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โดยแอมิเดชันของน้ำมันพืช



นางสาววันวิสาข์ สร้อยโสภี

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จุฬาลงกรณ์มหาวิทยาลัย

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**LUBRICITY ADDITIVES FOR DIESEL BY AMIDATION OF
VEGETABLE OILS**



Miss Wonwisa Sroisopee

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย
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Accepted by the Faculty of Science, Chulalongkorn University in
Partial Fulfillment of the Requirements for the Master's Degree

.....Dean of Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

Thesis Committee

.....Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

.....Thesis Advisor
(Associate Professor Amorn Petsom, Ph.D.)

.....Member
(Professor Sophon Roengsumran, Ph.D.)

.....Member
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

.....Member
(Assistant Professor Polkit Sangwanich, Ph.D.)

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ศึกษาสมบัติการหล่อลื่นสำหรับน้ำมันดีเซลจากการเติมสารประกอบเอมิคและเอสเทอร์ของกรดไขมัน โดยเอมิคของกรดไขมัน 9 ชนิดเตรียมได้จากกระบวนการเอมิเคชันของน้ำมันพืช 3 ชนิด ได้แก่ น้ำมันมะพร้าว น้ำมันปาล์ม และน้ำมันรำข้าว ทำปฏิกิริยากับไพรมารีเอมีนคือ เอทิลลามีน บิวทิลลามีน และเฮกซิลลามีน วิธีการเตรียมนี้สามารถเตรียมผลิตภัณฑ์ได้ 75-86 เปอร์เซ็นต์ สำหรับเอสเทอร์ของกรดไขมัน 9 ชนิดเตรียมได้จากกระบวนการทรานเอสเทอริฟิเคชันของน้ำมันพืช โดยทำปฏิกิริยากับแอลกอฮอล์ชนิดต่างๆ ได้แก่ เอทานอล 1-บิวทานอล และ 1-เฮกซานอลด้วยกรดซัลฟูริก สามารถเตรียมผลิตภัณฑ์ได้ 90-97 เปอร์เซ็นต์ การพิสูจน์เอกลักษณ์ทำได้โดยเทคนิคทางสเปกโทรสโกปี ได้แก่ อินฟราเรดสเปกโทรสโกปี แมสสเปกโตรเมตรี โพรตอนและคาร์บอนแมกเนติกเรโซแนนซ์สเปกโทรสโกปี ได้นำสารเติมแต่งที่สังเคราะห์ไปผสมกับน้ำมันดีเซล จากนั้นศึกษาสมบัติในการหล่อลื่นด้วยเครื่องมือ HFRR สารตัวอย่างทั้งหมดที่ความเข้มข้น 0.2 เปอร์เซ็นต์โดยน้ำหนัก สามารถทำให้ค่าความสึกหรอน้อยกว่า 460 ไมโครเมตร สำหรับสารเติมแต่งที่สังเคราะห์ได้ประเภทเอมิคของกรดไขมันพบว่า เอทิลลามีนของน้ำมันรำข้าวเป็นสารเติมแต่งเพื่อการหล่อลื่นที่ดีที่สุดเนื่องจากให้ค่าสึกหรอน้อยที่สุด สำหรับสารเติมแต่งประเภทเอสเทอร์ของกรดไขมัน เฮกซิลเอสเทอร์ของน้ำมันรำข้าวเป็นสารเติมแต่งเพื่อการหล่อลื่นสำหรับน้ำมันดีเซลที่ดีที่สุด นอกจากนี้สารเติมแต่งที่สังเคราะห์ได้ทั้งหมดไม่ทำให้สมบัติทางกายภาพของน้ำมันดีเซลเปลี่ยนแปลงไป

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จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.....

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KEYWORD: LUBRICITY ADDITIVES/ FATTY ACID AMIDES/ FATTY ACID ESTERS/ VEGETABLE OIL/ DIESEL FUEL

WONWISA SROISOPEE: LUBRICITY ADDITIVES FOR DIESEL BY AMIDATION OF VEGETABLE OILS. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D. 111 pp. ISBN: 974-17-4378-5

The influence of the addition of fatty acid amides and esters on the lubrication properties of base diesel fuels is studied in this work. Nine fatty acid amides could be prepared by amidation of three vegetable oils such as coconut oil, palm oil, and rice bran oil with primary amines such as ethylamine, butylamine, and hexylamine. This method of preparation gave about 75-86 % yield of products. Nine fatty acid esters were prepared from transesterification of vegetable oils with various alcohols such as ethanol, 1-butanol, and 1-hexanol in the presence of sulfuric acid, giving about 90-97 % yield of products. Their structures were identified by FT-IR, MS, ^1H -, and ^{13}C -NMR. The synthesized lubricity additives were blended with base diesel fuel, and then were investigated the lubricity performances using High Frequency Reciprocating Rig machine. All samples at concentration of 0.2 % by weight could provide satisfactory mean wear scar diameter of less than 460 μm . Considering the performances of fatty acid amides series, rice bran oil ethylamide was the best lubricity additive for diesel fuel, because it resulted in the lowest wear scar diameter value. For fatty acid esters series, rice bran oil hexyl ester was the best lubricity additive for diesel fuel. Moreover, all additives did not alter the physical properties of base diesel fuel.

Field of study Petrochemistry and polymer science **Student's signature**.....

Academic year 2003 **Advisor's signature**.....

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LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
CCI	Calculated Cetane Index
¹³ C-NMR	Carbon-13 Nuclear Magnetic Resonance
CO	Carbonmonoxide
cSt	Centistroke
δ	Chemical shift
°F	Degree Fahrenheit
d	Doublet (NMR)
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
g	Gram(s)
Hz	Hertz
HC	Hydrocarbon
ml	Mililiter(s)
m	Multiplet (NMR)
ppm	Part per million
¹ H-NMR	Proton Nuclear Magnetic Resonance
q	Quarter (NMR)
t _R	Retention time
rpm	Round per minute
s	Singlet (NMR)
Sp. Gr.	Specific Gravity
t	Triplet (NMR)
cm ⁻¹	Unit of wave number
WSD	Wear scar diameter
% wt	Weight percent
% yield	Yield percent

CHAPTER I

INTRODUCTION

1.1 Introduction

Diesel fuel is a fossil fuel, which in most refineries is made from distillate fractions of crude oil. Crude oil is a mixture of heavy and light hydrocarbons requiring different degrees of heat to produce different products. The boiling range of diesel fuel is approximately 160 to 330 °C. Diesel fuel is used in compression-ignition engine, which is the internal combustion engine. It is used in heavy-duty motor vehicles, such as heavy trucks, urban buses, and locomotives. The diesel engine relies on high temperature alone for ignition. Since this high temperature is the result of air compressing above the piston as it travels upward, diesel engines are often referred to as compression ignition engines [1].

Diesel powered cars have been increasingly popular, so diesel fuels are increasingly needed, especially for high-speed ones. It is expected that diesel demand and utilization will increase more in the next few decades. Many refineries have to produce increasingly diesel fuel with high quality, with enough quantity required. The consumption in Thailand is shown in Figure 1.1 [2].

However, further progress in diesel emission control is needed. Internal combustion engines lead to a number of pollutant emissions, which have a damaging impact on human's health and the environment, and are suspected to cause global climate changes. In order to reduce pollutant emissions, different types of "clean diesel" can be used to improve the combustion process. Generally, what is meant by "clean diesel" is low sulfur diesel.

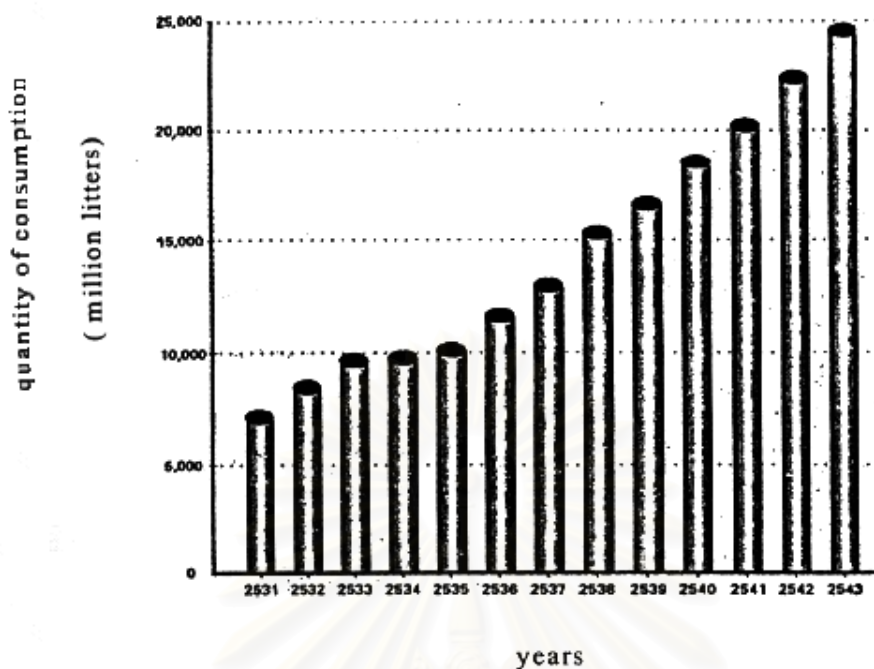


Figure 1.1 The quantity of high-speed diesel consumption in Thailand.

Diesel fuel normally contains relatively high levels of sulfur, which naturally occurs in all crude oils and is present in refined products. During combustion, sulfur compounds oxidize to form SO_2 and SO_3 . These compounds are part of the diesel engine's particulate emissions, which reduce air quality and also fall to the ground in the form of acid rain. Therefore, reducing fuel sulfur levels can result in lower particulate emissions.

For this reason, the Environmental Protection Agency (EPA) has established low sulfur requirements in diesel fuel. A minimum sulfur content of 0.05 % by weight is required. This is similar to regulations for diesel fuel in several countries around the world. All countries, which subscribe to the European Diesel Specification EN 590, produce diesel with sulfur content below 350 parts per million (ppm), while the agendas of fuel specifications for the year 2005 limit the sulfur content to 50 ppm. In 1999, Thailand limited sulfur in diesel fuel for "on-road" vehicles to a maximum of 500 ppm or 0.05 % by weight.

The introduction of low sulfur diesel fuels has been achieved by increasing the use of refining process such as hydrotreating or hydrocracking. This process involves the introduction of hydrogen in the refining process to remove sulfur and reduce aromatic hydrocarbons. However this process also tends to reduce the natural

lubricating properties of the fuel, *i.e.*, minimizes polyaromatic and polar compounds such as oxygen and nitrogen containing compounds [3, 4]. Moreover, the use of low sulfur diesel fuels has had the side effect of fuel injection systems inside diesel engines, causing many problems such as injector nozzle fouling and fuel pump failures, and results in wear or poor lubricity property. This problem can be solved by adding additives.

Lubricity additives are used to compensate for the poor lubricity of severely hydrotreated diesel fuels. They contain a polar group that is attached to metal surfaces, causing the additive to form a thin surface film. The film acts as a boundary lubricant when two metal surfaces come in contact. According to the present invention, it has been found that ester, carboxylic acid, amine, and amide compounds are useful as lubricity additives in low sulfur content diesel fuel [5].

In recent years fatty acid esters, commonly known as “biodiesel”, have successfully been used as diesel fuel lubricity improvers because they can be easily prepared from vegetable oils, are biodegradable and are produced at low cost. Biodiesel comprises of oxygen compounds which are fuels generally result in improved combustion quality. It leads to lower HC, CO, and particulate emissions. Biodiesel has been studied extensively in Europe and the U.S. for its effect on long-term engine wears, particularly with respect to those components normally lubricated by the fuel itself. Moreover, biodiesel offers superior lubricity even in very low blends. For example, a 1 % blend of biodiesel can improve lubricity by as much as 65 % [6, 7].

But even so past papers did not show that fatty acid amides, which can be prepared from vegetable oils, are used as lubricity additives. This research aims at the preparation of lubricity additives for diesel fuel by amidation of vegetable oils. Synthesis of fatty acid esters from transesterification of vegetable oils with alcohols is also studied. Their properties as lubricity additives are also compared.

The High Frequency Reciprocating Rig (HFRR) is used to measure fuel lubricity. The objective of this work is to assess the lubricating properties of diesel fuels blended with nine fatty acid esters and nine fatty acid amides of different structure. They should provide lubricity improvement down to the 460 μm wear scar diameter (WSD), which is the minimum requirement for an acceptable field performance [2].

1.2 Objectives and scope of the research

1.2.1 Objectives

1. To synthesize fatty acid esters and fatty acid amides from vegetable oils for use as lubricity additives in diesel fuel.
2. To study the properties of synthesized fatty acid esters and fatty acid amides blended with base diesel as lubricity additives.

1.2.2 Scope of the research

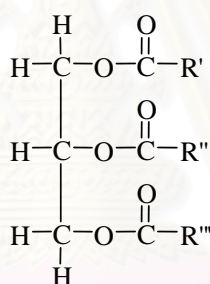
1. Literature survey of the relevant research works
2. Preparation of apparatus and chemical substances
3. Synthesis of fatty acid esters by transesterification of vegetable oils and of fatty acid amides by amidation of vegetable oils.
4. Characterization of fatty acid esters and fatty acid amides by spectroscopic methods such as FT-IR, MS, ^1H - and ^{13}C NMR.
5. Determination of lubrication properties and important physical properties of diesel fuel blended with fatty acid esters and fatty acid amides.
6. Summarizing of the results.

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 Vegetable oils

Fats and oils constitute a well-defined class of neutral and water insoluble substances that are produced in some quantity by animals and vegetable source [8]. Most vegetable oils have the triglyceride structure, which is represented in Scheme 2.1. These tri-esters are derived from glycerol and carboxylic acids known as fatty acids. Therefore, vegetable oils are commonly called triglycerides, although a more accurate name is triacylglycerols.



Whereas R', R'', R''' represent the hydrocarbon chain of fatty acid radicals.

Scheme 2.1 Structure of a triglyceride.

The fatty acids are almost always straight chains containing between 8 and 22 carbon atoms, and may be saturated, monounsaturated or polyunsaturated. Vegetable oil compositions are normally described in terms of their fatty acid content, referring to the acid ester moieties; actual fatty acids present in the oil are known as free fatty acids.

The difference chemical and physical properties of vegetable oils depend on the degree of unsaturation of the constituent fatty acids and chain length. Vegetable oils with a proportion of saturated fatty acids are solid or semi-solid at room temperature. The melting point of the fatty acids and their glycerides decrease from saturated to polyunsaturated types, whereas the volatility and boiling points change

only slightly. By chain length, the melting point, the boiling point of the fatty acids and their glycerides rises when chain length increase. There are many vegetable oils used a wide application in Thailand such as coconut oil, palm oil, and rice bran oil.

2.1.1 Coconut oil

The Coconut palm, *Cocos nucifera* L. [9] is a palm family. The coconut oil is the fats derived from the kernel oil of the coconut palm, which is white fat of bland taste having a peculiar, not unpleasant, odor of coconut meat. It is used for oil, food, fiber, and drink. Coconut oil is also an ingredient in many cosmetics, shampoos, and suntan products because it is resistant to spoilage and low in price. Coconut oil contains amounts of saturated fatty acids and their chemical compositions have a lot of short carbon chains that 47% of lauric acid (C12:0) and 17.5% of myristic acid (C14:0) are the main component acids [10]. Coconut oil is used as a viscosity improver the ability of the oil to lubricate over a wider temperature range. It furnishes the lauryl component of the lauryl methacrylate monomer form which most of this type of product is made.

2.1.2 Palm oil

The oil palm, *Elaeis guineensis*, [11] oil is derived from palm kernel oil. Palm oil is deep orange-red by the large amount of carotene. It is used for food, margarine, and soaps. It contains equal amounts of saturated and unsaturated fatty acids. Palm oil has long chain carbon of fatty acids in its composition that it contains 45% of palmitic acid (C16:0), 38% of oleic acids (C18:1) and 10% linoleic acid (C18:2) are the main component.

2.1.3 Rice bran oil

Rice bran oil, unlike other vegetable oils, has saturated and unsaturated fatty acids. Rice bran oil is deep orange-red. It contains long chain carbon of fatty acids, which are 14.4% of palmitic, 41.2% of oleic and 39.7% of linoleic acids.

Each vegetable oil is classified in terms of their fatty acid compositions. Typical fatty acid compositions of some vegetable oils (coconut oil, palm oil, and rice bran oil) are given in Table 2.1. In the table both non-systematic names and numerical

notation are given; for instant, 18:2 refers to a fatty acid with 18 carbons and two double bonds [12].

Table 2.1 Composition of fatty acids of vegetable oils

Fatty acid		% Fatty acid composition		
Non-systematic name	Numerical representation	Coconut oil	Palm oil	Rice bran oil
Caprylic acid	8:0	8	-	-
Capric acid	10:0	6	-	-
Lauric acid	12:0	47	-	-
Myristic acid	14:0	17.5	1	-
Palmitic acid	16:0	9	45	14.4
Palmitoleic acid	16:1	-	-	-
Stearic acid	18:0	3	4.5	1.3
Oleic acid	18:1	7	38	41.2
Linoleic acid	18:2	1.8	10	39.7
Linolenic acid	18:3	-	-	1.5

The main uses of fats and fatty acids are for food soap as a source of fatty acids, paints, protective coating, and industrial applications. Furthermore, they have a long history of use in lubrication. Actually, they were the main source of lubricants before the enormous growth of mineral oil-based products. Nowadays, there is a continuing use of vegetable oils in lubrication owing to price and overall performance. They can produce a wide variety of chemical products. These chemicals find use in many applications, including lubricants, either as additives or for the production of synthetic materials such as ester base fluids or amide compounds.

2.2 Lubricity additives made from vegetable oils: Biodiesel [6, 13]

Biodiesel is a clean-burning diesel fuel additive produced from vegetable oils instead of petroleum. Biodiesel is used in diesel engines to enhance engine combustion performance, improve engine lubrication, and reduce air and water pollution caused by the exhaust. The concept of using vegetable oil as a fuel dates

begins 1895. Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Diesel demonstrated his engine at the World Exhibition in Paris in 1900 using peanut oil as fuel.

Biodiesels are liquid transportation fuels made from plant matter instead of petroleum. Unlike gasoline and diesel, biodiesels contain oxygen. Therefore, adding biodiesels to petroleum products causes the fuel to combust more completely and improves air quality by sharply reducing the emissions, including particulate matter, which straight petroleum diesel fuel releases when it burns.

2.2.1 Flash Point and Sulfur Content

The flash point of a fuel is defined as the temperature to which the fuel must be heated to produce a vapor-air mixture above the surface of the fuel that will ignite when exposed to an ignition source such as a spark or flame. Due to the operating environment of underground mines, flash point is an important parameter. The flash point of biodiesel has been tested and reported by various sources. Specific testing at Southwest Research Institute concluded that the flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore pure biodiesel or blends of biodiesel with petroleum diesel is safer to store, handle, and use than conventional diesel fuel. In addition, the sulfur content of fuels utilized in underground mines is also regulated. Pure biodiesel is essentially sulfured free and results in a total reduction of SO₂ emissions as well sulfate aerosols in particulate matter. These reductions should assist in increasing both vehicle and catalyst life over time.

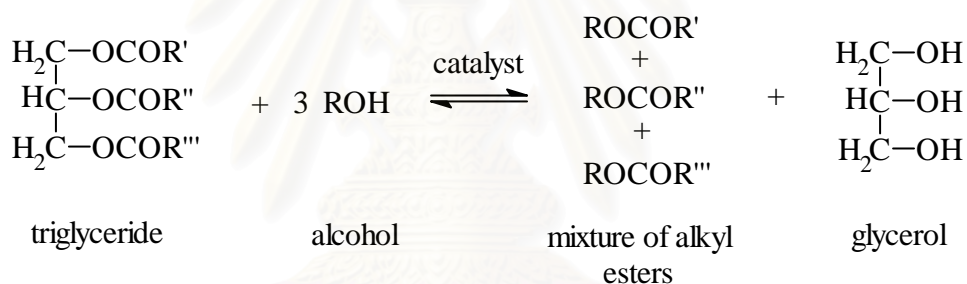
2.2.2 Lubricity Properties

Biodiesel improve the lubrication properties (lubricity) of the diesel fuel blend. Long term engine wear studies have been conducted in Europe and in the US. Porsche (Germany) determined that neat (100%) Biodiesel reduced long term engine wear in test diesel engines to less than half of what was observed in engines running on current low sulfur diesel fuel. Initial work on the lubricity of Biodiesel, performed by Mark-IV Group and the Southwest Research Institute in 1994, established a clear advantage to blending Biodiesel with petrodiesel to achieve superior lubrication.

Lubricity tests utilizing both the High Frequency Reciprocating Rigs (HFRR) and the Ball on Cylinder Lubricity Evaluator (BOCLE) have demonstrated the lubricity advantage of biodiesel. The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel, while fuel consumption, auto ignition, power output, and engine torque are relatively unaffected by biodiesel.

2.3 Transesterification of vegetable oils [14, 15, 16]

The process of converting vegetable oil into biodiesel fuel is called transesterification, which is a reaction between an ester and triglyceride with another compound that could either be an ester, alcohol or acid. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. (Scheme 2.2)



Scheme 2.2 Transesterification of vegetable oils.

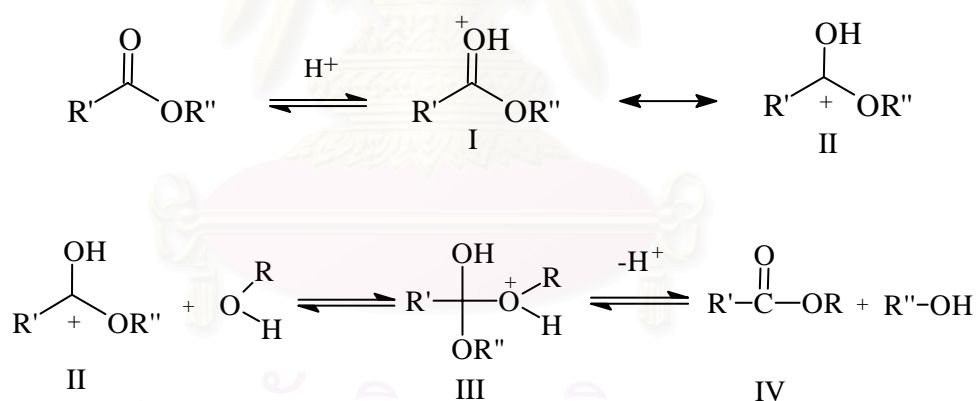
In the transesterification of vegetable oils, a triglyceride reacts with an alcohol and release three "ester chains" from the glycerin backbone of each triglyceride. The reaction requires heat and a strong acid or a strong base catalyst (e.g., hydroxide or lye), to achieve complete conversion of the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

The common aspect of synthetic consists in optimizing the reaction conditions, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content. The production processes for biodiesel are well known and based on the type of catalyst used.

2.3.1 Acid catalyzed transesterification of vegetable oils

The chemical reaction of acid catalyzed biodiesel production is shown in Scheme 2.3. The catalyst of this process is Bronsted acid, which is usually sulfuric acid. It gives very high yields in alkyl esters, but the reactions are slow.

The mechanism of the acid catalyzed transesterification of vegetable oils. The first step, the protonation of the carbonyl group of the ester leads to the carbocation I that after a nucleophilic attack of the alcohol produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+ .



R = alkyl group of the alcohol

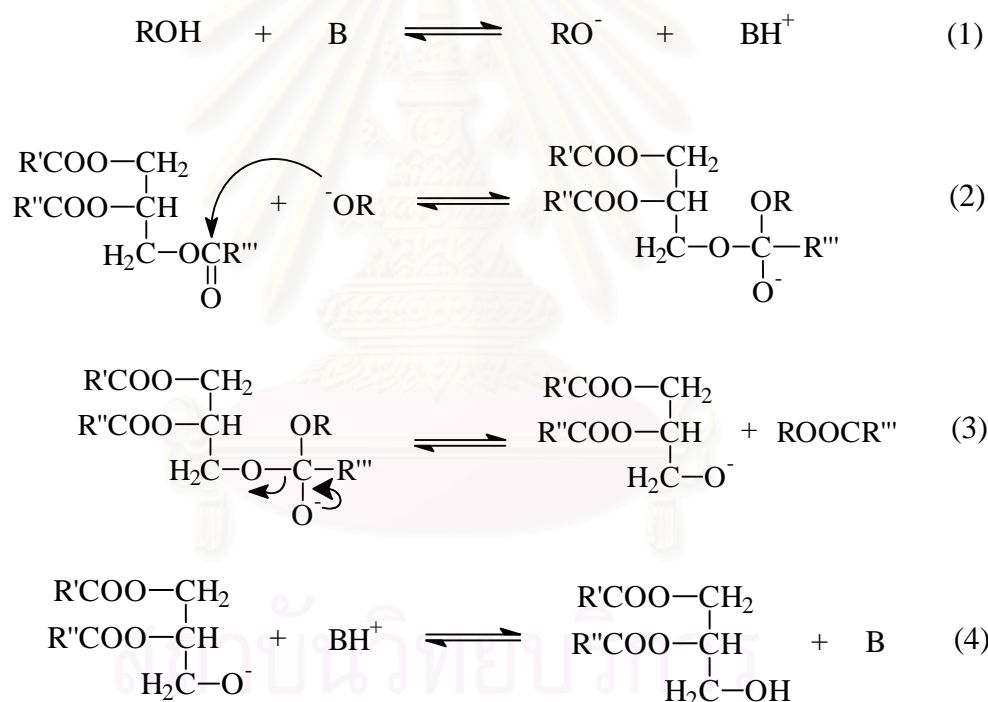
R' = carbon chain of the fatty acid

R'' = $\begin{array}{l} \text{O}^- \\ | \\ \text{—OH} \\ | \\ \text{—OH} \end{array}$; glyceride

Scheme 2.3 Mechanism of the acid-catalyzed transesterification of vegetable oils.

2.3.2 Base-Catalyzed transesterification of vegetable oils

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Scheme 2.4. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.



Scheme 2.4 Mechanism of the base-catalyzed transesterification of vegetable oils.

2.4 Lubricity additives made from vegetable oils: Fatty acid amides

Amides such as fatty acid amides, fatty alkanolamides and fatty diamides are important chemical intermediates for commerce with applications ranging. Fatty acid amides used for paper coatings and lubricants [17]. Fatty alkanolamides have a

multitude of uses such as detergents, shampoos, and lubricants. Fatty diamides also use for lubricants and release agents. Moreover the fatty acid amides are used as lubricity additives in diesel fuel because their structures have polar head group that form a surface film. These films are thick that they provide enough of protection to prevent metal-to-metal contact. Fatty acid amides have long chain fatty acids because they prepare from the fats or vegetable oils.

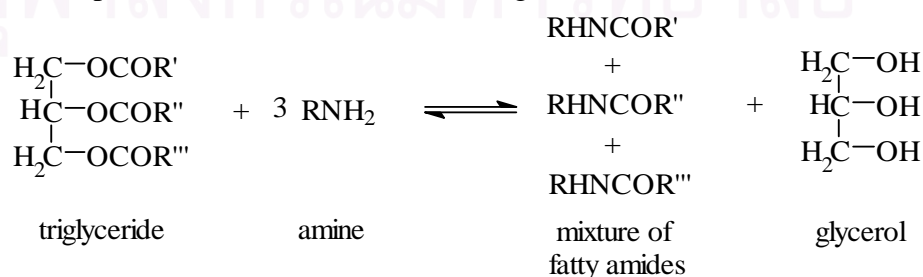
Industrially, secondary amides are produced from purified fatty acids and primary amines at high temperatures under moderate pressure. They are also produced by reacting fatty acyl chlorides with amines or, alternatively, by reacting fatty esters with amines while using sodium methoxide as a catalyst [18]. Not long after, fatty acid amides can also be prepared by direct amidation of triglycerides from fats or vegetable oils. There are three reaction conditions that are investigated;

1. Reflux with amines as solvents
2. Reflux with hexane as the solvent
3. Room temperature with amines as solvents

It was found that the reactions with amines as refluxing solvents were a simple procedure that required no base catalyst other than the amine itself and they gave high yield by this procedure.

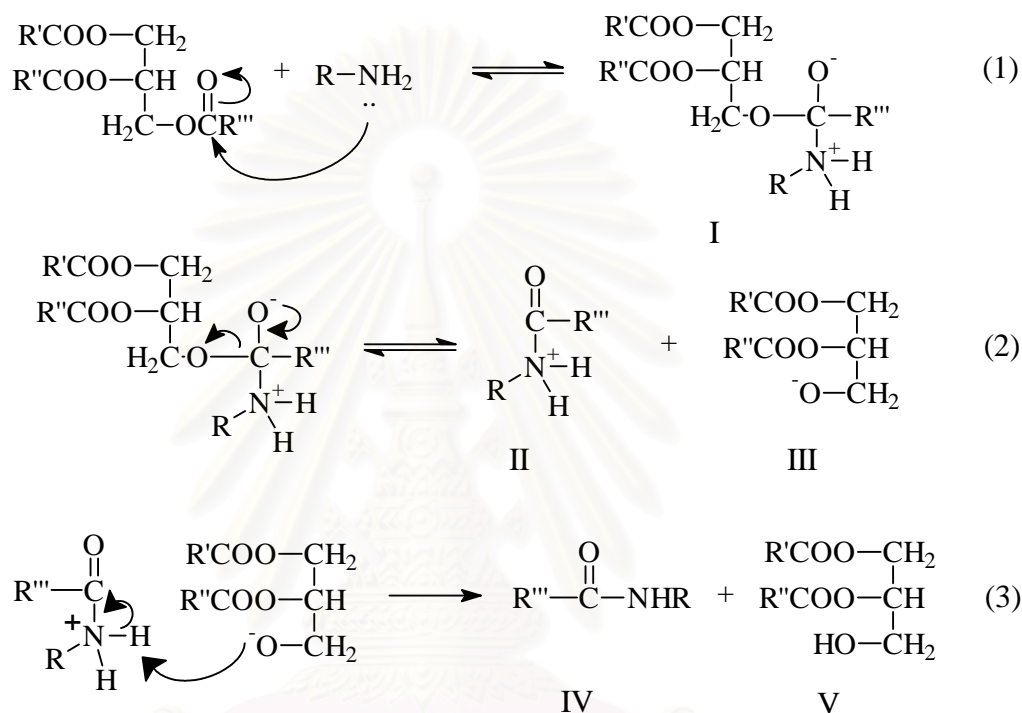
2.5 Amidation of vegetable oils [19, 20, 21]

Vegetable oils, containing naturally triglycerides, were reacted with primary amine. The products of this reaction are the mixtures of secondary amides and glycerol. This process is called amidation of vegetable oils (Scheme 2.5)



Scheme 2.5 Amidation of vegetable oils

The mechanism of the amidation of vegetable oils is shown in Scheme 2.6. The first step (Eq. 1) is the reaction of the base with the triglyceride. The nucleophilic of the amine attacks at the carbonyl group of the triglyceride, generates a tetrahedral intermediate I. The second step is an elimination mechanism; intermediate II and anion of the diglyceride (III) are formed. The latter deprotonates the intermediate II thus gives secondary amide.



Scheme 2.6 Mechanism of the amidation of vegetable oils.

2.6 Diesel fuel

Diesel fuel is a fossil fuel, which in most refineries is made from distillate fractions of crude oil. It is the portion of crude oil that distills out within the temperature range of approximately 160 to 330 °C (300-700°F), which is higher than the boiling range of gasoline (Figure 2.1). Diesel fuel is ignited in an internal combustion engine cylinder by the heat of air under high compression, which is any fuel suitable for burning in diesel engines. In contrast to motor gasoline, this is ignited by electrical spark.

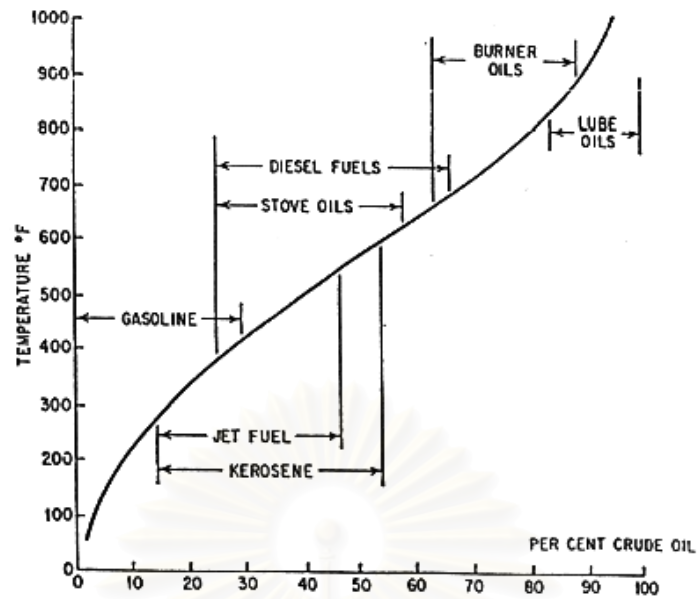


Figure 2.1 Proportion of diesel fuel and other petroleum products processed from crude petroleum.

2.7 Types of diesel fuels

There are three basic types of diesel fuels. High-speed diesel is normally used as a fuel for high-speed diesel engines operating above 1,000 rpm such as trucks, cars, buses, generating sets, locomotives, and pumping sets *etc.* Gas turbine requiring distillate fuels normally make use of high-speed diesel as fuel.

Medium-speed diesel is used for a wide range of purposes including generation of electricity, stationary power generators, railroads, and pipeline pumps. It operates range of 450 to 1,000 rpm. Low-speed diesel or marine diesel is commonly used on ships, fishing boats, and for generation of electricity. Low-speed diesel can operate below 300 rpm. Typical ranges of diesel engines are listed at Table 2.3.

Table 2.2 Typical ranges of diesel engines

Type	Speed Range	Conditions	Typing applications
Low Speed	< 300 rpm	Heavy load, constant speed Fairly high load	Marine main propulsion; electric power generation
Medium Speed	300-1000 rpm	Relatively constant speed	Marine auxiliaries; stationary power
High Speed	> 1000 rpm	Frequent and wide variation in load and speed	Generators; pumping units Road transport vehicles; diesel locomotives

2.8 Specification for diesel fuels

It has been critical to the successful development of diesel fuel and diesel-powered vehicles to have consensus among refiners, vehicle, and engine manufacturers, and other interested parties on the characteristics of diesel fuel necessary for satisfactory performance and reliable operation. Performance features desired of all diesel fuels, and the physical properties most directly related to them are summarized below [22].

Performance feature desired	Indicated by
1. Safety in handling	Flash point
2. Pumpability at low temperatures	Pour or cloud point, viscosity
3. Freedom from all suspended matter	Storage stability, suspended sediment tests
4. Readily atomized	Viscosity
5. Readily ignitable	Cetane number
6. Clean burning	Volatility, cetane number
7. Good fuel economy	API gravity
8. Major effect on engine wears	Sulfur

The properties generally considered to be most indicative of diesel fuel quality, however, are cetane number, volatility, viscosity, sulfur content, and API gravity. This section discussed the more important fuel characteristics as they relate to engine performance.

2.8.1 Density

Density is the mass per unit volume of diesel fuel at a given temperature. It can provide useful indications about a fuel's composition and performance related characteristics. In addition, the density gives an indication of other fuel characteristics, including specific energy, and ignition quality. There are two scales in use in the petroleum industry;

2.8.2 Specific gravity

The density of petroleum products is usually expressed as a specific gravity. The specific gravity is defined as the ratio of the mass of a volume of the fuel to the mass of the same volume of water. As it is a ratio there are no units. It is dependent on the temperature of both the fuel and the water. It will commonly be expressed as "Specific Gravity 60/60°F" which means that both the fuel and water were at 60°F.

2.8.3 API

An indication of density of crude oil or other liquid hydrocarbons as measured by a system recommended by the American Petroleum Institute (API), measured in degrees. For example, asphalt has an API gravity of 8° and gasoline has an API gravity of 50°. The API gravity is related to the specific gravity of the fuel by the following equation:

$$\text{API Gravity (}^{\circ}\text{C)} = 141.5/[\text{specific gravity } 60/60^{\circ}\text{F}]-131.5$$

API gravity is a useful measure of density for liquids lighter than water. API gravity of diesel fuel has a profound effect on engine power. As a general rule, there is 3-5% decrease in the thermal energy content of fuel for every 10 degrees increase in API gravity. This decrease in energy content will result in roughly the same percentage decrease in engine power. Use of fuels with higher API gravity will also result in higher fuel consumption.

2.8.4 Volatility

The volatility of a fuel is a measure of how readily it evaporates. The volatility indicates by distillation curve, which depends on the boiling range and the content of light fractions. Increasing the contents of lower boiling fractions increases the volatility of fuels. Diesel fuel is a mixture of hydrocarbon compounds with a range of boiling points. The distillation curve is determined by relating the fraction of a fuel sample, which is removed by heating a fuel sample to progressively higher temperatures. Typically, the initial point, which is the temperature at which the first drop of liquid leaves the condenser, the temperatures at each 10% of the liquid, characterizes the curve.

Important distillation points for determining fuel volatility are the 10%, 50%, 90%, and final boiling point. The highest temperature recorded during distillation is called the end point. Ideally, one would specify an end point in the definition of fuel properties. However, because a fuel's end point is difficult to measure with good repeatability, the fuel's 90% or 95% distillation point is commonly used.

The volatility or distillation of diesel strongly influences its performance especially in medium and high-speed engines. The volatility influences other properties such as viscosity, flash point, auto-ignition temperature, cetane number, and density.

The volatility of a diesel fuel has a major effect on engine performance because it determines how much fuel burns. For example:

1. A low T10 (temperature at which the first 10% of fuel is recovered) shows fuel is easily vaporized.
2. High T10 will cause poor starting.
3. If there is a wide temperature range between T10 and T50, the warm-up period may be long.
4. If T90 is too high - above 370°C - the fuel may not vaporize completely, causes smoking, and increased engine deposits

Too high a volatility typically causes vapor locks in the fuel system and poor penetration of the fuel spray in the combustion chamber. Both of these affect the running of the engine, reducing its power output, and increasing fuel consumption.

When volatility is too low, the fuel spray is poorly atomized and the fuel burns poorly. This reduces power output and increases fuel consumption. As a rule, volatility should be as high as possible without adversely affecting other characteristics of the fuel. In general, high volatile fuels are best suited for engines that experience frequently changing loads and speeds. They give better fuel economy and produce less exhaust smoke, odor, deposits, dilution of crankcase oil, and engine's wear.

2.8.5 Viscosity

Viscosity is a measure of fluid's resistance, which influences the spray pattern when the fuel is injected into the cylinder. The greater the viscosity, the less readily the liquid flows. The viscosity of petroleum oils is a strong function of temperature with the viscosity decreasing as the temperature increases. ASTM D445 is a standard test procedure for determining the kinematic viscosity of liquids. It provides a measure of the time required for a volume of liquid to flow under gravity through a calibrated glass capillary tube. The kinematic viscosity is then equal to the product of this time and a calibration constant for the tube, which is measured in stokes.

As one stokes is a large unit, kinematic viscosity is usually measured in centistokes (cSt). The term centistokes is being replaced by the preferred SI (System International unit) or one cSt = 1 mm²/s. For distillate fuels the reference temperature used is 40 °C. However for residual fuels 50 °C is still commonly used, even though the most common specification has a reference temperature of 100 °C.

Each fuel has its own temperature/viscosity relationship and this is shown for typical oil. As the relationship depends on its crude oil source and the refinery processes employed. Low-speed marine engines can use higher viscosity fuels than high-speed road transport engines and still run without excessive smoking.

In addition, viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps or injector plungers resulting in leakage or increased wears. Fuels, which do not meet viscosity requirements, can lead to performance complaints. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion and increased exhaust smoke and emissions.

2.8.6 Flash point

The flash point is the lowest temperature at which a combustible mixture can be formed above the liquid fuel that will ignite and spread over the liquid surface when a small flame is applied. It is dependent on both the lean flammability limit of the fuel as well as the vapor pressure of the fuel constituents. The flash point can be measured by ASTM D93 method using a Pensky-Martens closed cup tester. Heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid determine it. If the temperature is at or above the flash point, the vapor will ignite and can easily detectable flash.

Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of diesel fuel. Too low a flash point makes the fuel a fire hazard. Diesel with a very low flash might suggest a contamination with a more volatile and explosive fuel such as petrol.

Due to its higher flash point temperature, diesel fuel is inherently safer than many other fuels such as gasoline. For this reason, there are mandatory minimum values for flash point.

2.8.7 Pour point

The pour point is the lowest temperature at which a fuel can be handled without excessive amounts of wax crystals forming out of solution that the fuel is observed to flow. Definition from ASTM is the temperature at which a measured volume of fluid does not flow for 5 seconds when tilted horizontally. It is usually the lowest temperature at which a fuel can be pumped. If a fuel is below the pour point, wax will begin to separate out and this will block filters. Also, the wax will build up on tank bottoms and on heating coils. When heat is reapplied difficulties may be experienced in getting the wax to re-dissolve because of its insulating nature. In extreme cases, manual cleaning of tanks may be necessary.

2.9 Diesel fuel lubricity problems

Shortly after the introduction of the low sulfur fuels, it destroys some of the natural lubricant in diesel fuel. The diesel engine makes wear that is also an important property, which is used as an indicator of a fuel's ability to provide lubrication. Wear

causes many problems. It inhibits engine performance and shortens engine life. It leads to stalls, breakdowns and in severe cases, engine failure. There are three types of wear in an internal-combustion engine: abrasive wear, adhesive wear, and corrosive wear [23].

The first type of wear is abrasive. Abrasive wear occurs when a rough surface slides across a softer surface. The rougher surface digs into and scratches the softer surface. Dirt, metal-wear particles or metal-to-metal contact usually cause abrasive wear. They can actually use the oil as a transportation device to scour other parts of the engine. Abrasive wear is most common during the start up and shut down of the engine. The second type of wear is adhesive wear. If metal-to-metal contact occurs, the one metal may have fragments that break off and adhere to the other. Either lubrication breakdown or a lack of lubrication usually causes adhesive wear. Lubrication breakdown most commonly occurs when the oil film is too thin. And the third type of wear is corrosive wear. It occurs when a chemical attack corrodes the metal surface. The water, which remains unburned in the engine, may itself contain corrosive by products or can react with combustion by-products to form acidic compounds. For example, when combusted in diesel fuel it leaves a small amount of sulfur. These small amounts of sulfur and water in a diesel engine can react to form sulfuric acid, which can cause corrosive in the engine.

