, 2006b). In summary, the butanolysis reaction is monophasic throughout, which results in a faster initial rate of reaction but may yield lower overall conversion to butyl esters in comparison to methyl or ethyl esters.

2.6 Biodiesel Production from Waste Cooking Oil (Meng et al., 2008)

Currently, compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization. It is reported that approximately 70%–85% of the total biodiesel production cost arises from the cost of raw material. Use of low-cost feedstock such as WCO should help make biodiesel competitive in price with petroleum diesel. Numerous studies have been conducted on biodiesel production and emission testing in the past two decades. Most of the current challenges are targeted to reduce its production cost, as the cost of biodiesel is still higher than its petro-diesel counterpart. This opens a golden opportunity for the use of WCO as its production feedstock. Everywhere in the world, there is an enormous amount of waste lipids generated from restaurants, food processing industries and fast food shops everyday.

Reusing of these waste greases cannot only reduce the burden of the government in disposing the waste, maintaining public sewers and treating the oily wastewater, but also lower the production cost of biodiesel significantly. Furthermore, biodiesel fuel has been demonstrated to be successfully produced from waste edible oils by an alkali-catalyzed transesterification process, and can be considered as alternative fuels in diesel engines and other utilities. Our purpose is to find the most appropriate parameters for WCO transesterification reaction process.

CHAPTER III

RESEARCH METHOLOGY

3.1 General

The research had been carried out in a laboratory scale to study suitable reaction conditions for methyl ester production from waste cooking oil via batch transesterification using homogeneous base catalyst (Potassium hydroxide)

3.2 Experimental Equipment

1 Beaker 600 ml.

2 Stick glass

3 Spatula

4 Water bath

5 Tree blade paddle

6 Variable speed motor

7 Funnel

8 Thermometer

9 Hotplate

10 Weight scale

11 Gas chromatograph

3.3 Experimental Chemical

1. Methanol, Analytical grade : Merk.
2. Potassium hydroxide, Analytical grade : Carlo Erba
3. Tetrahydrofuran, Analytical grade : QReC
4. Methyl tertiary butyl ether (MTBE), Analytical grade: Carlo Erba
5. Diethyl ether (DEE), Analytical grade: J.T.Baker

6. Sulfuric acid, Analytical grade : J.T.Baker

3.4 Raw Material

Waste cooking oil using in the experiments was complimentary obtained from KFC.

3.5 Research Procedure

3.5.1 Analyze chemical properties of raw material for

1 Free fatty acid content

2 Free fatty acid composition in accordance with AOAC969.33, AOAC991.39 (2005)

3.5.2 Experimentation steps

1 Filter and heat the waste cooking oil to a temperature of approximately 120 degree Celsius for 60 minute in order to remove the impured water (100 g).

2 Mix methanol with potassium hydroxide at 60 degree Celsius to become Methoxide (34.04 g methanol with 2.6, 2.9 and 3.1 weight percent of Potassium hydroxide to methanol).

3 Mix cosolvent with the waste cooking oil at the required reaction temperature (0.2 mol ratio of cosolvent to waste cooking oil, 35 and 60 degree Celsius)

4 Heat or cool the methoxide obtained from step 3 to the required reaction temperature.

5 Pour the methoxide obtained from step 4 into the mixed oil and cosolvent in step 3. and stir at 200,250,400 and 550 rpm. Start counting the reaction time.

6 Terminate the reaction using sulfuric acid to neutralize the un-reacted base catalyst and to reduce soap produced from sponification of free fatty acids and base catalyst [1]

7 Pour the product into a funnel and leave it until methyl ester and glycerol is completely separated (3 hours).

8 Check the upper layer, methyl ester, of the separated product to remove the un-reacted excess methanol and cosolvent by distillation at a temperature approximately 100 degree Celsius.

9 Wash methyl ester with distillated water to remove the excess base catalyst, methanol, cosolvent and glycerol.

10 Pour methyl ester and water into a funnel and leave it until methyl ester and washing water is completely separated.

11 Wash methyl ester until the washing water is neutralize (pH7).

12 Remove washing water by heating the methyl ester at a temperature of approximately 120 degree Celsius for 1 hour duration.

13 Filter the methyl ester using filter paper no.1 and keep the sample for the analysis of ester composition by gas chromatograph.

3.5.3 Analyze percentage of produced methyl ester using gas chromatograph.

The content of fatty acid methyl ester (FAME) in product was analyzed by a GC-2010 gas chromatography (Shimadzu). Its column is SGE, BP20 GC capillary column (30m x 0.32mmi.d. x 0.25μm film thickness) capable to maintain temperature in the range of 20 – 250 degree Celsius. The temperature of the injector and the flame ionization detector (FID) was 210 and 250 ˚C, respectively. The chromatographic conditions are summarized in Table 3.1 below:-

Table 3.1 Chromatographic conditions

Condition	Value
Carrier gas (He) flow rate	30 mL/min
Detector temperature (FID)	250 °C
Split ratio	1 : 25
Injection part temperature	220 °C
Inject volume	1 μL
Column temperature	210 °C
Holding time	30 min

The ester content of fatty acid methyl ester is determined in accordance with EN14103:2003 (Fat and Oil Derivatives – Fatty Acid Methyl Ester (FAME) – Determination of ester and linolenic acid methyl ester contents) using methyl heptadecanoate ($C_{18}H_{36}O_2$) as an internal standard and use normal heptane as a solvent. Appendix B shows how to determine FAME content from gas chromatograph in accordance with EN 14103. Appendix E contains GC result for the products. Gas chromatography of the products was carried out by Scientific and Technological Research Equipment Center Chulalongkorn University.

CHAPTER IV

RESULTS AND DISSCUSION

4.1 Raw material properties

The chemical properties of the waste cooking oil feedstock, used for chicken frying provided by KFC (Siam Paragon Brach), from batch to batch used in the experiments were analyzed by Thailand Institute of Scientific and Technological Research using AOAC 969.33, AOAC 991.39 (2005) analytical standard with Gas Chromatography are shown in Table 4.1

Table 4.1: Fatty acid composition of waste cooking oil

		Molecular weight	% by weight
Free Fatty acid,			2.09
Fatty acid composition;			
Lauric acid	C12:0	200	0.41
Myristic acid	C14:0	228	0.96
Plamitic acid	C16:0	256	36.64
Palmitoleic acid	C16:1 n-7	254	0.54
Heptadecanoic acid	C17:0	270	0.10
Stearic acid	C18:0	284	3.60
Cis-9-Octadecenoic acid	C18:1 n-9	282	45.02
Cis-9,12-Octadecadienoic acid	C18:2 n-6	280	10.34
Cis-9,12,15-Octadecatrienoic acid	C18:3 n-3	280	0.86
Arachidic acid	C20:0	312	0.31
Cis-11-Eicosenoic acid	C20:1 n-9	310	0.25
Behenic acid	C22:0	340	0.10
Lignoceric acid	C24:0	368	0.06
Unidentified peak			0.81
Total fatty acid composition			100
Molecular weight			847.21

4.2 Effect of catalyst concentration

The concentration of the catalyst was the first parameter studied. The effect of KOH concentration on the transesterification of the WCO was investigated with its concentration varying from 2.6 to 3.1 wt% (based on the weight of raw oil). The operating conditions during the whole reaction process were fixed at: reaction temperature of 60°C, reaction time of 30 minutes, speed of 250 rpm and molar ratio of methanol to oil at 9:1.

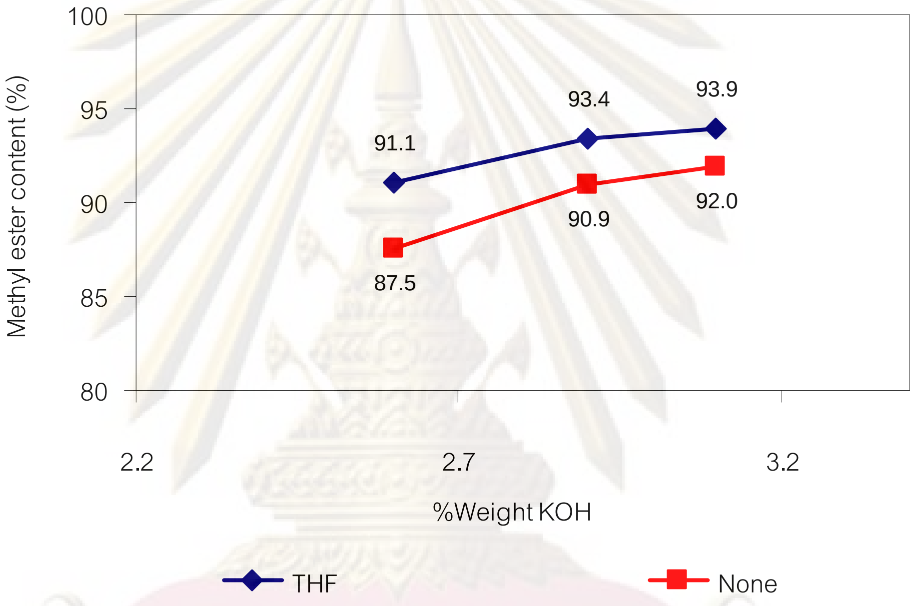


Figure 4.1 Effects of weight percent of Potassium Hydroxide to Methyl ester content (wt%)

From figure 4.1 shows that increasing of potassium hydroxide results in increasing of methyl ester due to increasing of catalyst is the increasing of chemical catalytic activity which help to break free fatty acid from triglyceride to have more reaction with alcohol. From the experiments found that increasing of potassium hydroxide to a certain point (more than 2.9 wt%) will create soap which is hard for product separation. At 2.6 wt% of potassium hydroxide to WCO, the product purification is quite easy.

4.3 Effect of speed

Mixing is an important factor for the transesterification reaction because methanol and oil is immiscible.

Ma et al. (1998b, 1999) studied the transesterification process of beef tallow with methanol. Because the solubility of methanol in beef tallow was 19% w/w at 100°C (Ma et al., 1998b), mixing was essential to disperse the methanol in beef tallow in order to start the reaction. They also pointed out that once the two phases were mixed and the reaction was started, stirring was no longer needed.

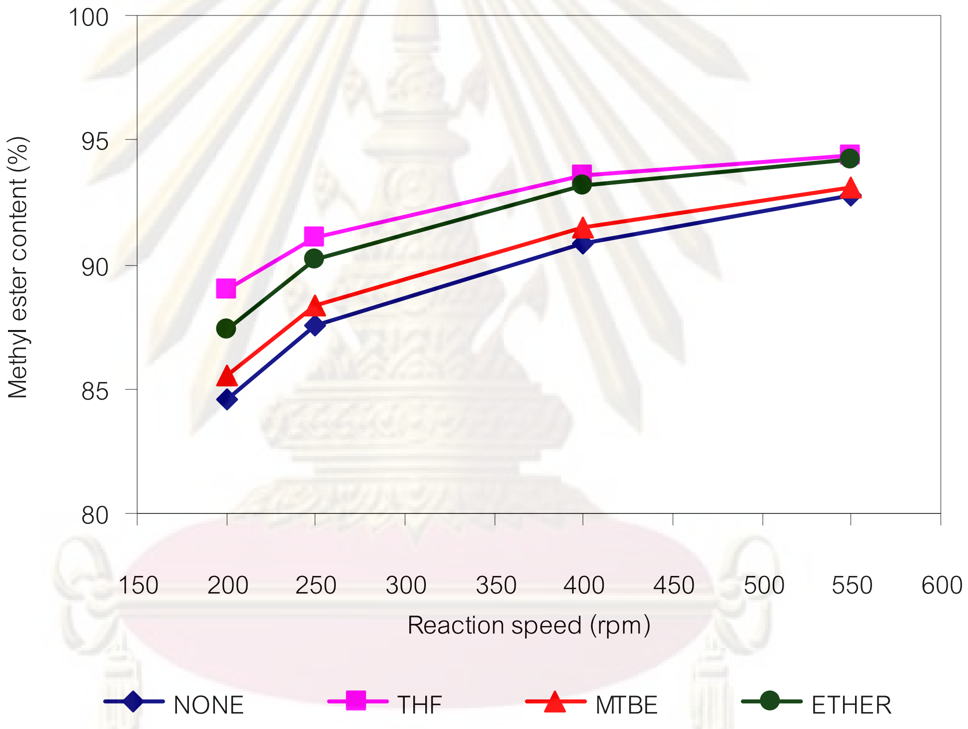


Figure 4.2 Effects of speed to Methyl ester content (wt%), Temp. 60 degree Celsius , 15 mins, 2.6%KOH

This research studied for the optimum speed using 9:1 constant molar ratio of methanol to oil, 2.6 wt% of potassium to oil, 60 °C and 15 minutes reaction time with varying stirring speed of 200, 250, 400 and 550 rpm. The paddle used in the experiments is three blade paddle, 5 cm diameter and 2.2 cm blade diameter. The beager is 9 cm diameter, 13 cm height with 3.2 cm chemical level in case of the reaction without cosolvent and 4.2 cm chemical level in case of using cosolvent. Distant between blades to bottom of the beager is 1.5 cm. The experimental results are shown in figure 4.2.

From the above figure, methyl ester contents in the product from gas chromatography analysis are:-

1) Reaction without cosolvent at 200, 250, 400 and 550 gave 84.6%, 87.5%, 90.8% and 92.8% methyl ester content, respectively.
2) Reaction with THF cosolvent at 200, 250, 400 and 550 gave 89.0%, 91.1%, 93.6% and 94.4% methyl ester content, respectively.
3) Reaction with MTBE cosolvent at 200, 250, 400 and 550 gave 85.6%, 88.3%, 91.5% and 93.1% methyl ester content, respectively.
4) Reaction with DEE cosolvent at 200, 250, 400 and 550 gave 87.4%, 90.2%, 93.1% and 94.2% methyl ester content, respectively.

Figure 4.2 shows that increasing of stirring speed will increase methyl ester content in the product due to increasing stirring speed resulting in smaller droplet size diameter of methanol from blade shearing. This will increase reaction surface for methanol, catalyst and oil resulting in faster reaction rate. In case of the reaction with tetrahydrofuran cosolvent, the highest content of 94.4 wt% methyl ester occurs at 550 rpm stirring speed. However, increasing of stirring speed from 250 rpm to 550 rpm enhances only 5.4 wt% additional methyl ester content whereas the reaction without cosolvent enhances 8.2 wt% methyl ester content from the same speed increasing.

4.4 Effect of temperature and time

Figure 4.3 shows result of the experiments which were carried to study the effects of reaction time using 2.6 wt% potassium hydroxide to WCO, 1:9 molar ratio of WCO to methanol, 400 rpm stirring speed at 35 °C and 60 °C reaction temperatures for 10, 15 and 30 minutes without cosolvent

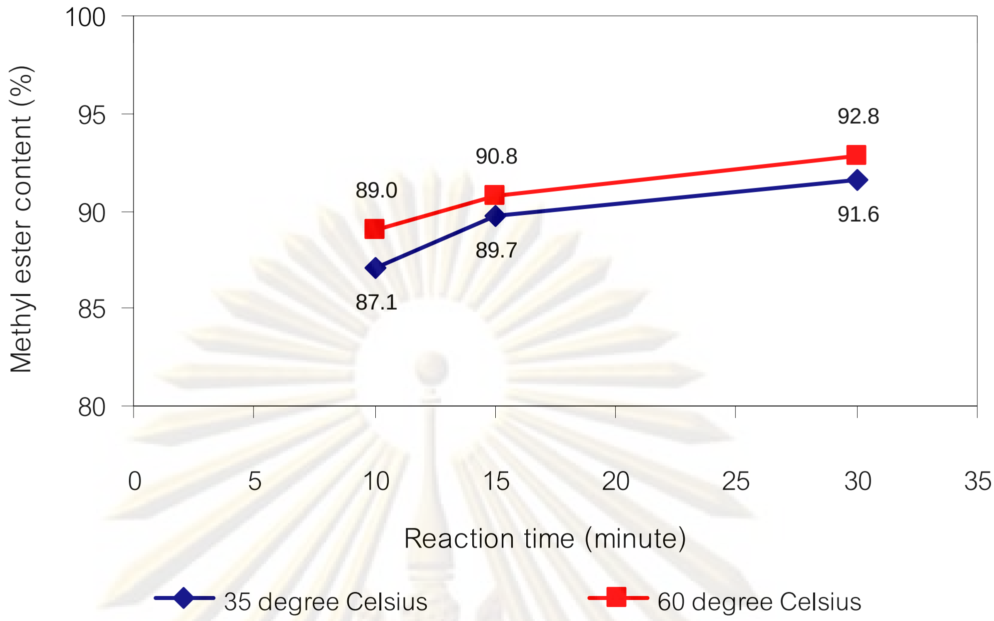


Figure 4.3 Effects of reaction temperature and time to Methyl ester content (wt%) for the reaction without cosolvent

From the above figure, methyl ester contents in the product from gas chromatography analysis are

1) At 35 °C reaction temperature and 10, 15, 30 min. reaction time gave 87.1%, 89.7%, 91.6% methyl ester content, respectively.
2) At 60 °C reaction temperature and 10, 15, 30 min. reaction time gave 89.0%, 90.8%, 92.8% methyl ester content, respectively.

Figure 4.3 shows that reaction temperature has a great effect to the reaction. This is due to higher temperature will increase energy for the reaction which results in greater percent of methyl ester. It was also found that at the first 10 to 15 minutes the increasing rate of methyl ester yield is quite high and will be lower at 30 minutes which is in line with the research by Darnoko (2000). Danoko studied the effect of reaction time on biodiesel production from palm oil via esterification reaction using 1 wt% potassium hydroxide, 50 °C reaction temperature and 90 minutes reaction time. The reaction rate is high in the first 5 minutes. Triglyceride was decreasing very fast whereas diglyceride and monoglyceride were increasing then.decreasing very fast. Reaction rate was slower after 15 minutes as can be seen from the slower increasing rate of methyl ester and the reaction tends to be in equilibrium after 30 minutes.

The study was also carried out using tetahydrofuran, MTBE and diethyl ether as a cosolvent to assist the transesterification at the same conditions with the result shown in figure 4.4, 4.5 and 4.6 respectively.

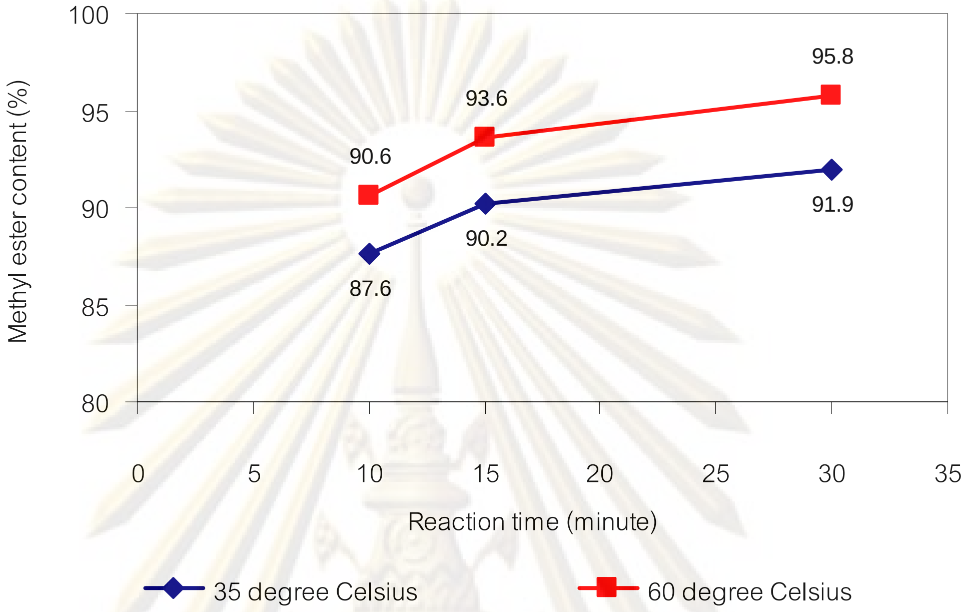


Figure 4.4 Effects of reaction temperature and time to Methyl ester content (wt%) for the reaction with tetahydrofuran cosolvent

The experimental results show the same trend with the reaction without cosolvent. However, using tetrahydrofuran as a cosolvent will result in higher methyl ester content in the product at the same experiment conditions due to tetahydrofuran cosolvent will assist in faster mixing of oil and methanol into the same phase even at low temperature, hence increasing the reaction rate and methyl ester content in the product.

From the above figure, methyl ester contents in the product from gas chromatography analysis are

1) At 35 °C reaction temperature and 10, 15, 30 min. reaction time gave 87.6%, 90.2%, 91.9% methyl ester content, respectively.
2) At 60 °C reaction temperature and 10, 15, 30 min. reaction time gave 90.6%, 93.6%, 95.8% methyl ester content, respectively.

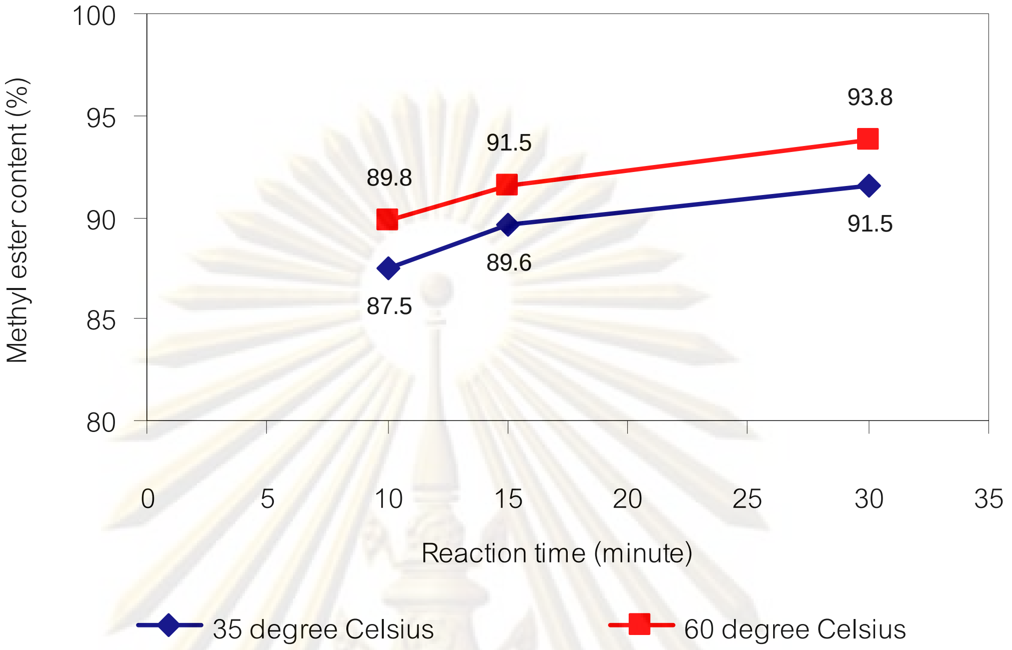


Figure 4.5 Effects of reaction temperature and time to Methyl ester content (wt%) for the reaction with MTBE cosolvent

From the above figure, methyl ester contents in the product from gas chromatography analysis are:-

1) At 35 °C reaction temperature and 10, 15, 30 min. reaction time gave 87.5%, 89.6%, 91.5% methyl ester content, respectively.
2) At 60 °C reaction temperature and 10, 15, 30 min. reaction time gave 89.8%, 91.5%, 93.8% methyl ester content, respectively.

