

ไบโอดีเซลแบบหลายหน้าที่จากสเต็มเซลล์



นางสาวดารณี เจริญสุข

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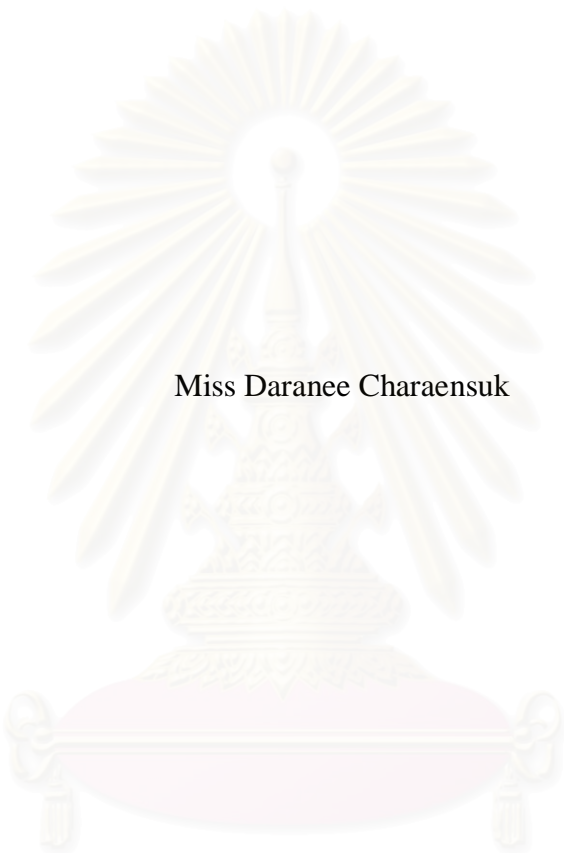
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

MULTIFUNCTIONAL BIODIESEL FROM SOAPSTOCKS



Miss Daranee Charaensuk

สถาบันวิทยบริการ
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science


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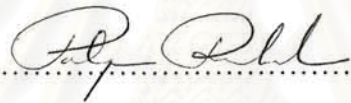
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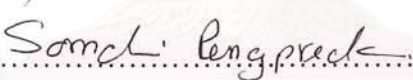
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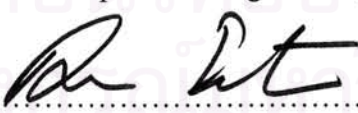

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งานวิจัยนี้เป็นการสังเคราะห์ไบโอดีเซลแบบหลายหน้าที่จากสต็อกสบู่ของน้ำมันพืช 3 ชนิด ได้แก่ น้ำมันปาล์ม น้ำมันรำข้าว น้ำมันถั่วเหลือง การเตรียมเมทิลเอสเทอร์ของสต็อกสบู่ได้จากการทำปฏิกิริยากับเมทานอล โดยมีกรดซัลฟูริก สามารถเตรียมผลิตภัณฑ์ 96-98 เปอร์เซ็นต์ แล้วนำมาทำปฏิกิริยาในเทอร์ชัน สามารถเตรียมผลิตภัณฑ์ได้ 92-95 เปอร์เซ็นต์ ทำการพิสูจน์เอกลักษณ์โดยเทคนิคทางสเปกโทรสโกปี ได้แก่ อินฟราเรดสเปกโทรสโกปี โปรตอนและคาร์บอนแมกเนติกเรโซแนนซ์สเปกโทรสโกปี ไบโอดีเซลที่สังเคราะห์ได้ สามารถละลายในน้ำมันดีเซลพื้นฐานได้ง่าย และมีประสิทธิภาพเพิ่มค่าซีเทนเพิ่มขึ้น 1.6, 2.0, 2.2, 2.3 และ 3.9 หน่วยสำหรับไบโอดีเซลจากสต็อกสบู่ของน้ำมันปาล์ม และ 6.8, 7.7, 7.9, 12.3 และ 13.4 หน่วยสำหรับไบโอดีเซลจากสต็อกสบู่ของน้ำมันถั่วเหลือง และ 3.6, 3.7, 4.5, 8.5 และ 8.7 หน่วยสำหรับไบโอดีเซลจากสต็อกสบู่ของน้ำมันรำข้าวที่ความเข้มข้น 0.50, 1.0, 2.0, 5.0, 10.0 เปอร์เซ็นต์โดยน้ำหนักตามลำดับ สำหรับคุณสมบัติการหล่อลื่นของไบโอดีเซลแบบหลายหน้าที่ทำการวิเคราะห์ด้วยเครื่องมือ HFRR ที่ความเข้มข้น 5 เปอร์เซ็นต์โดยน้ำหนัก พบว่า ไบโอดีเซลที่สังเคราะห์ได้จากสต็อกสบู่ของน้ำมันปาล์มสามารถทำให้ค่าสึกหรอน้อยกว่า 460 ไมโครเมตรในส่วนของ ค่าซีเทน และคุณสมบัติการหล่อลื่น ไบโอดีเซลจากสต็อกสบู่ของน้ำมันปาล์มเป็นสารเติมแต่งที่ดีที่สุด

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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KEYWORD: BIODIESEL/ CETANE NUMMBER/ CETANE IMPROVER/ DIESEL FUEL/ SOAPSTOCK/ VEGETABLE OIL/ NITRATE COMPOUNDS

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Multifunctional biodiesels could be synthesized from soapstocks such as palm oil, rice bran oil, and soy bean oil. Firstly, methyl ester of soapstocks could be prepared by reacting with methanol in the present of sulfuric acid to yield 96-98% of products. Finally, the nitration reaction was carried out to give 92-95% yield. Their structures were characterized by FT-IR, ^1H -, and ^{13}C -NMR. The multifunctional biodiesels could be easily blended with base diesel fuel. These compounds could rise in cetane number to 1.6, 2.0, 2.2, 2.3 and 3.9 units for multifunctional biodiesel from palm oil soapstock and 6.8, 7.7, 7.9, 12.3 and 13.4 units for multifunctional biodiesel from soy bean oil soapstock and 3.6, 3.7, 4.5, 8.5 and 8.7 units for multifunctional biodiesel from rice bran oil soapstock at the concentrations of 0.50%, 1.0%, 2.0%, 5.0% and 10.0% by weight, respectively. For lubricity performances, these multifunctional biodiesels were investigated by using High Frequency Reciprocating Rig machine. All samples at concentration of 5% by weight could provide mean wear scar diameter of multifunctional biodiesel from palm oil soapstock less than 460 μm . In the view of cetane number and lubricity performance, the multifunctional biodiesel from palm oil soapstock was the best additive for diesel fuel.

Field of study Petrochemistry and Polymer.Science. Student's signature Darane Charaensuk
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ABBREVIATIONS

ASTM	=	American Society for Testing and Materials
API	=	American Petroleum Institute
CCI	=	Calculated Cetane Index
¹³ C-NMR	=	Carbon-13 Nuclear Magnetic Resonance
cSt	=	Centistroke
CFR	=	Cooperative Fuel Research Council
°C	=	Degree Celcius
°F	=	Degree Fahrenheit
ml	=	Milliliter
% wt	=	Percent by weight
% yield	=	Percent yield
¹ H-NMR	=	Proton Nuclear Magnetic Resonance
rpm	=	Round per minute
Sp.Gr.	=	Specific Gravity
cm ⁻¹	=	Unit of wave number
PME	=	Palm oil methyl ester
PN	=	Palm oil nitrate
RN	=	Rice bran oil nitrate
SN	=	Soybean oil Nitrate
EHN	=	2-Ethylhexyl Nitrate

DEFINITIONS

Multifunctional biodiesel	=	Fatty compound containing nitrate and methyl ester groups.
Palm oil methyl ester	=	Methyl ester of palm oil soapstock.
Soybean oil methyl ester	=	Methyl ester of soybean oil soapstock.
Rice bran oil methyl ester	=	Methyl ester of rice bran oil soapstock.
Palm oil epoxide	=	Epoxide compound of palm oil methyl ester.
Soybean oil epoxide	=	Epoxide compound of soybean oil methyl ester.
Rice bran oil epoxide	=	Epoxide compound of rice bran oil methyl ester.
Palm oil nitrate	=	Nitrate product of methyl ester of palm oil soapstock.
Soybean oil nitrate	=	Nitrate product of methyl ester of soybean oil soapstock.
Rice bran oil nitrate	=	Nitrate product of methyl ester of rice bran oil soapstock.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Diesel fuel is a fossil fuel, which is made from distillate fraction of crude oil. Crude oil is a mixture of heavy and light hydrocarbon such as benzene, pentane, hexane, heptane, toluene, propane and butane. The boiling range of diesel fuel is approximately 160-390°C. Diesel fuel is used in compression-ignition 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 [1].

However, many countries have controlled diesel fuel as well as emission reductions from diesel engines. Furthermore, biodiesel engines can reduce the particulate matter, polycyclic aromatic hydrocarbon and improvements in combustion efficiency [2].

The demand for diesel fuel in Thailand consumed about 43 million liters per day of diesel in recent year, which was 46.6 % of total consumption of petroleum product. Therefore, the demanded for diesel fuel has been increased. The consumption of diesel fuel in Thailand is being continuously increased as shown in Figure 1.1 [3].

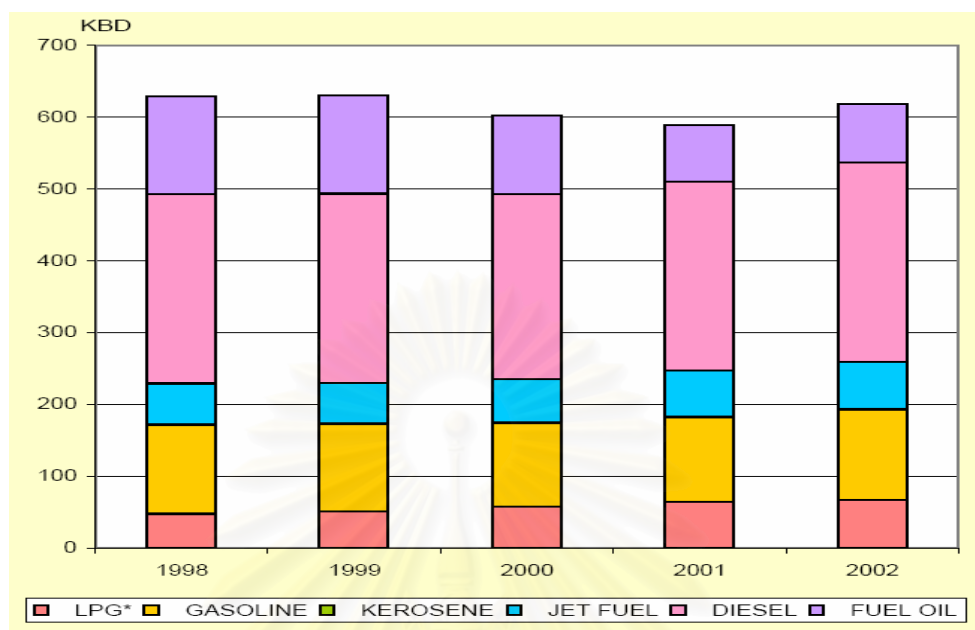


Figure 1.1 Oil products consumption in Thailand.

In the present, the world is confronted with the crises of fossil fuel reduction. Alternative fuels, energy conservation, energy efficiency and environmental protection have become necessary in recent year. The situation has led to the search for renewable fuels, such as alcohol, vegetable oils, biogas, biomass, biodiesel are becoming important.

Biodiesels and biofuels processed from biological materials such as vegetable oils, recycled cooking oils, animal fats are such fuels that can be blended with petroleum distillates for use in transportation engines and industrial processes to help offset increasing energy demand [4, 5].

Biodiesel is fatty acid esters, which have successfully been used as diesel fuel lubricity improvers because they prepared from vegetable oils, are biodegradable and are produced at low cost. Biodiesel comprises of oxygen compounds are fuels generally result in improved combustion quality [6].

This research, which is interesting to use soapstocks, as waste product from the vegetable oil refining process as multifunctional biodiesel by esterification of soapstocks with methanol using sulfuric acid as catalyst, followed by epoxidation and nitration reaction. The reaction conversion, performance of products of ester and nitration compound are especially well suited as biodiesel and additives for diesel fuels.

1.2 Objectives and Scope of the Research

1.2.1 Objectives

1. To synthesize multifunctional biodiesel from soapstocks.
2. To study the properties of multifunctional biodiesel from soapstocks.

1.2.2 Scope of the Research

1. Literature survey and study of the research works.
2. Preparation of equipments and chemicals.
3. Synthesis of multifunctional biodiesel from soapstocks of rice bran oil, soy bean oil, palm oil by esterification reaction, epoxidation reaction and nitration reaction.
4. Characterization of the synthesized multifunctional biodiesel by spectroscopic methods such as FT-IR and FT-NMR.
5. Determination of important physical properties of diesel fuel blended with multifunctional biodiesel.
6. Summarize the results.

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Vegetable oils

2.1.1 Soy bean oil

Soybean oil, *Leguminosae*, [7, 9] is a family, subfamily *Papilionaceae*, and the genus *Glycine max*. The soybean is a typical legume seed differing in color, size, and shape, depending upon variety. The common field varieties grown in the United States are nearly spherical and are yellow in color.

2.1.2 Palm oil

The oil palm, *Elaeis guineensis*, [7, 8] oil is derived from palm kernel oil. Palm oil is colored deep orange-red by the large amount of carotene. It is used in making vegetable, margarine, soap.

2.1.3 Rice bran oil

Rice bran oil, *Oryza sativa*, [10, 11] which makes up about 6% by weight of rough rice and contains about 15-20% of lipids. Rice bran oil is colored deep orange-red. It is used in salad oil, cooking.

Each vegetable oil has saturated and unsaturated fatty acid compositions. Typical fatty acid compositions of vegetable oils (soy bean oil, palm oil, and rice bran oil) are shown in Table 2.1 [6, 7, 8, 10 and 11].

Table 2.1 Composition of fatty acids of vegetable oils.

Fatty acid Common name	Numerical representation	% Fatty acid composition		
		Soy bean oil	Rice Bran oil	Palm oil
Myristic acid	14:0	-	-	1.0
Palmitic acid	16:0	11.5	14.4	45
Palmitoleic acid	16:1	-	-	-
Steric acid	18:0	4.0	1.3	4.5
Oleic acid	18:1	24.5	41.2	38.0
Linoleic acid	18:2	53.0	39.7	10.0
Linolenic acid	18:3	7	1.5	-

The fatty acids from oils, which are different saturated and unsaturated fatty acid. Rice bran oil is given oleic acid (18:1) referred to fatty acid with 18 carbon and one double bond. Palm oil is given palmitic acid (16:0) referred to fatty acid with 16 carbon and no double bond. The soy bean oil is given linoleic acid (18:2) referred to fatty acid with 18 carbon and two double bonds. Nowadays, vegetable oils produce a widespread in many applications such as biodiesel, lubricants, and additives.

2.2 Vegetable oil process [11, 12].

Extraction of oils from the vegetable materials in which they occur is accomplished by pressing or by solvent extraction. Both processes are widely used. Extraction by pressing, vegetable seeds must be finely ground. The ground material is adjusted to certain moisture content and warmed or cooked in a steam-jacketed vessel. For solvent extraction the seeds are ground in such a way as to produce the flakes rather than very fine particles. The flaked material is then extracted in suitable equipment by means of a low boiling point solvent.

Refining of oil is carried out to remove solid material such as phospholipids, free fatty acid, and colored impurities. A number of processes are employed for this purpose, including treatment with alkali and absorbent materials. A further process, known as deodorization, may be applied to edible oils. It consists of treatment with steam at high temperatures and under low pressure to remove volatile material such as residual solvent, certain free acids, and other substances which would give undesirable tastes or odors. A final treatment for edible oils may consist of hydrogenation and blending of the hydrogenated product with other oils to obtain a product of the desired characteristics.

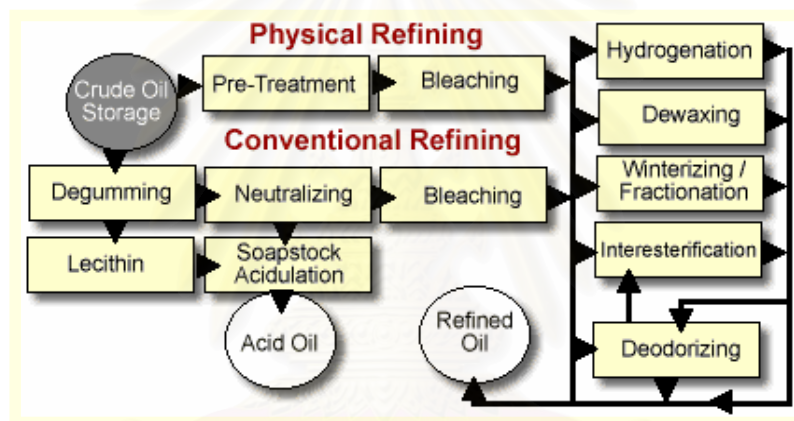


Figure 2.1 Vegetable oil process

2.3 Soapstock

Soapstock is a by product of the refining of edible vegetable oil process, that contains not only the salts of free fatty acids and consists largely of water, acylglycerides, phosphoglyceride, pigments. The price of soapstock can less than refined vegetable oil [13].

2.4 Biodiesel

Biodiesel produced from vegetable oil or animal fat including waste cooking oil. Biodiesel is used in diesel engine without modification because biodiesel has properties similar to petroleum diesel fuel. In comparison to diesel, biodiesel is higher

cetane number, low particulate emission including reduction of sulfur emissions, non-toxic and biodegradable.

Biodiesel is generally the ester that called an alkyl monoester. It produced from transesterification by reacting vegetable oils, such as soy bean, palm or rapeseed oil, with an alcohol as methanol or ethanol. It can be used in a blend or in pure form in conventional diesel engines [15].

2.4.1 Lubricity properties [6, 16, 17 and 18]

Biodiesel has successfully been used as diesel improvers. These mixtures of fatty acid methyl ester that the significant wear reduction was produced by oxygen compounds or carboxylic acid groups and used at a concentration of just a few parts per million.

The lubricity of varying concentrations fatty acid methyl ester in diesel fuel was demonstrated using the High Frequency Reciprocating Rig (HFRR) analysis method. The method used a sliding ball to scar a stable disk.

2.4.2 Flash point

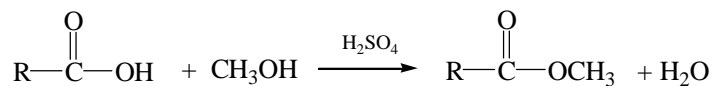
The flash point of a fuel is an important parameter that defined as the temperature is heated to produce a vapor-air mixture above the surface of the fuel that will ignite when exposed to an ignition source such as a spark or flame.

2.4.3 Sulfur content

The sulfur content of biodiesel is essentially sulfured free and results in a total reduction of SO₂ emissions as well sulfate aerosols.

2.5 Esterification process [18]

The process of converting carboxylic acid to biodiesel is called esterification that is reaction between carboxylic acid and alcohol by using acid catalyst, an ester is formed.



2.6 Diesel fuel

Diesel fuel is a fossil fuel that obtained from fractional distillation of the crude oil. The boiling range of distillate fuel is approximately 160-330°C (300-700°F), which is higher than the boiling range of gasoline (Figure 2.2).

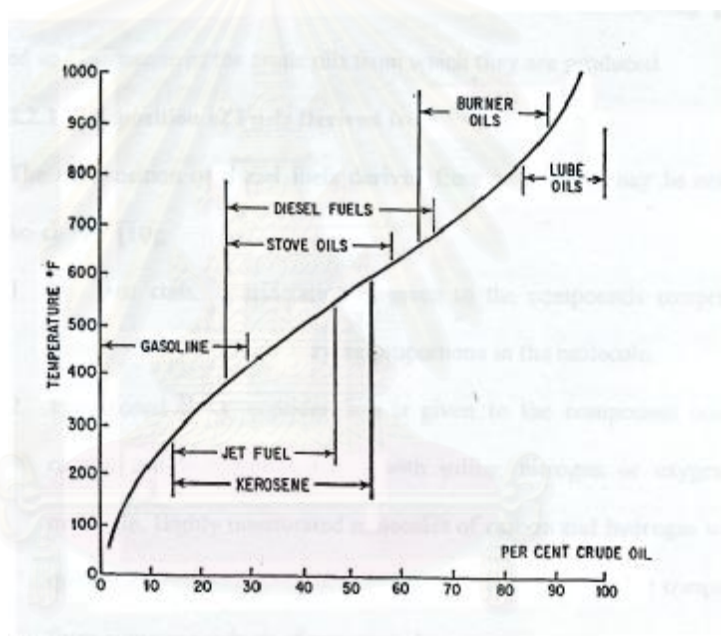


Figure 2.2 Proportion of diesel fuel and other petroleum products processed from crude petroleum.

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, 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 purpose 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 2.2.

Table 2.2 Typical ranges of diesel engines

Type	Speed Range	Conditions	Typing application
Low Speed	<300 rpm	Heavy load, constant speed	Marine main propulsion; electric power generation
Medium Speed	300-1000 rpm	Fairly high load 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

Although diesel engines vary widely in size speed, power output, and mechanical design, their fuel requirements are quite similar in many respects. Performance features desired of all diesel fuels, and the physical properties most directly related to them are summarized below. Fuel properties are presented in the order in which they are seen by the engine as the fuel flows from the storage tank, through the fuel system, to the combustion chamber, No attempt is made in the table to indicate relative importance [20].

<u>Performance Feature Desired</u>	<u>Indicated By</u>
1. Safety in handling	Flash point
2. Pump ability at low temperature	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 effects on engine wear and deposit	Sulfur

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

2.8.1 Cetane number

Cetane number is an index of a fuel's ignition quality. It is measured in a single cylinder, variable compression ratio diesel engine under fixed conditions of speed, load, jacket temperature, inlet air temperature, etc. The ignition quality of the test fuel is compared with mixtures of two reference hydrocarbon fuels, namely, cetane, which is assigned a rating of 100, and alpha-methyl-naphthalene which is assigned a rating of zero.

2.8.2 Volatility

A simple laboratory distillation test indicates the volatility or boiling range of a fuel. Important distillation points for determining fuel volatility are the 10%, 50%, 90%, and final boiling point. The higher than 50% and/or final boiling points, the more difficult it is to vaporize the fuel completely. High speed engines in particular require volatile fuels high boiling products cannot be vaporized in the short time

available for combustion, and sooty, incomplete burning results. It is very important in high speed engines to have volatile, readily vaporized fuels; the importance of fuel volatility decreases as speed decreases or, stated another way, as the time available for combustion increases.

2.8.3 Viscosity

Viscosity is a time measure of a fuel's resistance to flow, and is directly related to the ease with which the fuel is atomized in the combustion chamber. Too high a viscosity will result in the fuel spray penetrating too far into the combustion chamber; it wets the piston and cylinder walls, and then carbonizes on the hot combustion chamber surfaces. If fuel viscosity is too low, injector plungers and barrels, which depend on the fuel for lubrication, will tend to wear excessively.

2.8.4 Gravity

The gravity of petroleum oil is an index of the weight of a measured volume of the product. There are two scales in use in the petroleum industry; API gravity and specific gravity, the former being most widely used in the United States. The specific gravity of a petroleum oil or of mixtures of petroleum products with other substances is the ratio of the weight of a given volume of the material at a temperature of 60°F. to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air. The temperature requirements are shown by the expression, "Specific Gravity 60/60°F." For heavier products such as asphalt and liquid road materials a reference temperature of 77°F. is used instead of 60°F.

The API gravity of petroleum oil is based on an arbitrary hydrometer scale, which is related to specific gravity in accordance with the formula:

$$\text{Degree API} = \frac{141.5}{\text{Sp. Gr. } 60/60^\circ\text{F}} - 131.5 \quad (1)$$

2.8.5 Sulfur content

The sulfur content is associated with the corrosion and deposit forming tendencies of the fuel. A considerable amount of work has been done in an attempt to evaluate the harmful effects of sulfur in diesel fuels as a function of the percent sulfur contained in the fuel. There is evidence that high sulfur fuels cause more corrosion or deposits than low sulfur fuels. The problem that remains open, however, is how much does this corrosion or deposit formation cost in relation to added fuel costs to reduce the sulfur content.

2.8.6 Pour and Cloud points

Pour point, or the minimum temperature, at which a fuel remains liquid, is of importance in mobile installations where the fuel must be handled at or near atmospheric temperatures. If the fuel is to be pumped through filters, the cloud point, or that temperature at which crystals begin to form, is the minimum temperature at which engine operation is permissible. Operation below the cloud point will result in clogging of the fuel filters by wax.

2.8.7 Flash point

Fuel flash point is useful only as an index of fire hazard. Although flash point is an indication of the “readiness” of a fuel to ignite when exposed to a flame, it cannot be used for estimating auto-ignition temperature of diesel fuels.

2.8.8 Water and Sediment content

Water and sediment content reflects for the most part the care taken in the finishing and handling operations employed in preparing the fuel for the engine. Sediment in fuel leads to filter clogging and injector fouling, while water is harmful because it promotes rusting of critical steel injection equipment.

2.8.9 Ash content

The ash content is usually quite small. Large values reflect improper finishing in the production of fuels, particularly where treating steps are involved. In some cases it is known that ash-forming contaminants may be introduced to fuel mixtures through entrainment or otherwise in the distillation step employed to separate the diesel fuel from heavier stocks.

2.8.10 Carbon residue

Carbon residue content is an index of the carbonizing tendencies of a fuel. It reflects the presence of high-boiling or rather extremely low-volatility components present in a fuel; they crack down to a carbonaceous residue at the distillation temperatures of the fuel. These materials usually result from entrainment during separation of the diesel fuel by fractionation from higher-boiling fractions. A carbon residue value on diesel fuels is always determined on the 10% distillation residue in order to increase the accuracy of the test. The higher the carbon residue value, the greater will be the tendency for deposits to form on the fuel injector tip or in other parts of the combustion chamber.

2.9 Diesel ignition improvers

2.9.1 Cetane number

As previously stated, the most universally accepted measure of the ignition quality of diesel fuels is cetane number. The standard method for determining the cetane number of a diesel fuel is the ASTM D613 CFR engine technique. In this procedure the cetane number of a diesel fuel is determined by comparing its ignition quality with two reference fuel blends of known cetane numbers under standard operating conditions. This is done by varying the compression ratio for the sample and each reference fuel to obtain a fixed delay period between the start of injection and ignition. The compression ratio for the sample is bracketed by reference fuel

blends, which differ, by less than five cetane numbers, and the rating of the sample is calculated by interpolation.