While the lost wear protection occurred, diesel injection pump failures were reported. There are several types of diesel fuel injection systems being used by engine manufactures that depend on fuel lubricity in varying degrees. Of all systems being used, the rotary distributor injection pump is the one most dependent on lubricity because the fuel provides 100% lubrication to the internal parts of injection pump. As the rotary distributor injection pump is highly susceptible to boundary lubrication wear (i.e., when heavy metal-to-metal contact occurs with the fuel providing little or no lubrication), this potential wear becomes more severe with increasing ambient temperature and increasing loading on the engine [24].

2.10 Lubricity of diesel fuels

Since the introduction of low sulfur diesel fuel in 1993, there has been a considerable amount of effort by the automotive industry, users, and the petroleum industry to incorporate a “lubricity requirement” in commercial diesel fuel; namely,

ASTM D975. Because lubricity is the primary factors in determining diesel engine wear which describes the ability of a fluid to minimize friction between, and damage to, surfaces in relative motion under loaded conditions.

The lubrication mechanism is a combination of hydrodynamic lubrication and boundary lubrication. In hydrodynamic lubrication, a layer of liquid prevents contact between the opposing surfaces. For diesel fuel pumps and injectors, the liquid is the fuel itself; and viscosity is the key fuel property. Fuels with higher viscosity will provide better hydrodynamic lubrication. When high load and/or low speed have squeezed out much of the liquid that provides hydrodynamic lubrication, boundary lubrication becomes important. Now, small areas of the opposing surfaces are in contact. Boundary lubricants are compounds that form a protective anti-wear layer by adhering to the solid surfaces.

Many diesel fuels are good boundary lubricants. This is not due to the hydrocarbons that constitute the bulk of the fuel. Instead it is attributed to trace amounts of oxygen and nitrogen containing compounds and certain classes of aromatic compounds. However, when hydrotreating process is used on petroleum refineries, it removes not only sulfur but also it removes nitrogen, oxygen, and polyaromatic compound. The removal of these components might be responsible for lubricity of fuels. The use of fuels with poor lubricity can increase fuel pump and injector wears. The majority of low sulfur automotive diesel fuels marketed today are treated with an additive to enhance the lubricity of the base fuel. It is necessary to prepare the surface of the metal accordingly. It is possible to create a lubricant that forms a surface film over the surfaces, strongly adhering to the surface. These films are thick but they provide enough of a protection to prevent metal-to-metal contact. This type of boundary protection is known as boundary lubrication (figure 2.2).

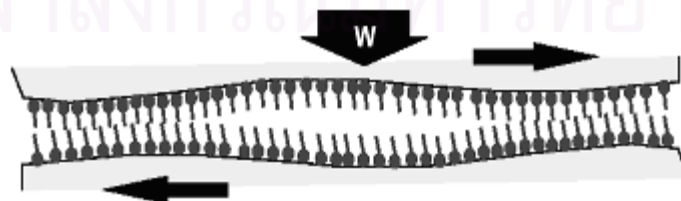


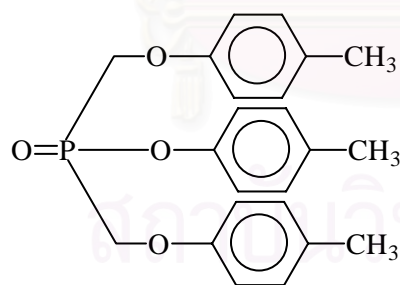
Figure 2.2 Boundary Lubrication

2.11 Lubricity additives

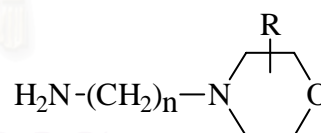
The need for diesel fuel lubricity has been recognized for many years. As previously described, lubricity additives are generally long slender molecules. They normally have a straight hydrocarbon chain consisting of at least ten carbon atoms. Hydrocarbons derived from natural products are ideal for such applications. The polar head group is the dominant factor in the effectiveness of the molecule as a lubricity additive. Such polar groups consist of (Scheme 2.7) [12]:

1. Carboxylic acids or derivatives (including their salts)
2. Phosphoric or phosphonic acids and, their derivatives
3. Amines, amides, imides, and their derivatives

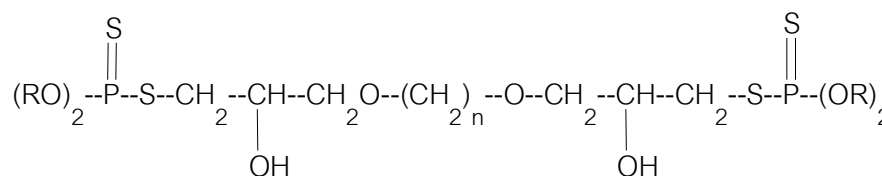
The past, traditional fuel lubricity additives contained sulfur, phosphorous, zinc, nitrogen or boron such as tri cresyl phosphate or TCP. These are called ash forming or catalyst-poisoning additives. Many additives also contribute to particulate emissions during combustion. Moreover, additives can form SO_x , NO_x , and PO_x emissions, which cause an increase in particulate and hydrocarbon emissions. Therefore there is a need in the art for diesel fuel additives that impart needed lubricity properties but provide minimal ash or preferably ash-less properties for the purposes of reducing ultimate emissions characteristics.



Tri cresyl phosphate or TCP



Aminoalkylmorpholine [25]



Dithiophosphoric diester-dialcohol

Scheme 2.7 Lubricity additives

Field experience has shown that in order to achieve the full benefits of the low sulfur diesel fuel, the lubricity additive must not only provide sufficient lubricity performance to protect sensitive diesel fuel pumps but must have no undesirable side effects. These potential side effects include:

1. Degrading the properties of the base fuel,
2. Interacting with crankcase lubricating oils,
3. Reducing the effects of other fuel additives present.

The oil and additive industries have developed a wide range of tests to evaluate the no-harm performance of lubricity additive packages and components.

Generally, the best additives are active organic compounds with long chain molecules and active end groups such as fatty acid, fatty acid ester, and fatty acid amide. These compounds bind tightly and intricately with each other, forming a film that builds up on the metal. Moreover they are no sulfur and prepare from vegetable oil.

2.12 Measurements of lubricity performances [2]

There are two methods that are commonly used to measure lubricity. One is the HFRR (High Frequency Reciprocating Rig) and the other is the BOCLE (Ball-on-Cylinder Lubricity Evaluator). The HFRR has been accepted by ISO and SAE. It was developed in Europe for testing diesel fuel lubrication. The drawback to this test is that there are currently only a few of these testing machines in the country. The BOCLE has been used for some time and there are several of these machines in labs throughout the country. Some as the test of choice is forwarding at the HFRR test, but others would also like to include the Scuffing BOCLE because it appears to have good correlation to the HFRR and BOCLE equipment is widely available.

Using the HFRR test procedure, according to CEC F-06-A-96 carried out all measurements. The temperature was 60 °C and the volume of fuel sample used was 2 ml. The relative humidity was kept between 50 and 55%, while the mean ambient temperature in the laboratory was approximately constant at 23 °C. The HFRR test also uses a steel ball that is placed on a flat surface. The ball is then rapidly vibrated back and forth with a stroke distance of one millimeter while 200 grams of weight is applied. After a given time the flat spot that has been worn into the ball is measured,

the size of the spot gives the lubrication qualities of the fuel being tested. The lubricating efficiency of the fuels was estimated by measuring the average wear scar diameter (WSD) of the spherical segment by using a photomicroscope. The wear scars quoted are corrected to give 1.4 WS values. The HFRR WS 1.4 parameter is the mean wear scar diameter normalized to a standard vapor pressure of 1.4 KPa.

In Europe lubricity is measured by HFRR method where an acceptable result is below 460 μm wear scar.



Figure 2.3 High Frequency Reciprocating Rig

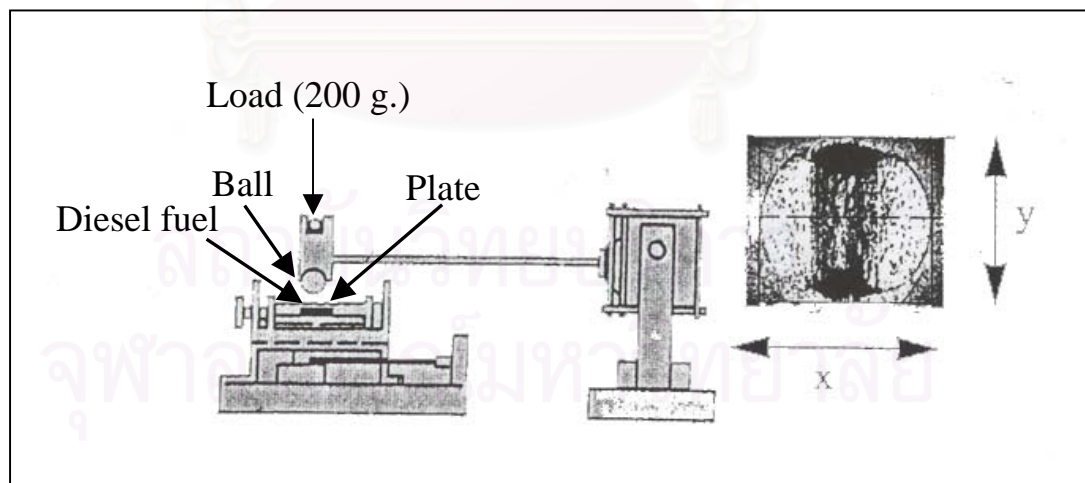


Figure 2.4 High Frequency Reciprocating Rig Test

2.13 Additives for diesel fuels

Additives are sometimes used to improve certain characteristics of diesel fuel. Additives for diesel fuel have many types, which were shown in Table 2.4 [2]. The using of additives, which are mixed in diesel fuel, depends on the produced diesel and its quality demanding to appropriate with the applications. For example, from the production, it can produce low sulfur diesel fuel that has high wear or low lubricating performance but the engine wants below 460 μm wear scar. Then lubricity additive is added for reducing wear in diesel engine.

Table 2.3 Additives for diesel fuels

Additives	Function
1. Cetane Improvers	-Increased cetane number -Enhanced ignitability
2. Oxidation Inhibitors	-Reduced sediment and gum occurring from reacting with oxygen during storage
3. Corrosion and Rust Inhibitors	-Reduced corrosion and rust in fuel lines throughout tanks for storage
4. Pour point Depressants	-Reduced pour point of fuel -Enhanced low temperature flow ability
5. Detergent-Dispersants	-Keep clean the fuel lines -Prevent combustion chamber deposits
6. Demulsifiers	-Emulsion prevention
7. Lubricating agent	-Lubricate pump system and fuel nozzle
8. Anti-foam	-Increased bubble breakability

This research established lubricity additives because of lubricating performances are the most important properties in diesel fuels.

2.14 Literature Reviews

Anastopoulos, G. [26], had reported that improved lubricating performances were achieved with ultra-low-sulfur diesel fuels by addition of a small amount of seven esters such as butyl caprate, hexyl laurate, octyl myristate, propyl palmitate, octyl palmitate, ethyl stearate, and hexyl oleate. Tribological experiments carried out on the high frequency reciprocating rig (HFRR) showed that the effective concentration of the additives was 500 ppm or higher. The behavior of the fatty acid esters as lubricity additives appeared to be a function of their kinematic viscosities. Fuel fractions having kinematic viscosities higher than 1.5 cSt at 40 °C gave the best response for all additives tested at concentration levels of 500 ppm or higher. For fuels having kinematic viscosities lower than 1.5 cSt at 40 °C, the required treat rate was 750 ppm for the more viscous additives octyl myristate, propyl palmitate, octyl palmitate, ethyl stearate, and hexyl oleate.

Drown, D. C. [6], discovered that the lubricating performance of diesel fuel could be substantially increased by the addition of a small amount of a methyl and ethyl monoalkyl esters of various vegetable oils such as methyl soy, methyl castor, ethyl soy, and ethyl castor. Tribological experiments carried out on the high frequency reciprocating rig, revealed that ethyl esters showed noticeable improvement compared to methyl esters in the wear properties of each ester tested. Esters of castor oil had improved lubricity over other oils with similar carbon chain-length (C_{18}) of fatty acids.

Anastopoulos, G. [13], examined the addition of specific types of fatty acid derivatives such as fatty acid methyl esters, or biodiesels, and tertiary amides on the lubrication properties of low sulfur diesel fuels. Fatty acid methyl esters were prepared from sunflower oil, corn oil, used fried oil, and olive oil, and two tertiary amides were lauric diethylamide, palmitic dibutylamide. The diesel fuels containing fatty acid derivatives were tested for lubricating performance on the HFRR procedure. They concluded that the biodiesels and tertiary amides could improve the low sulfur diesel lubricity.

Anastopoulos, G. [27], presented the impact of alkyl ethers and alcohol on the lubricity of automotive diesel. Seven ethers and five alcohols were used as lubricity additives on low sulfur diesel fuels. Using the HFRR method tested these lubricity additives, ethers and alcohols used provide satisfactory mean wear scar diameter of less than 460 μm , at the concentration levels of 750 ppm or higher. Among the ethers of the same molecular type, those having the oxygen in the middle of the molecule appeared to have better lubrication performance for some concentration ranges. Alcohols appear to be better lubricants than ethers at high concentrations.

In a study by Dmytryshyn, S. [28], fatty acid methyl esters were prepared by transesterification of four vegetable oils or fats such as canola oil, green seed canola oil, waste fryer grease, and unprocessed waste fryer grease. Their densities, viscosities, cloud points, pour points, lubricity properties, and thermal properties were reported. The diesel fuels containing 1 %volume of fatty acid methyl esters were tested for lubricating performance. The canola methyl ester was the only biodiesel sample that improved the lubricity performance. Another samples such as green seed methyl ester, waste fryer grease methyl ester, and unprocessed waste fryer grease methyl ester caused pitting on the rollers.

As the above reports showed, the lubricity additives containing ester, amine, amide, and oxy-group were outstanding in improving lubrication performance, especially at very low concentration level and had many times as effective as the commercial additives. From what has been mentioned, the need for further research of fatty acid esters and fatty acid amides is urgent.

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CHAPTER III

EXPERIMENTAL

3.1 Apparatus

All apparatus used in this experiment are listed in Table 3.1.

Table 3.1 Apparatus used in the experiment

Apparatus	Model	Manufacturer
Fourier-Transform Infrared Spectrophotometer	Impact 410	Nicolet
Fourier-Transform NMR Spectrometer	AC-F200 (200 MHz)	Bruker Spectrospin
Gas chromatography-Mass Spectrometry	MD-800 equipped with a 800 series GC	Fisson Instrument
Apparatus for API Gravity (glass thermometer)	-	-
Automatic viscometer	CAV-3	Cannon
Pensky-Martens Closed Flash Tester	PMFP 93	ISL
Automatic Pour Point Tester	ISL(CPP97-6)	ISL
Automatic Distillation Apparatus	PT 100	ISL

3.2 Chemicals

Reagents were obtained from various suppliers as shown in Table 3.2.

Table 3.2 Source of chemicals

Number	Materials	Company
1	Base high-speed diesel fuel	Petroleum Authority of Thailand (PTT)
2	ethylamine	FLUKA
3	<i>n</i> -butylamine	FLUKA
4	<i>n</i> -hexylamine	FLUKA
5	Ethanol	Merck
6	1-butanol	Merck
7	1-hexanol	Merck
8	Anhydrous sodium sulfate	Merck
9	Sodium hydrogen carbonate	Merck
10	96 % Sulfuric acid	Merck
11	Chloroform-D1	Merck
12	Coconut oil (food grade)	-
13	Palm oil (food grade)	Morakot Industries Public Co., Ltd
14	Rice bran oil (food grade)	Thai Edible oil Co., Ltd.

3.3 Synthesis of fatty acid amides by amidation of vegetable oils [19]

3.3.1 Synthesis of coconut oil ethylamide

Coconut oil (25.0 g) and ethylamine (13.5 g) were put in a 100 ml round-bottomed two-necked flask equipped with a condenser, thermometer, and mechanical stirrer. The mixture was heated to 40°C and stirred for 12 hours. After the completion of reaction, agitation was stopped. The reaction product was dissolved in dichloromethane and transferred into a 250 ml separatory funnel. The organic layer was washed with water, 0.5 % acetic acid, and water, respectively. After removing and discarding the aqueous layer, the organic portion was dried over anhydrous sodium sulfate and then filtered. The coconut oil ethylamide, obtained from the

dichloromethane layer by precipitation at 10°C, gave white powder (18.78 g, 75 % yield).

3.3.2 Synthesis of coconut oil butylamide

The synthesis of coconut oil butylamide was similar to that in Section 3.3.1, except coconut oil (25.0 g) and *n*-butylamine (21.9 g) were used. The mixture was heated to 78°C and stirred for 8 hours. The final product was white powder (18.83 g, 75 % yield).

3.3.3 Synthesis of coconut oil hexylamide

The synthesis of coconut oil hexylamide was similar to that in Section 3.3.1, except coconut oil (25.0 g) and *n*-hexylamine (30.4 g) were used. The mixture was heated to 131°C and stirred for 5 hours. The final product was white powder (19.55 g, 78 % yield).

3.3.4 Synthesis of palm oil ethylamide

The synthesis of palm oil ethylamide was similar to that in Section 3.3.1, except palm oil (25.0 g) and ethylamine (13.5 g) were used. The mixture was heated to 40°C and stirred for 12 hours. The final product was white powder (20.57 g, 82 % yield).

3.3.5 Synthesis of palm oil butylamide

The synthesis of palm oil butylamide was similar to that in Section 3.3.1, except palm oil (25.0 g) and *n*-butylamine (21.9 g) were used. The mixture was heated to 78°C and stirred for 8 hours. The final product was white powder (21.32 g, 85 % yield).

3.3.6 Synthesis of palm oil hexylamide

The synthesis of palm oil hexylamide was similar to that in Section 3.3.1, except palm oil (25.0 g) and *n*-hexylamine (30.4 g) were used. The mixture was heated to 131°C and stirred for 5 hours. The final product was white powder (21.53 g, 86 % yield).

3.3.7 Synthesis of rice bran oil ethylamide

The synthesis of rice bran oil ethylamide was similar to that in Section 3.3.1, except rice bran oil (25.0 g) and ethylamine (13.5 g) were used. The mixture was heated to 40°C and stirred for 12 hours. The final product was white powder (18.82 g, 75 % yield).

3.3.8 Synthesis of rice bran oil butylamide

The synthesis of rice bran oil butylamide was similar to that in Section 3.3.1, except rice bran oil (25.0 g) and *n*-butylamine (21.9 g) were used. The mixture was heated to 78°C and stirred for 8 hours. The final product was white powder (19.55 g, 78 % yield).

3.3.9 Synthesis of rice bran oil hexylamide

The synthesis of rice bran oil hexylamide was similar to that in Section 3.3.1, except rice bran oil (25.0 g) and *n*-hexylamine (30.4 g) were used. The mixture was heated to 131°C and stirred for 5 hours. The final product was white powder (20.53 g, 82 % yield).

3.4 Synthesis of fatty acid esters by transesterification of vegetable oils [16]

3.4.1 Synthesis of coconut oil ethyl ester

Coconut oil (25.0 g) was mixed with 100 ml ethanol and 2.5 ml of 96 % sulfuric acid in a 250 ml round-bottomed two-necked flask equipped with a condenser, thermometer, and mechanical stirrer. The mixture was heated to 78°C and stirred for 15 hours. After the completion of reaction, agitation was stopped. The mixture was dissolved with dichloromethane and transferred into a 250 ml separatory funnel. The organic layer was washed with water, sodium hydrogen carbonate, and water, respectively. After removing and discarding the aqueous layer, the organic portion was dried over anhydrous sodium sulfate and then filtered. Finally, solvent (dichloromethane) was removed by distillation at atmospheric pressure to give coconut oil ethyl ester (22.58 g, 90 % yield) as clear yellowish liquid.

3.4.2 Synthesis of coconut oil butyl ester

The synthesis of coconut oil butyl ester was similar to that in Section 3.4.1, except coconut oil (25.0 g) and 1-butanol (100 ml) were used. The mixture was heated to 117°C and stirred for 7 hours. The final product was clear yellowish liquid (22.96 g, 92 % yield).

3.4.3 Synthesis of coconut oil hexyl ester

The synthesis of coconut oil hexyl ester was similar to that in Section 3.4.1, except coconut oil (25.0 g) and 1-hexanol (100 ml) were used. The mixture was heated to 156°C and stirred for 5 hours. The final product was clear yellowish liquid (24.28 g, 97 % yield).

3.4.4 Synthesis of palm oil ethyl ester

The synthesis of palm oil ethyl ester was similar to that in Section 3.4.1, except palm oil (25.0 g) and ethanol (100 ml) were used. The mixture was heated to 78°C and stirred for 15 hours. The final product was clear yellowish liquid (22.80 g, 91 % yield).

3.4.5 Synthesis of palm oil butyl ester

The synthesis of palm oil butyl ester was similar to that in Section 3.4.1, except palm oil (25.0 g) and 1-butanol (100 ml) were used. The mixture was heated to 117°C and stirred for 7 hours. The final product was clear yellowish liquid (23.37 g, 93 % yield).

3.4.6 Synthesis of palm oil hexyl ester

The synthesis of palm oil hexyl ester was similar to that in Section 3.4.1, except palm oil (25.0 g) and 1-hexanol (100 ml) were used. The mixture was heated to 156°C and stirred for 5 hours. The final product was clear yellowish liquid (23.74 g, 95 % yield).

3.4.7 Synthesis of rice bran oil ethyl ester

The synthesis of rice bran oil ethyl ester was similar to that in Section 3.4.1, except rice bran oil (25.0 g) and ethanol (100 ml) were used. The mixture was heated to 78°C and stirred for 15 hours. The final product was clear yellowish liquid (23.93 g, 96 % yield).

3.4.8 Synthesis of rice bran oil butyl ester

The synthesis of rice bran oil butyl ester was similar to that in Section 3.4.1, except rice bran oil (25.0 g) and 1-butanol (100 ml) were used. The mixture was heated to 117°C and stirred for 7 hours. The final product was clear yellowish liquid (23.66 g, 95 % yield).

3.4.9 Synthesis of rice bran oil hexyl ester

The synthesis of rice bran oil hexyl ester was similar to that in Section 3.4.1, except rice bran oil (25.0 g) and 1-hexanol (100 ml) were used. The mixture was heated to 156°C and stirred for 5 hours. The final product was clear yellowish liquid (22.62 g, 90 % yield).

3.5 Characterization and determination of the synthesized lubricity additives (fatty acid amides and fatty acid esters)

3.5.1 Characterization of the synthesized lubricity additives

The synthesized lubricity additives were characterized by using instruments as follows:

1. Fourier-Transform Infrared Spectrophotometer
2. Fourier-Transform NMR Spectrometer
3. Mass Spectrometer (MS)

Results were summarized in Chapter IV. The spectra of fatty amides were shown in appendix A and the spectra of fatty acid esters were shown in appendix B.

3.5.2 Determination of properties and lubricity performances of base diesel fuel blended with synthesized lubricity additives

Blended base diesel fuels containing 0.2 % by weight of synthesized lubricity additives were determined for their properties and lubricity performances.

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1) Base diesel fuel blended with fatty acid amides

The blended base diesel fuels were prepared by blending synthesized fatty acid amides (0.2 g) and xylene (0.4 g) in base diesel fuel (100 g). The synthesized lubricity additives were as follows:

1. Coconut oil ethylamide
2. Coconut oil butylamide
3. Coconut oil hexylamide
4. Palm oil ethylamide
5. Palm oil butylamide
6. Palm oil hexylamide
7. Rice bran oil ethylamide
8. Rice bran oil butylamide
9. Rice bran oil hexylamide

2) Base diesel fuel blended with fatty acid esters

The blended base diesel fuels were prepared by blending synthesized fatty acid esters (0.2 g) in base diesel fuel (100 g). The synthesized lubricity additives were as follows:

1. Coconut oil ethyl ester
2. Coconut oil butyl ester
3. Coconut oil hexyl ester
4. Palm oil ethyl ester
5. Palm oil butyl ester
6. Palm oil hexyl ester
7. Rice bran oil ethyl ester
8. Rice bran oil butyl ester
9. Rice bran oil hexyl ester

3) The physical properties of the blended base diesel fuels were determined as shown in Table 3.3.

Table 3.3 Test methods of the blended base diesel fuels

Property	Method
API Gravity	ASTM D1298
Viscosity	ASTM D445
Flash point	ASTM D93
Pour Point	ASTM D97
Distillation	ASTM D86

4) The lubricity performances of the base diesel fuels blended with synthesized lubricity additives were determined by using High Frequency Reciprocating Rig (HFRR) test procedure, according to CEC F-06-A-96.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of fatty acid amides

Fatty acid amides could be prepared by amidation of vegetable oils with primary amines. The temperature of the reactions was maintained at boiling point of amines, *i.e.*, 40, 78, and 131°C for ethylamine, butylamine, and hexylamine, respectively. Synthetic results were shown in Table 4.1.

Table 4.1 Summary of synthetic results of fatty acid amides

Compound	Characteristics	% yield
Coconut oil ethylamide	White powder	75
Coconut oil butylamide	White powder	75
Coconut oil hexylamide	White powder	78
Palm oil ethylamide	White powder	82
Palm oil butylamide	White powder	85
Palm oil hexylamide	White powder	86
Rice bran oil ethylamide	White powder	75
Rice bran oil butylamide	White powder	78
Rice bran oil hexylamide	White powder	82

4.2 Characteristics of fatty acid amides

Fatty acid amides were characterized by IR, ¹H-, ¹³C-NMR, and MS spectroscopy. IR results were summarized in Table 4.2, ¹H-NMR in Table 4.3, ¹³C-NMR in Table 4.4, and MS in Table 4.5. The spectra were shown separately in Appendix A.

Table 4.2 The absorption assignments of the synthesized fatty acid amides

Compound	IR peak assignment				Figure
	N-H stretching, 2 nd amide	C=O stretching, ester	C=O stretching, amide	N-H bending, 2 nd amide	
Coconut oil	-	1740	-	-	A1
Coconut oil ethylamide	3303	-	1638	1552	A2
Coconut oil butylamide	3296	-	1641	1552	A9
Coconut oil hexylamide	3319	-	1638	1552	A14
Palm oil	-	1746	-	-	A19
Palm oil ethylamide	3297	-	1635	1551	A20
Palm oil butylamide	3299	-	1638	1548	A27
Palm oil hexylamide	3307	-	1638	1552	A31
Rice bran oil	-	1750	-	-	A35
Rice bran oil ethylamide	3297	-	1640	1551	A36
Rice bran oil butylamide	3296	-	1638	1556	A42
Rice bran oil hexylamide	3315	-	1634	1548	A46

For the parent coconut oil, palm oil, and rice bran oil, absorption band of ester C=O stretching at 1740, 1746, and 1750 cm^{-1} were clearly seen in Figure A1, A19, and A35. When these vegetable oils were reacted with primary amines, these peaks disappeared. IR spectra of all synthesized fatty acid amides indicated important absorption bands of one N-H spike for a secondary amide and amide C=O stretching. These bands were clearly observed at about 3300 and 1640 cm^{-1} respectively. The result was confirmed by using ^1H -, ^{13}C -NMR, and mass spectra.

Table 4.3 The assignments of $^1\text{H-NMR}$ spectra of fatty acid amides

Structure	Compound	Chemical shift, ppm (Multiplicity)		Figure
		a	b	
$\text{RCONHCH}_2\text{CH}_3$ b a	Coconut oil ethylamide	3.24 (m)	5.45 (s)	A4
	Palm oil ethylamide	3.23 (m)	5.65 (s)	A22
	Rice bran oil ethylamide	3.25 (m)	5.59 (s)	A38
$\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil butylamide	3.22 (m)	5.59 (s)	A10
	Palm oil butylamide	3.21 (m)	5.56 (s)	A28
	Rice bran oil butylamide	3.32 (m)	5.57 (s)	A43
$\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil hexylamide	3.19 (m)	5.65 (s)	A15
	Palm oil hexylamide	3.20 (m)	5.65 (s)	A32
	Rice bran oil hexylamide	3.19 (m)	5.76 (s)	A47

Table 4.4 The assignments of ^{13}C -NMR spectra of fatty acid amides

Structure	Compound	Chemical shift, ppm (Carbon type)		Figure
		a	b	
$\text{RCONHCH}_2\text{CH}_3$ b a	Coconut oil ethylamide	36.84 (CH ₂)	173.18 (C)	A6
	Palm oil ethylamide	36.89 (CH ₂)	173.08 (C)	A24
	Rice bran oil ethylamide	36.83 (CH ₂)	173.12 (C)	A40
$\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil butylamide	39.19 (CH ₂)	173.20 (C)	A11
	Palm oil butylamide	39.18 (CH ₂)	173.13 (C)	A29
	Rice bran oil butylamide	39.16 (CH ₂)	173.14 (C)	A44
$\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil hexylamide	39.47 (CH ₂)	173.16 (C)	A16
	Palm oil hexylamide	39.48 (CH ₂)	173.16 (C)	A33
	Rice bran oil hexylamide	39.49 (CH ₂)	173.49 (C)	A48

Table 4.5 The fragmentation ion in the mass spectra of fatty acid amides

Compound	Fragmentation ion peak			Products	Figure
	t _R	m/z	Structure		
Coconut oil ethylamide	17.48	227	CH ₃ (CH ₂) ₁₀ CONHC ₂ H ₅	Lauric acid ethylamide	A7
	19.04	255	CH ₃ (CH ₂) ₁₂ CONHC ₂ H ₅	Myristic acid ethylamide	A8
Coconut oil butylamide	18.46	255	CH ₃ (CH ₂) ₁₀ CONH(CH ₂) ₃ CH ₃	Lauric acid butylamide	A12
	20.19	283	CH ₃ (CH ₂) ₁₂ CONH(CH ₂) ₃ CH ₃	Myristic acid butylamide	A13
Coconut oil hexylamide	21.81	283	CH ₃ (CH ₂) ₁₀ CONH(CH ₂) ₅ CH ₃	Lauric acid hexylamide	A17
	22.36	311	CH ₃ (CH ₂) ₁₂ CONH(CH ₂) ₅ CH ₃	Myristic acid hexylamide	A18
Palm oil ethylamide	1.82	283	CH ₃ (CH ₂) ₁₄ CONHC ₂ H ₅	Palmitic acid ethylamide	A25
	2.61	309	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CONHC ₂ H ₅	Oleic acid ethylamide	A26
Palm oil butylamide	2.00	311	CH ₃ (CH ₂) ₁₄ CONH(CH ₂) ₃ CH ₃	Palmitic acid butylamide	A30
		337	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CONH(CH ₂) ₃ CH ₃	Oleic acid butylamide	
Palm oil hexylamide	2.20	339	CH ₃ (CH ₂) ₁₄ CONH(CH ₂) ₅ CH ₃	Palmitic acid hexylamide	A34
		365	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CONH(CH ₂) ₅ CH ₃	Oleic acid hexylamide	
Rice bran oil ethylamide	2.09	309	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CONHC ₂ H ₅	Oleic acid ethylamide	A41
		307	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ CONHC ₂ H ₅	Linoleic acid ethylamide	
Rice bran oil butylamide	2.13	337	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CONH(CH ₂) ₃ CH ₃	Oleic acid butylamide	A45
		335	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ CONH(CH ₂) ₃ CH ₃	Linoleic acid butylamide	
Rice bran oil hexylamide	1.85	365	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ CONH(CH ₂) ₅ CH ₃	Oleic acid hexylamide	A49
		363	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ CONH(CH ₂) ₅ CH ₃	Linoleic acid hexylamide	

4.3 Synthesis of fatty acid esters

Fatty acid esters could be prepared by transesterification of vegetable oils with alcohols in the presence of 96 % sulfuric acid. The temperature of the reactions was maintained at boiling point of alcohols, *i.e.*, 78, 117, and 156°C for ethanol, 1-butanol, and 1-hexanol, respectively. Synthetic results were shown in Table 4.6.

Table 4.6 Summary of synthetic results of fatty acid esters

Compound	Characteristics	% yield
Coconut oil ethyl ester	clear yellowish liquid	90
Coconut oil butyl ester	clear yellowish liquid	92
Coconut oil hexyl ester	clear yellowish liquid	97
Palm oil ethyl ester	clear yellowish liquid	91
Palm oil butyl ester	clear yellowish liquid	93
Palm oil hexyl ester	clear yellowish liquid	95
Rice bran oil ethyl ester	clear yellowish liquid	96
Rice bran oil butyl ester	clear yellowish liquid	95
Rice bran oil hexyl ester	clear yellowish liquid	90

4.4 Characteristics of fatty acid esters

Fatty acid esters were characterized by IR, ¹H-, ¹³C-NMR, and MS spectroscopy. IR results were summarized in Table 4.7, ¹H-NMR in Table 4.8, ¹³C-NMR in Table 4.9, and MS in Table 4.10. The spectra were shown separately in Appendix B.

Table 4.7 The absorption assignments of the synthesized fatty acid esters

Compound	IR peak assignment			Figure
	C-H stretching, aliphatic	C=O stretching, ester	C-O stretching	
Coconut oil ethyl ester	2854, 2924	1741	1171	B1
Coconut oil butyl ester	2854, 2932	1735	1172	B6
Coconut oil hexyl ester	2850, 2928	1735	1168	B11
Palm oil ethyl ester	2854, 2924	1743	1180	B16
Palm oil butyl ester	2854, 2924	1735	1176	B21
Palm oil hexyl ester	2854, 2924	1735	1174	B26
Rice bran oil ethyl ester	2853, 2920	1730	1184	B30
Rice bran oil butyl ester	2858, 2932	1738	1180	B34
Rice bran oil hexyl ester	2854, 2928	1735	1172	B38

From Table 4.7, IR spectra of fatty acid esters, it showed that there was no absorption band of alcohol O-H stretching group of ethanol, which was a starting material at 3300 cm^{-1} in the produced obtained. The result was confirmed by using ^1H -, ^{13}C -NMR, and mass spectra.

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Table 4.8 The assignments of $^1\text{H-NMR}$ spectra of fatty acid esters

Structure	Compound	Chemical shift, ppm (Multiplicity)		Figure
		a	b	
$\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ a b	Coconut oil ethyl ester	2.10 (t)	3.95 (q)	B2
	Palm oil ethyl ester	2.21 (t)	4.04 (q)	B17
	Rice bran oil ethyl ester	2.27 (t)	4.05 (q)	B31
$\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ a b	Coconut oil butyl ester	2.17 (t)	3.94 (t)	B7
	Palm oil butyl ester	2.21 (t)	3.99 (t)	B22
	Rice bran oil butyl ester	2.17 (t)	3.96 (t)	B35
$\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ a b	Coconut oil hexyl ester	2.17 (t)	3.94 (t)	B12
	Palm oil hexyl ester	2.17 (t)	3.95 (t)	B27
	Rice bran oil hexyl ester	2.11 (t)	3.88 (t)	B39

Table 4.9 The assignments of ^{13}C -NMR spectra of fatty acid esters

Structure	Compound	Chemical shift, ppm (Carbon type)		Figure
		a	b	
$\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil ethyl ester	59.78 (CH ₂)	173.34 (C)	B3
	Palm oil ethyl ester	59.97 (CH ₂)	173.64 (C)	B18
	Rice bran oil ethyl ester	59.97 (CH ₂)	173.59 (C)	B32
$\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil butyl ester	63.81 (CH ₂)	173.53 (C)	B8
	Palm oil butyl ester	63.94 (CH ₂)	173.75 (C)	B23
	Rice bran oil butyl ester	63.99 (CH ₂)	173.82 (C)	B36
$\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ b a	Coconut oil hexyl ester	64.13 (CH ₂)	173.55 (C)	B13
	Palm oil hexyl ester	64.12 (CH ₂)	173.53 (C)	B28
	Rice bran oil hexyl ester	64.03 (CH ₂)	173.33 (C)	B40

Table 4.10 The fragmentation ion in the mass spectra of fatty acid esters

Compound	Fragmentation ion peak			Products	Figure
	t _R	m/z	Structure		
Coconut oil ethyl ester	12.59	228	CH ₃ (CH ₂) ₁₀ COOC ₂ H ₅	Lauric acid ethyl ester	B4
	14.20	256	CH ₃ (CH ₂) ₁₂ COOC ₂ H ₅	Myristic acid ethyl ester	B5
Coconut oil butyl ester	14.47	256	CH ₃ (CH ₂) ₁₀ COO(CH ₂) ₃ CH ₃	Lauric acid butyl ester	B9
	15.43	284	CH ₃ (CH ₂) ₁₂ COO(CH ₂) ₃ CH ₃	Myristic acid butyl ester	B10
Coconut oil hexyl ester	18.20	284	CH ₃ (CH ₂) ₁₀ COO(CH ₂) ₅ CH ₃	Lauric acid hexyl ester	B14
	19.75	312	CH ₃ (CH ₂) ₁₂ COO(CH ₂) ₅ CH ₃	Myristic acid hexyl ester	B15
Palm oil ethyl ester	14.51	284	CH ₃ (CH ₂) ₁₄ COOC ₂ H ₅	Palmitic acid ethyl ester	B19
	16.22	310	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOC ₂ H ₅	Oleic acid ethyl ester	B20
Palm oil butyl ester	17.94	312	CH ₃ (CH ₂) ₁₄ COO(CH ₂) ₃ CH ₃	Palmitic acid butyl ester	B24
	19.75	338	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COO(CH ₂) ₃ CH ₃	Oleic acid butyl ester	B25
Palm oil hexyl ester	1.34	340	CH ₃ (CH ₂) ₁₄ COO(CH ₂) ₅ CH ₃	Palmitic acid hexyl ester	B29
		366	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COO(CH ₂) ₅ CH ₃	Oleic acid hexyl ester	
Rice bran oil ethyl ester	15.93	310	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOC ₂ H ₅	Oleic acid ethyl ester	B33
		308	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOC ₂ H ₅	Linoleic acid ethyl ester	
Rice bran oil butyl ester	17.37	338	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COO(CH ₂) ₃ CH ₃	Oleic acid butyl ester	B37
		336	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COO(CH ₂) ₃ CH ₃	Linoleic acid butyl ester	
Rice bran oil hexyl ester	19.03	366	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COO(CH ₂) ₅ CH ₃	Oleic acid hexyl ester	B41
		364	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COO(CH ₂) ₅ CH ₃	Linoleic acid hexyl ester	

4.5 Determination of lubricity performances of base diesel fuel blended with synthesized lubricity additives.

The lubricity performances of the base diesel fuels blended with synthesized lubricity additives were determined by using High Frequency Reciprocating Rig (HFRR) test procedure, according to CEC F-06-A-96. The lubricating efficiency of the fuels was estimated by measuring the mean wear scar diameter (WSD) value. If samples gave lower wear scar diameter value, it could be indicated that they had higher lubricity performances. Table 4.11 showed the lubricity performances of palm oil butylamide, which were blended in base diesel fuel. The lubricity test of palm oil butylamide at concentration of 0.05 % by weight did not appear to be suited to increase the lubricity of the fraction to an acceptable level. Although the wear scar diameter value decreased from 546 μm to 468 μm , it did not reach the desired limit value of 460 μm . Nevertheless the lubricity of the samples tested improved with increasing concentration of additives, where the declining wear of 468 μm to 419 μm from 0.05 to 0.2 % by weight of additive was clearly seen. A concentration of 0.2 % by weight of palm oil butylamide gave mean wear scar diameter of less than 460 μm , which was the minimum requirement for an acceptable field performance.

Table 4.11 Lubricity performances of the blend of palm oil butylamide with base diesel fuel.

Concentration (% by weight)	Blended composition	Lubricity performance (Mean wear scar diameter, μm)
0	Base	527
0.05	Base + palm oil butylamide	468
0.2	Base + palm oil butylamide	419

To investigate the impact of adding additives on the lubrication properties of diesel fuels, another synthesized lubricity additives such as palm oil ethylamide, palm oil hexylamide, and fatty acid esters were added into the base diesel fuel at the same concentration of 0.2 % by weight. Tables 4.12 and 4.13 showed the results of the

lubricity testing for 0.2 % by weight of secondary fatty acid amides and fatty acid esters, respectively.

Table 4.12 Lubricity performances of the blend of 0.2 % by weight of fatty acid amides with base diesel fuel.

Blended composition	Lubricity performance (Mean wear scar diameter, μm)
Base + coconut oil ethylamide	373
Base + coconut oil butylamide	424
Base + coconut oil hexylamide	448
Base + palm oil ethylamide	318
Base + palm oil butylamide	419
Base + palm oil hexylamide	431
Base + rice bran oil ethylamide	299
Base + rice bran oil butylamide	391
Base + rice bran oil hexylamide	397

From Table 4.12, it could be seen that nine fatty acid amides at concentration of 0.2 % by weight gave the wear scar diameter lower of less than 460 μm . Type of fatty acid compositions of vegetable oils had a significant effect on the lubricity improvement of base diesel fuel. It was found that the synthesized fatty acid amides prepared from rice bran oil gave the lubricity performances better than palm oil, which was better than coconut oil, respectively. Rice bran oil comprised of the longest carbon chain of fatty acids, which are 41.2 % of oleic acid (C18:1) and 39.7 % of linoleic acid (C18:2). Palm oil had shorter carbon chain of fatty acids than rice bran oil. It contained 45 % of palmitic acid (C16:0) and 38 % of oleic acid (C18:1). Coconut oil contained a shortest carbon chains, 47 % of lauric acid (C12:0) and 17.5 % of myristic acid (C14:0). The length of carbon chain of fatty acids had influenced the improving lubricity of base diesel fuel. The longer chain of fatty acids, the lower wear scar diameter values.

Moreover, the length of carbon chain of amines also had an effect on improving lubricity of diesel fuel. The longer chain of amines, the higher wear scar

diameter values. Therefore, hexylamide of all vegetable oils gave the highest wear scar diameter values compared to butylamide and ethylamide. Among various fatty amides studies, it could be concluded that rice bran oil ethylamide was the best lubricity additive for diesel fuel.

Table 4.13 Lubricity performances of the blend of 0.2 % by weight of fatty acid esters with base diesel fuel.

Blended composition	Lubricity performance (Mean wear scar diameter, μm)
Base + palm oil ethyl ester	376
Base + palm oil butyl ester	367
Base + palm oil hexyl ester	356
Base + rice bran oil ethyl ester	369
Base + rice bran oil butyl ester	348
Base + rice bran oil hexyl ester	344

From Table 4.13, it could be seen that six fatty acid esters at concentration of 0.2 % by weight gave the wear scar diameter lower less than 460 μm . Similar to the case of lubricity improvement by fatty acid amides, the type of fatty acid compositions of vegetable oils also had significant effect on the lubricity improvement of base diesel fuel. Fatty acid esters prepared from rice bran oil had lubricity performances better than palm oil esters. The longer chain of alcohol gave the lower wear scar diameter values. Moreover, hexyl ester of rice bran oil and palm oil gave the highest wear scar diameter values than butyl ester and ethyl ester. In a series of lubricity performances of fatty acid esters, it could be concluded that rice bran oil hexyl ester was the best lubricity additive for diesel fuel.