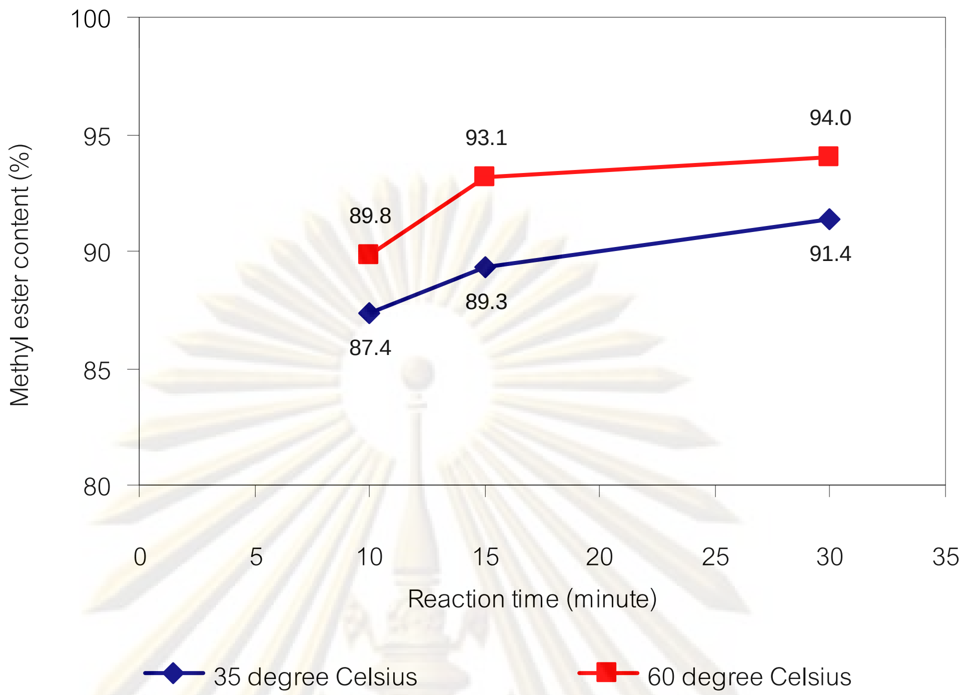


Figure 4.6 Effects of reaction temperature and time to Methyl ester content (wt%) for the reaction with dimethyl ether (DEE) cosolvent

From the above figure, methyl ester contents in the product from gas chromatography analysis are:-

1) At 35 °C reaction temperature and 10, 15, 30 min. reaction time gave 87.4%, 89.3%, 91.4% methyl ester content, respectively.
2) At 60 °C reaction temperature and 10, 15, 30 min. reaction time gave 89.8%, 93.1%, 94.0% methyl ester content, respectively.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. In this study, the optimum concentration of catalyst, KOH, is 2.6 wt% which is lesser than the threshold concentration limit that cause difficulty for glycerol separation due to soap formation from excess amount of catalyst with free fatty acids.

2. Addition of cosolvent into the reaction mixture making oil miscible with methanol. Because mass transfer in the one-phase reaction is superior to that in the two-phase reaction, due to an increase in the contact surface, the production rate of methyl ester by the one-phase reaction increases. Therefore, the initial addition of a cosolvent enhances the miscibility of oil to methanol and reduces the time required to form the one-phase system.

3. Using tetrahydrofuran as a cosolvent resulted in higher methyl ester content than diethyl ether in which diethyl ether cosolvent gave higher methyl ester content than MTBE cosolvent. The maximum methyl ester content obtained from the alcali-catalyzed transesterification of waste cooking oil and methanol (1:9 molar ratio) without cosolvent using 2.6 wt% KOH and 400 rpm stirring speed was 92.8 wt% at 60 °C reaction temperature and 30 minutes reaction time while the reaction at the same condition with 0.2 mol% tetrahydrofuran, DEE and MTBE cosolvent gave methyl ester content 95.8, 94.0 and 93.8 wt% respectively.

4. In this study, the experiments to observe the effects of stirring speed also had been carried out by varying stirring speed from 250 to 550 rpm using 9:1 molar ratio of methanol to waste cooking oil, 2.6 wt% KOH, 60 °C and 15 minutes reaction time, found that the maximum methyl ester contents for the reaction with and without tetrahydrofuran cosolvent were 94.4 and 92.8 wt%, at the maximum stirring speed of 550 rpm, respectively. However, the increasing of

stirring speed from 200 rpm to 550 rpm enhances only 5.4 wt% additional methyl ester content for the reaction with tetrahydrofuran cosolvent whereas the reaction without cosolvent enhances 8.2 wt% methyl ester content from the same speed increasing. Hence, stirring speed has more effect on the reaction without cosolvent.

5. It also observed that increasing the reaction time (upto 30 minutes) and reaction temperature (upto 60 °C) also resulted in higher methyl ester content in the product.

5.2 Recommendations

1. The addition of diethyl ether to the reaction as a cosolvent can improve the reaction rate and methyl ester content but with less efficiency than tetrahydrofuran. However, due to the fact that diethyl ether is cheaper than tetahydrofuran, the comparative economics study between tetrahydrofuran and diethyl ether is recommended.
2. In order to obtain methyl ester content to meet with the biodiesel standard, i.e. 96.5 wt% minimum, it was found that even using tetrahydrofuran in the reaction temperature 60 °C at 30 minutes still could not achieve that value (the experiment result was 95.8 wt%), so further study by increasing stirring speed, methanol to oil molar ratio or catalyst concentration is recommended.

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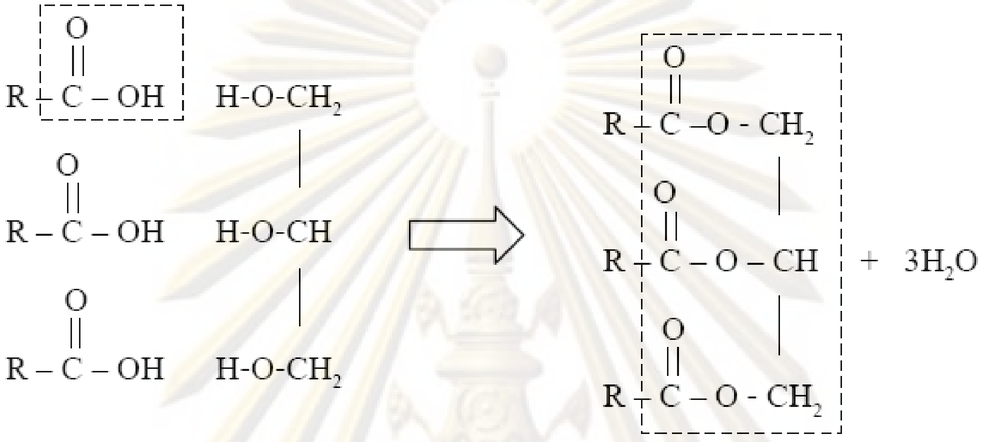
APPENDICES

APPENDIX A

REACTION CHEMISTRY CALCULATION

Waste Cooking Oil Molecular Weight Calculation



3 Fatty Acids + Glycerol Triglyceride + Water

From Triglyceride formation reaction, the molecular weight of triglyceride can be obtained from the following equation:-

$$MW_{TG} = 3\,R_{avg} + 38$$

$$R_{avg} = \sum \frac{[\%F_{AN} \times MW_n]}{100} + 38$$

Where

MW_{TG} is average molecular weight of triglyceride

R_{avg} is average Molecular weight of fatty acid less COOH

$\%F_{AN}$ is %wt of each fatty acid in waste cooking oil

MW_n is Molecular weight of each fatty acid

R_{AVG} = (0.41x200.32) + (0.96x228.36) + (36.64x256.43) + (0.54x254.41) + (0.1x270.45) + (3.6x284.48) + (45.02x282.46) + (10.34x280.45) + (0.86x280.45) + (0.31x312.53) + (0.25x310.51) + (0.1x340.59) + (0.06x368.64) = 269.74 g/mol

MW_{TG} = (3x265.1) +38

= 847.21 g/mol

Table A1 Chemical physical properties

Chemical	Density (g/ml)	Molecular Weight
Waste cooking oil	-	847.21
Methanol	0.79	32.04
Tetrahydrofulan	0.88	72.11
MTBE	0.74	88.15
Diethyl Ether (DEE)	0.71	74.12

Methanol Quantity Calculation

The experiment used waste cooking oil 100 g

Molar ratio of methanol to oil is 9

Waste cooking oil 100 g equals to 100/847.21 = 0.120 mol

Hence, methanol used is 9 x 0.120 = 1.06 mol or 1.06 x 32.04 = 34.04 g

or 32.04/ 0.79 = 43.09 ml

Catalyst Quantity Calculation

The experiment used 2.6 %wt catalyst to waste cooking oil

Hence, catalyst quantity used is (2.6/100) x 100 =2.6 g

Tetrahydrofuran Quantity Calculation

Methanol used in the experiment is 1.06 mol

Used 0.2 molar ratio of tetrahydrfuran to methanol

Hence, tatrahydrofuran used is 0.2 x 1.06 = 0.21 mol

or 0.21 x 72.11 = 15.14 g or 10.38/ 0.88 = 17.21 ml

MTBE Quantity Calculation

Methanol used in the experiment is 1.06 mol

Used 0.2 molar ratio of MTBE to methanol

Hence, MTBE used is 0.2 x 1.06 = 0.21 mol

or 0.21 x 88.15 = 18.51 g or 12.69/ 0.74 = 25.01 ml

DEE Quantity Calculation

Methanol used in the experiment is 1.06 mol

Used 0.2 molar ratio of DEE to methanol

Hence, DEE used is 0.2 x 1.06 = 0.21 mol

or 0.21 x 74.12 = 15.57 g or 15.57/ 0.71 = 21.92 ml

APPENDIX B

DETERMINATION OF METHYL ESTER CONTENT

Analysis of Methyl Ester Content in the Product

Methyl ester content in the product is determined from gas chromatograph in accordance with EN 14103: 2003 using methyl hetadecanoate (C17:0) as an internal standard and uses normal heptane (n-C_7H_{16}) as a solvent. Methyl ester content is calculated using the following formula:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} x \frac{C_{EI} x V_{EI}}{m} x100$$

Where

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

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

C_{EI} is the concentration, in mg/ml, of methyl heptadecanoate solution being used

V_{EI} is the volume, in ml, of the methyl haptadecanoate solution being used

m is the mass, in mg, of the sample

APPENDIX C
COSOLVENT SELECTION

Solvent selection criteria are:-

1. The selected cosolvents shall be inert to the reaction

2. The selected cosolvent shall have a boiling point lower and near to the boiling point of methanol to simplify the solvent recycle by flashing them out of the product at the boiling point of methanol.

3. The selected cosolvents shall be soluble in both methanol and triglyceride. Due to methanol is a polar substance while triglyceride which contains a long chain alkyl (hydrocarbon) group is non-polar, hence they are immiscible. So, the selected cosolvents which can be solute in both methanol and triglyceride shall have both polar and non-polar parts in their molecules.

The following table summarized the properties of cosolvents selected for the study.

Table C.1 Properties of selected cosolvent

Chemical	Formula	Molecular Wt	Density (g/ml)	Solubility in Water (20 °C)	Boiling Point (°C)
Tetrahydro Furan	C_4H_8O	72.11	0.88	Soluble	67
MTBE	$C_5H_{12}O$	85.15	0.74	26 g/l	55.2
Diethyl ether	$C_4H_{10}O$	74.12	0.71	69 g/l	34.6

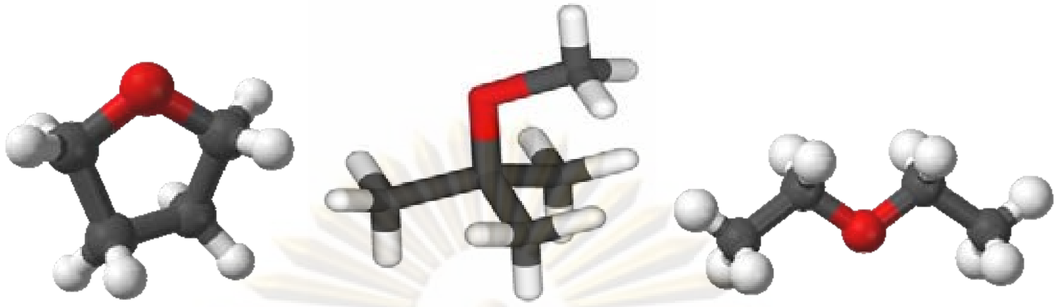


Fig. C.1 Molecular Structure of Tetrahydrofuran, MTBE and Diethyl Ether

The above figures show molecular structure of THF, MTBE and DEE from the left to right respectively. It can be seen that all these cosolvents have both polar part (at hydrogen atom) and non-polar part (at oxygen atom). MTBE and diethyl ether have lower boiling point than the melting point of waste cooking oil which requires higher reaction temperature. However, these cosolvents were selected due to they have lower and near boiling point to that of methanol, soluble in both methanol and triglyceride and the reaction will be carried out in a closed reactor. The boiling point of the solution will also be raised by the high content of both methanol and the non volatile triglyceride.

APPENDIX D

ERROR ANALYSIS

In order to check the accuracy/ error of the experimental result, three samples were tested at the same reaction conditions, i.e. 9:1 mol MeOH/ Oil, 2.6 wt% KOH, 60 °C, 15 minutes, 550 rpm, with THF cosolvent. The results are shown in the figure below.

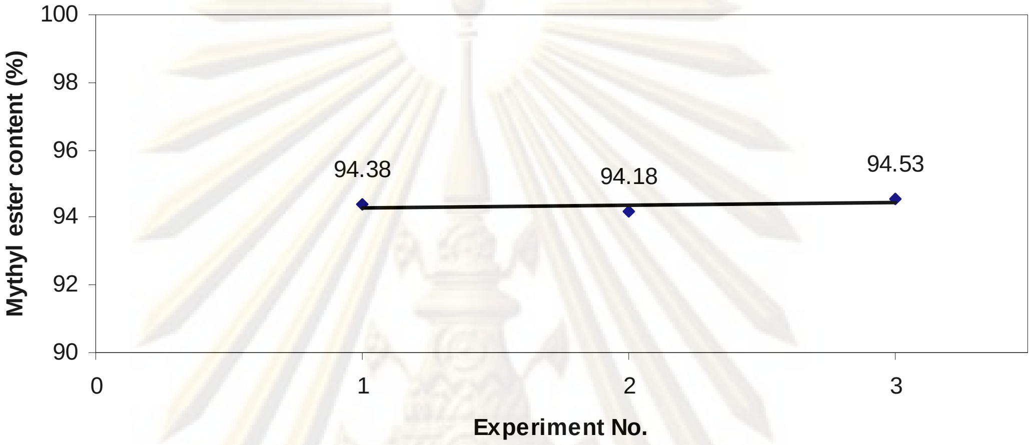


Fig. D.1 Methyl ester content from experiments at the same reaction conditions

Reaction condition: 9:1 mol MeOH/ Oil, 2.6 wt% KOH, 60 °C, 15 minutes, 550 rpm, with THF cosolvent

From the above results

- average methyl ester content is 94.37 wt%
- maximum methyl ester content (from experiment no. 3) is 94.53 wt% or +0.17% error from the average value
- minimum methyl ester content (from experiment no. 2) is 94.18 wt% or -0.19 % error from the average value

It can be concluded that if the different of methyl ester content from the different experiment conditions is less than 0.35 wt% (94.18 – 94.53), the result can be considered that these conditions yield the same methyl ester content.

APPENDIX E

EXPERIMENTAL DATA

1. Experimental Data

Sample No.	Cosolvent	Reaction Condition			
		%KOH	Speed (rpm)	Teperature (^{o}C)	Time (min)
W01	-	2.6	250	60	15
W02	-	2.9	250	60	15
W03	-	3.1	250	60	15
W04	THF	2.6	250	60	15
W05	THF	2.9	250	60	15
W06	THF	3.1	250	60	15
W07	-	2.6	200	60	15
W08	-	2.6	400	60	15
W09	-	2.6	550	60	15
W10	THF	2.6	200	60	15
W11	THF	2.6	400	60	15
W12	THF	2.6	550	60	15
W13	MTBE	2.6	200	60	15
W14	MTBE	2.6	250	60	15
W15	MTBE	2.6	400	60	15
W16	MTBE	2.6	550	60	15
W17	DEE	2.6	200	60	15
W18	DEE	2.6	250	60	15
W19	DEE	2.6	400	60	15
W20	DEE	2.6	550	60	15
W21	-	2.6	400	35	10
W22	-	2.6	400	35	15
W23	-	2.6	400	35	30

Sample No.	Cosolvent	Reaction Condition			
		%KOH	Speed (rpm)	Teperature (^{o}C)	Time (min)
W24	-	2.6	400	60	10
W25	-	2.6	400	60	30
W26	THF	2.6	400	35	10
W27	THF	2.6	400	35	15
W28	THF	2.6	400	35	30
W29	THF	2.6	400	60	10
W30	THF	2.6	400	60	30
W31	MTBE	2.6	400	35	10
W32	MTBE	2.6	400	35	15
W33	MTBE	2.6	400	35	30
W34	MTBE	2.6	400	60	10
W35	MTBE	2.6	400	60	30
W36	DEE	2.6	400	35	10
W37	DEE	2.6	400	35	15
W38	DEE	2.6	400	35	30
W39	DEE	2.6	400	60	10
W40	DEE	2.6	400	60	30
W41	THF	2.6	550	60	15
W42	THFR	2.6	550	60	15

2. Gas Chromatography Analysis for Methyl Ester Content in Product

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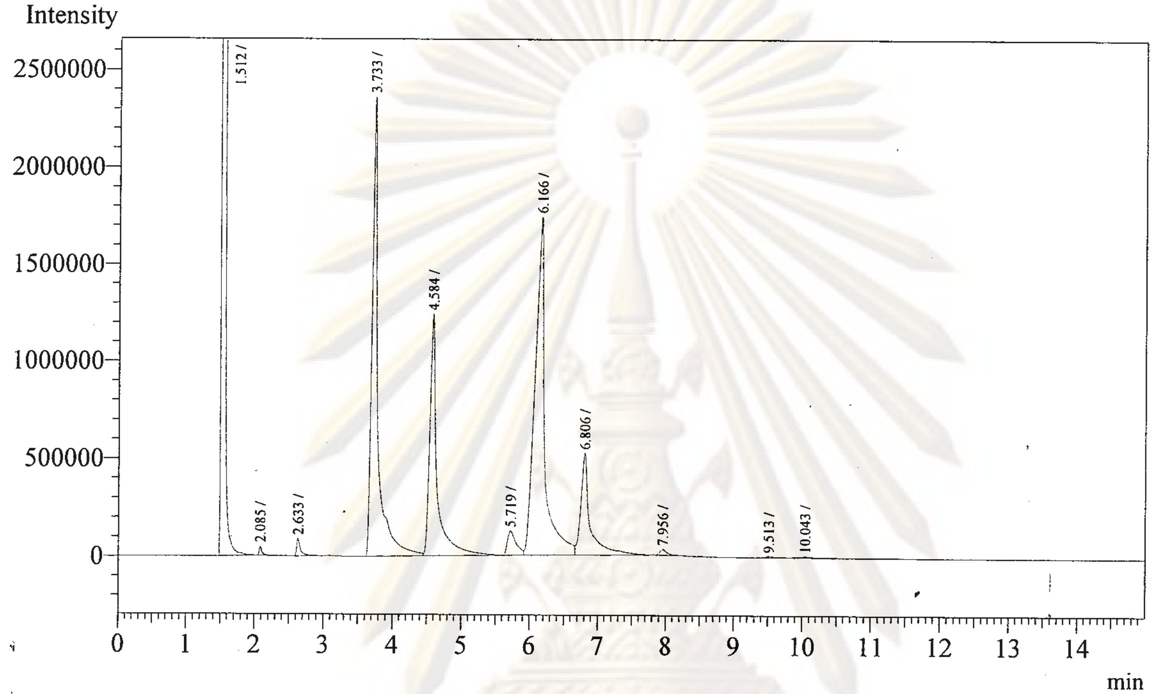

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3	2.633	325900	88434	0.000				
4	3.733	14752100	2351680	0.000				
x 5	4.584	9331350	1240420	0.000		V		
6	5.719	1094114	124893	0.000				
7	6.166	17824871	1736414	0.000		V		
8	6.806	4985709	520708	0.000		SV		
9	7.956	194948	28905	0.000				
10	9.513	69694	7299	0.000				
11	10.043	75066	6028	0.000				
Total		803691969	20344346					