The cetane number scale is based on two primary reference fuels. One, normal cetane (n-hexadecane), has excellent ignition qualities and, consequently, a very short ignition delay. A cetane number 100 was arbitrarily assigned to this fuel. The second fuel, alphas-methylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alphas-methylnaphthalene was replaced as a primary reference fuel by heptamethyl nonane, which has a cetane number of 15 as determined by use of the two original primary reference fuels.

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (Cetane No. = 100) in a blend with heptamethylnonane (Cetane No.15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number:

$$\text{Cetane No.} = \% \text{ n-cetane} + 0.15 (\% \text{ heptamethylnonane}) \quad (2)$$

When fuel is injected into the combustion chamber of a diesel engine, ignition does not occur immediately. The interval between the beginning of the fuel injection and its self-ignition is known as the ignition delay period. This delay period depends on the fuel, the engine and its design, and on the operating conditions.

High-speed diesel engines normally are supplied with fuels in the range of 45 to 55 cetane number. The actual cetane number required in any given service depend on engine design and size, speed and load variations, and on starting and atmospheric conditions. Exhaust smoking and odor are affected only indirectly by cetane number.

Diesel fuels of high cetane number differ from those of lower cetane number by having a shorter ignition lag when injected into the diesel-engine cylinder. High-cetane fuel also is ignited at a lower compressed-air temperature than low-cetane fuel. These characteristics result in the differences in the performance of high-cetane and low-cetane fuels in operating engines as described below [21]:

Starting. The higher the cetane number, the lower the temperature at which the engine can be started, but the range of starting temperatures differs for different engines. Furthermore, there is a lower limit for each engine below which starting cannot be achieved by using higher cetane fuel alone. A practical example: if a given engine would start on 35 cetane fuel with intake at 60°F, it might start at 30°F on 60 cetane fuel, but it could not be expected to start at 0°F with 85 cetane fuel.

Warm-up. After starting at low temperatures, engines can be brought to a state of steady running, without misfiring or emitting white smoke, more quickly on high-cetane fuel than on low-cetane fuel.

Combustion Knock. Combustion roughness, or diesel knock, as well as shock loading of pistons, bearings and other engine parts, results when a fuel having too low cetane number is used for the size and type of engine and conditions under which it is being operated. Use of higher-cetane fuel will give smoother combustion and reduce the noise and stress on the parts. The small, high-speed engines in automotive service usually require fuel of higher than 40 cetane number, although large-bore, slow-speed engines can utilize fuel of lower-cetane quality.

Engine Deposits. Low-cetane fuels may cause more rapid accumulation of varnish and carbonaceous deposits while the engine is idling at light-load operation than high-cetane fuels of the same grade. Such deposits are probably the result of the fuel composition per se rather than the result of poor combustion due to late ignition or low cetane number.

Smoke, Fumes and Odor. High-cetane fuel will help reduce the production of acrid odor and fumes (cold smoke) during light-load, cool-running conditions; but ignition quality has only a minor effect on black (hot) smoke. In some types of engine very high cetane fuel, 60 or higher, causes more smoke than fuel of lower cetane number.

Power and Fuel Consumption. Ignition quality has a negligible influence on output and economy. Low-cetane fuels, however, as long as they satisfy the cetane requirement of the engine, tend to give slightly more power at maximum output or lower fuel consumption than high-cetane fuels. This is because low-cetane fuels generally are heavier and, therefore, contains more heat units per gallon.

In the majority of diesel engines, the ignition delay period is shorter than the duration of injection. Under such circumstances, the total combustion period can be considered to be divided into the following four stages:

1. Ignition delay
2. Rapid pressure rise
3. Constant pressure or controlled pressure rises
4. Burning on the expansion stroke

The rapid pressure rise results from the large number of ignition points and the accumulation of fuel during the ignition delay period. Following this stage, the rate of combustion can be controlled to a much greater degree by controlling the injection rate, since the fuel is being injected into flame. Because the rapid pressure rise represents uncontrolled and inefficient combustion resulting from the burning of fuel accumulated during the ignition delay period, it is desirable to limit ignition delay to minimum. This limitation can be accomplished mechanically by the development and selection of a spray pattern configuration properly tailored to the combustion chamber. The use of high fuel injection pressures and high fuel/air turbulence to promote rapid fuel jet break-up and thorough fuel distribution can reduce ignition delay.

Although the reduction of ignition delay by mechanical means is important, the nature of the fuel is the primary factor in reducing the time consumed by ignition delay. Physical characteristics, such as viscosity, gravity, and mid-boiling point are influential. On the other hand, hydrocarbon type is important only as it affects the physical characteristics of the fuel. Since the ignition delay characteristics of diesel fuels directly influence the interval of uncontrolled combustion during injection and as a result, the overall engine performance, this property is of primary importance, thus becomes desirable to have a numerical basis for evaluating the fuel ignition delay and for measuring and predicting this property.

The hydrocarbon composition of diesel fuel is believed to influence ignition quality and combustion characteristics, depending on the degree of fuel-air mixing obtained before complete combustion. For ignition quality or low-temperature ignitability, long chain normal paraffins have a high cetane number. Highly branched chain paraffins and aromatics (compact structure) have a low cetane number. Olefins and naphthenes are intermediate. It is obvious that fuels having a high cetane number have a low octane number. We have also seen that aromatics in gasoline have very high octane numbers. This reversal of desirable fuel properties when comparing diesel and gasoline suggests an inverse relationship between cetane and octane numbers, as illustrated in Figure 2.3.

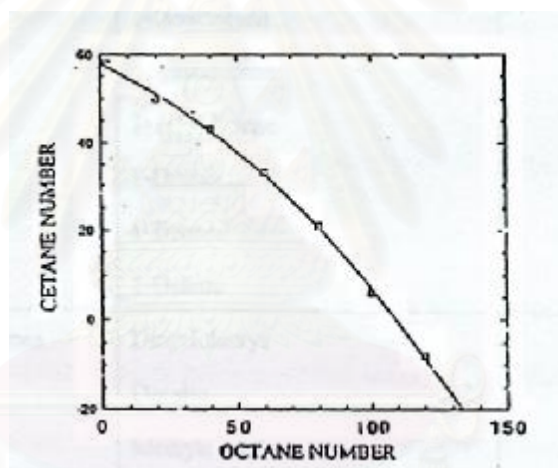


Figure 2.3 The inverse relationship between cetane and octane numbers [21].

The cetane numbers of a variety of compounds are shown in Table 2.3. As a rule, for compounds having the same number of carbon atoms, the cetane number drops in the order n-alkane > alkene > cycloalkane > alkyl aromatic.

2.9.2 Cetane index

Since the determination of cetane number by engine testing requires special equipment, as well as being time consuming and costly, alternative methods have

been developed for calculating estimates of cetane number. The calculation is based upon equations involving values of other known characteristics of the fuel.

One of the most widely used methods is based on the Calculated Cetane Index formula. The formula represents a means for directly estimating the ASTM cetane number of distillate fuels from API gravity and mid-boiling point [19]. The index value as computed from the formula is termed the Calculated Cetane Index. The Calculated Cetane Index is not an optional method for expressing ASTM cetane number. It is a supplementary tool for predicting cetane number with considerable accuracy when used with due regard for its limitations. It may be conveniently employed for approximating cetane number where the quantity of sample is too small for an engine rating. In cases where the cetane number of a fuel has been initially established, the index is useful as a cetane number check on subsequent samples of that fuel, provided its source and mode of manufacture remain unchanged.

Calculated Cetane Index is determined by 2 methods.

1. It may be conveniently determined by means of the alignment chart in Figure 2.4.

2. It is determined from the following formula [23]:

2.1 When it is not applicable to fuels containing additives for raising cetane number.

$$\begin{aligned} \text{Calculated Cetane Index (CCI)} = & -420.34 + 0.016G^2 + 0.192G \log M \\ & + 65.01 (\log M)^2 - 0.0001809 M^2 \end{aligned} \quad (3)$$

2.2 When it is applicable to fuels containing additives for raising cetane number. The calculated cetane index improver is determined from the equation 2 plus equation 3.

$$\text{Improver value} = 0.1742 (0.1G)^{1.4444} (0.01M)^{1.0052} \{\ln (1+17.5534D)\} \quad (4)$$

Where:

G = API gravity, determined by Test Method D287 or D1298.

M = Mid-boiling temperature (°F), determined by Test Method D86 and corrected to standard barometric pressure.

D = Percent weight of cetane improver, % weight.

Therefore;

$$\text{CCI improved} = \text{CCI} + \text{Improver value} \quad (5)$$

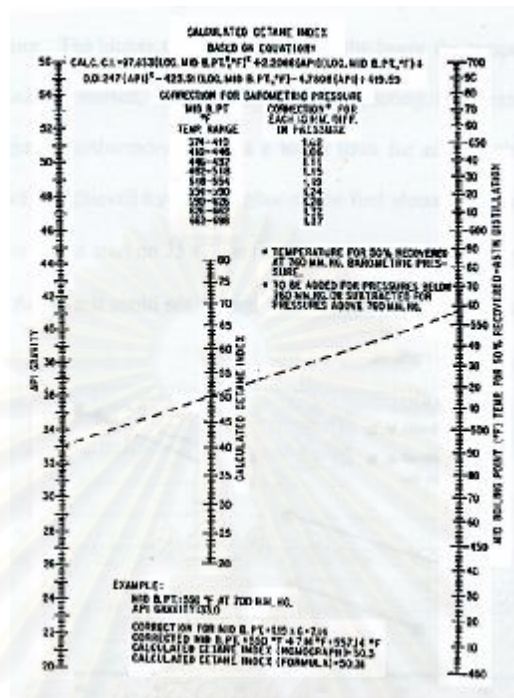


Figure 2.4 Nomograph for calculated cetane index [22].

The Calculated Cetane Index formula possesses certain inherent limitations, which must be recognized in its application. These are:

It is not applicable to fuels containing additives for raising cetane number. It is not applicable to pure hydrocarbons, synthetic fuels, alkylates or coal-tar products. Substantial inaccuracies in correlation may occur if used for crude oils, residuals or products having a volatility of below 500°F end point. Correlation of index values with ASTM cetane number is dependent to a great extent upon the accuracy of determination of both API gravity and mid-boiling point. A difference of 2°F in the mid-boiling point represents a difference of approximately 0.4 in index value. Within the range of 30 to 60 cetane number, the expected correlation of the calculated cetane index with the ASTM cetane number will be somewhat less than ± 2 cetane numbers for 75 percent of the distillate fuels evaluated. Errors in correlation may be greater for fuels whose cetane numbers are outside this range.

2.9.3 Cetane improver

Cetane improvers are compounds, which readily decompose to give free radicals and thus enhance the rate of chain initiation in diesel combustion. They promote fast oxidation of fuels and thus improve their ignition characteristics. They are specialty chemicals which, when added to diesel, improve diesel's cetane number similar to the way ethanol and ETBE improve the octane rating of gasoline. At concentrations less than 0.15%, cetane improvers can reduce ignition delay times of diesel fuel. Fundamentally, the cetane improver concentration is another degree of freedom in designing a diesel fuel. In practice, this degree of freedom is often capable of simultaneously decreasing NO_x, hydrocarbon and particulate emissions. Cetane improvers are considered a key technology to provide cleaner burning diesel fuel.

They are key additives for making premium diesel. Chemical compounds such as alkyl nitrates, ether nitrates, dinitrates of polyethylene glycols and certain peroxides are known cetane improvers.

The isooctyl nitrate product, in view of its good response and low production costs, is the most cost-effective additive and is now almost exclusively used in all commercial applications with hydrocarbon-based fuels. The weak RO-NO₂ bond in isooctyl nitrate provides the available source of the free radicals required enhancing diesel combustion.

2.10 Additives for diesel fuel

Apart from a few exceptions treatment of diesel fuel with additives has only recently become important. For this relatively late development in diesel fuels, compared with gasoline, two main reasons exist; First a significant progress occurred in diesel engine technology from about the mid-1970s, which made improved diesel fuel quality seem desirable, especially with respect to lower exhaust emissions. Second an anticipated change in the middle distillate quality became apparent at the same time and made the use of additive very attractive.

Commercial diesel fuel may contain a variety of additives to enhance or impart certain desirable properties. Among those which may be found in current fuels are ignition quality improvers, oxidation inhibitors, biocides, rust preventives, metal

deactivators, pour point depressants, demulsifiers, smoke suppressants, detergent-dispersants, conductivity improvers, dyes and de-icers. Diesel fuel additives are shown by class and function in Table 2.4. As with any system in which a variety of additives may be used, care should be taken to avoid incompatibilities among additives and unanticipated interactions which may produce undesirable fuel effects.

Table 2.3 Commercial diesel fuel additives-function and type [22].

Class or Function	Class or Function
1. Ignition Quality Improvers: Raise Cetane Number thereby promoting faster starts and less white smoke.	-Alkyl nitrates
2. Oxidation Inhibitors: Minimize oxidation and gum and precipitate formation, improve storage life	-Alkyl amines and amine-containing complex materials
3. Biocides: Inhibit the growth of bacteria and fungi which feed on hydrocarbons, help prevent filter-clogging caused by these organisms.	-Boron compounds, ethers of ethylene glycol, quaternary amine compounds
4. Rust Preventives: Minimize rust formation in fuels systems and storage facilities.	-Organic acids and amine salts
5. Metal Deactivator: Deactivates copper ions which are powerful oxidation catalysis.	-N,N-disalicylidene-1,2-propane diamine
6. Pour Point Depressants: Reduce the pour point and improve low-temperature fluidity properties by modifying the wax crystal growth, structure, and/or agglomeration.	-Generally consist of polymeric materials such as polyolefins, polyacrylates and ethylene-vinyl chloride copolymers
7. Demulsifiers and Dehazers: Improve the separation of water from distillate fuels and prevent haze.	-Surface-active materials which increase the rate of water/oil separation

This research established multifunction biodiesel that have cetane improvers and lubricity additives because of ignition quality and lubricating performances are the most important properties in diesel fuels.

2.11 Literature Reviews

Hass, M.J. *et al.* [13], synthesized fatty acid methyl ester from soy bean soapstock by saponification followed by acid catalyzed esterification. The biodiesel from soy bean soapstock was similar to biodiesel produced from refined soy oil. Petroleum diesel containing 20 % volume of biodiesel from soy bean soapstock was reduced total hydrocarbons, particulate matter and carbon monoxide relative to petroleum diesel.

Anastopoulos, G. *et al.* [16], examined the impact of esters of monocarboxylic fatty acid improved lubricating performances were achieved with ultra-low-sulfur diesel fuel by addition of a small amount of seven esters. Tribological experiments carried out on the high-frequency reciprocating rig (HFRR) showed that the effective concentration of the additives was 500 ppm or higher.

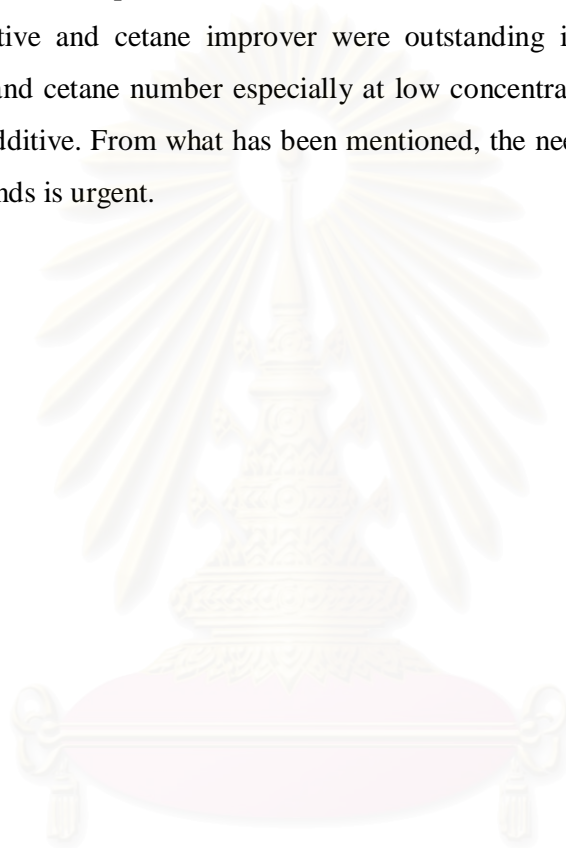
Drown, D. C. *et al.* [6], had reported that the lubricating performance of diesel fuel were increased by the addition of a small amount of a methyl and ethyl monoalkyl esters of various vegetable oils such as methyl soy, methyl castor, ethyl soy, ethyl castor. Tribological experiments carried out on the high-frequency reciprocating testrig (HFRR). The results were obtained that the esters of castor oil had improved lubricity over than other oils.

Dmytryshyn, S.L. *et al.* [23], produced fatty acid methyl esters by transesterification of four vegetable oils such as canola oil, greenseed canola oil, processed wastes fryer grease and unprocessed waste fryer grease. The diesel fuel was blended with 1 % volume of fatty acid methyl ester were tested for lubricating performance and showed properties similar to diesel fuel.

Suppes, G.J. *et al.* [24], synthesized nitrate compound from oleic acid as cetane improver by epoxidation, hydrolysis and nitration reaction. The product improved abilities similar to 2-Ethyl hexyl nitrate. Lubricity tests indicated that the product has good lubricity enhancing capabilities.

Moreover, several studies by Boonlaksiri [7] synthesized nitrate compound as cetane improver from fatty acid wastes, Pongthanomsak [9] synthesized nitrate compound as cetane improver from vegetable oils. The products were effective in increasing cetane number.

As the above reports showed, biodiesel and additive in diesel fuel such as the lubricity additive and cetane improver were outstanding in improving lubrication performance and cetane number especially at low concentration level as effective as commercial additive. From what has been mentioned, the need for further research of these compounds is urgent.



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CHAPTER III

EXPERIMENTAL

3.1 Apparatus

1. Fourier-Transform NMR Spectrometer: Mercury (400MHz); Varian
2. Fourier-Transform Infrared Spectrophotometer: Model Impact410; Nicolet
3. Gas Chromatography-Mass Spectrometry: Fisson Instrument
4. Differential Scanning Calorimeter: Model DSC822; Metter Toledo
5. Elemental Analyzer: Leco CHN-2000
6. High Frequency Reciprocating Rig: CEC F-06-A-96
7. Automatic Distillation Apparatus: Model MP626; Herzog
8. Pensky-Martens Closed Flash Tester: Model ISL(PMFP93); Perzoo
9. Automatic Pour Point Tester: Model ISL(CPP97-6); ISL
10. Cannon Automatic Viscometer: Model CAV-3; Cannon
11. Apparatus for API Gravity
12. Cetane-2000 Diesel Fuel Analyzer; PetroSpec

3.2 Chemicals

1. Soybean oil soapstock; Thanakorn Vegetable Oil Product Co.,Ltd.
2. Palm oil soapstock; Siam Union Sahamitr Co.,Ltd
3. Rice bran oil soapstock; Thai Edible Oil Co;Ltd.
4. Dichloromethane: analytical grade; Lab-Scan
5. Methanol: analytical grade; Merck
6. Hexane: analytical grade; Lab-Scan
7. 96% Sulfuric acid: analytical grade; Carlo Erba
8. 65% Nitric acid: analytical grade; Merck
9. 50% Hydrogen peroxide: analytical grade ; Merck
10. Glacial acetic acid: analytical grade; Carlo Erba
11. Sodium hydrogen carbonate: analytical grade; Carlo Erba
12. Anhydrous sodium sulfate: analytical grade; Carlo Erba
13. Chloroform-D: NMR spectroscopy grade; Merck
14. Diesel fuel base; Petroleum Authority of Thailand

3.3 Synthesis of multifunctional biodiesel from palm oil soapstock

3.3.1 Synthesis of palm oil methyl ester

Palm oil soapstock (200 g.), methanol (750 g.) and 96% sulfuric acid (25 ml.) were put in the 1000 ml of two-neck round bottom flask equipped with reflux condenser, thermometer, and mechanical stirrer. The mixture was refluxed at 65 °C and stirrer for 10 hours. After the reaction completed, the mixture was allowed to separate. Then the reaction mixture was transferred into the separating funnel and the aqueous layer was removed, the organic layer was washed with water (500 ml.), 5% sodium hydrogen carbonate solution (300 ml.), water (200ml.) and saturated sodium chloride solution (200 ml.), respectively. After removing and discarding the aqueous layer, the organic portion was dried over anhydrous sodium sulfate and then filtered. The organic solvent was removed on rotary evaporator to give 195.6 g (yield = 97.80%) of palm oil methyl ester as a yellow liquid.

3.3.2 Synthesis of palm oil epoxide

Palm oil methyl ester (100 g.) was mixed with hexane (100 g.) in a 500 ml. round bottom flask equipped with mechanical stirrer. The mixture was stirred for 30 minute. Preparation of peracetic acid desired amounts of glacial acetic acid (44.45 g.) and 96% sulfuric acid (1.2g.) were added in the 500 ml. round bottom flask equipped with mechanical stirrer. Then 50% hydrogen peroxide (75.55 g.) was slowly added over 1 hour at room temperature. After that peracetic acid was slowly added in the mixture and stirred for 6 hours. After the reaction completed, the mixture was allowed to separate. After removing the aqueous layer, the organic layer was washed with water (100 ml.), 5% sodium hydrogen carbonate solution (100 ml.), water (100ml.) and saturated sodium chloride solution (100 ml.), respectively.

The organic portion was dried over anhydrous sodium sulfate and then filtered. The organic solvent was removed on rotary evaporator to give 94.50g (yield = 94.50%) of palm oil epoxide as a pale yellow liquid.

3.3.3 Synthesis of palm oil nitrate

In the 500 ml. of round bottom flask, 65% nitric acid (103.47g.) and 96% sulfuric acid (217.97g.) were added. The mixture was stirred on ice-bath and maintaining temperature at 0 ± 2 °C. The palm oil epoxide (50 g.) in dichloromethane (50 ml.) was added drop wise to the flask and temperature was kept at 0 ± 2 °C. The reaction was stirred for 4 hours. After the reaction completed, the mixture was allowed to separate. After removing the aqueous layer, the organic layer was washed with water (100 ml.), 5% sodium hydrogen carbonate solution (100 ml.), water (100ml.) and saturated sodium chloride solution (100 ml.), respectively. The organic portion was dried over anhydrous sodium sulfate and then filtered. The organic solvent was removed on rotary evaporator to give 47.50g (yield = 95%) of palm oil nitrate as a brown liquid.

3.4 Synthesis of multifunctional biodiesel from rice bran oil soapstock

3.4.1 Synthesis of rice bran oil methyl ester

The synthesis of rice bran oil methyl ester was similar to that Section 3.3.1, except rice bran oil soapstock (200g.) and methanol (680 g.) and 96% sulfuric acid (25 ml.), the subtitle compound was prepared to give 193 g. (yield =96.5 %) of rice bran oil methyl ester as yellow liquid.

3.4.2 Synthesis of rice bran oil epoxide

The synthesis of rice bran epoxide was similar to that Section 3.3.2., except rice bran oil methyl ester (100g.), hexane (100g.), glacial acetic acid (40.55g.), 96% sulfuric acid (1.05 g.) 50% hydrogen peroxide(68.9 g.), the subtitle compound was prepared to give 93.5 g. (yield =93.5 %) of rice bran oil epoxide as yellow liquid.

3.4.3 Synthesis of rice bran oil nitrate

The synthesis of rice bran oil epoxide was similar to that Section 3.3.3., except rice bran oil epoxide (50 g.), 65% nitric acid (87.93g.) and 96% sulfuric acid (185.24 g.) the subtitle compound was prepared to give 47.21 g. (yield = 94.43 %) of rice bran oil nitrate as brown liquid.

3.5 Synthesis of multifunctional biodiesel from soybean oil soapstock

3.5.1 Synthesis of soybean oil methyl ester

The synthesis of soybean oil methyl ester was similar to that Section 3.3.1, except soybean oil soapstock (200g.) and methanol (685 g.) and 96% sulfuric acid (25 ml.), the subtitle compound was prepared to give 197.2 g. (yield = 98.6 %) of soybean oil methyl ester as yellow liquid.

3.5.2 Synthesis of soybean oil epoxide

The synthesis of rice bran oil epoxide was similar to that Section 3.3.2., except soybean oil methyl ester (100g.), hexane (100g.), glacial acetic acid (42.89g.), 96% sulfuric acid (1.15 g.) 50% hydrogen peroxide(72.85 g.), the subtitle compound was prepared to give 92.35 g. (yield = 92.35 %) of soybean oil epoxide as yellow liquid.

3.5.3 Synthesis of soybean oil nitrate

The synthesis of soy bean oil epoxide was similar to that Section 3.3.3., except soybean oil epoxide (50 g.), 65% nitric acid (89.19g.) and 96% sulfuric acid (187.87 g.) the subtitle compound was prepared to give 46.17 g. (yield = 92.34 %) of soybean oil nitrate as brown liquid.

3.6 Characterization and determination of the synthesized multifunctional biodiesels.

3.6.1 Characterization of the multifunctional biodiesels.

The synthesized multifunctional biodiesels were characterized by using instruments as follows:

1. Fourier-Transform Infrared Spectrophotometer
2. Fourier-Transform NMR Spectrometer
3. Gas Chromatography-Mass Spectrometry
4. Differential Scanning Calorimeter
5. Elemental Analyzer

The result was shown in appendix A.

3.6.2 Determination of cetane number of base diesel fuel blended with multifunctional biodiesel.

Blended base diesel fuels containing with 0.5%, 1.0%, 2.0%, 5.0%, and 10.0% by weight of multifunctional biodiesels were determined of cetane number using Cetane -2000 Diesel Fuel Analyzer.

1. The blended base diesel fuels were prepared by blending synthesized multifunctional biodiesels. The synthesized nitrate compounds were follows:

- 1) Palm oil nitrate
- 2) Rice bran oil nitrate
- 3) Soy bean oil nitrate

2. The physical properties of the base diesel fuel blended with synthesized multifunctional biodiesels were determined as shown in Table 3.1.

Table 3.1 Test method of the blended base diesel fuel.

Property	Method
Mid-boiling point	ASTM D 86
API gravity	ASTM D 1298
Pour point	ASTM D 97
Viscosity	ASTM D 445
Flash point	ASTM D 93
Color	ASTM D 1500
Cetane Index	ASTM D976

3. The lubricity performances of the base diesel fuels blend with multifunctional biodiesels 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 multifunctional biodiesel from soapstocks

Methyl ester of soapstocks could be prepared by esterification of soapstocks with methanol using sulfuric acid as a catalyst. Epoxidation of methyl ester product with peracetic acid gave an epoxide product. Then nitrate compound could be prepared from the nitration of epoxide compound with concentrated nitric acid and concentrated sulfuric acid. The conditions of nitration reaction were varied which shown in Table 4.1. The synthetic results were shown in Table 4.2.