4.6 Determination of physical properties of fatty acid amides and fatty acid esters in base diesel fuel

There were many properties considered being most indicative of diesel fuel quality such as API gravity, specific gravity, viscosity, pour point, and flash point. There were presented in Table 4.14 and distillation of the diesel fuels blended with synthesized lubricity additives was presented in Table 4.15 respectively.

Table 4.14 Physical properties of the base diesel fuels blended with 0.2 % by weight of secondary fatty acid amides and fatty acid esters.

Blended composition	API gravity	Specific gravity	Viscosity (cSt)	Pour point (°C)	Flash point (°C)
Base	38.1	0.8343	3.546	-5	82
Base + coconut oil ethylamide	38.1	0.8343	3.536	-5	81
Base + coconut oil butylamide	38.1	0.8343	3.544	-5	80
Base + coconut oil hexylamide	38.1	0.8343	3.551	-5	81
Base + palm oil ethylamide	38.1	0.8343	3.553	-5	81
Base + palm oil butylamide	38.1	0.8343	3.562	-5	81
Base + palm oil hexylamide	38.1	0.8343	3.574	-5	81
Base + rice bran oil ethylamide	38.1	0.8343	3.560	-5	81
Base + rice bran oil butylamide	38.1	0.8343	3.565	-5	81
Base + rice bran oil hexylamide	38.1	0.8343	3.572	-5	81
Base + coconut oil ethyl ester	38.1	0.8343	3.566	-5	80
Base + coconut oil butyl ester	38.1	0.8343	3.568	-5	81
Base + coconut oil hexyl ester	38.1	0.8343	3.570	-5	80
Base + palm oil ethyl ester	38.1	0.8343	3.568	-5	80
Base + palm oil butyl ester	38.1	0.8343	3.569	-5	81
Base + palm oil hexyl ester	38.1	0.8343	3.575	-5	81
Base + rice bran oil ethyl ester	38.1	0.8343	3.561	-5	80
Base + rice bran oil butyl ester	38.1	0.8343	3.567	-5	82
Base + rice bran oil hexyl ester	38.1	0.8343	3.572	-5	83

Note that API gravity, specific gravity, and pour point of all compositions were 38.1, 0.8343, and -5°C respectively. Values of the viscosity indicated that all of samples had slightly higher viscosity than diesel fuel, except for coconut oil ethylamide, and coconut oil butylamide. The flash point of these synthesized lubricity additives blended with diesel fuel changed slightly, *i.e.*, $80\text{-}83^{\circ}\text{C}$ as compared with the value of base diesel fuel without lubricity additives (82°C).

Table 4.15 Distillation of the base diesel fuels blended with 0.2 % by weight of fatty acid amides and fatty acid esters.

Blended composition	Distillation ($^{\circ}\text{C}$)			
	Initial boiling	10 %	50 %	90 %
Base	193.5	228.0	288.2	354.9
Base + coconut oil ethylamide	191.0	227.5	288.9	355.1
Base + coconut oil butylamide	190.1	226.8	289.0	352.7
Base + coconut oil hexylamide	190.5	227.0	288.8	352.4
Base + palm oil ethylamide	191.3	228.2	288.7	353.2
Base + palm oil butylamide	193.3	230.2	289.4	353.9
Base + palm oil hexylamide	191.1	227.3	288.9	353.0
Base + rice bran oil ethylamide	191.2	227.8	289.9	355.7
Base + rice bran oil butylamide	192.9	228.3	289.6	354.2
Base + rice bran oil hexylamide	190.9	227.4	289.4	355.3
Base + coconut oil ethyl ester	194.2	229.5	287.4	351.2
Base + coconut oil butyl ester	196.1	229.0	288.0	350.2
Base + coconut oil hexyl ester	191.2	229.1	287.1	350.3
Base + palm oil ethyl ester	193.8	230.3	288.9	352.3
Base + palm oil butyl ester	193.5	229.7	288.8	352.5
Base + palm oil hexyl ester	191.7	229.3	288.7	353.6
Base + rice bran oil ethyl ester	191.6	228.2	288.0	352.7
Base + rice bran oil butyl ester	196.8	230.0	288.8	351.6
Base + rice bran oil hexyl ester	195.7	228.7	288.8	350.9

From Table 4.15, it could be seen that the fatty acid amides and fatty acid esters did not make any change to the distillation of the base diesel fuel, and all of blended base diesel fuels gave the similar value as base diesel fuel.

From these results, it was concluded that these synthesized lubricity additives blended with diesel fuel increased the lubricity performance, but they did not change any physical properties as compared with the value of base diesel fuel without lubricity additives. They could be used according to the specification of diesel fuel.



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CHAPTER V

CONCLUSION

5.1 CONCLUSION

Nine fatty acid amides could be prepared by amidation of various vegetable oils, *i.e.*, coconut oil, palm oil, and rice bran oil, with primary amines such as ethylamine, butylamine, and hexylamine. This method of preparation gave about 75-86 % yield of products. The obtained fatty acid amides were coconut oil ethylamide, coconut oil butylamide, and coconut oil hexylamide, *etc.* These compounds were dissolved in xylene and then were blended with base diesel fuel at the concentration of 0.2 % by weight.

Nine fatty acid esters could be prepared by transesterification of vegetable oils with various alcohols such as ethanol, 1-butanol, and 1-hexanol in the presence of sulfuric acid. This method of preparation gave about 90-97 % yield of products. The obtained compounds were coconut oil ethyl ester, coconut oil butyl ester, and coconut oil hexyl ester, *etc.* They were easily soluble in base diesel fuel, and were blended with base diesel fuel also at the concentration of 0.2 % by weight.

The lubricity properties of synthesized lubricity additives were investigated using High Frequency Reciprocating Rig machine. From the results of tests, it could be concluded that all samples could provide satisfactory mean wear scar diameter of less than 460 μm . In the other words, they had good lubricity properties which were at acceptable field performance. Among various fatty acid amides studies, rice bran oil ethylamide was the best lubricity additive for diesel fuel. For a series of fatty acid esters, rice bran oil hexyl ester was the best one. Moreover, all samples did not alter physical properties of the base diesel fuel.

5.2 Further study

1. Because of high cost for determining lubricity performances by using HFRR machine, this research could run lubricity test of all samples at concentration of only 0.2 % by weight. An optimum level of additive, resulting in an acceptable wear scar diameter value less than 460 μm , has therefore not yet been sought. Consequently, future study should vary the concentration of samples in the range of, for example 0-0.2 % by weight, in order to specify the lowest dosage of synthesized lubricity additives that will give the lowest wear scar diameter value.

2. The utilization of synthesized fatty acid amides and fatty acid esters in the future needs more studies in engine performance tests to support such as the effect on polycyclic aromatic hydrocarbons emission of diesel engine, and ignition quality of diesel fuel.



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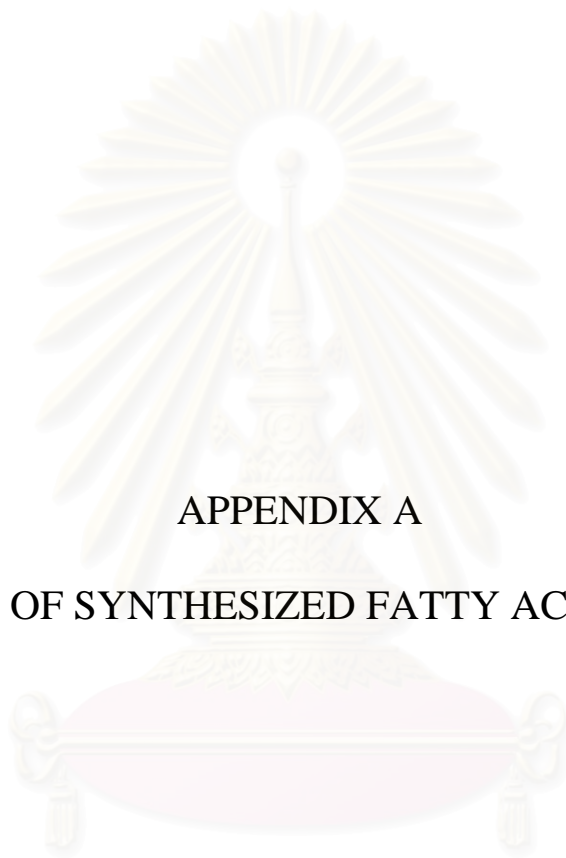


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APPENDICES

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APPENDIX A

SPECTRA OF SYNTHESIZED FATTY ACID AMIDES

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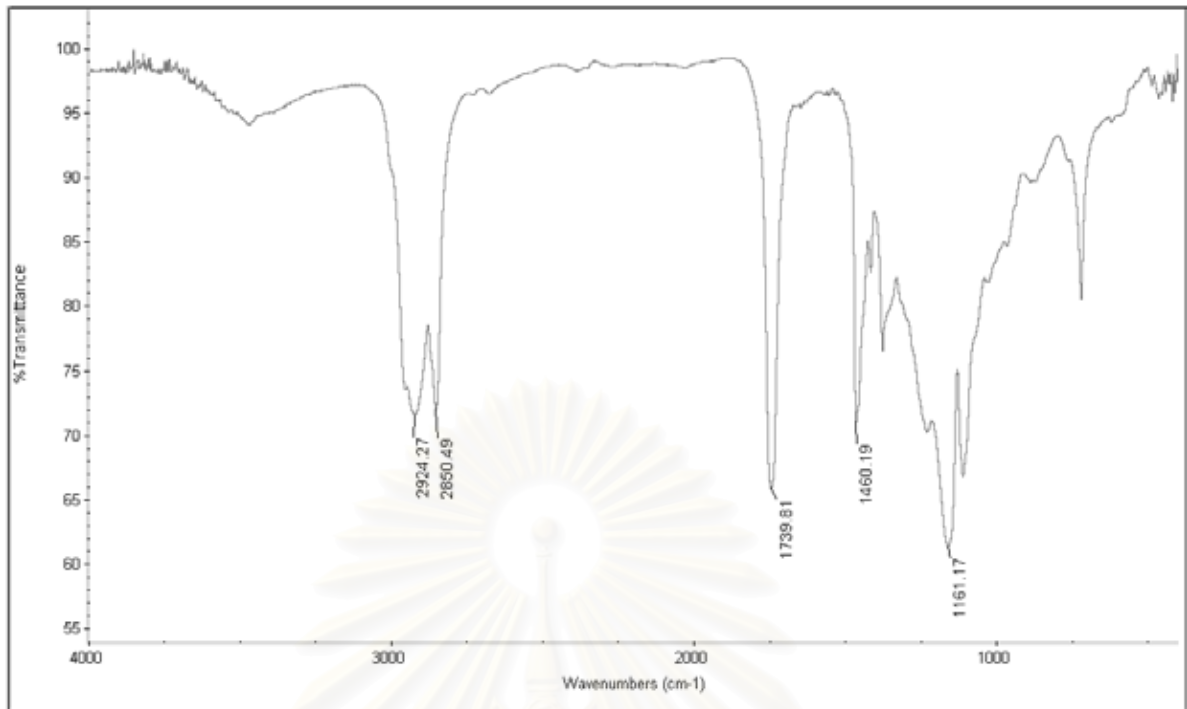


Figure A1 FTIR spectrum of coconut oil (NaCl)

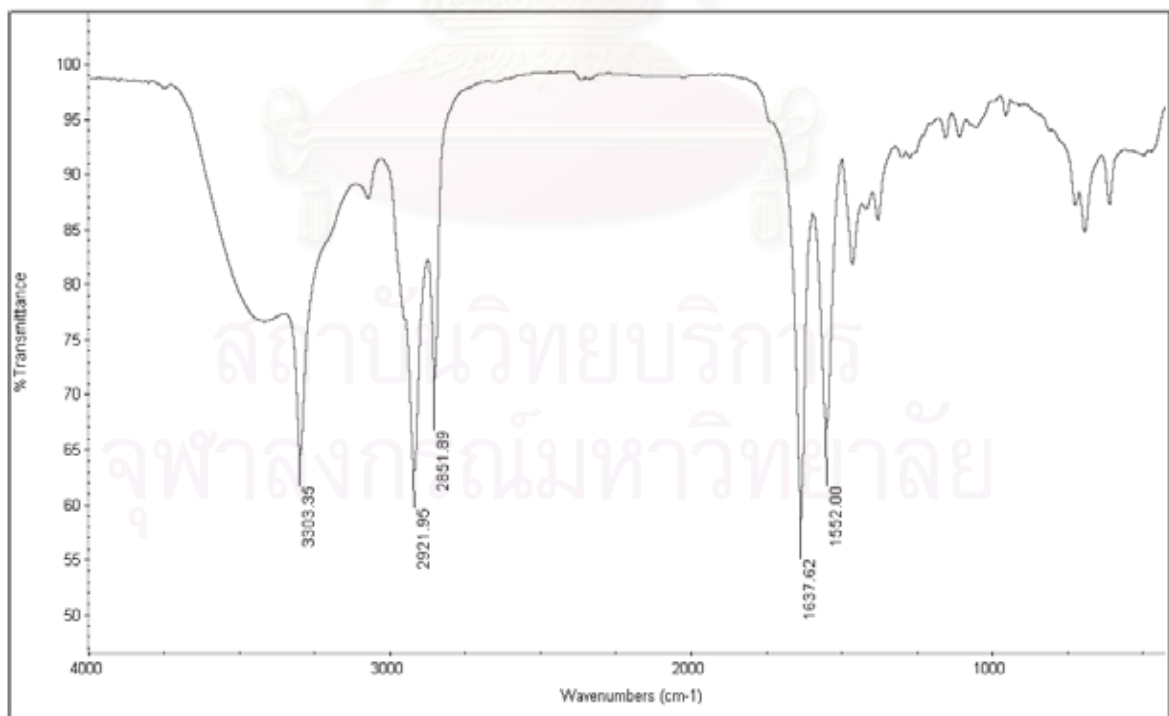


Figure A2 FTIR spectrum of coconut oil ethylamide (NaCl)

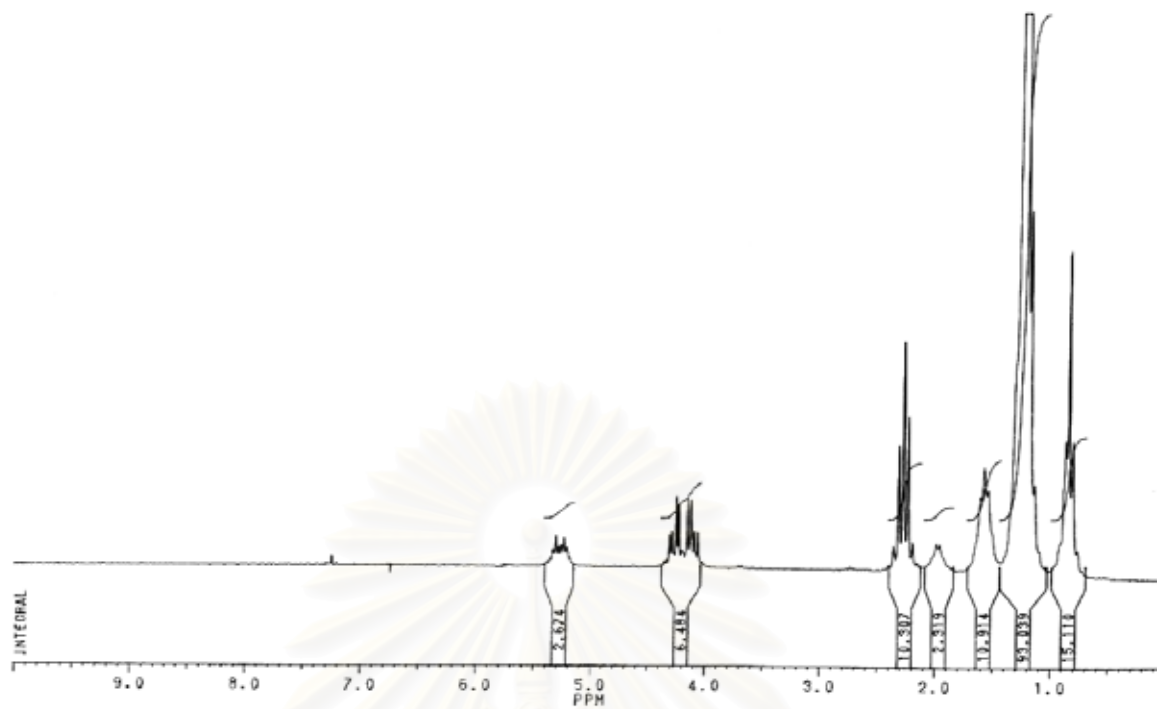


Figure A3 ¹H-NMR spectrum of coconut oil (CDCl₃)

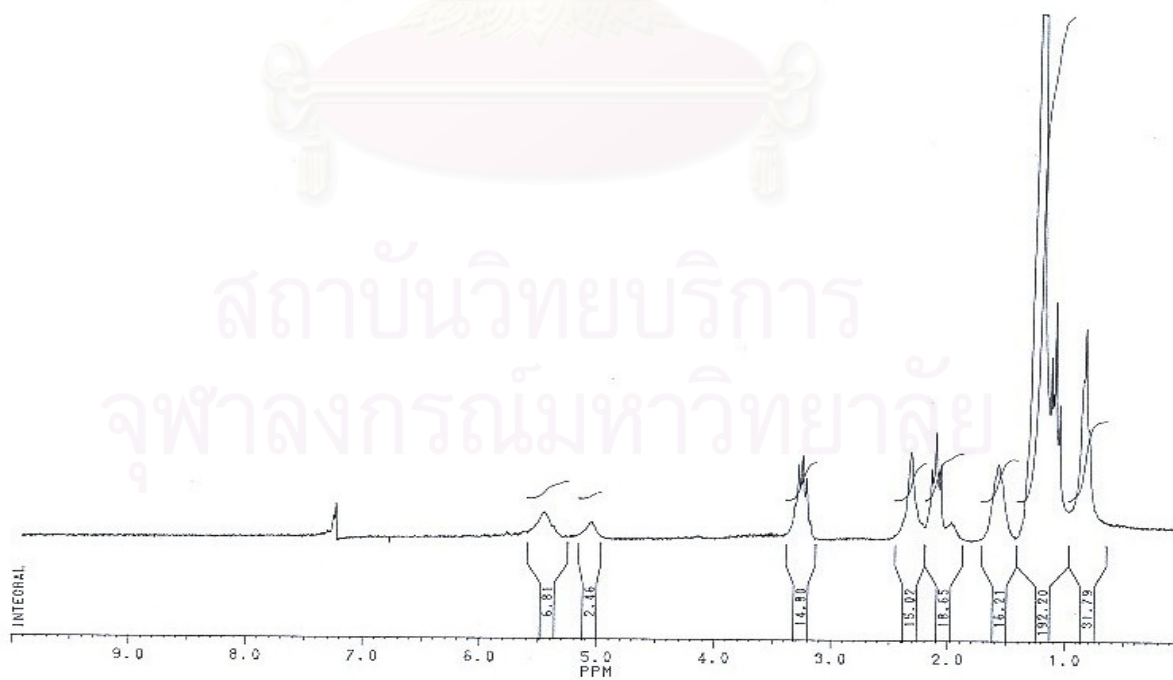


Figure A4 ¹H-NMR spectrum of coconut oil ethylamide (CDCl₃)

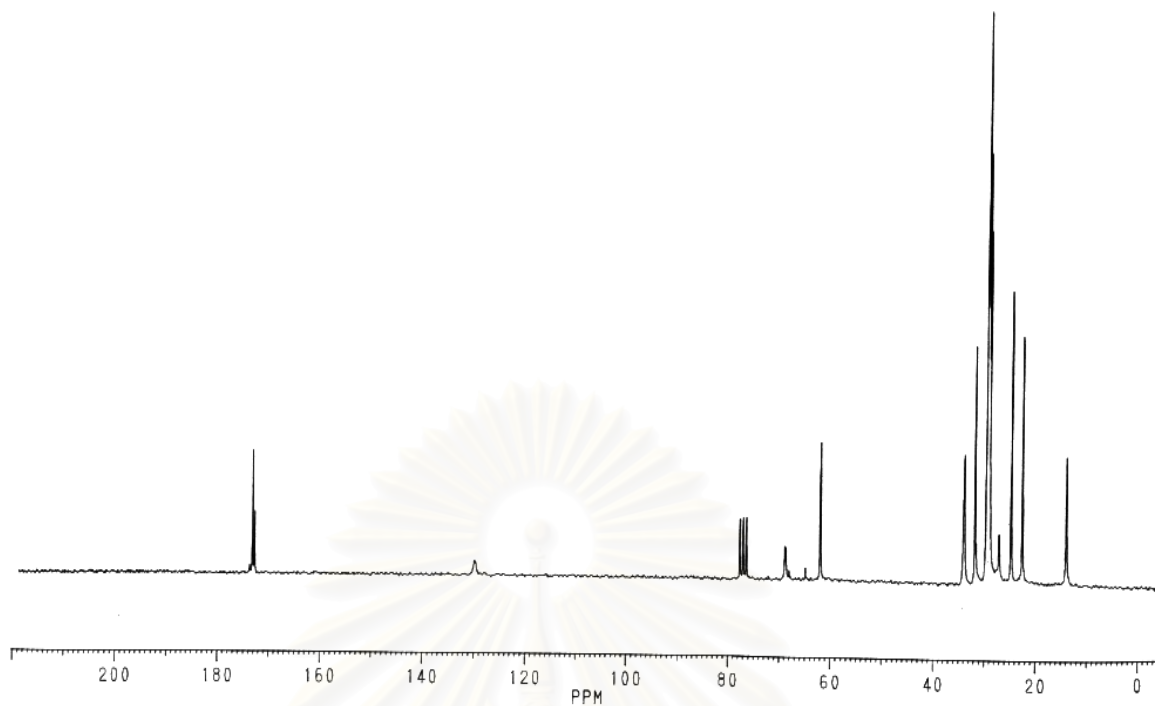


Figure A5 ^{13}C -NMR spectrum of coconut oil (CDCl_3)

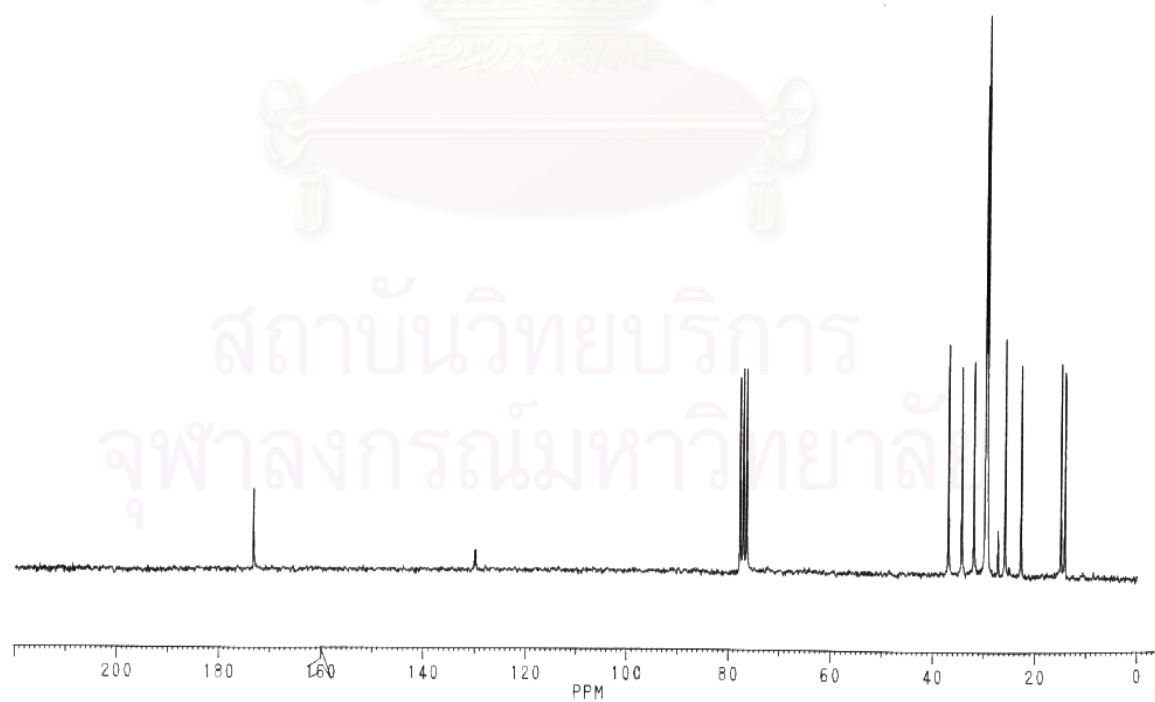


Figure A6 ^{13}C -NMR spectrum of coconut oil ethylamide (CDCl_3)

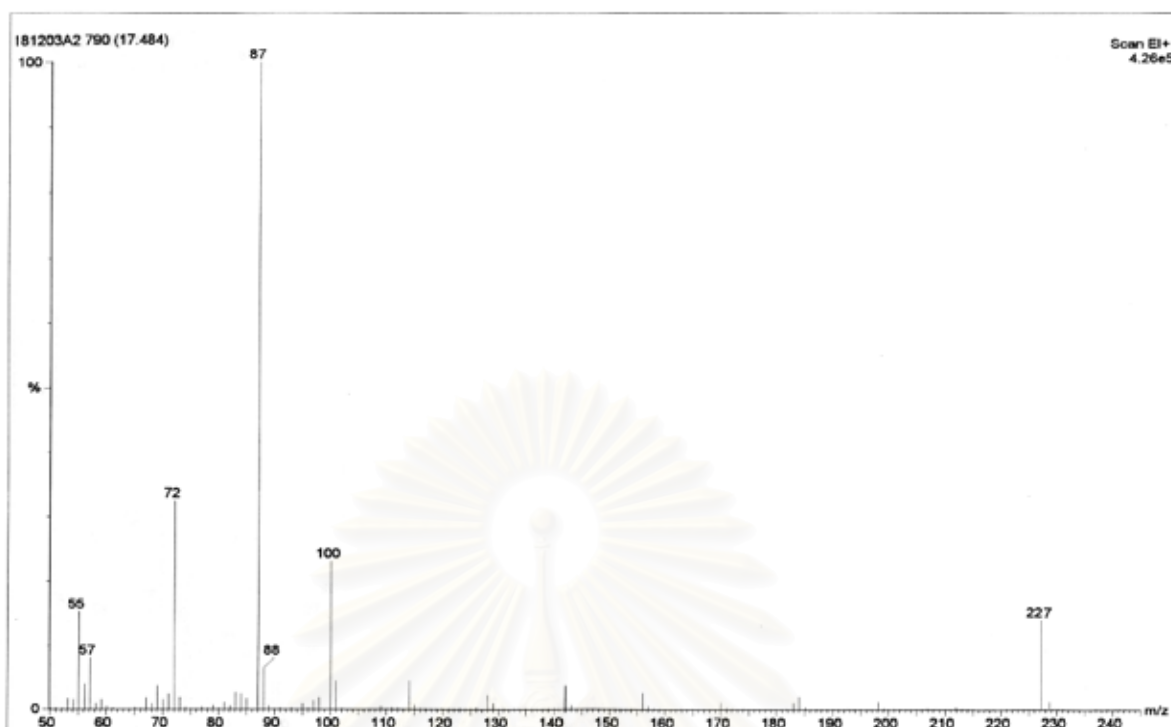


Figure A7 Mass spectrum of coconut oil ethylamide at retention time of 17.48 min.

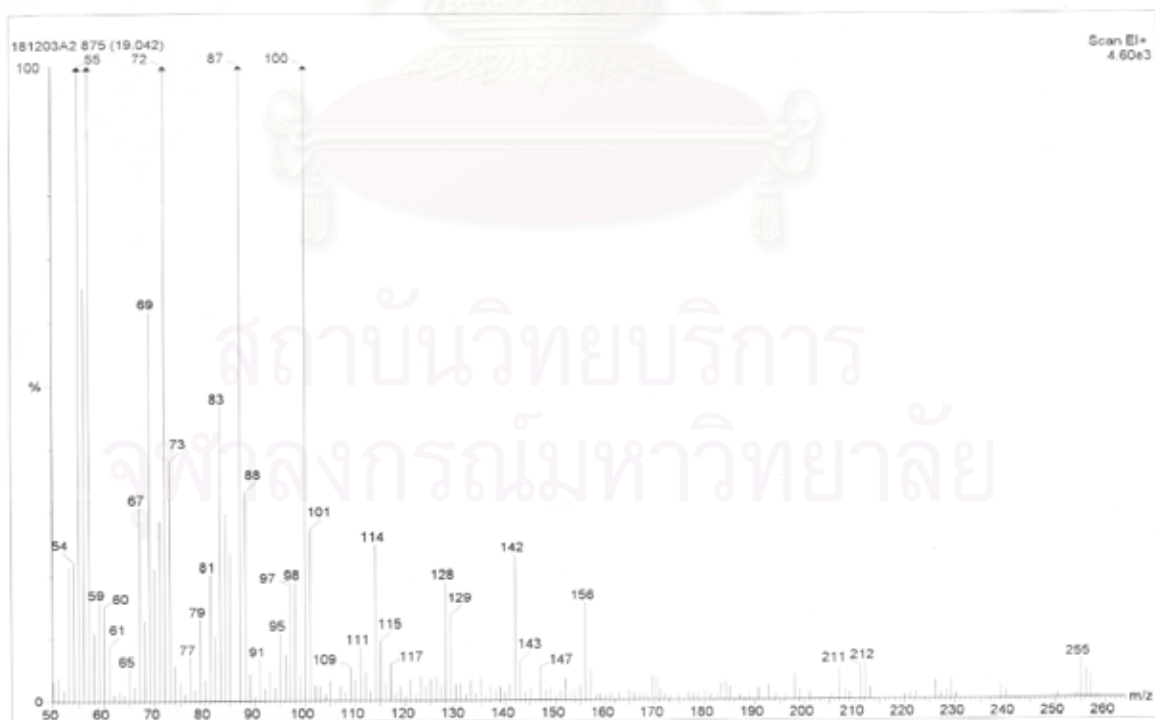


Figure A8 Mass spectrum of coconut oil ethylamide at retention time of 19.04 min.

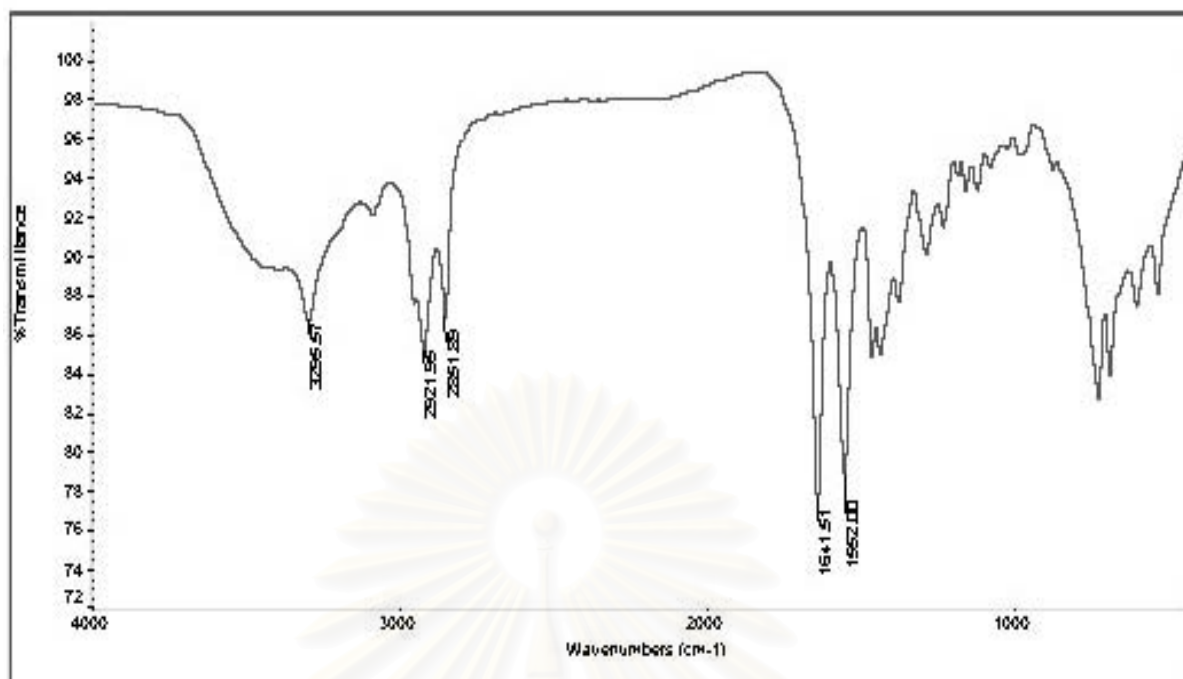


Figure A9 FTIR spectrum of coconut oil butylamide (NaCl)

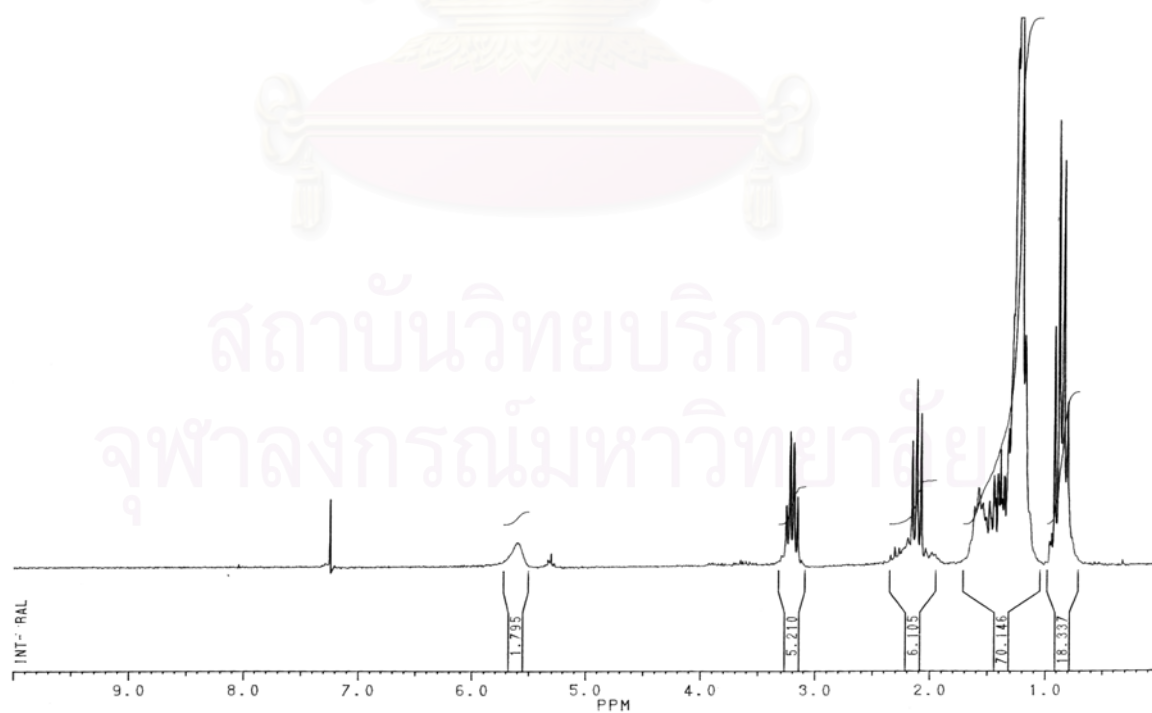


Figure A10 ¹H-NMR spectrum of coconut oil butylamide (CDCl₃)

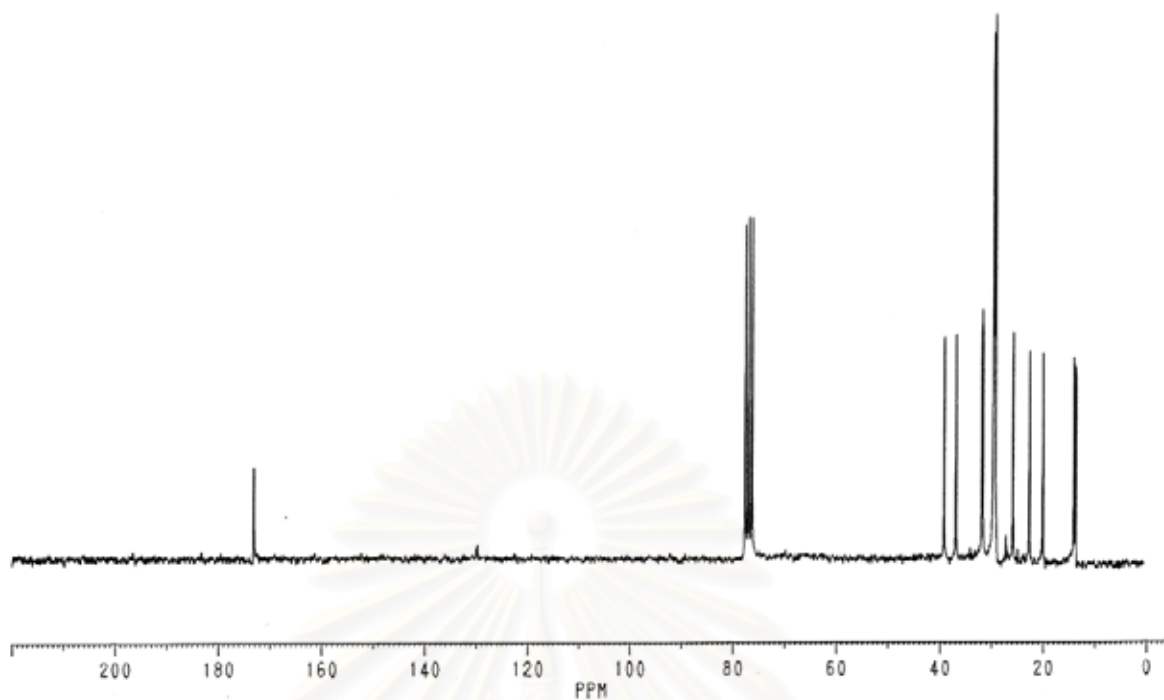


Figure A11 ^{13}C -NMR spectrum of coconut oil butylamide (CDCl_3)

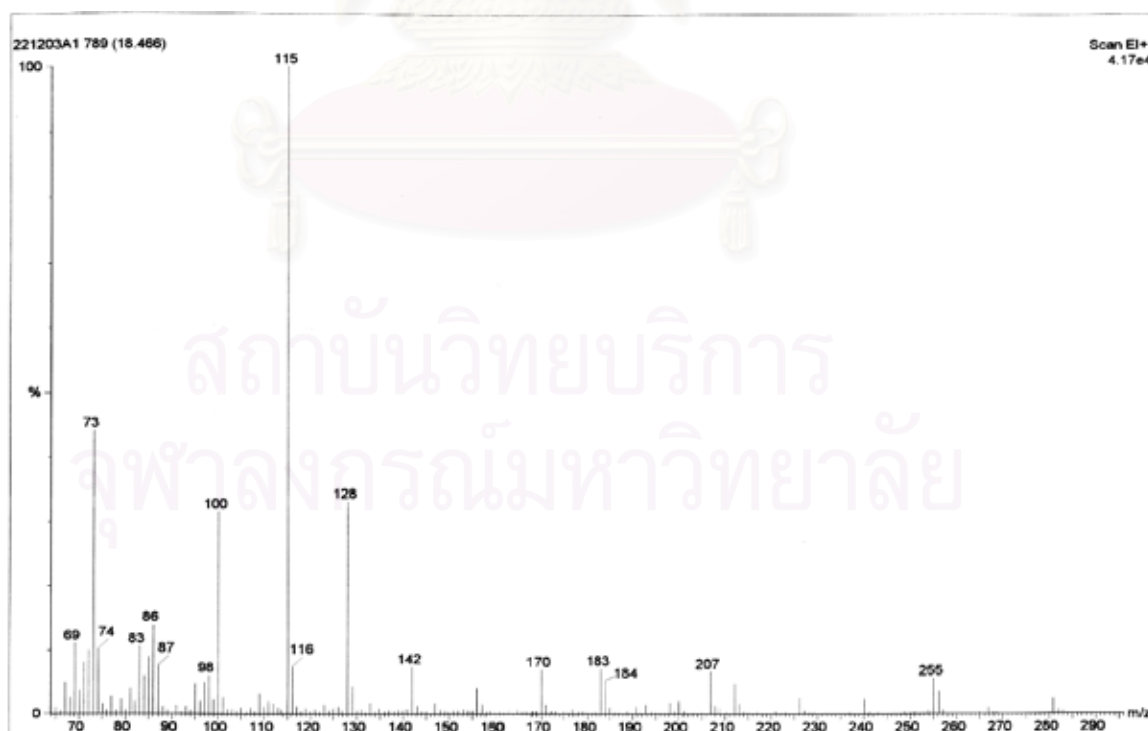


Figure A12 Mass spectrum of coconut oil butylamide at retention time of 18.46 min.