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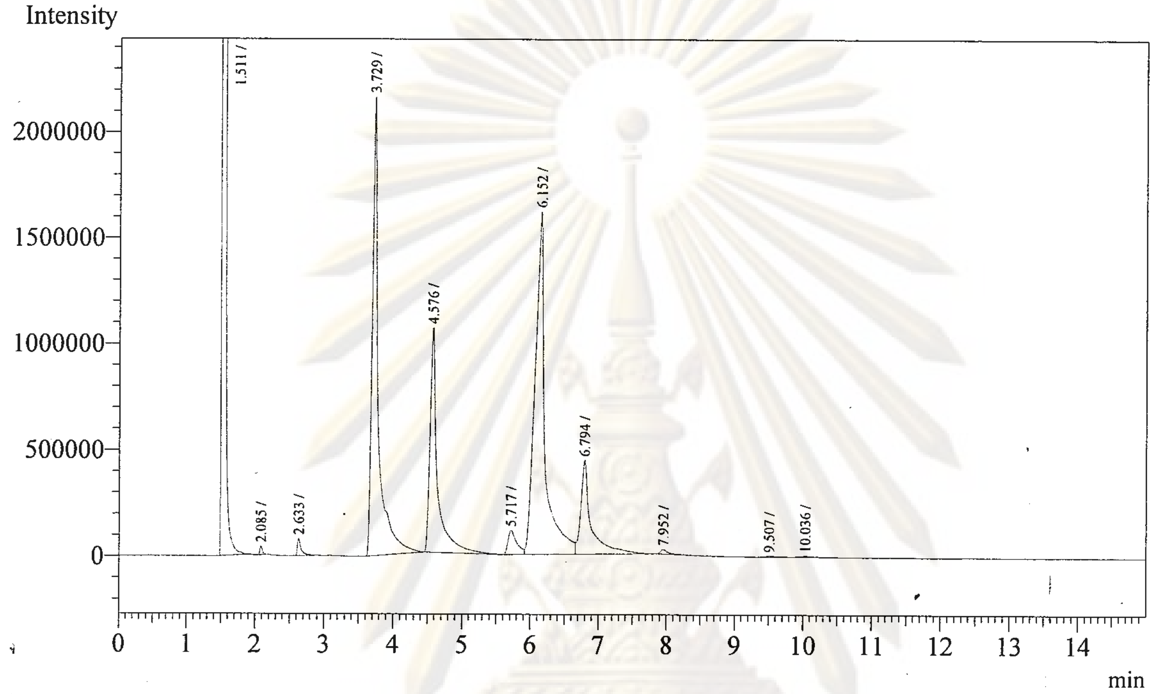

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4	3.729	13810955	2155142	0.000				
x 5	4.576	8007650	1057631	0.000				
6	5.717	1004721	113796	0.000				
7	6.152	16818942	1614566	0.000		V		
8	6.794	4666376	441971	0.000		V		
9	7.952	152217	22458	0.000				
10	9.507	62622	6401	0.000				
11	10.036	60700	5178	0.000				
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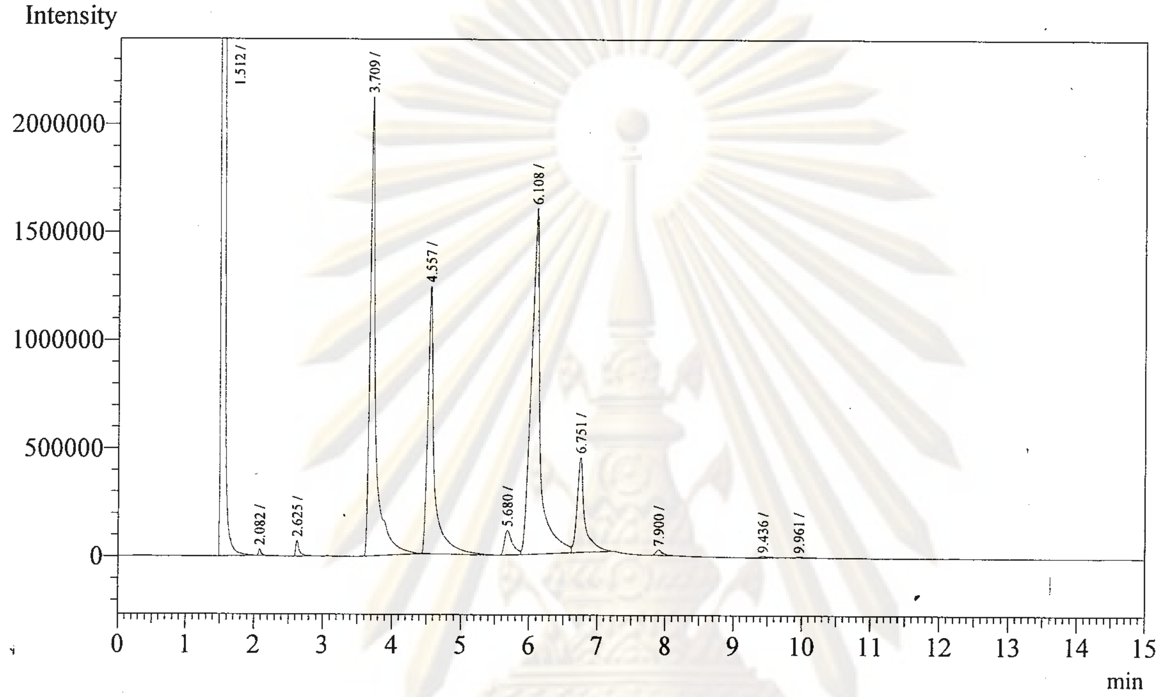

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3	2.625	265194	73614	0.000				
4	3.709	15936526	2120428	0.000				
5	4.557	8530774	1236565	0.000				
6	5.680	931493	114202	0.000				
7	6.108	18532922	1596150	0.000		V		
8	6.751	3461421	440547	0.000		V		
9	7.900	167168	25487	0.000				
10	9.436	63185	6653	0.000				
11	9.961	59976	5271	0.000				
Total		815727774	21940013					

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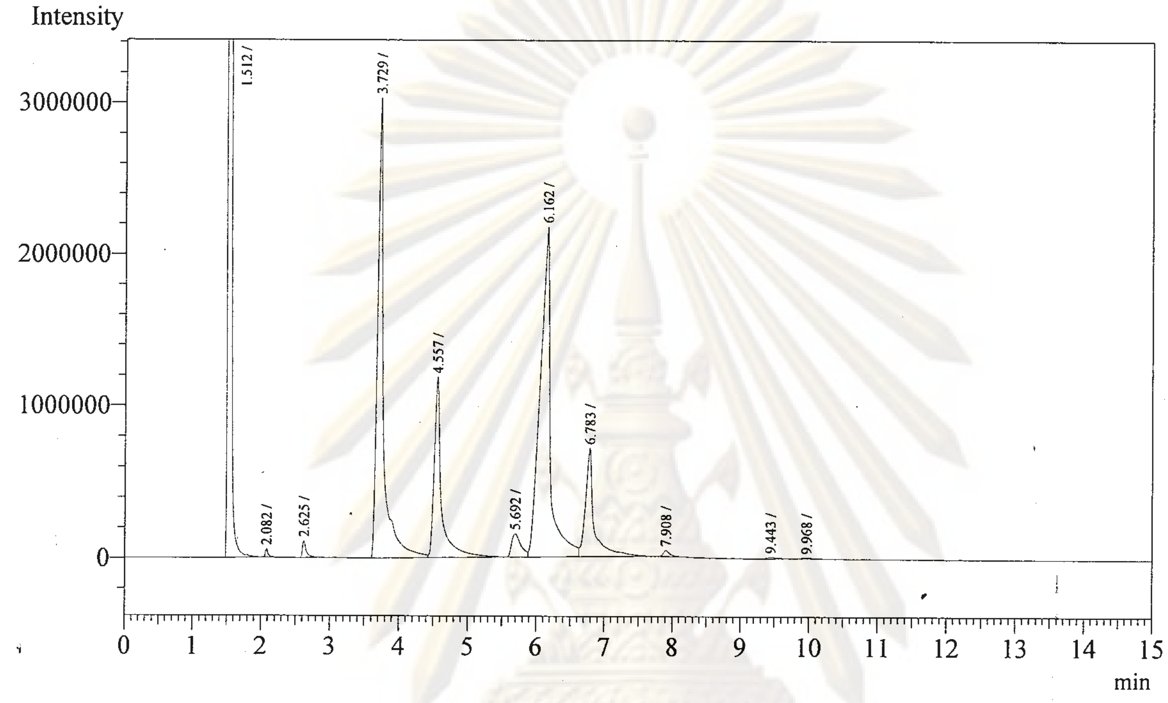

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3	2.625	419016	111548	0.000				
4	3.729	19298333	3015089	0.000				
5	4.557	8899216	1184728	0.000		V		
6	5.692	1457971	153928	0.000				
7	6.162	13364601	2173325	0.000		V		
8	6.783	6433991	713236	0.000		V		
9	7.908	258202	40637	0.000				
10	9.443	102939	10744	0.000				
11	9.968	86796	8104	0.000				
Total		794856687	09738974					

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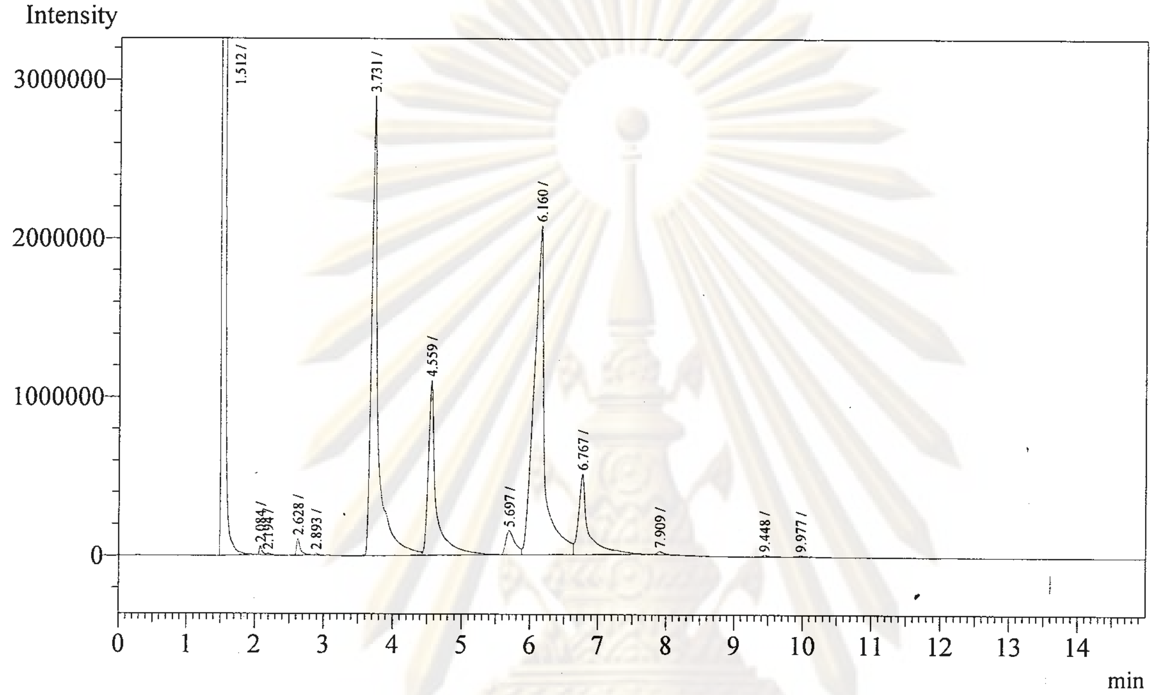

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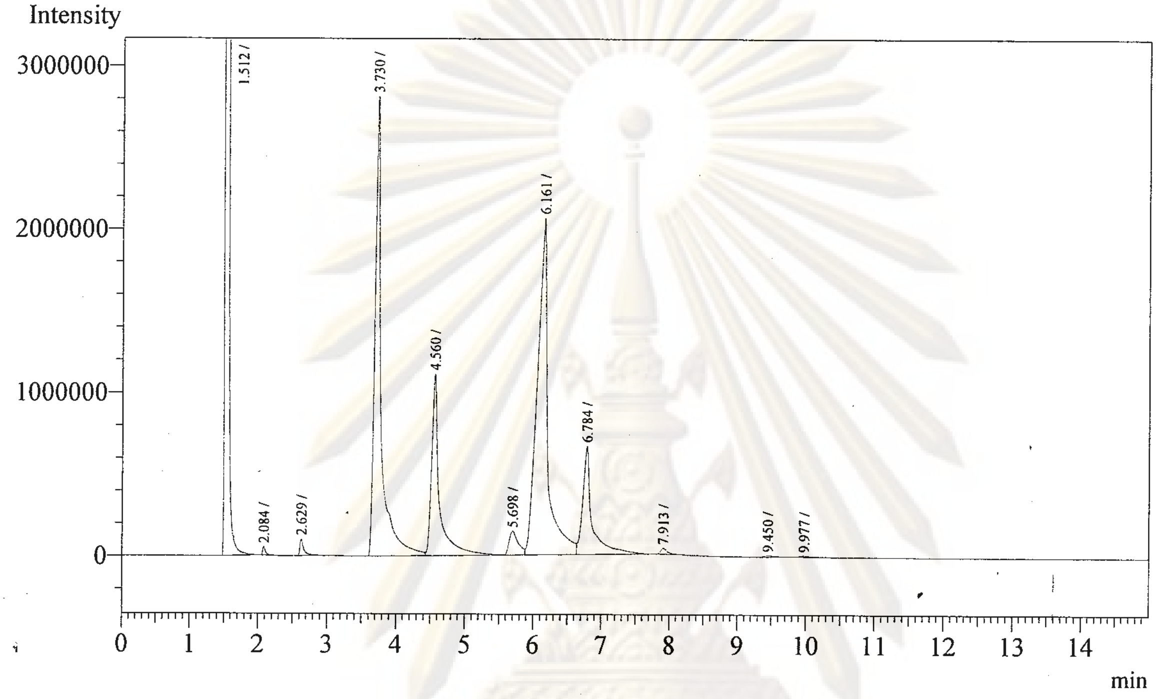
1	1.512	755338646	06785900	0.000		S		
2	2.084	156610	55722	0.000				
3	2.194	51343	11125	0.000		V		
4	2.628	407829	103702	0.000				
5	2.893	42634	12017	0.000				
6	3.731	19570277	2894299	0.000				
7	4.559	8824964	1102032	0.000		V		
8	5.697	1402268	152158	0.000				
9	6.160	12858817	2065428	0.000		V		
10	6.767	5135998	506332	0.000		V		
11	7.909	123285	18818	0.000				
12	9.448	93093	9520	0.000				
13	9.977	86360	7390	0.000				
Total		804092124	13724443					

Analysis Date & Time : 15/7/2552 8:59:55
User Name : Admin
Vial# : 5
Sample Name : W06
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

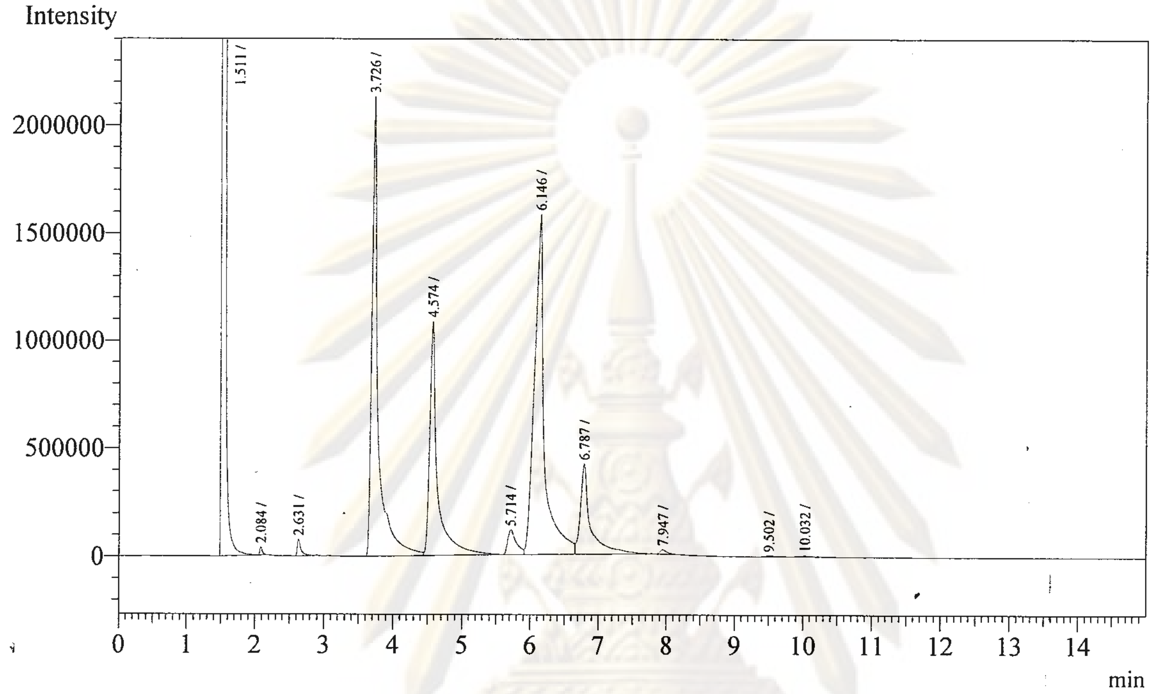
Data Name : D:\ACID\FA20.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.512	751559275	98286000	0.000		S		
2	2.084	150135	51979	0.000				
3	2.629	397430	101923	0.000				
4	3.730	18751649	2806947	0.000				
5	4.560	8820721	1107889	0.000		V		
6	5.698	1347866	145369	0.000				
7	6.161	12765883	2055062	0.000		V		
8	6.784	6451127	661997	0.000		V		
9	7.913	240596	36437	0.000				
10	9.450	90545	9480	0.000				
11	9.977	83964	7426	0.000				
Total		803659191	05270509					

Analysis Date & Time : 2/7/2552 12:25:49
User Name : Admin
Vial# : 10
Sample Name : W07
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

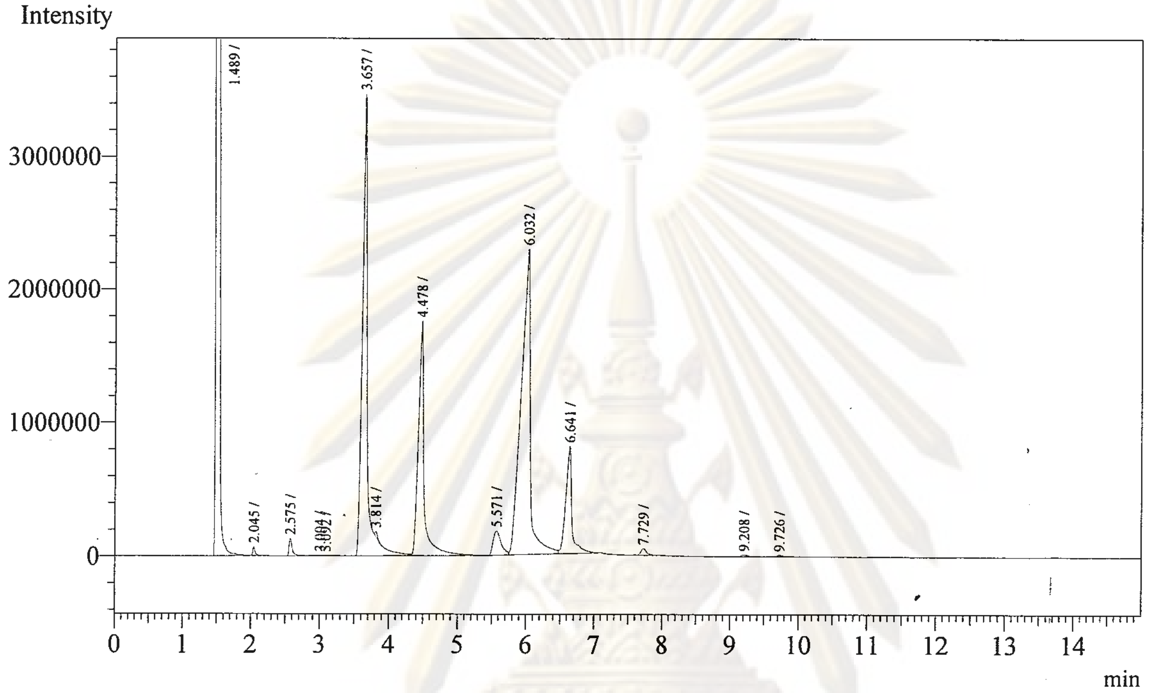
Data Name : D:\ACID\FA14.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.511	749766515	12023128	0.000		S		
2	2.084	91516	37690	0.000				
3	2.631	292156	77372	0.000				
4	3.726	13832799	2127947	0.000				
5	4.574	8526352	1084066	0.000		V		
6	5.714	1001591	114413	0.000				
7	6.146	16292871	1576607	0.000		V		
8	6.787	4368912	418219	0.000		V		
9	7.947	142570	20907	0.000				
10	9.502	63464	6432	0.000				
11	10.032	65563	5236	0.000				
Total		794444309	17492017					

Analysis Date & Time : 2/9/2552 10:28:01
User Name : Admin
Vial# : 9
Sample Name : W08
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

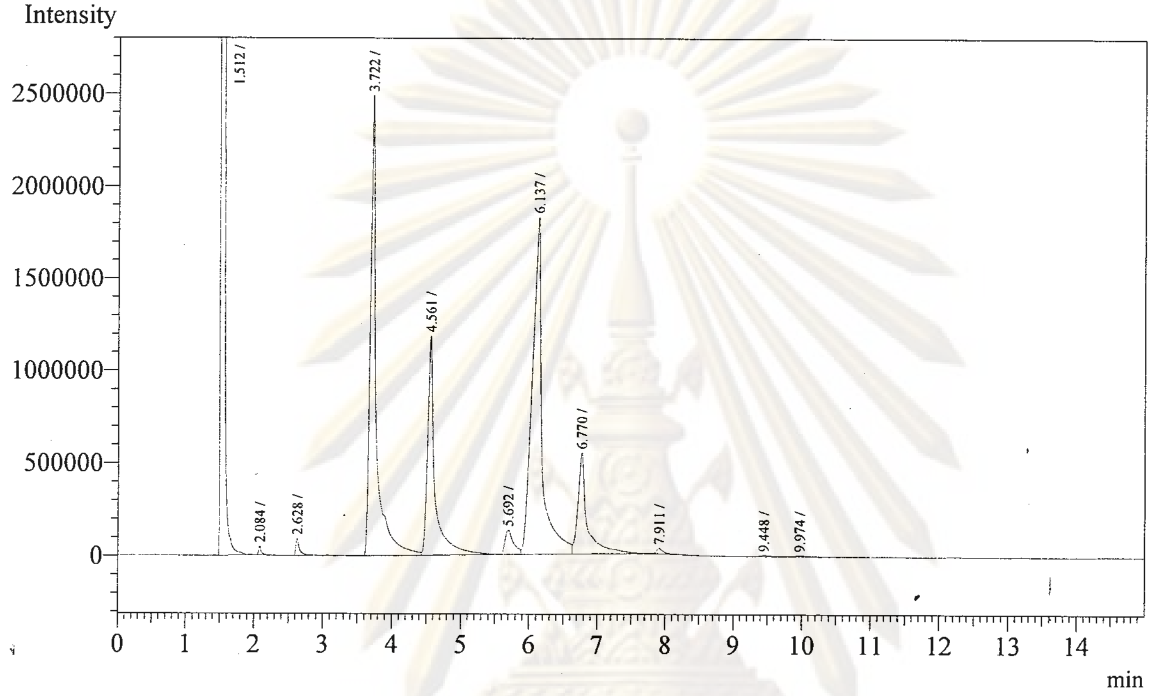
Data Name : D:\ACID\FA98.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.489	827075413	63935951	0.000		S		
2	2.045	158205	66995	0.000				
3	2.575	416701	132128	0.000		S		
4	3.004	30157	6691	0.000				
5	3.092	40845	3889	0.000		V		
6	3.657	17953999	3454167	0.000		S		
7	3.814	90207	35990	0.000		T		
8	4.478	10434884	1757403	0.000		V		
9	5.571	1499229	182884	0.000				
10	6.032	21891889	2288754	0.000		V		
11	6.641	5061915	799210	0.000		V		
12	7.729	281875	50804	0.000				
13	9.208	109843	13730	0.000				
14	9.726	107074	10797	0.000				
Total		885152236	72739393					