Table 4.1 Variation condition of nitration reaction of epoxide compound from methyl ester of soapstock.

Condition	Reaction Time (hr.)			
	4	6	8	10
Molar ratio (Oil : HNO ₃ : H ₂ SO ₄)				
1:3:6	*	*	*	**
1:5:10	*	*	**	**
1:6:12	**	**	**	**

Note; (*) = incomplete reaction

(**) = complete reaction

Table 4.2 Summary of the synthetic results of compound.

Compound	Characteristics	% yield
Palm oil methyl ester	yellow liquid	97.80
Palm oil epoxide	yellow liquid	94.50
Palm oil nitrate	brown liquid	95.00
Rice bran oil methyl ester	yellow liquid	96.50
Rice bran oil epoxide	yellow liquid	93.50
Rice bran oil nitrate	brown liquid	94.43
Soybean oil methyl ester	yellow liquid	98.60
Soybean oil epoxide	yellow liquid	92.35
Soybean oil nitrate	brown liquid	92.34

4.2 Characteristics of synthesized compounds

4.2.1 Palm oil methyl ester

The IR spectra of palm oil soapstock and palm oil methyl ester were shown in Figure A1 and A2, respectively. The important absorption bands of palm oil soapstock and palm oil methyl ester were listed in Table 4.3

Table 4.3 The absorption assignments of palm oil soapstock and palm oil methyl ester.

Wave number (cm ⁻¹)		Assignments
Palm oil soapstock	Palm oil methyl ester	
3005	3005	=C-H Stretching
2851	2849	C-H Stretching, Aliphatic
1740	1742	C=O Stretching
1654	1654	C=C Stretching
1461	1461	C-H Bending, Aliphatic
1162	1167	C-O Stretching

The IR spectrum of palm oil soapstock (Figure A1) and palm oil methyl ester (Figure A2) could not be distinguished. The result was confirmed by using ¹H-NMR and ¹³C-NMR spectra.

The ¹H-NMR spectra of palm oil soapstock and palm oil methyl ester were shown in Figure A3 and A4, respectively. Some signals of soapstock of palm oil and palm oil methyl ester were shown in Table 4.4

Table 4.4 The assignments of $^1\text{H-NMR}$ spectra of palm oil soapstock and palm oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ ,ppm)	
		Palm oil soapstock	Palm oil methyl ester
a	m	0.77-0.83	0.74-0.81
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.15-1.95	1.12-1.92
q	t	2.19-2.26	2.15-2.22
s	s	-	3.54
t,u,v	m	4.01-4.27	-
i,j	m	5.19-5.28	5.20-5.25

From the $^1\text{H-NMR}$ spectrum of palm oil methyl ester (Figure A4) as comparing with palm oil soapstock (Figure A3), it could be observed that the signal at $\delta_{\text{H}}3.54$ ppm was belonged to the protons of methoxy group of methyl ester.

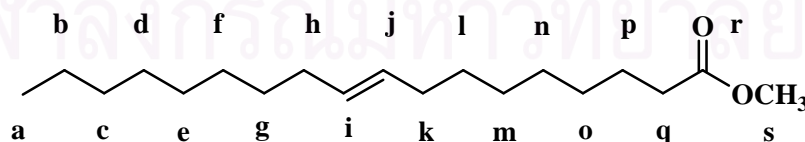
The $^{13}\text{C-NMR}$ spectra of palm oil soapstock and palm oil methyl ester were shown in Figure A5 and A6, respectively. The important signals of palm oil soapstock and palm oil methyl ester were shown in Table 4.5

Table 4.5 The assignments of ^{13}C -NMR spectra of palm oil soapstock and palm oil methyl ester.

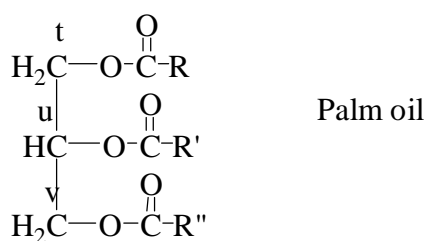
Position of Carbon	Chemical Shift (δ ,ppm)	
	Palm oil Soapstock	Palm oil methyl ester
a	14.05	14.00
b,c,d,e,f,g,h,k,l,m,n,o,p	22.55-33.94	22.61-31.86
q	34.09	33.90
s	-	51.12
t,v	62.00	-
u	68.86	-
i,j	127.83-130.01	127.79-129.93
r	172.60-173.01	173.90

From the ^{13}C -NMR spectra of palm oil methyl ester (Figure A6) as comparing with palm oil soapstock (Figure A5), it was clearly seen that the signals at δ_{C} 62 ppm and δ_{C} 68 ppm belong to the carbon of glycerol moiety of triglyceride were absent, and the signal at δ_{C} 51 ppm belonged to the carbon of methoxy group of methyl ester were shown instead.

From the results of spectra data, it could be concluded that the product was palm oil methyl ester and its structure was as follows:



Palm oil methyl ester



4.2.2 Palm oil epoxide

The IR spectrum of palm oil epoxide was shown in Figure A9. The absorption bands of palm oil epoxide were listed in Table 4.6.

Table 4.6 The absorption assignments of palm oil epoxide.

Wave number (cm ⁻¹)		Assignments
Palm oil methyl ester	Palm oil epoxide	
-	3467	O-H Stretching
3005	-	=C-H Stretching
2849	2849	C-H Stretching, Aliphatic
1742	1741	C=O Stretching
1654	-	C=C Stretching
1461	1461	C-H Bending, Aliphatic
1167	1162	C-O Stretching

From the IR spectrum of palm oil epoxide (Figure A9) as comparing with palm oil methyl ester (Figure A2), it could be observed that the absorption bands at 3005 cm⁻¹ and 1654 cm⁻¹ were observed in the spectrum of palm oil methyl ester due to the presence of double bond in fatty acid chain, while they could not be observed in spectrum of palm oil epoxide

The ¹H-NMR spectrum of palm oil epoxide was shown in Figure A10. The important signals of palm oil epoxide were shown in Table 4.7.

Table 4.7 The assignments of ^1H -NMR spectrum of palm oil epoxide.

Position of Proton	Multiplicity	Chemical Shift (δ ,ppm)
a	m	0.71-0.77
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.09-1.51
q	t	2.11-2.19
i,j	m	2.68-2.76
s	s	3.54

From the ^1H -NMR spectrum of palm oil epoxide (Figure A10) as comparing with palm oil methyl ester (Figure A4), it could be observed that the signal between δ_{H} 5.20 ppm to δ_{H} 5.25 ppm belonged to the alkene protons of long chain fatty acid were absent, due to the formation of epoxide product. The signal at δ_{H} 2.68 to 2.76 ppm belonged to the proton in epoxide group.

The ^{13}C -NMR spectrum of palm oil epoxide was shown in Figure A11. The important signals of palm oil epoxide were shown in Table 4.8.

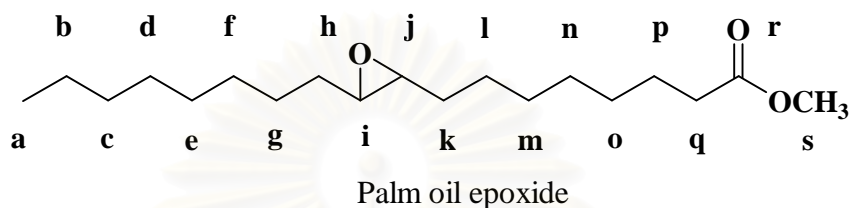
Table 4.8 The assignments of ^{13}C -NMR spectrum of palm oil epoxide.

Position of Carbon	Chemical Shift (δ ,ppm)
a	14.02
b,c,d,e,f,g,h,k,l,m,n,o,p	22.62-31.86
q	34.00
s	51.32
i,j	57.13-57.17
r	174.23

From the ^{13}C -NMR spectrum of palm oil epoxide (Figure A11) as comparing with palm oil methyl ester (Figure A6), it could be observed that the signals of olefinic carbon ($-\text{C}=\text{C}-$) at δ_{C} 127.79 to 129.93 ppm were absent, due to the formation

of epoxide product. The signal at δ_c 57.13 to 57.17 ppm belonged to the carbons in epoxide group.

From the results of these spectral data, it could be concluded that the product was palm oil epoxide was and its structure was as follow:



4.2.3 Palm oil nitrate

The IR spectrum of palm oil nitrate was shown in Figure A12. The important absorption bands of palm oil nitrate were listed in Table 4.9.

Table 4.9 The absorption assignments of palm oil nitrate.

Wave number (cm ⁻¹)		Assignments
Palm oil epoxide	Palm oil nitrate	
3467	-	O-H Stretching
2849	2863	C-H Stretching, Aliphatic
1741	1742	C=O Stretching
-	1632	NO ₂ Asymmetric Stretching
1461	1461	C-H Bending, Aliphatic
-	1271	NO ₂ Symmetric Stretching
1162	1167	C-O Stretching
	853	N-O Stretching Vibration

From the IR spectrum of palm oil nitrate (Figure A12) as comparing with palm oil epoxide (Figure A9), it could be observed that there was no absorption band of OH stretching at 3467 cm⁻¹ but the absorption bands of NO₂ (asymmetric and symmetric) stretching and NO stretching were clearly observed at

1632, 1271 and 853 cm^{-1} , respectively. The result was confirmed by using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra.

The $^1\text{H-NMR}$ spectrum of palm oil nitrate was shown in Figure A13. The important signals of palm oil nitrate were shown in Table 4.10.

Table 4.10 The assignments of $^1\text{H-NMR}$ spectrum of palm oil nitrate.

Position of Proton	Multiplicity	Chemical Shift (d,ppm)
a	m	0.75-0.81
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.12-1.59
q	t	2.26-2.24
s	s	3.56
i,j	m	5.06-5.16

From the $^1\text{H-NMR}$ spectrum of palm oil nitrate (Figure A13) as comparing with palm oil epoxide (Figure A10), it could be observed that the signals at δ_{H} 3.18 to 3.26 ppm belonged to the protons of carbon that connected hydroxy group were absent, due to the formation of nitrate product. The signals at δ_{H} 5.06 ppm to δ_{H} 5.16 ppm belonged to the protons of carbon that connected nitrate group.

The $^{13}\text{C-NMR}$ spectrum of palm oil nitrate was shown in Figure A14. The important signals of palm oil nitrate were shown in Table 4.11.

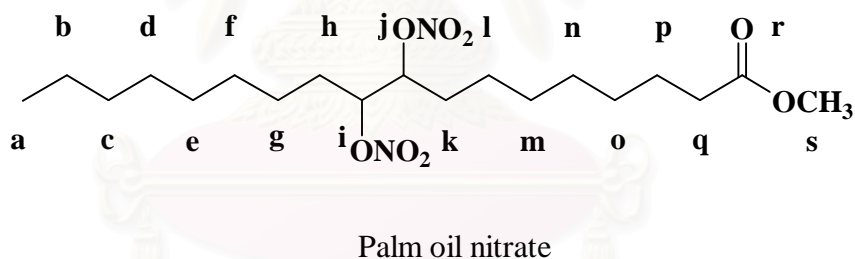
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จุฬาลงกรณ์มหาวิทยาลัย

Table 4.11 The assignments of ^{13}C -NMR spectrum of palm oil nitrate.

Position of Carbon	Chemical Shift (δ ,ppm)
a	13.79
b,c,d,e,f,g,h,k,l,m,n,o,p	22.34-31.84
q	33.92
s	51.19
i,j	81.62-81.67
r	174.06

From the ^{13}C -NMR spectrum of palm oil nitrate (Figure A14) as comparing with palm oil epoxide (Figure A11), it could be observed that the signals of the carbons at δ_c 81.62 to 81.67 ppm belonged to the carbons that connected nitrate group.

From the results of the spectral data, it could be concluded that the product was palm oil nitrate and its structure was as follows:



4.2.4 Soybean oil methyl ester

The IR spectra of soybean oil soapstock and soybean oil methyl ester were shown in Figure A16 and A17, respectively. The important adsorption bands of soybean oil soapstock and soybean oil methyl ester were listed in Table 4.12

Table 4.12 The absorption assignments of soybean oil soapstock and soybean oil methyl ester.

Wave number (cm ⁻¹)		Assignments
Soybean oil soapstock	Soybean oil methyl ester	
3006	3006	=C-H Stretching
2860	2859	C-H Stretching, Aliphatic
1740	1740	C=O Stretching
1655	1655	C=C Stretching
1460	1460	C-H Bending, Aliphatic
1161	1171	C-O Stretching

The IR spectrum of soybean oil methyl ester (Figure A 17) and soybean oil soapstock (Figure A 16) could not be distinguished. The result was confirmed by using ¹H-NMR and ¹³C-NMR

The ¹H-NMR spectra of soybean oil soapstock and soybean oil methyl ester were shown in Figures A18 and A19, respectively. The important signals of soybean oil soapstock and soybean oil methyl ester were shown in Table 4.13.

Table 4.13 The assignments of $^1\text{H-NMR}$ spectra of soybean oil soapstock and soybean oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ ,ppm)	
		Soybean oil soapstock	Soybean oil methyl ester
a	m	0.81-0.87	0.75-0.81
b,c,d,e,k,l,m,n,o,p	m	1.18-2.02	1.12-1.96
q	t	2.23-2.30	2.15-2.22
h	m	2.69-2.75	2.63-2.69
s	s	-	3.54
t,u,v	m	4.05-4.30	-
f,g,i,j	m	5.22-5.34	5.14-5.29

From the $^1\text{H-NMR}$ spectrum of soybean oil methyl ester (Figure A19) as comparing with soybean oil soapstock (Figure A18), it could be observed that the signal between δ_{H} 4.05 ppm to δ_{H} 4.30 ppm belonged to the proton of glycerol moiety of triglyceride were absent, due to the formation of methyl ester. The signal at δ_{H} 3.54 ppm was belonged to the protons of methoxy group of methyl ester.

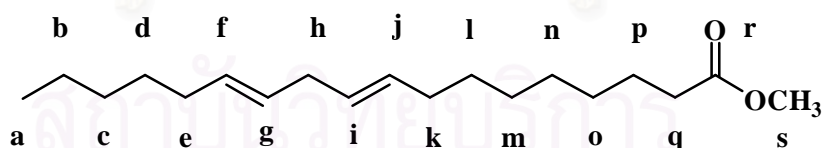
The $^{13}\text{C-NMR}$ spectra of soybean oil soapstock and soybean oil methyl ester were shown in Figures A20 and A21, respectively. The important signals of soybean oil soapstock and soy bean oil methyl ester were shown in Table 4.14.

Table 4.14 The assignments of ^{13}C -NMR spectra of soybean oil soapstock and soybean oil methyl ester.

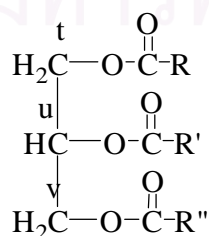
Position of Carbon	Chemical Shift (δ ,ppm)	
	Soybean oil soapstock	Soybean oil methyl ester
a	14.03	13.95
b,c,d,e,h,k,l,m,n,o,p,q	22.55-34.10	22.51-33.93
s	-	51.18
t,v	62.02	-
u	68.87	-
f,g,i,j	127.07-131.79	127.03-131.73
r	172.63-173.03	173.95

From the ^{13}C -NMR spectrum of soybean oil methyl ester (Figure A21) as comparing with soybean oil soapstock (Figure A20), it was clearly seen that the signals at δ_c 62.02 ppm and δ_c 68.87 ppm belonged to the carbons of glycerol moiety of triglyceride were absent, and the signal at δ_c 51.18 ppm belonged to the carbon of methoxy group of methyl ester was shown instead.

From the results of these spectral data, it could be concluded that the product was soybean oil methyl ester and its structure was as follows:



Soybean oil methyl ester



Soybean oil

4.2.5 Soybean oil epoxide

The IR spectrum of soybean oil epoxide was shown in Figure A24. The important absorption bands of soybean oil epoxide were listed in Table 4.15.

Table 4.15 The absorption assignments of soybean oil epoxide.

Wave number (cm ⁻¹)		Assignments
Soybean oil methyl ester	Soybean oil epoxide	
-	3453	O-H Stretching
3006	-	=C-H Stretching
2859	2864	C-H Stretching, Aliphatic
1740	1740	C=O Stretching
1655	-	C=C Stretching
1465	1455	C-H Bending, Aliphatic
1171	1171	C-O Stretching

From the IR spectrum of soybean oil epoxide (Figure A24) as comparing with soybean oil methyl ester (Figure A17), it could be observed that the absorption bands at 3006 cm⁻¹ and 1655 cm⁻¹ were observed in the spectrum of soybean oil methyl ester due to the presence of double bond in fatty acid chain, while they could not be observed in the spectrum of soybean oil epoxide. It also showed the characteristic absorption band of OH stretching at 3453 cm⁻¹. The result was confirmed by using ¹H-NMR and ¹³C-NMR spectra.

The ¹H-NMR spectrum of soybean oil epoxide was shown in Figure A25. The important signals of soybean oil epoxide were shown in Table 4.16.

Table 4.16 The assignments of $^1\text{H-NMR}$ spectrum of soy bean oil epoxide.

Position of Proton	Multiplicity	Chemical Shift (δ ,ppm)
a	m	0.77-0.81
b,c,d,e,h,k,l,m,n,o,p	m	1.14-1.54
q	t	2.15-2.26
f,g,i,j	m	3.29-3.50
s	s	3.55

From the $^1\text{H-NMR}$ spectrum of soybean oil epoxide (Figure A25) as comparing with soybean oil methyl ester (Figure A19), it could be observed that the signal between δ_{H} 5.14 ppm to δ_{H} 5.29 ppm belonged to the alkene protons of long chain fatty acid were absent, and the signals at δ_{H} 3.29 to 3.50 ppm belonged to the protons of carbon that connected to a hydroxy group (likely from ring opening of dihydroxy product) were shown instead.

The $^{13}\text{C-NMR}$ spectrum of soybean oil epoxide was shown in Figure A26. The important signals of soybean oil epoxide were shown in Table 4.17.

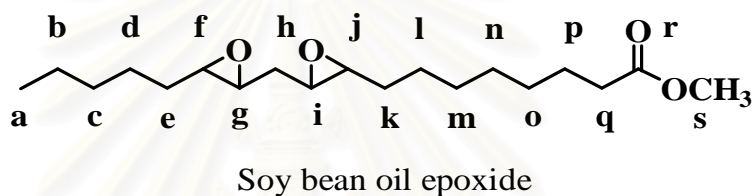
Table 4.17 The assignments of $^{13}\text{C-NMR}$ spectrum of soybean oil epoxide

Position of Carbon	Chemical Shift (δ ,ppm)
a	13.97
b,c,d,e,h,k,l,m,n,o,p,q	22.55-33.92
s	51.28
f,g,i,j	56.47-57.13
r	174.19

The $^{13}\text{C-NMR}$ spectrum of soybean oil epoxide (Figure A26) showed the difference from that of palm oil epoxide spectrum (Figure A11). That was because in soybean oil had linoleic acid (53%) more than palm oil (10%). Thus the influences of

linoleic acid make the spectrum different. When comparing the ^{13}C -NMR spectrum of soybean oil epoxide with that of soybean oil methyl ester (Figure A21), it could be observed that the signals of olefinic carbon ($-\text{C}=\text{C}-$) at δ_c 127.03 to 131.73 ppm were absent, due to the formation of epoxide product. The signals at δ_c 56.47 to 57.13 ppm were belonged to the carbons in epoxide group. In addition, it could be observed the signals at δ_c 71.29 to 84.03 ppm which resulting from the ring opening hydroxy product.

From the results of these spectral data, it could be concluded that the product was soybean oil epoxide and its structure was as follows:



4.2.6 Soybean oil nitrate

The IR spectrum of soybean oil nitrate was shown in Figure A27. The important absorption bands of soybean oil nitrate were listed in Table 4.18.

Table 4.18 The absorption assignments of soybean oil nitrate.

Wave number (cm^{-1})		Assignments
Soybean oil epoxide	Soybean oil nitrate	
3453	-	O-H Stretching
2864	2864	C-H Stretching, Aliphatic
1740	1740	C=O Stretching
-	1639	NO_2 Asymmetric Stretching
1455	1456	C-H Bending, Aliphatic
-	1271	NO_2 Symmetric Stretching
1171	1191	C-O Stretching
-	854	N-O Stretching Vibration

From the IR spectrum of soybean oil nitrate (Figure A27) as comparing with soybean oil epoxide (Figure A24), it could be observed that there was no absorption band of OH stretching 3453 cm^{-1} but the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1639, 1271 and 854 cm^{-1} respectively. The result was confirmed by using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra.

The $^1\text{H-NMR}$ spectrum of soybean oil nitrate was shown in Figure A28. The important signals of soybean oil nitrate were shown in Table 4.19.

Table 4.19 The assignments of $^1\text{H-NMR}$ spectrum of soybean oil nitrate.

Position of Proton	Multiplicity	Chemical Shift (δ ,ppm)
a	m	0.75-0.79
b,c,d,e,h,k,l,m,n,o,p	m	1.16-1.55
q	t	2.16-2.24
s	s	3.56
f,g,i,j	m	5.08-5.14

From the $^1\text{H-NMR}$ spectrum of soybean oil nitrate (Figure A28) as comparing with soybean oil epoxide (Figure A25), it could be observed that the signal at δ_{H} 3.29 to 3.50 ppm belonged to the protons of carbon that connected to a hydroxy group were absent, due to formation of nitrate product. The signals at δ_{H} 5.08 ppm to δ_{H} 5.14 ppm belonged to the proton of carbon that connected to a nitrate group.

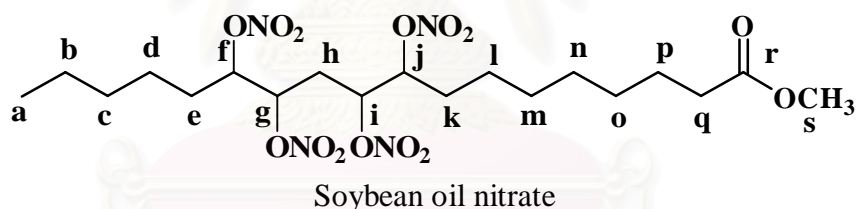
The $^{13}\text{C-NMR}$ spectrum of soybean oil nitrate was shown in Figure A29. The important signals of soybean oil nitrate were shown in Table 4.20.

Table 4.20 The assignments of ^{13}C -NMR spectrum of soybean oil nitrate.

Position of Carbon	Chemical Shift (δ ,ppm)
a	13.83
b,c,d,e,h,k,l,m,n,o,p,q	22.31-34.35
s	51.31
f,g,i,j	77.13-84.20
r	174.09

From the ^{13}C -NMR spectrum of soybean oil nitrate (Figure A29) as comparing with soybean oil epoxide (Figure A27), it could be observed that the signals of the carbons at δ_c 77.13 to 84.20 ppm belonged to the carbon connected to the nitrate group.

From the results of these spectral data, it could be concluded that the product was soybean oil nitrate and its structure was as follows:



4.2.7 Rice bran oil methyl ester

The IR spectra of rice bran oil soapstock and rice bran oil methyl ester were shown in Figure A31 and A32, respectively. The important adsorption bands of rice bran oil soapstock and rice bran oil methyl ester were listed in Table 4.21

Table 4.21 The absorption assignments of rice bran oil soapstock and rice bran oil methyl ester.

Wave number (cm ⁻¹)		Assignments
Rice bran oil soapstock	Rice bran oil methyl ester	
3007	3007	=C-H Stretching
2860	2851	C-H Stretching, Aliphatic
1741	1745	C=O Stretching
1654	1654	C=C Stretching
1456	1460	C-H Bending, Aliphatic
1157	1166	C-O Stretching

The IR spectrum of rice bran oil methyl ester (Figure A 32) and rice bran oil soapstock (Figure A 31) could not be distinguished. The result was confirmed by using ¹H-NMR and ¹³C-NMR

The ¹H-NMR spectra of rice bran oil soapstock and rice bran oil methyl ester were shown in Figures A33 and A34, respectively. The important signals of rice bran oil soapstock and rice bran oil methyl ester were shown in Table 4.22.

Table 4.22 The assignments of ¹H-NMR spectra of rice bran oil soapstock and rice bran oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Rice bran oil soapstock	Rice bran oil methyl ester
a	m	0.77-0.83	0.74-0.81
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.15-1.95	1.12-1.92
q	t	2.19-2.26	2.15-2.22
s	s	-	3.54
t,u,v	m	4.01-4.27	-
i,j	m	5.19-5.28	5.20-5.25

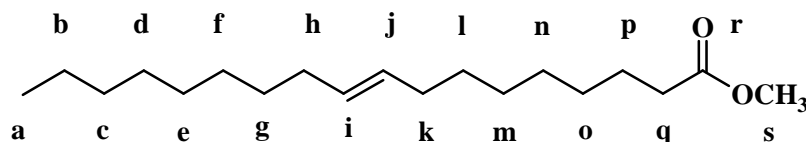
From the $^1\text{H-NMR}$ spectrum of rice bran oil methyl ester (Figure A34) as comparing with rice bran oil soapstock (Figure A33), it could be observed that the signal at δ_{H} 3.54 ppm was belonged to the protons of methoxy group of methyl ester.

The $^{13}\text{C-NMR}$ spectra of rice bran oil soapstock and rice bran methyl ester were shown in Figures A35 and A36, respectively. The important signals of rice bran oil soapstock and rice bran oil methyl ester were shown in Table 4.23.

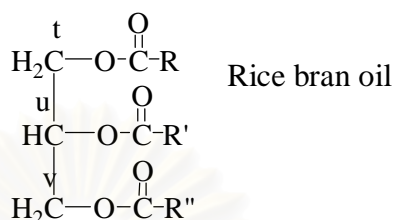
Table 4.23 The assignments of $^{13}\text{C-NMR}$ spectra of rice bran oil soapstock and rice bran oil methyl ester.

Position of Carbon	Chemical Shift (δ ,ppm)	
	Rice bran oil soapstock	Rice bran oil methyl ester
a	14.05	14.00
b,c,d,e,f,g,h,k,l,m,n,o,p	22.55-33.94	22.61-31.86
q	34.09	33.90
s	-	51.18
t,v	62.02	-
u	68.87	-
i,j	127.83-130.01	127.79-129.93
r	172.60-173.01	173.90

Form the $^{13}\text{C-NMR}$ spectrum of rice bran oil methyl ester (Figure A36) as comparing with rice bran oil soapstock (Figure A35), it was clearly seen that the signals at δ_{C} 62.02 ppm and δ_{C} 68.87 ppm belonged to the carbons of glycerol moiety of triglyceride were absent, and the signal at δ_{C} 51.18 ppm belonged to the carbon of methoxy group of methyl ester was shown instead. From the results of these spectral data, it could be concluded that the product was rice bran oil methyl ester and its structure was as follows:



Rice bran oil methyl ester



Rice bran oil

4.2.8 Rice bran oil epoxide

The IR spectrum of rice bran oil epoxide was shown in Figure A39. The absorption bands of rice bran oil epoxide were listed in Table 4.24.