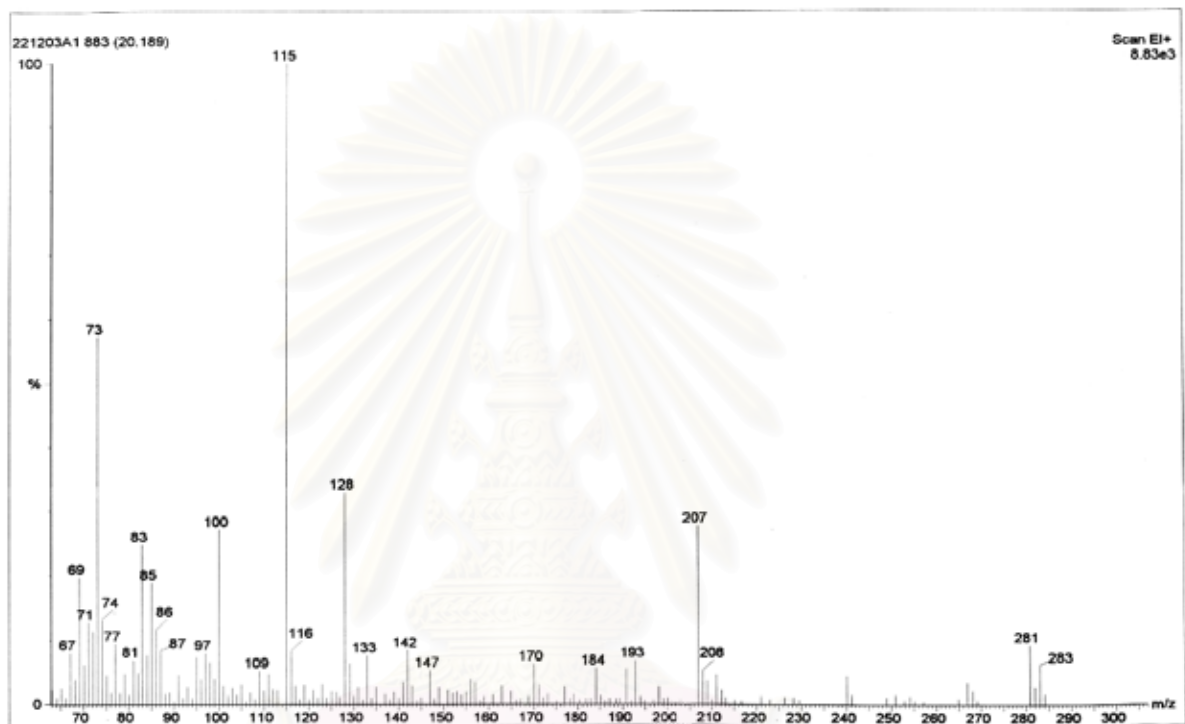


Figure A13 Mass spectrum of coconut oil butylamide at retention time of 20.19 min.

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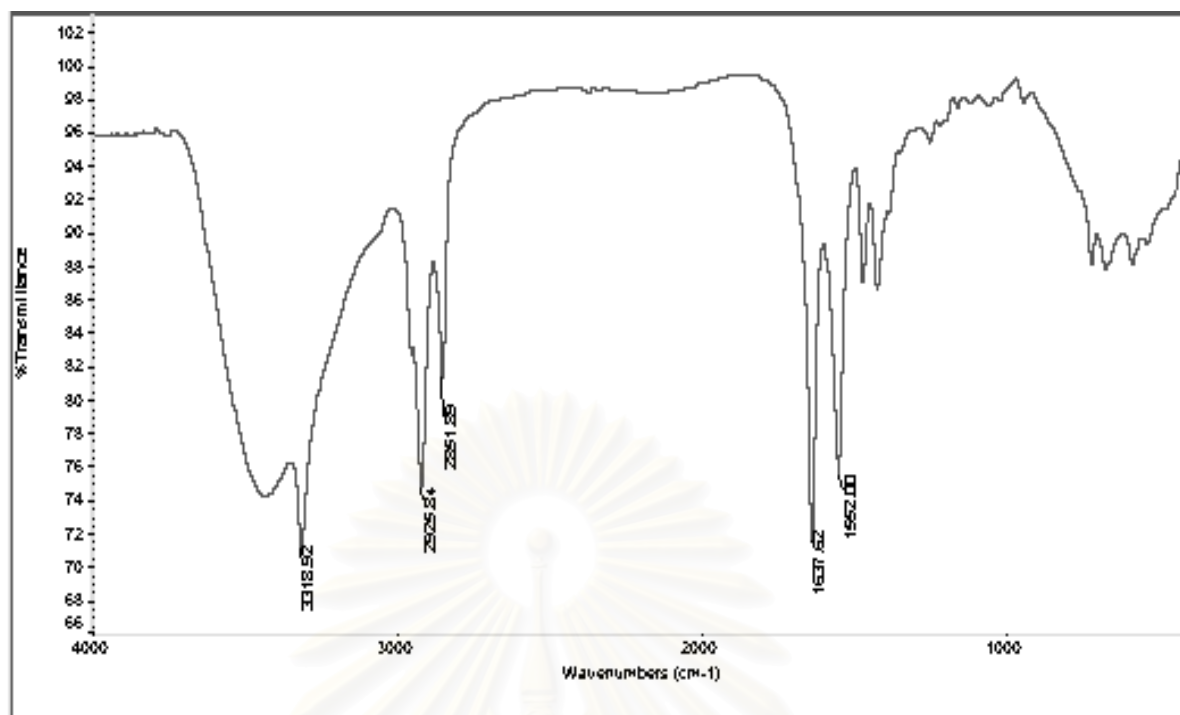


Figure A14 FTIR spectrum of coconut oil hexylamide (NaCl)

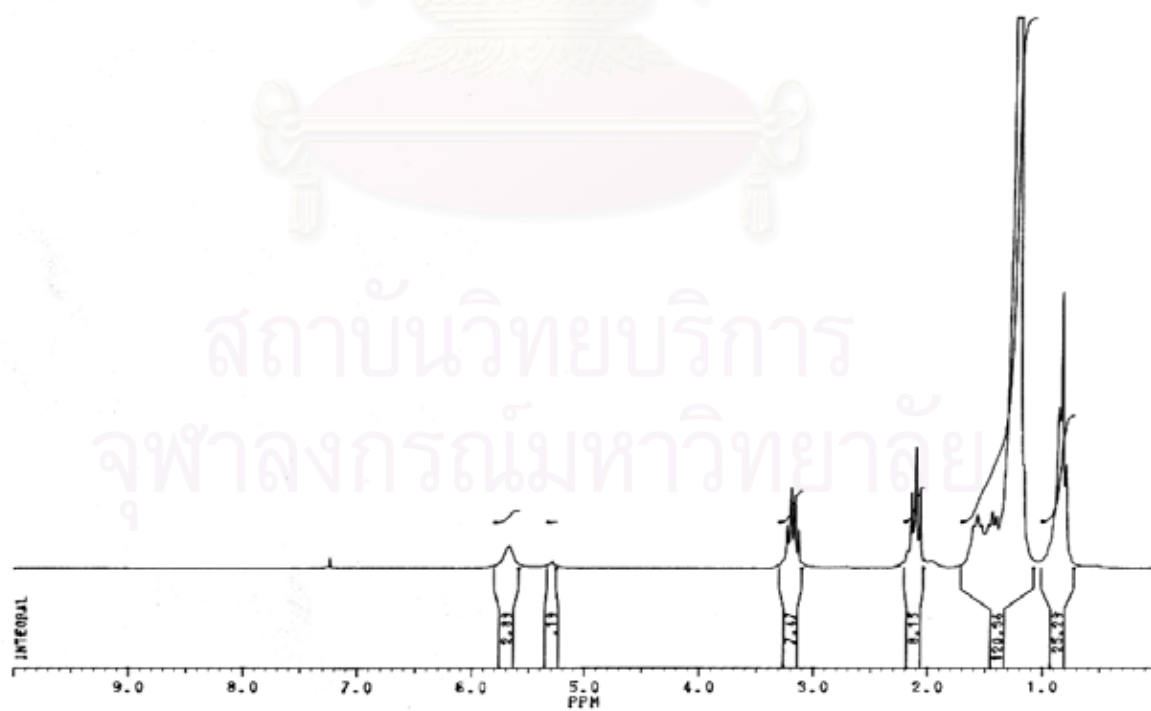


Figure A15 ¹H-NMR spectrum of coconut oil hexylamide (CDCl₃)

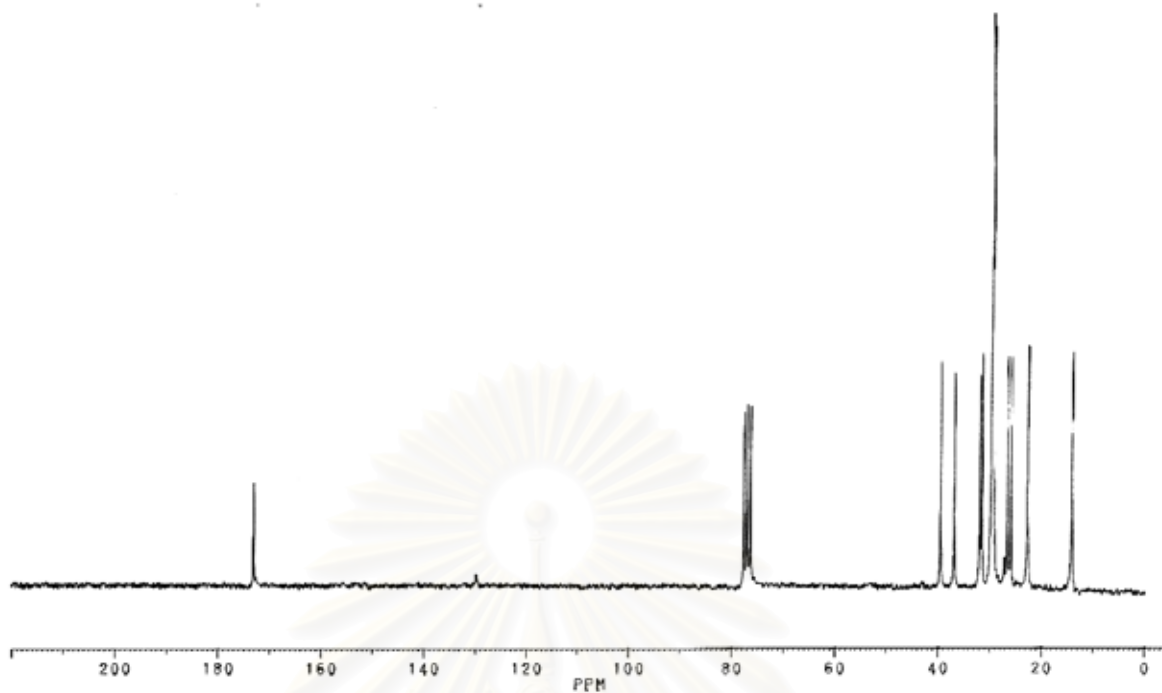


Figure A16 ^{13}C -NMR spectrum of coconut oil hexylamide (CDCl_3)

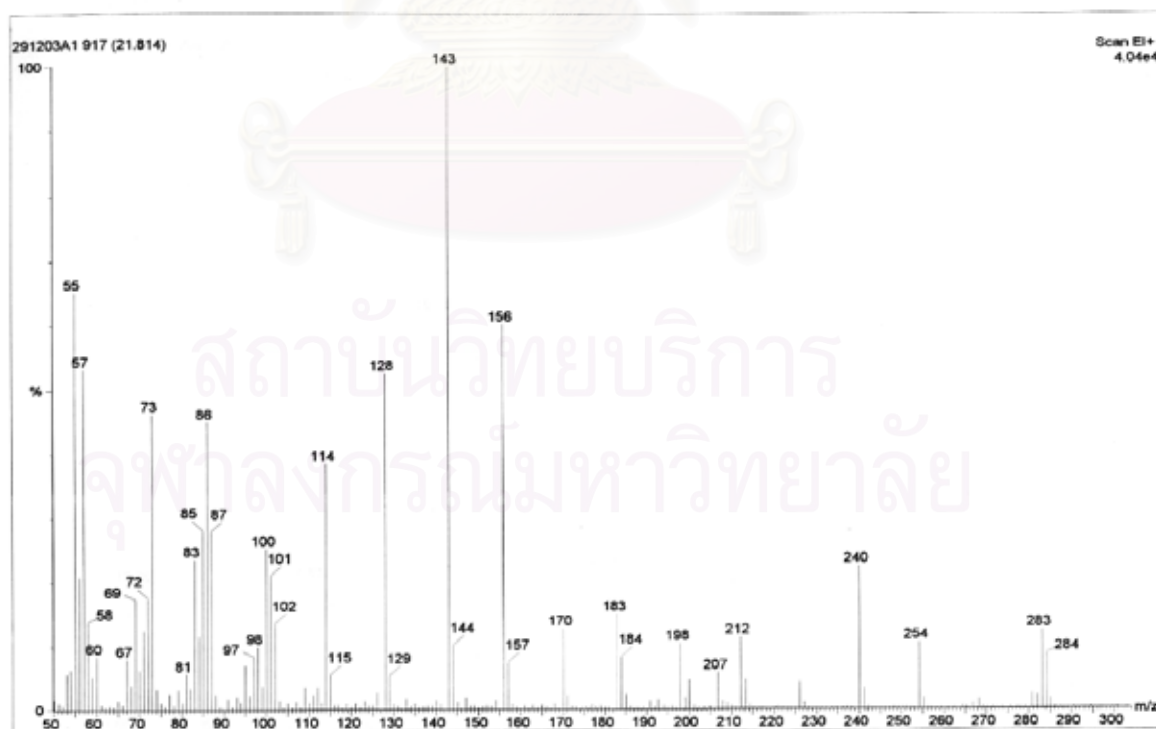


Figure A17 Mass spectrum of coconut oil hexylamide at retention time of 21.81 min.

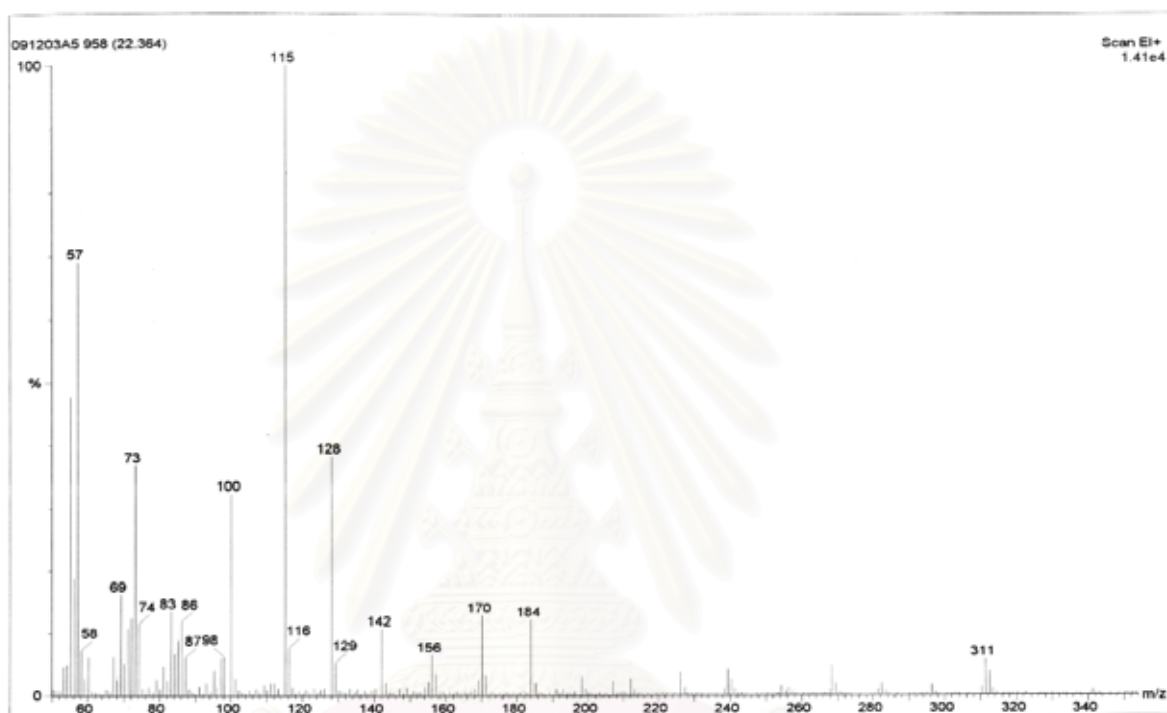


Figure A18 Mass spectrum of coconut oil hexylamide at retention time of 20.19 min.

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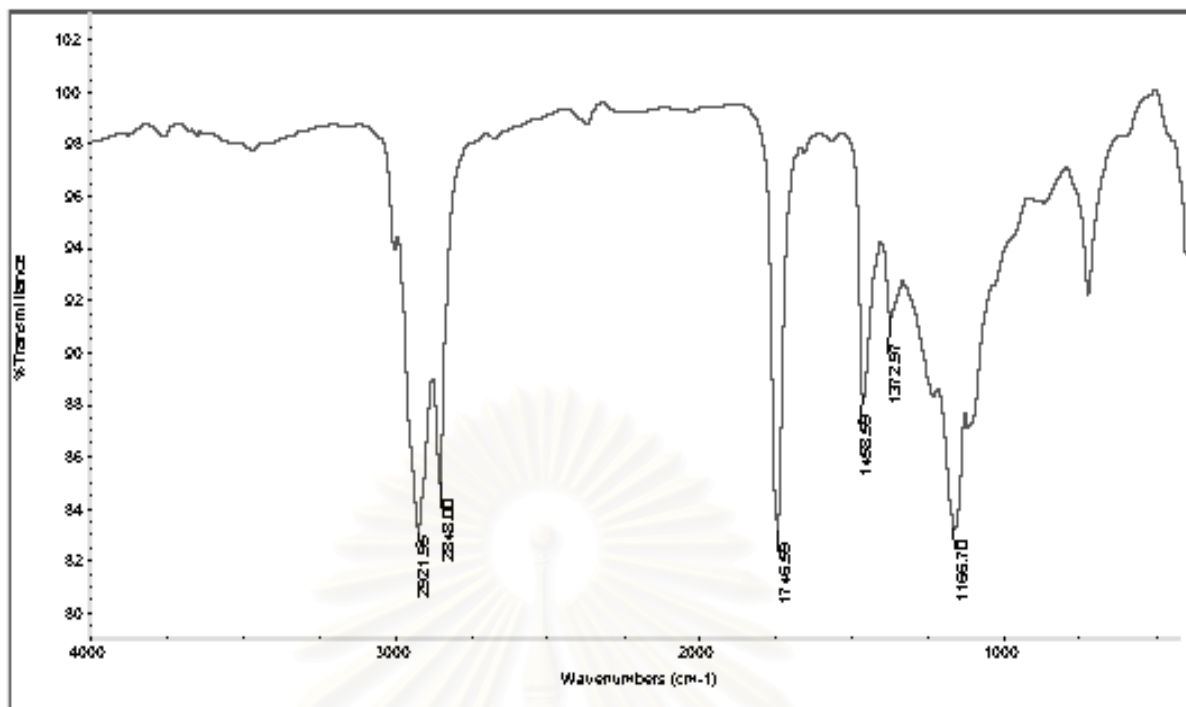


Figure A19 FTIR spectrum of palm oil (NaCl)

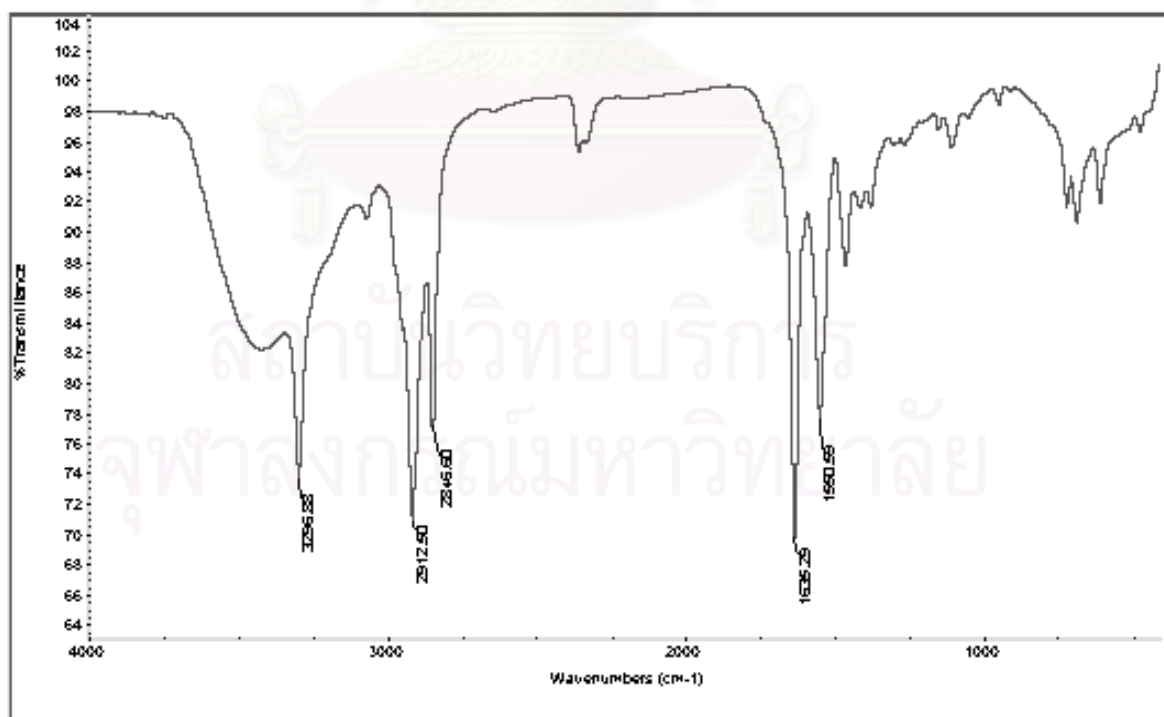


Figure A20 FTIR spectrum of palm oil ethylamide (NaCl)

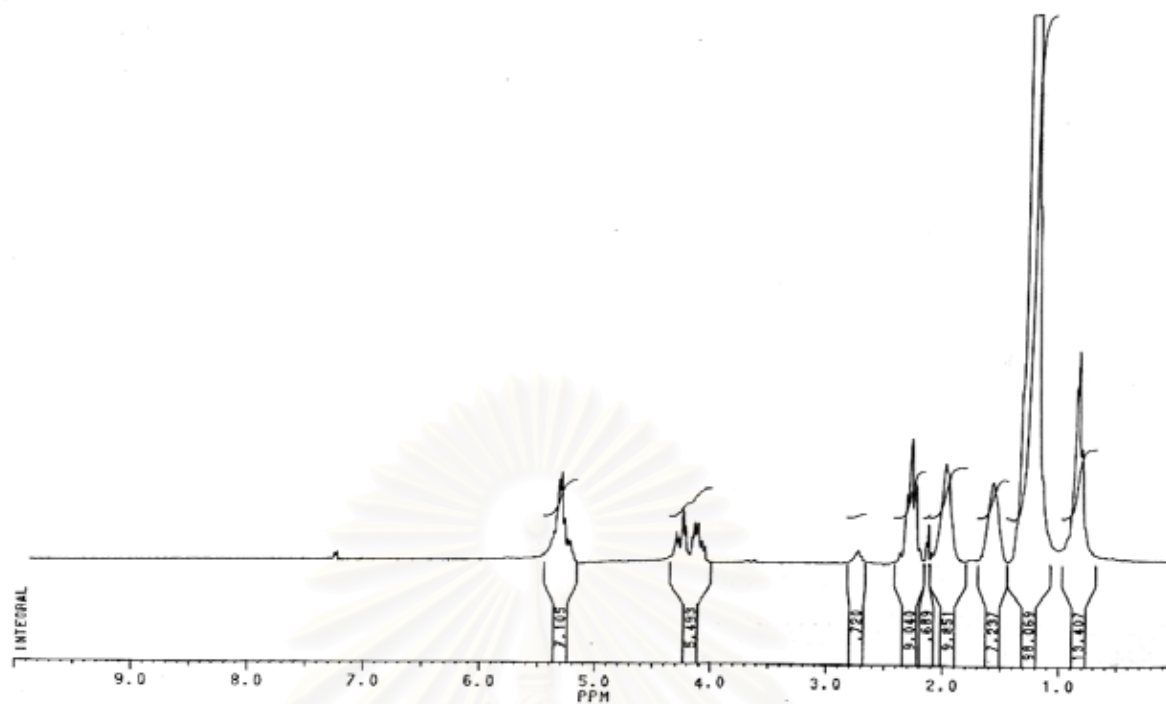


Figure A21 ¹H-NMR spectrum of palm oil (CDCl₃)

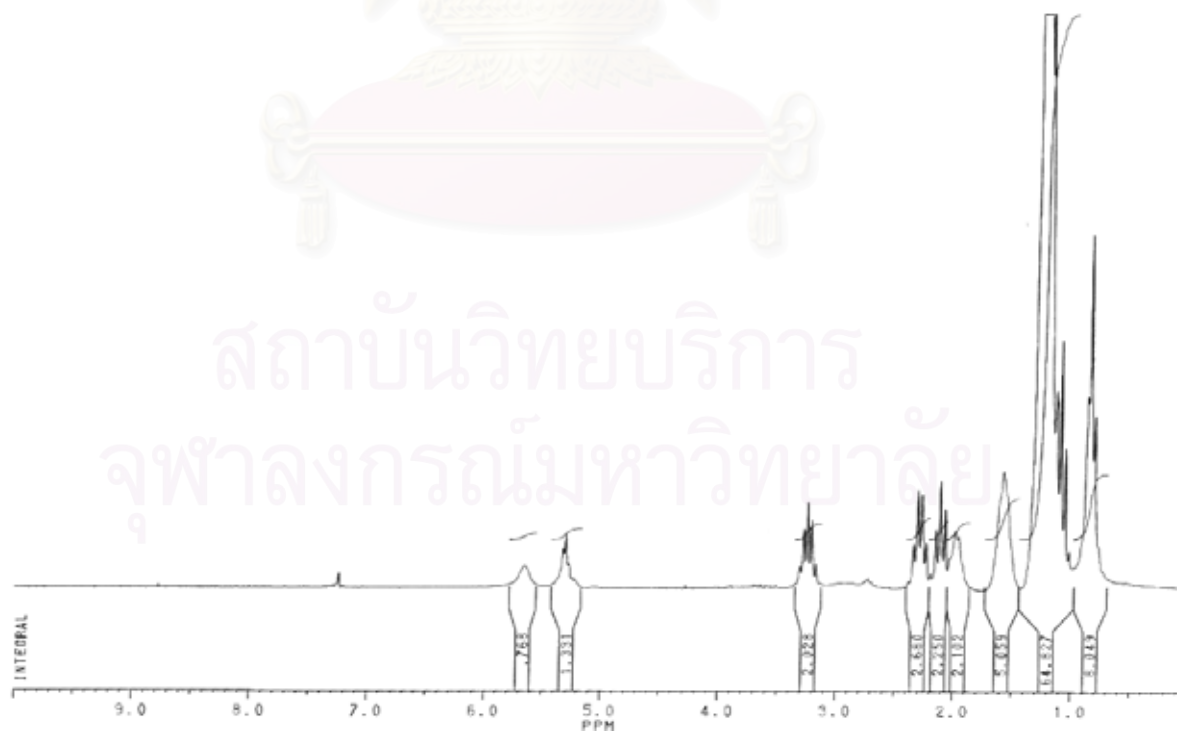


Figure A22 ¹H-NMR spectrum of palm oil ethylamide (CDCl₃)

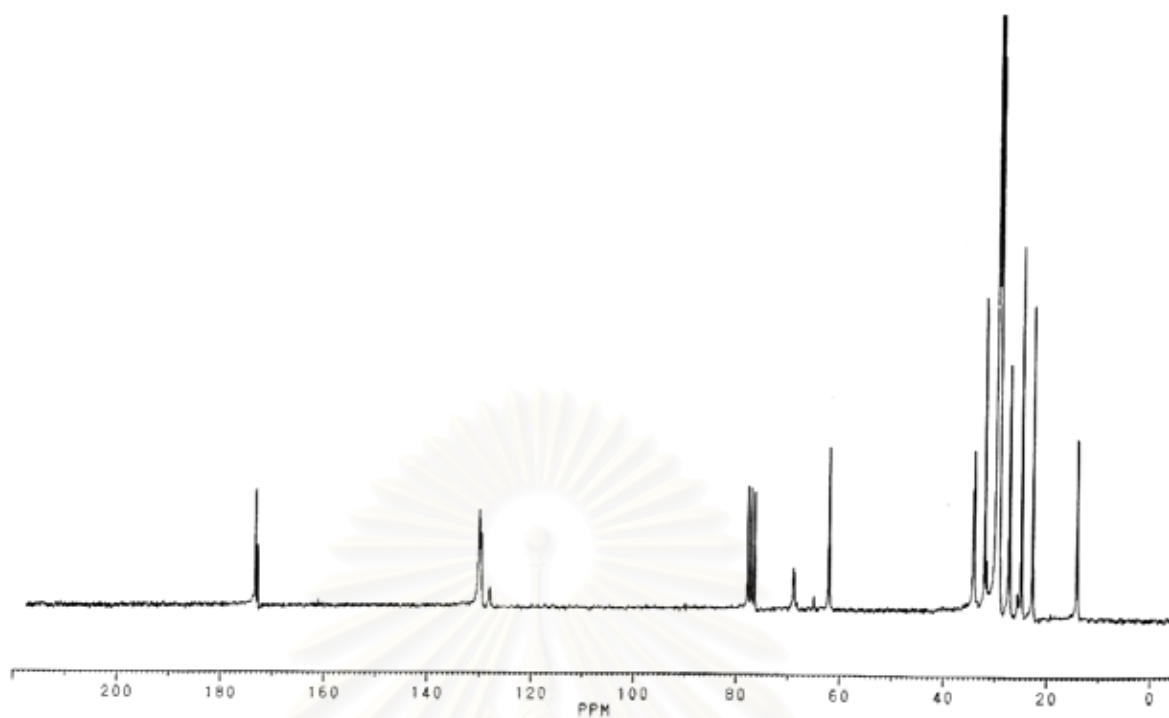


Figure A23 ^{13}C -NMR spectrum of palm oil (CDCl_3)

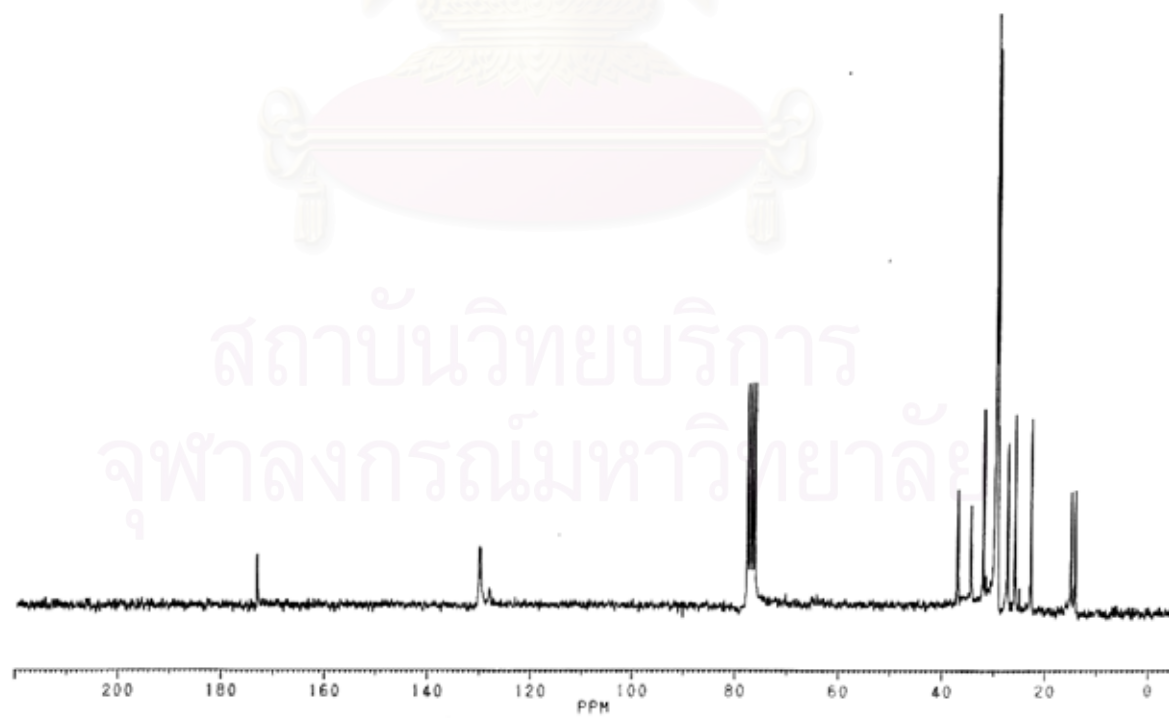


Figure A24 ^{13}C -NMR spectrum of palm oil ethylamide (CDCl_3)

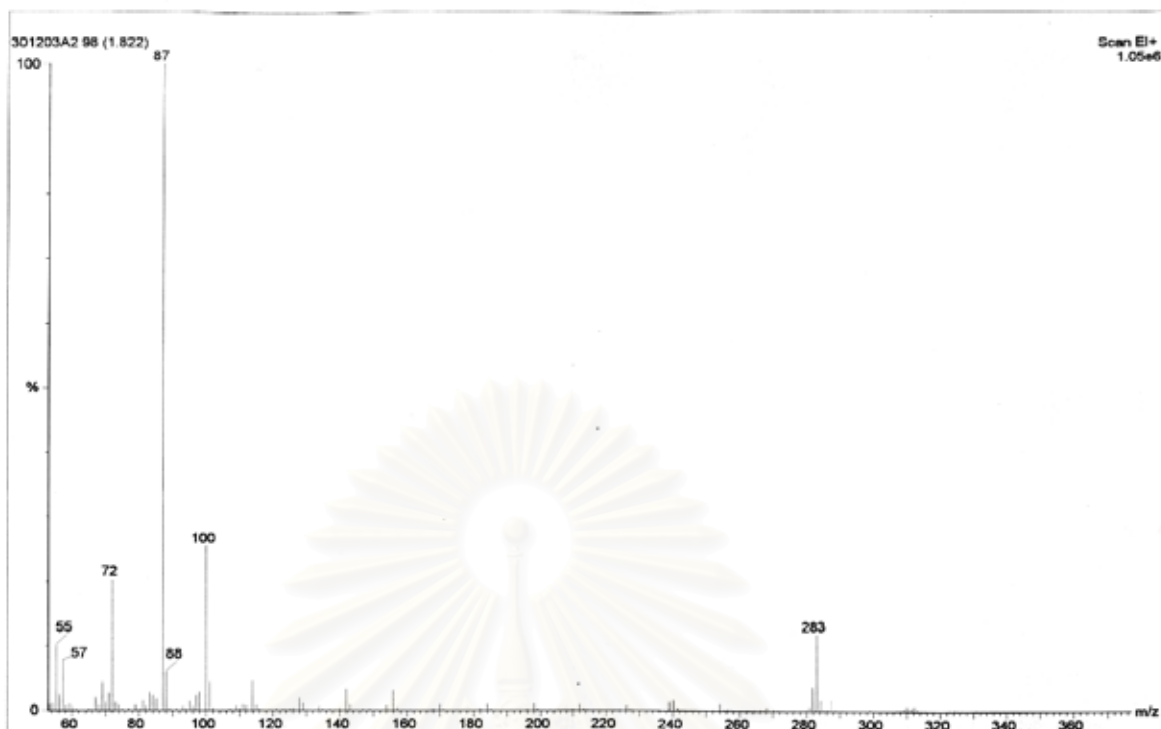


Figure A25 Mass spectrum of palm oil ethylamide at retention time of 1.82 min.

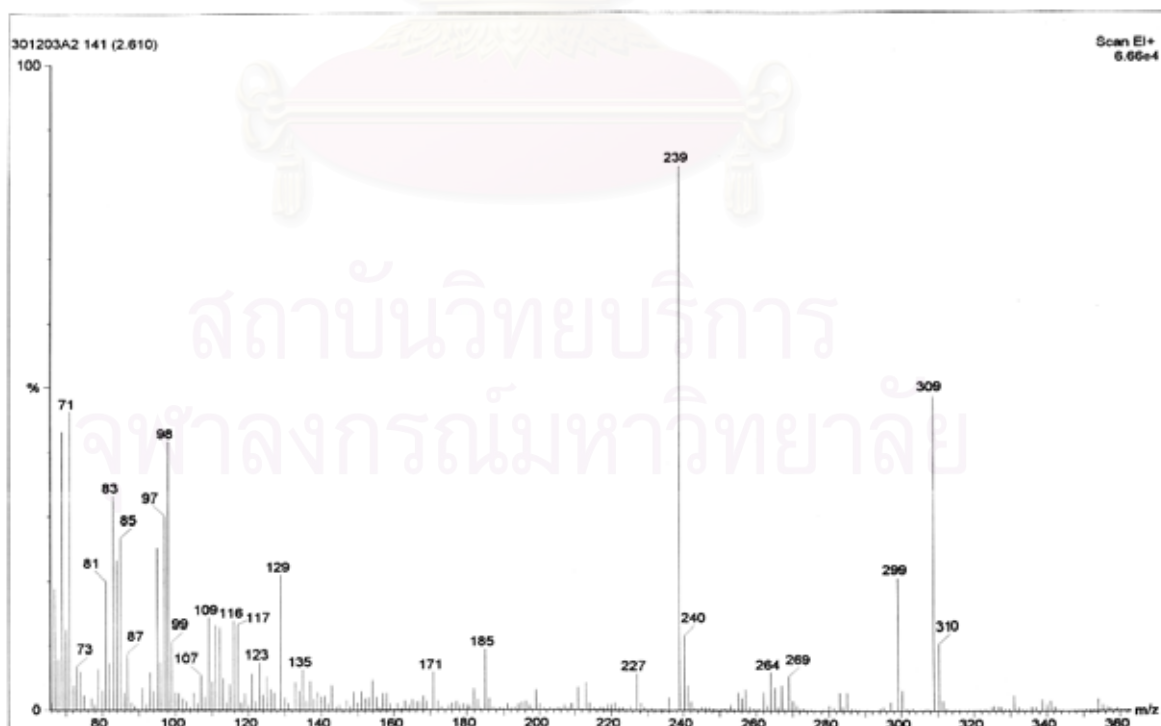


Figure A26 Mass spectrum of palm oil ethylamide at retention time of 2.61 min.