Analysis Date & Time : 15/7/2552 8:26:39
User Name : Admin
Vial# : 3
Sample Name : W09
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

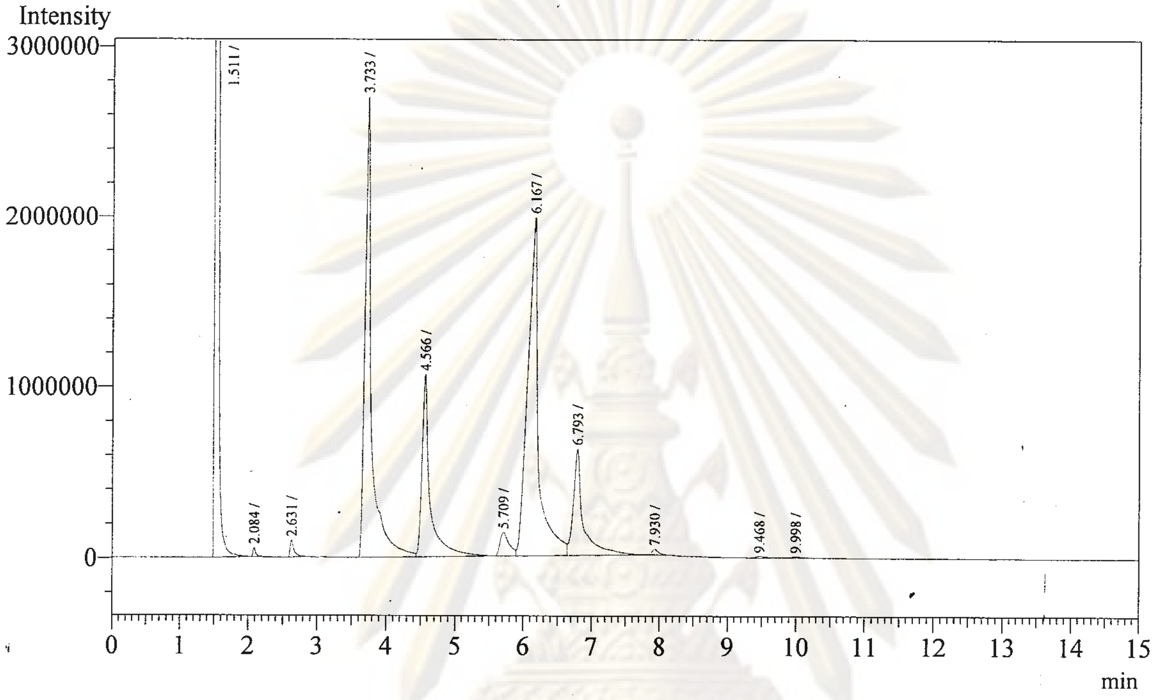
Data Name : D:\ACID\FA18.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.512	769904423	12189700	0.000		S		
2	2.084	131723	47762	0.000				
3	2.628	334072	89883	0.000				
4	3.722	15578180	2485937	0.000				
5	4.561	8850290	1184315	0.000		V		
6	5.692	1137229	131594	0.000				
7	6.137	18811391	1819029	0.000		V		
8	6.770	5256570	546323	0.000		V		
9	7.911	197717	30096	0.000				
10	9.448	73635	7813	0.000				
11	9.974	74207	6302	0.000				
Total		820349437	18538754					

Analysis Date & Time : 15/7/2552 7:53:23
User Name : Admin
Vial# : 1
Sample Name : W10
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

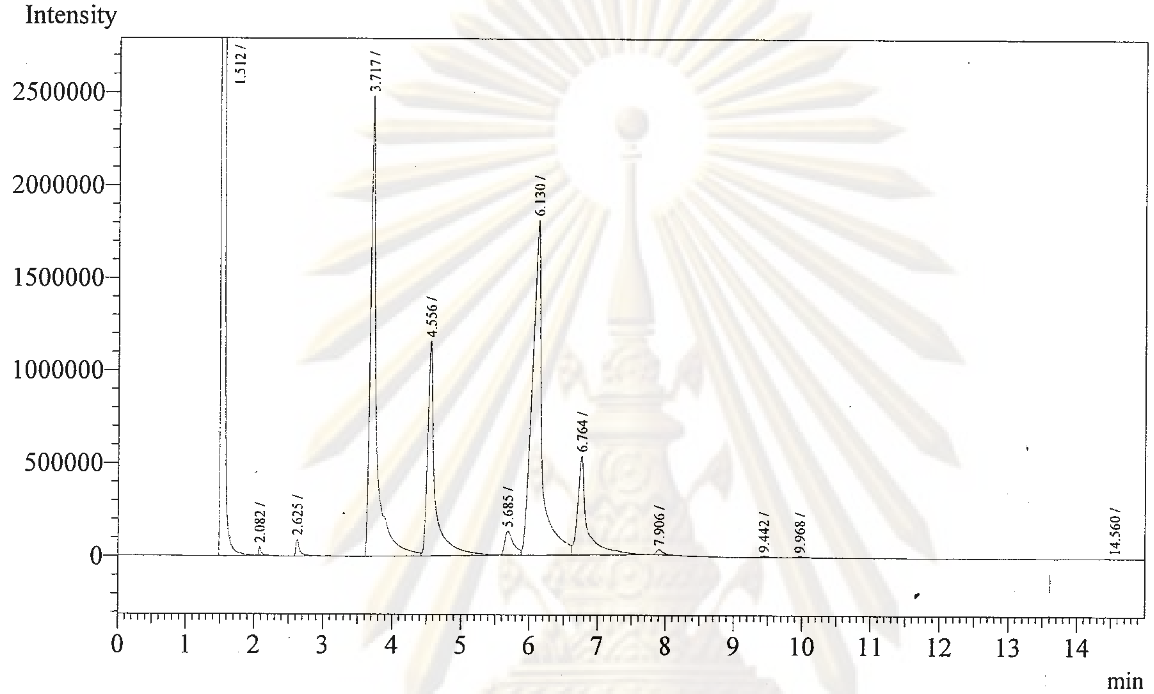
Data Name : D:\ACID\FA16.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.511	760230427	12797043	0.000		S		
2	2.084	157767	52728	0.000				
3	2.631	394590	99714	0.000				
4	3.733	18539460	2693718	0.000				
5	4.566	8769657	1064580	0.000		V		
6	5.709	1290834	138044	0.000				
7	6.167	12305436	1981083	0.000		V		
8	6.793	6356630	621493	0.000		V		
9	7.930	226919	33295	0.000				
10	9.468	82261	8448	0.000				
11	9.998	84295	6958	0.000				
Total		808438276	19497104					

Analysis Date & Time : 15/7/2552 9:33:12
User Name : Admin
Vial# : 7
Sample Name : W11
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

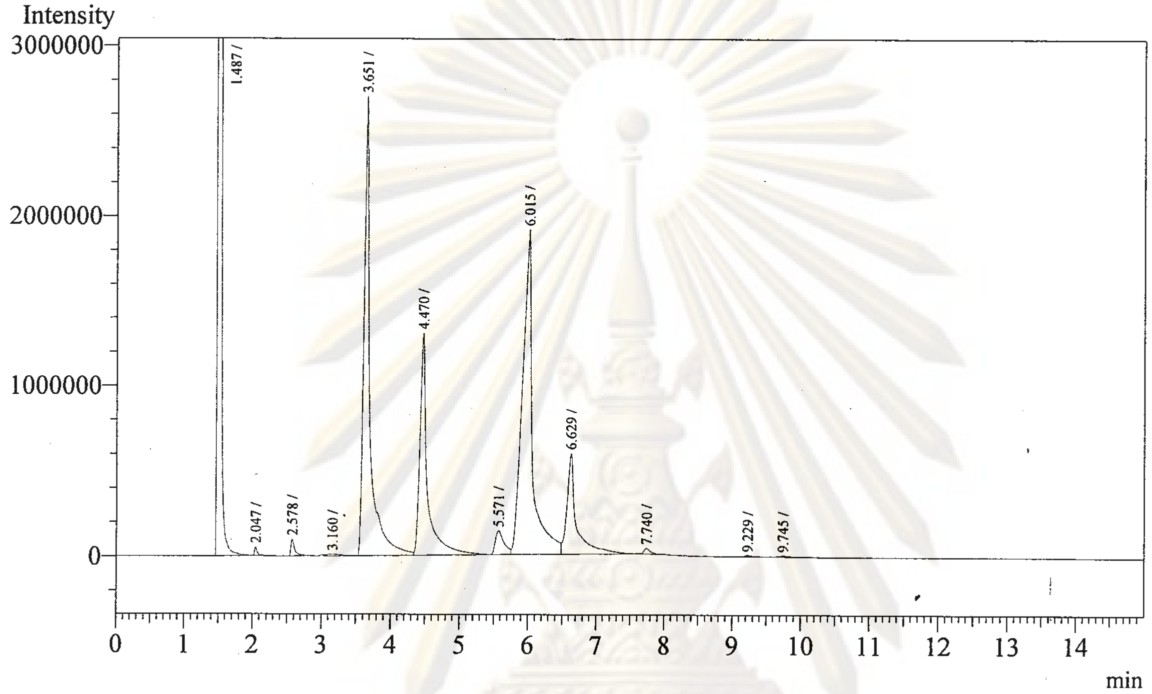
Data Name : D:\ACID\FA22.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.512	760806311	13801118	0.000		S		
2	2.082	129156	46545	0.000				
3	2.625	334766	90716	0.000				
4	3.717	15590150	2478416	0.000				
5	4.556	8779845	1154932	0.000		V		
6	5.685	1145748	129393	0.000				
7	6.130	18611126	1805663	0.000		V		
8	6.764	5146845	533247	0.000		V		
9	7.906	189391	28244	0.000				
10	9.442	73252	7729	0.000				
11	9.968	70458	6127	0.000				
12	14.560	58524	2138	0.000				
Total		810935572	20084268					

Analysis Date & Time : 6/8/2552 10:10:52
User Name : Admin
Vial# : 6
Sample Name : W12
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

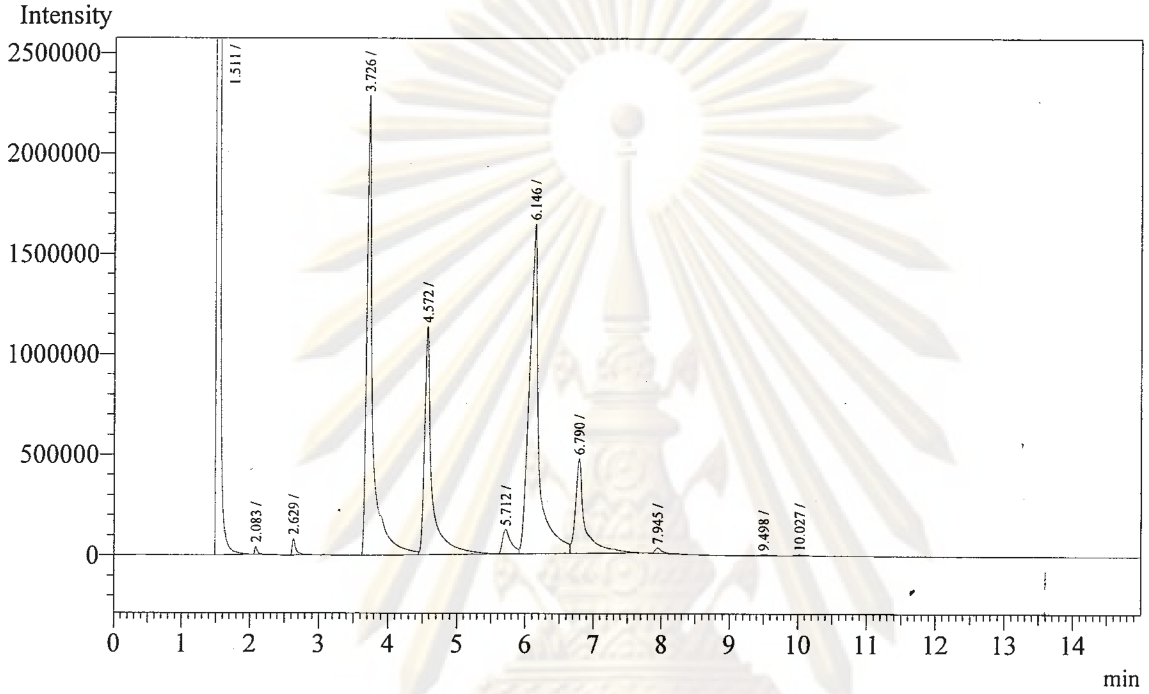
Data Name : D:\ACID\FA39.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.487	813871361	55917711	0.000		S		
2	2.047	143329	50826	0.000				
3	2.578	378512	99470	0.000				
4	3.160	142637	9993	0.000		V		
5	3.651	17332024	2693846	0.000				
6	4.470	9940107	1302161	0.000		V		
7	5.571	1234725	140602	0.000				
8	6.015	20044951	1904343	0.000		V		
9	6.629	5756487	590620	0.000		V		
10	7.740	209852	32398	0.000				
11	9.229	80509	8831	0.000				
12	9.745	79738	6857	0.000				
Total		869214232	62757658					

Analysis Date & Time : 2/7/2552 12:09:10
User Name : Admin
Vial# : 9
Sample Name : W13
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

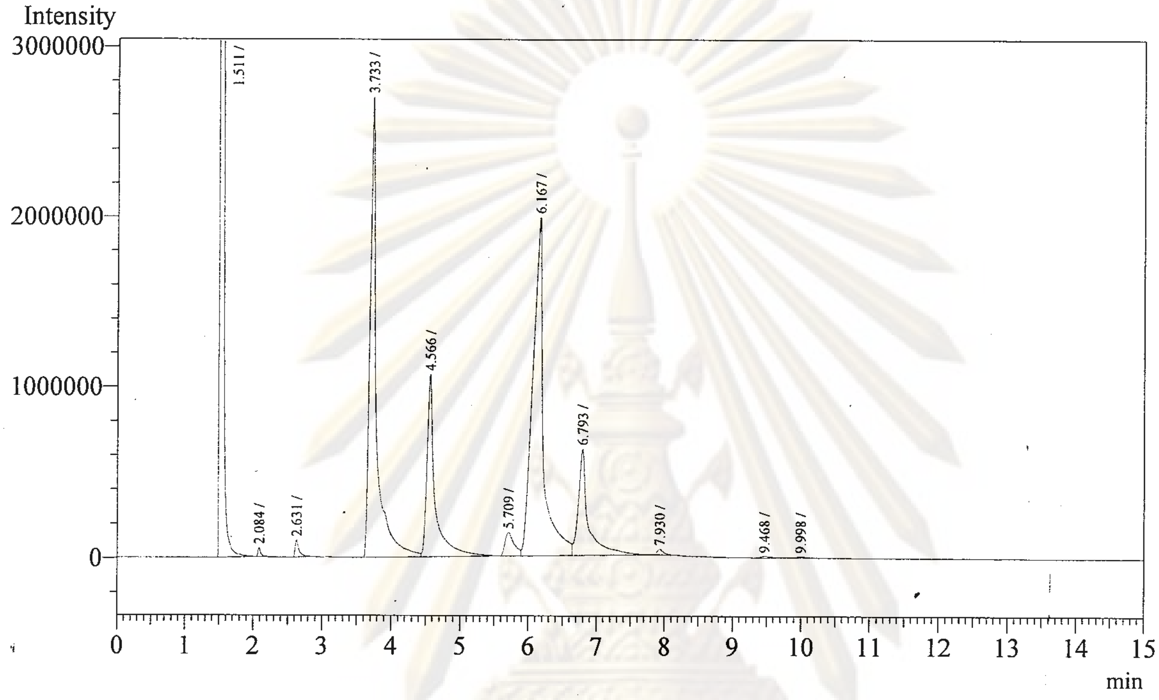
Data Name : D:\ACID\FA13.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.511	751123714	13907984	0.000				
2	2.083	109864	40641	0.000				
3	2.629	301768	82056	0.000				
4	3.726	14203254	2284916	0.000				
5	4.572	8542127	1133783	0.000		V		
6	5.712	1044043	121266	0.000				
7	6.146	16408978	1636310	0.000		V		
8	6.790	4627001	471832	0.000		V		
9	7.945	176534	26312	0.000				
10	9.498	66437	6962	0.000				
11	10.027	66440	5497	0.000				
Total		796670160	19717559					

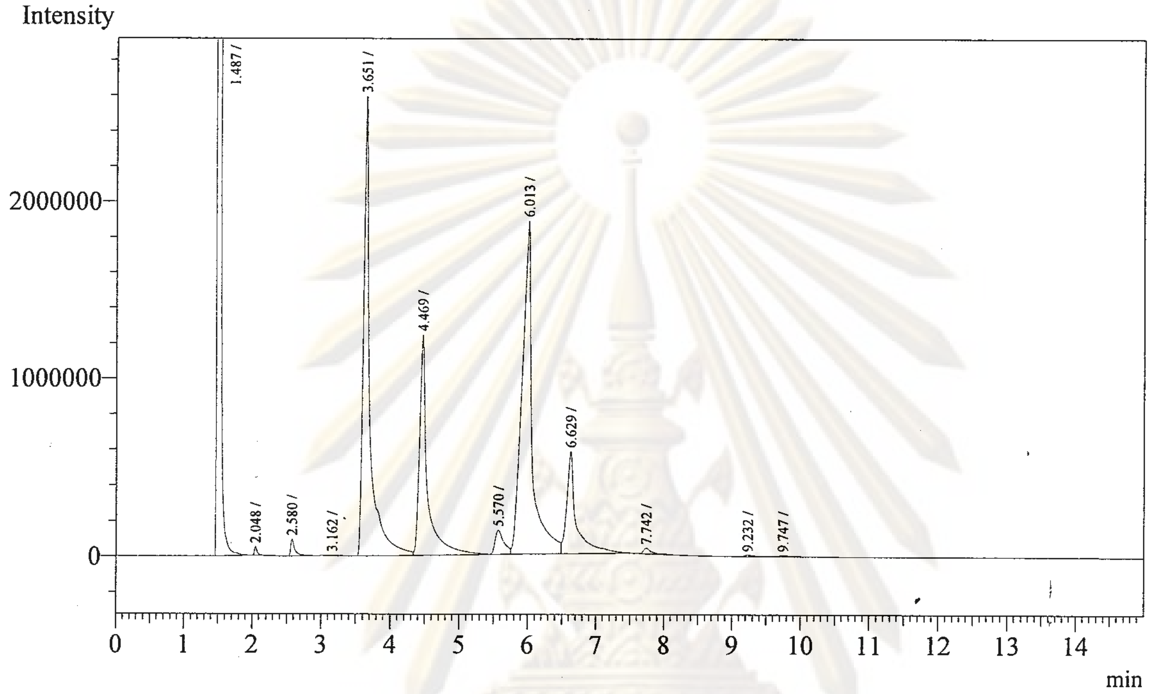
Analysis Date & Time : 15/7/2552 7:53:23
User Name : Admin
Vial# : 1
Sample Name : W14
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

Data Name : D:\ACID\FA16.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.511	760230427	12797043	0.000		S		
2	2.084	157767	52728	0.000				
3	2.631	394590	99714	0.000				
4	3.733	18539460	2693718	0.000				
5	4.566	8769657	1064580	0.000		V		
6	5.709	1290834	138044	0.000				
7	6.167	12305436	1981083	0.000		V		
8	6.793	6356630	621493	0.000		V		
9	7.930	226919	33295	0.000				
10	9.468	82261	8448	0.000				
11	9.998	84295	6958	0.000				
Total		808438276	19497104					