Table 4.24 The absorption assignments of rice bran oil epoxide.

Wave number (cm ⁻¹)		Assignments
Rice bran oil methyl ester	Rice bran oil epoxide	
-	3450	O-H Stretching
3007	-	=C-H Stretching
2851	2847	C-H Stretching, Aliphatic
1745	1738	C=O Stretching
1654	-	C=C Stretching
1460	1464	C-H Bending, Aliphatic
1166	1166	C-O Stretching

From the IR spectrum of rice bran oil epoxide (Figure A39) as comparing with rice bran oil methyl ester (Figure A32), it could be observed that the absorption bands at 3007 cm⁻¹ and 1654 cm⁻¹ were observed in the spectrum of rice bran oil methyl ester due to the presence of double bond in fatty acid chain, while they could not be observed in spectrum of rice bran oil epoxide.

The $^1\text{H-NMR}$ spectrum of rice bran oil epoxide was shown in Figure A40. The important signals of rice bran oil epoxide were shown in Table 4.25.

Table 4.25 The assignments of $^1\text{H-NMR}$ spectrum of rice bran oil epoxide.

Position of Proton	Multiplicity	Chemical Shift (d,ppm)
a	m	0.71-0.77
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.09-1.51
q	t	2.11-2.19
i,j	m	2.68-2.76
s	s	3.54

From the $^1\text{H-NMR}$ spectrum of rice bran oil epoxide (Figure A40) as comparing with rice bran oil methyl ester (Figure A34), it could be observed that the signal between δ_{H} 5.20 ppm to δ_{H} 5.25 ppm belonged to the alkene protons of long chain fatty acid were absent, due to the formation of epoxide product. The signal at δ_{H} 2.68 to 2.76 ppm belonged to the proton in epoxide group.

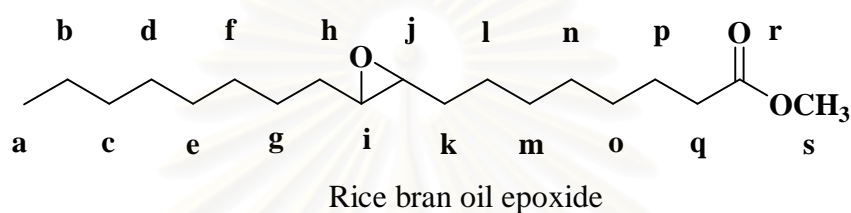
The $^{13}\text{C-NMR}$ spectrum of rice bran oil epoxide was shown in Figure A41. The important signals of rice bran oil epoxide were shown in Table 4.26.

Table 4.26 The assignments of $^{13}\text{C-NMR}$ spectrum of rice bran oil epoxide.

Position of Carbon	Chemical Shift (d,ppm)
a	14.02
b,c,d,e,f,g,h,k,l,m,n,o,p	22.62-31.86
q	34.00
s	51.32
i,j	57.13-57.17
r	174.23

From the ^{13}C -NMR spectrum of rice bran oil epoxide (Figure A41) as comparing with rice bran oil methyl ester (Figure A36), it could be observed that the signals of olefinic carbon ($-\text{C}=\text{C}-$) at δ_{C} 127.79 to 129.93 ppm were absent, due to the formation of epoxide product. The signal at δ_{C} 57.13 to 57.17 ppm belonged to the carbons in epoxide group.

From the results of these spectral data, it could be concluded that the product was rice bran oil epoxide and its structure was as follow:



4.2.9 Rice bran oil nitrate

The IR spectrum of rice bran oil nitrate was shown in Figure A42. The important absorption bands of rice bran oil nitrate were listed in Table 4.27.

Table 4.27 The absorption assignments of rice bran oil nitrate.

Wave number (cm^{-1})		Assignments
Rice bran oil epoxide	Rice bran oil nitrate	
3450	-	O-H Stretching
2847	2853	C-H Stretching, Aliphatic
1738	1735	C=O Stretching
-	1643	NO_2 Asymmetric Stretching
1464	1458	C-H Bending, Aliphatic
-	1275	NO_2 Symmetric Stretching
1166	1166	C-O Stretching
	858	N-O Stretching Vibration

From the IR spectrum of rice bran oil nitrate (Figure A42) as comparing with rice bran oil epoxide (Figure A39), it could be observed that there was no absorption band of OH stretching at 3450 cm^{-1} but the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1643, 1275 and 858 cm^{-1} , respectively. The result was confirmed by using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra.

The $^1\text{H-NMR}$ spectrum of rice bran oil nitrate was shown in Figure A43. The important signals of rice bran oil nitrate were shown in Table 4.28.

Table 4.28 The assignments of $^1\text{H-NMR}$ spectrum of rice bran oil nitrate.

Position of Proton	Multiplicity	Chemical Shift (δ ,ppm)
a	m	0.75-0.81
b,c,d,e,f,g,h,k,l,m,n,o,p	m	1.12-1.59
q	t	2.26-2.24
s	s	3.56
i,j	m	5.06-5.16

From the $^1\text{H-NMR}$ spectrum of rice bran oil nitrate (Figure A43) as comparing with rice bran oil epoxide (Figure A40), it could be observed that the signals at δ_{H} 5.06 ppm to δ_{H} 5.16 ppm belonged to the protons of carbon that connected nitrate group.

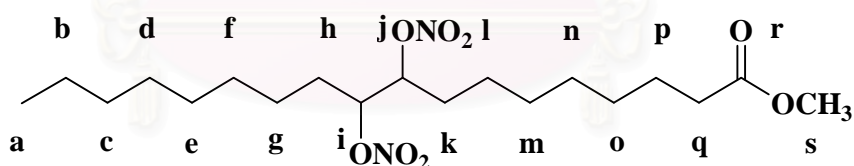
The $^{13}\text{C-NMR}$ spectrum of rice bran oil nitrate was shown in Figure A44. The important signals of rice bran oil nitrate were shown in Table 4.29.

Table 4.29 The assignments of ^{13}C -NMR spectrum of rice bran oil nitrate.

Position of Carbon	Chemical Shift (δ ,ppm)
a	13.79
b,c,d,e,f,g,h,k,l,m,n,o,p	22.34-31.84
q	33.92
s	51.19
i,j	81.62-81.67
r	174.06

From the ^{13}C -NMR spectrum of rice bran oil nitrate (Figure A44) as comparing with rice bran oil epoxide (Figure A41), it could be observed that the signals at δ_c 81.62 to 81.67 ppm belonged to the carbons connected to the nitrate group.

From the results of the spectral data, it could be concluded that the product was rice bran oil nitrate and its structure was as follows:



Rice bran oil nitrate

4.3 Characterization of 2-ethylhexyl nitrate

The IR spectra of 2-ethylhexyl nitrate was shown in Figures A46, respectively. The important absorption bands of 2-ethylhexyl nitrate was listed in Table 4.30.

Table 4.30 The absorption assignments of 2-Ethylhexyl nitrates.

Wave number (cm ⁻¹)	Assignment
2863	C-H Stretching, Aliphatic
1631	NO ₂ Asymmetric Stretching
1460, 1374	C-H Bending, Aliphatic
1279	NO ₂ Symmetric Stretching
984	C-O Stretching
856	O-N Stretching Vibration

From the IR spectrum of 2-ethylhexyl nitrate (Figure A46) it could be observed that the absorption bands of NO₂ (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1631, 1279 and 856 cm⁻¹ respectively. The result was confirmed by using ¹H-NMR and ¹³C-NMR spectra.

The ¹H-NMR spectra of 2-ethylhexyl nitrate were shown in Figures A47, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.31.

Table 4.31 The assignments of ¹H-NMR spectrum of 2-ethylhexyl nitrate.

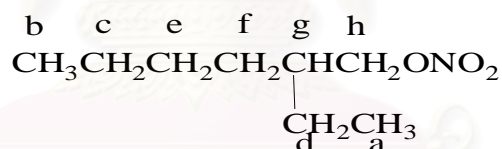
Chemical Shift (δ,ppm)	Multiplicity	Position of Proton	Number of Protons
0.85-0.92	m	a, b	6
1.27-1.48	m	c, d, e, f	8
1.60-1.78	m	g	1
4.38	d	h	2

The ¹³C-NMR spectra of 2-ethylhexyl nitrate were shown in Figures A48, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.32.

Table 4.32 The assignments of ^{13}C -NMR spectrum of 2-ethylhexyl nitrate.

Position of Carbon	Carbon Type	Chemical Shift of Nitrate(δ ,ppm)
a	CH_3	11.14
b	CH_3	14.25
c	CH_2	23.43
d	CH_2	23.10
e	CH	28.34
f	CH_2	29.21
g	CH_2	41.21
h	CH_2	78.19

From the results of the spectral data, it could be concluded that the product was 2-ethylhexyl nitrate and its structure was as follows:

**Table 4.33** The assignments of fragmentation ion peak of methyl ester

Compound	Fragmentation ion peak			
	t_R	m/z	Products	Figure
Palm oil methyl ester	14.50	284	Palmitic acid methyl ester	A7
	19.10	296	Oleic acid methyl ester	A8
Soybean oil methyl ester	19.09	296	Oleic acid methyl ester	A22
	20.04	294	Linoleic acid methyl ester	A23
Rice bran oil methyl ester	14.48	284	Palmitic acid methyl ester	A37
	19.09	296	Oleic acid methyl ester	A38

4.4 Determination of cetane number of multifunctional biodiesel in base diesel fuel.

The cetane numbers of the blend of multifunctional biodiesel with base diesel fuel at concentration in the range of 0.5% to 10.0 % weight were shown in Table 4.34.

Table 4.34 Cetane number of synthesized multifunctional biodiesel blended with base diesel fuel.

Concentration (% weight)	Cetane Number				
	Base + PMS	Base+PN	Base+SN	Base+RN	Base+EHN
0.05	-	-	-	-	59.5
0.10	-	-	-	-	60.8
0.20	-	-	-	-	64.0
0.50	-	55.5	57.5	60.7	68.4
1.00	-	55.9	57.6	61.6	69.6
2.00	54.2	56.1	58.4	61.8	71.9
5.00	54.6	56.2	62.4	66.2	-
10.00	55.1	57.8	62.6	67.3	-

Note: Base = base diesel fuel
PMS = palm oil methyl ester
PN = multifunctional biodiesel from palm oil soapstock
RN = multifunctional biodiesel from rice bran oil soapstock
SN = multifunctional biodiesel from soybean oil soapstock
EHN = 2-ethylhexyl nitrate

The physical properties of synthesized multifunctional biodiesel blended with base diesel fuel at concentration of 10% by weight were shown in Table 4.35.

Table 4.35 Physical properties of base diesel fuel blended with synthesized multifunctional biodiesel from soapstocks.

Properties	Base	Base + 10.00% PN	Base + 10.00% SN	Base + 10.00% RN
Mid-Boiling Point (°F)	530.6	527.0	538.52	532.4
API Gravity@ 60 °F	39.51	39.23	38.95	39.14
Viscosity	2.863	2.881	2.914	2.886
Pour Point (°C)	-2	-2	-2	-2
Flash Point (°C)	59.1	56.0	59.1	55.1
Density @ 15(°C)	0.827	0.824	0.826	0.825
Color	0.6	0.6	1.0	0.9
Cetane Index	52	57	59	58
Cetane Number	52.0	60.0	60.2	60.1

The synthesized multifunctional biodiesel from soapstocks were easily soluble in base diesel fuel and did not change any physical properties within the specification of diesel fuel at the concentration of 0.5% to 10.0% by weight.

Figure 4.1, showed the relationship between the cetane number and concentration (%wt) of multifunctional biodiesels and EHN in base diesel fuel.

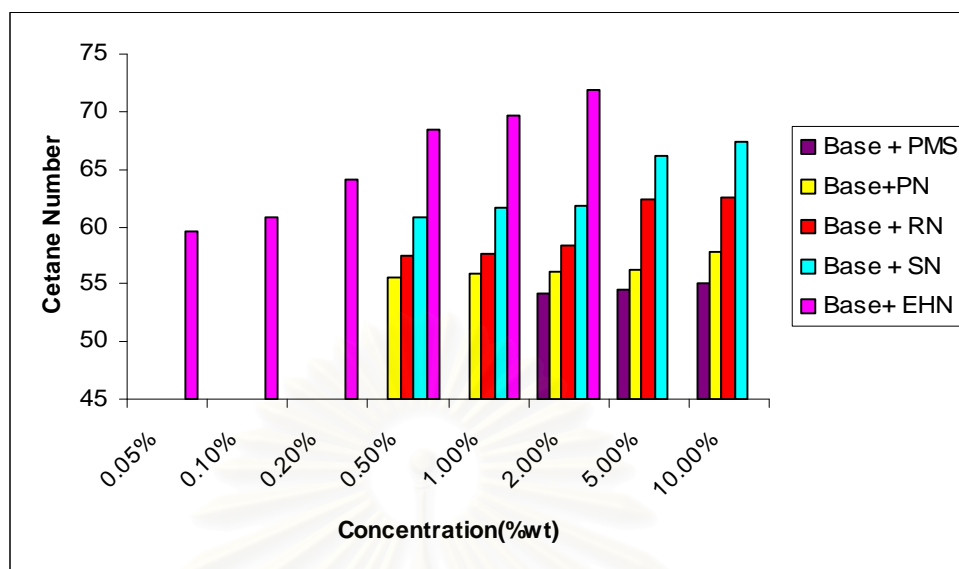


Figure 4.1 Relationship between the cetane number of multifunctional biodiesel in base diesel fuel and concentration (% wt).

From the relationship between the cetane number and concentration (%wt) of multifunctional biodiesel in base diesel fuel it could be seen that the cetane number of multifunctional biodiesel was increased when concentration increased. Multifunctional biodiesel from soybean oil soapstock gave cetane number higher than multifunctional biodiesels from rice bran oil soapstock and palm oil soapstock. Thus, it could be concluded that these multifunctional biodiesels could be used as cetane improver for diesel fuel, as compared EHN.

From Figure 4.1, it could be seen that 2-ethylhexyl nitrate (EHN) gave the highest cetane number at low concentration as compare with the others.

4.5 Determination of lubricity performance of base diesel fuel blended with multifunctional biodiesel.

The lubricity performances of the base diesel fuels blended with multifunctional biodiesels were investigated 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 had

higher lubricity performance, it could be given lower wear scar diameter value. Table 4.38 showed the lubricity performances of multifunctional biodiesels blended in base diesel fuel at the same concentration of 5% by weight. The results showed that only the multifunctional biodiesel from palm oil soapstock gave mean wear scar diameter of 373 μm which was less than 460 μm of the standard.

Table 4.36 The element composition of products.

Nitrate Compounds	Element analysis value (%)			C:N Ratio
	C	H	N	
Palm oil nitrate	49.3542	8.1379	1.6780	29.4125
Rice bran oil nitrate	53.5342	9.2844	2.5318	21.1447
Soy bean oil nitrate	57.3254	9.4394	2.5084	22.8533

Table 4.37 Lubricity performance of the blends of 5% by weight of multifunctional biodiesels with base diesel fuel.

Blended composition	Lubricity performance (Mean wear scar diameter, μm)
Base diesel fuel	421
Base+ biodiesel from palm oil soapstock	373
Base+ biodiesel from rice bran oil soapstock	472
Base+ biodiesel from soybean oil soapstock	545
Standard	< 460

According to C/N ratio in Table 4.36 and lubricity performance in Table 4.37, it could be concluded that multifunctional biodiesel from palm oil soapstock gave lubricity performance better than multifunctional biodiesels from rice bran oil soapstock and soybean oil soapstock. This result could be explained from C/N ratio,

as multifunctional biodiesel from palm oil soapstock had C/N ratio of 29.41, which was higher than C/N ratio of 22.85, 21.14 from multifunctional biodiesels from soybean oil soapstock and rice bran oil soapstock. It could be concluded that more C/N ratio gave better lubricity performance.

4.6 DSC analysis of multifunctional biodiesels.

It could be seen from Figure 4.2 the results shown that DSC scan of these products gave a very sharp intense exotherm peak at 195-197 °C, respectively.

According to the DSC peak, the nitrate groups in these multifunctional biodiesels are thermally more stable than EHN.

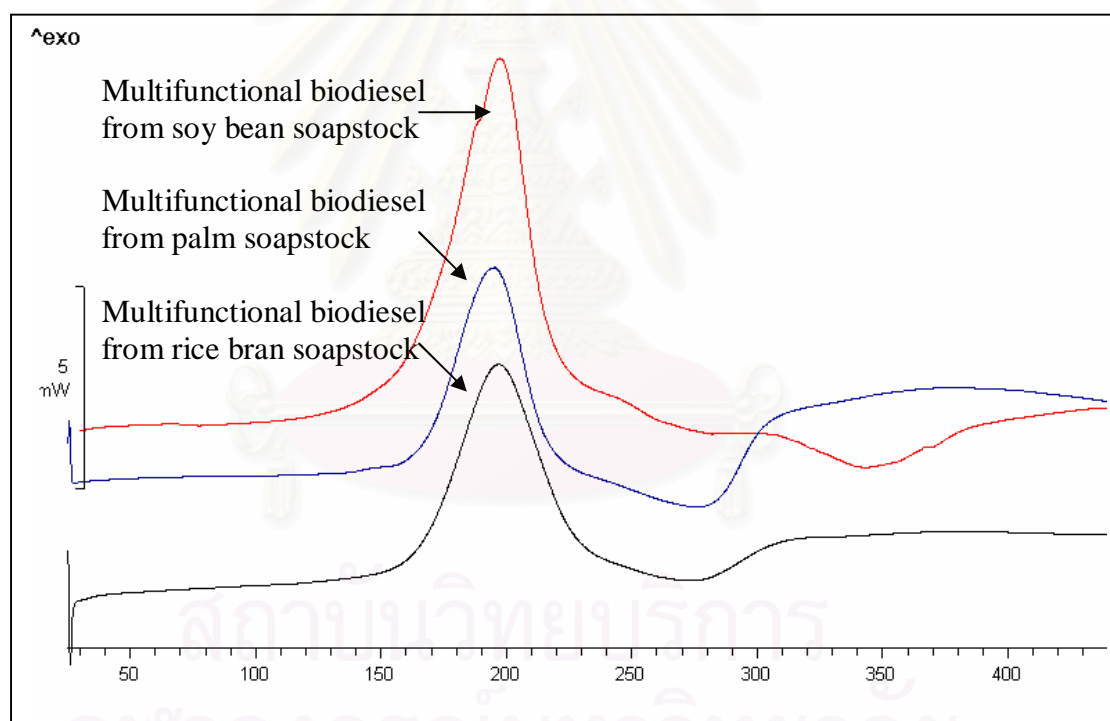


Figure 4.2 DSC of multifunctional biodiesel from soapstocks.

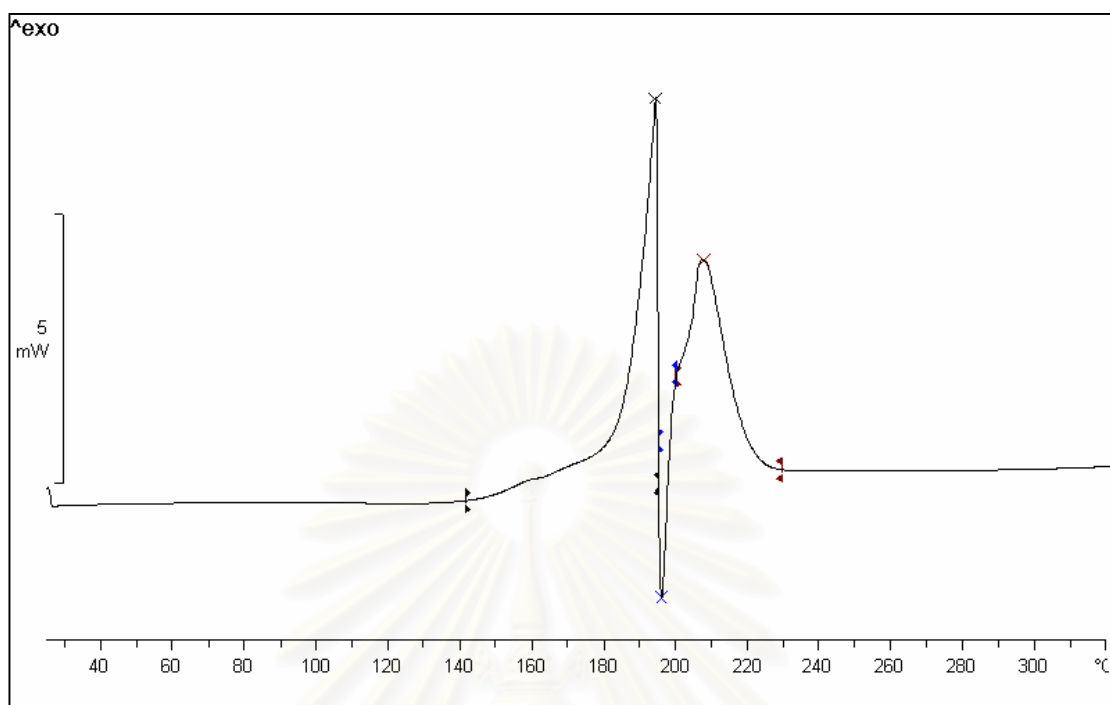


Figure 4.3 DSC of 2-ethylhexyl nitrate.

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CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The multifunctional biodiesel from soapstock such as soy bean oil, rice bran oil, palm oil could be synthesized. Firstly, the esterification of fatty acid with methanol using sulfuric acid as catalyst gave a methyl ester product (96-98% yield). Then, the epoxidation of methyl ester product with peroxy acid gave an epoxide compound (92-95% yield). Finally the nitration of epoxide compound with concentrated nitric acid and concentrated sulfuric acid gave a multifunctional biodiesel (92-95% yield).

The products were easily soluble in base diesel fuel and did not change any physical properties such as API gravity, viscosity *etc.* when blend with base diesel fuel at the concentration of 0.05% to 10.0% by weight. The product from soy bean soapstock increased a cetane number more than rice bran soapstock and palm soapstock at the same concentration.

The lubricity test at concentration of 5% by weight of each product for palm oil, rice bran oil, soy bean oil were carried out by using High Frequency Reciprocating Rig machine. The result showed that only the product of palm oil gave the satisfaction of mean wear scar diameter was 426 μm compared with the standard value of less than 460 μm . Considering the performances of multifunctional biodiesel from palm oil soapstock was the best lubricity additive for diesel fuel.

5.2 Further study

1. The utilization of synthesized multifunctional biodiesel need more studies on engine performance tests such as emission of NO_x and CO etc.
2. New source of cheaper oil need to be studied.
3. More lubricity performance tests need to be done on various concentrations.