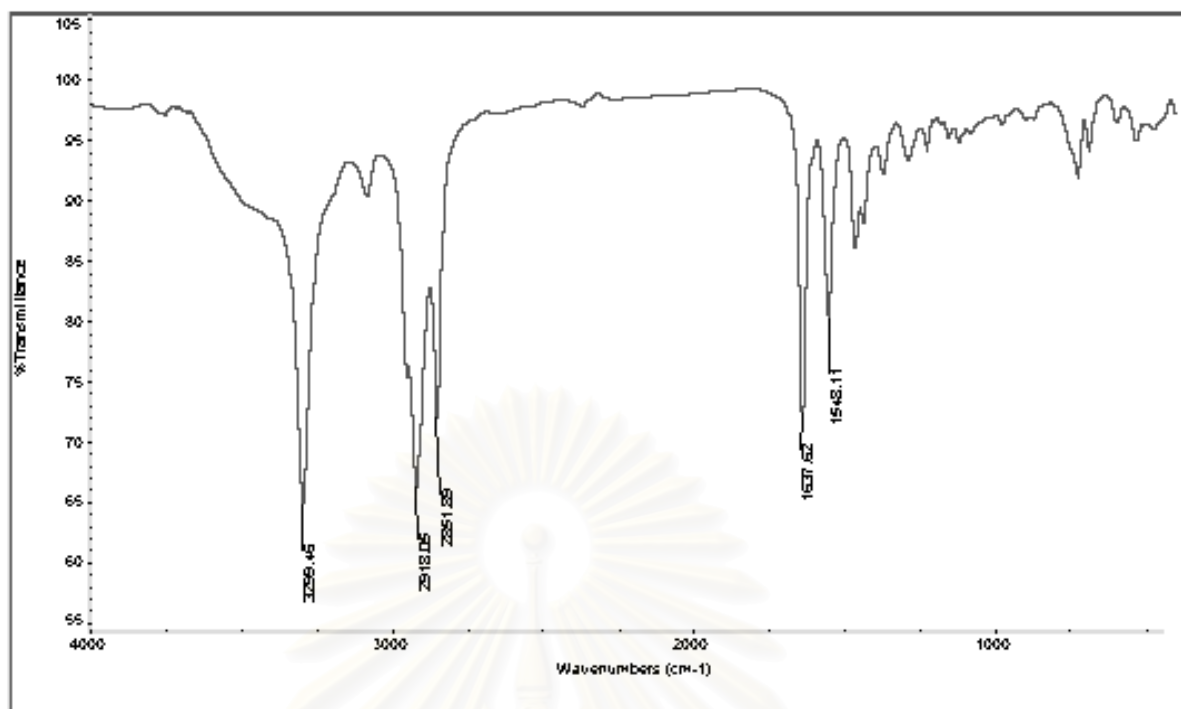


Figure A27 FTIR spectrum of palm oil butylamide (NaCl)

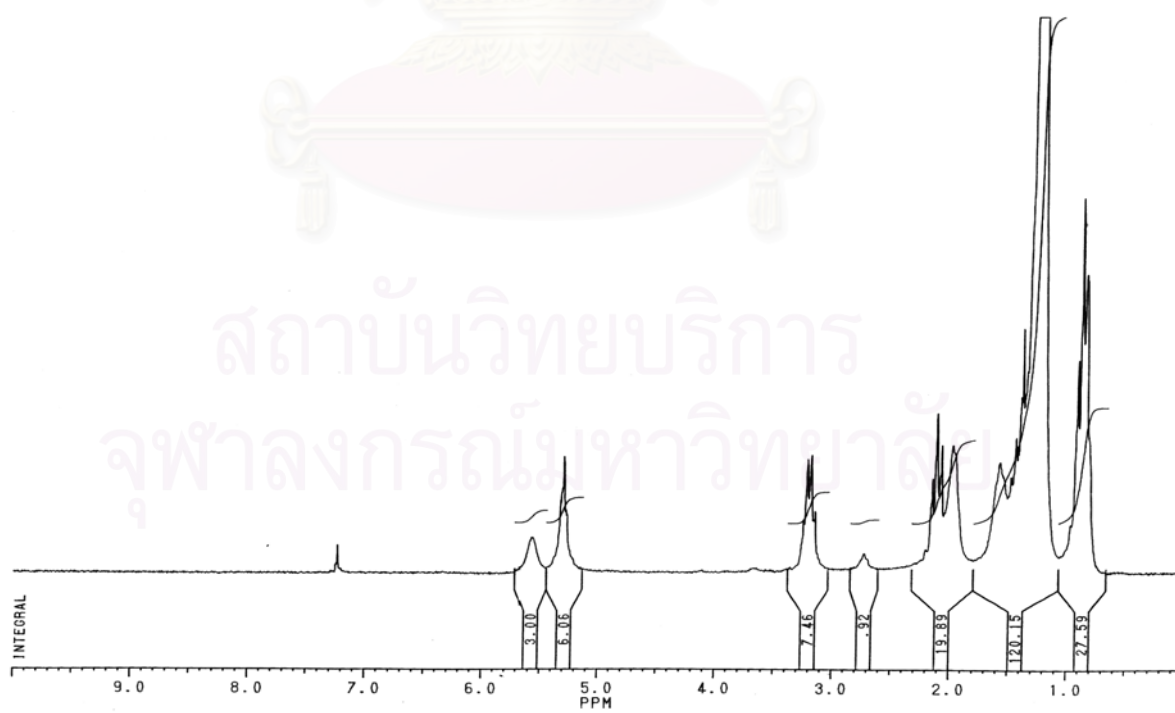


Figure A28 ¹H-NMR spectrum of palm oil butylamide (CDCl₃)

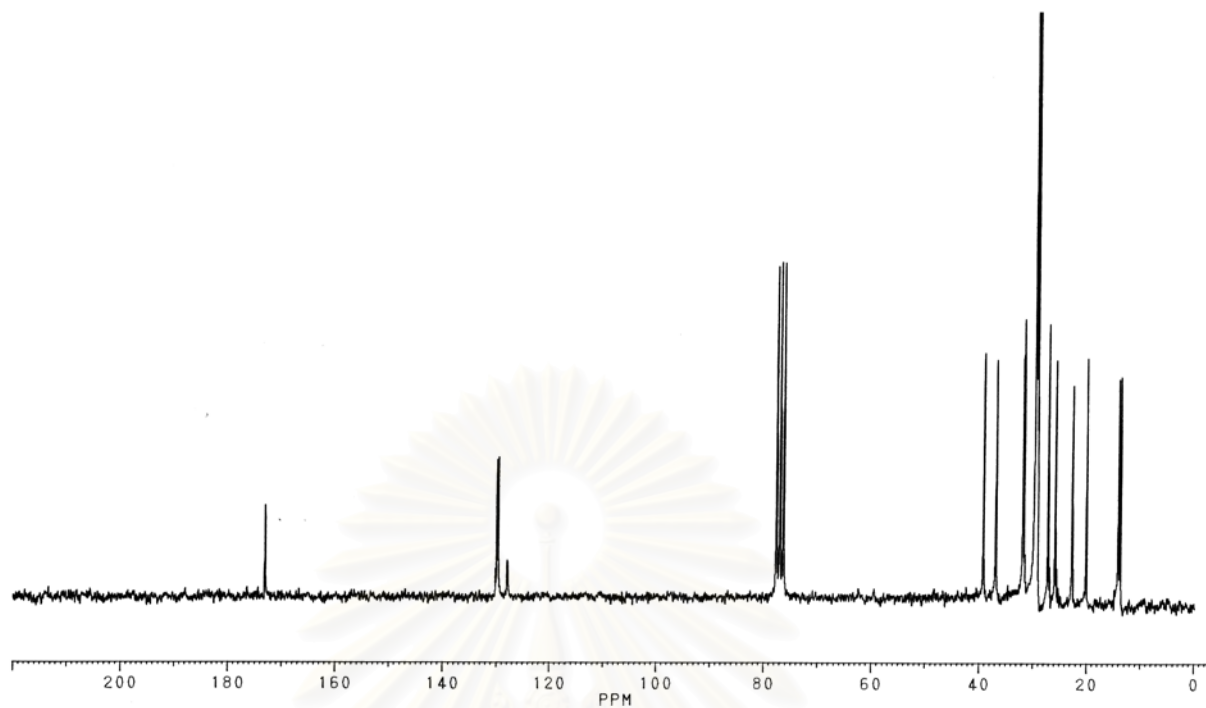


Figure A29 ^{13}C -NMR spectrum of palm oil butylamide (CDCl_3)

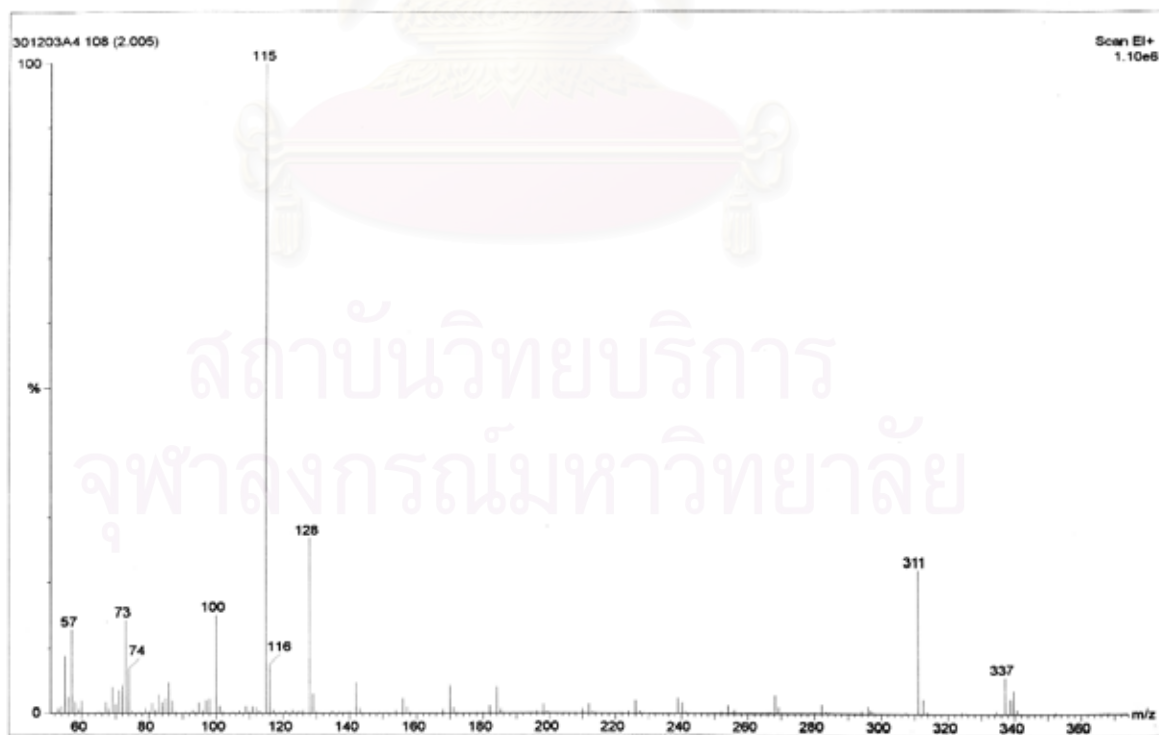


Figure A30 Mass spectrum of palm oil butylamide at retention time of 2.00 min.

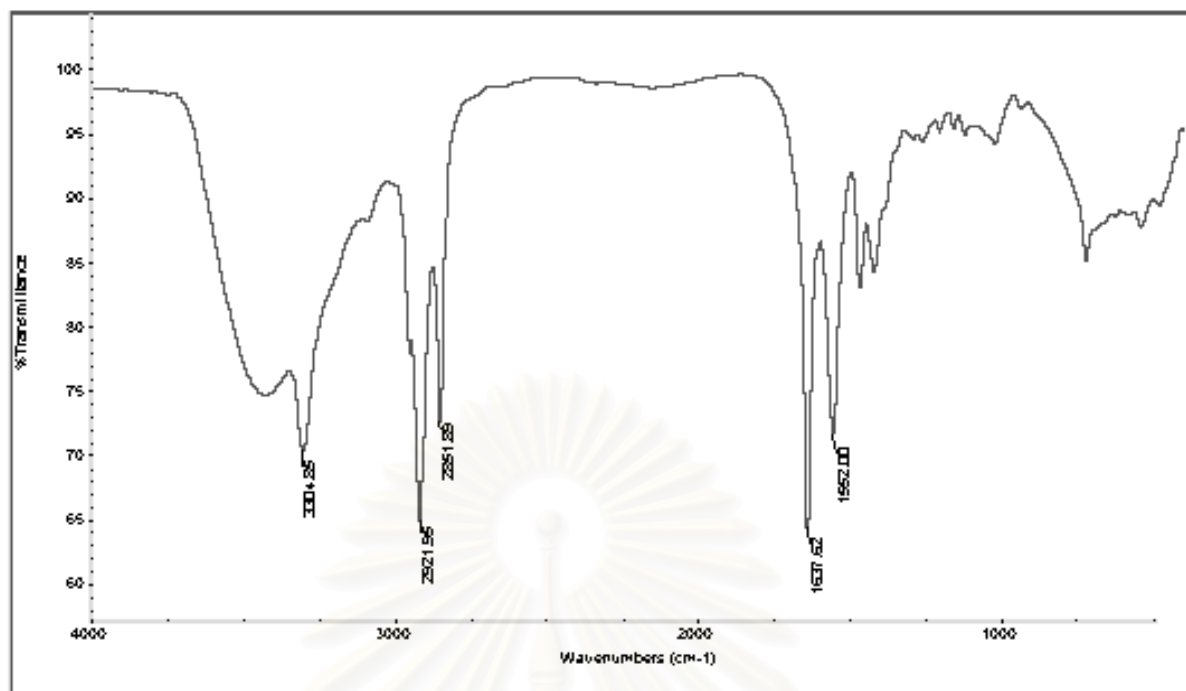


Figure A31 FTIR spectrum of palm oil hexylamide (NaCl)

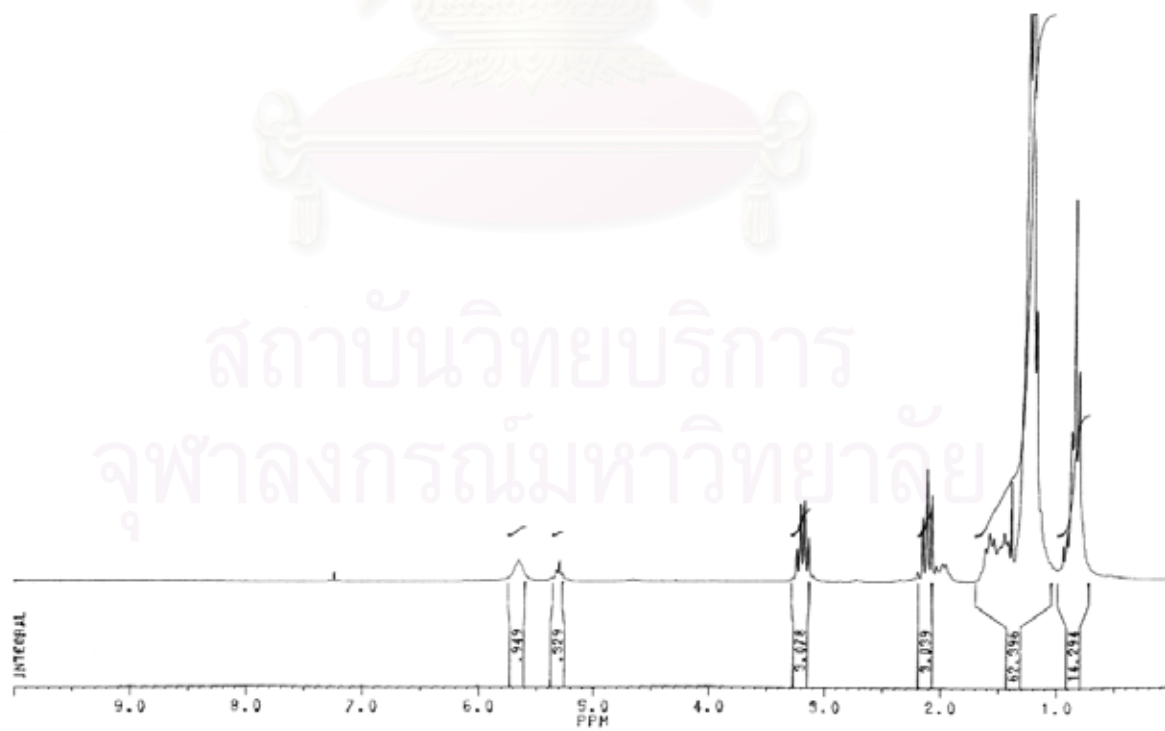


Figure A32 $^1\text{H-NMR}$ spectrum of palm oil hexylamide (CDCl_3)

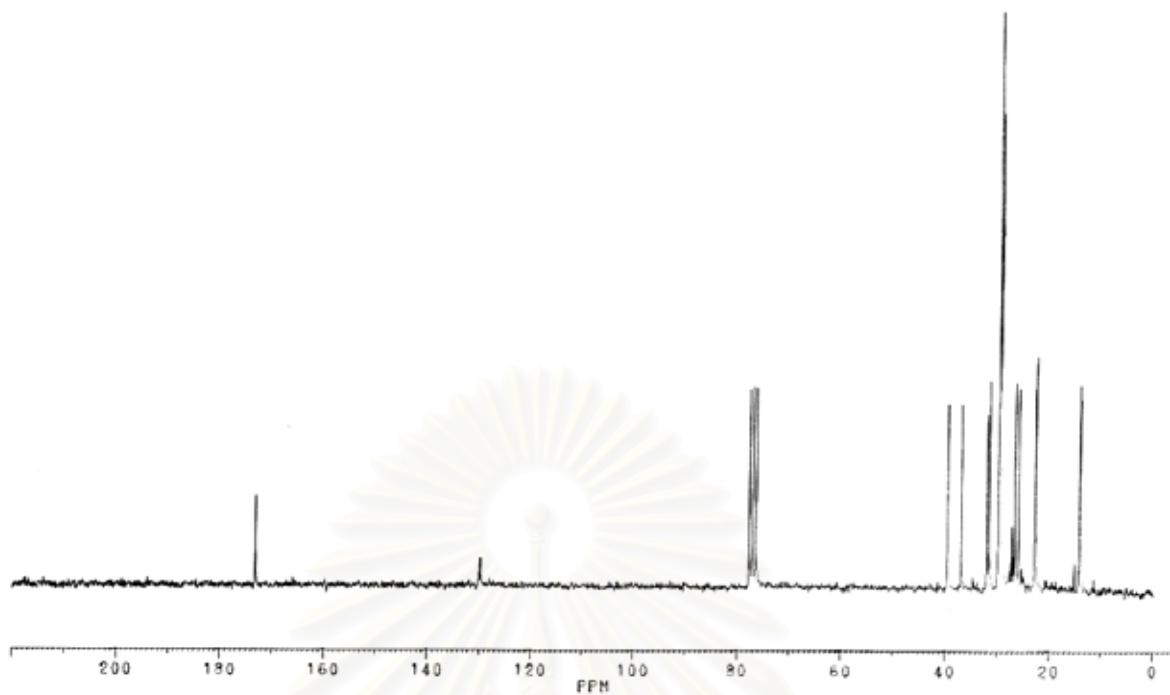


Figure A33 ^{13}C -NMR spectrum of palm oil hexylamide (CDCl_3)

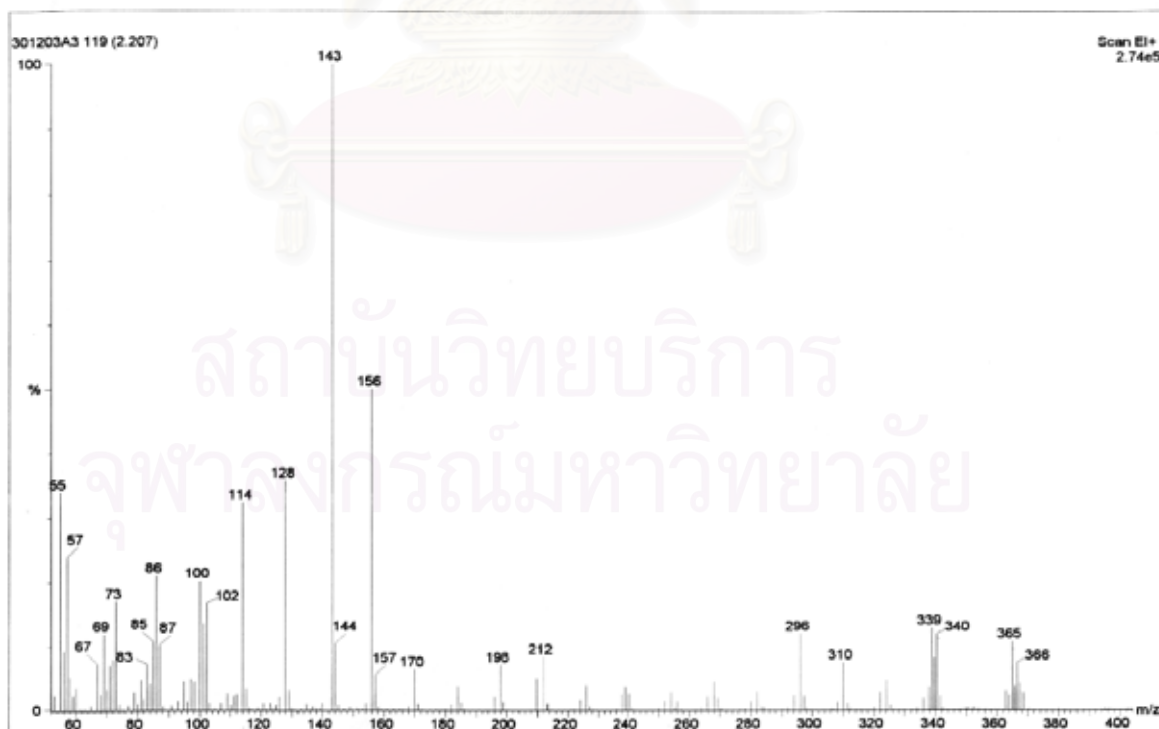


Figure A34 Mass spectrum of palm oil hexylamide at retention time of 2.20 min.

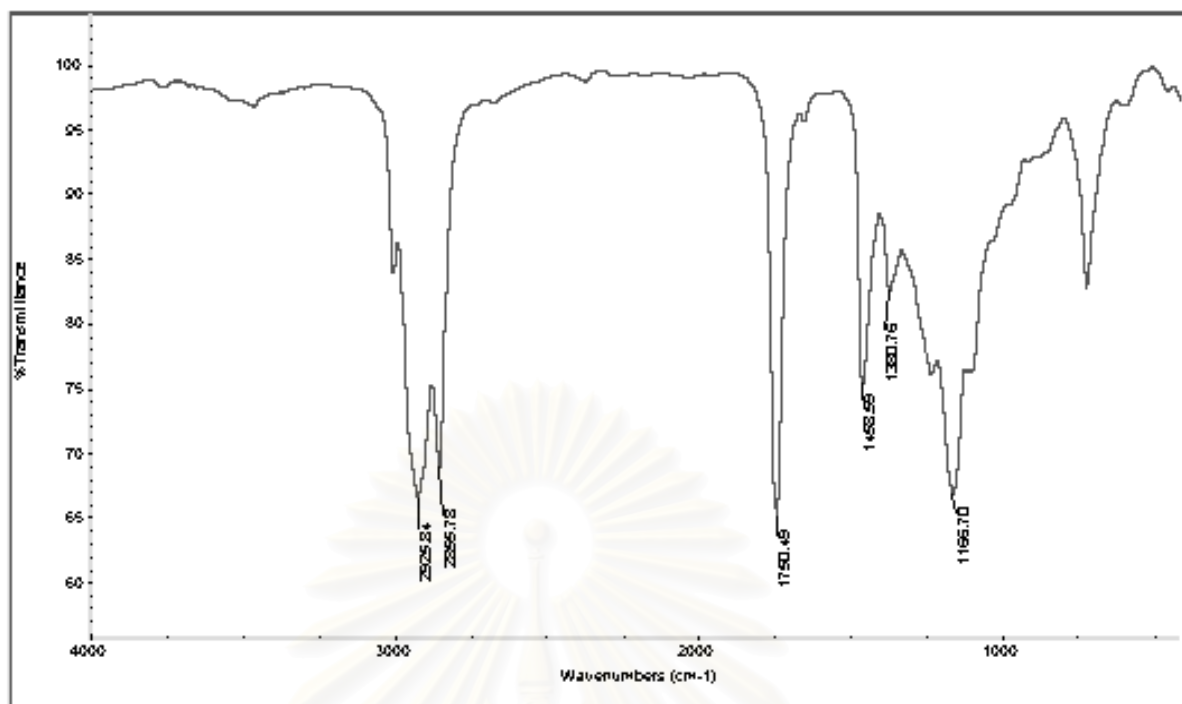


Figure A35 FTIR spectrum of rice bran oil (NaCl)

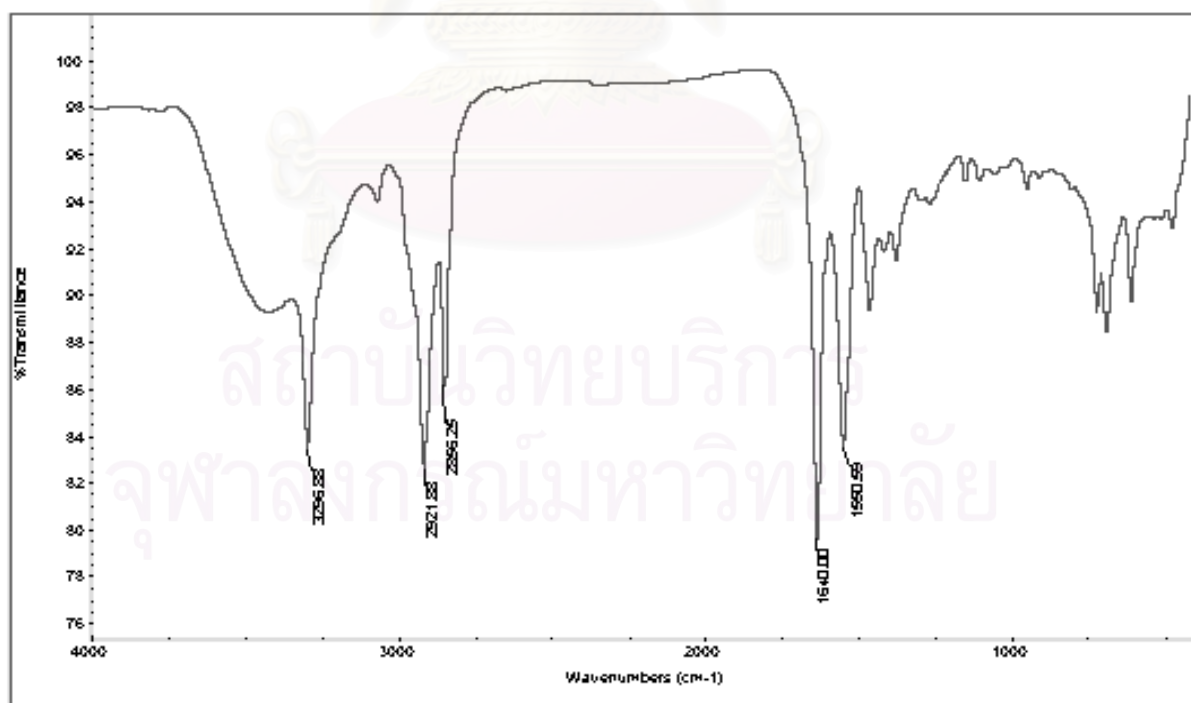


Figure A36 FTIR spectrum of rice bran oil ethylamide (NaCl)

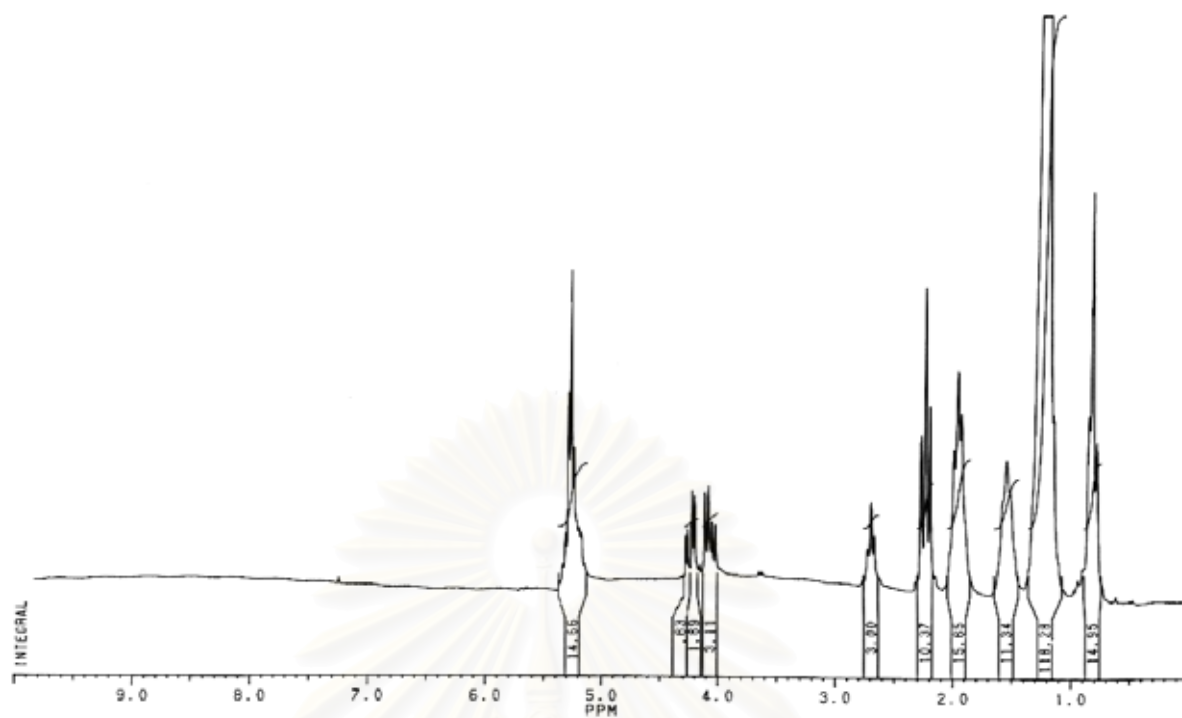


Figure A37 $^1\text{H-NMR}$ spectrum of rice bran oil (CDCl_3)

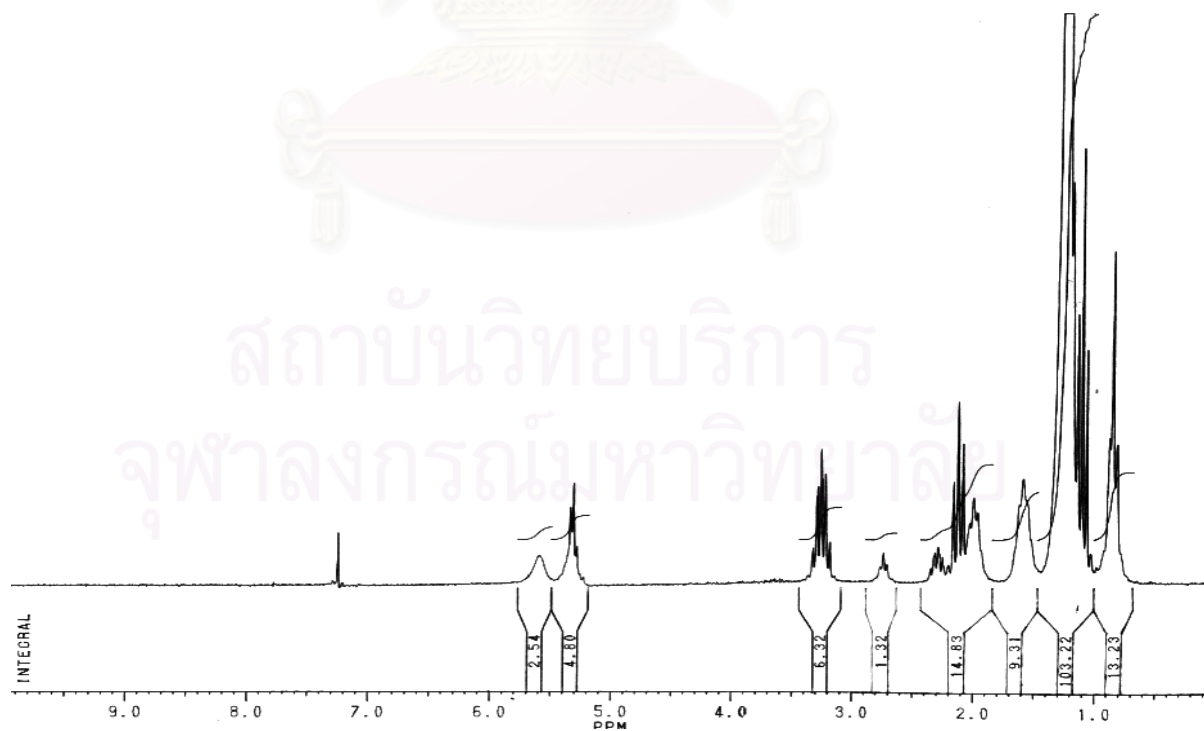


Figure A38 $^1\text{H-NMR}$ spectrum of rice bran oil ethylamide (CDCl_3)

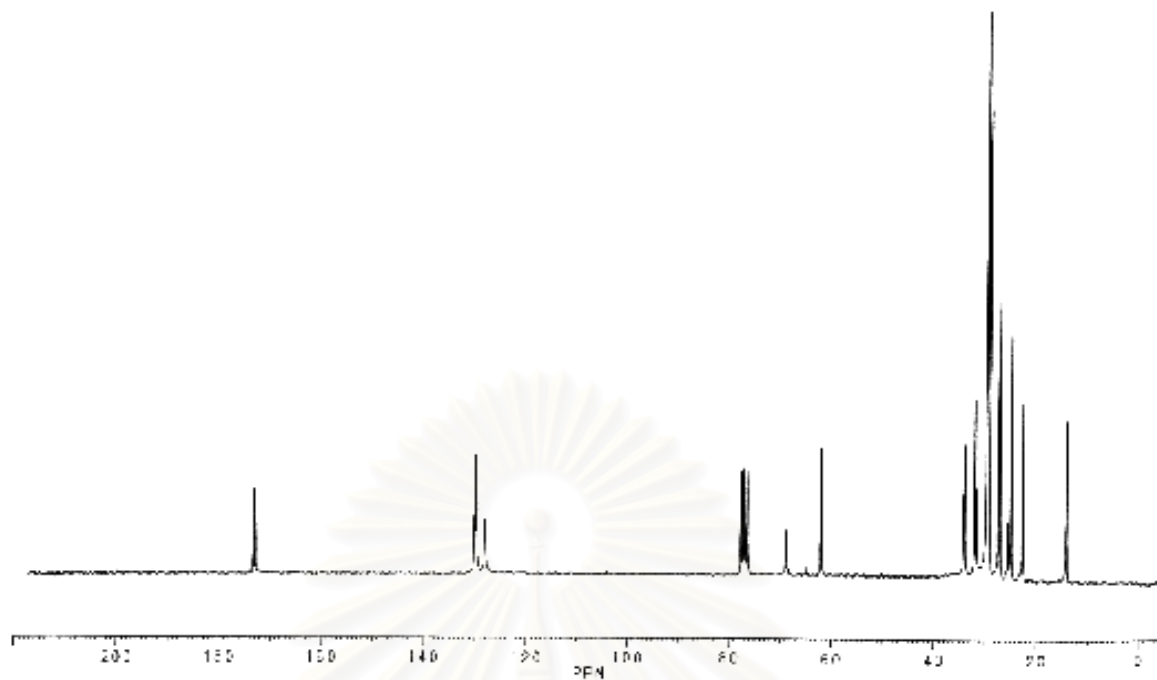


Figure A39 ^{13}C -NMR spectrum of rice bran oil (CDCl_3)

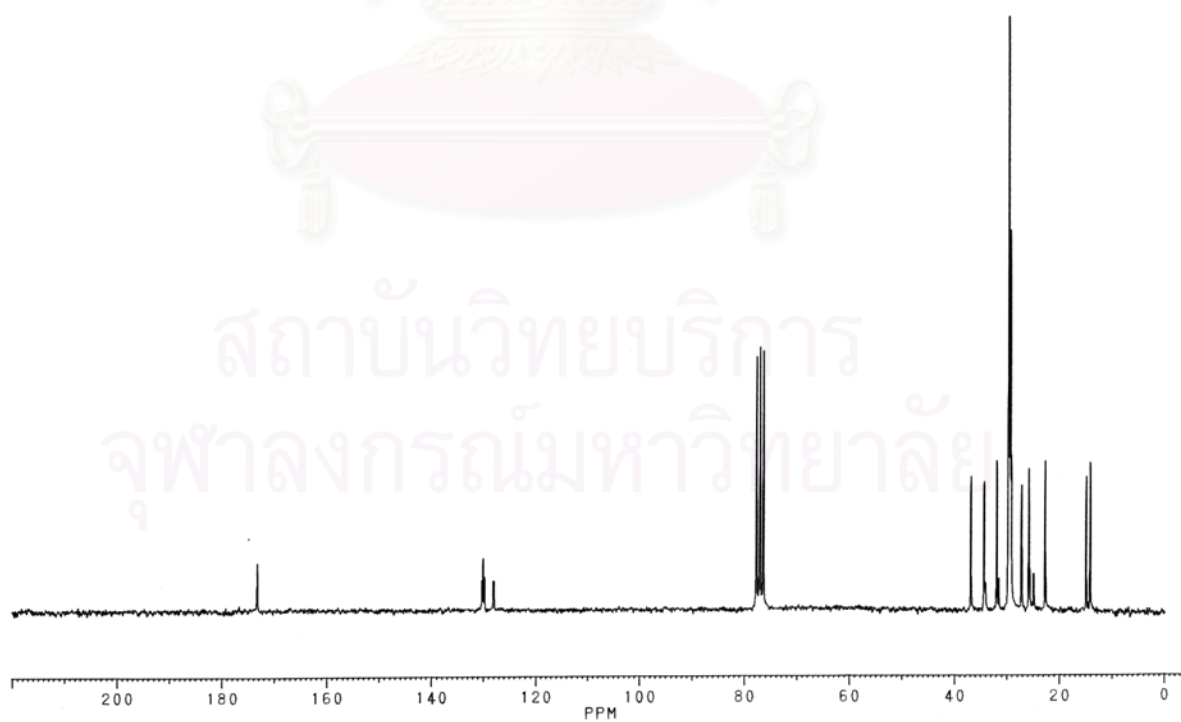


Figure A40 ^{13}C -NMR spectrum of rice bran oil ethylamide (CDCl_3)

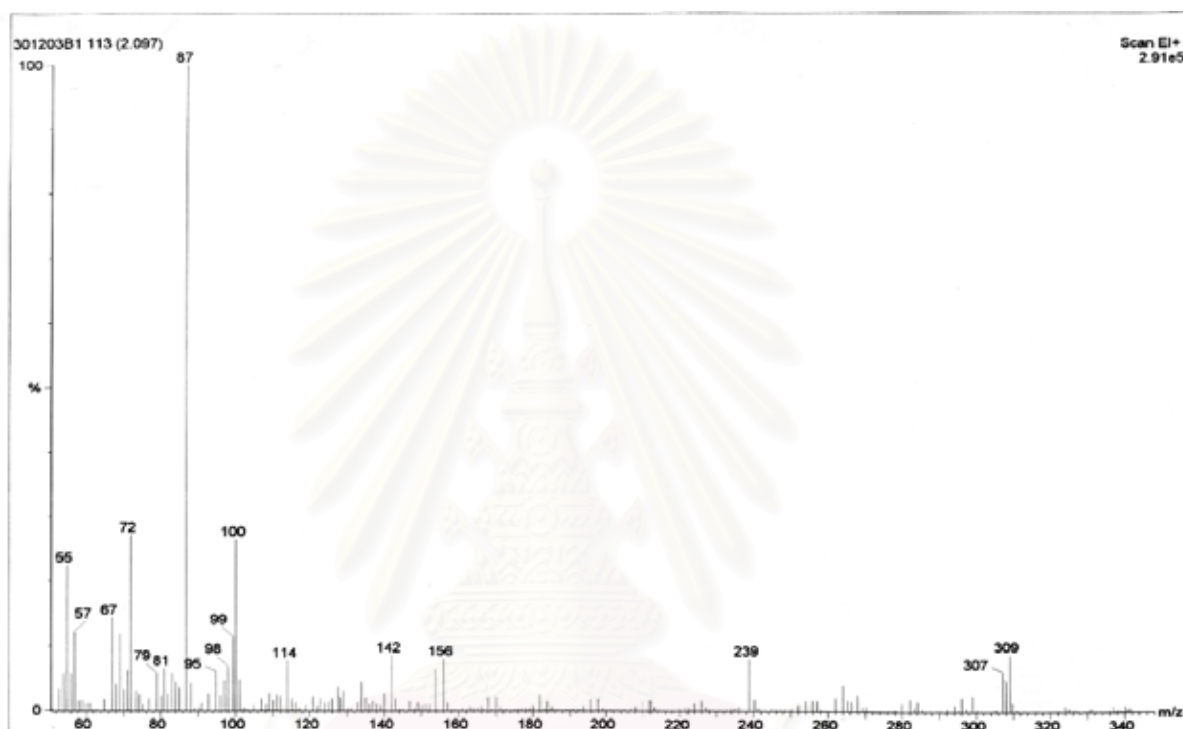


Figure A41 Mass spectrum of rice bran oil ethylamide at retention time of 2.09 min.

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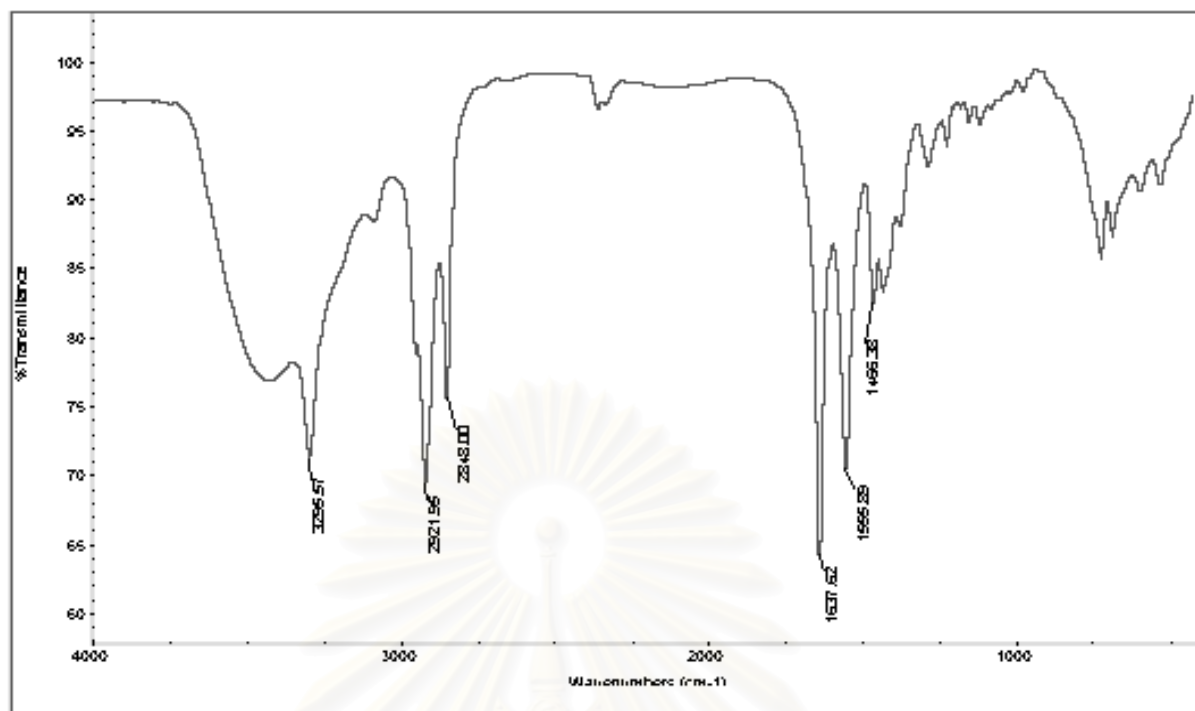


Figure A42 FTIR spectrum of rice bran oil butylamide (NaCl)

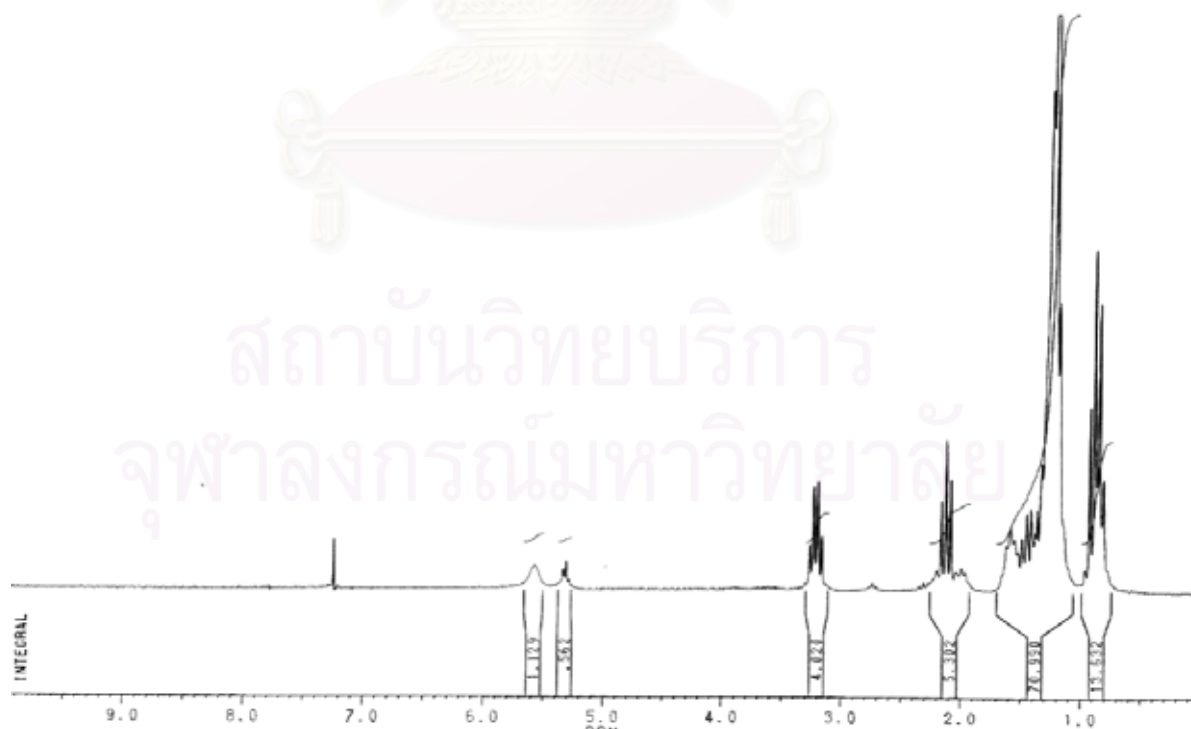


Figure A43 ¹H-NMR spectrum of rice bran oil butylamide (CDCl₃)

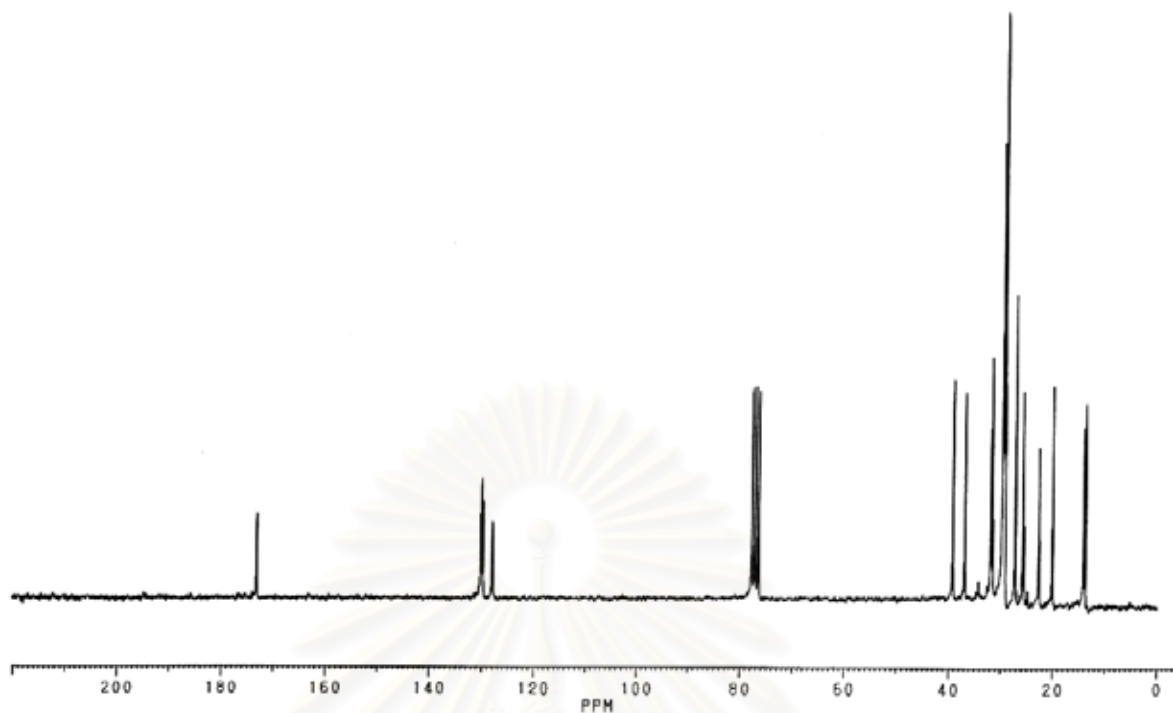


Figure A44 ^{13}C -NMR spectrum of rice bran oil butylamide (CDCl_3)

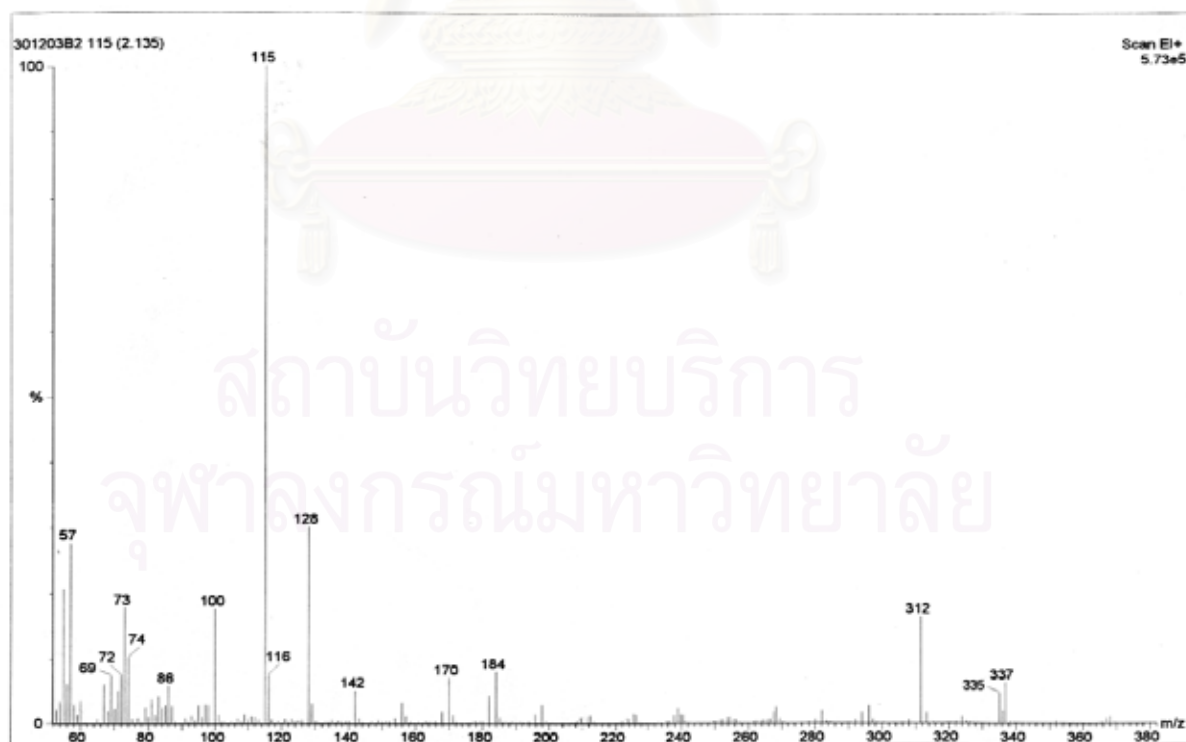


Figure A45 Mass spectrum of rice bran oil butylamide at retention time of 2.09 min.