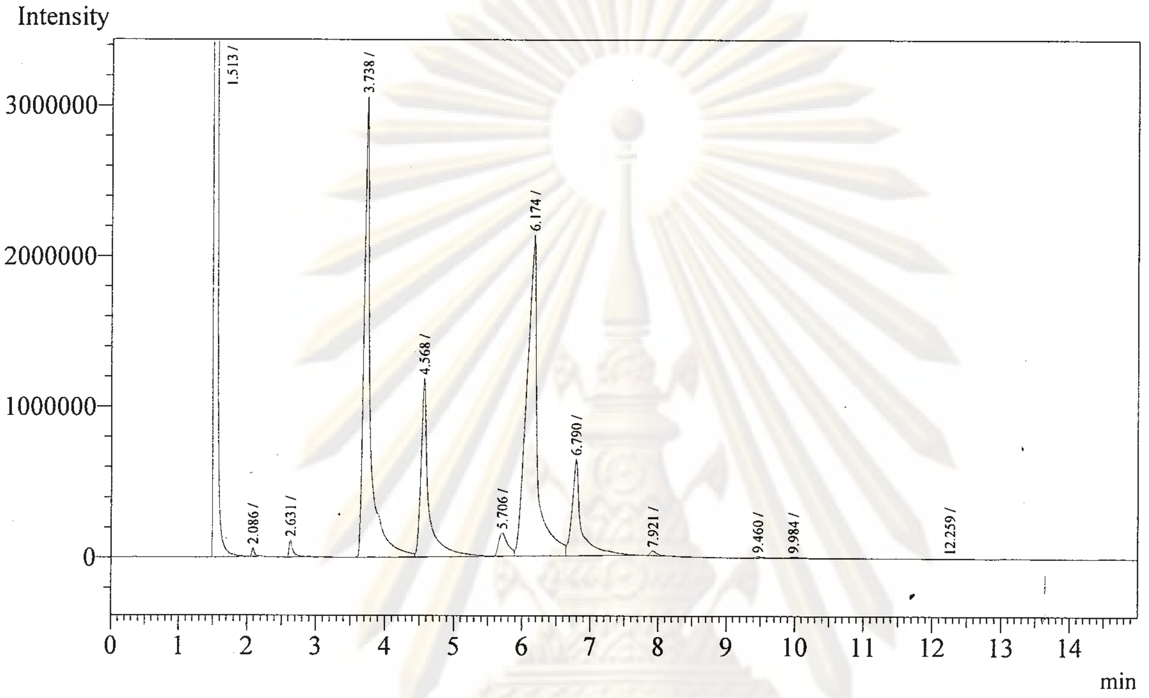
Analysis Date & Time	: 7/8/2552 9:20:55
User Name	: Admin
Vial#	: 3
Sample Name	: W15
Sample ID	: UNK-0001
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:
Data Name	: D:\ACID\FA36.gcd
Method Name	: D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.487	814616996	03448812	0.000		S		
2	2.048	114595	64080	0.000				
3	2.580	575173	248087	0.000				
4	3.162	592515	5594708	0.000		V		
5	3.651	17025813	139163	0.000				
6	4.469	9412986	2147218	0.000		V		
7	5.570	1265248	422193	0.000				
8	6.013	19052158	1708217	0.000		V		
9	6.629	5236814	10558	0.000		V		
10	7.742	451572	526299	0.000				
11	9.232	38208	8562	0.000				
12	9.747	31994	6875	0.000				
Total		868414072	14324772					

Analysis Date & Time : 15/7/2552 8:10:00
User Name : Admin
Vial# : 2
Sample Name : W16
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

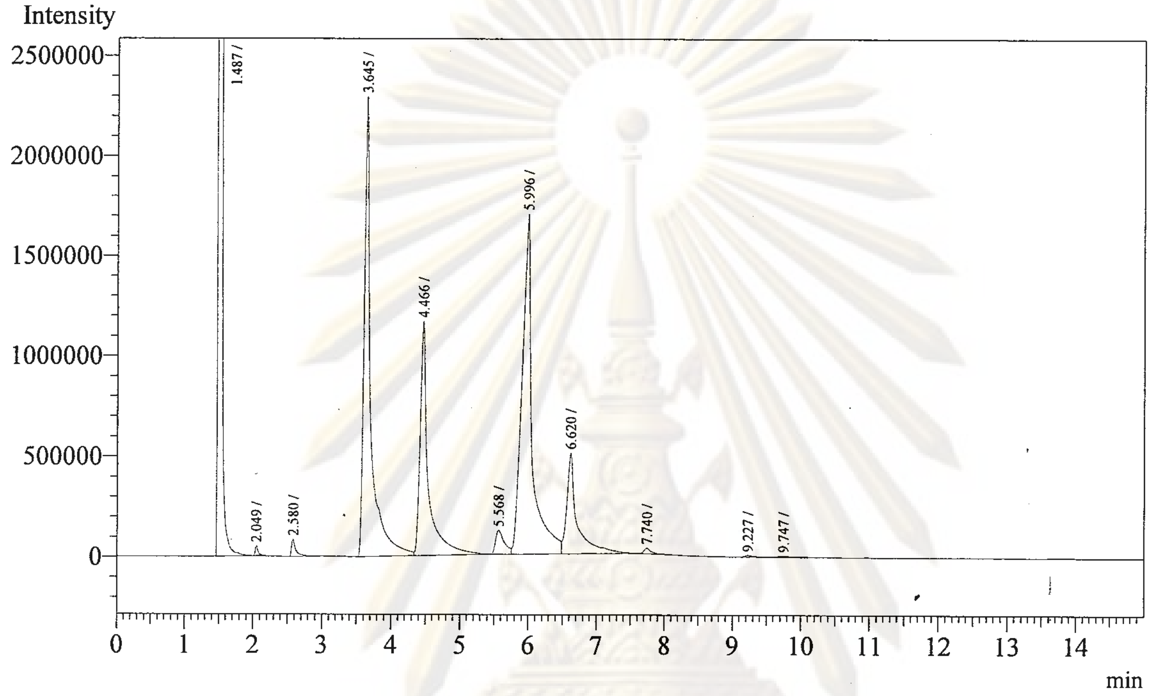
Data Name : D:\ACID\FA17.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.513	761169105	05017008	0.000		S		
2	2.086	157241	57221	0.000				
3	2.631	429046	110801	0.000				
4	3.738	20549158	3038587	0.000				
5	4.568	9318935	1183288	0.000		V		
6	5.706	1443971	154919	0.000				
7	6.174	13941741	2125148	0.000		V		
8	6.790	6245132	637733	0.000		V		
9	7.921	201519	30678	0.000				
10	9.460	92531	9787	0.000				
11	9.984	92004	7705	0.000				
12	12.259	35257	1486	0.000				
Total		813675640	12374361					

Analysis Date & Time : 6/8/2552 9:37:34
User Name : Admin
Vial# : 4
Sample Name : W17
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

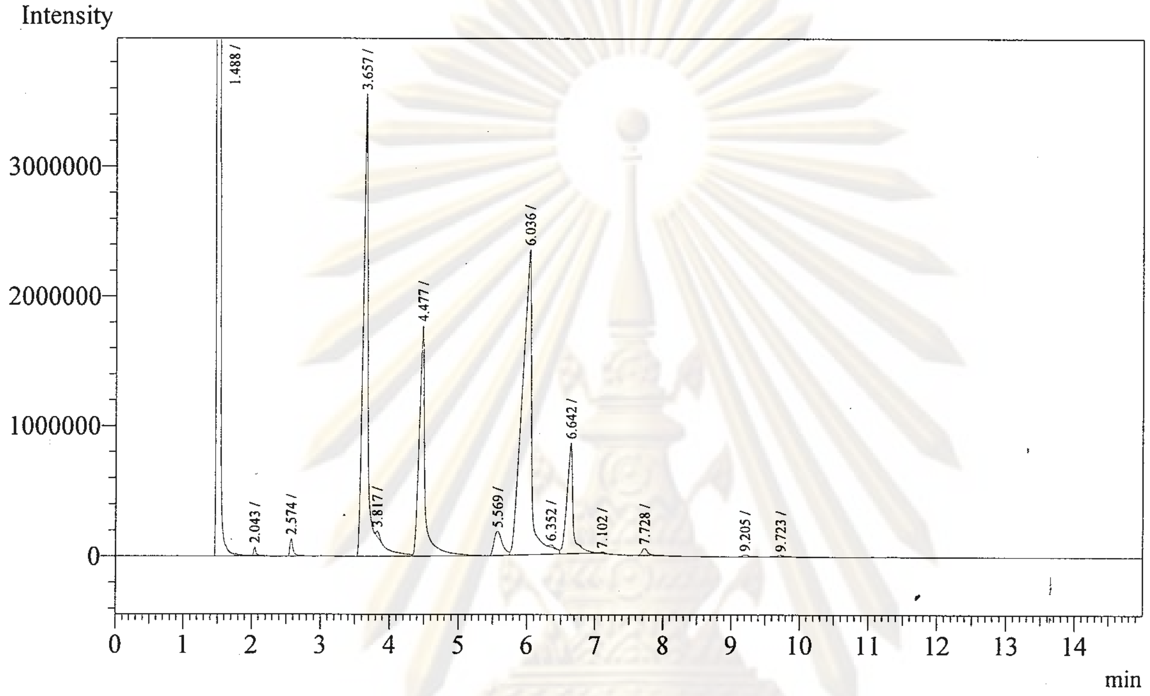
Data Name : D:\ACID\FA37.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.487	813995239	53050852	0.000		S		
2	2.049	151935	49711	0.000				
3	2.580	378563	86352	0.000				
4	3.645	15834470	2288758	0.000				
5	4.466	9629643	1164353	0.000		V		
6	5.568	1073723	120774	0.000				
7	5.996	17992196	1692775	0.000		V		
8	6.620	5305735	502461	0.000		V		
9	7.740	222917	28183	0.000				
10	9.227	68180	7247	0.000				
11	9.747	68857	5778	0.000				
Total		864721458	58997244					

Analysis Date & Time	: 2/9/2552 12:57:57
User Name	: Admin
Vial#	: 18
Sample Name	: W18
Sample ID	: UNK-0001
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:

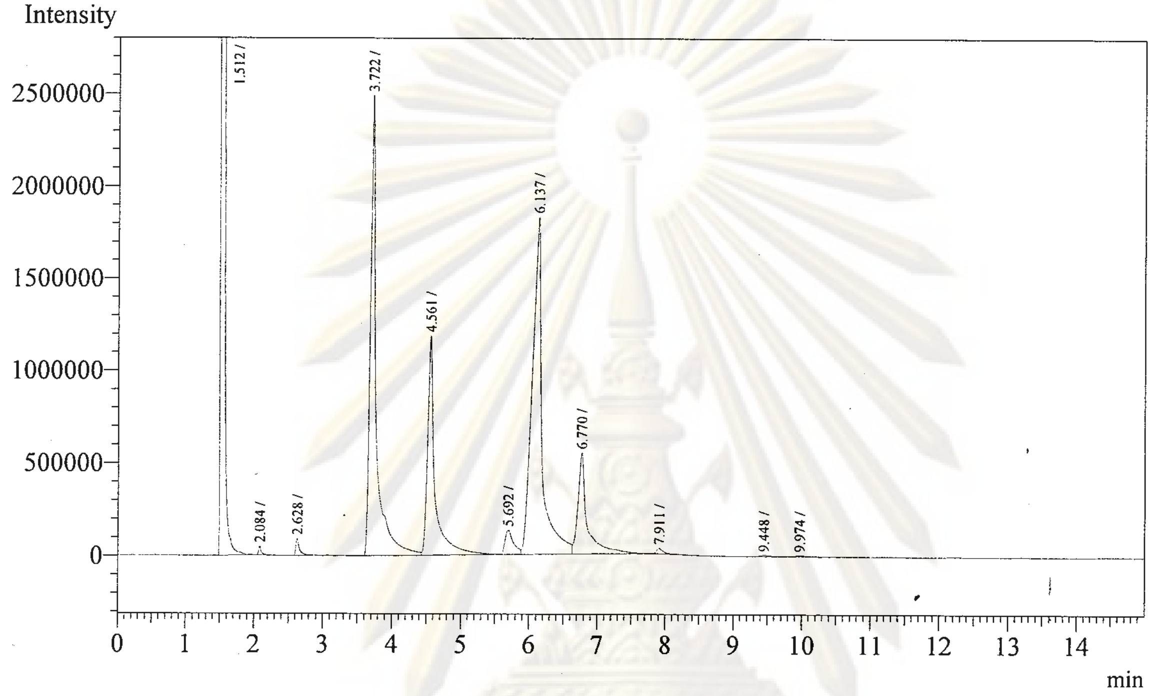
Data Name	: D:\ACID\FA107.gcd
Method Name	: D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.488	829522611	72723642	0.000		S		
2	2.043	166179	69743	0.000				
3	2.574	437220	135083	0.000				
4	3.657	18733450	3543735	0.000		S		
5	3.817	148122	40226	0.000		T		
6	4.477	10625783	1771353	0.000		V		
7	5.569	1575853	186669	0.000				
8	6.036	23102628	2350215	0.000		SV		
9	6.352	81444	20547	0.000		T		
10	6.642	5365513	849639	0.000		V		
11	7.102	46831	10329	0.000				
12	7.728	303592	54748	0.000				
13	9.205	116507	14670	0.000				
14	9.723	114437	11471	0.000				
Total		890340170	81782070					

Analysis Date & Time : 15/7/2552 8:26:39
User Name : Admin
Vial# : 3
Sample Name : W19
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

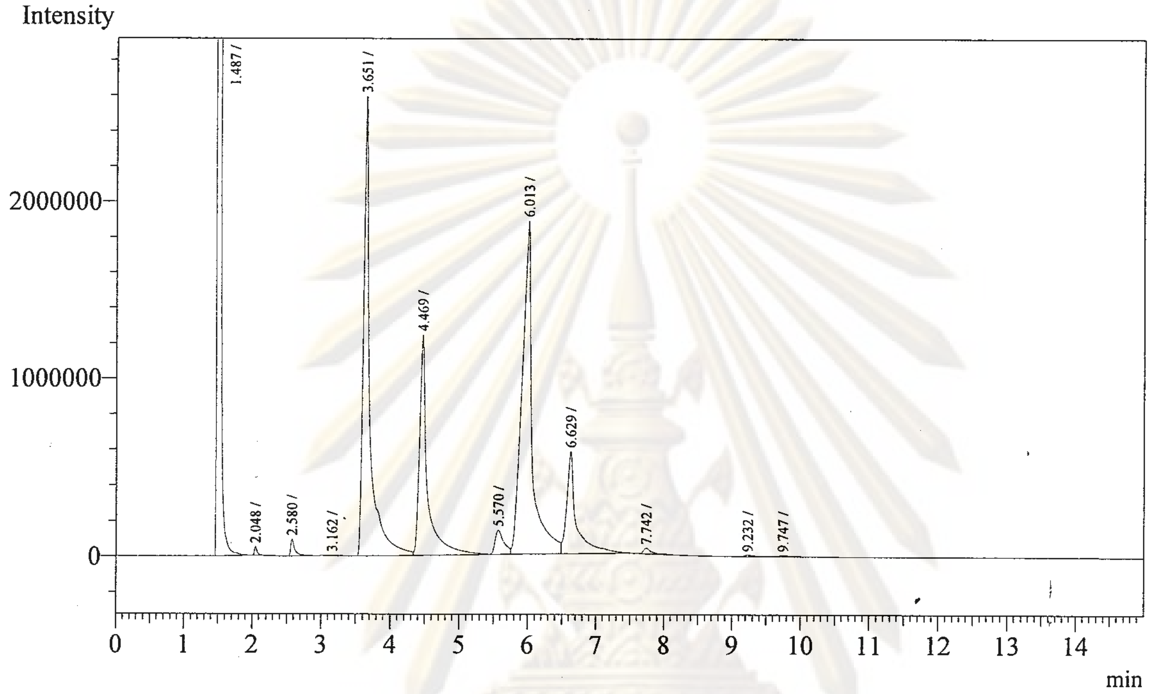
Data Name : D:\ACID\FA18.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.512	769904423	12189700	0.000		S		
2	2.084	131723	47762	0.000				
3	2.628	334072	89883	0.000				
4	3.722	15578180	2485937	0.000				
5	4.561	8850290	1184315	0.000		V		
6	5.692	1137229	131594	0.000				
7	6.137	18811391	1819029	0.000		V		
8	6.770	5256570	546323	0.000		V		
9	7.911	197717	30096	0.000				
10	9.448	73635	7813	0.000				
11	9.974	74207	6302	0.000				
Total		820349437	18538754					

Analysis Date & Time : 6/8/2552 9:20:55
User Name : Admin
Vial# : 3
Sample Name : W20
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

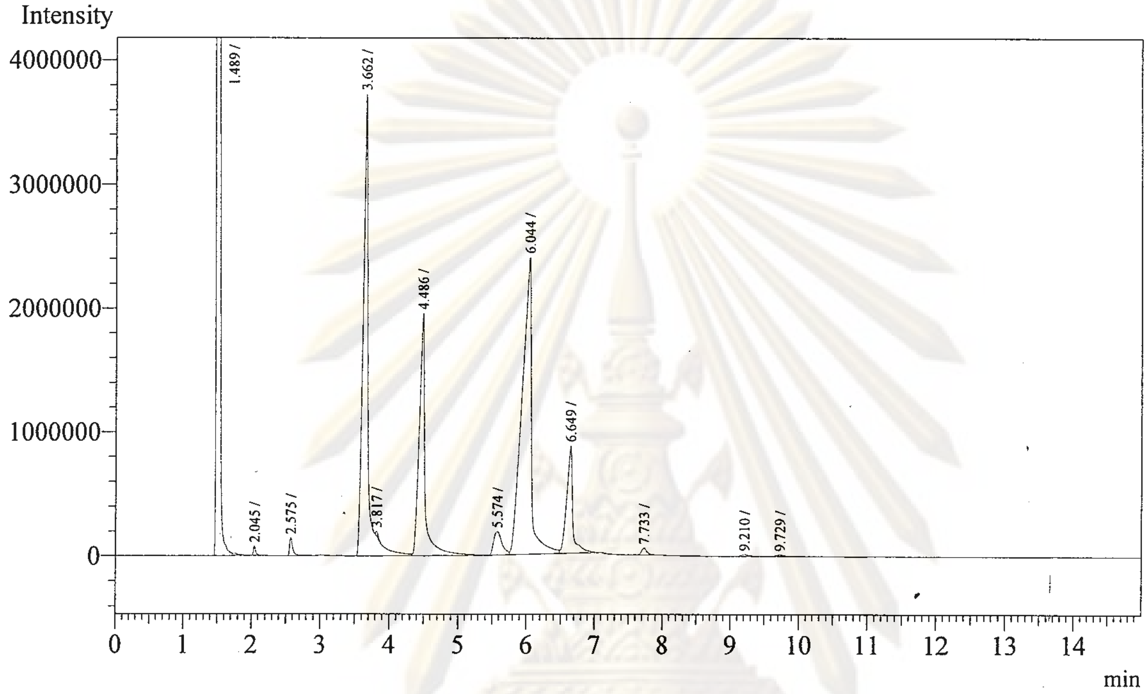
Data Name : D:\ACID\FA36.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.487	814789043	53086313	0.000		S		
2	2.048	148456	50012	0.000				
3	2.580	376879	95063	0.000				
4	3.162	49010	4031	0.000		V		
5	3.651	17299495	2582679	0.000				
6	4.469	9837418	1239264	0.000		V		
7	5.570	1211372	135520	0.000				
8	6.013	19936401	1876173	0.000		V		
9	6.629	5710056	574225	0.000		V		
10	7.742	250429	32108	0.000				
11	9.232	78796	8460	0.000				
12	9.747	79232	6622	0.000				
Total		869766587	59690470					

Analysis Date & Time : 2/9/2552 10:11:21
User Name : Admin
Vial# : 8
Sample Name : W21
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

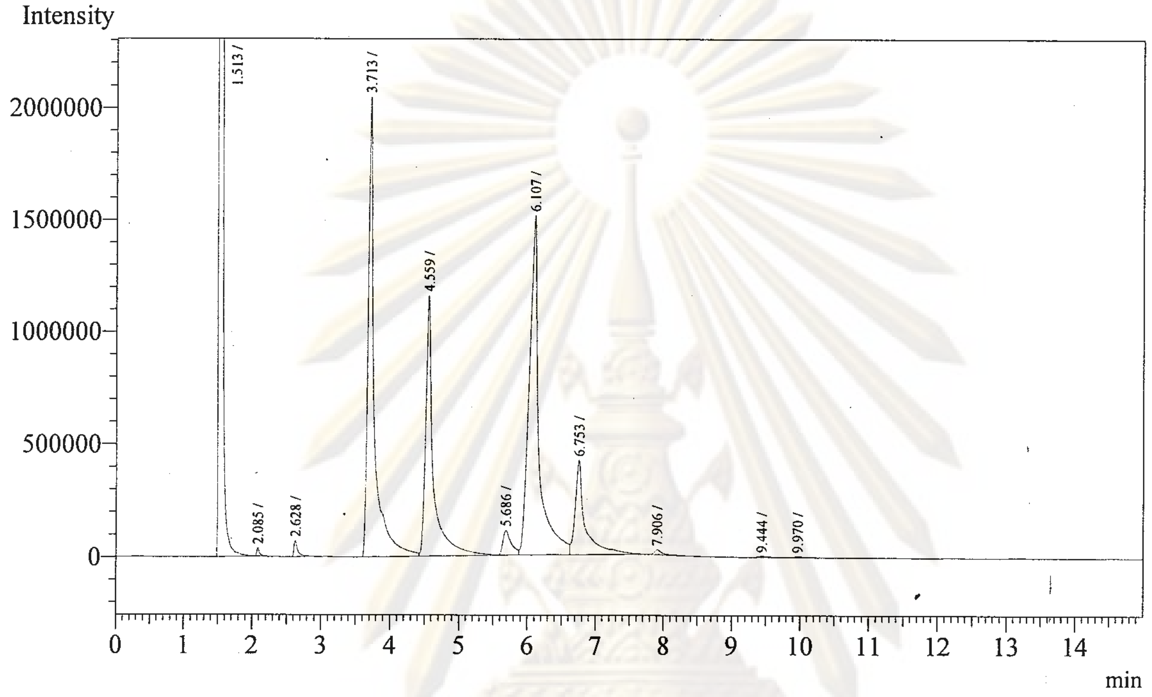
Data Name : D:\ACID\FA97.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.489	827956010	63832559	0.000		S		
2	2.045	176914	75018	0.000				
3	2.575	456600	143832	0.000		S		
4	3.662	19542648	3705315	0.000		S		
5	3.817	89432	37197	0.000		T		
6	4.486	11694542	1948906	0.000		V		
7	5.574	1625709	190655	0.000				
8	6.044	23589038	2390224	0.000		V		
9	6.649	5454951	866166	0.000		V		
10	7.733	307935	56068	0.000				
11	9.210	118182	14942	0.000				
12	9.729	110182	11594	0.000				
Total		891122143	73272476					

Analysis Date & Time : 15/7/2552 8:43:16
User Name : Admin
Vial# : 4
Sample Name : W22
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