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APPENDICES

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APPENDIX A
SPECTRA OF SYNTHESIZED COMPOUNDS

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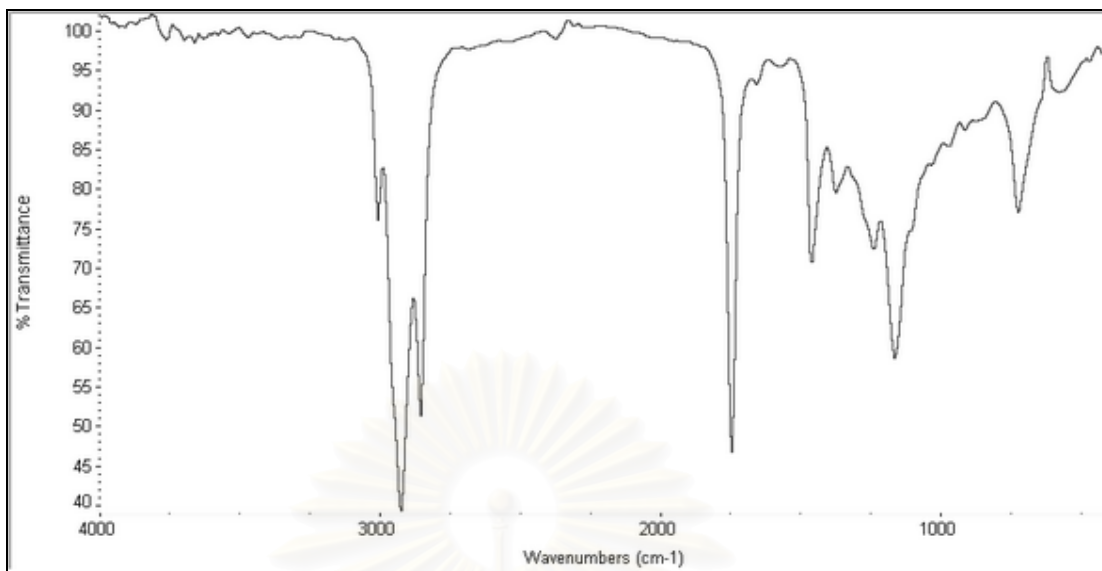


Figure A1 FTIR spectrum of palm oil soapstock (NaCl)

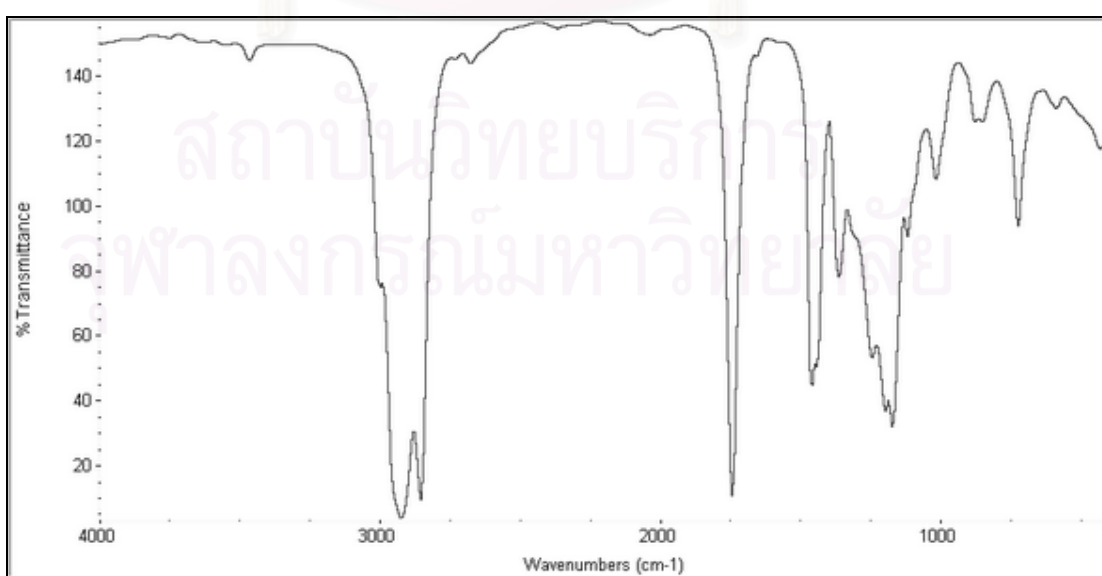


Figure A2 FTIR spectrum of palm oil methyl ester (NaCl)

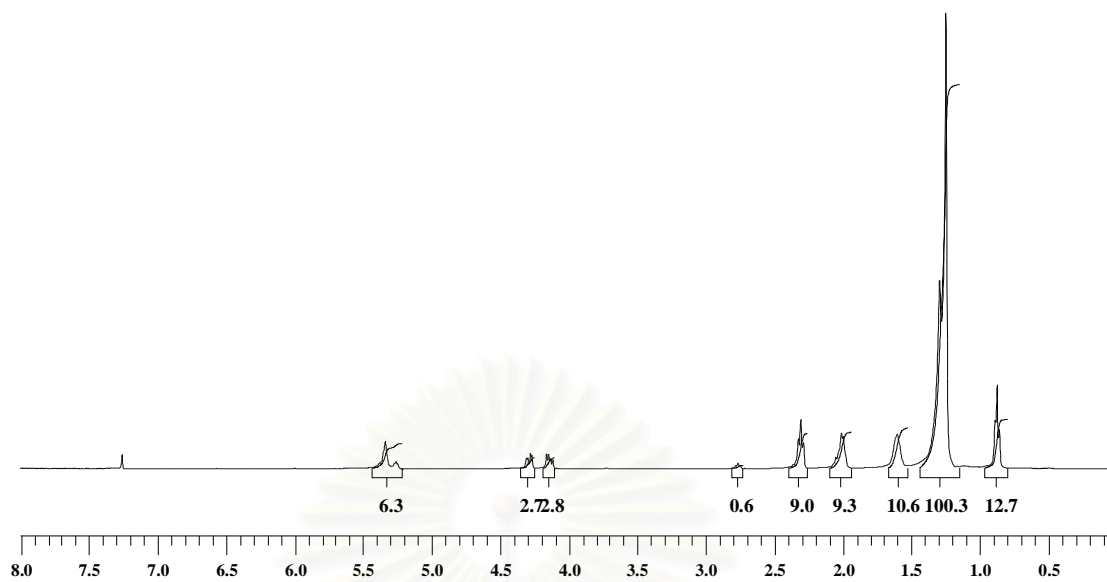


Figure A3 $^1\text{H-NMR}$ spectrum of palm oil soapstock (CDCl_3)

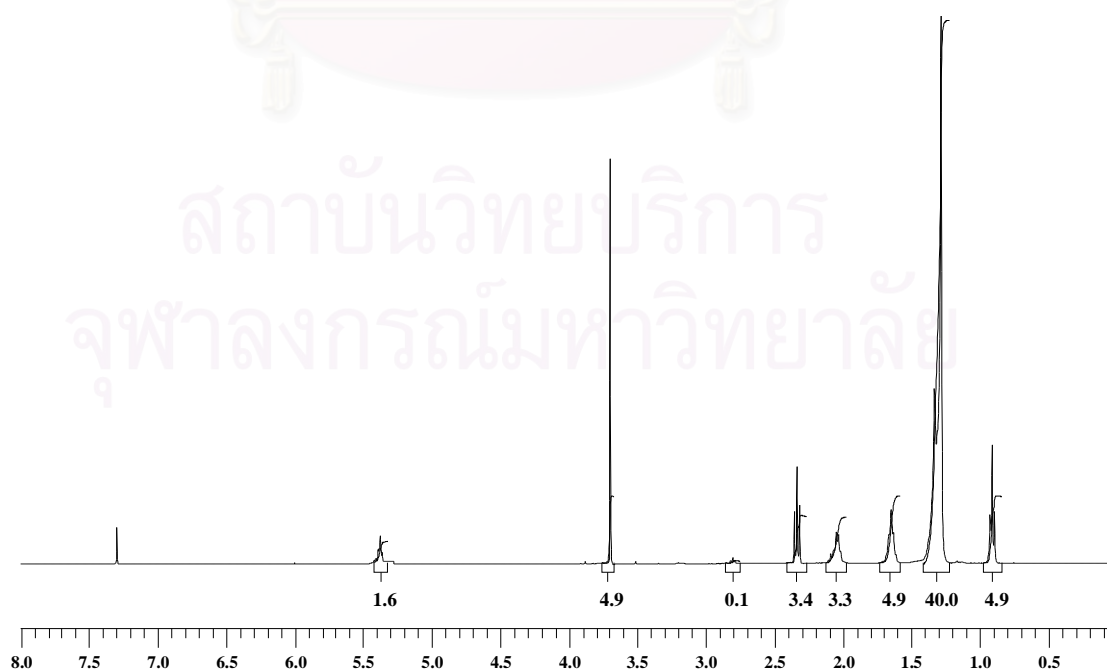


Figure A4 $^1\text{H-NMR}$ spectrum of palm oil methyl ester (CDCl_3)

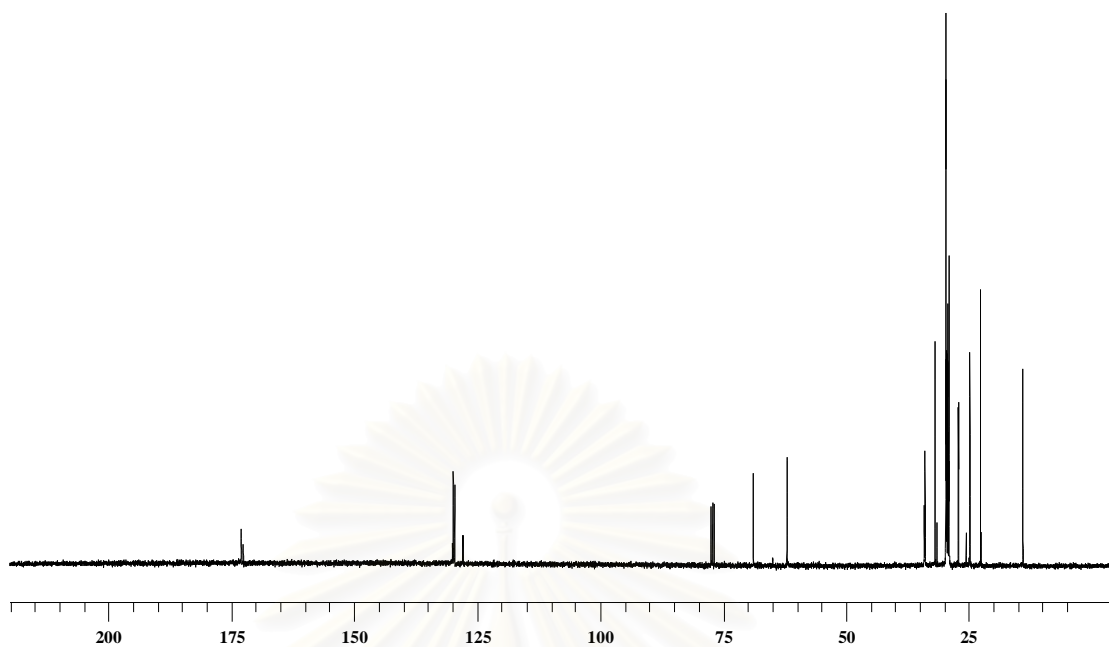


Figure A5 ^{13}C -NMR spectrum of palm oil soapstock (CDCl_3)

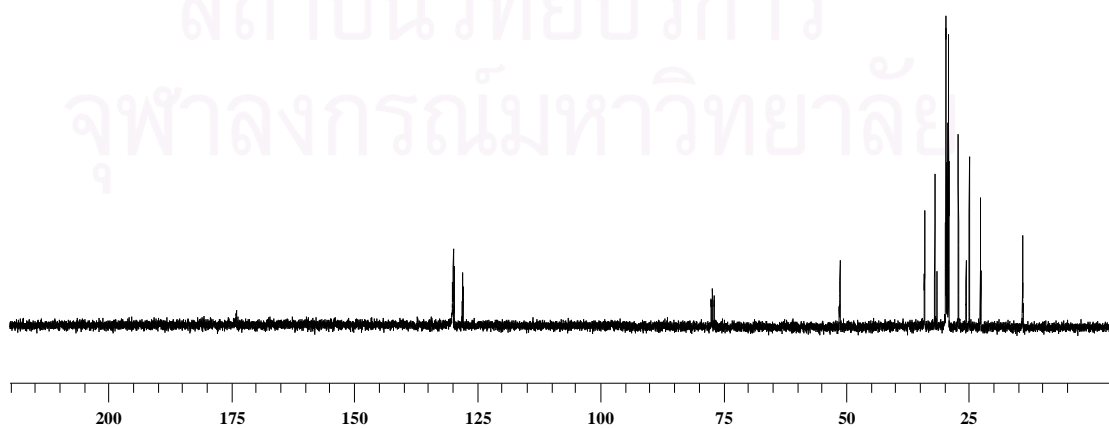


Figure A6 ^{13}C -NMR spectrum of palm oil methyl ester (CDCl_3)

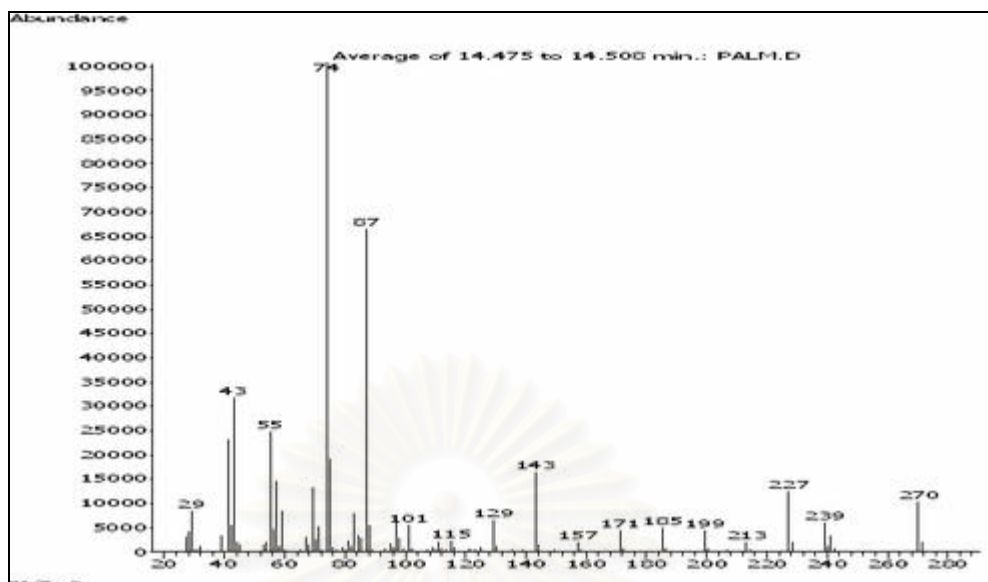


Figure A7 Mass spectrum of palm oil methyl ester at retention time of 14.50 min.

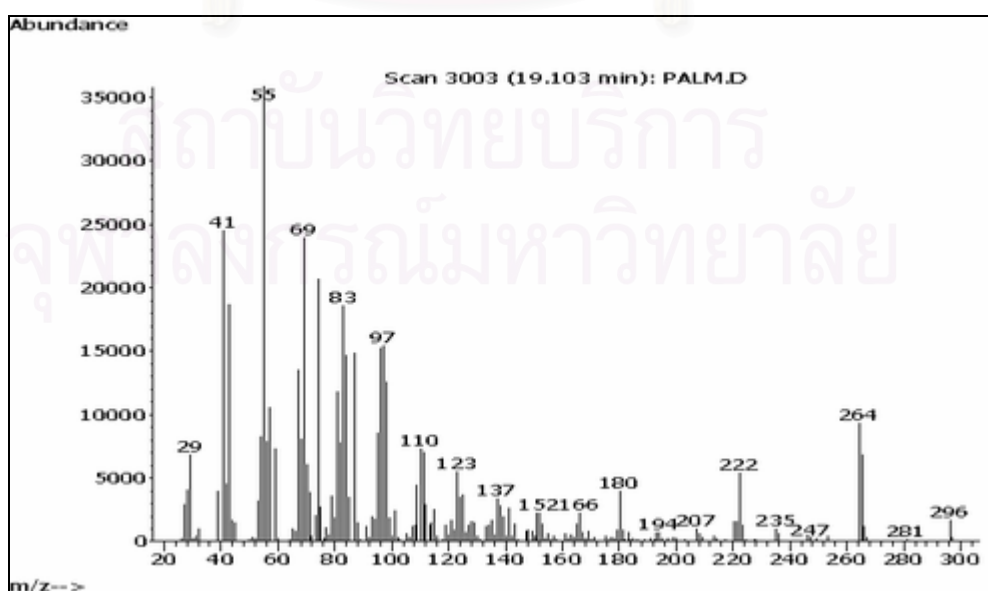


Figure A8 Mass spectrum of palm oil methyl ester at retention time of 19.10 min

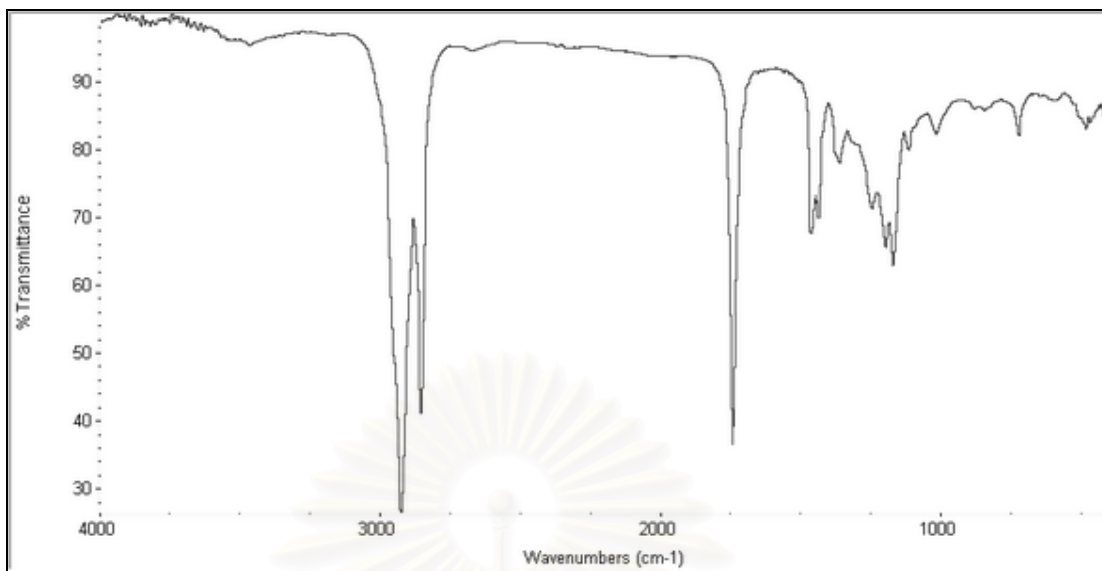


Figure A9 FTIR spectrum of palm oil epoxide (NaCl)

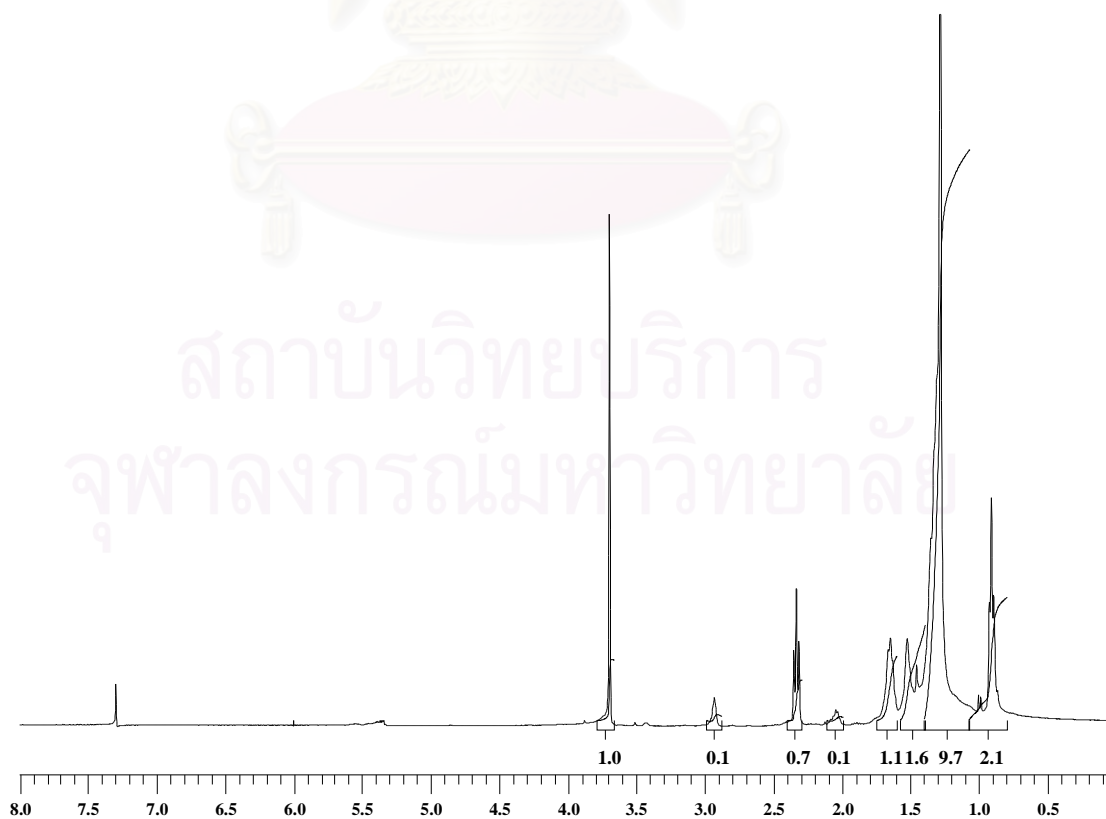


Figure A10 $^1\text{H-NMR}$ spectrum of palm oil epoxide (CDCl_3)

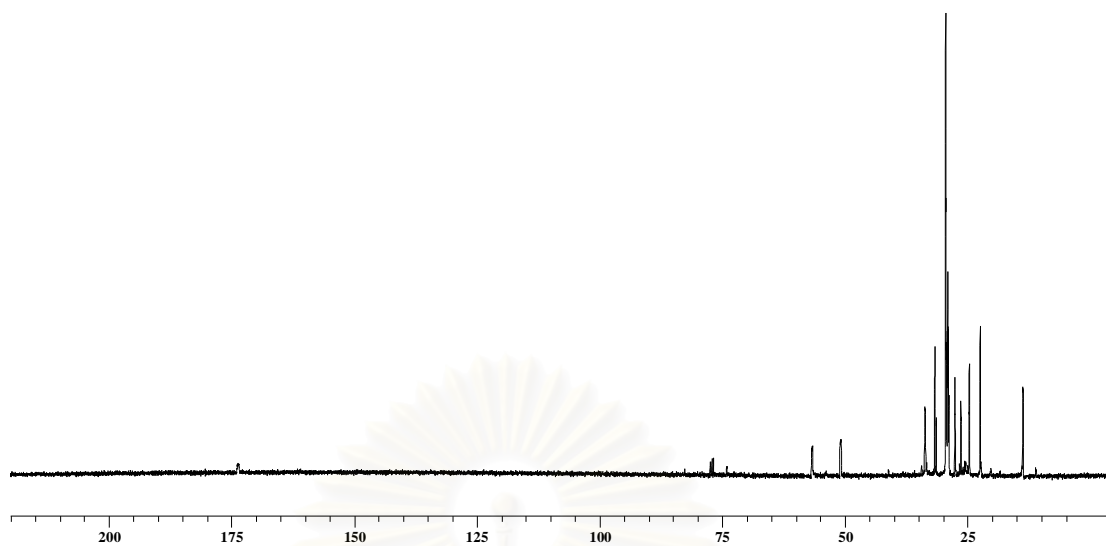


Figure A11 ^{13}C -NMR spectrum of palm oil epoxide (CDCl_3)

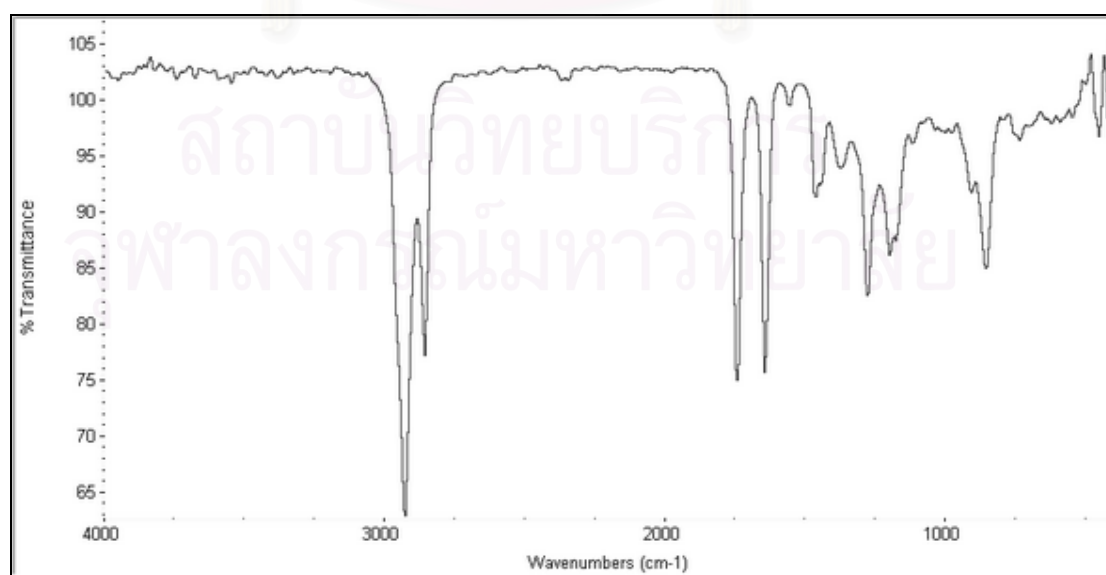


Figure A12 FTIR spectrum of palm oil nitrate (NaCl)

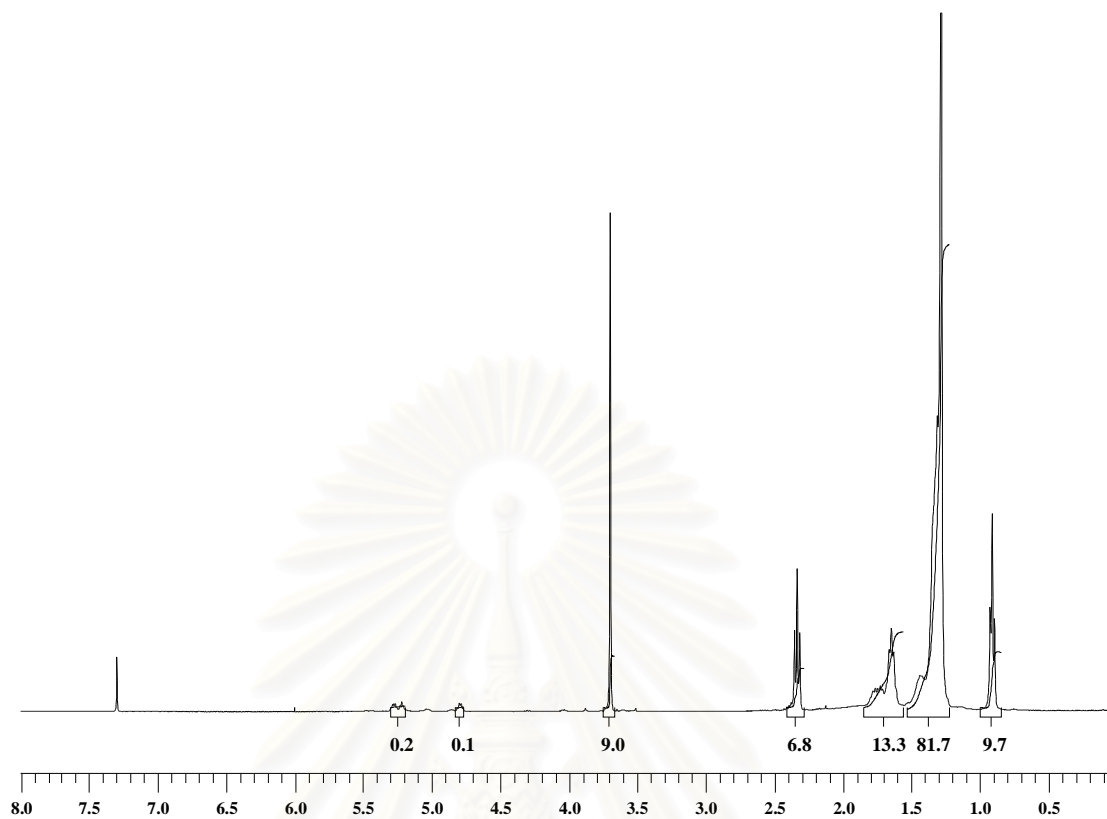


Figure A13 $^1\text{H-NMR}$ spectrum of palm oil nitrate (CDCl_3)

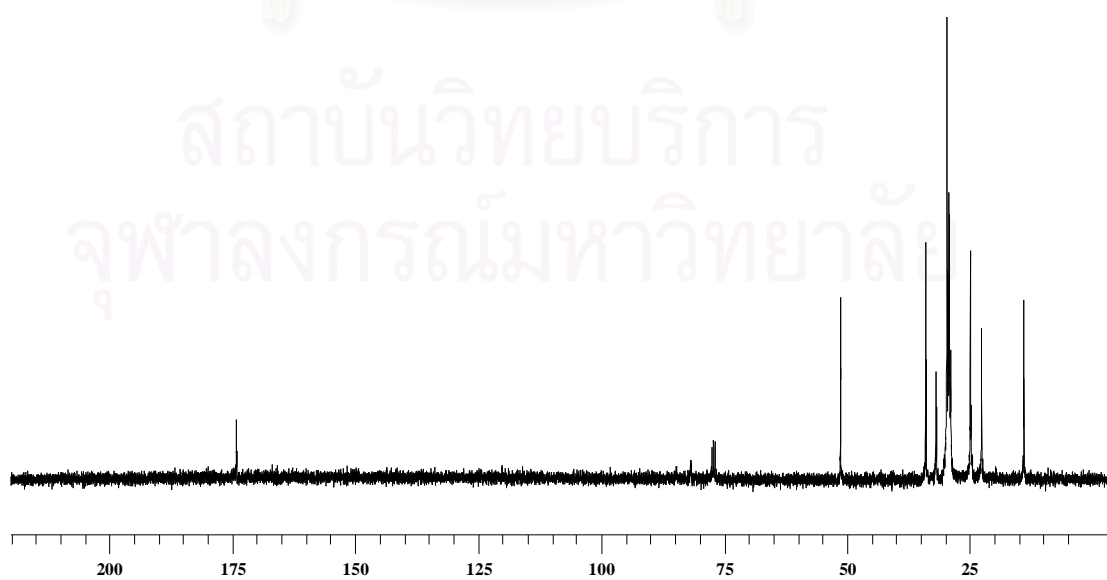


Figure A14 $^{13}\text{C-NMR}$ spectrum of palm oil nitrate (CDCl_3)

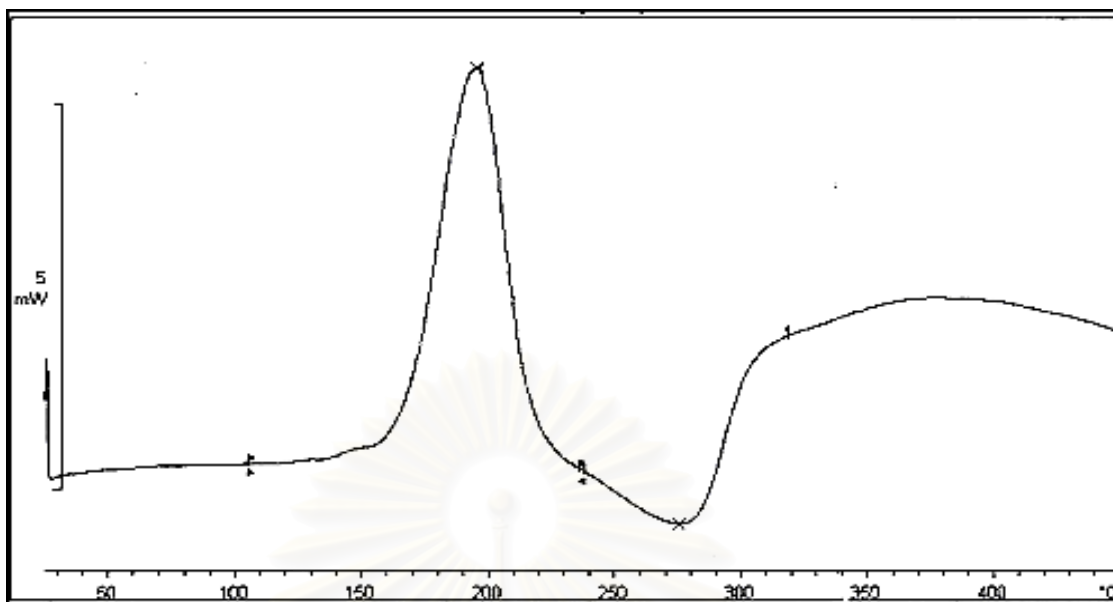


Figure A15 DSC of palm oil nitrate

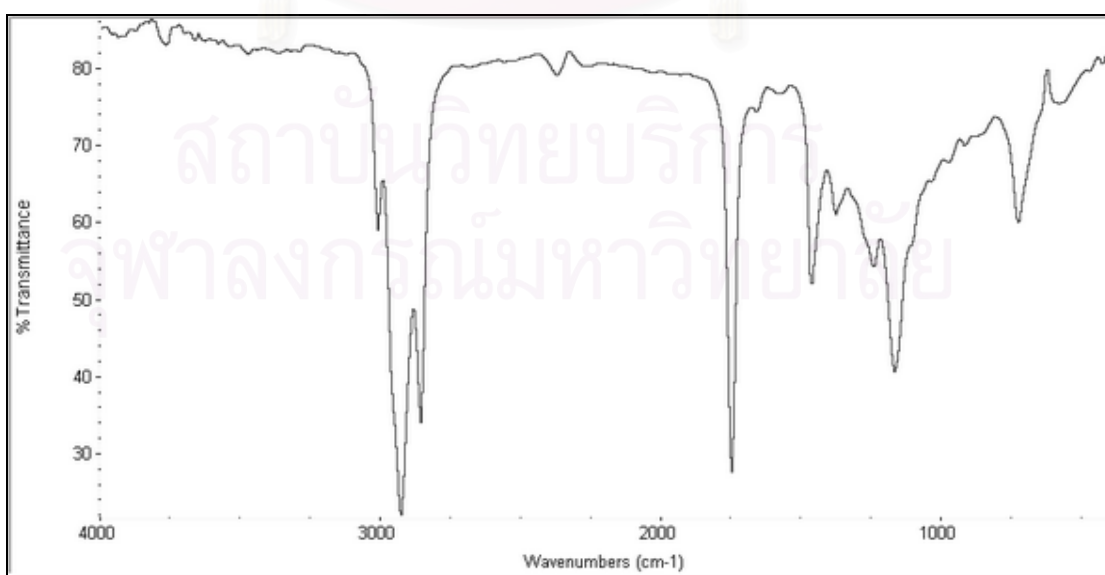


Figure A16 FTIR Spectrum of soybean oil soapstock (NaCl)

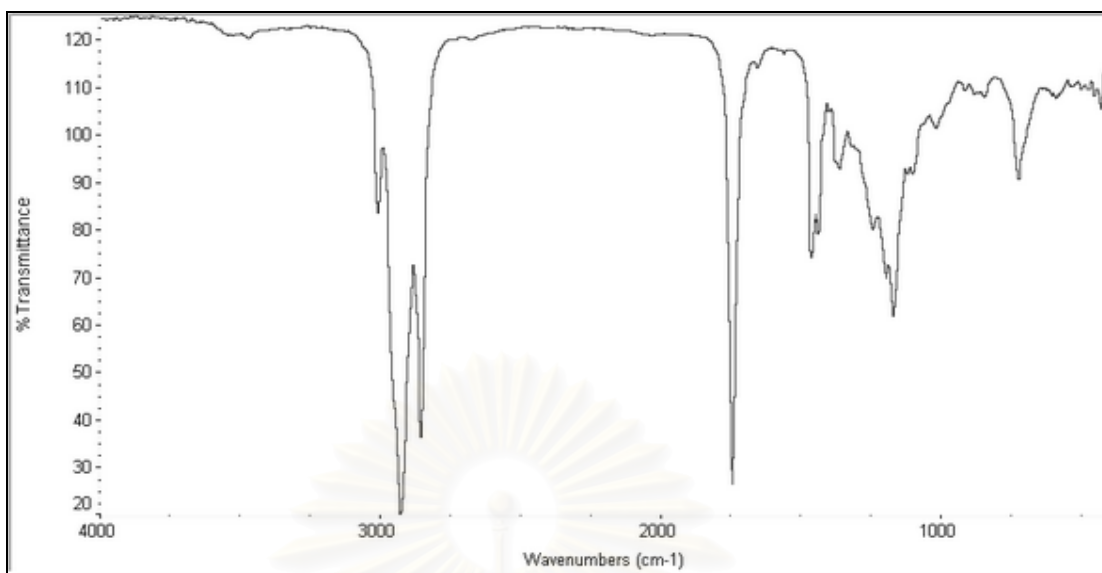


Figure A17 FTIR Spectrum of soybean oil methyl ester (NaCl)

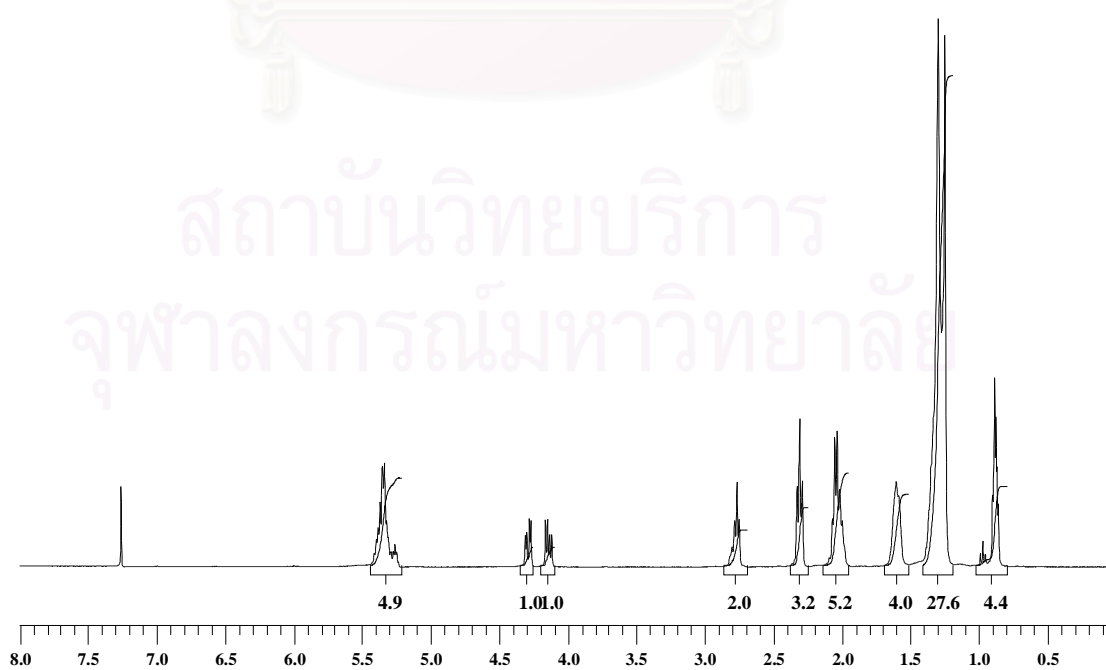


Figure A18 ¹H-NMR spectrum of soybean oil soapstock (CDCl₃)

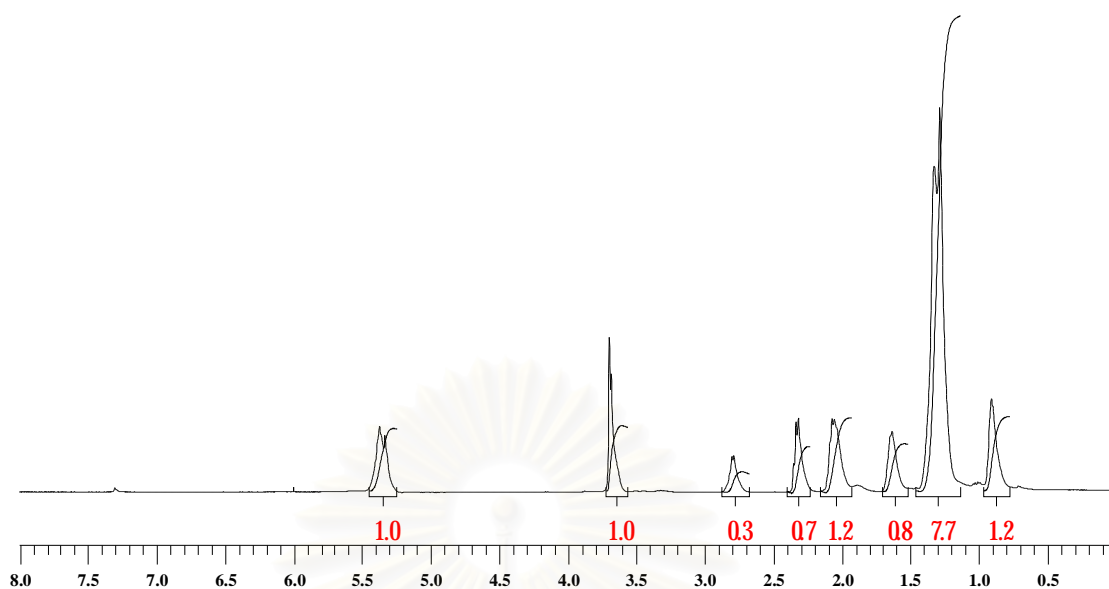


Figure A19 $^1\text{H-NMR}$ spectrum of soybean oil methyl ester (CDCl_3)

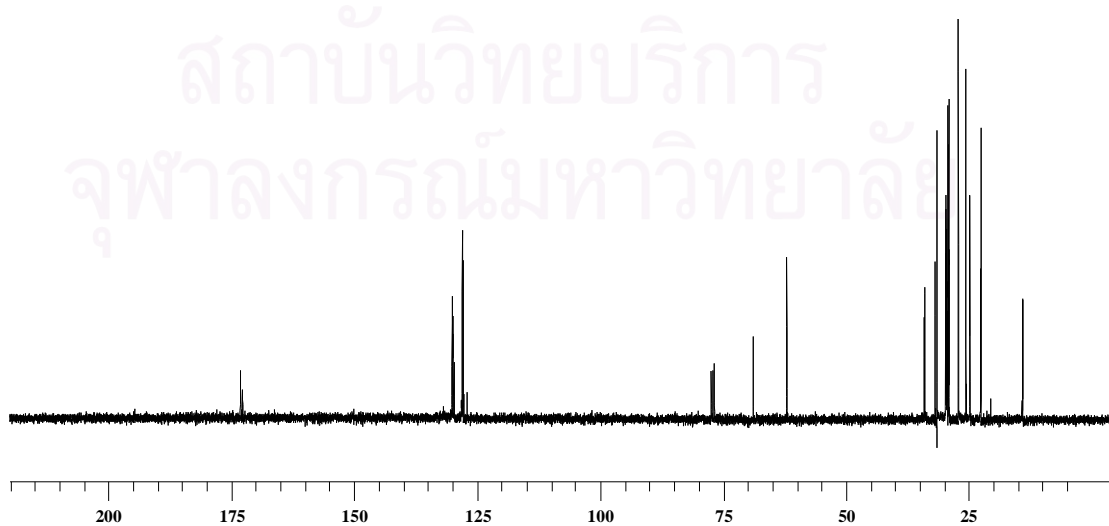


Figure A20 $^{13}\text{C-NMR}$ spectrum of soybean oil soapstock (CDCl_3)

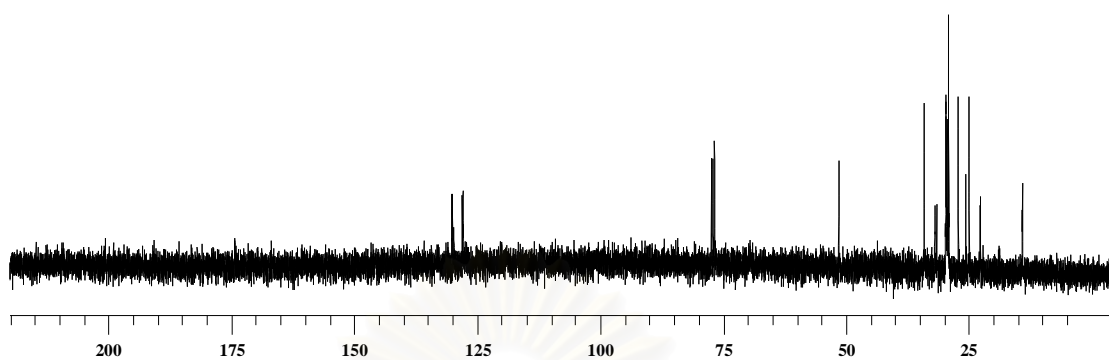


Figure A21 ^{13}C -NMR spectrum of soybean oil methyl ester (CDCl_3)

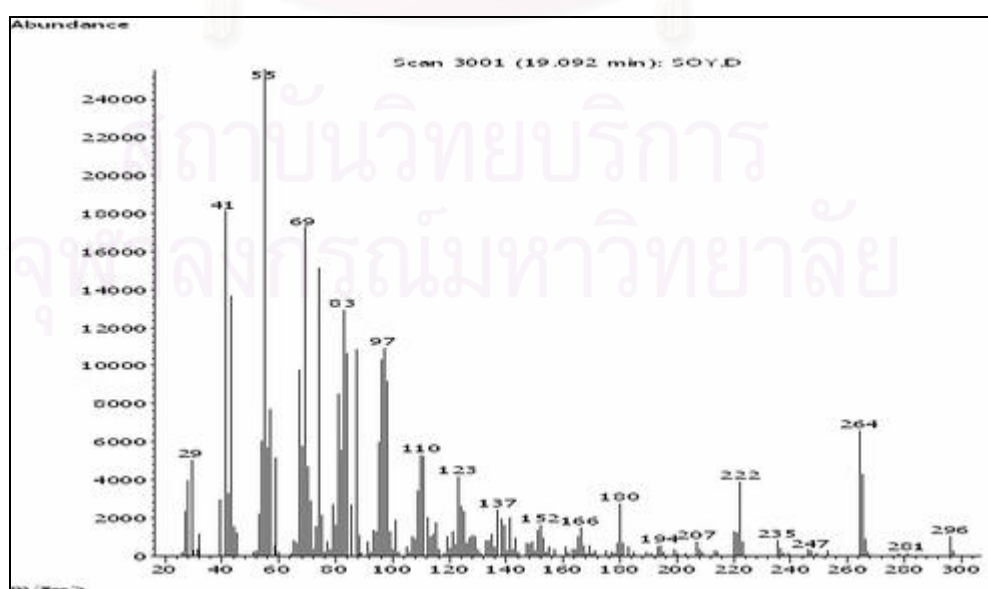


Figure A22 Mass spectrum of soybean oil methyl ester at retention time of 19.09 min.

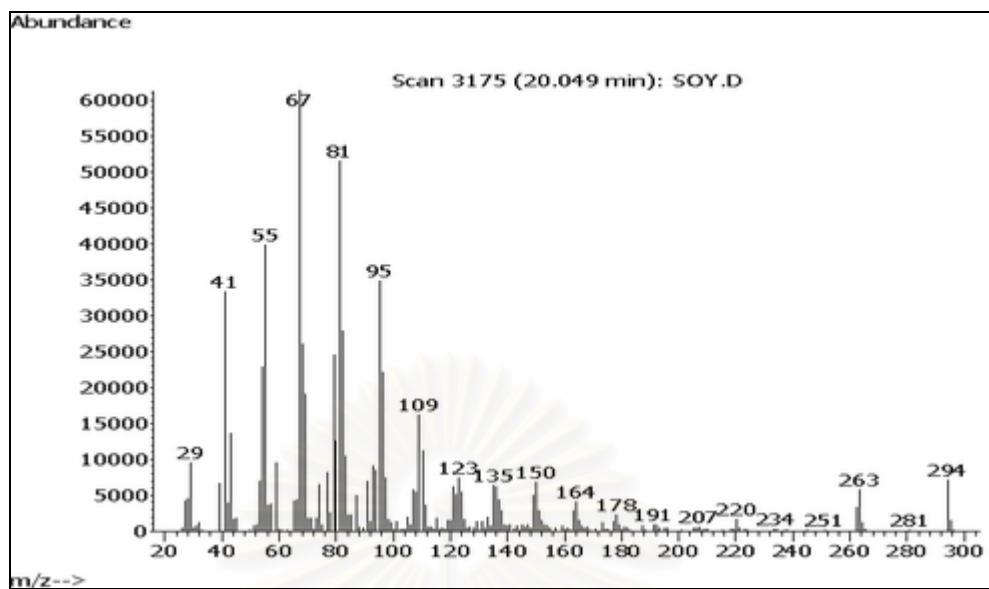


Figure A23 Mass spectrum of soybean oil methyl ester at retention time of 20.05 min.

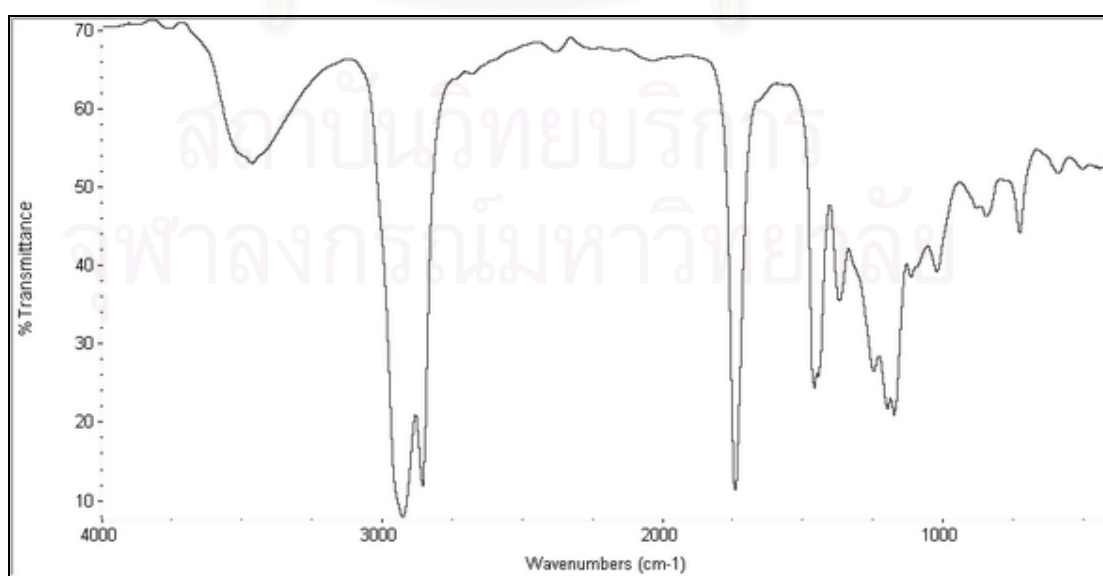


Figure A24 FTIR spectrum of soybean oil epoxide (NaCl)

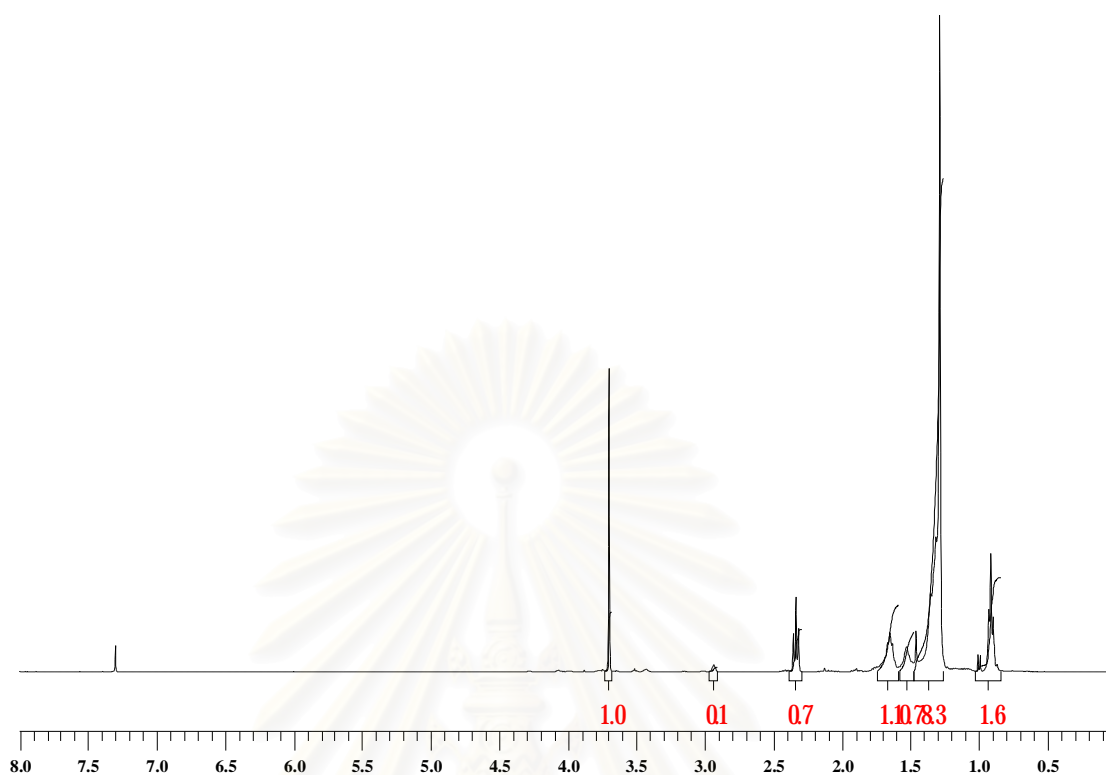


Figure A25 $^1\text{H-NMR}$ spectrum of soybean oil epoxide (CDCl_3)

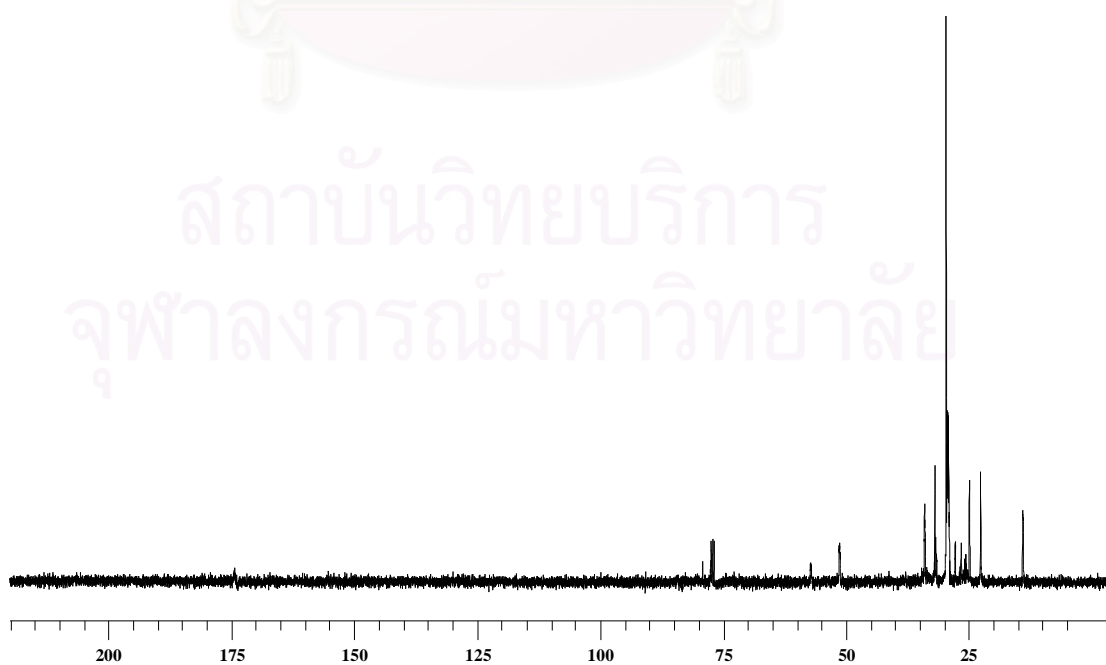


Figure A26 $^{13}\text{C-NMR}$ spectrum of soybean oil epoxide (CDCl_3)