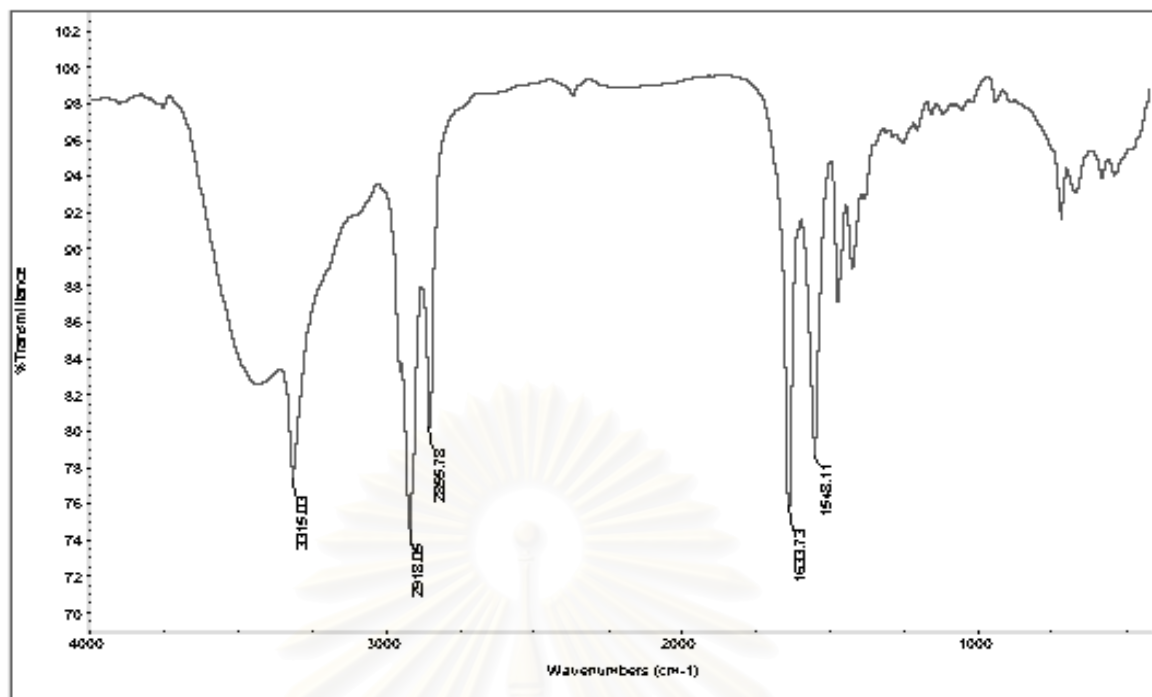


Figure A46 FTIR spectrum of rice bran oil hexylamide (NaCl)

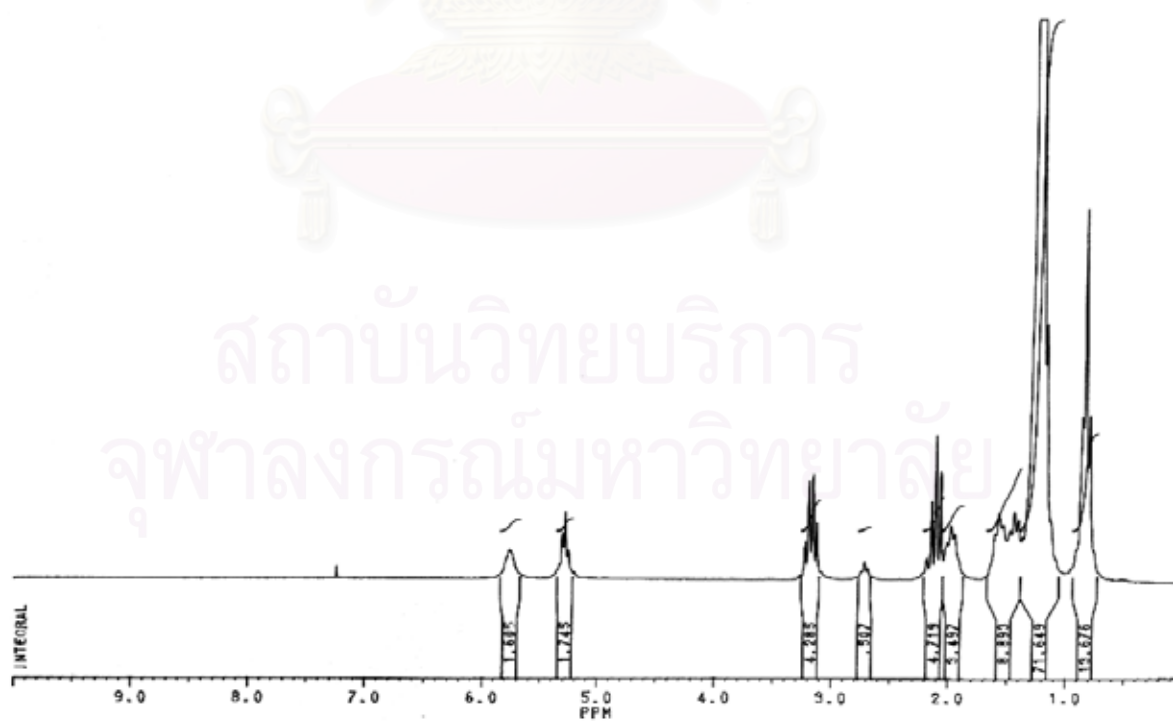


Figure A47 ¹H-NMR spectrum of rice bran oil hexylamide (CDCl₃)

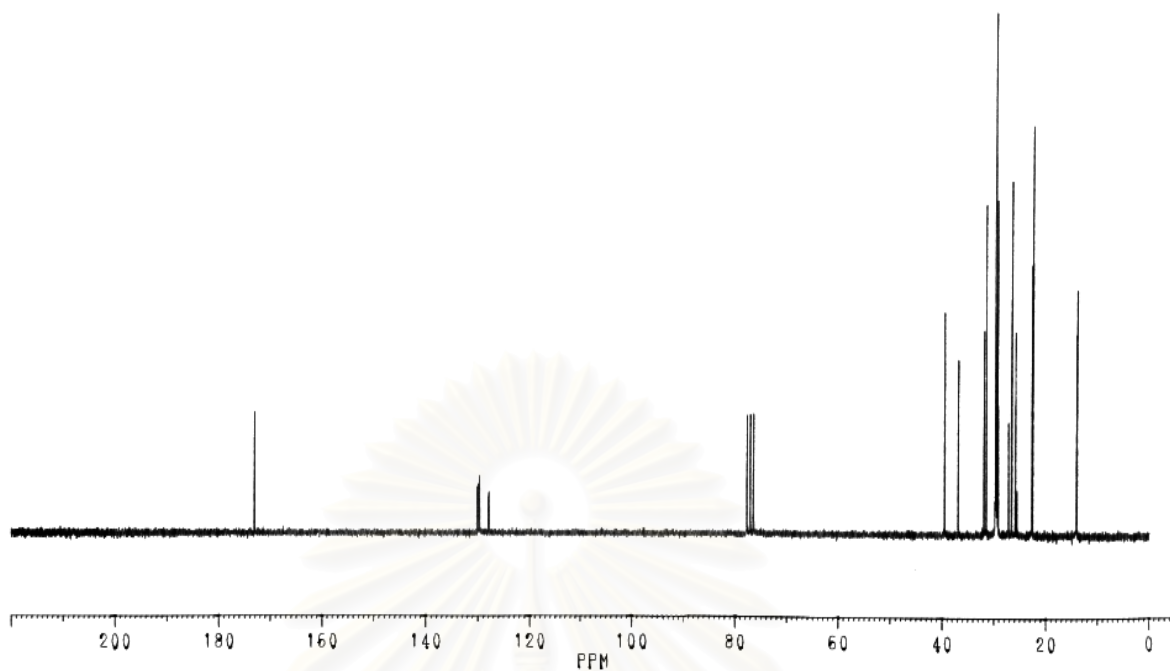


Figure A48 ^{13}C -NMR spectrum of rice bran oil hexylamide (CDCl_3)

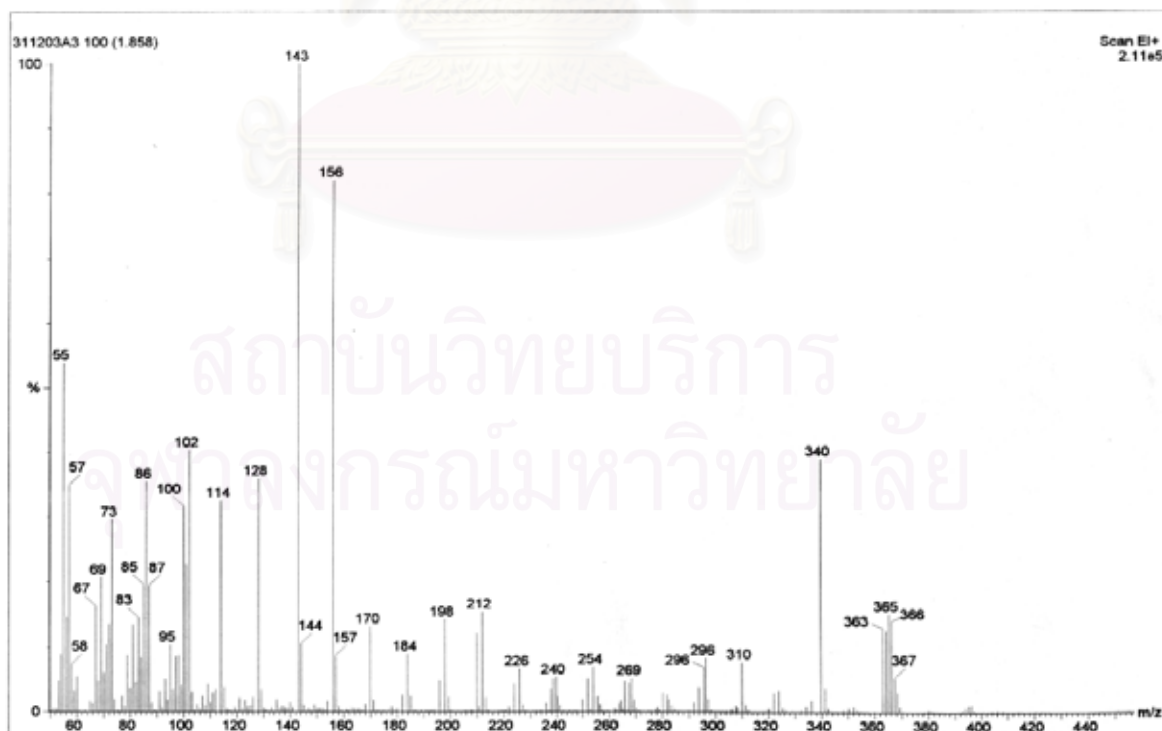


Figure A49 Mass spectrum of rice bran oil hexylamide at retention time of 1.85 min.



APPENDIX B

SPECTRA OF SYNTHESIZED FATTY ACID ESTERS

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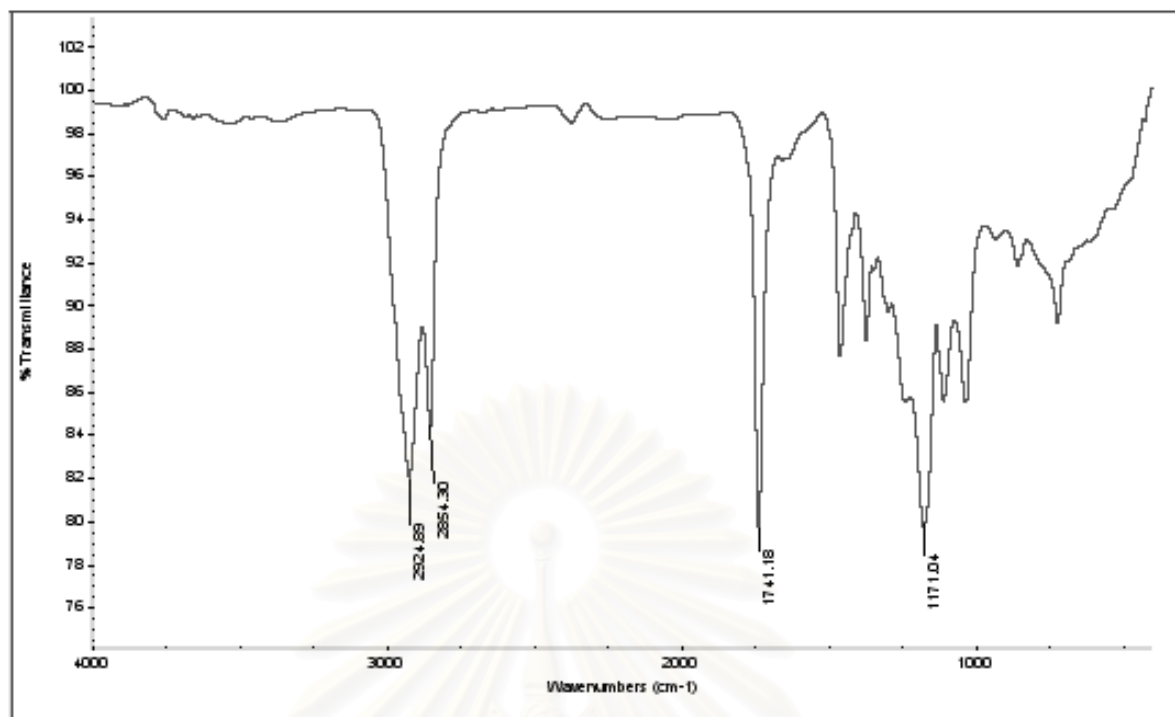


Figure B1 FTIR spectrum of coconut oil ethyl ester (NaCl)

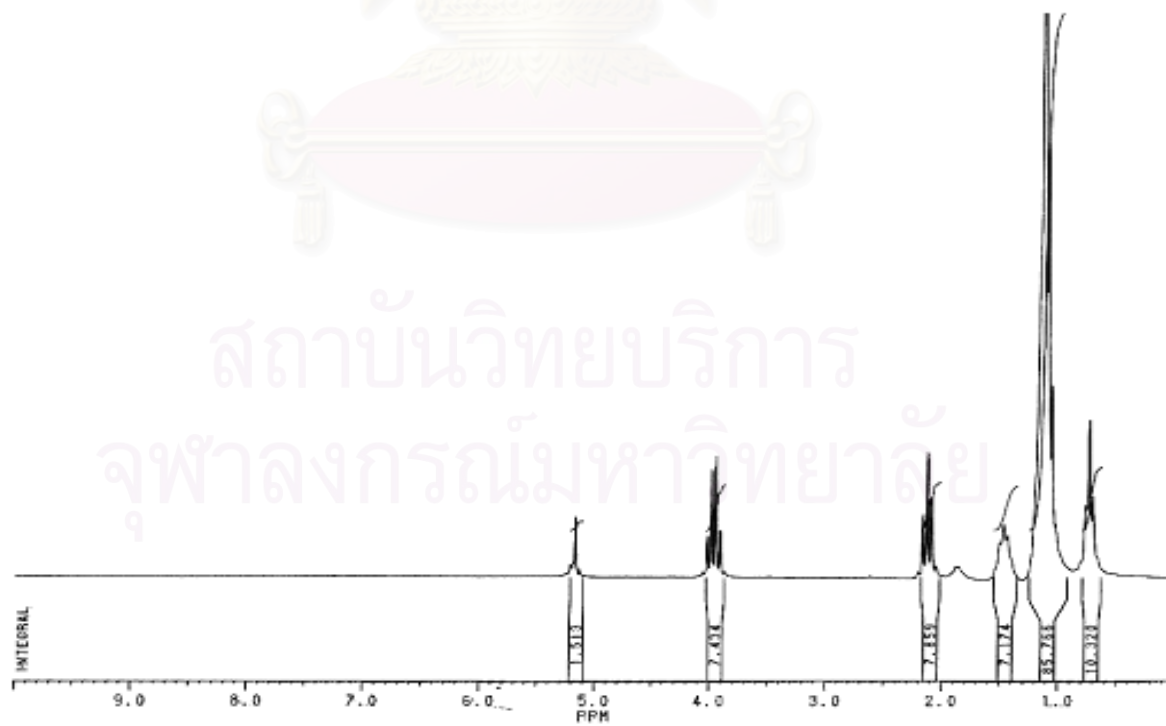


Figure B2 ¹H-NMR spectrum of coconut oil ethyl ester (CDCl₃)

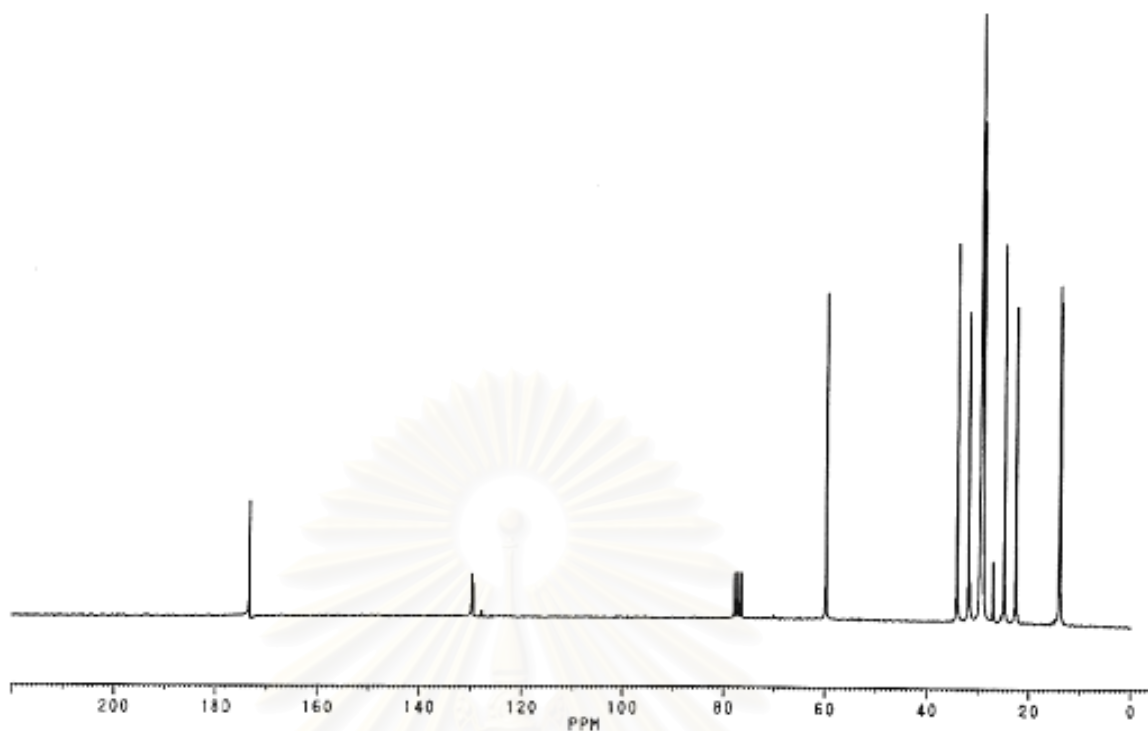


Figure B3 ^{13}C -NMR spectrum of coconut oil ethyl ester (CDCl_3)

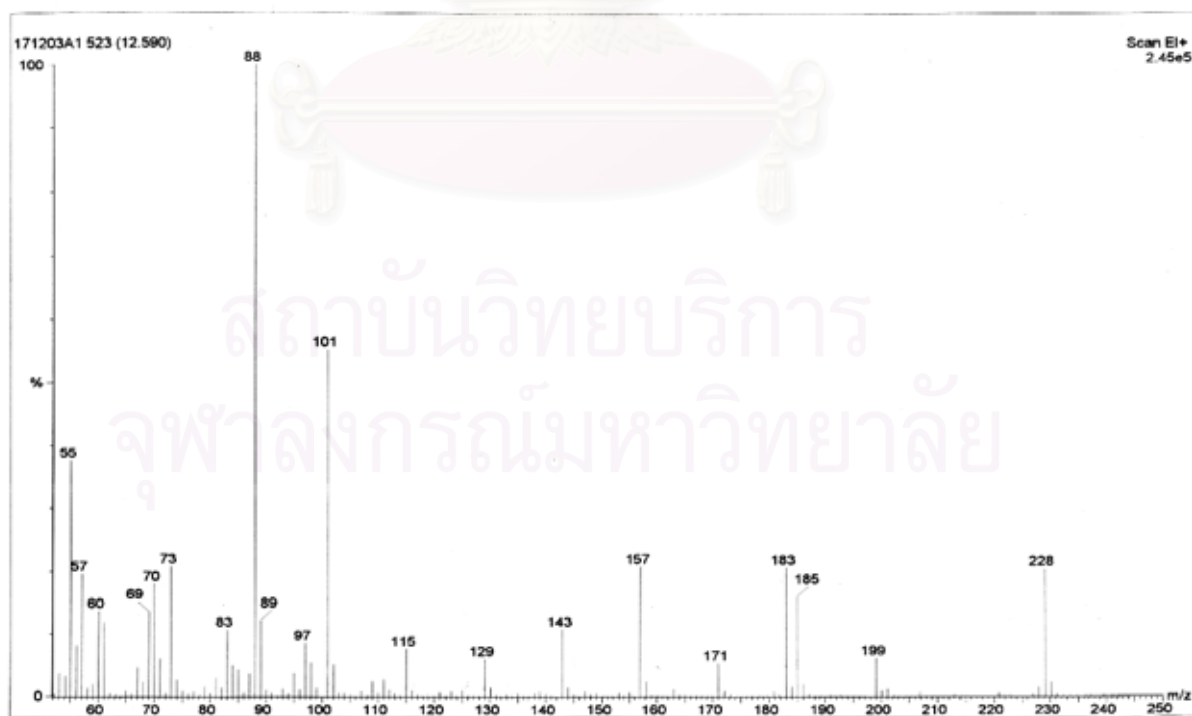


Figure B4 Mass spectrum of coconut oil ethyl ester at retention time of 12.59 min.

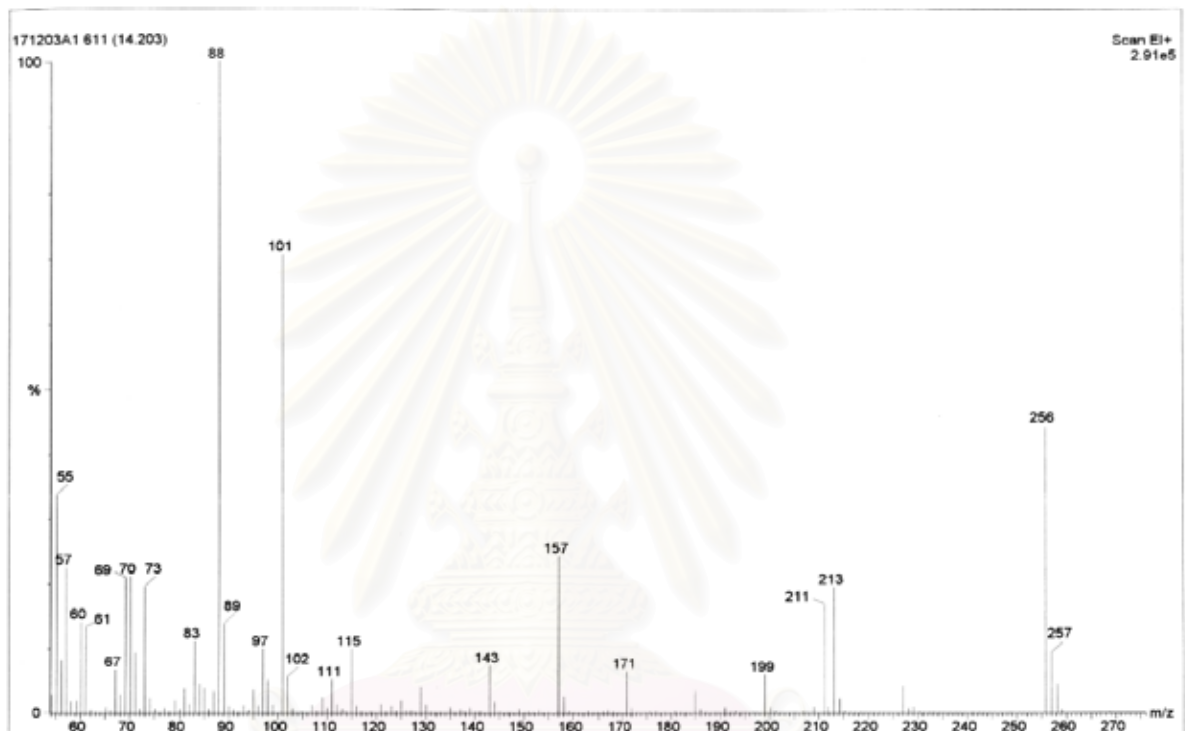


Figure B5 Mass spectrum of coconut oil ethyl ester at retention time of 14.20 min.

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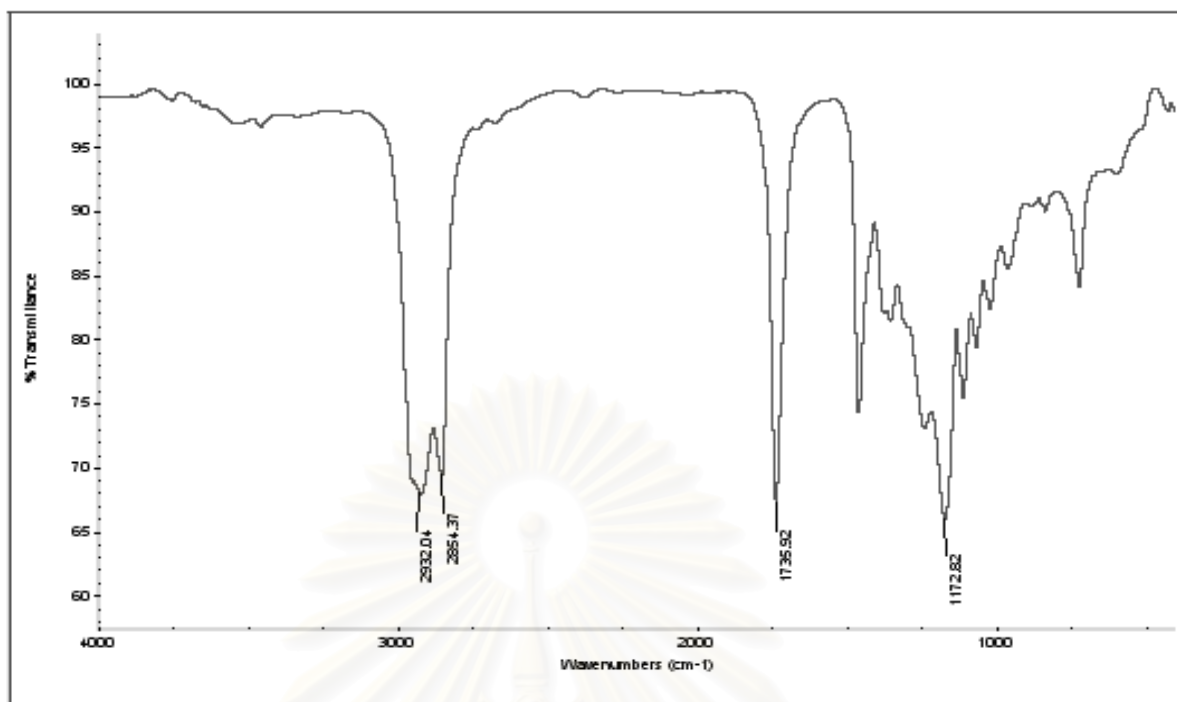


Figure B6 FTIR spectrum of coconut oil butyl ester (NaCl)

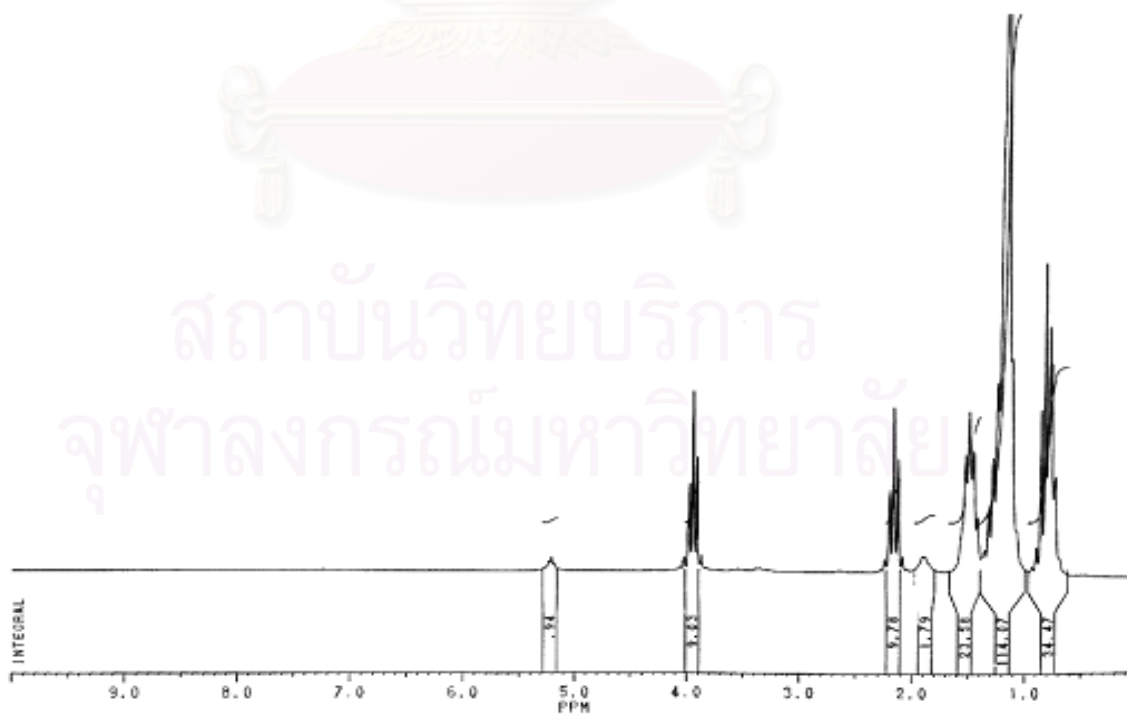


Figure B7 ¹H-NMR spectrum of coconut oil butyl ester (CDCl₃)

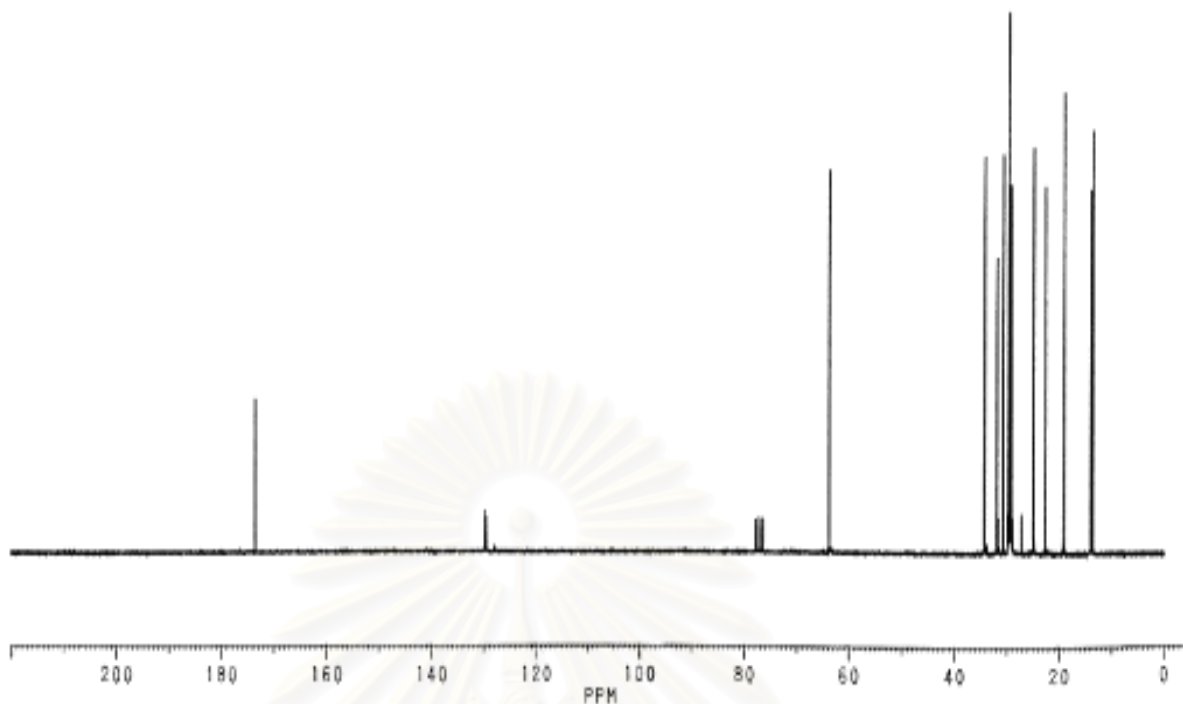


Figure B8 $^{13}\text{C-NMR}$ spectrum of coconut oil butyl ester (CDCl_3)

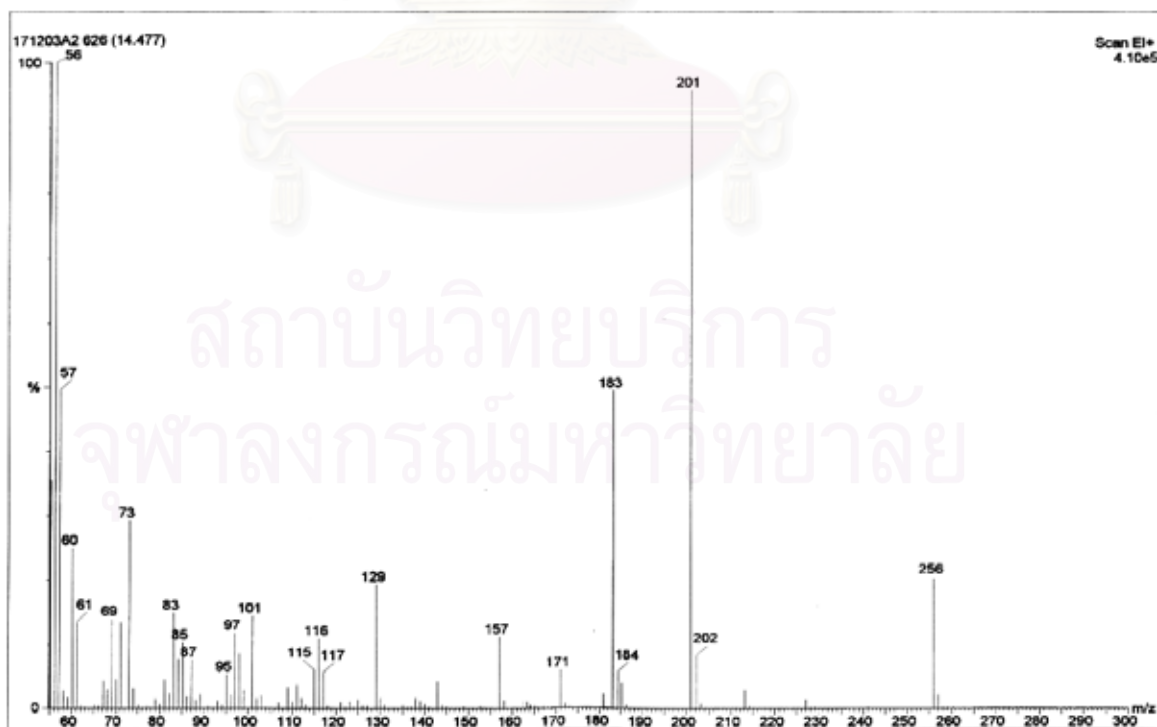


Figure B9 Mass spectrum of coconut oil butyl ester at retention time of 14.47 min.

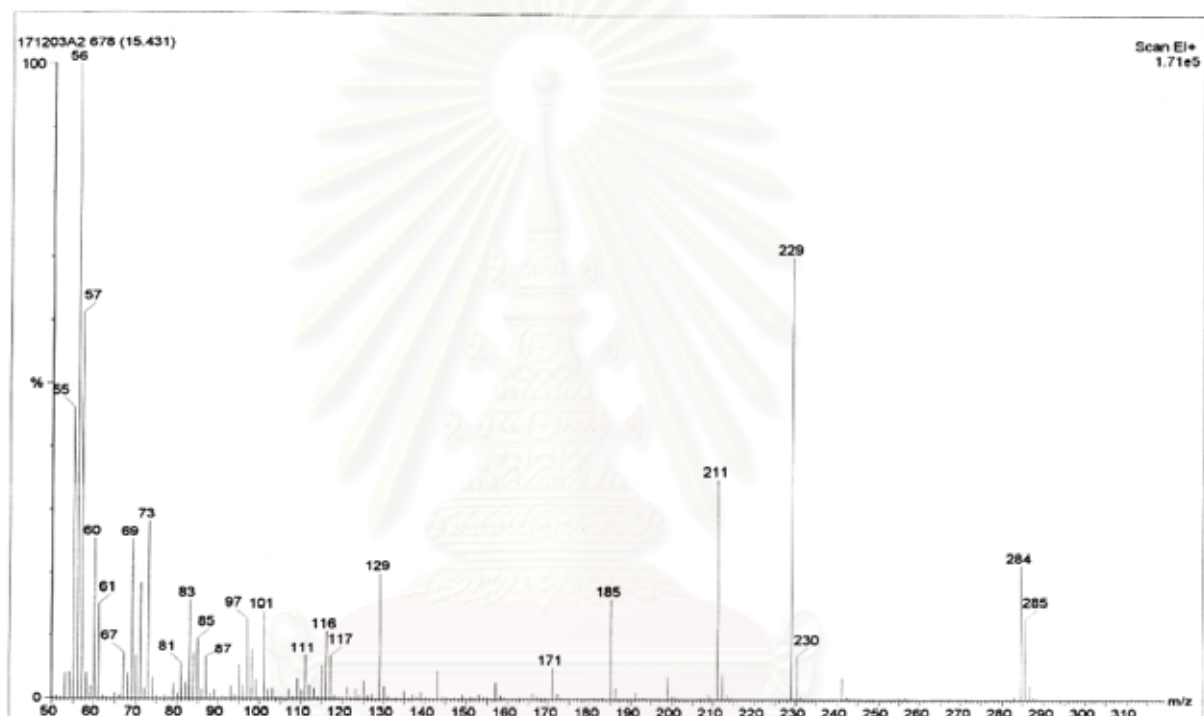


Figure B10 Mass spectrum of coconut oil butyl ester at retention time of 15.43 min.