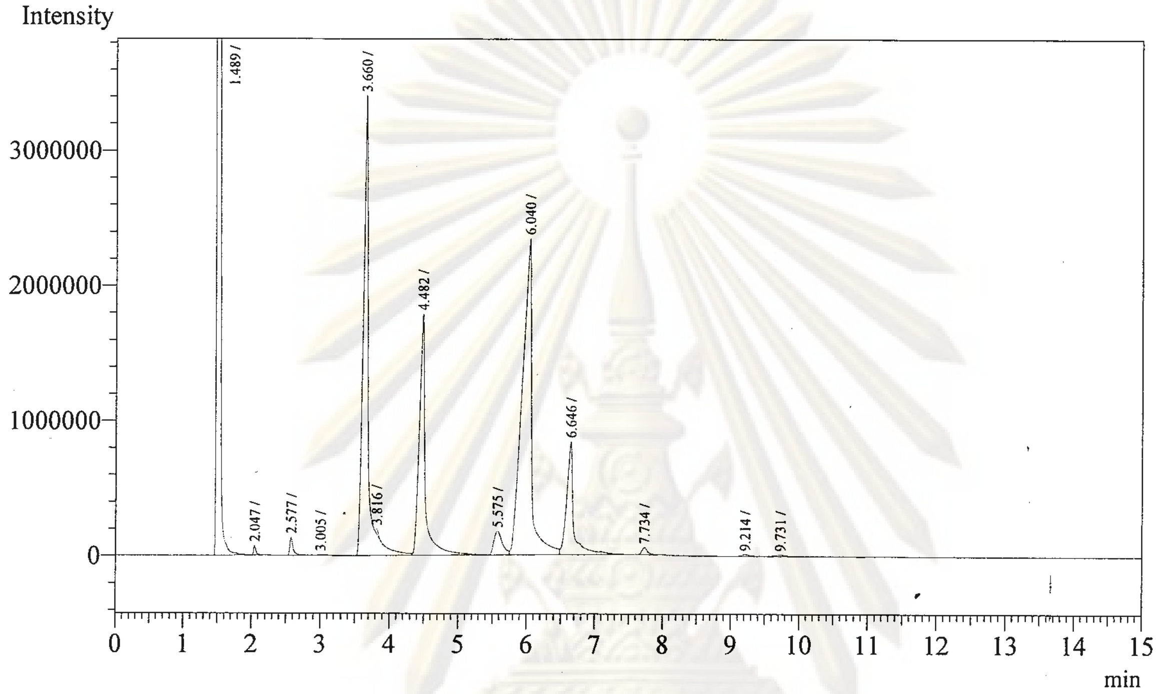
Data Name : D:\ACID\FA19.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.513	766196836	06905680	0.000		S		
2	2.085	104711	37154	0.000				
3	2.628	274963	72237	0.000				
4	3.713	13245429	2047176	0.000				
5	4.559	8999349	1156929	0.000		V		
6	5.686	925957	110069	0.000				
7	6.107	22598242	1511058	0.000		V		
8	6.753	4329883	418855	0.000		V		
9	7.906	181712	22695	0.000				
10	9.444	58862	6038	0.000				
11	9.970	56702	4748	0.000				
Total		816972646	12292639					

Analysis Date & Time : 2/9/2552 9:54:40
User Name : Admin
Vial# : 7
Sample Name : W23
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

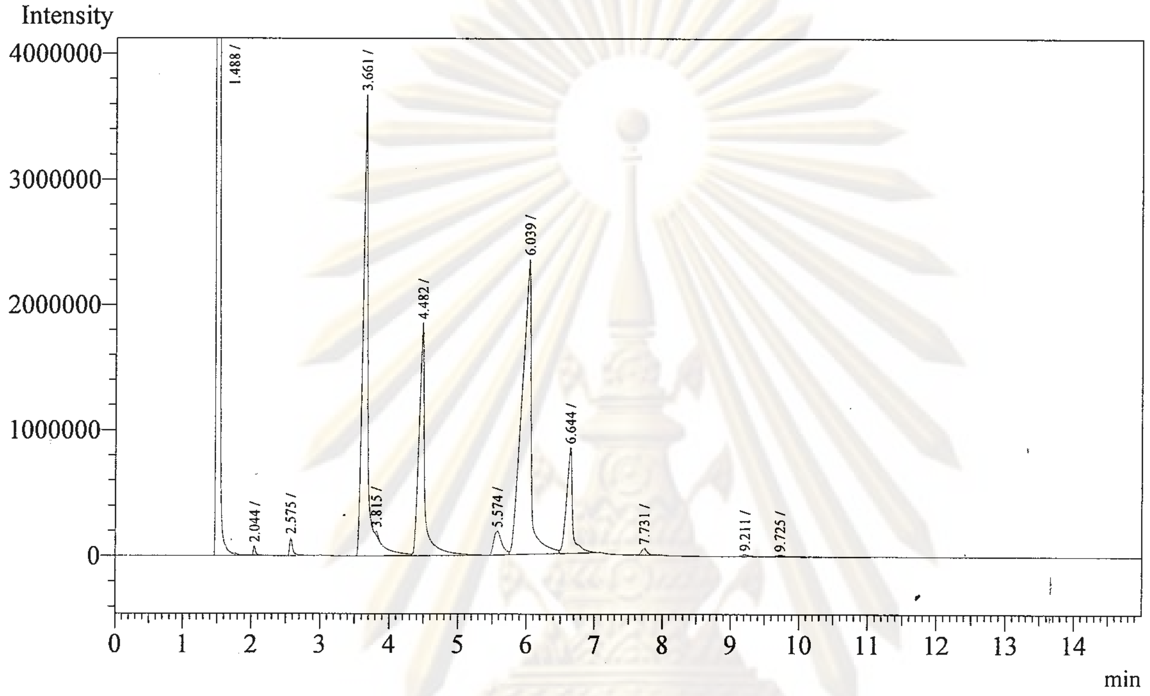
Data Name : D:\ACID\FA96.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.489	828774217	59339000	0.000		S		
2	2.047	171000	71169	0.000				
3	2.577	437695	133517	0.000		S		
4	3.005	48057	6520	0.000				
5	3.660	18354500	3374575	0.000		S		
6	3.816	82608	33411	0.000		T		
7	4.482	11054721	1785061	0.000		V		
8	5.575	1521030	176483	0.000				
9	6.040	23477076	2338635	0.000		V		
10	6.646	6143744	836776	0.000		SV		
11	7.734	292528	51981	0.000				
12	9.214	108881	13434	0.000				
13	9.731	110335	10853	0.000				
Total		890576392	68171415					

Analysis Date & Time	: 2/9/2552 11:34:45
User Name	: Admin
Vial#	: 13
Sample Name	: W24
Sample ID	: UNK-0001
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:

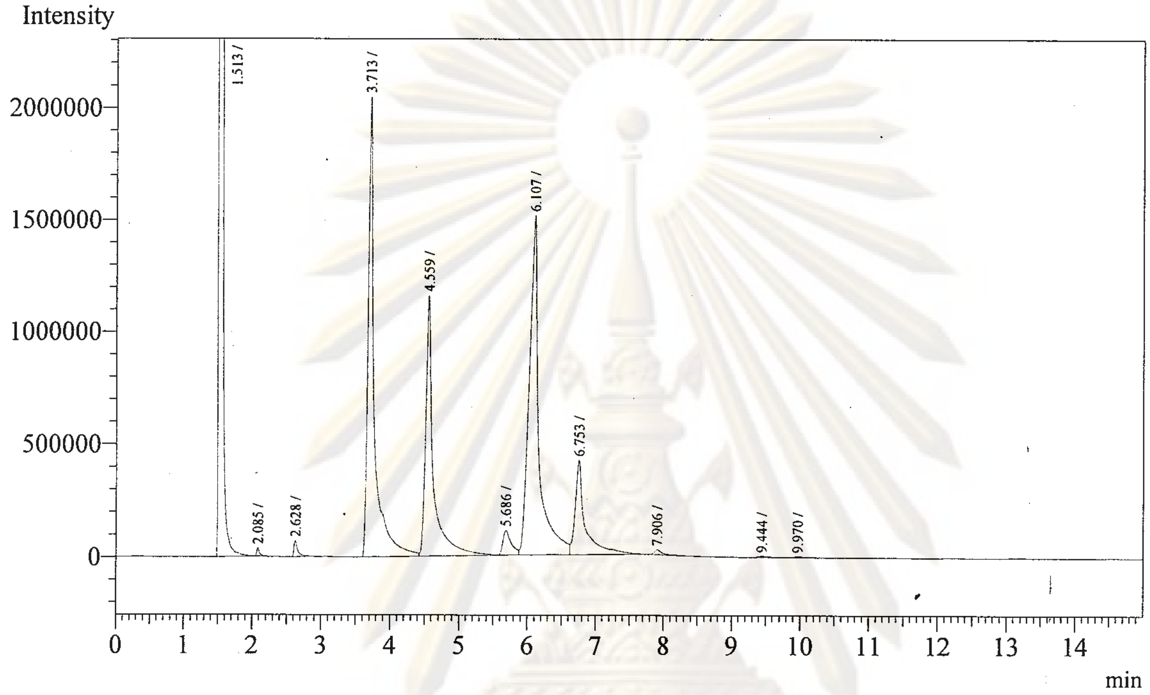
Data Name	: D:\ACID\FA102.gcd
Method Name	: D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.488	826175954	65877003	0.000		S		
2	2.044	170722	71453	0.000				
3	2.575	450873	140578	0.000				
4	3.661	19460249	3663600	0.000		S		
5	3.815	83470	34119	0.000		T		
6	4.482	11169015	1852046	0.000		V		
7	5.574	1597508	190138	0.000				
8	6.039	22969002	2345925	0.000		V		
9	6.644	5330624	840777	0.000		V		
10	7.731	298653	53960	0.000				
11	9.211	116117	14597	0.000				
12	9.725	112252	11226	0.000				
Total		887934439	75095422					

Analysis Date & Time : 16/7/2552 8:43:16
User Name : Admin
Vial# : 4
Sample Name : W25
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

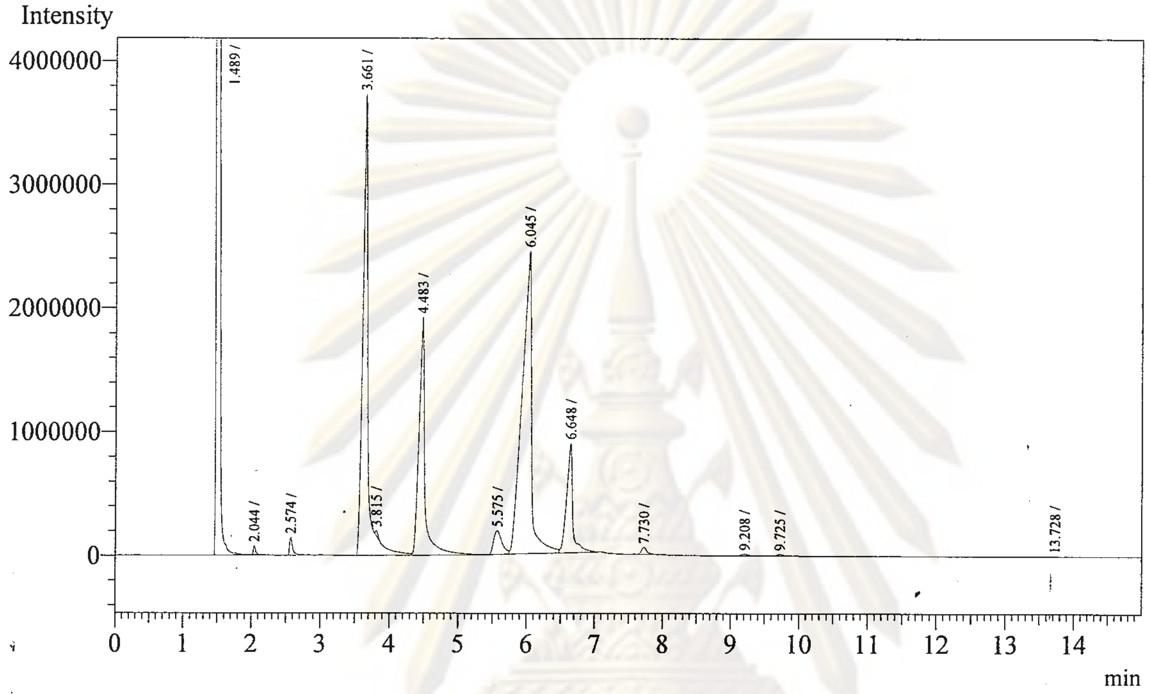
Data Name : D:\ACID\FA19.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.513	766196836	06905680	0.000		S		
2	2.085	129712	37154	0.000				
3	2.628	279481	72237	0.000				
4	3.713	21222132	2047176	0.000				
5	4.559	8900226	1156929	0.000		V		
6	5.686	982917	110069	0.000				
7	6.107	15260509	1511058	0.000		V		
8	6.753	4375315	418855	0.000		V		
9	7.906	152793	22695	0.000				
10	9.444	64247	6038	0.000				
11	9.970	56702	4748	0.000				
Total		817620870	12292639					

Analysis Date & Time	: 2/9/2552 11:01:18
User Name	: Admin
Vial#	: 11
Sample Name	: W26
Sample ID	: UNK-0001
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:

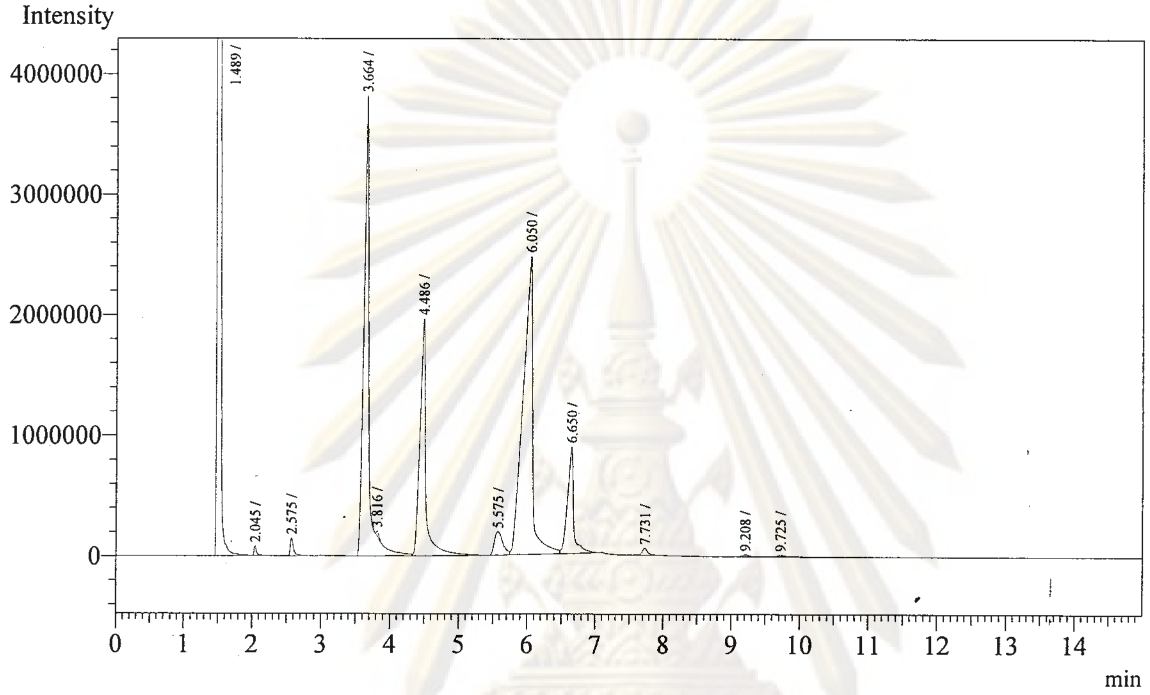
Data Name	: D:\ACID\FA100.gcd
Method Name	: D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.489	824887148	67064301	0.000		S		
2	2.044	177372	74794	0.000				
3	2.574	462534	144033	0.000		S		
4	3.661	19754879	3718731	0.000		S		
5	3.815	99429	39989	0.000		T		
6	4.483	11691467	1920743	0.000		V		
7	5.575	1654931	193382	0.000				
8	6.045	24285040	2444611	0.000		V		
9	6.648	5618148	886111	0.000		V		
10	7.730	317585	57622	0.000				
11	9.208	122488	15424	0.000				
12	9.725	120629	11973	0.000				
13	13.728	46503	1319	0.000				
Total		889238153	76573033					

Analysis Date & Time	: 2/9/2552 10:44:37
User Name	: Admin
Vial#	: 10
Sample Name	: W27
Sample ID	: UNK-0001
Sample Type	: Unknown
Injection Volume	: 1.00
ISTD Amount	:

Data Name	: D:\ACID\FA99.gcd
Method Name	: D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.489	823879768	59659249	0.000		S		
2	2.045	184983	77304	0.000				
3	2.575	478966	148635	0.000		S		
4	3.664	20364051	3789898	0.000		S		
5	3.816	96355	38434	0.000		T		
6	4.486	11954882	1961654	0.000		V		
7	5.575	1697517	194140	0.000				
8	6.050	24858393	2471422	0.000		V		
9	6.650	5634981	883444	0.000		V		
10	7.731	314744	57276	0.000				
11	9.208	125608	15910	0.000				
12	9.725	121054	12310	0.000				
Total		889711302	69309676					

```
Analysis Date & Time   : 2/9/2552 11:18:01
User Name              : Admin
Vial#                  : 12
Sample Name            : W28
Sample ID              : UNK-0001
Sample Type            : Unknown
Injection Volume       : 1.00
ISTD Amount            :

Data Name              : D:\ACID\FA101.gcd
Method Name            : D:\ACID\FATTY  ACID-2.gcm
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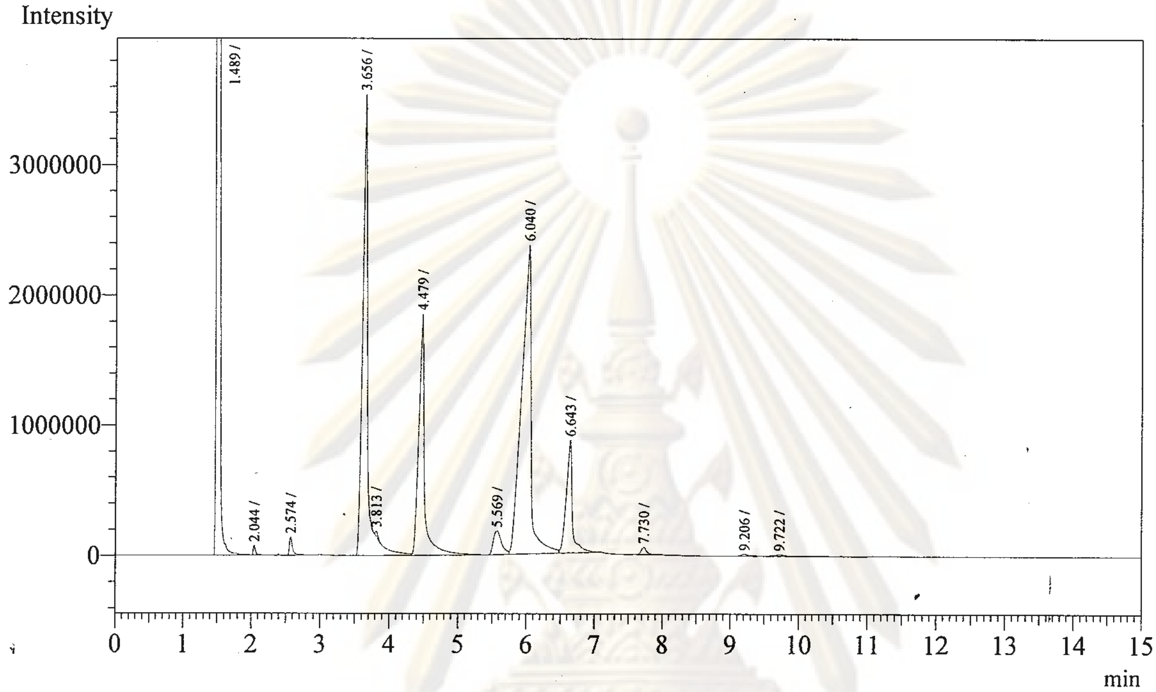
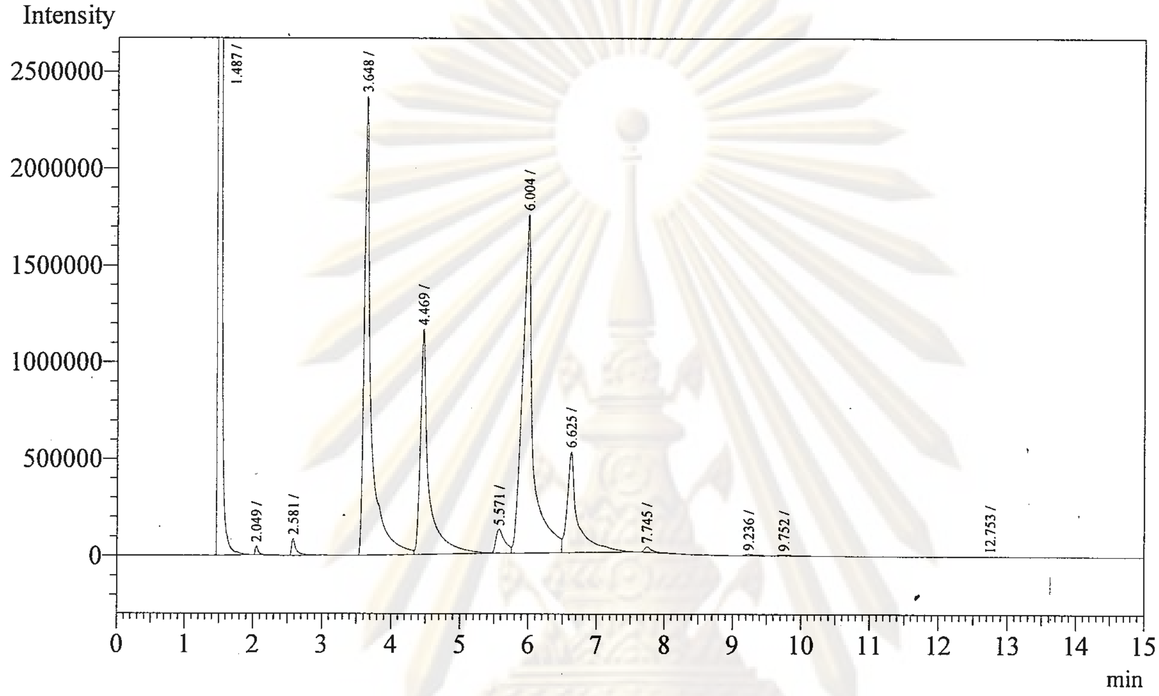