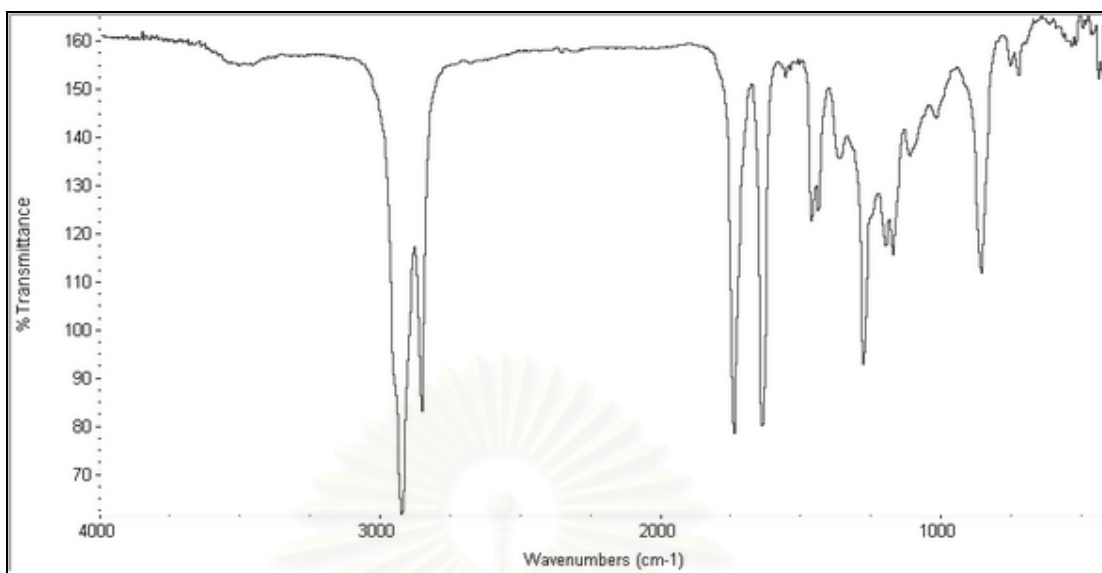


Figure A27 FTIR spectrum of soybean oil nitrate (NaCl)

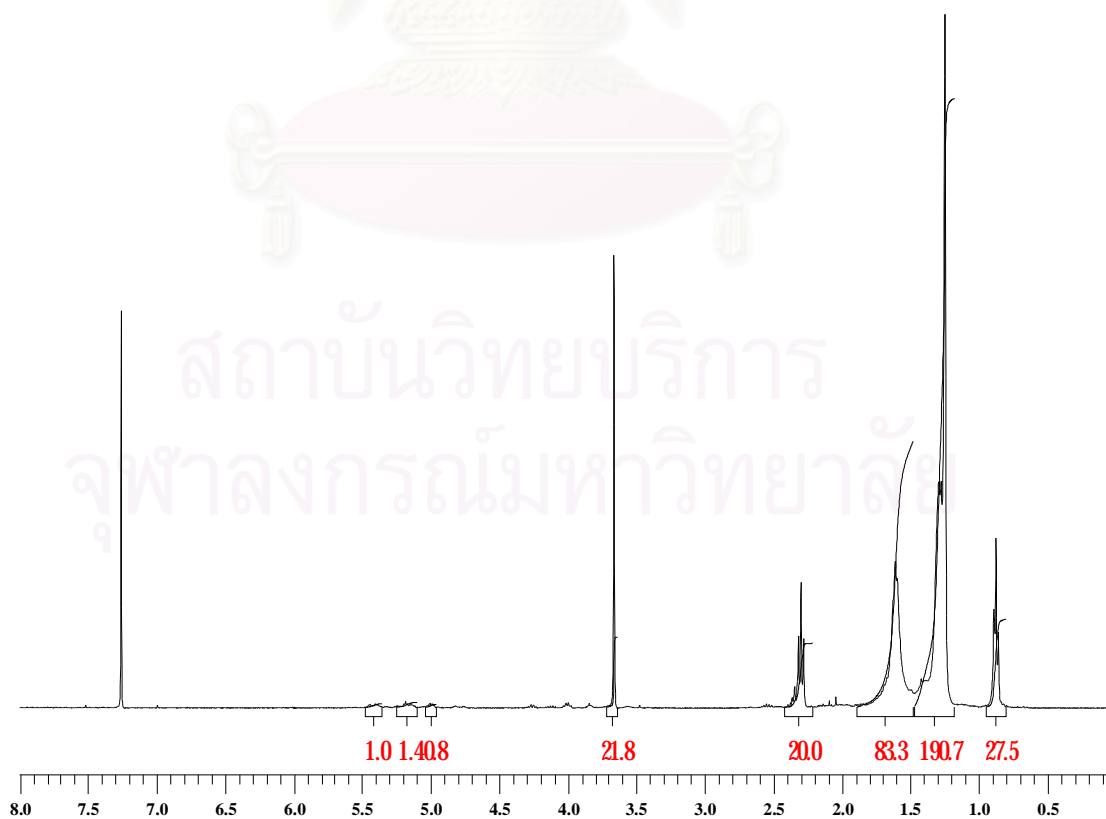


Figure A28 $^1\text{H-NMR}$ spectrum of soybean oil nitrate (CDCl_3)

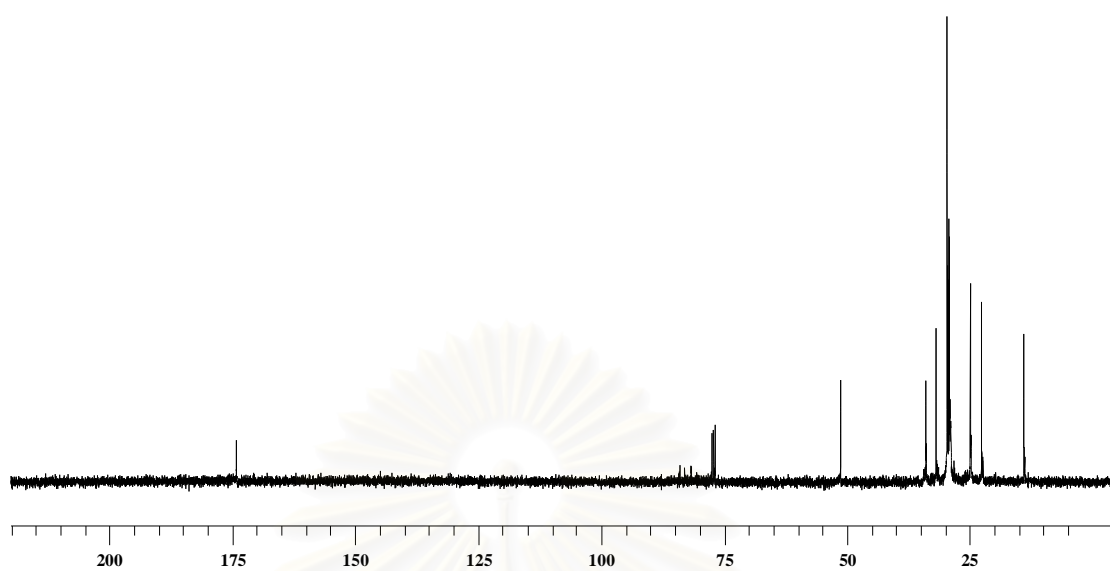


Figure A29 ^{13}C -NMR spectrum of soybean oil nitrate (CDCl_3)

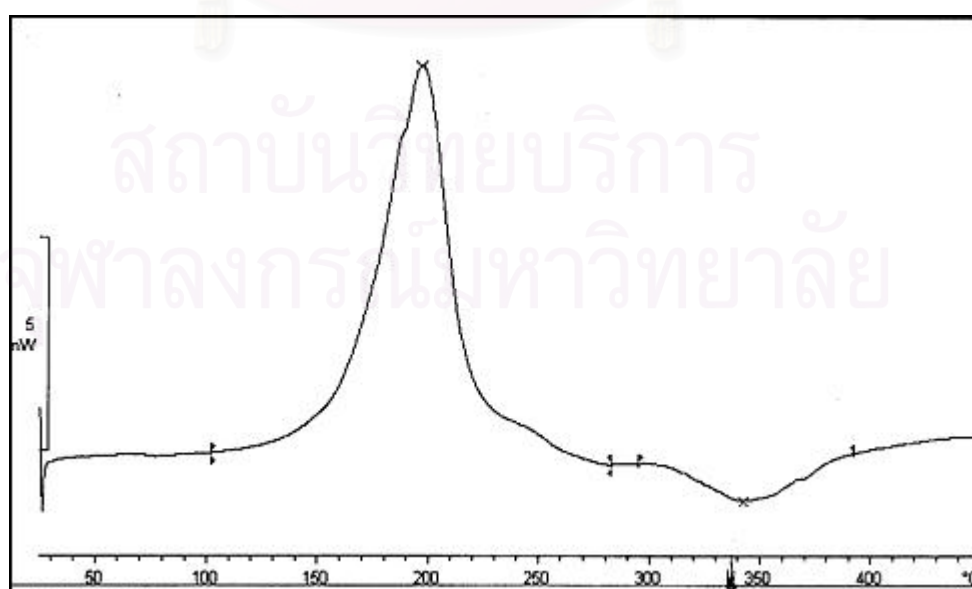


Figure A30 DSC of soybean oil nitrate

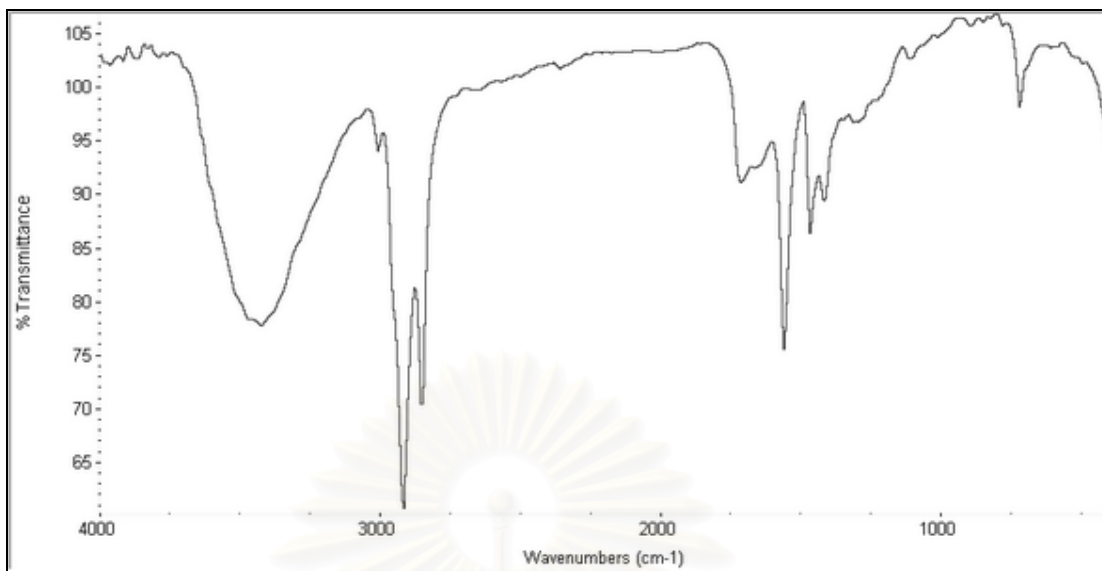


Figure A31 FTIR Spectrum of rice bran oil soapstock (NaCl)

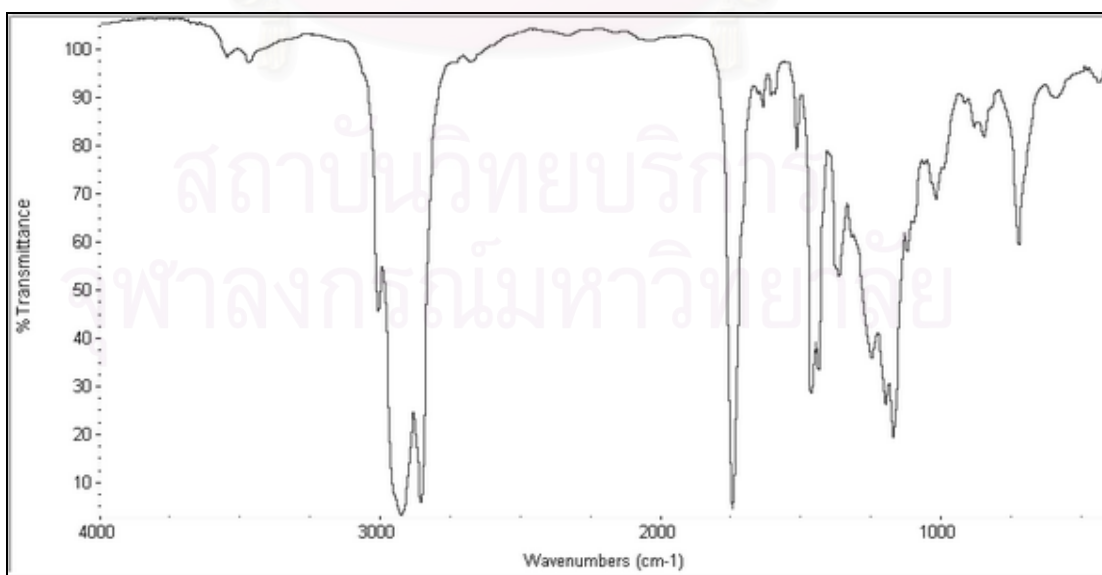


Figure A32 FTIR Spectrum of rice bran oil methyl ester (NaCl)

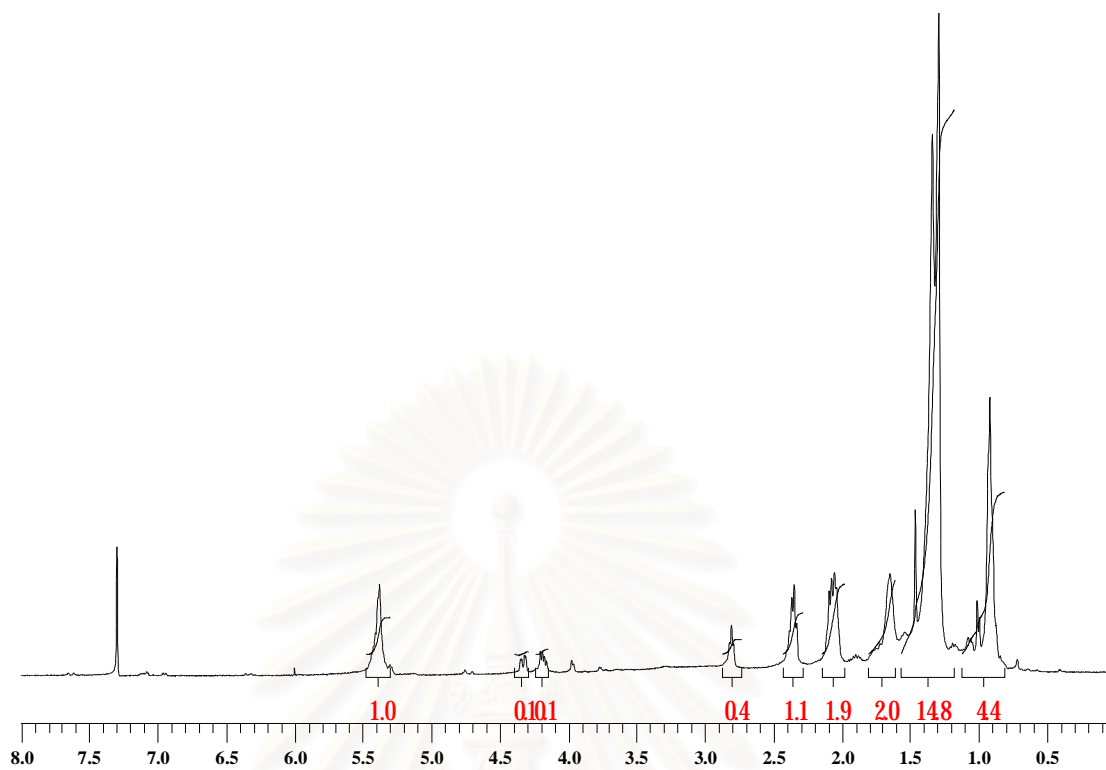


Figure A33 ¹H-NMR spectrum of rice bran oil soapstock (CDCl₃)

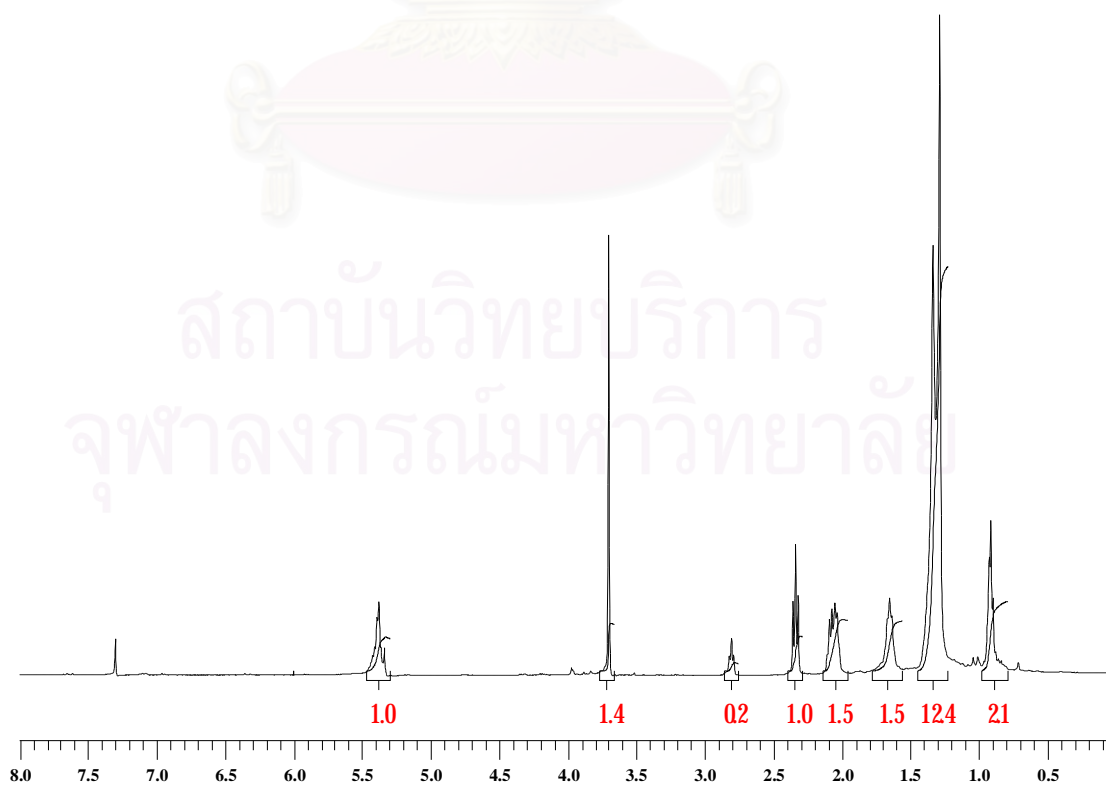


Figure A34 ¹H-NMR spectrum of rice bran oil methyl ester (CDCl₃)

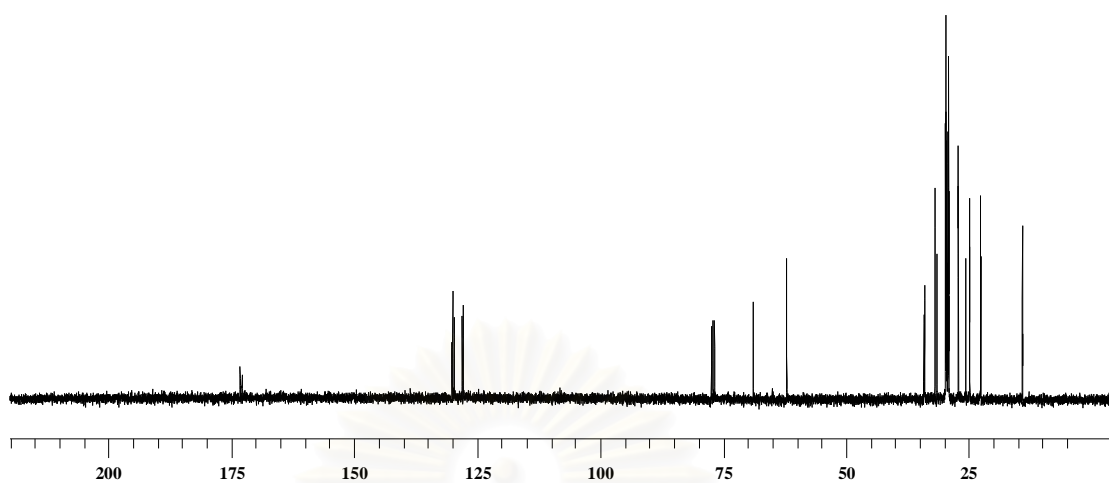


Figure A35 ^{13}C -NMR spectrum of rice bran oil soapstock (CDCl_3)

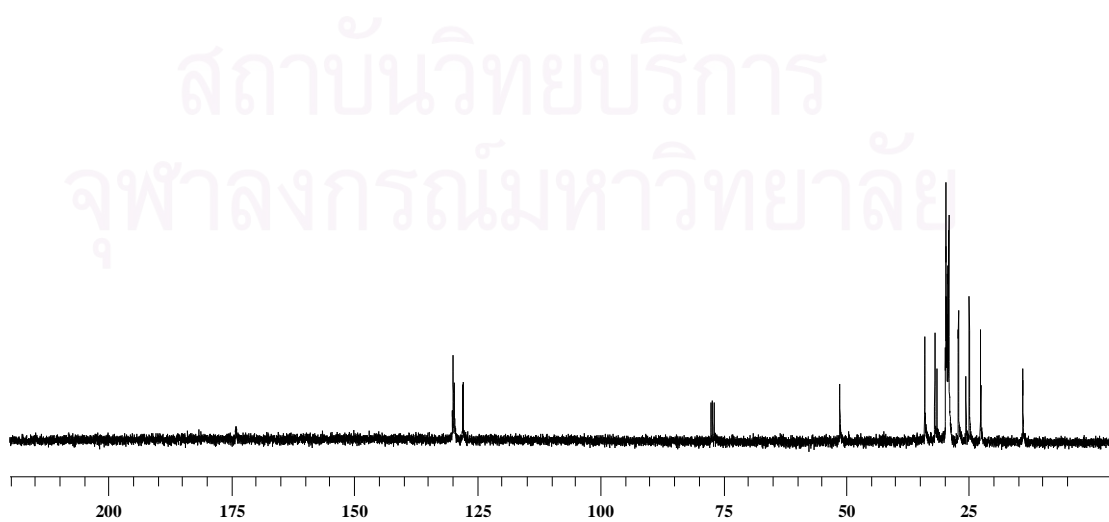


Figure A36 ^{13}C -NMR spectrum of rice bran oil methyl ester (CDCl_3)

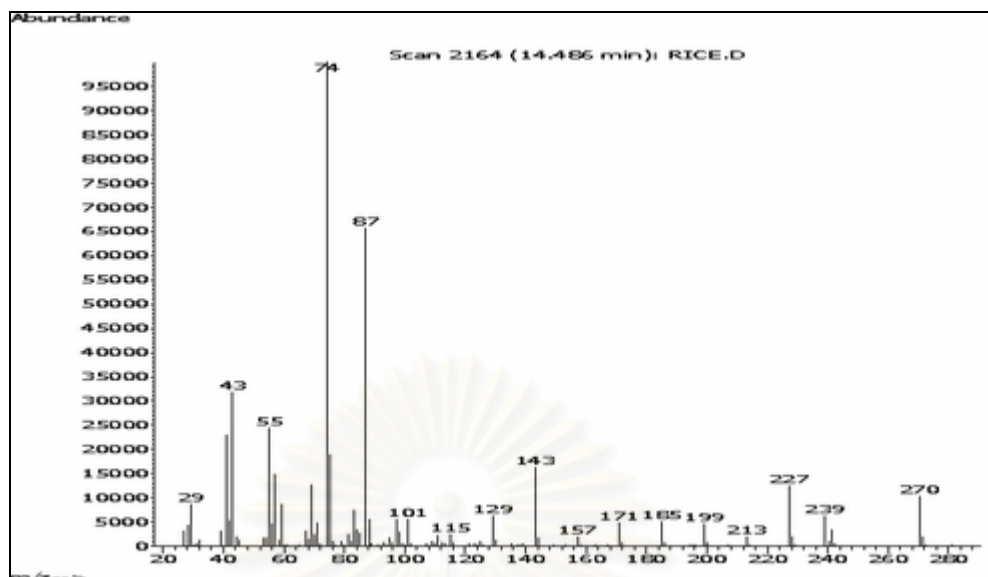


Figure A37 Mass spectrum of rice bran oil methyl ester at retention time of 14.49 min.

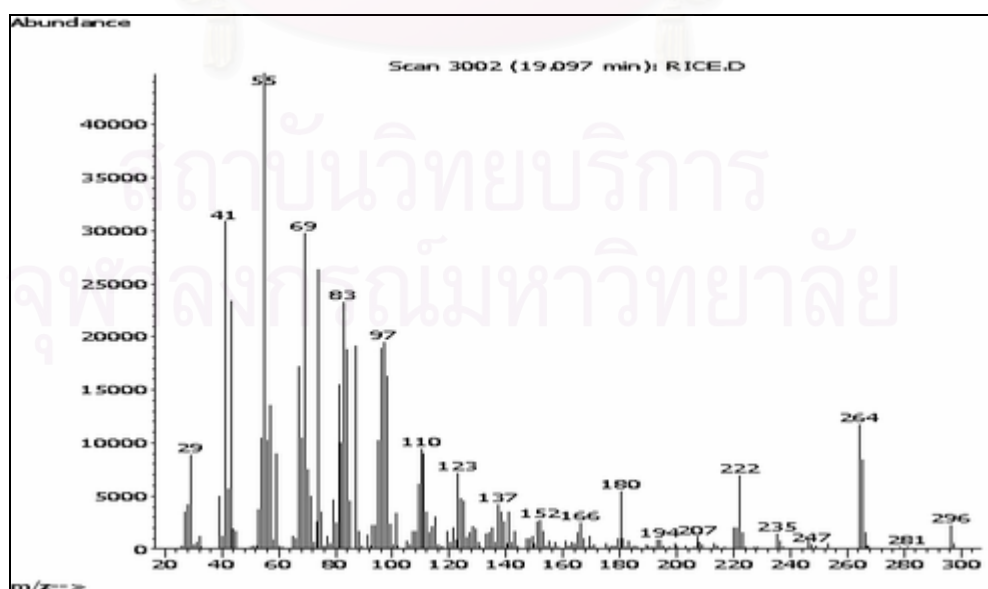


Figure A38 Mass spectrum of rice bran oil methyl ester at retention time of 19.10 min

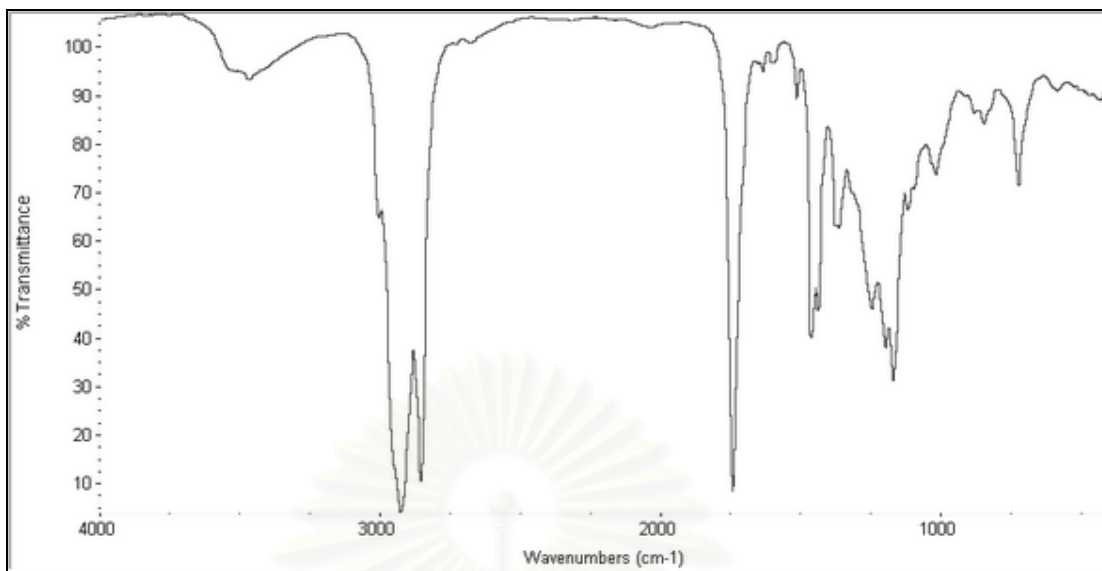


Figure A39 FT-IR spectrum of rice bran oil epoxide (NaCl)

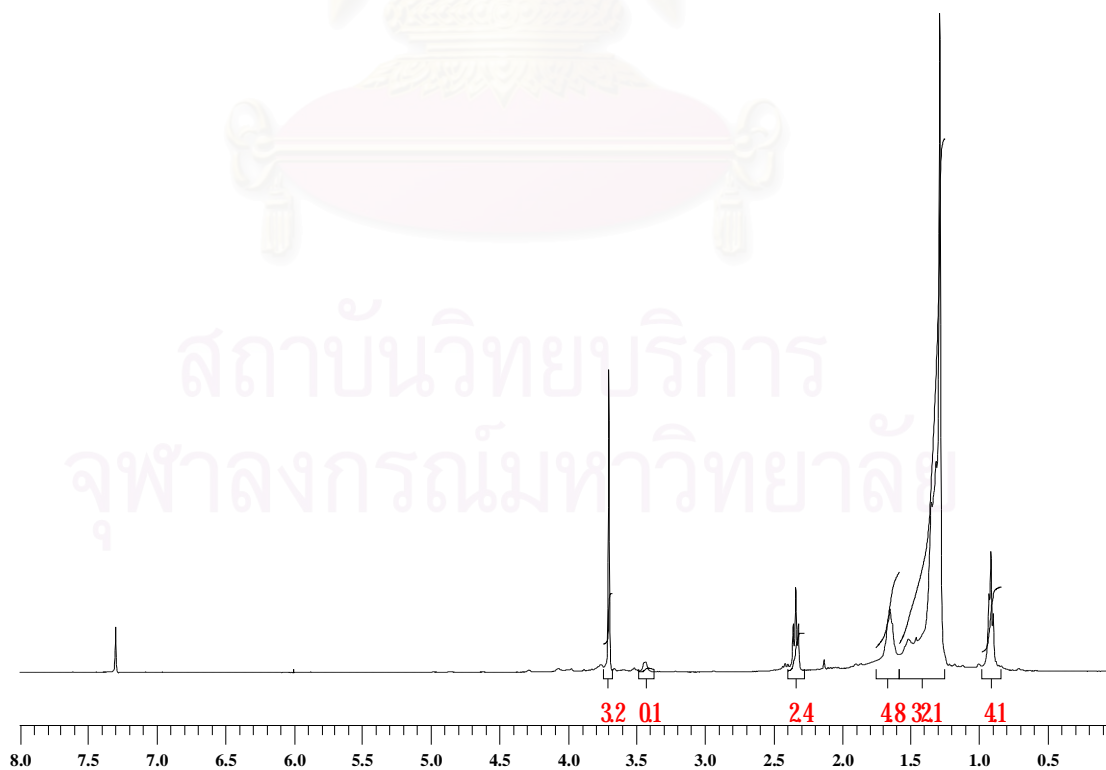


Figure A40 $^1\text{H-NMR}$ spectrum of rice bran oil epoxide (CDCl_3)

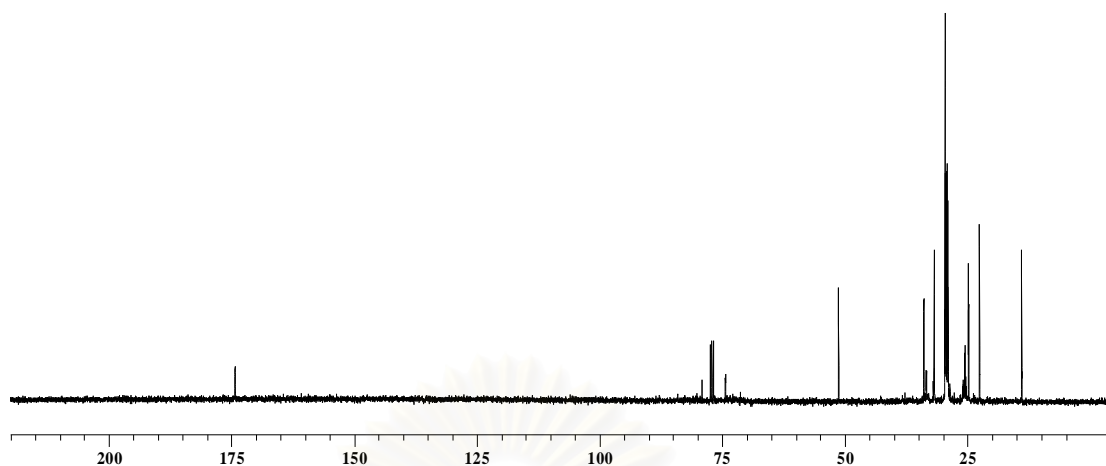


Figure A41 ^{13}C -NMR spectrum of rice bran oil epoxide (CDCl_3)

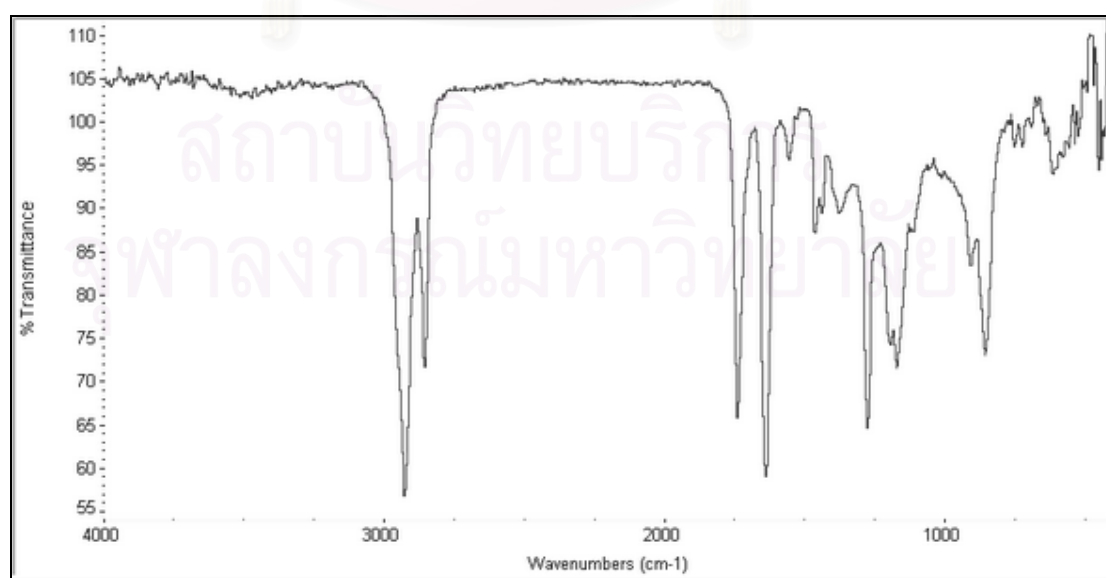


Figure A42 FT-IR spectrum of rice bran oil nitrate (NaCl)

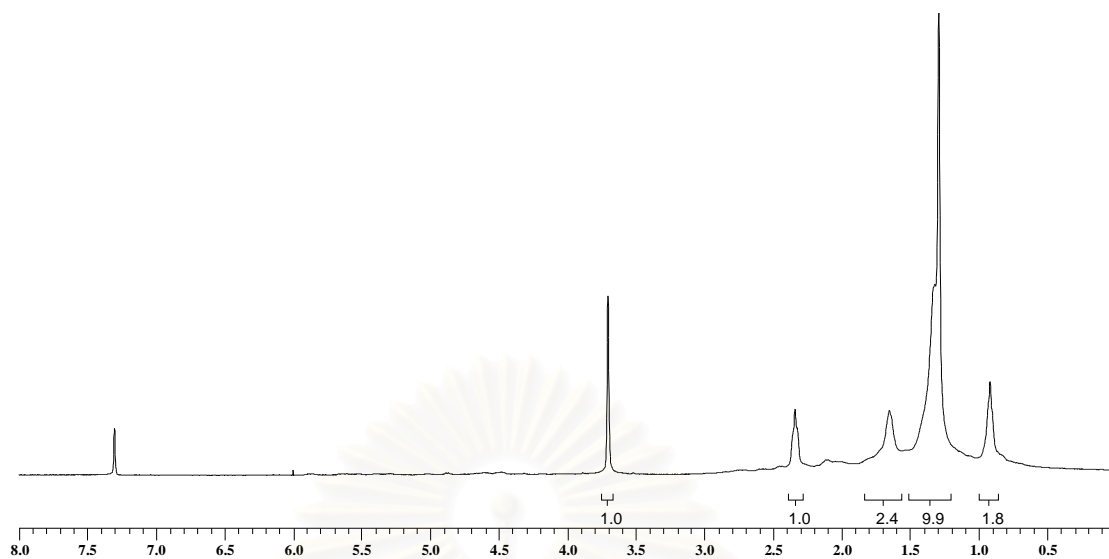


Figure A43 $^1\text{H-NMR}$ spectrum of rice bran oil nitrate (CDCl_3)

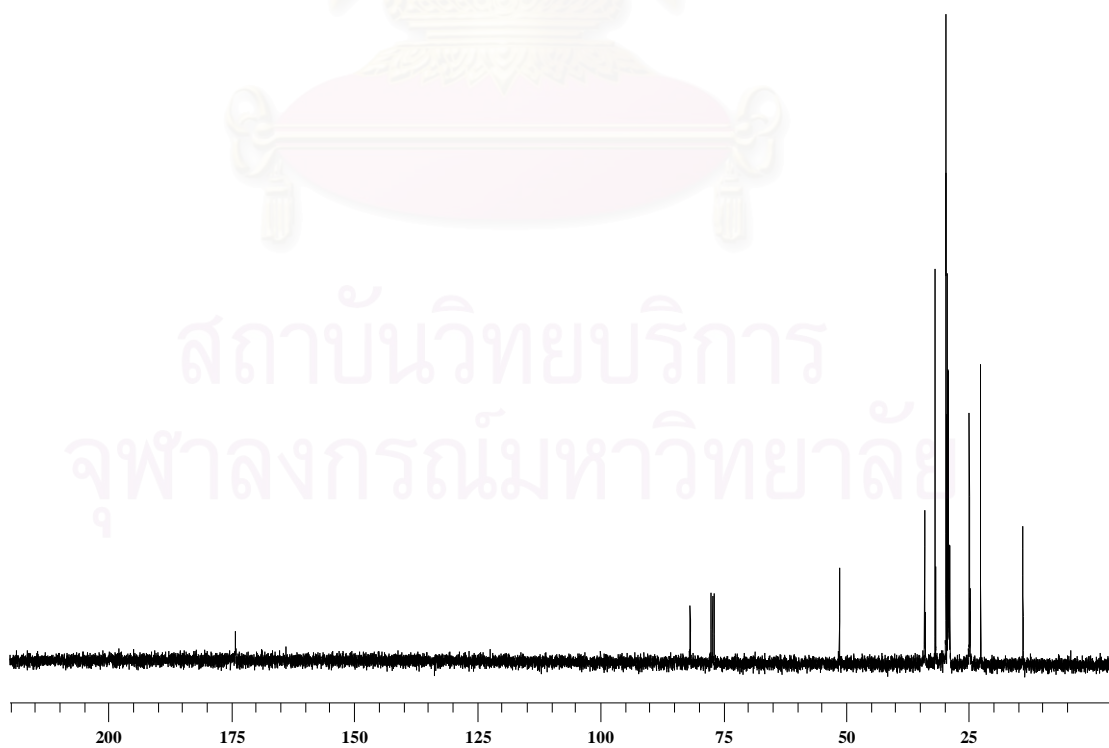


Figure A44 $^{13}\text{C-NMR}$ spectrum of rice bran oil nitrate (CDCl_3)

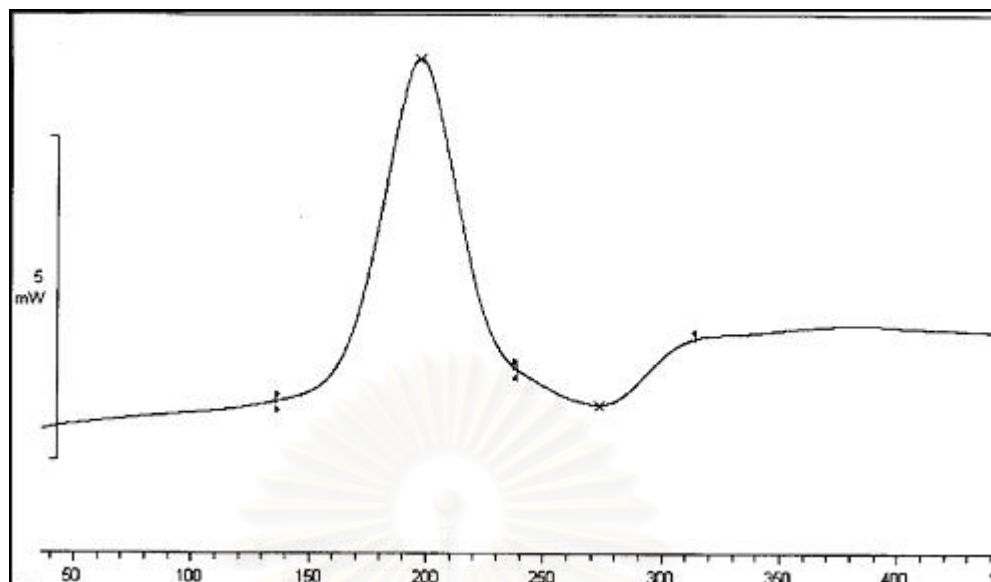


Figure A45 DSC of rice bran oil nitrate

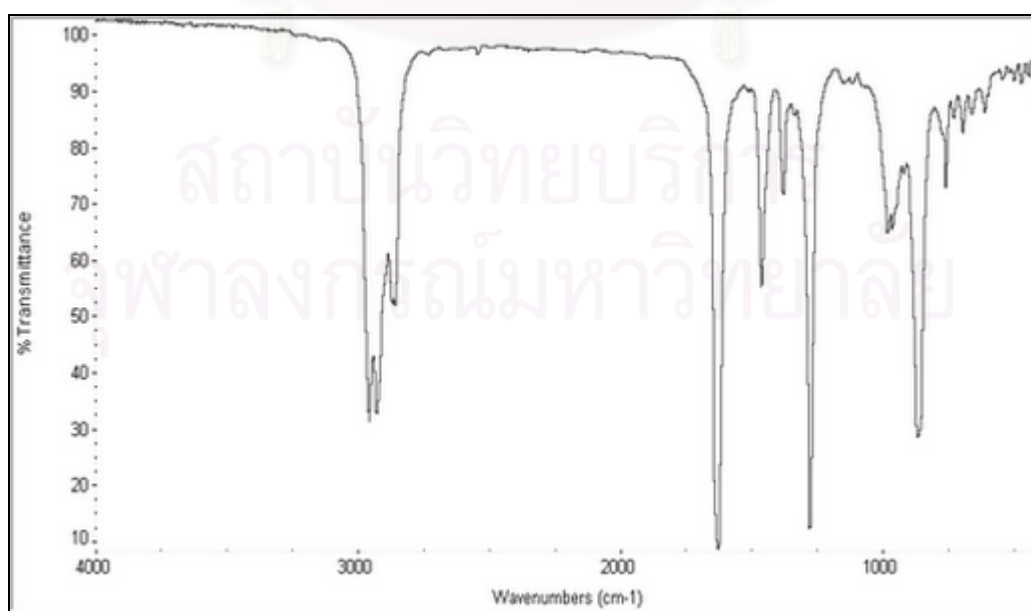


Figure A46 FTIR spectrum of 2-ethylhexyl nitrate (NaCl)

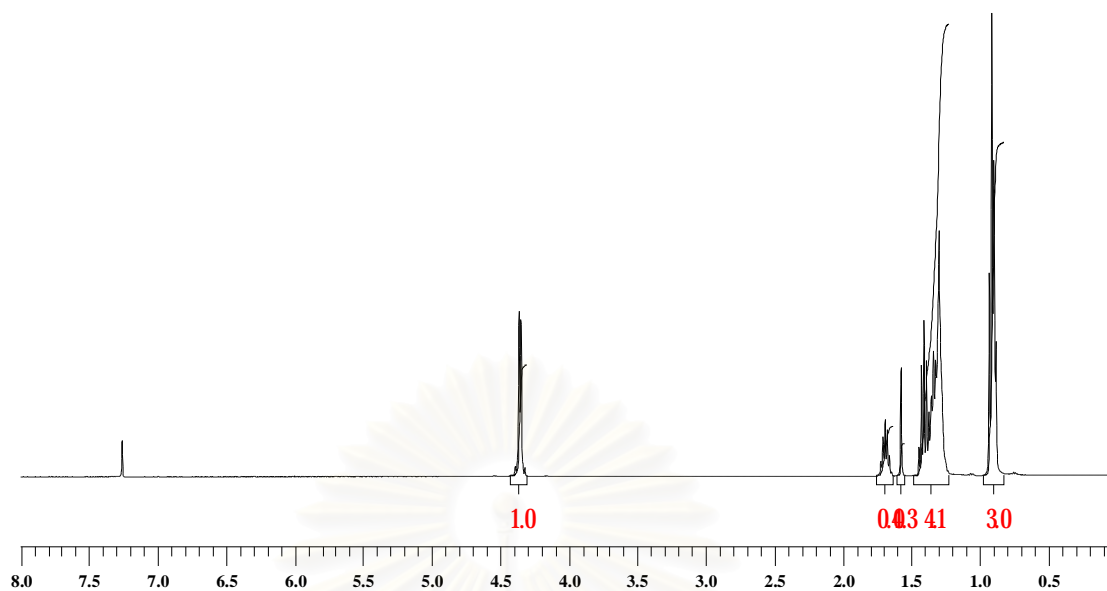


Figure A47 ^1H -NMR spectrum of 2-ethylhexyl nitrate (CDCl_3)

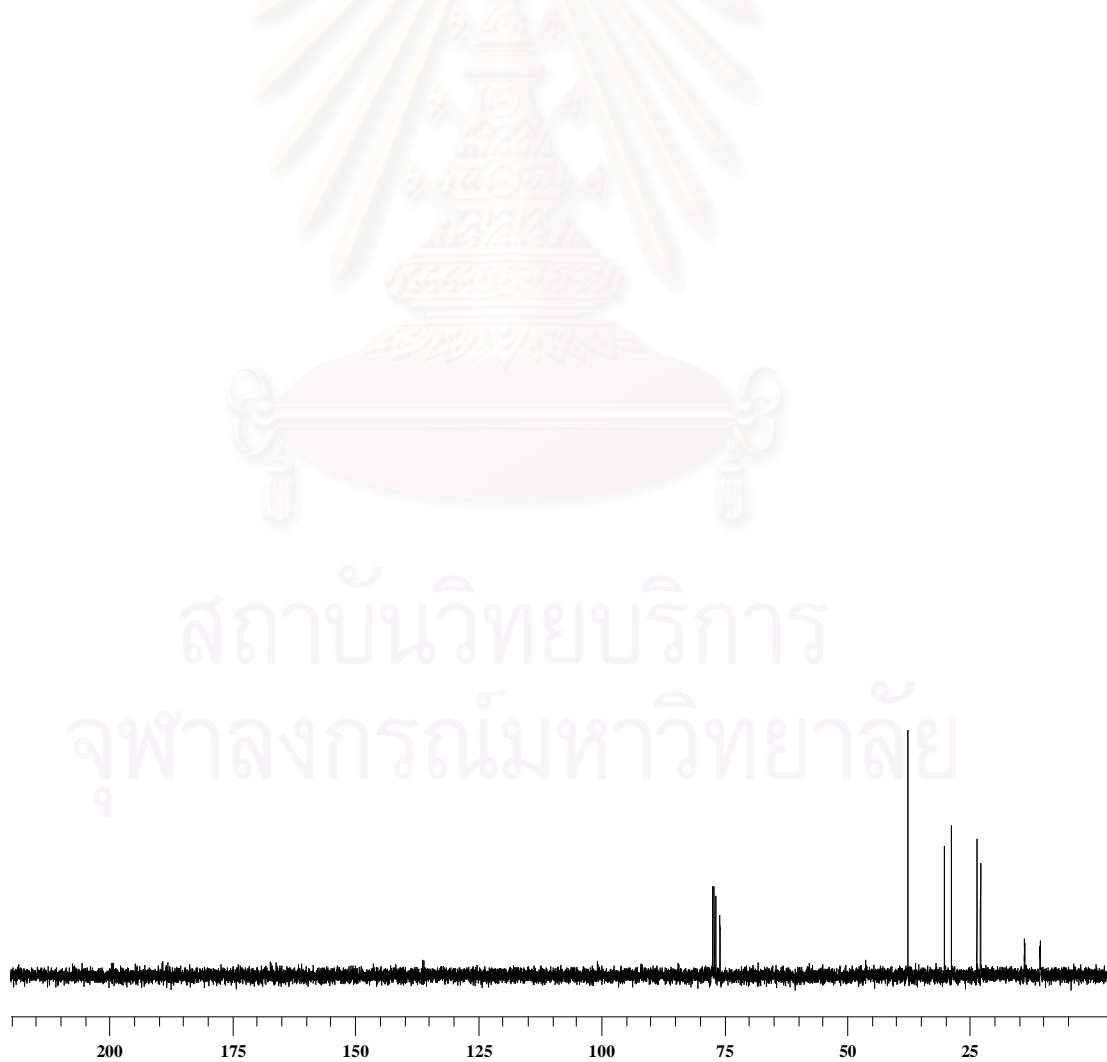


Figure A48 ^{13}C -NMR spectrum of 2-ethylhexyl nitrate (CDCl_3)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX B

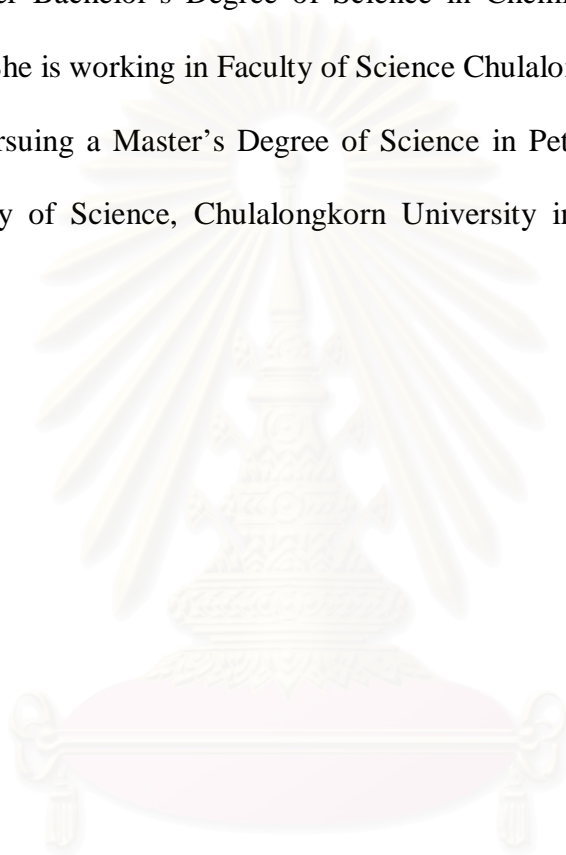
SPECIFICATION AND TEST METHOD FOR DIESEL FUEL IN THAILAND

Characteristics	Specification		
	High-Speed Engine	Low-Speed Engine	Methods
Density at 15.6/15.6 °C	0.81-0.87	0.92	ASTM D1286
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	max 357	-	ASTM D 86
(temperature of 90% distillation)			
Color	max 4.0	-	ASTM D 1500
Detergent Additive	Test by the Standard CUMMINS Tandem L-10 (Superior Level)	-	-

VITA

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She is pursuing a Master's Degree of Science in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2003 and graduated in 2005.



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