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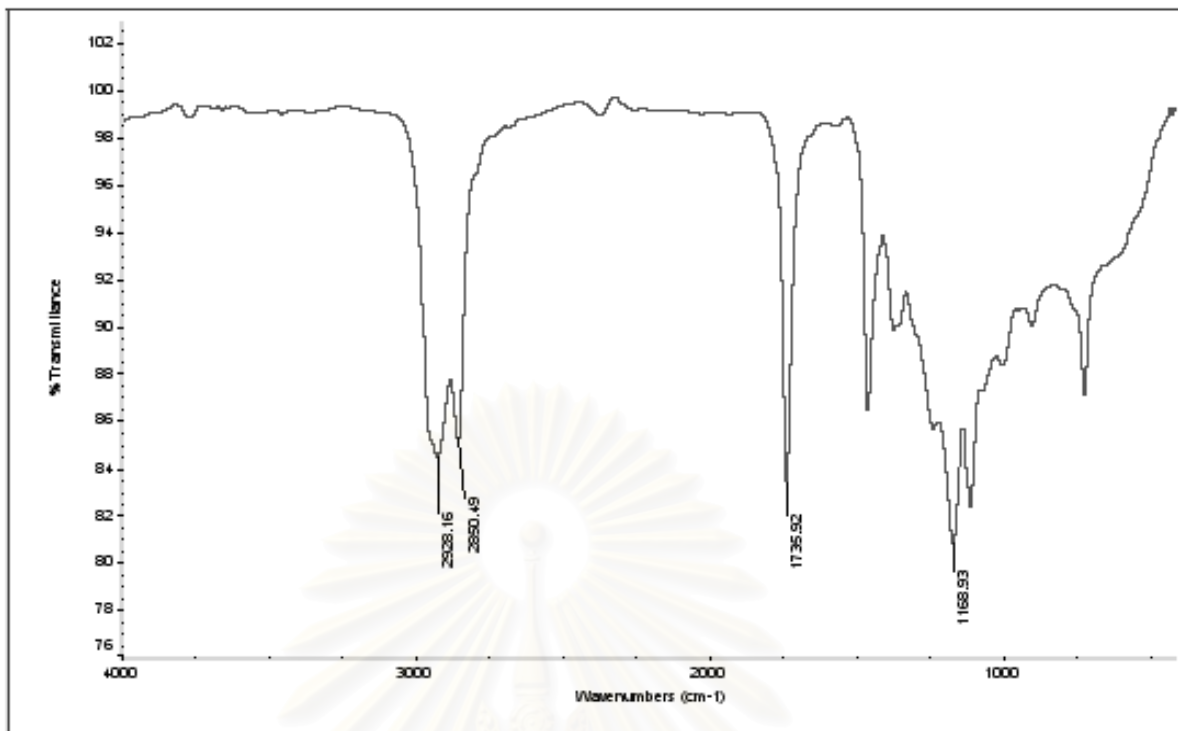


Figure B11 FTIR spectrum of coconut oil hexyl ester (NaCl)

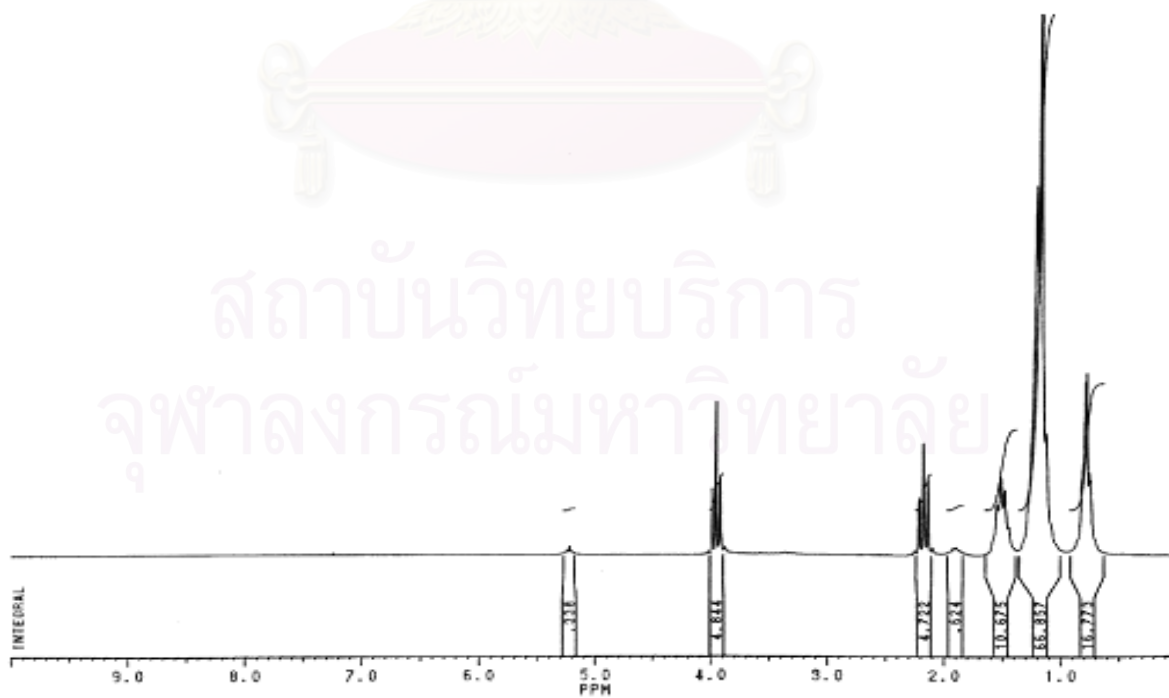


Figure B12 ¹H-NMR spectrum of coconut oil hexyl ester (CDCl₃)

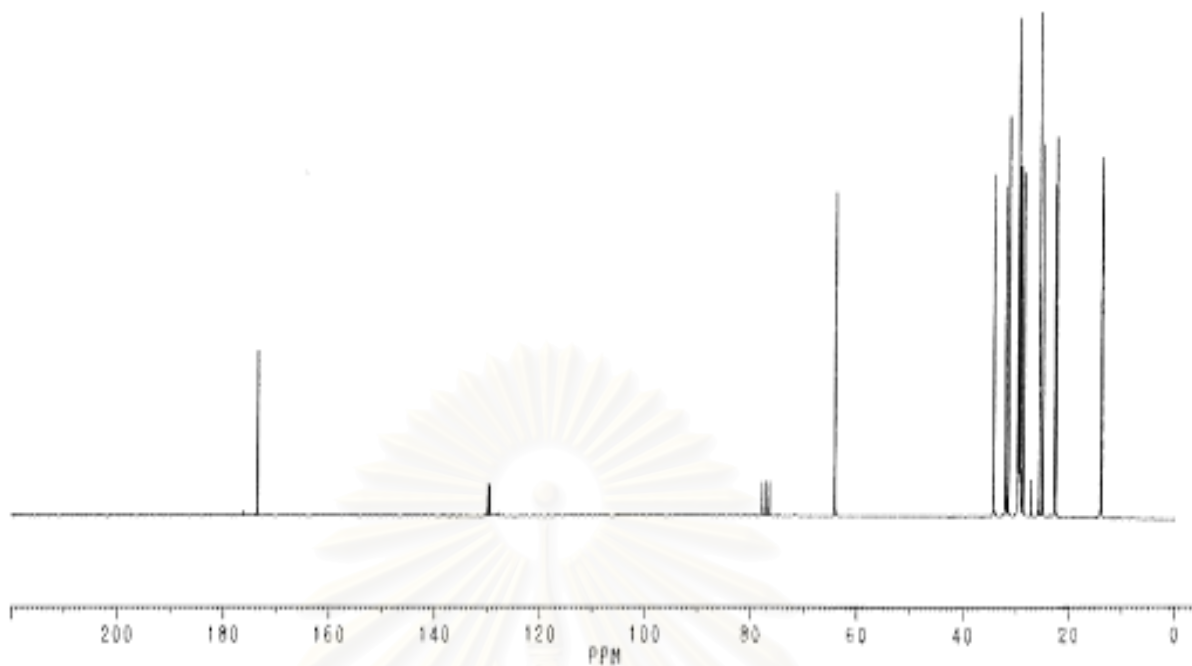


Figure B13 ^{13}C -NMR spectrum of coconut oil hexyl ester (CDCl_3)

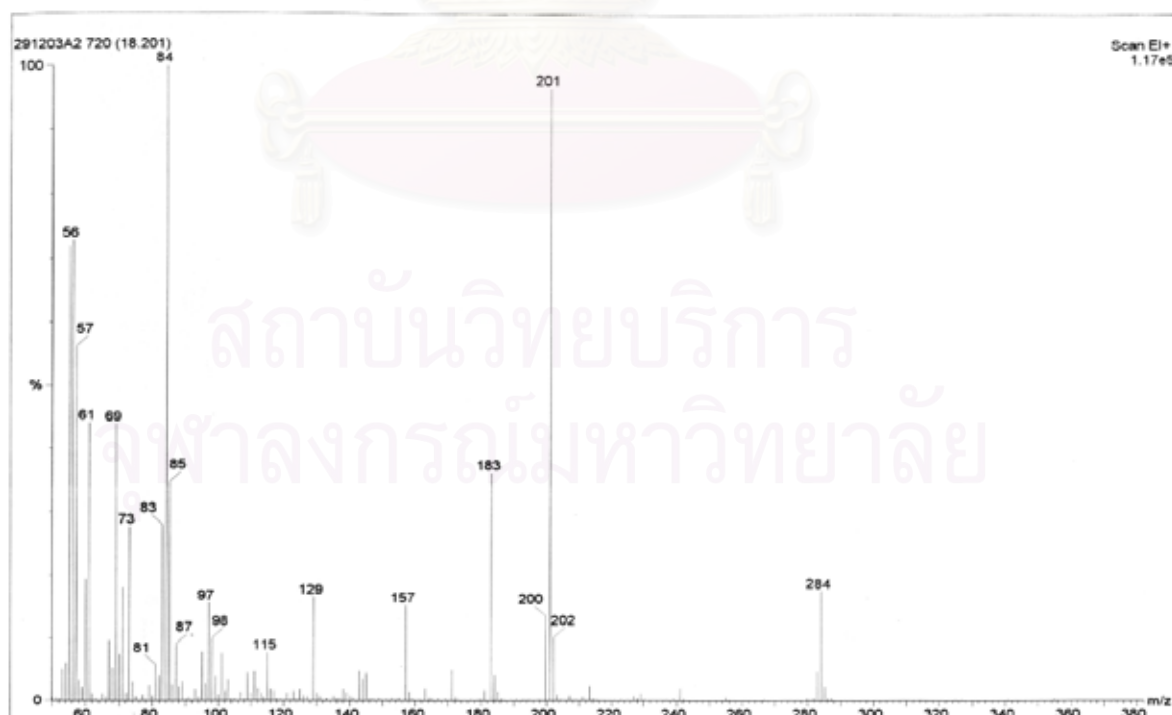


Figure B14 Mass spectrum of coconut oil hexyl ester at retention time of 18.20 min.

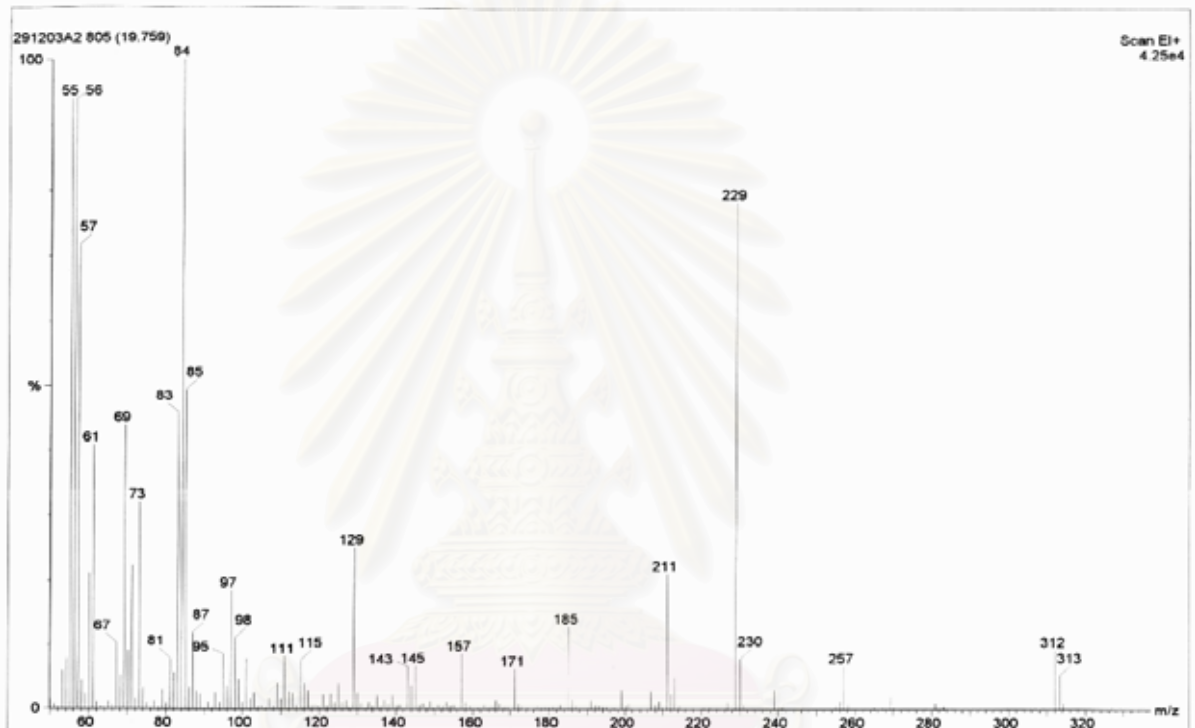


Figure B15 Mass spectrum of coconut oil hexyl ester at retention time of 19.75 min.

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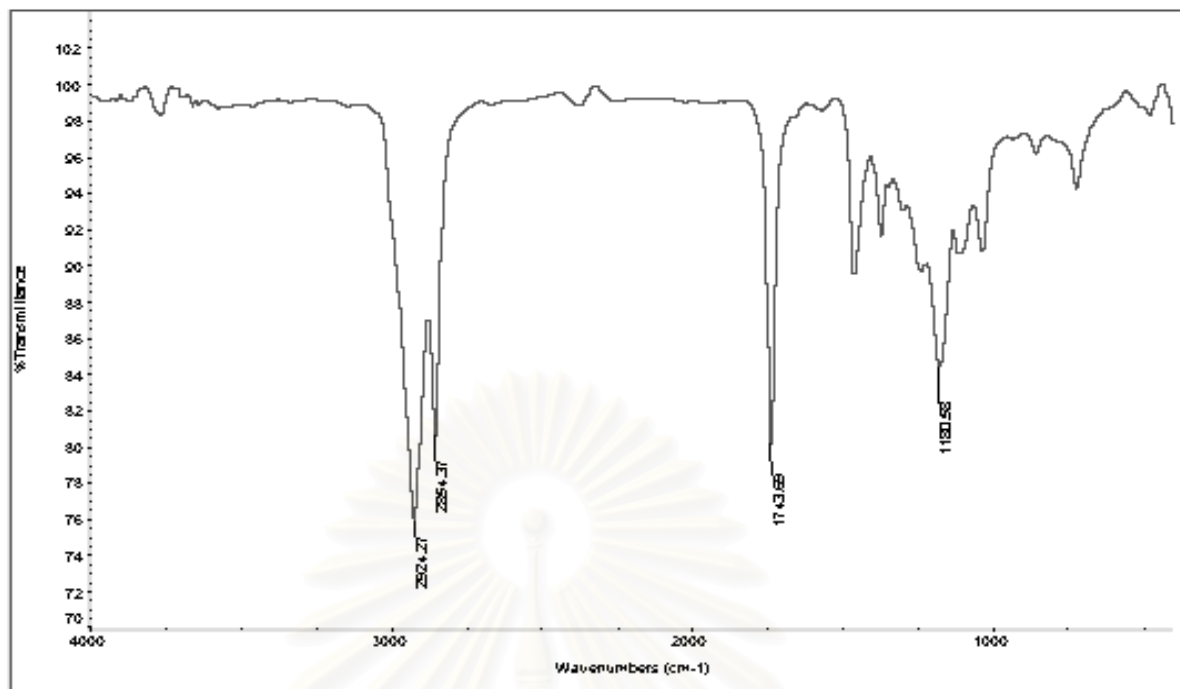


Figure B16 FTIR spectrum of palm oil ethyl ester (NaCl)

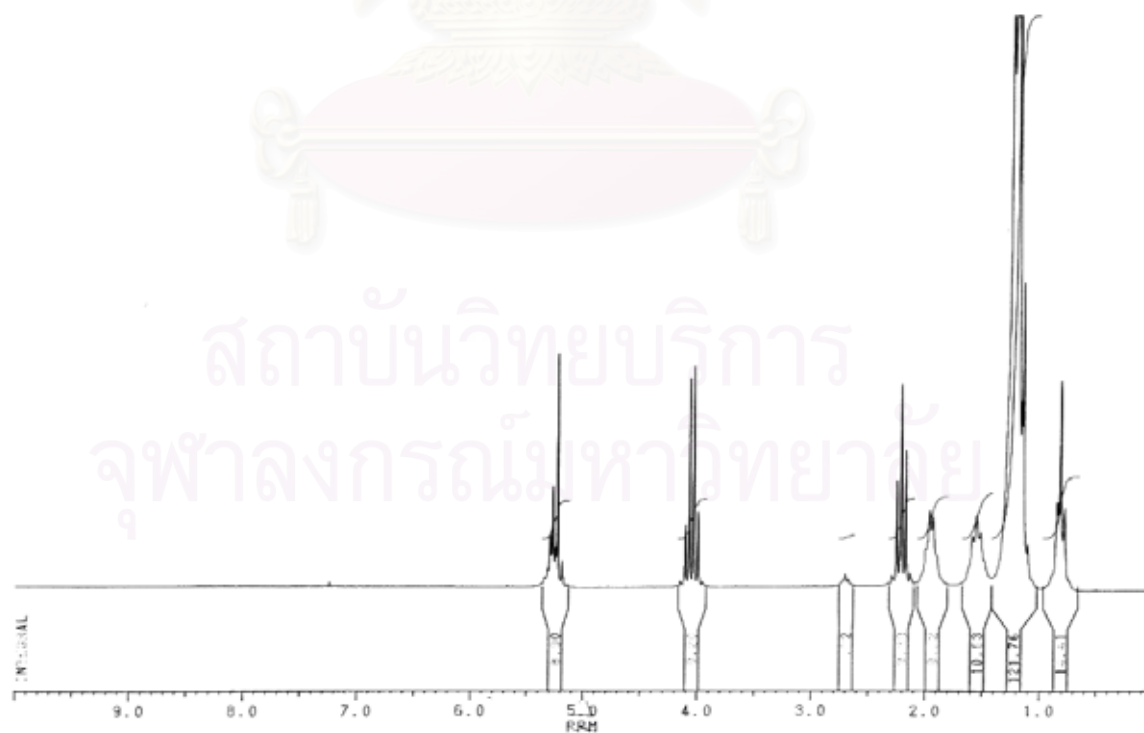


Figure B17 ¹H-NMR spectrum of palm oil ethyl ester (CDCl₃)

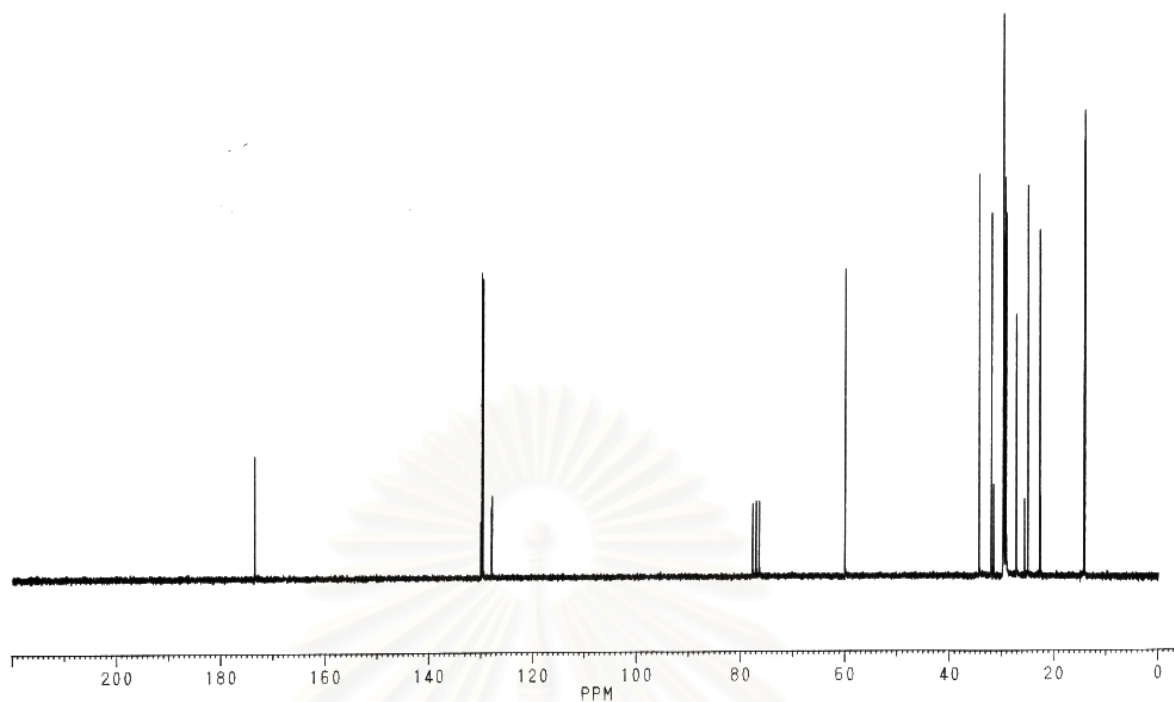


Figure B18 ^{13}C -NMR spectrum of palm oil ethyl ester (CDCl_3)



Figure B19 Mass spectrum of palm oil ethyl ester at retention time of 14.51 min.

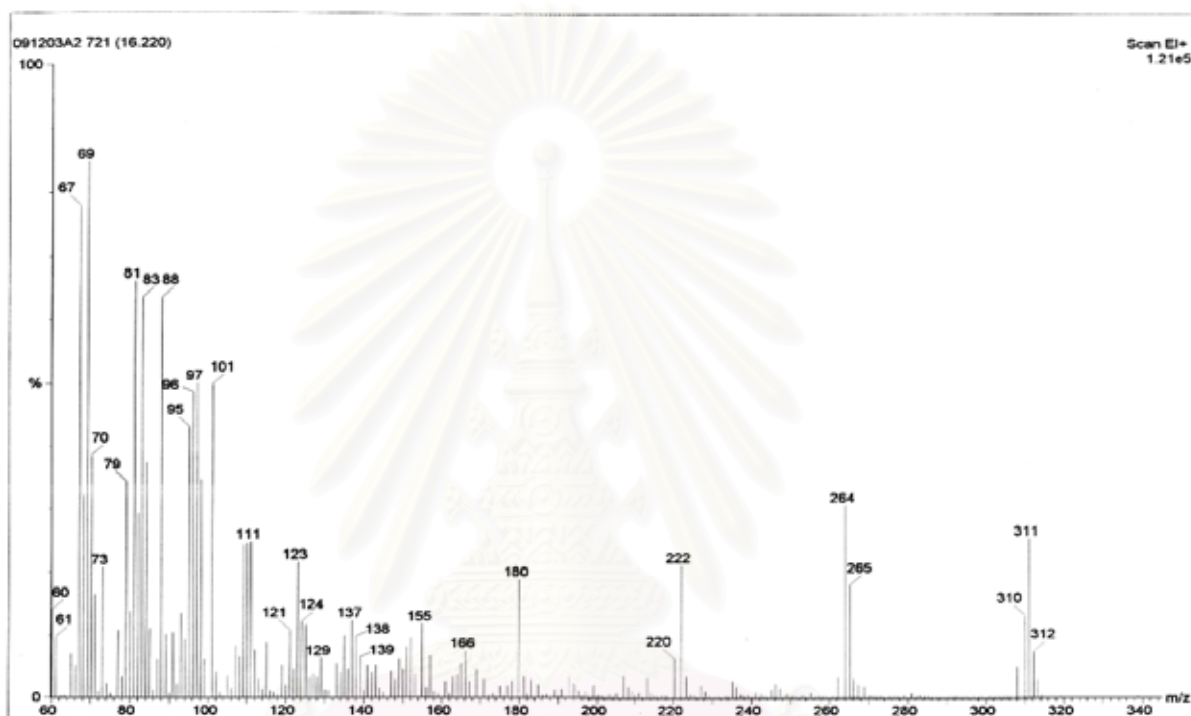


Figure B20 Mass spectrum of palm oil ethyl ester at retention time of 16.22 min.

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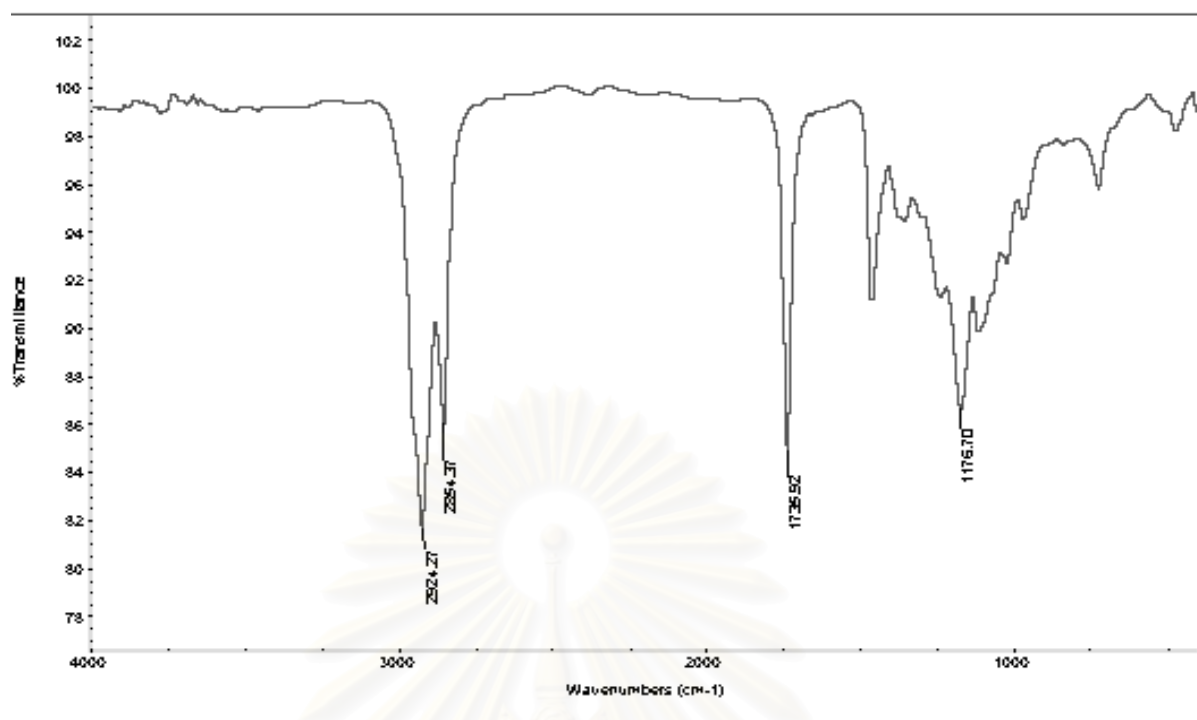


Figure B21 FTIR spectrum of palm oil butyl ester (NaCl)

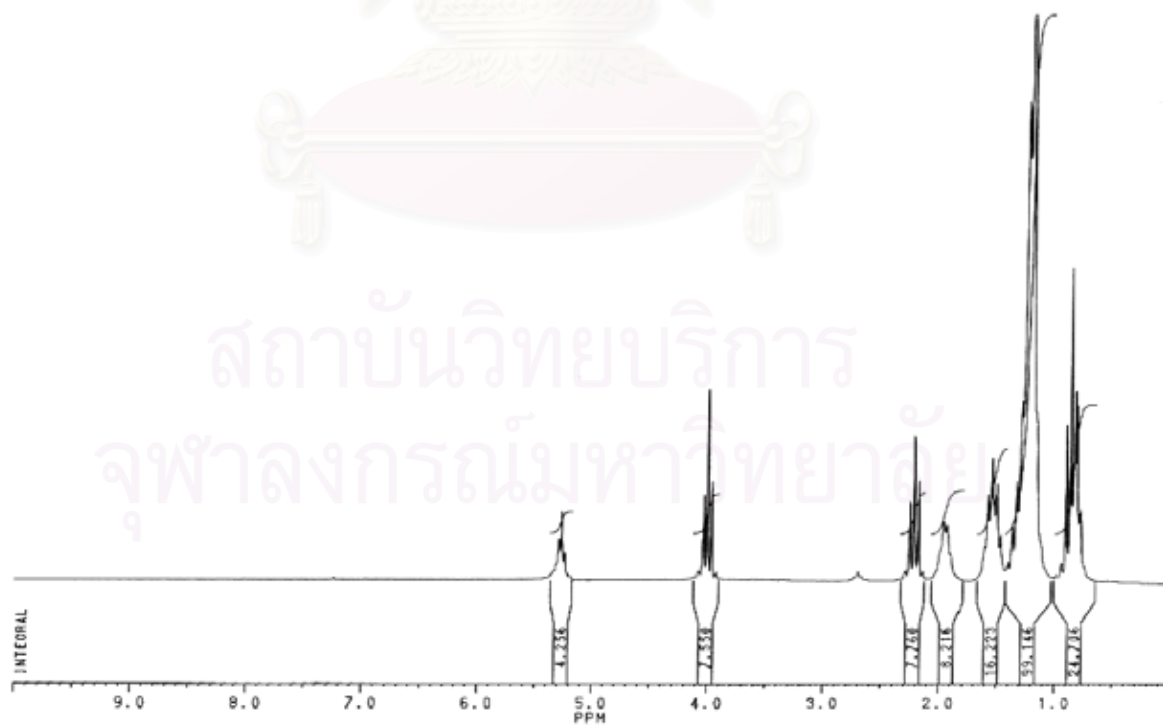


Figure B22 ¹H-NMR spectrum of palm oil butyl ester (CDCl₃)

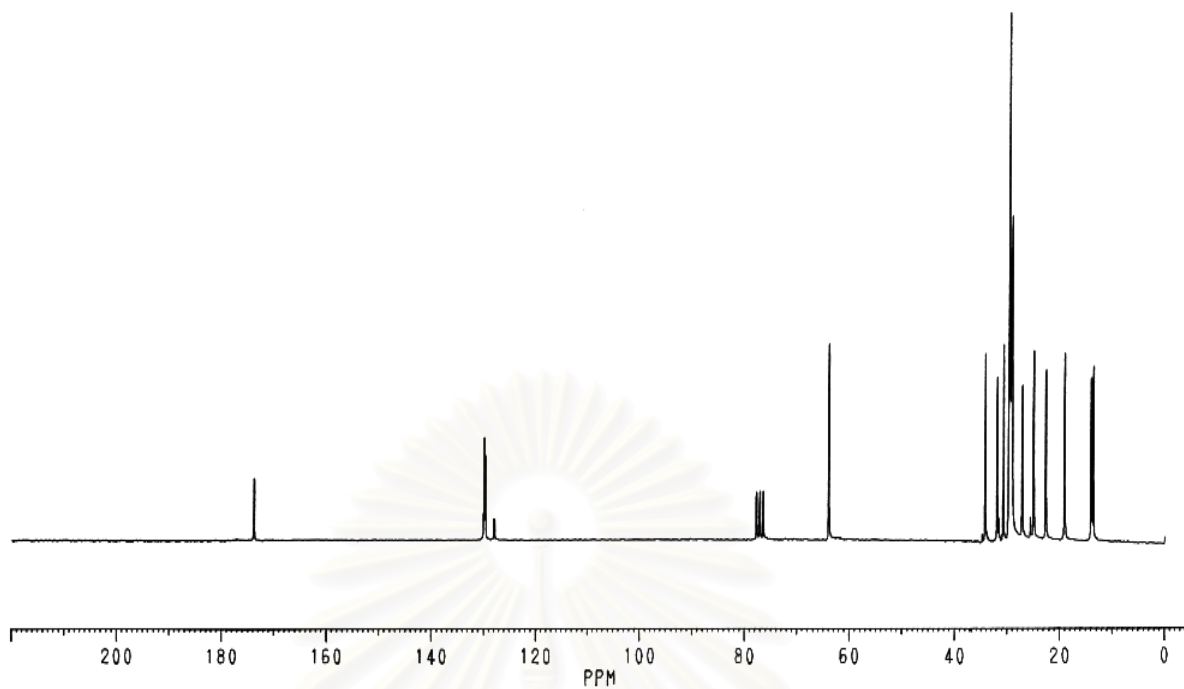


Figure B23 ^{13}C -NMR spectrum of palm oil butyl ester (CDCl_3)

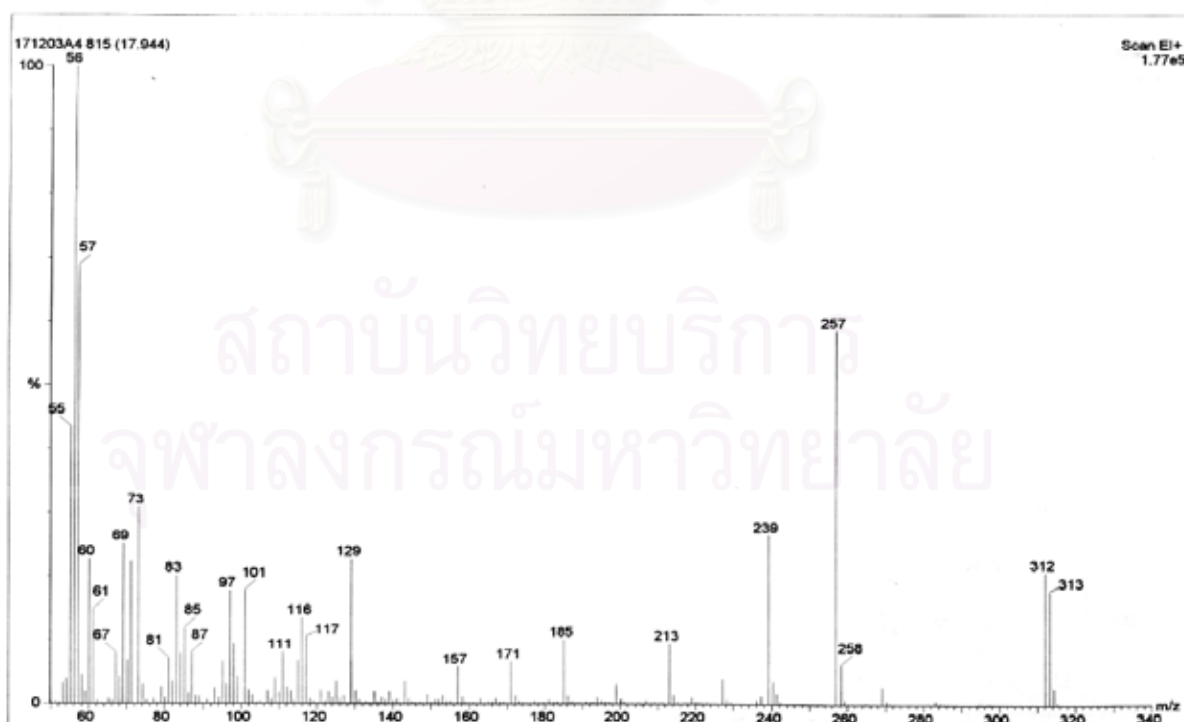


Figure B24 Mass spectrum of palm oil butyl ester at retention time of 17.94 min.

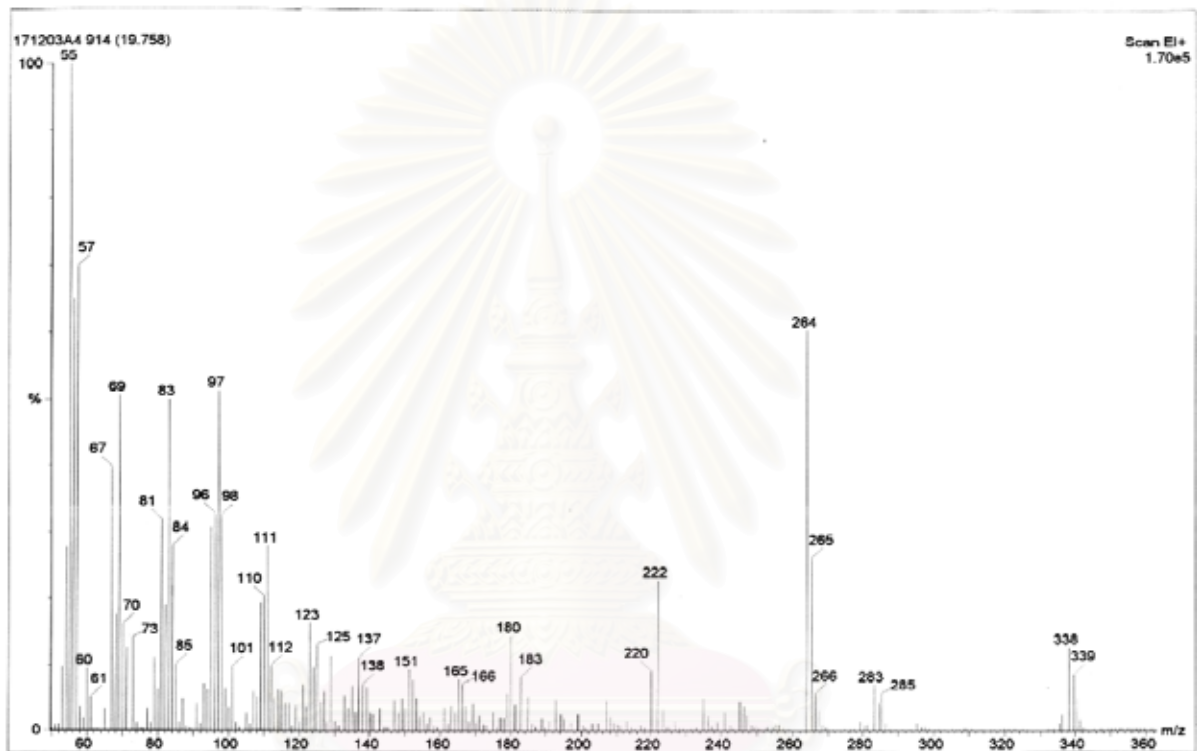


Figure B25 Mass spectrum of palm oil butyl ester at retention time of 19.75 min.