```
Peak#  Ret.Time      Area     Height    Conc.  Unit Mark  ID#     Cmpd Name
    1     1.489  828019784 71665937    0.000        S
    2     2.044     169141    73258    0.000
    3     2.574     440798   139210    0.000        S
    4     3.656   18432600  3531062    0.000        S
    5     3.813      94594    38247    0.000        T
    6     4.479   11028690  1849689    0.000         V
    7     5.569    1556917   183300    0.000
    8     6.040   23353418  2364047    0.000         V
    9     6.643    5419845   866261    0.000         V
   10     7.730     309445    56093    0.000
   11     9.206     116565    14835    0.000
   12     9.722     118520    11814    0.000
Total            889060317 80793753
```

Analysis Date & Time : 6/8/2552 10:27:30
User Name : Admin
Vial# : 7
Sample Name : W29
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

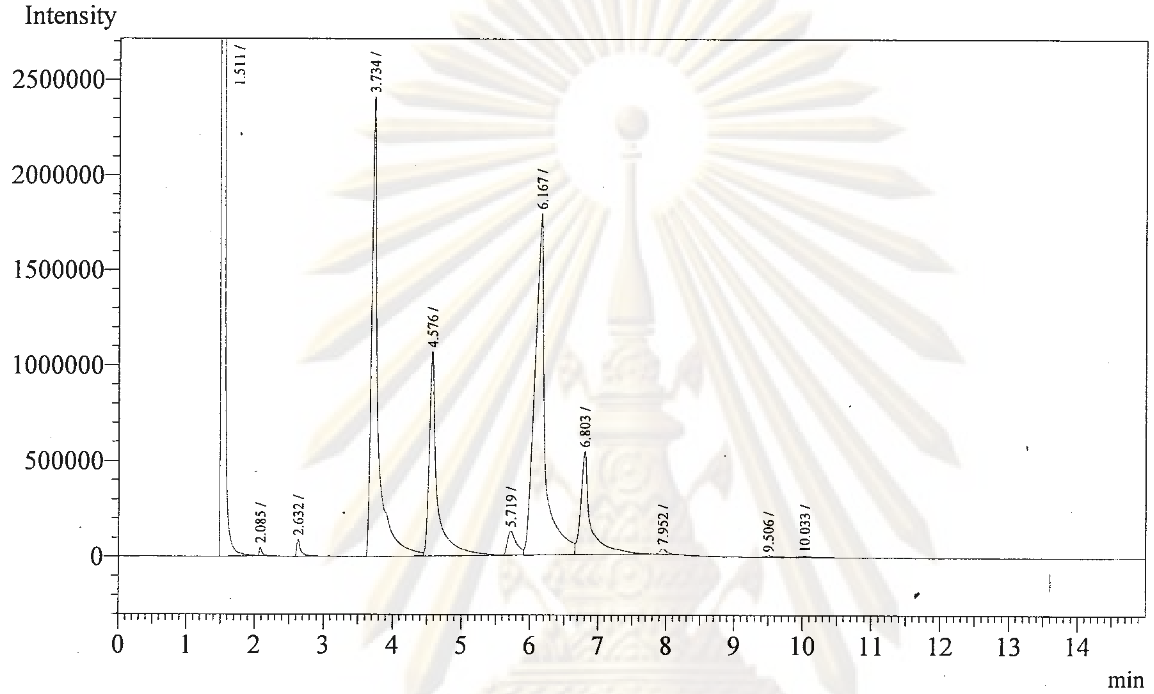
Data Name : D:\ACID\FA40.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.487	807178092	47874643	0.000		S		
2	2.049	143459	46703	0.000				
3	2.581	395346	87240	0.000				
4	3.648	16780634	2370713	0.000				
5	4.469	9837058	1163961	0.000		V		
6	5.571	1114101	124544	0.000				
7	6.004	18983927	1746223	0.000		V		
8	6.625	5680326	522677	0.000		V		
9	7.745	237549	28800	0.000				
10	9.236	70540	7344	0.000				
11	9.752	71032	5833	0.000				
12	12.753	32605	962	0.000				
Total		860524669	53979643					

Analysis Date & Time : 2/7/2552 12:42:26
User Name : Admin
Vial# : 11
Sample Name : W30
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

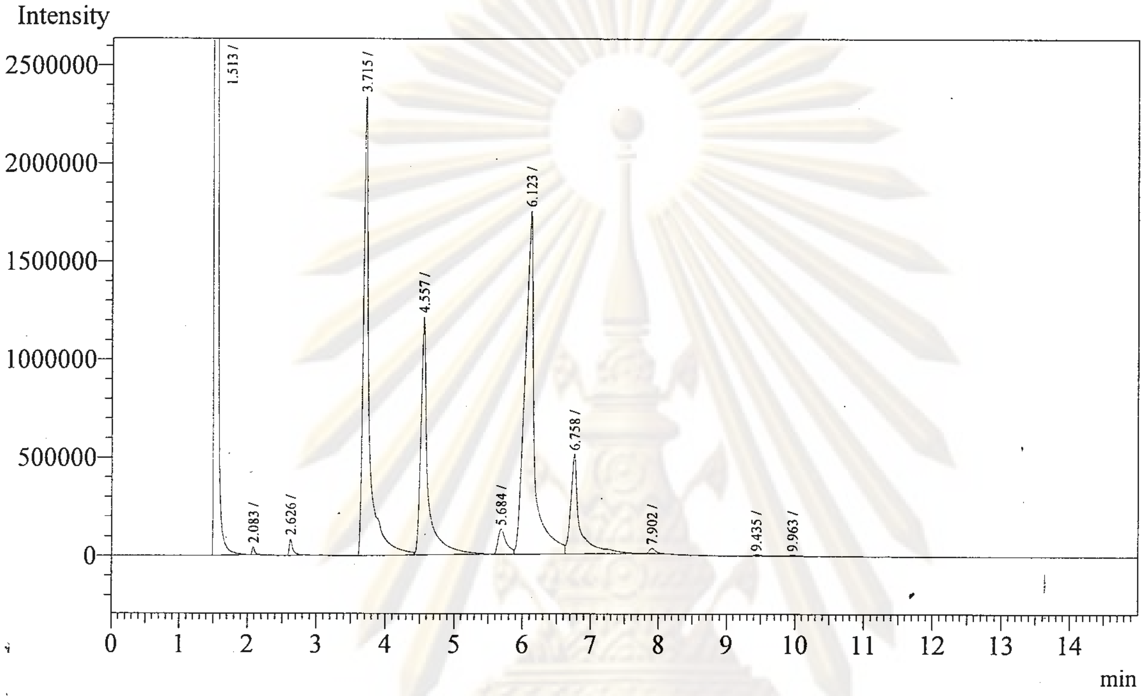
Data Name : D:\ACID\FA15.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.511	741469939	04925790	0.000		S		
2	2.085	132983	46487	0.000				
3	2.632	347148	89323	0.000				
4	3.734	16112046	2399507	0.000				
5	4.576	8627517	1071214	0.000		V		
6	5.719	1159383	127263	0.000				
7	6.167	19258317	1790548	0.000		V		
8	6.803	5449251	539906	0.000		V		
9	7.952	198678	29067	0.000				
10	9.506	74189	7734	0.000				
11	10.033	76140	6206	0.000				
Total		792905591	11033045					

Analysis Date & Time : 15/7/2552 10:39:47
User Name : Admin
Vial# : 11
Sample Name : W31
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

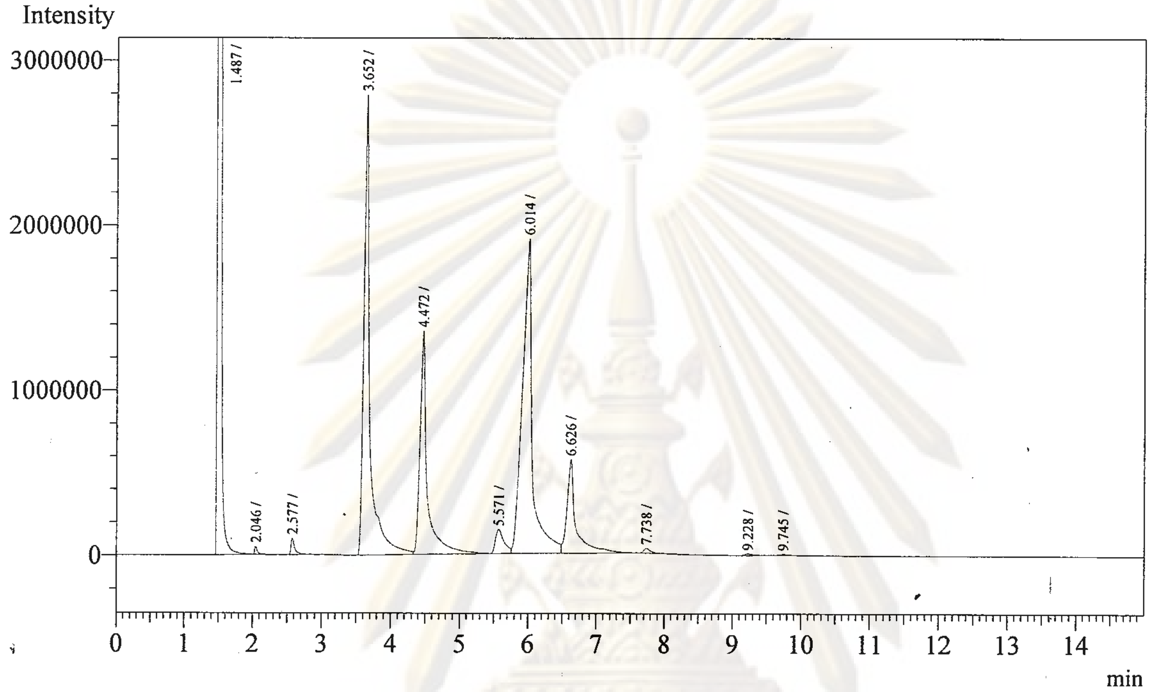
Data Name : D:\ACID\FA26.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.513	755464899	02189232	0.000		S		
2	2.083	115376	40487	0.000				
3	2.626	305717	83372	0.000				
4	3.715	14300999	2332650	0.000				
5	4.557	8800843	1213886	0.000		V		
6	5.684	1073793	127262	0.000				
7	6.123	17314310	1745825	0.000		V		
8	6.758	4723399	506935	0.000		V		
9	7.902	176568	27328	0.000				
10	9.435	70531	7698	0.000				
11	9.963	67289	6023	0.000				
Total		802413724	08280698					

Analysis Date & Time : 6/8/2552 9:04:18
User Name : Admin
Vial# : 2
Sample Name : W32
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

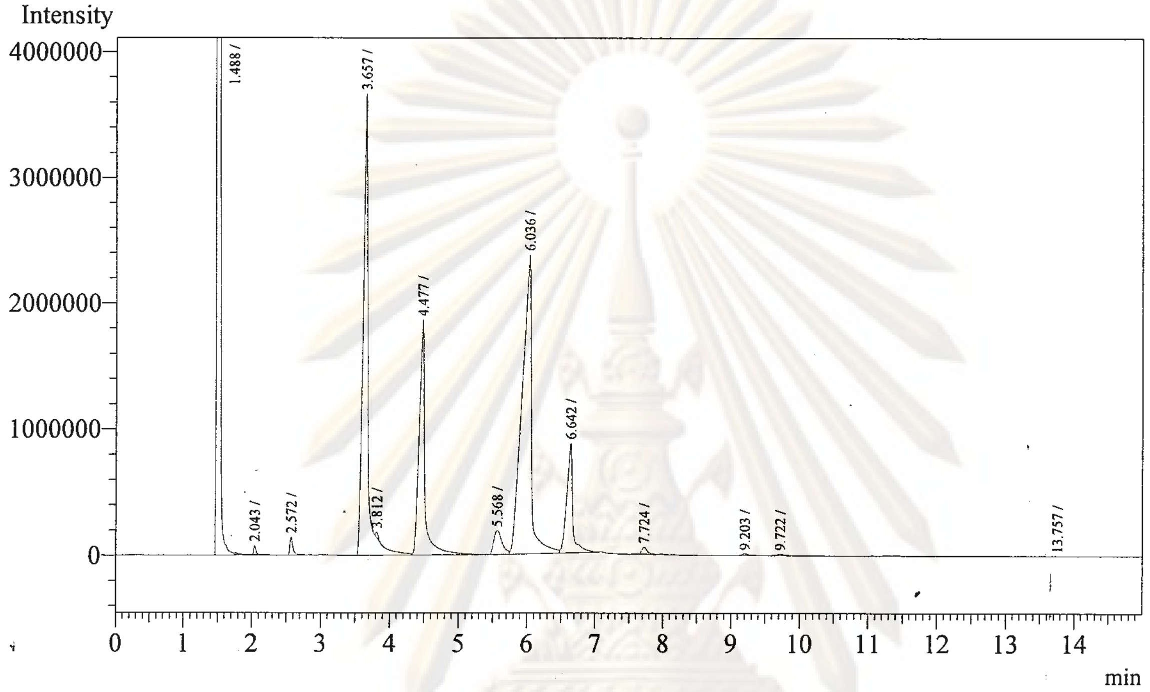
Data Name : D:\ACID\FA35.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.487	834690003	66128827	0.000		S		
2	2.046	138387	48415	0.000		S		
3	2.577	374350	101088	0.000				
4	3.652	17272849	2785756	0.000				
5	4.472	9919359	1353630	0.000		V		
6	5.571	1266805	145451	0.000				
7	6.014	19530107	1905650	0.000		V		
8	6.626	5202565	566420	0.000		V		
9	7.738	186652	29326	0.000				
10	9.228	83804	9168	0.000				
11	9.745	79666	7106	0.000				
Total		888744547	73080837					

Analysis Date & Time : 2/9/2552 12:08:01
User Name : Admin
Vial# : 15
Sample Name : W33
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

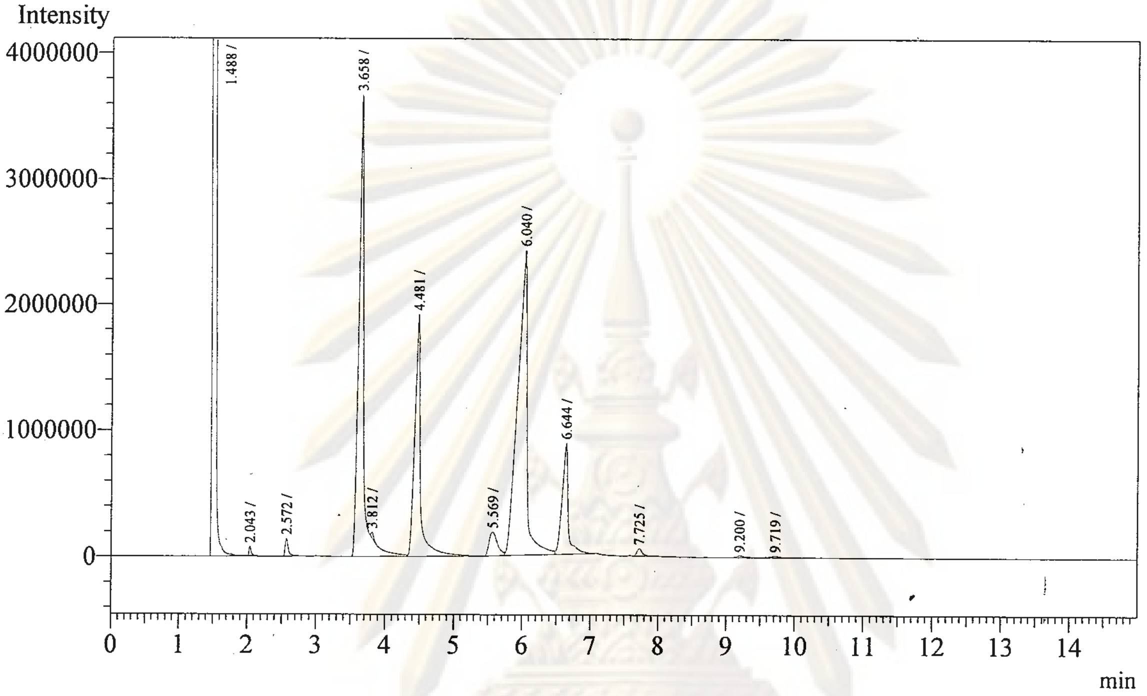
Data Name : D:\ACID\FA104.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.488	835401040	78951523	0.000		S		
2	2.043	170743	75020	0.000				
3	2.572	442405	141579	0.000		S		
4	3.657	18798139	3652383	0.000		S		
5	3.812	106039	41917	0.000		T		
6	4.477	10901996	1860759	0.000		V		
7	5.568	1604862	190830	0.000				
8	6.036	23122332	2371073	0.000		V		
9	6.642	5382435	867479	0.000		V		
10	7.724	311013	57306	0.000				
11	9.203	119211	15251	0.000				
12	9.722	117084	11923	0.000				
13	13.757	35480	1015	0.000				
Total		896512779	88238058					

Analysis Date & Time : 2/9/2552 11:51:23
User Name : Admin
Vial# : 14
Sample Name : W34
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

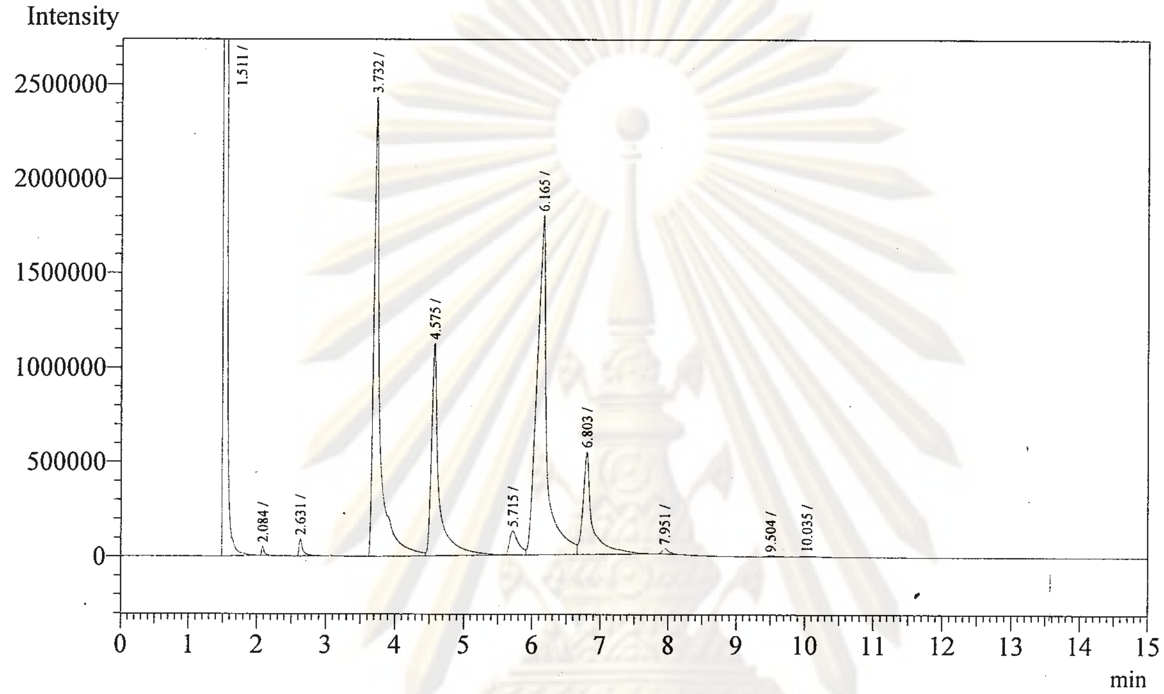
Data Name : D:\ACID\FA103.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.488	828119673	71324312	0.000		S		
2	2.043	174533	74803	0.000				
3	2.572	454381	141945	0.000		S		
4	3.658	19219647	3639626	0.000		S		
5	3.812	107911	42004	0.000		T		
6	4.481	11483398	1909727	0.000		V		
7	5.569	1620027	189264	0.000				
8	6.040	23858244	2421013	0.000		V		
9	6.644	5536646	878057	0.000		V		
10	7.725	318743	58801	0.000				
11	9.200	121516	15568	0.000				
12	9.719	114735	12203	0.000				
Total		891129454	80707323					

Analysis Date & Time : 2/7/2552 11:52:31
User Name : Admin
Vial# : 8
Sample Name : W35
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

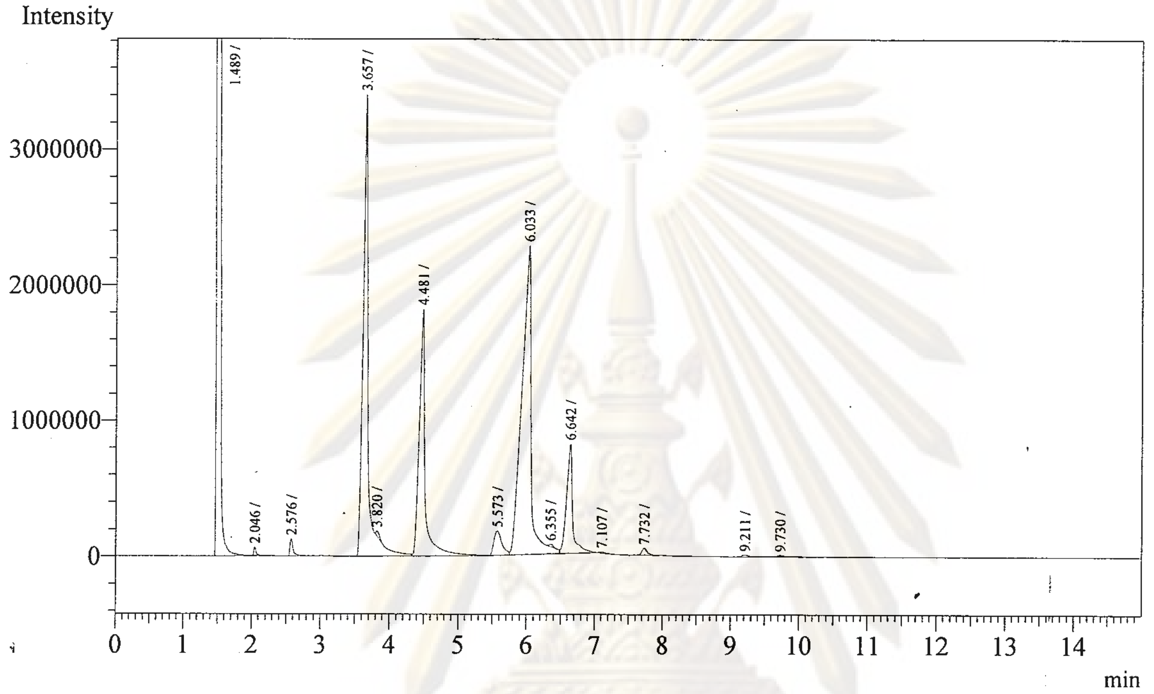
Data Name : D:\ACID\FA12.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.511	756168906	19561890	0.000		S		
2	2.084	134234	49581	0.000				
3	2.631	341262	91815	0.000				
4	3.732	15539691	2430042	0.000				
5	4.575	8635281	1124452	0.000		V		
6	5.715	1148752	128332	0.000				
7	6.165	18763748	1792766	0.000		V		
8	6.803	5285411	543849	0.000		V		
9	7.951	202513	30092	0.000				
10	9.504	74430	7788	0.000				
11	10.035	75306	6261	0.000				
Total		806369534	25766868					

Analysis Date & Time : 2/9/2552 9:04:34
User Name : Admin
Vial# : 4
Sample Name : W36
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

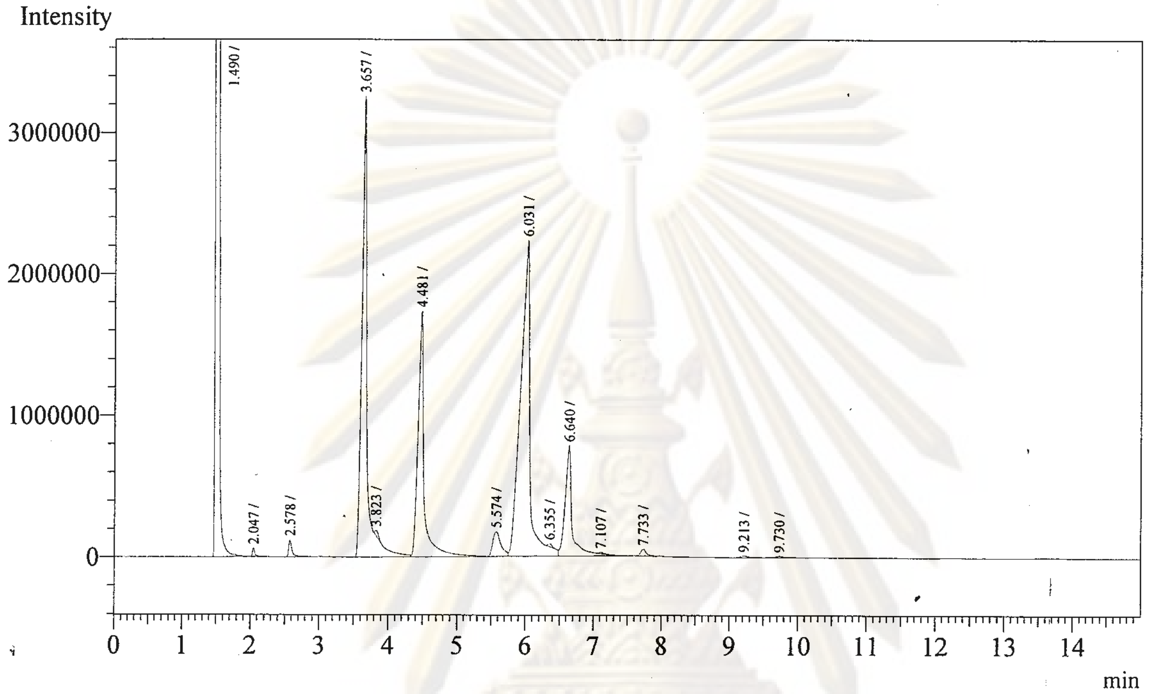
Data Name : D:\ACID\FA93.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.489	837645919	64315748	0.000		S		
2	2.046	147803	62829	0.000				
3	2.576	402538	126196	0.000				
4	3.657	17744376	3390524	0.000		S		
5	3.820	135079	36040	0.000		T		
6	4.481	10893290	1816150	0.000		V		
7	5.573	1473039	179946	0.000				
8	6.033	22024031	2273552	0.000		SV		
9	6.355	79004	20293	0.000		T		
10	6.642	5079272	805248	0.000		V		
11	7.107	45360	10055	0.000				
12	7.732	278466	50329	0.000				
13	9.211	106500	13275	0.000				
14	9.730	102751	10477	0.000				
Total		896157428	73110662					

Analysis Date & Time : 2/9/2552 9:37:57
User Name : Admin
Vial# : 6
Sample Name : W37
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

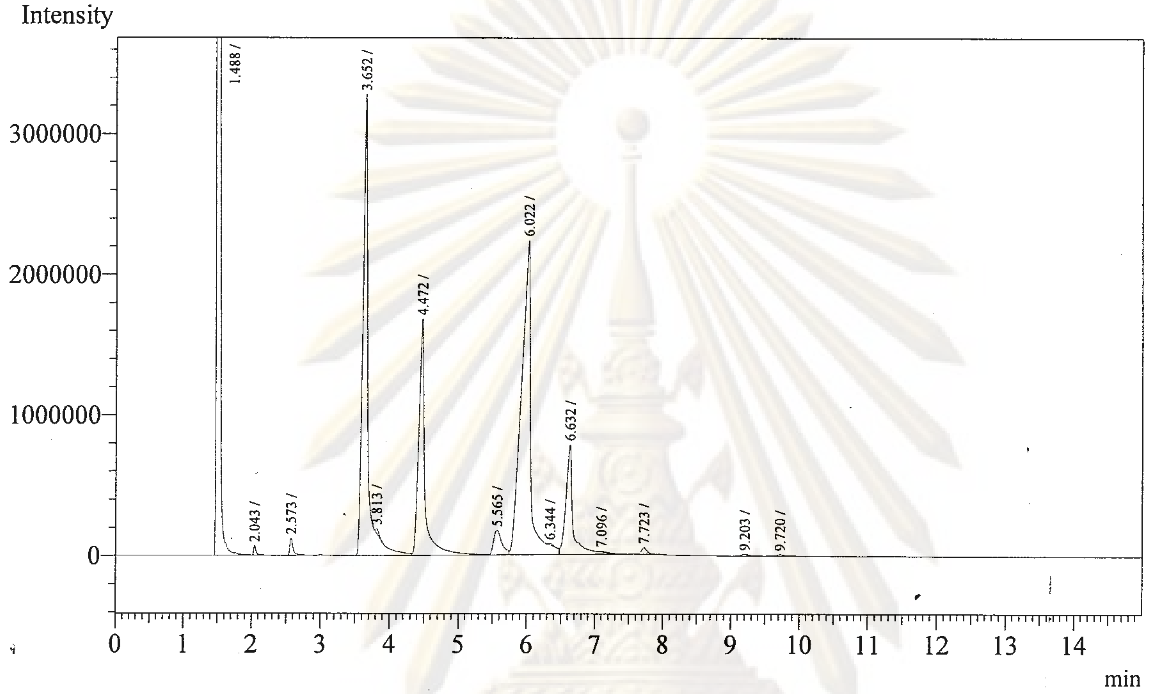
Data Name : D:\ACID\FA95.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.490	826022280	60062510	0.000		S		
2	2.047	145664	60470	0.000				
3	2.578	395255	120652	0.000				
4	3.657	17410628	3243985	0.000		S		
5	3.823	141099	35410	0.000		T		
6	4.481	10673572	1730176	0.000		V		
7	5.574	1457781	175167	0.000				
8	6.031	21873615	2228549	0.000		SV		
9	6.355	90252	22120	0.000		T		
10	6.640	5783810	781877	0.000		SV		
11	7.107	47190	10211	0.000		T		
12	7.733	270988	47880	0.000				
13	9.213	103123	12781	0.000				
14	9.730	105346	9984	0.000				
Total		884520603	68541772					

Analysis Date & Time : 2/9/2552 12:41:18
User Name : Admin
Vial# : 17
Sample Name : W38
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

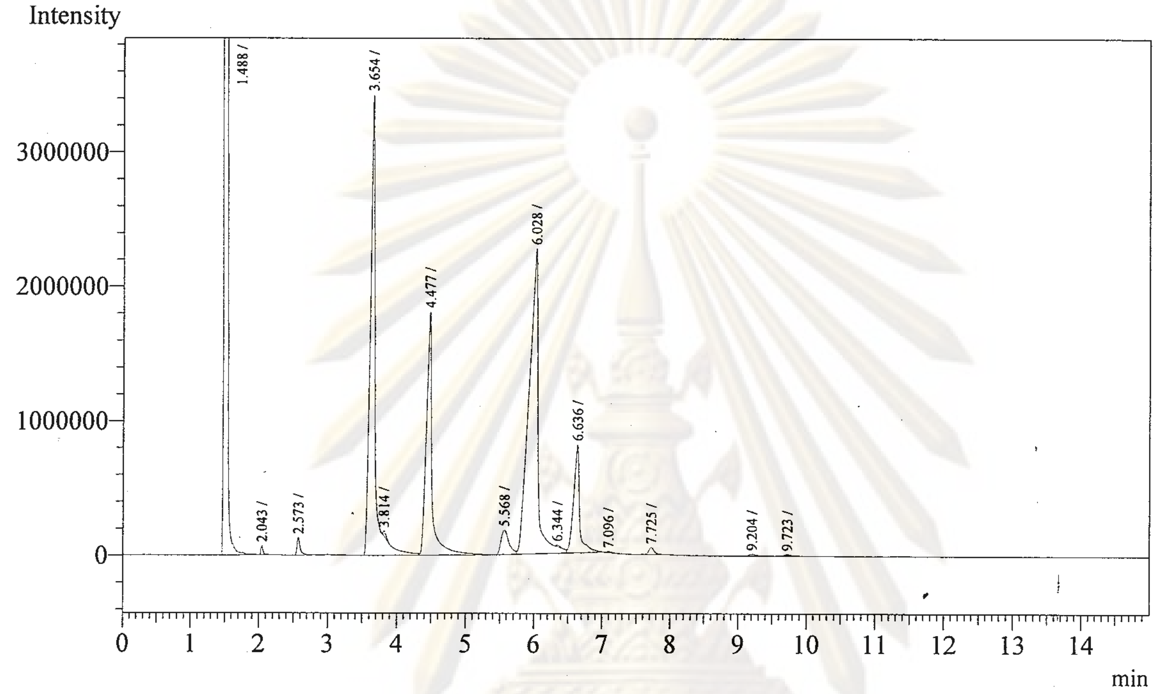
Data Name : D:\ACID\FA106.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.488	832843909	75018161	0.000		S		
2	2.043	159170	66009	0.000				
3	2.573	407616	124321	0.000				
4	3.652	17631306	3271299	0.000		S		
5	3.813	101254	29713	0.000		T		
6	4.472	10442678	1679206	0.000		V		
7	5.565	1473064	174705	0.000				
8	6.022	21863214	2236541	0.000		SV		
9	6.344	39687	11704	0.000		T		
10	6.632	5790577	780440	0.000		SV		
11	7.096	37410	8097	0.000		T		
12	7.723	273971	48377	0.000				
13	9.203	104624	12680	0.000				
14	9.720	103821	10036	0.000				
Total		891272301	83471289					

Analysis Date & Time : 2/9/2552 12:24:38
User Name : Admin
Vial# : 16
Sample Name : W39
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

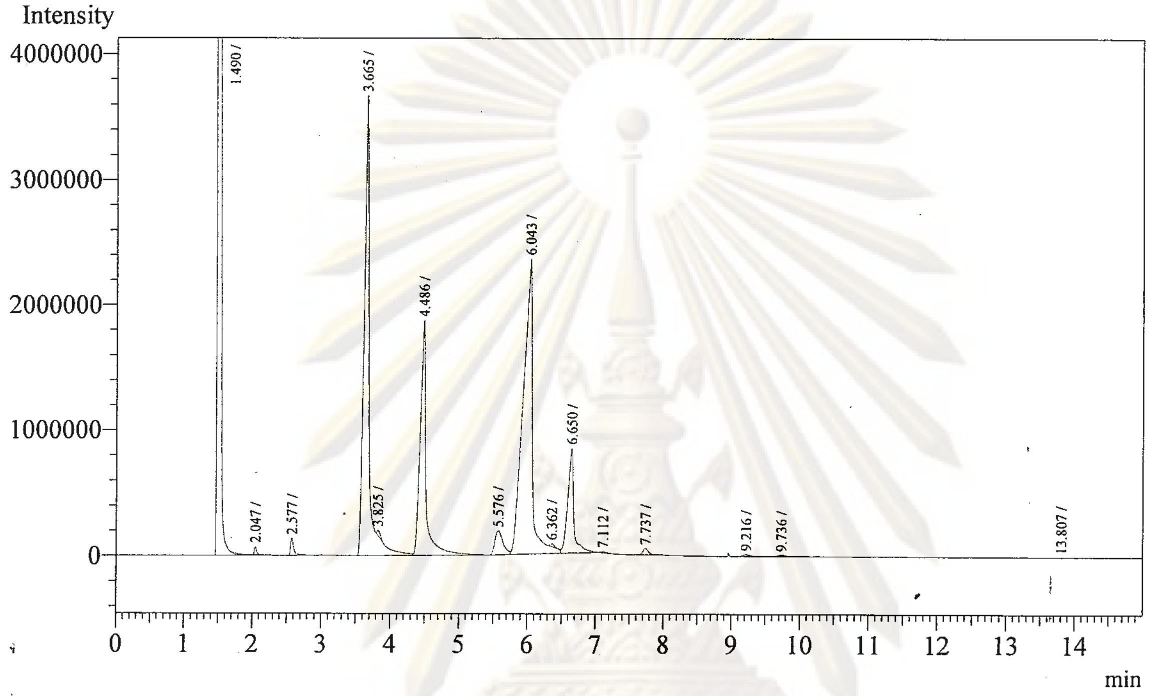
Data Name : D:\ACID\FA105.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.488	830197773	73614348	0.000		S		
2	2.043	159586	68311	0.000				
3	2.573	412932	129788	0.000				
4	3.654	17625697	3391916	0.000		S		
5	3.814	114412	35163	0.000		T		
6	4.477	10667583	1805686	0.000		V		
7	5.568	1476985	181949	0.000				
8	6.028	21608176	2267819	0.000		SV		
9	6.344	40336	11209	0.000		T		
10	6.636	5019163	803192	0.000		V		
11	7.096	36393	8006	0.000				
12	7.725	284349	51581	0.000				
13	9.204	109232	13844	0.000				
14	9.723	101746	10752	0.000				
Total		887854363	82393564					

Analysis Date & Time : 2/9/2552 9:21:14
User Name : Admin
Vial# : 5
Sample Name : W40
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

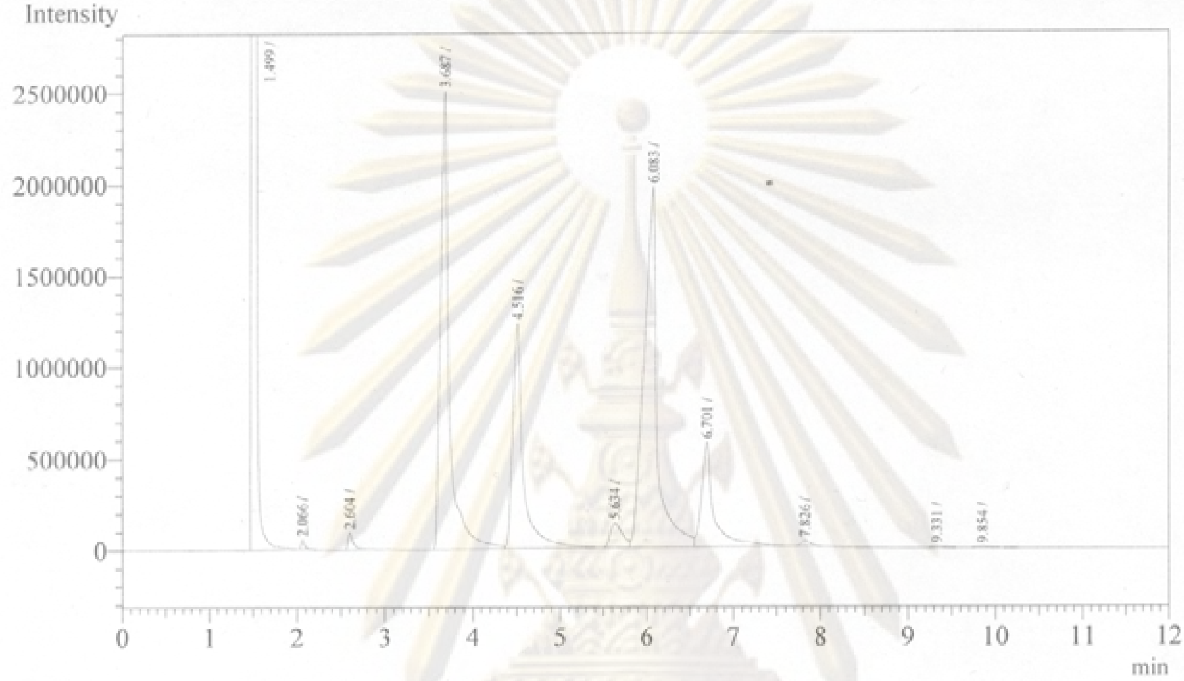
Data Name : D:\ACID\FA94.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.490	830574305	63011345	0.000		S		
2	2.047	159703	67236	0.000				
3	2.577	442019	136252	0.000				
4	3.665	19601612	3643049	0.000		S		
5	3.825	138899	36659	0.000		T		
6	4.486	11300354	1869906	0.000		V		
7	5.576	1595965	191338	0.000				
8	6.043	22881646	2345922	0.000		SV		
9	6.362	90951	23417	0.000		T		
10	6.650	5276963	832000	0.000		V		
11	7.112	51883	11126	0.000				
12	7.737	286963	51846	0.000				
13	9.216	113896	14466	0.000				
14	9.736	110134	10973	0.000				
15	13.807	32705	942	0.000				
Total		892657998	72246477					

Analysis Date & Time : 23/9/2552 12:48:15
User Name : Admin
Vial# : 3
Sample Name : ~~S41~~ W41
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

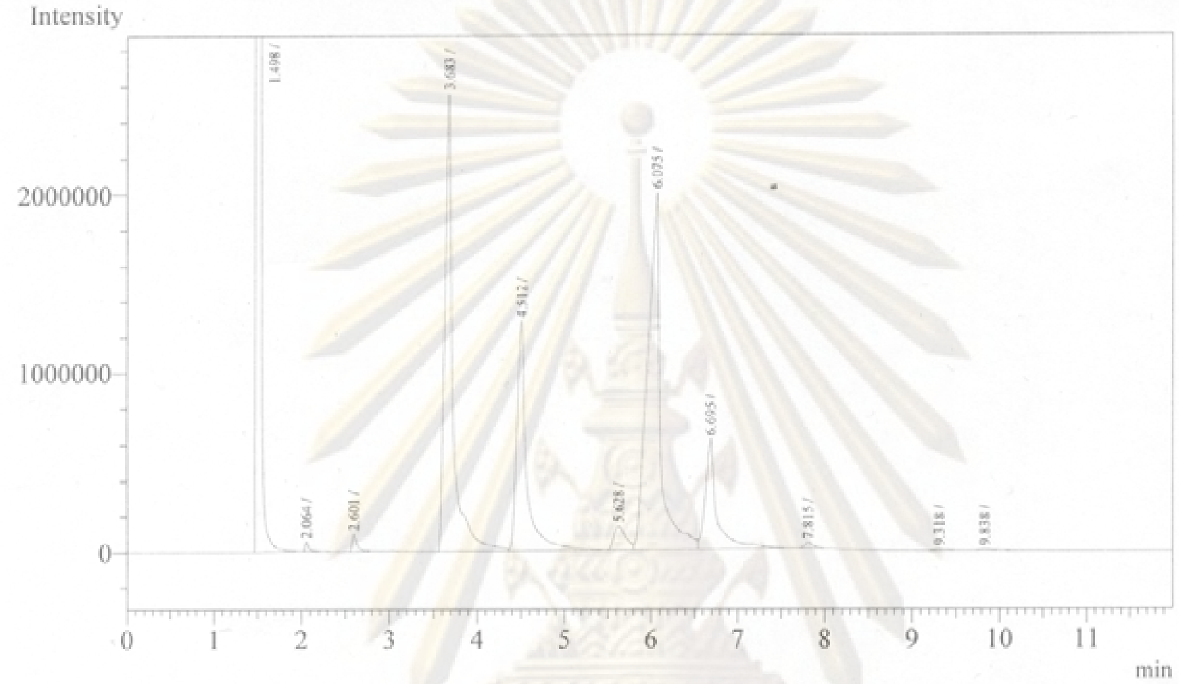
Data Name : D:\ACID\FA122.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.499	854172035	68820142	0.000		S		
2	2.066	158908	53164	0.000				
3	2.604	387526	95113	0.000				
4	3.687	17427259	2501403	0.000				
5	4.516	10275612	1230242	0.000		V		
6	5.634	1318980	132575	0.000				
7	6.083	21275966	1970137	0.000		V		
8	6.701	5573348	570852	0.000		V		
9	7.826	207856	29485	0.000				
10	9.331	86916	8684	0.000				
11	9.854	89345	7063	0.000				
Total		910973751	75418860					

Analysis Date & Time : 23/9/2552 13:01:52
User Name : Admin
Vial# : 4
Sample Name : ~~S42~~ W42
Sample ID : UNK-0001
Sample Type : Unknown
Injection Volume : 1.00
ISTD Amount :

Data Name : D:\ACID\FA123.gcd
Method Name : D:\ACID\FATTY ACID-2.gcm



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	1.498	861523263	77094388	0.000		S		
2	2.064	165286	55586	0.000				
3	2.601	396089	99259	0.000				
4	3.683	17083109	2547394	0.000				
5	4.512	10173752	1281896	0.000		V		
6	5.628	1285344	132861	0.000				
7	6.075	21012562	1995102	0.000		V		
8	6.695	5756586	615487	0.000		SV		
9	7.815	234046	35201	0.000				
10	9.318	85233	8717	0.000				
11	9.838	87674	7228	0.000				
Total		917802944	83873119					

BIOGRAPHY

Miss Thepyanee Lodcam was born in Udorn Thani province on April 13, 1982, she graduated from Chulalongkorn University and received Bachelor degree in Chemical Science in 2004. In 2006 she entered the Graduate School of Chulalongkorn University to continue her study of Chemical Engineering.