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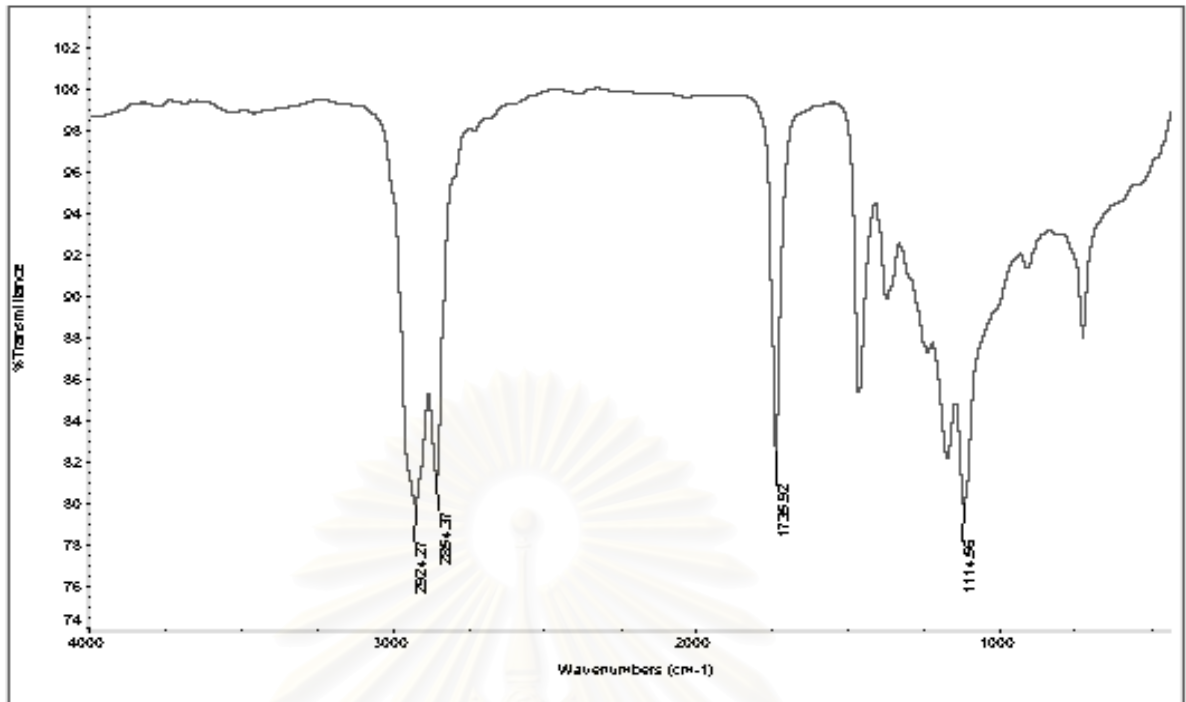


Figure B26 FTIR spectrum of palm oil hexyl ester (NaCl)

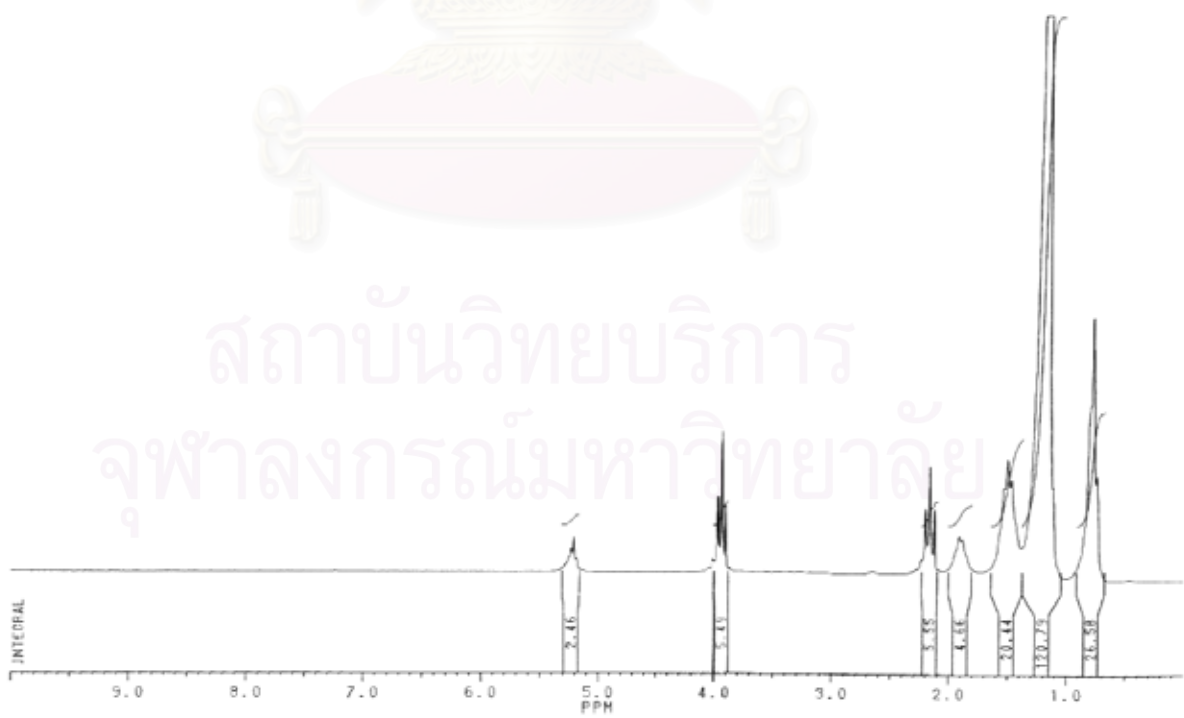


Figure B27 ¹H-NMR spectrum of palm oil hexyl ester (CDCl₃)

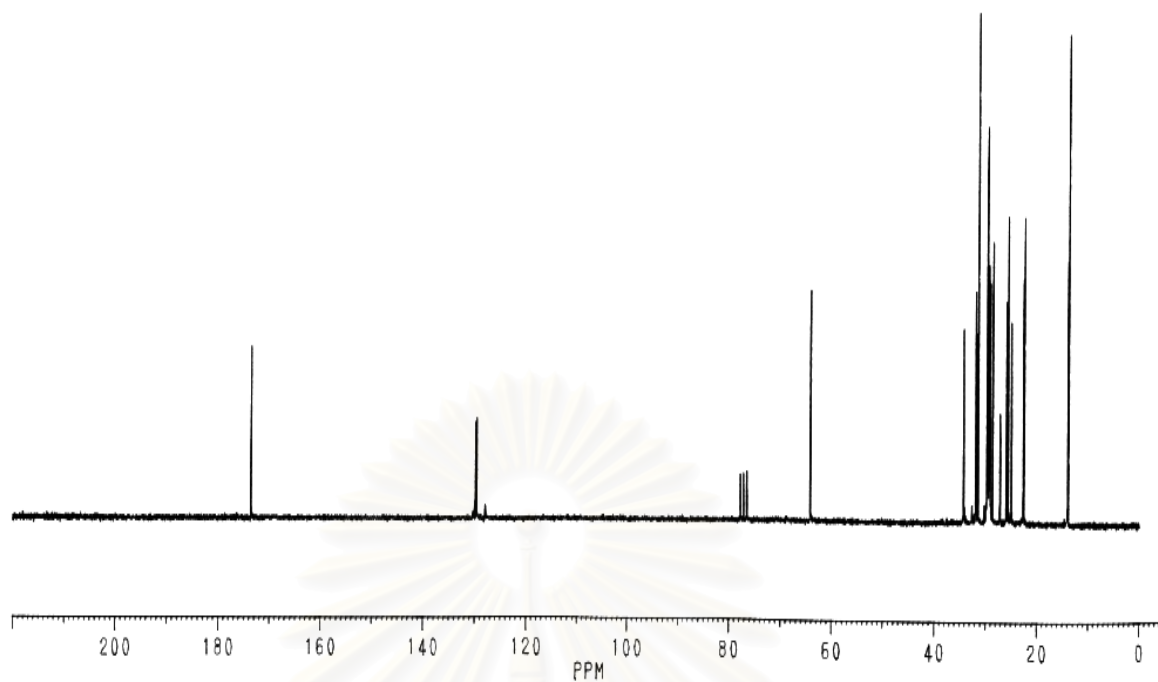


Figure B28 ^{13}C -NMR spectrum of palm oil hexyl ester (CDCl_3)

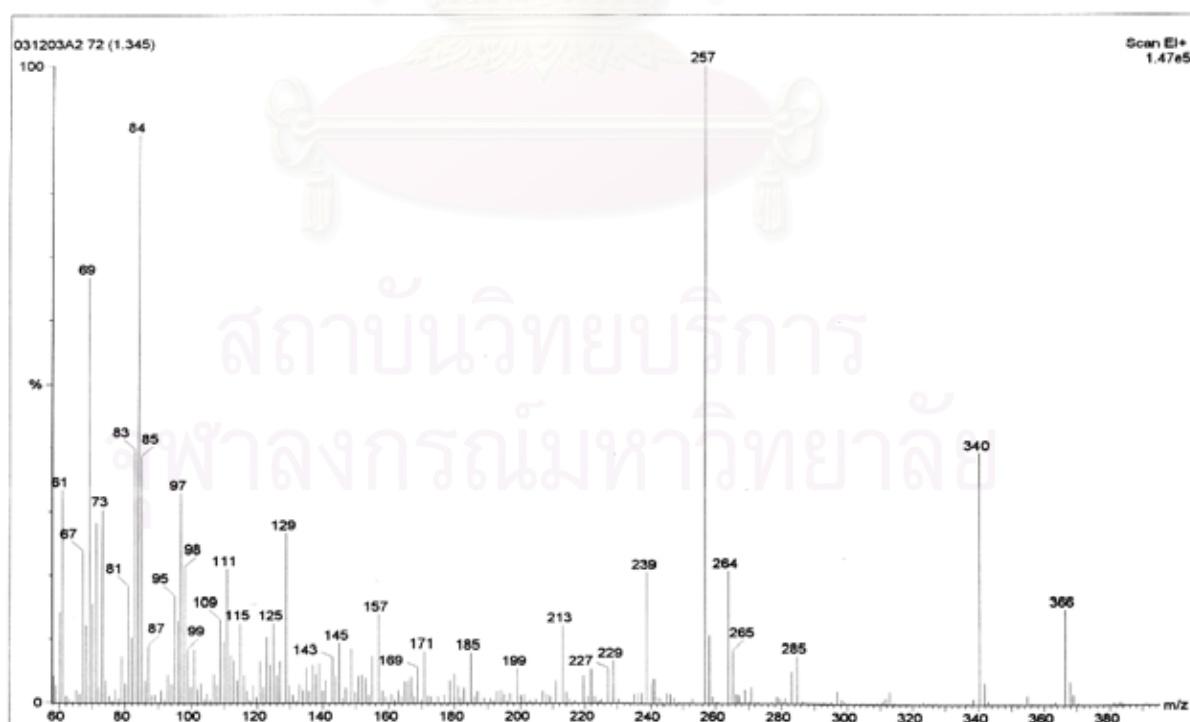


Figure B29 Mass spectrum of palm oil hexyl ester at retention time of 1.34 min.

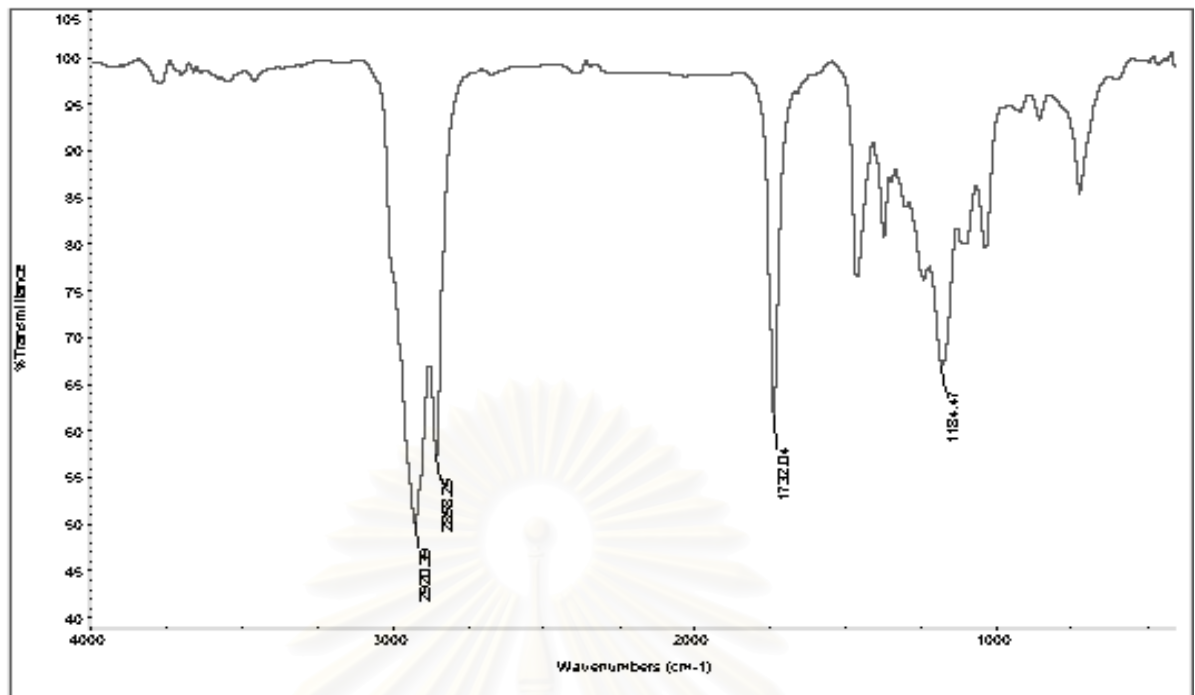


Figure B30 FTIR spectrum of rice bran oil ethyl ester (NaCl)

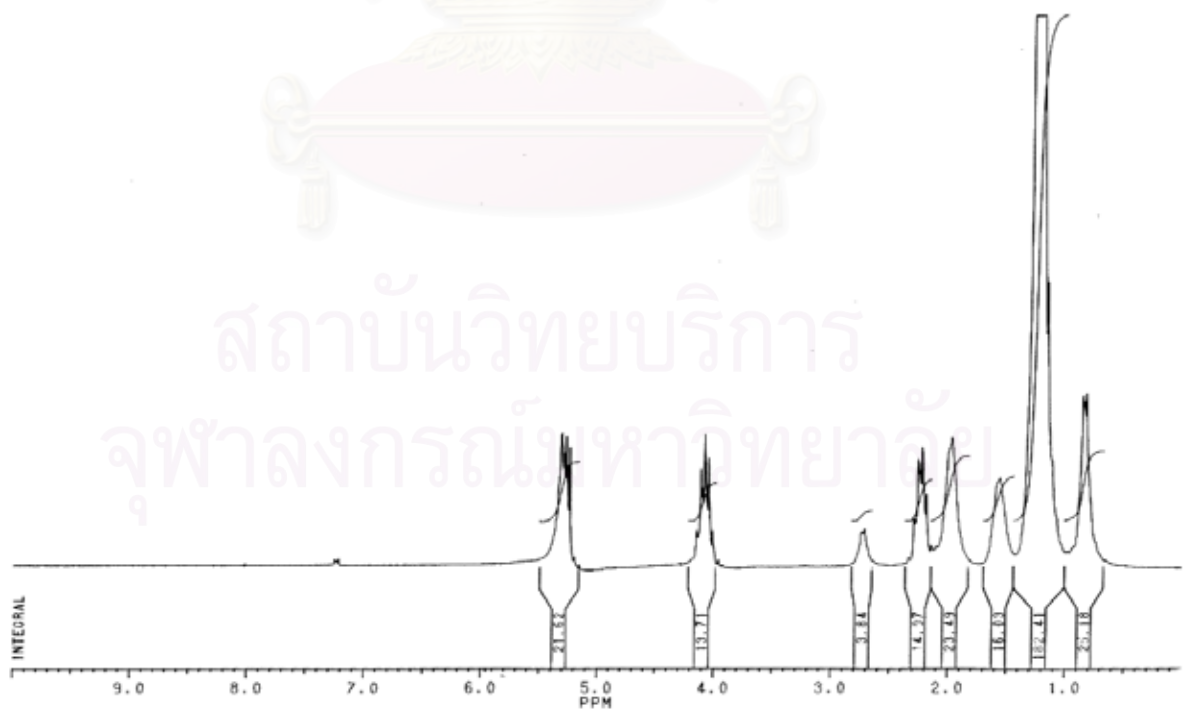


Figure B31 ¹H-NMR spectrum of rice bran oil ethyl ester (CDCl₃)

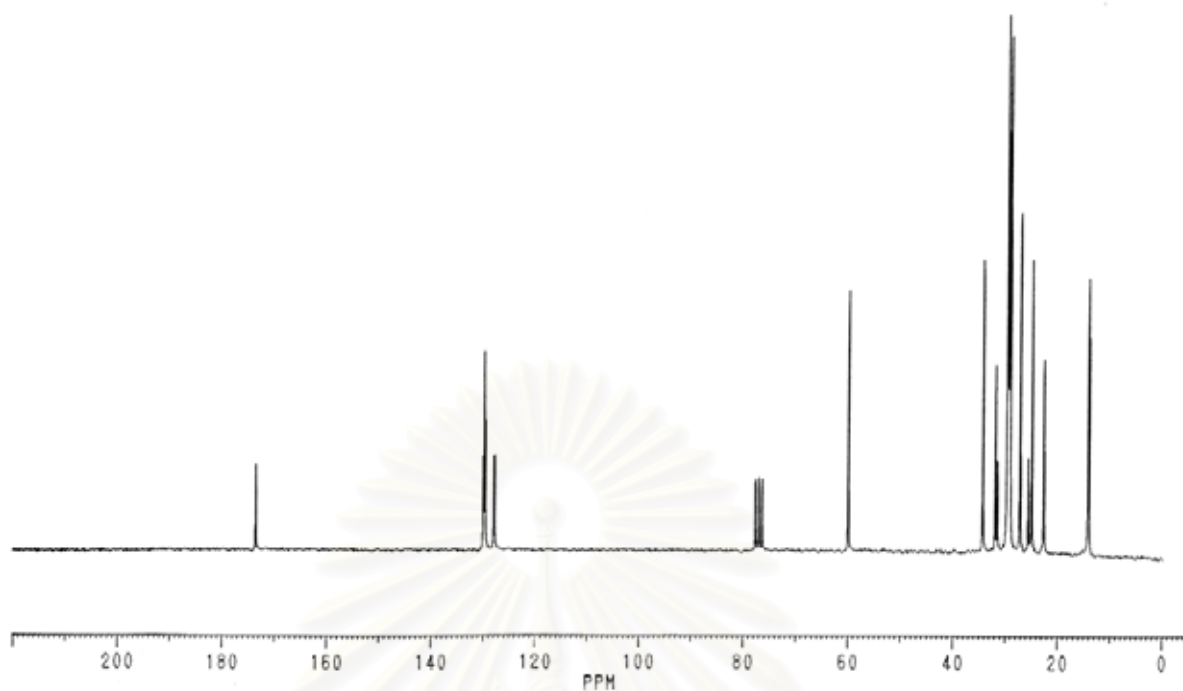


Figure B32 ^{13}C -NMR spectrum of rice bran oil ethyl ester (CDCl_3)

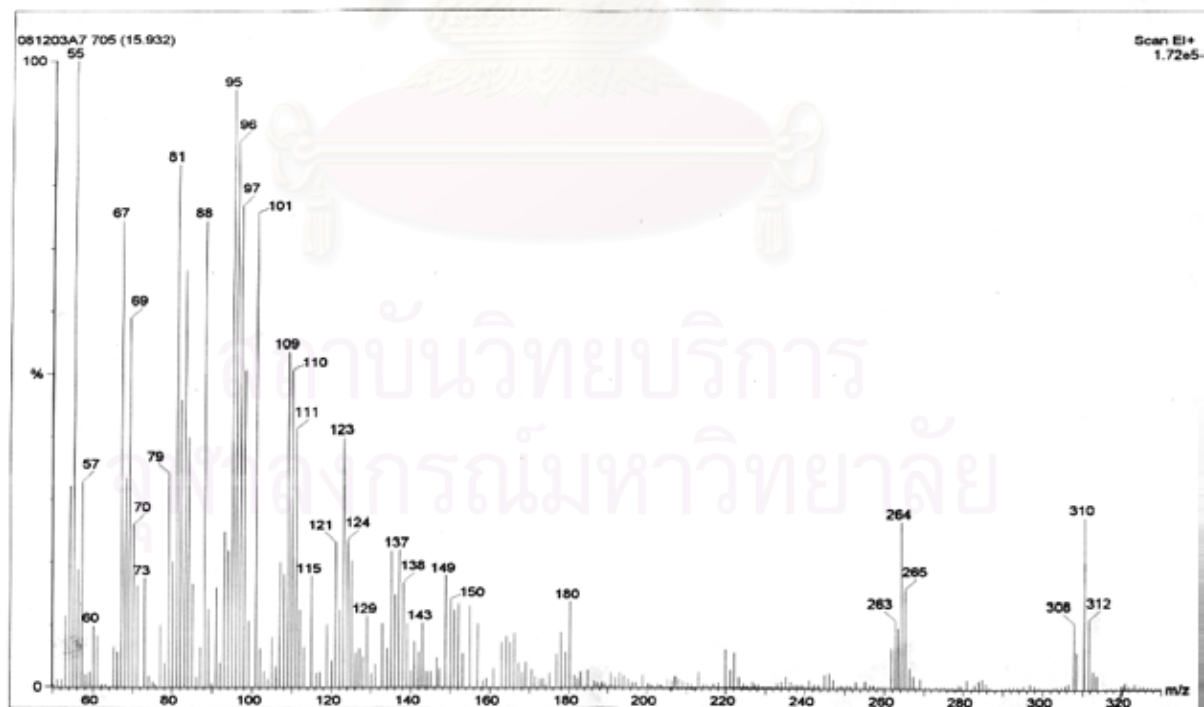


Figure B33 Mass spectrum of rice bran oil ethyl ester at retention time of 15.93 min.

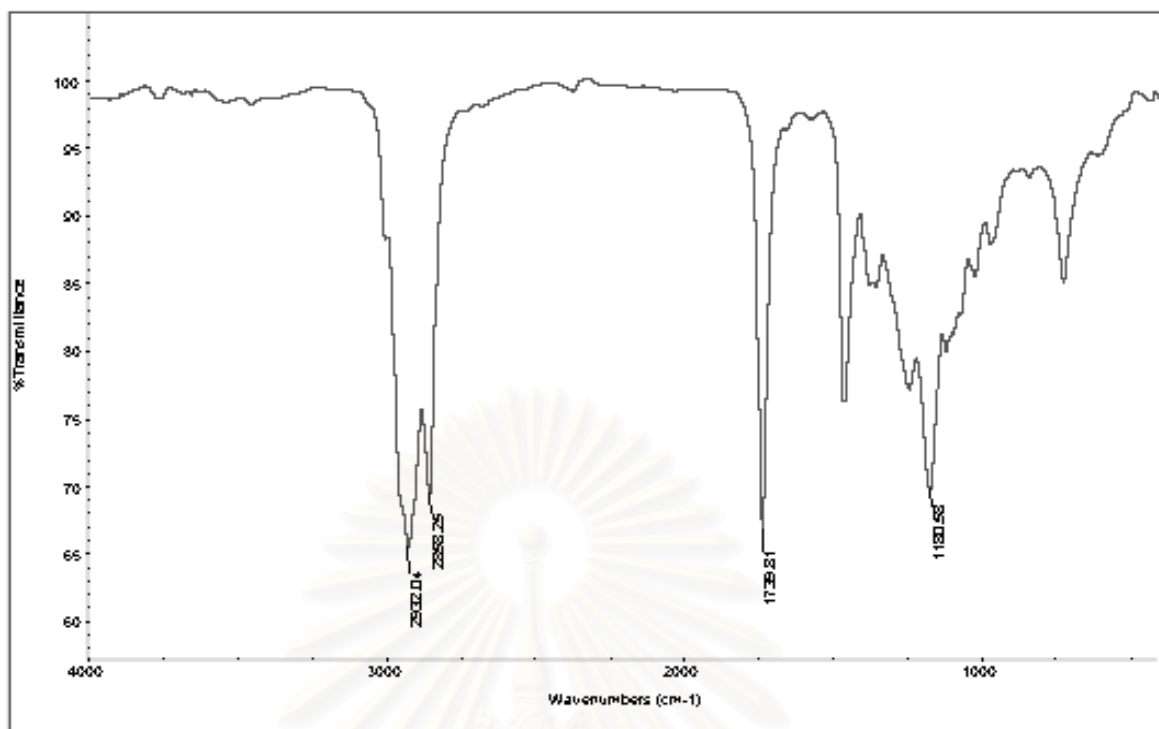


Figure B34 FTIR spectrum of rice bran oil butyl ester (NaCl)

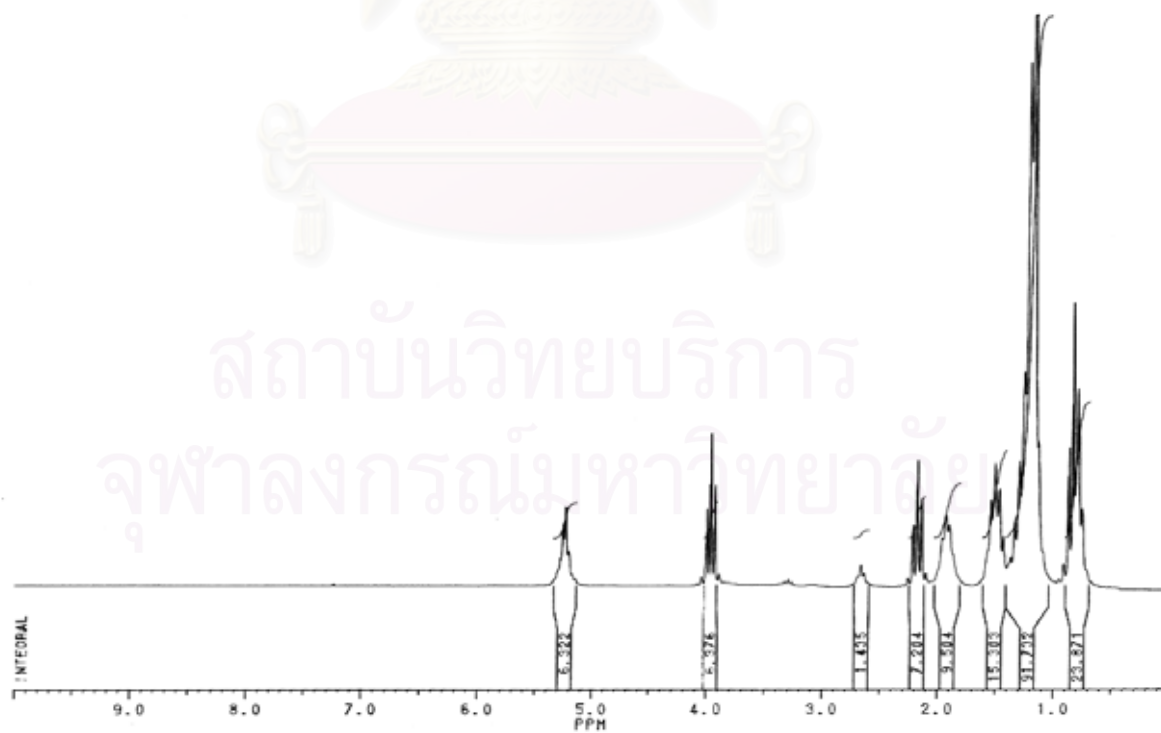


Figure B35 ¹H-NMR spectrum of rice bran oil butyl ester (CDCl₃)

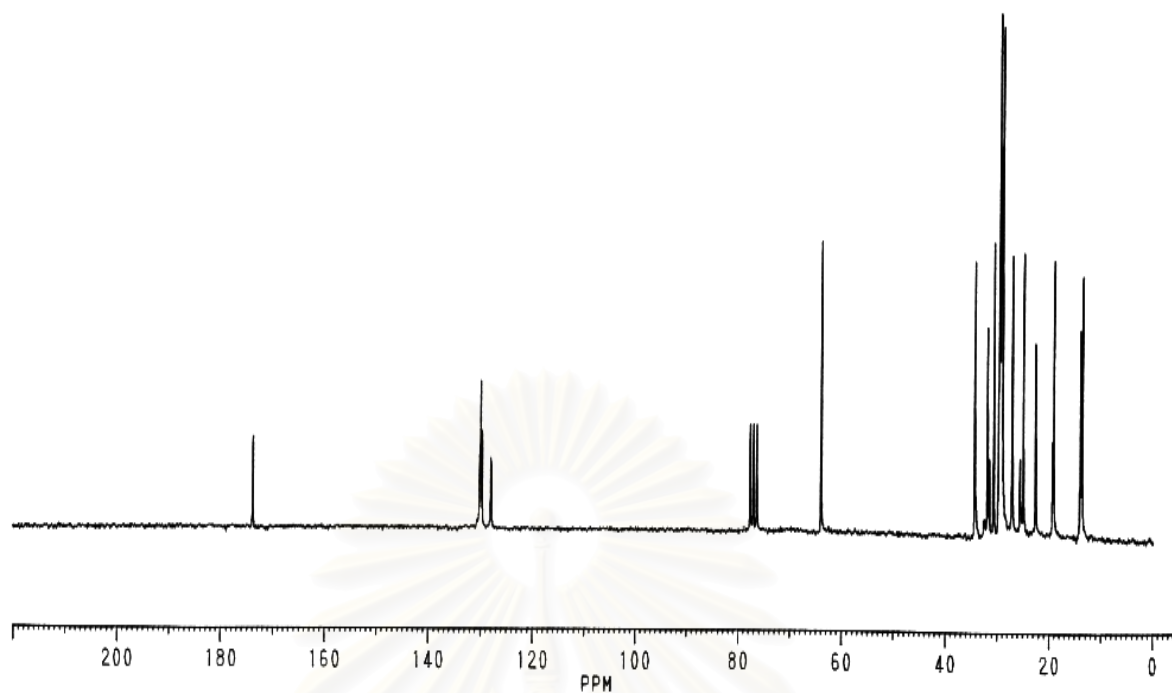


Figure B36 ^{13}C -NMR spectrum of rice bran oil butyl ester (CDCl_3)

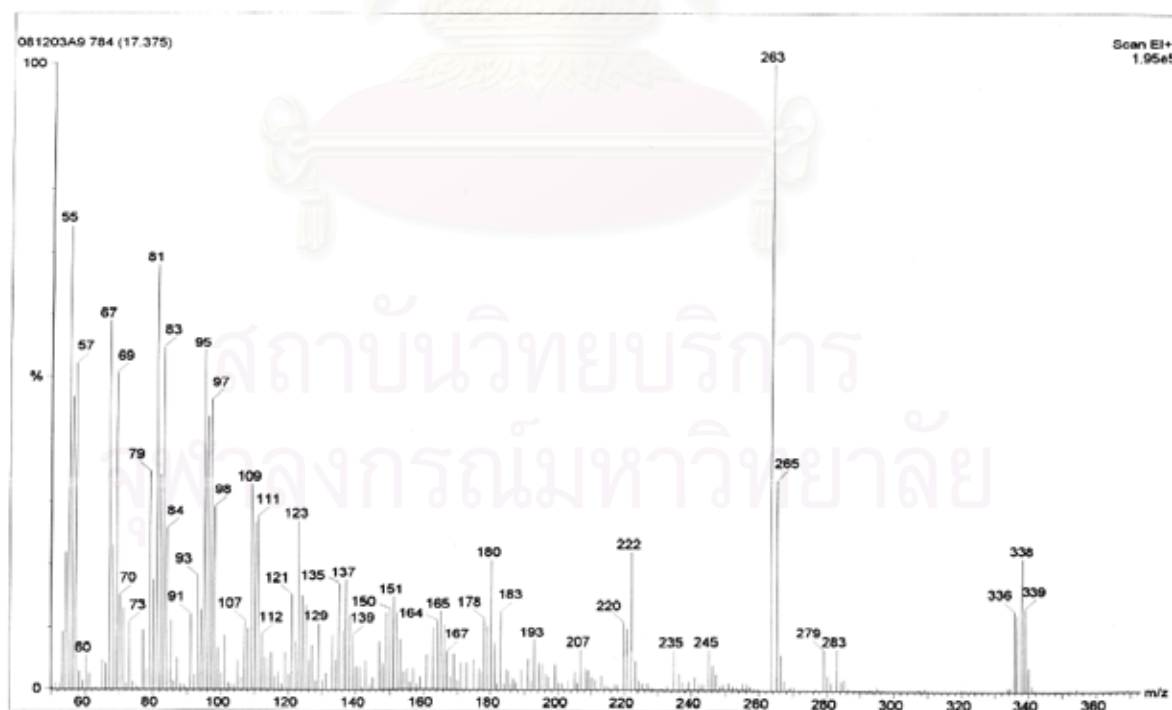


Figure B37 Mass spectrum of rice bran oil butyl ester at retention time of 17.37 min.

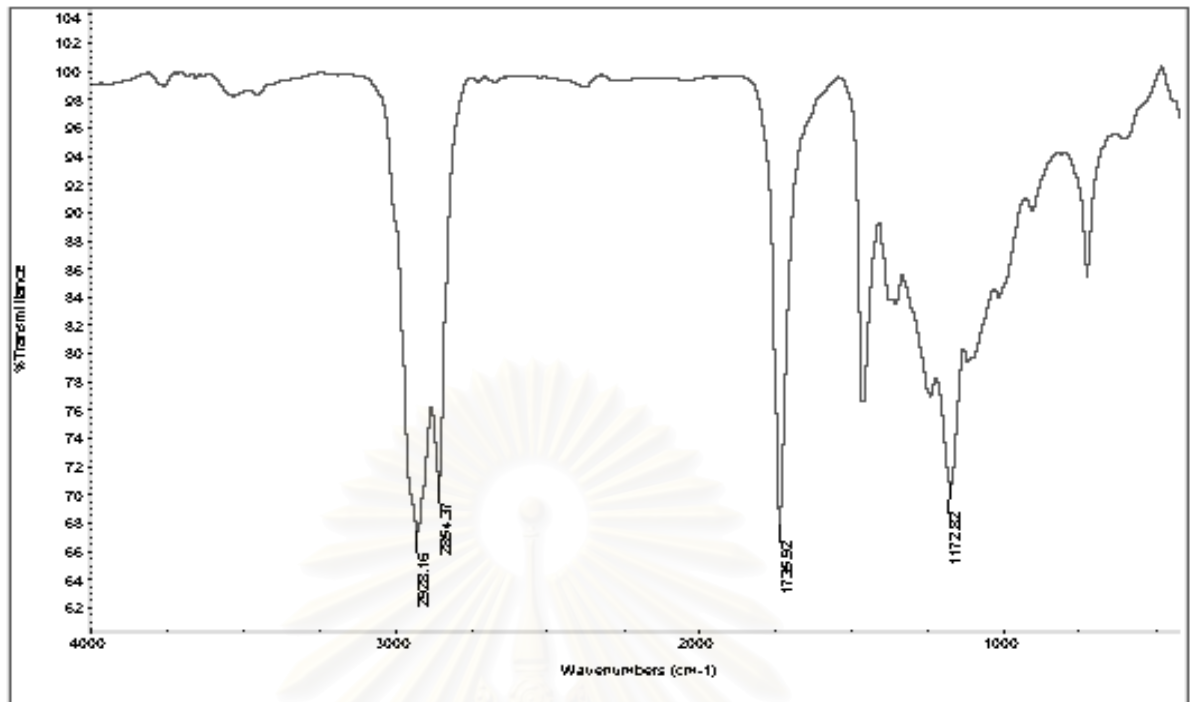


Figure B38 FTIR spectrum of rice bran oil hexyl ester (NaCl)

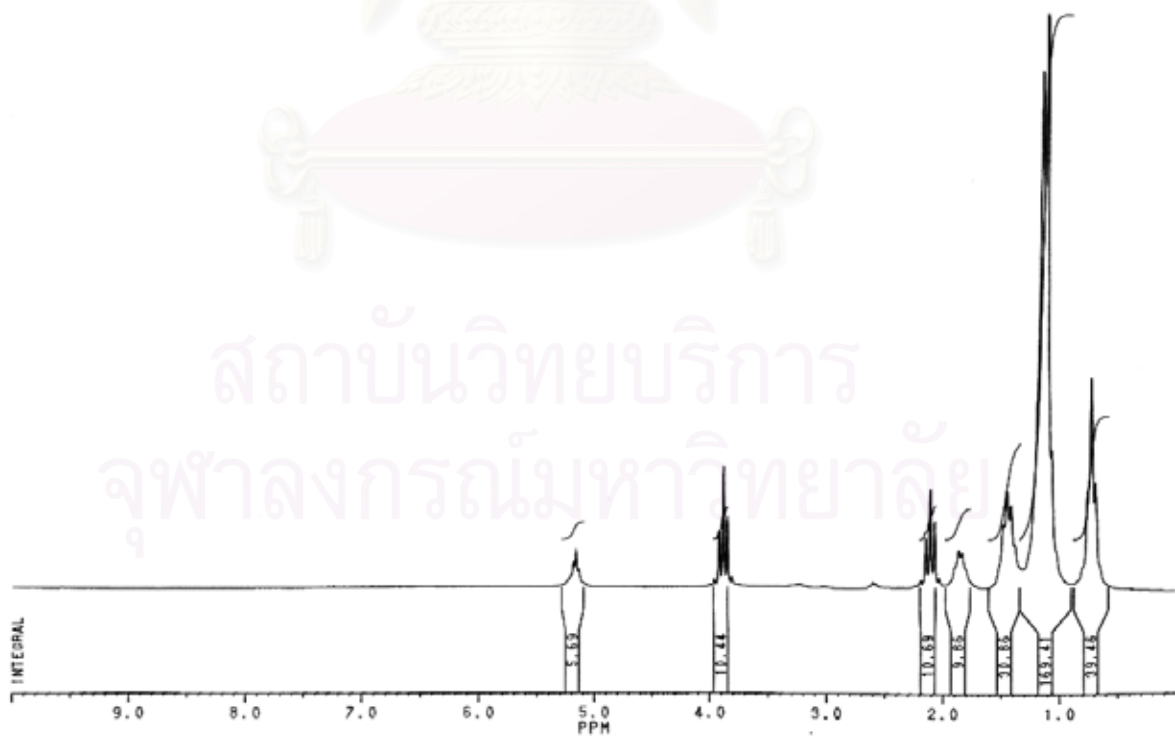


Figure B39 ¹H-NMR spectrum of rice bran oil hexyl ester (CDCl₃)

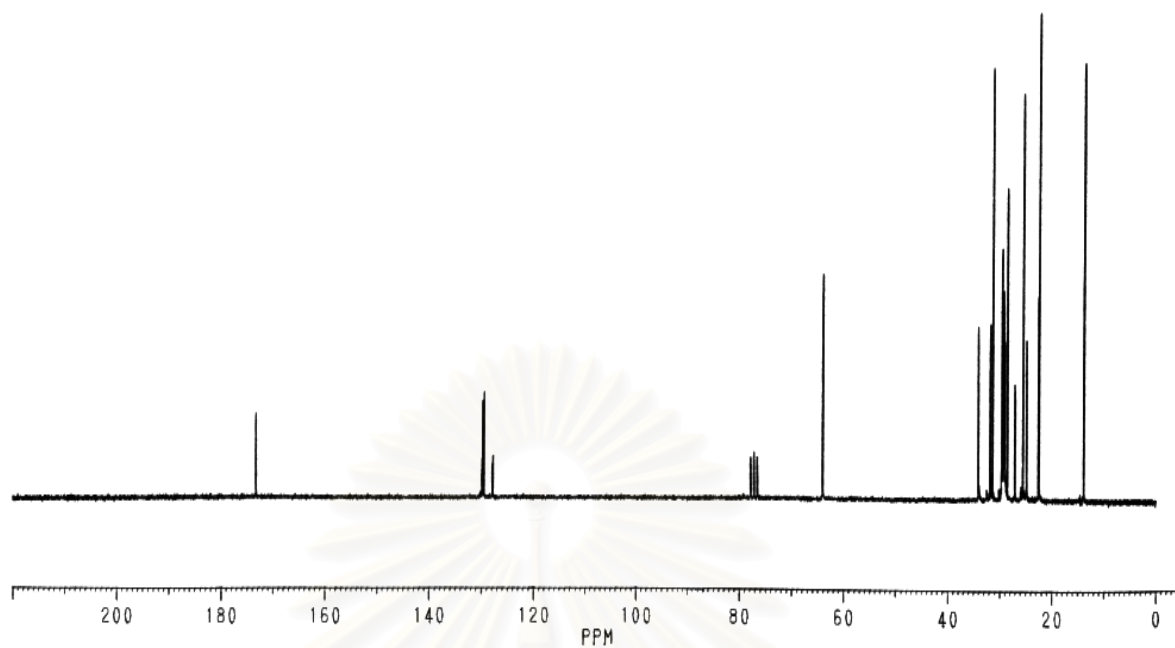


Figure B40 ^{13}C -NMR spectrum of rice bran oil hexyl ester (CDCl_3)

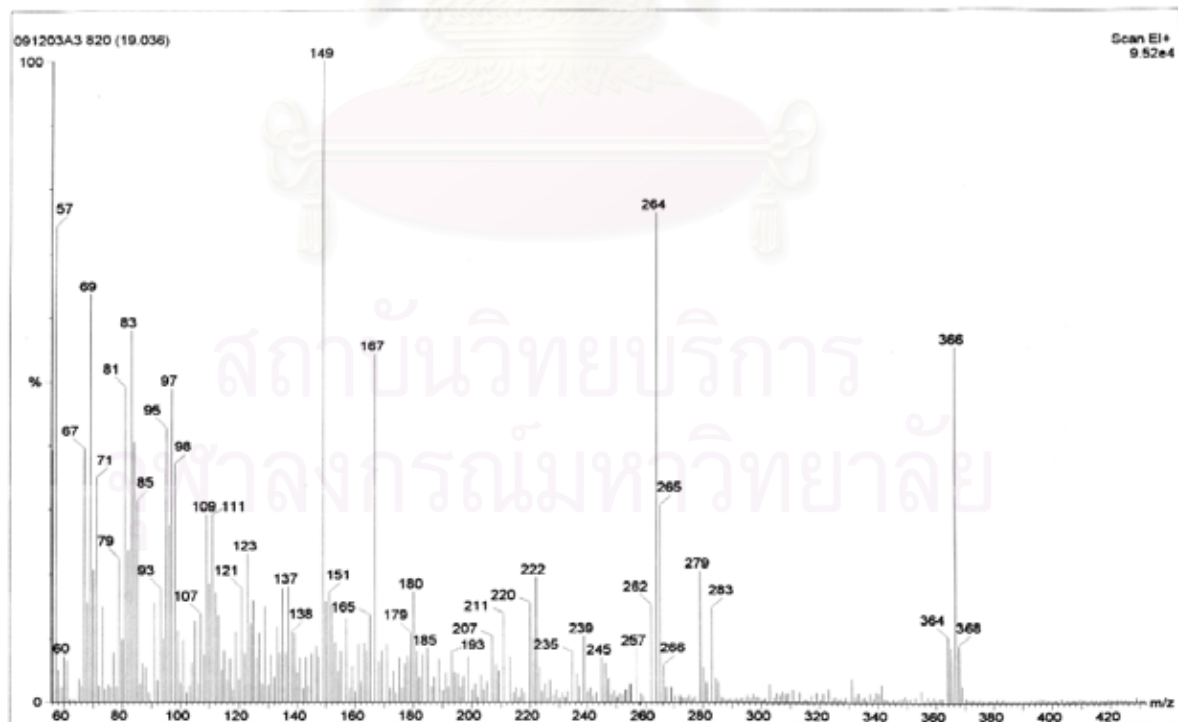


Figure B41 Mass spectrum of rice bran oil hexyl ester at retention time of 19.03 min.

APPENDIX C

SPECIFICATION AND TEST METHOD FOR DIESEL FUEL IN THAILAND

Characteristics	Specification		
	High-speed Engine	Low-speed Engine	Methods
Density at 15.6/15.6°C	0.81	0.92	ASTM D 1286
Cetane number	min 47	min 45	ASTM D 613
or calculated cetane index	min 47	min 45	ASTM D 976
Viscosity at 40°C, cSt	1.8-4.1	max 8.0	ASTM D 445
or at 50°C, cSt		max 6.0	
Pour point, °C	max 10	max 16	ASTM D 97
Sulfur content, % wt.	max 0.25	max 1.5	ASTM D 129
Copper strip corrosion, number	max 1	-	ASTM D 130
Carbon Residue, % wt.	max 0.05	-	ASTM D 189
Water and sediment, % vol.	max 0.05	max 0.3	ASTM D 2709
Ash content, % wt.	max 0.01	max 0.02	ASTM D 482
Flash point, °C	min 52	min 52	ASTM D 93
Distillation (temperature of 90% distillation)	max 357	-	ASTM D 86
Color	max 4.0	-	ASTM D 1500

VITA

Miss Wonwisa Sroisopee was born on February 18, 1979, in Nakhonprathom, Thailand. She graduated with Bachelor's Degree of Science from Department of Chemistry, Faculty of Science, Chulalongkorn University in 2001. She attended the Master's Degree of Science Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in 2003.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย