การสังเคราะห์สารประกอบไดออลไนเทรตจากของเสียกรดไขมันเพื่อใช้เป็นสารเพิ่มค่าซีเทน

นาย ชูศักดิ์ บุญลักษณ์ศิริ

SYNTHESIS OF DIOL NITRATE COMPOUNDS FROM FATTY ACID WASTES AS CETANE IMPROVERS

Mr. Choosak Boonlaksiri

Thesis Title   SYNTHESIS OF DIOL NITRATE COMPOUNDS FROM FATTY ACID WASTES AS CETANE IMPROVERS

By   Mr. Choosak Boonlaksiri

Field of Study   Petrochemistry and Polymer Science

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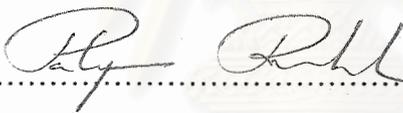
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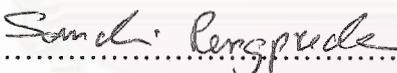
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ชูศักดิ์ บุญลักษณ์ศิริ : การสังเคราะห์สารประกอบไดออลไนเทรตจากของเสียกรดไขมัน
เพื่อใช้เป็นสารเพิ่มค่าซีเทน (SYNTHESIS OF DIOL NITRATE COMPOUNDS FROM
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สารประกอบไกลคอลไนเทรตสามารถสังเคราะห์ได้ด้วยการนำของเสียกรดไขมัน จาก
น้ำมันถั่วเหลืองและน้ำมันมะพร้าว มาทำปฏิกิริยาเอสเทอร์ริฟิเคชั่นกับเอทีลีนไกลคอล โดยใช้กรด
ซัลฟิวริกเข้มข้นเป็นตัวเร่งปฏิกิริยา และทำปฏิกิริยาไนเทรชัน ด้วยกรดไนตริกเข้มข้นและซัลฟิวริก
เข้มข้น ที่อุณหภูมิ 0-2 องศาเซลเซียส โดยมีไดคลอโรมีเทนเป็นตัวทำละลาย ได้พิสูจน์เอกลักษณ์
สารไนเทรตที่โดยการวิเคราะห์ด้วยเทคนิคทางสเปกโทรสโกปี ได้แก่ อินฟราเรดสเปกโทรสโกปี
และนิวเคลียร์แมกเนทิกเรโซแนนซ์สเปกโทรสโกปี   สารประกอบไนเทรตที่สังเคราะห์ได้สามารถ
ละลายในน้ำมันดีเซลพื้นฐานได้ง่าย จากการตรวจสอบค่าเลขซีเทนพบว่า สารเหล่านี้ให้ค่าเลขซี
เทนเพิ่มขึ้นประมาณ 0.5, 0.7, 2.0, 3.9, 5.6 และ 7.1 หน่วย สำหรับสารประกอบไนเทรตที่
สังเคราะห์ได้จากของเสียกรดไขมันที่มาจากน้ำมันถั่วเหลือง และ 0.4, 0.5, 1.4, 2.7, 4.0 และ 5.1
หน่วย สำหรับสารประกอบไนเทรตที่สังเคราะห์ได้จากของเสียกรดไขมันที่มาจากน้ำมันมะพร้าว ที่
ความเข้มข้น 0.05, 0.10, 0.25, 0.50, 0.75 และ 1.00 เปอร์เซ็นต์โดยน้ำหนักตามลำดับ โดยที่
สารประกอบไนเทรตที่สังเคราะห์ได้มีแนวโน้มทำให้ค่าซีเทนของน้ำมันดีเซลพื้นฐานเพิ่มขึ้น ได้

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต...

ปีการศึกษา............2546.................   ลายมือชื่ออาจารย์ที่ปรึกษา...............................

CHOOSAK BOONLAKSIRI: SYNTHESIS OF DIOL NITRATE COMPOUNDS FROM FATTY ACID WASTES AS CETANE IMPROVERS. THESIS ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 91 PAGES. ISBN 974-17-4288-6

Glycol nitrate compounds could be prepared by nitration of fatty acid ethylene glycol ester such as soybean fatty acid waste and coconut fatty acid waste with concentrated nitric acid and concentrated sulfuric acid, while maintaining the temperature of the reaction at $0\pm2\,^{\circ}C$ in the presence of dichloromethane. The nitrate compounds obtained were identified by spectroscopic techniques, such as Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy. The nitrate compounds could be easily blended with base diesel fuel. They were effective in increasing cetane number to 0.5, 0.7, 2.0, 3.9, 5.6 and 7.1 units for soybean fatty acid ethylene glycol nitrate and 0.4, 0.5, 1.4, 2.7, 4.0 and 5.1 units for coconut fatty acid ethylene glycol nitrate at concentrations of 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00% by weight, respectively. These synthesized nitrate compounds had potential to be used to improve cetane number of base diesel fuel.

Field of study...……Petrochemistry and Polymer Science…. Student's signature……………...………………..

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

ACKNOWLEDGEMENTS

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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
^{1}H-NMR	=	Proton Nuclear Magnetic Resonance
MPa	=	Mega Pascal
ml	=	Milliliter
Sp.Gr.	=	Specific Gravity
rpm	=	Round per minute
cm^{-1}	=	Unit of wave number
%wt	=	Weight percent
%yield	=	Yield percent

CHAPTER I

INTRODUCTION

1.1 Introduction

At present, humans get many profits from petroleum. These include transportation, energy, food, medicine and daily equipment. Therefore, the living of human necessarily associates with using of petroleum. Thus, there are always searching, exploration and drilling the new petroleum sources.

Diesel fuel is obtained from crude oil, which is a mixture of hydrocarbons such as benzene, pentane, hexane, heptane, toluene, propane and butane. Diesel fuels are middle distillates, generally boiling within the range of 170-390°C. Blending two or more refinery streams such as light gas oil (LGO) normally produces them, heavy gas oil (HGO) and kerosene. In a complex refinery with several downstream cracking capabilities, more middle-distillate stream may be available for blending. The proportions of the different components in the finished blend will be determined by their individual characteristics and the requirements of the diesel fuel specification such as distillation, viscosity, cetane, cold properties, etc [2].

Diesel engine has now extended over a much wider range of applications than any other engines currently in use. Within the past eighty years diesel engines have been used wherever engine power has been required. They are found driving small and large electric power generating and pumping units; in the main propulsion of ships and their auxiliaries; in large and small road vehicles; they are used for off road

agricultural and civil engineering vehicles and machinery and also for railway locomotives. Whilst few examples now exist, diesel engines usually power the lighter than airships and in the past have seen application in winged aircraft. They find no favour today for this latter purpose because other engine types have far higher power to weight ratios. It must also be said that diesel engines are not unique to any one part of the world. They will be found everywhere where man needs to augment his own work capability [3]. Therefore, the demand for diesel fuel has been increased. The consumptions of diesel fuel are being continuously increased as shown in Figure 1.1[4].
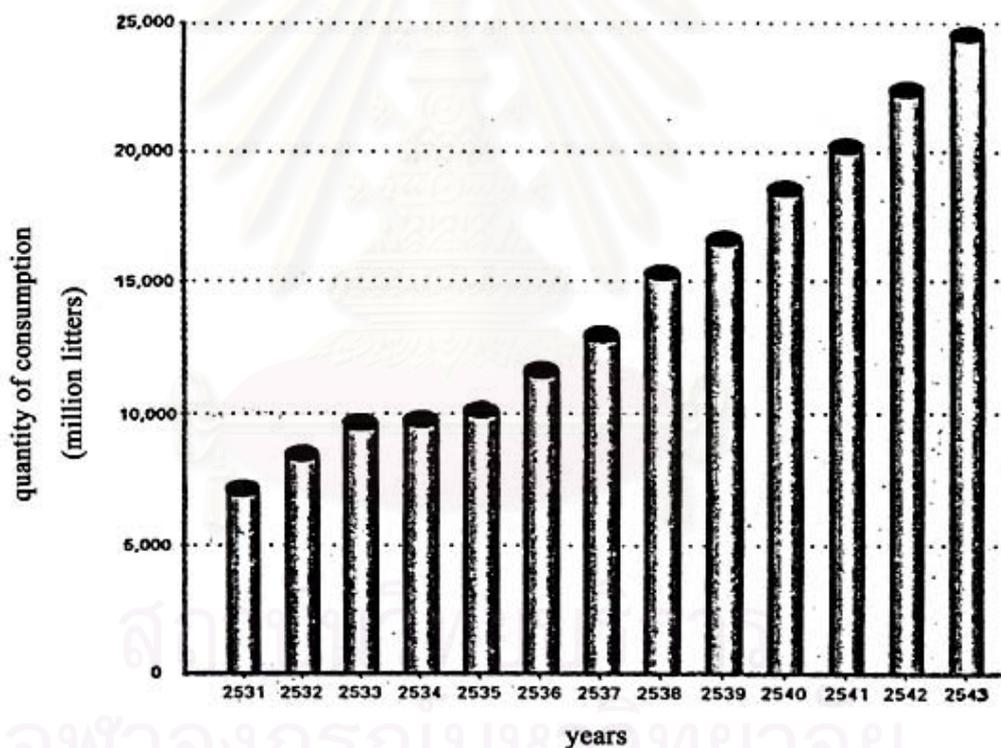
Figure 1.1   The quantity of high speed diesel consumption in Thailand.

For diesel fuel, ignition quality is important operational parameter. It is expressed in term of cetane number, which number has been developed on a basis very similar to that adopted for measuring the ignition quality of gasoline in term of

octane number. If ignition delays too long, the amount of fuel in the chamber increases and upon ignition results in a rough running engine and increases smoke. A short ignition delay results in smooth engine operation and decreases smoke. So a high cetane number indicates a low ignition delay period, and hence better performance as a diesel fuel.

Thus an increase in cetane number of diesel fuel corresponds to a decrease in the ignition delay period can be performed into two methods.

1. Cracking of diesel fuel having low cetane number, such as by thermal cracking, catalytic cracking and hydrocracking.

2. Addition cetane improver, which will decrease ignition delay period so that result of the diesel engines is more easily start. Many types of additives have been used to raise the cetane number of diesel fuel. Such additives usually contain nitrogen or sulfur, both of which are known cetane improvers under certain circumstances. These include peroxides, nitrites, nitrates, nitrosocarbamates, tetrazoles, and the like.

Refer to the two methods as above, it was found that the cracking of diesel fuel process needed high cost and had not obtained the sufficient cetane number. Being the advantage cost over cracking of diesel fuel and higher cetane number needs, addition of cetane improver was substitutionally considered.

Cetane improvers have been used for many years to improve the ignition quality of diesel fuels [5]. The cetane-improving agents of the present invention can be incorporated in the hydrocarbon – based fuels disclosed here in any suitable manner. These materials are normally soluble in paraffinic as well as aromatic hydrocarbons, therefore, can be incorporated directly in the fuels [6].

Cetane improvers are special chemicals, which improve cetane number of diesel fuel similar to ethanol and MTBE improve the octane rating of gasoline. At concentrations less than 0.15%, cetane improvers can reduce ignition delay times of diesel fuels. 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 particular emissions [7]. The use of cetane improvers is increasing due to the increased demand for diesel fuel.

Vegetable oil or used vegetable oil will be converted into methyl ester formed by trans-esterification, which is called biodiesel. In recent years, biodiesel becomes more important as new power resource which can be substituted for diesel fuel. From the literature review, it was found that the properties of biodiesel are similar to that of diesel fuel and it can be used as a replacement for diesel.

In this research, it is interesting to use acid waste, as normally used for animal feeding, from the vegetable oil producing process as a cetane improver. This can be synthesized by reaction between acid waste and ethylene glycol [7] using conc. sulfuric acid as catalyst, followed by nitration reaction. These nitrate compounds are especially well suited as additives for diesel fuels and biodiesel. Furthermore nitrate compounds can be used as lubricant in diesel fuel. [8]

1.2 Objectives and Scope of the Research

1.2.1 Objectives

1. To synthesize diol nitrate compounds from acid wastes for using as cetane improvers in diesel fuel.

2. To study the properties of synthesized diol nitrate compounds blended with base diesel as cetane improvers.

1.2.2 Scope of the Research

1. Literature survey of the relevant research works.

2. Preparation of apparatus and chemical substance.

3. Synthesis of diol nitrate compounds by nitration reaction.

4. Characterizing of synthesized diol nitrate compounds by spectroscopic methods such as FT-IR and FT-NMR.

5. Determination of cetane index, cetane number and important physical properties of diesel fuel blended with synthesized nitrate compounds.

6. Summarizing of the results.
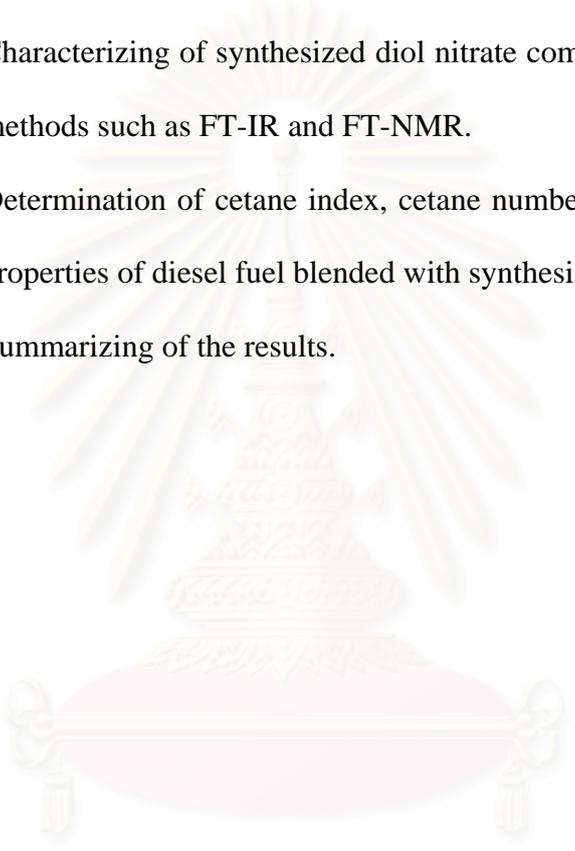
CHAPTER II

THEORETICAL CONSIDERATION

2.1 Diesel Engines

The diesel engine differs from the Otto engine in the heterogeneous combustion of its mixture and the self-ignition of the fuel. The temperature necessary for self-ignition is produced in the compression stroke, in which compression of air to ca. 3.0-5.5 MPa leads to temperatures of 700-900°C. Fuel is injected into the heated air shortly before the end of the compression stroke, where it self-ignites. In principle the diesel engine can be either of the four- or two-stroke type. In practice, four-stroke engines are found in the vast majority of vehicles, whereas the two-stroke process is used in large ship or simpler truck engines. In the diesel engine, air is generally taken in unthrottled and the fuel-air ratio varies with the quantity of fuel injected (quality governing) thus leading to a very lead fuel-air mixture.

The diesel engine must achieve compression temperatures and pressures, which are adequate to enable starting from cold and to give acceptable smooth combustion when running. In high-speed automotive diesel engines, this is obtained by the use of compression ratios of between 12:1 and 23:1, depending on cylinder size, combustion system and whether the engine is turbocharged. It is the typically high compression ratio of the diesel engine, which dictated the need for its general mechanical robustness and also leads to its high-indicated efficiency characteristics.

After compression ratio, the main factors affecting combustion in the diesel engine are combustion chamber design and fuel injection characteristics. The time from start of fuel injection to end of combustion is very small, and during this a fuel-air mixture has to be formed which will ignite within a reasonable delay period. Good mixing of fuel and air is essential and adequate oxygen has to be available for combustion to be completed early in the expansion stroke.

In general, two combustion chamber forms are principally used in automotive diesel engine applications. These are the direct injection system as illustrated in Figure 2.1 and the pre-chamber, indirect injection system shown in Figure 2.2 [4].
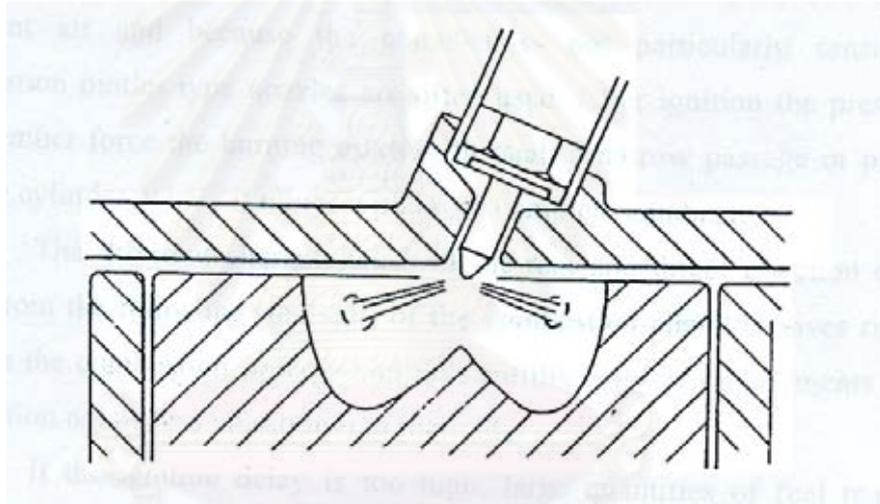
Figure 2.1   Direct injection combustion system.[4]
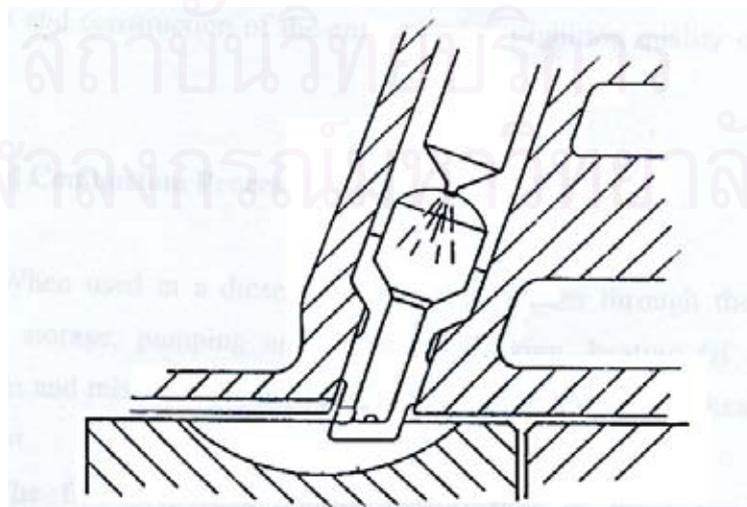
Figure 2.2   Indirect injection combustion system.[4]

With the deep bowl direct injection system the required fuel-air mixing is achieved by direct injection of fuel into an open cylinder into which air has been introduced with a high degree of rotational movement. The air movement is initiated during the induction stroke by correctly sited and shaped inlet ports which causes the air to swirl in the cylinder. The swirl continues as the piston rises during compression.

In contrast, in the pre-chamber indirect injection system air is forced into a pre-chamber during the compression stroke. Fuel is injected into the turbulent air and because the chamber is not particularly sensitive to atomization pintle-type nozzles are often used. After ignition the pressure in the chamber forces the burning mixture through a narrow passage or passages into the cylinder, where it mixes with air to complete combustion [9].

The different characteristics of indirect and direct injection engines result from the following: the split of the combustion chamber gives rise to a delay in the combustion process and thus fulfills comfort requirements (lower combustion noise; less vibrations) in particular.

If the ignition delay is too high, large quantities of fuel reach the combustion chamber unburned. The length of ignition delay depends on both the design and construction of the engine and the ignition quality of the diesel fuel.

2.1.1 The Diesel Combustion Process

Combustion fuel in a liquid state is injected in the cylinder at a precise rate ensures that the combustion pressure is forced on the piston too early nor too late. The fuel enters the cylinder where the heated compressed air is present.

Fuel will burn only when it is in a vaporized state (attained through addition of heat) and intimately mixed with a supply of oxygen. All these conditions are present in the cylinder. When the first minute droplet of fuel enters the combustion chamber,

it is quickly surrounded by its own vapor because the compression temperature at this point is about 343 °C (650 °F). Heat is withdrawn from the air surrounding the droplet causing it to vaporize. It takes time for the heat to build up again and cause the vapor to ignite since the core of the droplet is still liquid and relatively cold. One ignition has started and a flame is present, the heat required for continuos vaporizing is supplied from that released by combustion and the higher compression temperature. The liquid droplet surrounded by its own vapor, burns as fast as fresh oxygen is supplied. This process continues unchanged until the fuel oil is burned or the oxygen is used up [10].

2.1.2 Combustion of Diesel Fuel Oils

Both physical and chemical processes are involved to any combustion process. In the diesel engine, the physical processes include transportation of the fuel and air into the combustion chamber, mixing of fuel and air, and provision of environmental conditions favorable to chemical reaction. The chemical processes involve self-ignition or auto-ignition of the fuel and finally extensive chemical reaction that liberates the potential energy in the fuel.

2.1.3 General Outline of Combustion in the Diesel Engine

In any combustion process, there are at least three basic requirements;

1. Formation of a mixture of fuel and air.
2. Ignition of the fuel-air mixture.
3. Completion of combustion of the fuel-air mixture

In the diesel engine, these requirements are met as indicated diagrammatically in Fig. 2.3
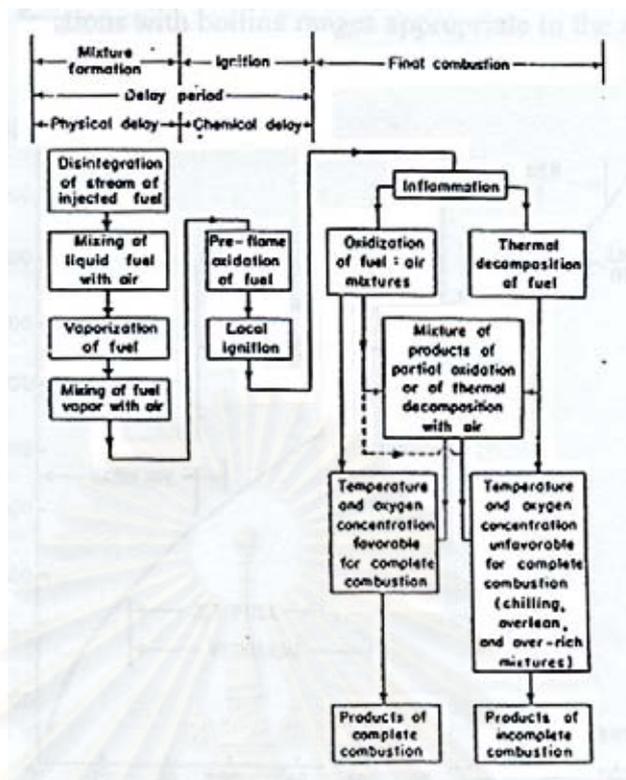
Figure 2.3 Outline of combustion process in the diesel engine.[10]

Ignition in the diesel engine occurs as the result of auto-ignition of the fuel. This is accomplished by the direct oxidation of the fuel, the rate of which is comparatively slow at first and accelerates rapidly until ignition occurs. After ignition, the mixture inflames and combustion may proceed as indicated in Fig. 2.3, either by rapid oxidation of mixtures of fuel and air or by rapid oxidation of products of thermal decomposition of the fuel. If mixing is complete under conditions favorable for combustion, then combustion is complete. If mixing is inadequate of if combustion reactions or thermal decomposition reactions are chilled, products of incomplete combustion will result.

2.2 Diesel Fuel

Fuel for diesel engine is obtained from fractional distillation of the crude oil to separate it into fractions with boiling ranges appropriate to the major fuel application.
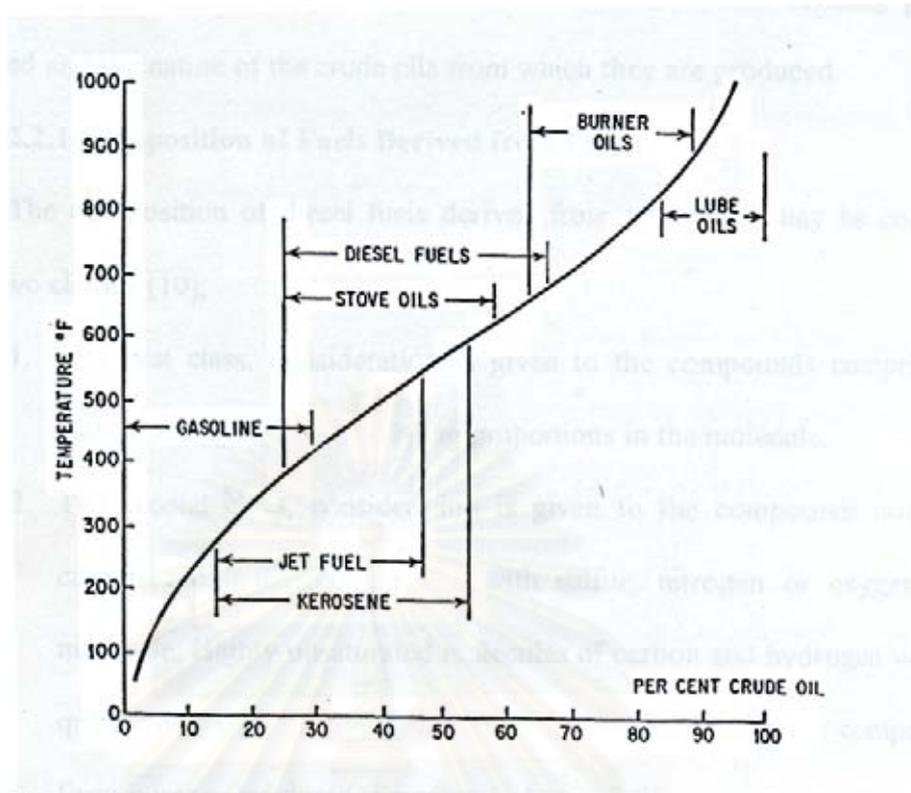
Figure 2.4 Proportion of diesel fuel and other petroleum products processed from crude petroleum.[11]

The boiling range of distillate fuel is approximately 150-370°C (300-700°F). It is a general property of hydrocarbons that the more volatile they are the higher temperatures for spontaneous ignition. It is for this reason that the less volatile middle distillate fractions of petroleum crude and even residues are more readily applicable to diesel engines than gasoline or lighter fractions.

With reference to Fig. 2.4 [11], the more common designation is that portion of the distillation curve from 25 to 65 percent of the crude-oil barrel, or within the temperature ranges of 375-725°F. Other properties are evaluated and characteristics are determined which influence the fuel performance value in a specific application. In the diesel fuel classification many properties are considered significant by the American Society for Testing Materials, such as cetane number, viscosity, carbon residue, sulfur content, flash point, pour point, ash, and copper-strip corrosion.

The properties of commercial fuel oils depend on the refining practices employed and the nature of the crude oils from which they are produced.

2.2.1 Composition of Fuel Derived from Petroleum

The composition of diesel fuels derived from petroleum may be considered under two classes [10];

1. The first class, consideration is given to the compounds comprising on carbon and hydrogen in varying proportions in the molecule.

2. The second class, consideration is given to the compounds comprising carbon and hydrogen together with sulfur, nitrogen or oxygen in the molecule. Highly unsaturated molecules of carbon and hydrogen which are quite reactive and tend to polymerize or to react with other compounds to form gums or products of extremely low volatility.

Class I Component

Diesel fuels are mixtures comprising these hydrocarbons boiling within the range from about $350°F$ to about $700°F$. It is possible to further classify such hydrocarbon mixtures into four main types: parpffins, olefins, naphthenes and aromatics.

1. Paraffins, both straight chain and moderately branched. Generally, one may consider that for diesel fuel, in the formula varies from 9 to 20 carbon atoms.

2. Olefins structurally undefined.

3. Naphthenes consisting of major proportions of five and six carbon rings with multiple and short parpffinic side chains.

4. Aromatics consisting of major proportions of mononuclear compounds and multiple and short paraffinic side chains.

Class II Components

Those derivatives of hydrocarbons containing sulfur, nitrogen or oxygen, together with such compounds of the diolefin type which are quit reactive to form high molecular weight.

Sulfur derivatives – In the most simple forms sulfur exists as mercaptans, sulfides, and disulfides. These compounds are produced in the conventional treating operations. Other sulfur compounds are known to exist in diesel-fuel fractions from petroleum.

Nitrogen derivatives – These nitrogen compounds are considered to be basic in nature but very little more is known as to the actual structural form in which they are present in crude oils.

Oxygen derivatives – Hydrocarbon derivatives containing oxygen are also present in some crudes such as naphthenic acids.

Highly unsaturated hydrocarbons – The breaking down of high molecular weight hydrocarbons to molecules of lower molecular weight produces an increase in the unsaturation of the products.

2.2.2 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 [12].

Performance Feature Desired	Indicated By
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	$^{\circ}$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) $^{\circ}$API gravity. This section discussed the more important fuel characteristics as they relate to engine performance.

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.

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.

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.

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:

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

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.

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.

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.

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.

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.

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.

2.3 Specification for Diesel Fuels

2.3.1 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, alphamethylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alphamethylnaphthalene 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 [11]:

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

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 [11]:

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 engines 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. Ignition delay can be reduced by the use of high fuel injection pressures and high fuel/air turbulence to promote rapid fuel jet break-up and through fuel distribution.

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 [13]. 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, It 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, the 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 2.5.
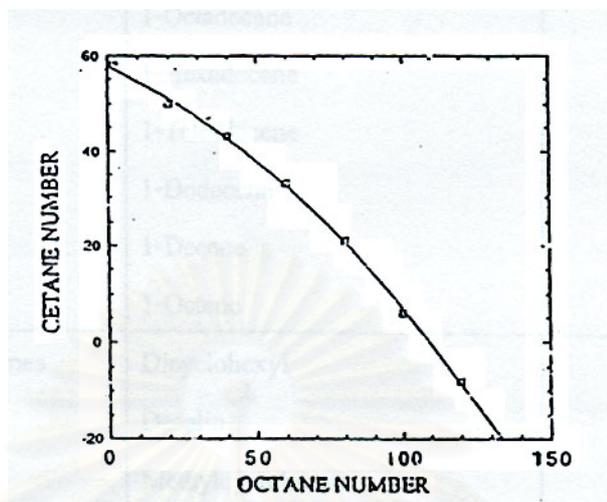
Figure 2.5 The inverse relationship between cetane and octane numbers.

The cetane numbers of a variety of compounds are shown in Table 2.1. 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 [14].
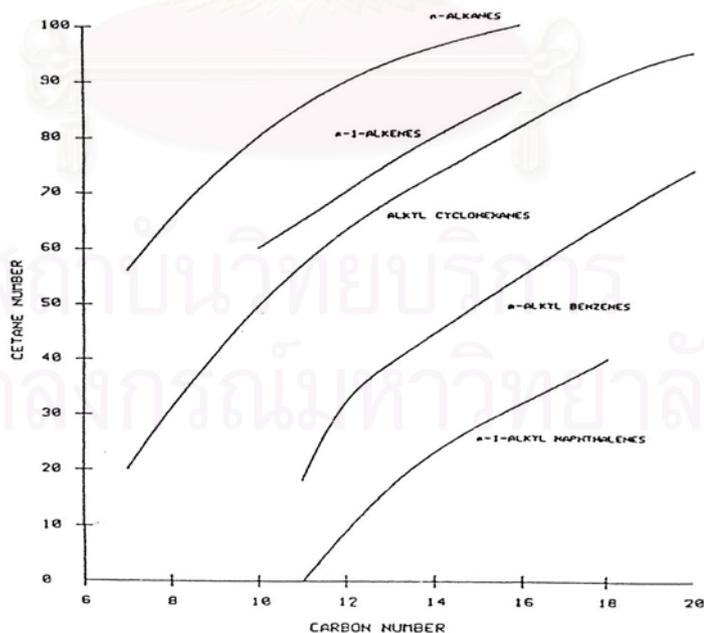
Figure 2.6 Cetane number of pure hydrocarbons.

Table 2.1 Cetane number for pure organic compounds.[14]

Chemical Structure	Compounds	Cetane Number
Normal Paraffins	Hexadecane	100.0
	Tetradecane	96.1
	Dodecane	87.6
	Decane	76.9
	Octane	63.8
	Heptane	56.3
Olefins	1-Octadecene	90.0
	1-Hexadecene	84.2
	1-Tetradecene	82.7
	1-Dodecene	71.3
	1-Decene	60.2
	1-Octene	40.5
Naphthenes	Dicyclohexyl	47.4
	Decalin	42.1
	Methylcyclohexane	20.0
Aromatics	n-Nonylbenzene	50
	n-Hexylbenzene	26
	n-Amylbenzene	8
	n-Diisopropylbenzene	-12

2.3.2 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 [15]. 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 2.7.

2. It is determined from the following formula [16]:

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

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

   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;

CCI improved   =   CCI + Improver value   (4)
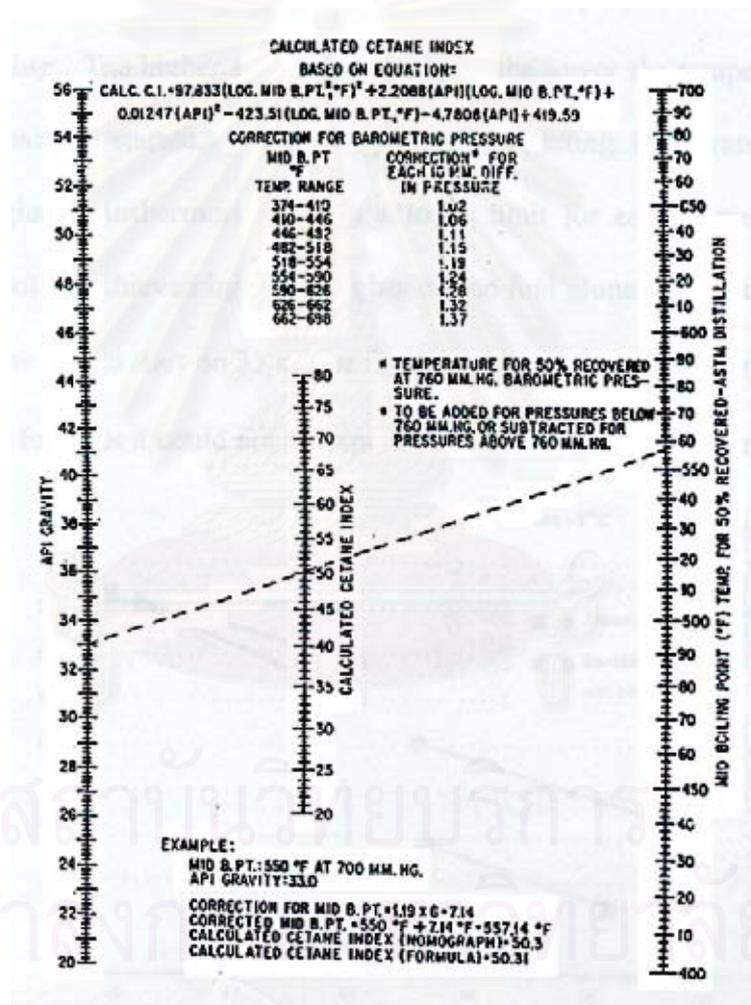
Figure 2.7 Nomograph for calculated cetane index.[16]

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.

2.3.3 The Cetane Quality of Diesel Fuels and Diesel Fuel Component.

The cetane quality of diesel fuel has traditionally been high, and importance is attached to the performance benefits this offers in terms of:

1. Improved cold starting

2. Reduced smoke emission during warm-up

3. Reduced noise

4. Reduced fuel consumption and exhaust emissions

5. Improved engine durability

The scope of refiners to produce diesel fuel of high cetane quality varies significantly with the types of crude oil processed and the process units available within the refinery. In general, throughout the world the conversion refinery utilizing catalytic cracking predominates, and the diesel fuel blending components typically available are shown in Table 2.2 and 2.3, the effect of crude source on light gas oil

quality being illustrated by the data in Table 2.2 and the effect of component type by

the data in Table 2.3.

Table 2.2 Effect of crude source on diesel fuel blending component quality.[15]

Property/crude source	Light gas oil ex Kuwait crude	Light gas oil ex Forties crude	Light gas oil ex Nigerian crude
Density (kg/1 at 15°C)	0.8517	0.8558	0.8785
Viscosity (cSt at 40°C)	4.5	4.6	4.5
Cloud point (°C)	4	6	-8
Cold filter plugging point (°C)	-4	1	-11
ASTM distillation 50% distilled at °C	304	294	283
Sulfur (%wt)	1.40	0.19	0.13
Cetane number (ASTM D613)	54.1	52.2	40.9

Table 2.3 Effect of component type on diesel fuel blending component quality.[15]

Property/Component type	Kerosene ex North Sea crude	Light gas oil ex North Sea crude	Light cracked gas oil ex North Sea crude	
			Non-hydrotreated	Hydrotreated
Density (kg/1 at 15°C)	0.8011	0.8558	0.9613	0.9294
Viscosity (cSt at 40°C)	1.2	4.6	3.1	3.0
Cloud point (°C)	-58	6	-11	-11
Cold filter plugging point (°C)	-58	1	-9	-9
ASTM distillation 50% distilled at °C	190	294	276	273
Sulfur (%wt)	0.03	0.19	1.35	0.24
Cetane number (ASTM D613)	41.3	52.2	21.0	24.1

Trends in the production and use of petroleum products are dictating that increased quantities of the lower cetane quality components are used in diesel fuel blending. Projections are that, without the use of additives, marked falls in the cetane quality of diesel fuels could occur. In this situation cetane improvers are invaluable, as they provide refiners and blenders with a simple and effective means of achieving operational flexibility on a day-to-day basis.

Current experience would suggest that cetane number improvers are being increasingly used to:

1. Upgrade diesel fuel quality to meet specification requirements in conversion refineries where there is a requirement to use increasing quantities of cracked components in diesel fuel production.

2. Provide the flexibility required to process significant quantities of low cetane naphthenic crude oils when geographic or economic conditions dictate this.

3. Upgrade diesel fuel quality to give the premium grade products now being marketed by many oil companies in certain markets throughout the world [8].

2.3.4 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 [7]. 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 [17].

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 $RO-NO_2$ bond in isooctyl nitrate provides the available source of the free radicals required to enhance diesel combustion [9].

Nitrates have historically been the chemical functional groups that lead to good cetane improver performance. Agricultural feedstock were pursued on the basis of the

following criteria: (1) relatively low cost (<$0.40 per pound as compared to EHN costs typically >$0.50 per pound), and (2) chemical functional groups that allow nitration at a carbon: nitrogen ratio >6. Triglycerides meet these criteria. In addition, triglycerides have carbon-carbon ∂-bonds and ester bonds, both of which can be chemically modified leading to high nitration yields. Hydrocarbon emissions (HC) generally do not correlate well with cetane number since, to a first approximation, hydrocarbon emissions are dominated by fuel volatility. In addition, typical variations in engine operation will have a greater impact than a cetane improver additive.

2.4 Fuel Properties Affecting Ignition Delay

2.4.1 Fuel Rating

A discussion of the effect of fuel properties on ignition delay must be prefaced by a discussion of methods for evaluating fuels to determine these effects. In the case of diesel fuels, this is done in the familiar CFR engine by matching, under standard test conditions, the ignition delay of the unknown fuel with the ignition delay of a reference fuel.

Since high cetane fuels ignite in the CFR engine at lower temperatures and pressures than low cetane fuels, it is apparent that the cetane number permits us to put fuels in the proper order with respect to the ease with which they may be ignited by compression. It is, therefore, useful in rating fuels and as a basis for correlating data on certain fuel performance factors in engines. It should be emphasized that the cetane number has no quantitative significance, since it tells us only that Fuel A is better than Fuel B, but not how much better.

To attach quantitative significance to the cetane number, it is necessary to study the performance of the fuel under the particular environment in which we are

interested. This point is illustrated in Figure 2.8, which shows the relation between cetane number and ignition delay in tests in three different engines, and between cetane number and ignition delay in bomb tests. This figure emphasizes the importance of the environment in attaching quantitative significance to the cetane number. This is indicated by the effect of speed on the ignition delay of a given cetane number fuel in one engine, by the effect of compression ratio in another engine, and by the comparison between bomb and engine experiments.
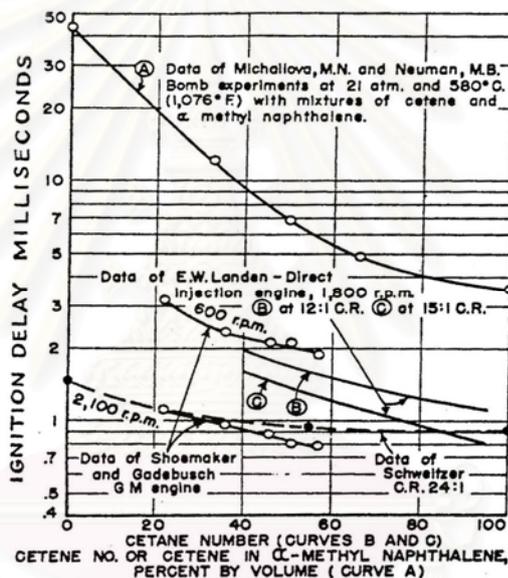
Figure 2.8 Relation between ignition delay and cetane number in tests in engines and

bombs.[10]
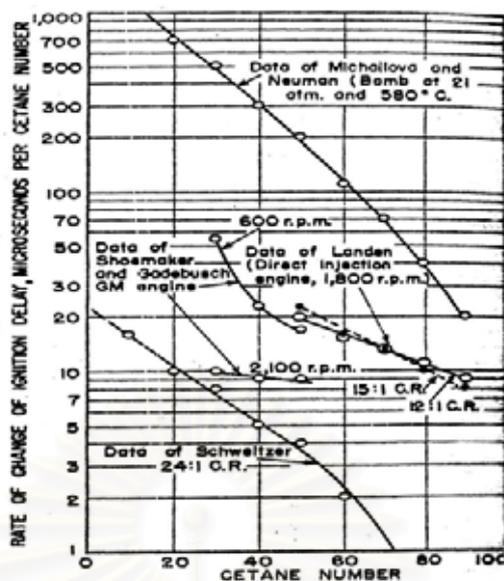
Figure 2.9 Variation of rate of change of ignition delay with cetane number.[10]

Closer study of Figure 2.8 shows that, in the low range of cetane numbers, a given increase in cetane number corresponds to a greater decrease in ignition delay than in the high range. This may be seen more clearly in Figure 2.9, which shows the relation between cetane number and decrease in ignition delay in microseconds per unit increase in cetane number. From the standpoint of ignition delay, it is evident that, in most instances, the cetane number is a larger unit at low cetane than at high cetane numbers. However, this does not seem to be true in the case of one engine at 1800 r.p.m., and therefore, this further emphasizes the importance of environment in attaching quantitative significance to the cetane number. These results also emphasize the limitations of cetane number as a means of rating fuels quantitatively [10].

2.4.2 Effect of Chemical Structure

The effect on cetane number of adding one side chain to a normal paraffin hydrocarbon is shown in Figure 2.10. The data were obtained by Petrov in a bomb

which had been calibrated against a CFR engine. Figure 2.10 shows quantitatively that, in every instance, the addition of one side chain to a normal paraffin hydrocarbon reduces the cetane number. In general, the side chain was added near the middle carbon atom of the normal paraffin and this should be recognized in any conclusions drawn. Data were obtained on side chains containing one to seven carbon atoms; but in Figure 2.10 it is very difficult to separate the effect of length of side chain on cetane number, because in no instance was the length of the main chain held constant nor did the length of the side chain increase systematically.
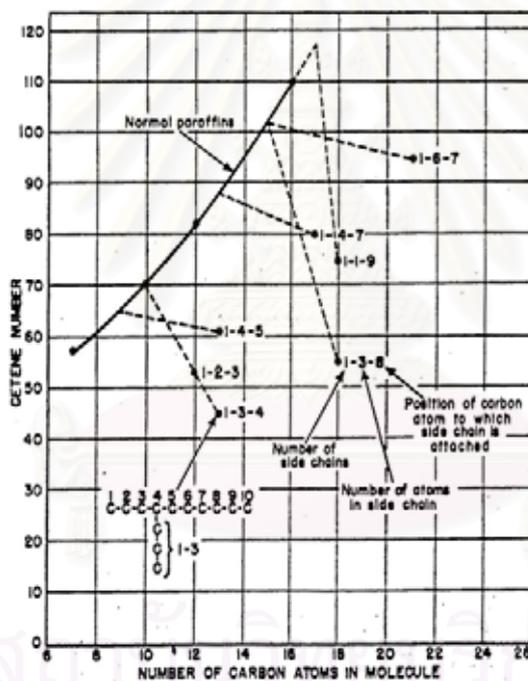
Figure 2.10 Cetane number of n-alkyl paraffin hydrocarbons.[10]

In order to overcome this difficulty, the results have been plotted as shown in Figure 2.11. The ordinate is the ratio of the cetane number of the hydrocarbon with one side chain to the cetane number of the normal paraffin hydrocarbon to which the side chain is added. By plotting this ratio against the number of carbon atoms in the molecule, the indications are that we have essentially a linear relation in the case of

three and four carbon side chains. Even though we have only two experimental points, it seems reasonable to expect that if, as an example, the line for a three carbon side chain is extrapolated to a molecule containing only three carbon atoms, there will obviously be no side chain and therefore the ratio should be unity. The limited data seem to support this reasoning. Even if this reasoning is not valid, we can still use Figure 2.10 for interpolation and slight extrapolation.
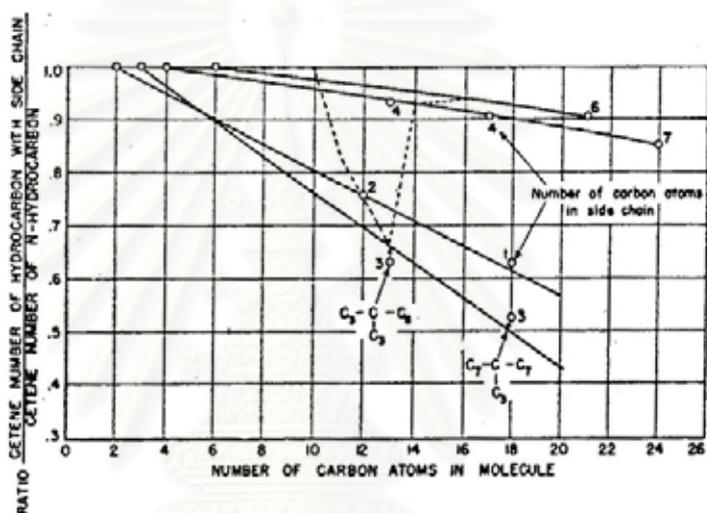
Figure 2.11 Effect of adding n-alkyl side chains on cetane number of paraffin hydrocarbons.[10]

By interpolation, using Figures 2.10 and 2.11, it can now estimate the effect of adding different length side chains to a given normal paraffin hydrocarbon, say, for example, decane. Thus it can estimate the cetane number of methyldecane, ethyldecane, propyldecane, butyldecane, etc. Such an estimate is shown graphically in Figure 2.12 for n-alkyldecanes and n-alkylpentadecanes. It will be observed that, in both instances, a progressive and significant reduction in cetane number is indicated, as one, two, and three carbon atoms are added in the side chain. However, the addition of a side chain containing four or more carbon atoms gives a hydrocarbon

having a cetane number only slightly less than that of the normal paraffin to which the side chain has been added. These results strongly indicate that an unbranched side chain containing three carbon atoms or, in other words, a propyl side chain, results in a chemical structure that is more resistant to oxidation than any other structure in the homologous series of n-paraffins having one n-alkyl side chain (mono n-alkyl n-paraffins). Admittedly, this statement is based on very meager evidence, if there are other instances where a three-carbon side chain results in maximum stability toward oxidation.
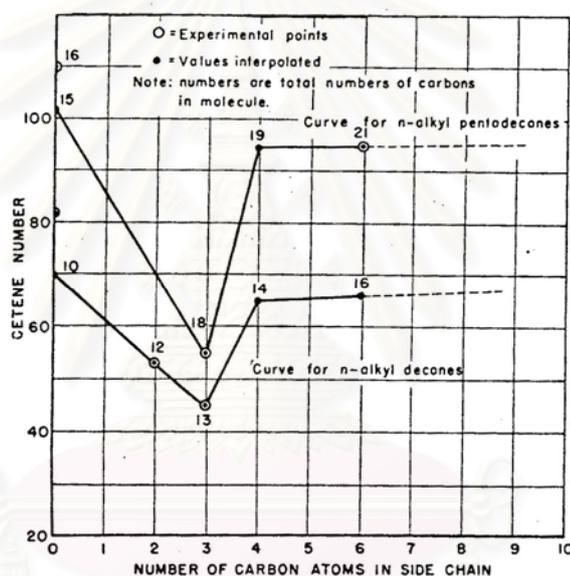
Figure 2.12 Relation between cetane number and number of carbon atoms in a single side chain in n-alkyl paraffin hydrocarbons.[10]

2.4.3 Effect of Thermal Stability

The effect of the thermal stability of a fuel on its ignitability was studied by Boerlage and van Dyck. In their tests, the thermal stability of the fuel was measured by the rate at which the fuel cracked or decomposed into lower molecular weight hydrocarbons. The results of these tests are shown in Figure 2.13, which indicates

good correlation between rate of cracking and cetane number in eight out of ten fuels. These results clearly show that low thermal stability of a fuel is associated with high oxidation rate. The reason for this association probably is related to the high reactivity of hydrocarbon free radicals produced in the thermal decomposition process.
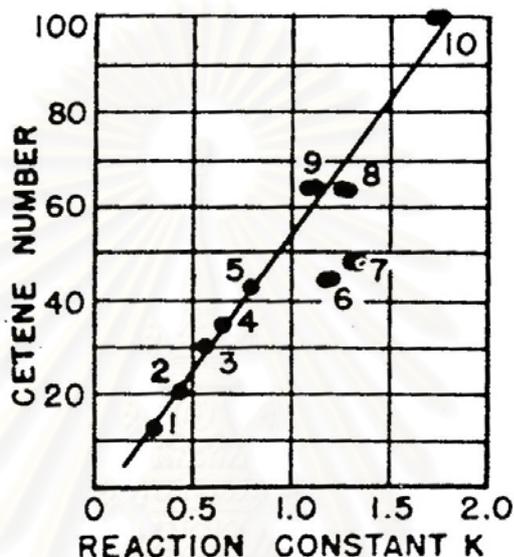
Figure 2.13 Reaction constant K in relation to cetane number. (cracking temperature 635°C).[10]

2.4.4 Ignition Accelerators

The rate of the chemical reactions preceding the auto-ignition of a fuel may be increased by the addition of ignition accelerators. Numerous compounds have been proposed as ignition accelerators, but probably the most effective, reasonably stable accelerator is acetone peroxide, and the most effective semi-commercially available accelerator is amyl nitrate. The average increase in cetane number obtained in tests of nine different fuels in shown in Figure 2.14, in relation to the concentration of ignition

accelerator. It will be observed that significant improvement is obtained with comparatively small additions of accelerator.
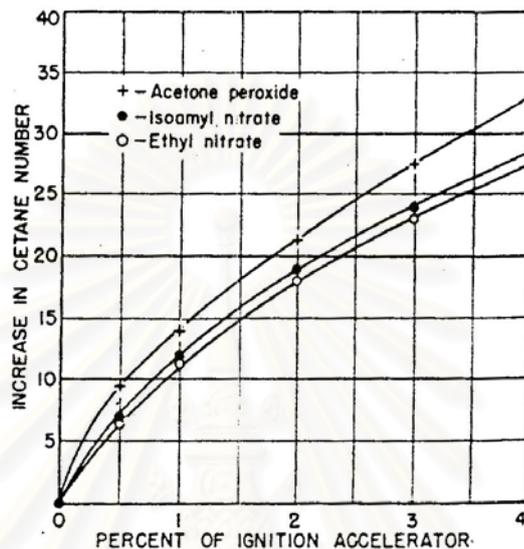
Figure 2.14 Average increases in cetane number of 9 test fuels in relation to concentration of ignition accelerator.[18]

Let us now see what is the probable mechanism of ignition acceleration and why comparatively small additions of accelerator produced such a marked effect. This question has been considered by Broeze and Hinze, who show that their results on the reduction in ignition delay by accelerators can be explained on the basis of chain-reaction theory. It is probable, therefore, that the accelerators or their thermal decomposition products enter into chain-branching reactions. In connection with the effect of alkyl nitrates, it is significant to note that NO_2 in certain concentrations accelerates the reaction between hydrogen and oxygen and between carbon monoxide and oxygen.

2.4.5 Effect of Physical Properties of Fuel

The interrelation between the physical properties of a fuel and cetane number is shown in Figure 2.15, which was developed by Blackwood and Cloud. It is evident from this chart that boiling point, viscosity, and gravity are so interrelated with cetane number that in correlating data on combustion performance with cetane number, considerable care must be exercised to make sure that the effects observed are not due to changes in one of the physical properties of the fuel. This is particularly true of volatility which, as we have already seen, is related to the air required for combustion and therefore affects mixture distribution.
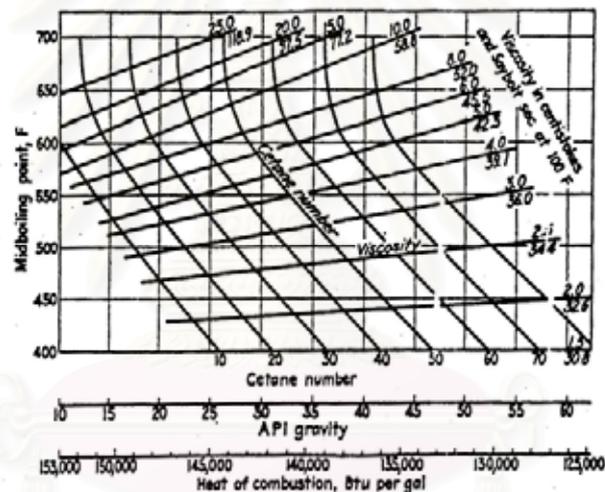
Figure 2.15 Interrelated properties of diesel fuels.[10]

2.5 Diesel Fuel Additives

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 [18].

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, demulsifies, 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 2.4 Commercial diesel fuel additives-function and type.[19]

Class or Function	Common Additive Type
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

Table 2.4(continued) Commercial diesel fuel additives-function and type.[19]

Class or Function	Common Additive Type
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. Demulsifies and Dehazers: Improve the separation of water from distillate fuels and prevent haze.	Surface-active materials which increase the rate of water/oil separation
8. Smoke Suppressants: Minimize exhaust smoke by catalyzing more complete combustion of carbonaceous materials or by helping to maintain fuel spray patterns	Catalyst types are generally over based barium compounds. Maintenance of spray patterns is helped by detergents.

This research established cetane improvers because of ignition quality are the most important properties in diesel fuels.

2.6 Fatty acid wastes

Soybean is the family *Leguminosae,* subfamily *Papilinaceae,* 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 yellow color.

Table 2.5 Fatty acid composition of soybean acid waste.

Component acids	Amount of fatty acid composition (wt%)
Palmitic acids (C 16:0)	7-12
Stearic acid (C 18:0)	2-6
Oleic acid (C 18:1)	15-33
Linoleic acid (C 18:2)	35-60
Linolenic acid (C 18:3)	2-13

Coconut (*Cocos nucifera*) is a palm family. It is used for oil, food, fiber and drink. Coconut is also an ingredient in many cosmetics, shampoos and suntan products, because coconut oil is resistant to spoilage and low in price. Coconut oil contains amounts of saturated fatty acids, which lauric and myristic acids are the main component acids.

Table 2.6 Fatty acid composition of coconut acid waste.

Component acids	Amount of fatty acid composition (wt%)
Caprylic acid (C 8:0)	10-12
Capric acid (C 10:0)	7-10
Lauric acid (C12:0)	50-55
Myristic acid (C14:0)	17-20
Palmitic acids (C 16:0)	7-10
Stearic acid (C 18:0)	2-5

2.7 Literature Reviews

Suppes, G.J. *et al*. [7] synthesized organic acid glycol nitrates as cetane improver from five acids ranging from C_6 to C_{18} by acid catalyzed esterification of organic acids with ethylene glycol followed by nitration of the terminal alcohol group to fatty acid glycol nitrate. Fatty acid glycol nitrates with carbon numbers between 8 and 14 exhibited the best performance. All organic acid glycol nitrates evaluated cetane improver capabilities that were up to 60% of the efficacy of 2-ethylhexyl nitrate (EHN)

Suppes, G.J. *et al*. [20] synthesized nitrate derivatives of soybean oil and evaluated for diesel fuel additives to develop as a renewable cetane improver, alternative to 2-ethylhexyl nitrate (EHN) which currently dominates the cetane improver market. The products exhibited NO*x*-reducing capabilities similar to that of EHN when used in a diesel fuel. They also provided significant lubricity enhancement to the fuels at the same concentrations used to provide the cetane enhancement. Depending on the product, these additives exhibit increased stability and lower

volatility than EHN. Commercially competitive enhancements of both ignition-related properties and lubricity where achieved in a single product.

Liotta, F.T. Jr. [21] reported that improved cetane rating was achieved with a base diesel fuel having a cetane number of 43 by the addition of a small amount of methyl benzyl alcohol nitrate (MBAN). In addition to the blends containing MBAN, blends were prepared using the same concentrations of the commercial cetane number improver, 2-ethylhexyl nitrate. The results revealed that MBAN was slightly less effective than the commercial material but it had a cost advantage over the commercial material. In fact, cetane improvers containing benzene ring tend to decrease cetane number but MBAN are comprised of nitrate groups induced the higher cetane number. It could be depicted that cetane improvement additive in the presence of nitrogen and oxygen in the molecular structure was used to increase cetane number.

Moreover, several studies by Siraprapakit, S. [22], Suttipitakwong, C. [23], Vasaruchtragul, J. [24] and Khankasikham, T. [25] revealed that a diesel fuel containing dinitrate compounds such as triethylene glycol nitrate, 1,10-decane dinitrate and tripropylene glycol dinitrate increased cetane number. The results were directly compared to the response obtained with a commercial cetane improver, 2-ethylhexyl nitrate. It was found that these dinitrate compounds gave higher increased cetane number than commercial cetane improver.

As the above reports showed, the cetane improvers containing nitro, nitrate and oxy- group were an outstanding cetane improver, especially at very low concentrations and had many times as effective as the commercial additive. Hence, the available cetane number. From what has been mentioned, the need for further research of these compounds is urgent.

CHAPTER III

EXPERIMENTAL

3.1 Apparatus

1. Fourier-Transform NMR Spectrometer: Model AC-F 200 (200MHz); Bruker Spectrospin

2. Fourier-Transform Infrared Spectrophotometer: Model Impact410; Nicolet

3. Automatic Distillation Apparatus: Model MP626; Herzog

4. Pensky-Martens Closed Flash Tester: Model ISL(PMFP93); Perzoo

5. Automatic Pour Point Tester: Model ISL(CPP97-6); ISL

6. Cannon Automatic Viscometer: Model CAV-3; Cannon

7. Apparatus for API Gravity

8. PetroSpecCetane-2000 Diesel Fuel Analyzer

3.2 Chemicals

1. Soybean fatty acid waste; Thanakorn Vegetable Oil Product Co.,Ltd.

2. Coconut fatty acid waste; Siam Union Sahamitr Co.,Ltd

3. Ethylene glycol: analytical grade; Merck

4. 2-Ethyl-1-hexanol: analytical grade; Fluka

5. Dichloromethane: analytical grade; Lab-Scan

6. 96% Sulfuric Acid: analytical grade; Carlo Erba

7. 65% Nitric acid: analytical grade; Merck

8. Sodium hydrogen carbonate: analytical grade; Merck

9. Anhydrous sodium sulfate: analytical grade; Merck

10. Chloroform-D: NMR spectroscopy grade: Merck

11. Diesel fuel base; Petroleum Authority of Thailand

3.3 Synthesis of Fatty Acid Ethylene Glycol Nitrate

3.3.1 Synthesis of Soybean Fatty Acid Ethylene Glycol Ester

In the 250 ml round bottom flask equipped with condenser and Dean-stark apparatus, soybean fatty acid waste (10 g.), ethylene glycol (50 g.), 96% sulfuric acid (1.5 ml.), toluene (70 ml.) as solvent were added. The reaction was refluxed for 4 to 6 hours. During the reaction period, the generated water was distilled off. After this period, the reaction was cooled down to room temperature gradually. Then the reaction mixture was transferred into the separating funnel and the aqueous phase was drawn off. The organic phase was then washed with water (100 ml.), 15% aqueous sodium hydrogen carbonate solution (100 ml.), water (100 ml.) and saturated sodium chloride solution (100 ml.), respectively. The organic phase was then dried over anhydrous sodium sulfate, and concentrated on the rotary evaporator to give soybean fatty acid ethylene glycol ester, as a brown liquid (9.86 g.) (yield = 98.6%).

3.3.2 Synthesis of Soybean Fatty Acid Ethylene Glycol Nitrate

In the 250 ml of round bottom flask, a mixture of 65% nitric acid (7.35 g.) and 96% sulfuric acid (15.55 g.) was stirred on ice-bath and maintained temperature at $0\pm2^{\circ}$C. The solution of soybean fatty acid ethylene glycol ester (5 g.) in dichloromethane (30 ml.) was added dropwise to the mixture and temperature was kept at 0-2 $^{\circ}$C. The reaction was stirred for 6 hours and maintained temperature at 0-2 $^{\circ}$C, then the reaction mixture was transferred to a separating funnel and the aqueous phase was removed. The organic phase was then washed with water (50 ml.), 15% aqueous sodium hydrogen carbonate solution (50 ml.), water (50 ml.) and saturated sodium chloride solution (50 ml.), respectively. The organic phase was then dried over anhydrous sodium sulfate, and concentrated on the rotary evaporator to give

soybean fatty acid ethylene glycol nitrate, as a dark brown liquid (4.72 g.) (yield = 94.4%). The product was further purified by silica gel column chromatography, using 10% ethyl acetate/hexane as an eluant, to give pure product, as a yellow liquid (3.65 g.).

3.3.3 Synthesis of Coconut Fatty Acid Ethylene Glycol Ester

By starting with coconut fatty acid waste (10 g.) using a process analogous that described in 3.3.1, the subtitle compound was prepared to give coconut fatty acid ethylene glycol ester, as a light brown liquid (9.78 g.) (yield = 97.8%).

3.3.4 Synthesis of Coconut Fatty Acid Ethylene Glycol Nitrate

In the 250 ml round bottom flask, a mixture of 65% nitric acid (7.35 g.) and 96% sulfuric acid (15.55 g.) was stirred on ice-bath and maintained temperature at $0\pm2^{\circ}$C. The solution of coconut fatty acid ethylene glycol ester (5 g.) in dichloromethane (30 ml.) was added dropwise to the mixture and temperature was kept at 0-2 $^{\circ}$C. The reaction was stirred for 6 hours and maintained temperature at 0-2 $^{\circ}$C, then the reaction mixture was transferred to a separating funnel and the aqueous phase was removed. The organic phase was then washed with water (50 ml.), 15% aqueous sodium hydrogen carbonate solution (50 ml.), water (50 ml.) and saturated sodium chloride solution (50 ml.), respectively. The organic phase was then dried over anhydrous sodium sulfate, and concentrated on the rotary evaporator to give coconut fatty acid ethylene glycol nitrate, as a yellow liquid (4.54 g.) (yield = 90.80%).

3.4 Synthesis of 2-Ethylhexyl Nitrate

In the 250 ml round bottom flask, 50 ml. of dichloromethane were added to 96% sulfuric acid (6.13 g.) and 65% nitric acid (3.88 g.). 2-Ethyl-1-hexanol (2.6 g.) were then slowly added to the well-agitated mixture whilst maintaining the temperature at 0-2 $^{\circ}$C. The mixture was stirred for over an hour and then the reaction mixture was transferred to a separating funnel. The aqueous phase (comprising mainly strong sulfuric acid) was removed. The organic phase was then washed with water (100 ml.), 15% aqueous sodium hydrogen carbonate solution (100 ml.), water (100 ml.) and saturated sodium chloride solution (100 ml.), respectively. The organic phase was then dried over anhydrous sodium sulfate, and concentrated on the rotary evaporator to give 2-ethylhexyl nitrate, as a colorless liquid (3.26 g.) (yield = 93.14%).

3.5 Characterization and Determination of the Synthesized Nitrate Compounds

3.5.1 Characterization of the Synthesized Nitrate Compounds

The synthesized nitrate compounds were characterized by using instruments as follows:

1. Fourier-Transform Infrared Spectrophotometer

2. Fourier-Transform NMR Spectrometer

The result was shown in appendix A.

3.5.2 Determination of Cetane Number of Base Diesel Fuel Blended with Synthesized Nitrate Compounds

Blended base diesel fuels containing 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00% by weight of synthesized nitrate compounds were determined of

their cetane numbers by Cetane-2000 Diesel Fuel Analyzer (ASTM D613). The physical properties of the base diesel fuels were determined as shown in Table 3.1.

Table 3.1 Test method of the base diesel fuels

Property	Method
Mid-boiling point	ASTM D86
API gravity	ASTM D1298
Pour point	ASTM D97
Flash point	ASTM D93
Viscosity	ASTM D445
Cetane index	ASTM D976

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Fatty Acid Ethylene Glycol Nitrate Compounds from Fatty Acid Wastes

Fatty acid ethylene glycol nitrate compounds could be prepared from esterification of fatty acid wastes with ethylene glycol using concentrated sulfuric acid as a catalyst, followed by the nitration reaction. The details of these reactions were described in sections 3.3.1, 3.3.2, 3.3.3 and 3.3.4, respectively. Moreover, condition of nitration reaction were varied which shown in Table 4.1

Table 4.1 Variation of nitration reaction of fatty acid ethylene glycol ester

Conditions	Mole ratio (glycol ester : acid)			Amount of time (hrs.)		
Temperature(°C)	1:1	1:3	1:5	4	6	8
-78 °C	-	-	-	-	-	-
-20 °C	-	-	-	-	-	-
0 °C	*	**	**	*	**	**
15 °C	*	**	**	*	**	**

Note;　(-)　=　no reaction

(*)　=　incomplete reaction

(**)　=　complete reaction

From Table 4.1, the optimum condition of nitration reaction was performed at temperature 0 °C, mole ratio 1:3:6 and reaction time 6 hours, due to the completion of reaction. Some of the spectra of no reaction and non complete reaction, as compare

with starting fatty acid ethylene glycol ester compound (Figure A27), were shown in Figures A28, A29, respectively.

4.2 Characteristics of Synthesized Fatty Acid Ethylene Glycol Ester Compounds

4.2.1 Soybean Fatty Acid Ethylene Glycol Ester

The IR spectra of soybean fatty acid waste and soybean fatty acid ethylene glycol ester were shown in Figures A1 and A2, respectively. The important absorption bands of soybean fatty acid waste and soybean fatty acid ethylene glycol ester were listed in Table 4.2.

Table 4.2 The absorption assignments of soybean fatty acid waste and soybean fatty acid ethylene glycol ester.

Wave number (cm^{-1})		Assignments
Soybean fatty acid waste	Soybean fatty acid ethylene glycol ester	
-	3443	O-H Stretching
2855	2851	C-H Stretching, Aliphatic
1742	1731	C=O Stretching
1458	1462	C-H Bending, Aliphatic
1162	1174	C-O Stretching

From the IR spectrum of soybean fatty acid ethylene glycol ester (Figure A2) as comparing with soybean fatty acid waste (Figure A1), it could be seen that the absorption bands of OH stretching of alcohol functional group was clearly observed at 3443 cm^{-1} as no absorption band of OH stretching in the IR spectrum of soybean fatty acid waste. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of soybean fatty acid waste and soybean fatty acid ethylene glycol ester were shown in Figures A3 and A4, respectively. Some signals of soybean fatty acid waste and soybean fatty acid ethylene glycol ester were shown in Table 4.3.

Table 4.3 The assignments of ^{1}H-NMR spectra of soybean fatty acid waste and soybean fatty acid ethylene glycol ester.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Soybean fatty acid waste	Soybean fatty acid ethylene glycol ester
a	*t*	0.89	0.81
b	*m*	1.60	1.55
c, d, e, f	*m*	1.29	1.24
g	*m*	2.01	1.96
h	*t*	2.31	2.27
i	*m*	5.38	5.29
k	*s*	10.77	-
l	*t*	-	4.11
m	*t*	-	3.72
n	*s*	-	2.79

From the ^{1}H-NMR spectrum of soybean fatty acid ethylene glycol ester (Figure A4) as comparing with soybean fatty acid waste (Figure A3), it could be observed that the signal at δ_H 10.77 ppm belonged to the protons of carboxylic acid group was absent, due to the formation of soybean fatty acid ethylene glycol ester. The signals at δ_H 3.72 ppm and 4.11 ppm were belonged to the protons of soybean fatty acid

ethylene glycol ester at position m and l and that at δ_H 2.79 ppm was belonged to the proton of hydroxyl group of ethylene glycol.

The ^{13}C-NMR spectra of soybean fatty acid waste and soybean fatty acid ethylene glycol ester were shown in Figures A5 and A6, respectively. Some signals of soybean fatty acid waste and soybean fatty acid ethylene glycol ester were shown in Table 4.4.

Table 4.4 The assignments of ^{13}C-NMR spectra of soybean fatty acid waste and soybean fatty acid ethylene glycol ester.

| Position of Carbon	Chemical Shift (δ,ppm)	
	Soybean fatty acid waste	Soybean fatty acid ethylene glycol ester
a	14.07	14.03
b	22.57	22.55
c	24.64	24.85
d	27.17	27.14
e	29.35	29.31
f	31.51	31.65
g, h	34.09	34.12
i	127.92,129.95	128.01,129.51
j	180.33	174.20
l	-	65.78
m	-	60.93

From the ^{13}C-NMR spectrum of soybean fatty acid ethylene glycol ester (Figure A6) as comparing with soybean fatty acid waste (Figure A5), it could be seen the

signal at δ_c 60.93 ppm and δ_c 65.78 ppm were belonged to the carbons of soybean fatty acid ethylene glycol ester at position m and n. The signals of carbonyl group of soybean fatty acid waste at δ_c 180.33 were shifted to 174.20 ppm, due to the formation of soybean fatty acid ethylene glycol ester.

From the results of the spectral data, it could be concluded that the product was soybean fatty acid ethylene glycol ester and its structure was as follows:

$$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{f}{CH_2}-\underset{}{(CH_2)_n}-\underset{e}{CH_2}-\underset{d}{CH_2}-\underset{g}{CH}=\underset{i}{CH}-\underset{i}{CH_2}-\underset{g}{CH_2}-\underset{d}{(CH_2)_n}-\underset{e}{CH_2}-\underset{c}{CH_2}-\underset{h}{\overset{\overset{O}{\|}}{C}}-\underset{k}{OH}$$

Soybean fatty acid waste

$$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{f}{CH_2}-\underset{}{(CH_2)_n}-\underset{e}{CH_2}-\underset{d}{CH_2}-\underset{g}{CH}=\underset{i}{CH}-\underset{i}{CH_2}-\underset{g}{CH_2}-\underset{d}{(CH_2)_n}-\underset{e}{CH_2}-\underset{c}{CH_2}-\underset{h}{\overset{\overset{O}{\|}}{C}}-O-\underset{l}{CH_2}-\underset{m}{CH_2}-\underset{n}{OH}$$
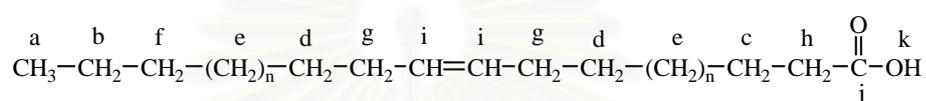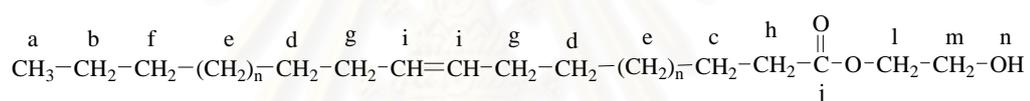
Soybean fatty acid ethylene glycol ester

4.2.2 Soybean Fatty Acid Ethylene Glycol Nitrate

The IR spectra of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate were shown in Figures A2 and A7, respectively. The important absorption bands of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate were listed in Table 4.5.

Table 4.5 The absorption assignments of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate.

Wave number (cm^{-1})		Assignments
Soybean fatty acid ethylene glycol ester	Soybean fatty acid ethylene glycol nitrate	
3443	-	O-H Stretching
2851	2855	C-H Stretching, Aliphatic
1731	1742	C=O Stretching
-	1637	NO_2 Asymmetric Stretching
1462	1458	C-H Bending, Aliphatic
-	1275	NO_2 Symmetric Stretching
1174	1162	C-O Stretching
-	855	N-O Stretching Vibration

From the IR spectrum of soybean fatty acid ethylene glycol nitrate (Figure A7) as comparing with that soybean fatty acid ethylene glycol ester (Figure A2), it could be observed that there was no the absorption band of OH stretching 3443 cm^{-1} but the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1637, 1275 and 855 cm^{-1} respectively. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate were shown in Figures A4 and A8, respectively. The important signals of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate were shown in Table 4.6.

Table 4.6 The assignments of ^{1}H-NMR spectra of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Soybean fatty acid ethylene glycol ester	Soybean fatty acid ethylene glycol nitrate
l	*t*	4.11	4.60
m	*t*	3.72	4.28
n	*s*	2.79	-

From the ^{1}H-NMR spectrum of soybean fatty acid ethylene glycol nitrate (Figure A8) as comparing with soybean fatty acid ethylene glycol ester (Figure A4), it could be observed that the signal at δ_H 2.79 ppm belonged to the proton of hydroxyl group of soybean fatty acid ethylene glycol ester was absent, due to nitrate reaction. The signals at δ_H 4.28 ppm and 4.60 ppm were belonged to the protons of soybean fatty acid ethylene glycol nitrate at position m and l which shifted from δ_H 3.72 ppm and 4.11 ppm, due to the influence of nitrate group.

The ^{13}C-NMR spectra of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate were shown in Figures A6 and A9, respectively. The important signals of soybean fatty acid ethylene glycol nitrate were shown in Table 4.7.

Table 4.7 The assignments of ^{13}C-NMR spectra of soybean fatty acid ethylene glycol ester and soybean fatty acid ethylene glycol nitrate.

Position of Carbon	Chemical Shift (δ,ppm)	
	Soybean fatty acid ethylene glycol ester	Soybean fatty acid ethylene glycol nitrate
l	65.78	59.93
m	60.93	70.52

* It was determined by DEPT spectra as shown in Figure A19

From the ^{13}C-NMR spectrum of soybean fatty acid ethylene glycol nitrate (Figure A9) as comparing with soybean fatty acid ethylene glycol ester (Figure A6), it could be seen that the signals at δ_c 70.52 ppm and δ_c 59.93 ppm were belonged to the carbons of soybean fatty acid ethylene glycol nitrate at position m and l which shifted from δ_c 60.93 ppm and δ_c 65.78 ppm, due to the influence of nitrate group.

From the results of the spectral data, it could be concluded that the product was soybean fatty acid ethylene glycol nitrate and its structure was as follows:

$$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{f}{CH_2}-\underset{}{(CH_2)_n}-\underset{e}{CH_2}-\underset{d}{CH_2}-\underset{g}{CH}=\underset{i}{CH}-\underset{i}{CH_2}-\underset{g}{CH_2}-\underset{d}{(CH_2)_n}-\underset{e}{CH_2}-\underset{c}{CH_2}-\overset{h}{\underset{j}{C}}\overset{O}{\underset{\parallel}{}}-O-\underset{l}{CH_2}-\underset{m}{CH_2}-ONO_2$$
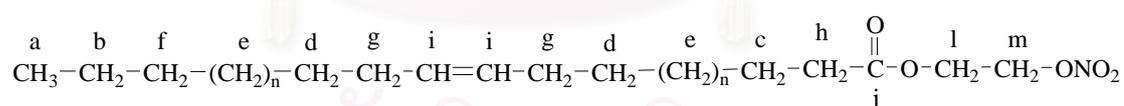
Soybean fatty acid ethylene glycol nitrate

4.2.3 Coconut Fatty Acid Ethylene Glycol Ester

The IR spectra of coconut fatty acid waste and coconut fatty acid ethylene glycol ester were shown in Figures A10 and A11, respectively. The important absorption bands of coconut fatty acid waste and coconut fatty acid ethylene glycol ester were listed in Table 4.8.

Table 4.8 The absorption assignments of coconut fatty acid waste and coconut fatty acid ethylene glycol ester.

Wave number (cm^{-1})		Assignments
Coconut fatty acid waste	**Coconut fatty acid ethylene glycol ester**	
-	3431	O-H Stretching
2855	2855	C-H Stretching, Aliphatic
1711	1742	C=O Stretching
1458	1462	C-H Bending, Aliphatic
1166	1174	C-O Stretching

From the IR spectrum of coconut fatty acid ethylene glycol ester (Figure A11) as comparing with coconut fatty acid waste (Figure A10), it could be seen that the absorption bands of OH stretching of alcohol functional group was clearly observed at 3431 cm^{-1} as no absorption band of OH stretching in the coconut fatty acid waste spectrum. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of coconut fatty acid waste and coconut fatty acid ethylene glycol ester were shown in Figures A12 and A13, respectively. Some signals of coconut fatty acid ethylene glycol ester were shown in Table 4.9.

Table 4.9 The assignments of ^{1}H-NMR spectra of coconut fatty acid waste and coconut fatty acid ethylene glycol ester.

| Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Coconut fatty acid waste	Coconut fatty acid ethylene glycol ester
a	*t*	0.83	0.78
b	*m*	1.58	1.53
c, d, e, f	*m*	1.22	1.17
g	*m*	2.27	2.25
j	*t*	-	4.10
k	*t*	-	3.71
l	*s*	-	2.87

From the ^{1}H-NMR spectrum of coconut fatty acid ethylene glycol ester (Figure A13) as comparing with coconut fatty acid waste (Figure A12), it could be observed that the signals at δ_H 3.71 and 4.10 ppm belonged to the protons of coconut fatty acid ethylene glycol ester at positions m and l and that at δ_H 2.87 ppm was belonged to the proton of hydroxyl group of ethylene glycol.

The ^{13}C-NMR spectra of coconut fatty acid waste and coconut fatty acid ethylene glycol ester were shown in Figures A14 and A15, respectively. Some signals of coconut fatty acid waste and coconut fatty acid ethylene glycol ester were shown in Table 4.10.

Table 4.10 The assignments of ^{13}C-NMR spectra of coconut fatty acid waste and coconut fatty acid ethylene glycol ester.

Position of Carbon	Chemical Shift (δ,ppm)	
	Coconut fatty acid waste	**Coconut fatty acid ethylene glycol ester**
a	14.04	14.00
b	22.66	22.60
c	24.83	24.81
d	29.25	28.86
e	29.60	29.54
f	31.90	31.83
g	34.08	34.07
i	180.24	174.20
j	-	65.70
k	-	60.71

From the ^{13}C-NMR spectrum of coconut fatty acid ethylene glycol ester (Figure A15) as comparing with coconut fatty acid waste (Figure A14), it could be seen that the signals at δ_c 60.71 and 65.70 ppm were belonged to the carbons of coconut fatty acid ethylene glycol ester at positions k and j. The signal of carbonyl group of coconut fatty acid waste at δ_c 180.24 was shifted to 174.20 ppm, due to the formation of coconut fatty acid ethylene glycol ester.

From the results of the spectral data, it could be concluded that the product was coconut fatty acid ethylene glycol ester and its structure was as follows:

$$CH_3-CH_2-CH_2-CH_2-(CH_2)_n-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

a b f d e d c g   h

i

Coconut fatty acid waste

$$CH_3-CH_2-CH_2-CH_2-(CH_2)_n-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-OH$$

a   b   f   d   e   d   c   g   j   k   l

i
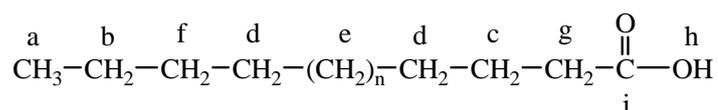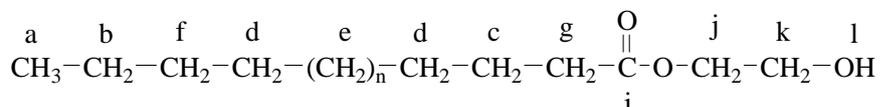
Coconut fatty acid ethylene glycol ester

4.2.4 Coconut Fatty Acid Ethylene Glycol Nitrate

The IR spectra of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate were shown in Figures A11 and A16, respectively. The important absorption bands of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate were listed in Table 4.11.

Table 4.11 The absorption assignments of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate.

Wave number (cm^{-1})		Assignments
Coconut fatty acid ethylene glycol ester	Coconut fatty acid ethylene glycol nitrate	
3431	-	O-H Stretching
2855	2851	C-H Stretching, Aliphatic
1742	1742	C=O Stretching
-	1637	NO_2 Asymmetric Stretching
1462	1454	C-H Bending, Aliphatic
-	1275	NO_2 Symmetric Stretching
1174	1162	C-O Stretching
-	851	N-O Stretching Vibration

From the IR spectrum of coconut fatty acid ethylene glycol nitrate (Figure A16) as comparing with coconut fatty acid ethylene glycol ester (Figure A11), it could be observed that there was no absorption band of OH stretching 3431 cm^{-1} but the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1637, 1275 and 851 cm^{-1}, respectively. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate were shown in Figures A13 and A17, respectively. Some signals of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate were shown in Table 4.12.

Table 4.12 The assignments of ^{1}H-NMR spectra of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Coconut fatty acid ethylene glycol ester	Coconut fatty acid ethylene glycol nitrate
j	*t*	4.10	4.61
k	*t*	3.71	4.30
l	*s*	2.87	-

From the ^{1}H-NMR spectrum of coconut fatty acid ethylene glycol nitrate (Figure A17) as comparing with coconut fatty acid ethylene glycol ester (Figure A13), it could be observed that the signal at δ_H 2.87 ppm belonged to the proton of hydroxyl group of coconut fatty acid ethylene glycol ester was absent, due to nitration reaction. The signals at δ_H 4.30 and 4.61 ppm were belonged the protons of coconut fatty acid

ethylene glycol nitrate at positions k and j which shifted from δ_H 3.71 to 4.10 ppm, due to the influence of nitrate group.

The ^{13}C-NMR spectra of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate were shown in Figures A15 and A18, respectively. The important signals of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate were shown in Table 4.13.

Table 4.13 The assignments of ^{13}C-NMR spectra of coconut fatty acid ethylene glycol ester and coconut fatty acid ethylene glycol nitrate.

Position of Carbon	Chemical Shift (δ,ppm)	
	Coconut fatty acid ethylene glycol ester	Coconut fatty acid ethylene glycol nitrate
j	65.70	59.88
k	60.71	70.55

* It was determined by DEPT spectra as shown in Figure A20

From the ^{13}C-NMR spectrum of coconut fatty acid ethylene glycol nitrate (Figure A18) as comparing with coconut fatty acid ethylene glycol ester (Figure A15), it could be seen that the signals at δ_c 70.55 and 59.88 ppm were belonged to the carbons of coconut fatty acid ethylene glycol nitrate at positions k and j which shifted from δ_c 60.71 to 65.70 ppm due to the influence of nitrate group.

From the results of the spectral data, it could be concluded that the product was coconut fatty acid ethylene glycol nitrate and its structure was as follows:

$$\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{f}{CH_2}-\underset{d}{CH_2}-\underset{e}{(CH_2)_n}-\underset{d}{CH_2}-\underset{c}{CH_2}-\underset{g}{CH_2}-\overset{\overset{O}{\underset{\|}{}}}{\underset{i}{C}}-O-\underset{j}{CH_2}-\underset{k}{CH_2}-ONO_2$$
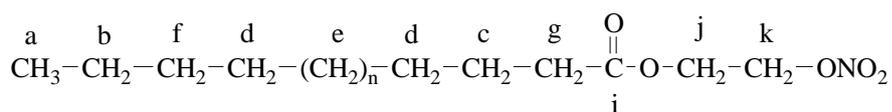
Coconut fatty acid ethylene glycol nitrate

4.3 Characteristics of 2-Ethylhexyl Nitrate

The IR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A21 and A22, respectively. The important absorption bands of 2-ethylhexyl nitrate were listed in Table 4.14.

Table 4.14 The absorption assignments of 2-ethylhexyl nitrate.

Wave number (cm^{-1})	Assignment
2868	C-H Stretching, Aliphatic
1634	NO$_2$ Asymmetric Stretching
1465, 1383	C-H Bending, Aliphatic
1275	NO$_2$ Symmetric Stretching
978	C-O Stretching
866	O-N Stretching Vibration

From the IR spectrum of 2-ethylhexyl nitrate (Figure A22) comparing with that of 2-ethyl-1-hexanol (Figure A21), it could be observed that there was no absorption band of OH stretching 3200-3500 cm^{-1} but the absorption bands of NO$_2$ (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1634, 1280 and 866 cm^{-1} respectively. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A23 and A24, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.15.

Table 4.15 The assignments of ^{1}H-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* (*J* = 6 Hz)	h	2

The ^{13}C-NMR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A25 and A26, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.16.

Table 4.16 The assignments of ^{13}C-NMR spectrum of 2-ethylhexyl nitrate.

Position of Carbon	Carbon Type	Chemical Shift of Nitrate(δ,ppm)	Chemical Shift of Alcohol(δ,ppm)
a	CH_3	11.14	11.20
b	CH_3	14.25	14.14
c	CH_2	23.43	23.42
d	CH_2	23.70	23.73
e	CH_2	28.34	29.58
f	CH_2	29.21	30.59
g	CH	42.21	42.31
h	CH_2	78.19	65.21

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

$$\overset{b}{C}H_3\overset{c}{C}H_2\overset{e}{C}H_2\overset{f}{C}H_2\overset{g}{C}H\overset{h}{C}H_2ONO_2$$

$$\underset{d \quad a}{CH_2CH_3}$$
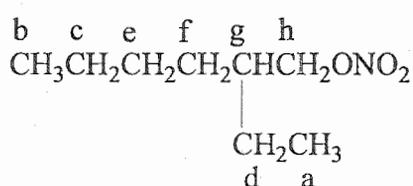
4.4 Determination of Cetane Number of Synthesized Nitrate Compounds in Base Diesel Fuel.

These compounds were brought to determine their cetane number and physical properties as shown in Tables 4.17 and 4.18

Table 4.17 Cetane number of the blend of synthesized nitrate compounds with based diesel fuel.

Concentration (%weight)	Cetane Number					
	Base	EHN	SW	SGN	CW	CGN
0.05	52.7	54.2	52.6	53.1	52.5	52.9
0.10	52.7	56.0	52.6	53.3	52.5	53.1
0.15	52.7	57.0	-	-	-	-
0.20	52.7	58.3	-	-	-	-
0.25	52.7	-	52.3	54.3	52.3	53.7
0.50	52.7	-	52.0	55.9	51.8	54.5
0.75	52.7	-	51.7	57.3	51.5	55.5
1.00	52.7	-	51.4	58.5	51.1	56.2

Note: Base = Base Diesel Fuel

SW = Soybean Acid Waste

SGN = Soybean Fatty Acid Ethylene Glycol Nitrate

CW = Coconut Waste Acid

CGN = Coconut Fatty Acid Ethylene Glycol Nitrate

EHN = 2-Ethylhexyl Nitrate

Table 4.18 Physical properties of base diesel fuel.

Properties	Base	Base + 1.00% SGN	Base + 1.00% CGN
Mid-Boiling Point ($^{\circ}$F)	554.78 °F	556.18	556.52
API Gravity@ 60 $^{\circ}$F	38.90	38.58	38.60
Pour Point	1 °C	2 °C	2 °C
Flash Point	63	64	64
Viscosity	3.31	3.43	3.41
Cetane Index	58.24	57.78	57.84
Cetane Number	52.7	55.9	54.5

Table 4.17 showed the cetane number of the blend of synthesized nitrate compounds with base diesel fuel at the concentration of 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00% by weight, respectively. It could be seen that cetane number was increased when the nitrate compounds was added. An increased cetane number was proportioned with an amount of nitrate compounds, but it would be decreased with fatty acid wastes, as shown in Figure 4.1. In addition, even though these compounds could not increase a cetane number as much as 2-ethylhexylnitrate (EHN), but the value of acid wastes could be considerably high. These nitrate compounds did not change their physical properties within the specification of diesel fuel (Table 4.18).

From slope of Figure 4.2 shown that the soybean fatty acid ethylene glycol nitrate gave cetane number more than coconut fatty acid ethylene glycol nitrate because purification of soybean fatty acid ethylene glycol nitrate removed wax to increase cetane number.
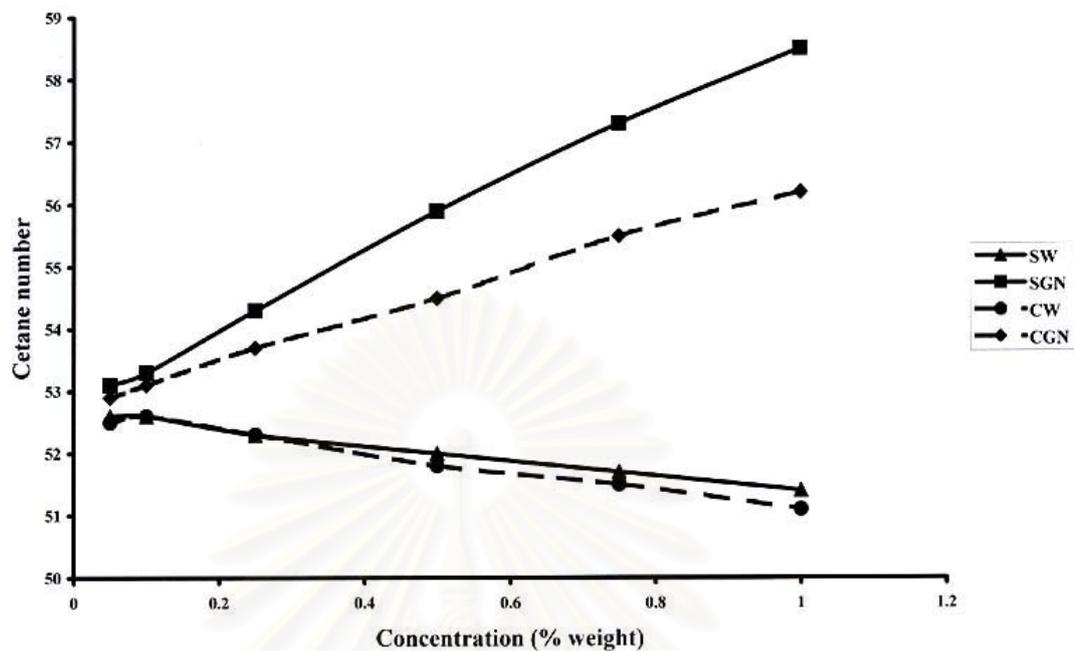
Figure 4.1 Cetane number of fatty acid wastes comparing with nitrate compounds.
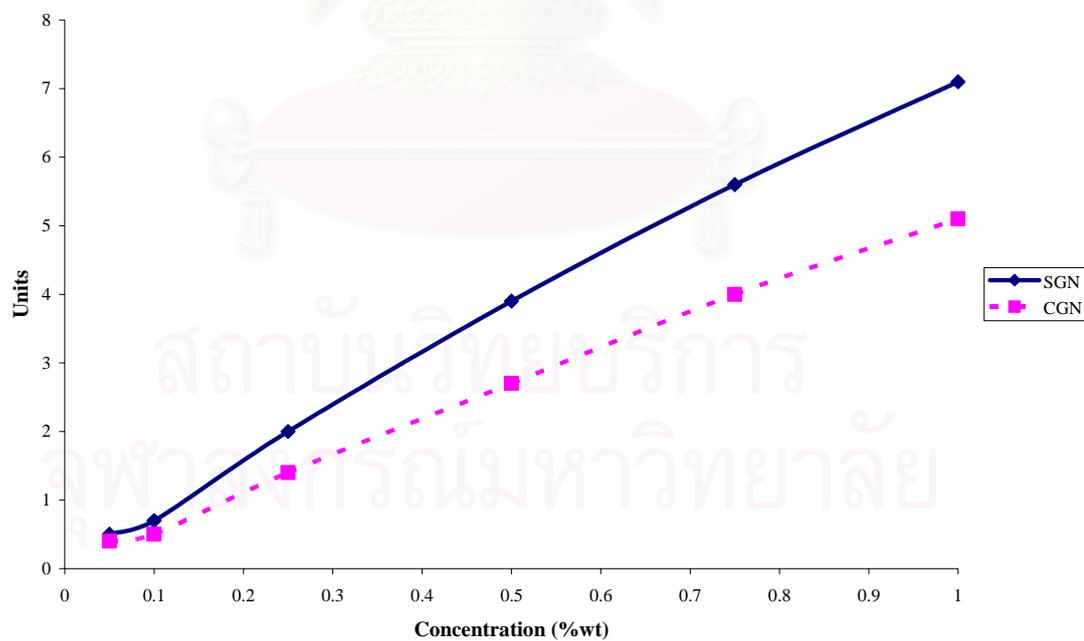
Figure 4.2 Increasing units of the synthesize glycol nitrate compounds at similar concentration.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

Nitrate compounds could be prepared from esterification of acid wastes with ethylene glycol using concentrated sulfuric acid as a catalyst, followed by the nitration reaction.

In this study, all of nitrate compounds were obtained in high yield. The cetane number was improved by these nitrate compounds. These nitrate compounds were easily soluble in base diesel fuel which did not change their physical properties within the specification of diesel fuel at the concentration of 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00% by weight. The cetane number of the blended base diesel fuel was increased approximately for 0.5, 0.7, 2.0, 3.9, 5.6 and 7.1 units for soybean fatty acid ethylene glycol nitrate and 0.4, 0.5, 1.4, 2.7, 4.0 and 5.1 units for coconut fatty acid ethylene glycol nitrate at concentrations of 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00% by weight, respectively. Although these nitrate compounds gave lower cetane numbers as comparing with 2-ethylhexyl nitrate, the commercial cetane improver, but the value of acid wastes could be considerably high. So, these nitrate compounds had potential to be used for improving cetane number in base diesel fuel.

5.2 Suggestions for the future work

1) Cetane improvers generally contain nitrogen and some concerning with the formation of addition NO_X has been raised, therefore, future shouldstudies focus on low-nitrogen cetane improvers and nitrogen free cetane improvers.

2) From this study, synthesized nitrate compounds were obtained from ethylene glycol could improve cetane number, therefore future studies used other diol alcohol such as 1,4-butanediol, 1,6-hexadiol, 1,8-octadiol, 1,10-decadiol.

REFERENCES

1. การปิโตรเลียมแห่งประเทศไทย. ส่วนควบคุมคุณภาพและส่วนบริการเทคนิคตลาดพาณิชย์ *ความรู้เกี่ยวกับปิโตรเลียม ฉบับปี 2000.* พิมพ์ครั้งที่ 1. กุมภาพันธ์ 2543.

2. Nikanjam, M. "Low Emissions Diesel Fuel", *US. Patent No. 5,389,111*, Feb. 14, (**1995**).

3. Hobson, G.D. "Modern Petroleum Technology Part 2". 5th ed. New York: John Wiley & Sons, (**1984**), pp.823-828.

4. ศูนย์วิจัยและพัฒนา การปิโตรเลียมแห่งประเทศไทย. *หนังสือชุดปิโตรเลียมน่ารู้* พิมพ์ครั้งที่ 1, 2539, หน้า 2, 13, 15.

5. Poirer, M.A., Steere, D.V., and Krogh, J.A. "Cetane Improver Compositions Comprising Nitrated Fatty Acid Derivatives" *US Patent 5,454,842*, (**1995**).

6. Purcell, R.F., and Hallock, L.L. "Cetane Improver for Diesel Fuel" *US Patent 4,549,883*, (**1985**).

7. Suppes, G.J., Zhi Chen, Ying Rui, Mason, M., Heppert, J.A., "Synthesis and Cetane Improver Performance of Fatty Acid Glycol Nitrates" *Fuel* (**1999**), Vol.78, pp. 73-81.

8. Drown, D.C., Harper, K., Frame, E., "Screening Vegetable Oil Alcohol Esters as Fuel Lubricity Enhancers" *J. Am. Oil. Chem. Soc.* (**2001**), 78, no.6

9. Russel, T.J. "Additives Influencing Diesel Fuel Combustion" *Gasoline and Diesel Fuel Additives*. New York: John Wiley & Sons, (**1989**), pp. 65-88.

10. The American Society of Mechanical Engineers. "Diesel Fuel Oils Production, Characteristics, and Combustion" New York: (**1947**), pp. 59, 78-79, 88-89.

11. Virgil, B.G. *Petroleum Products Handbook* 1st ed. New York: McGraw-Hill, (**1960**), pp. 6-2 - 6-11.

12. Patberg, J.B. "Petroleum & Chemical Processes" *Exxon Research and Engineering Company*, (**1976**).

13. Popovich, M. "Fuels and Lubricants. London": John Wiley & Sons, (**1959**), pp. 134-145.

14. Schobert, H.H. "The Chemistry of Hydrocarbon Fuels" 2nd ed. London: Buterwork-Heinemann, (**1991**), pp. 197-202.

15. Allinson, J.P. "Criteria for Quality of Petroleum Products" 1st ed. Great Britain: Applied Science Publishers, (**1975**), pp. 121-141.

16. Collins, J.M., and Unzelman, G.H. "Better Cetane Prediction Equations Developed" *Oil & Gas Journal*. June 7, (**1982**), pp. 148-160.

17. Filbey, A.H. "Diesel Fuel Composition" *US. Patent No. 4,406,665*, Sep. 27, (1**983**).

18. Clothier, P., Aguda, B., Moise, A., and Pritchard, H. "How do Diesel Fuel Ignition Improvers Works" *Chemical Society Reviews*, 1993, pp. 101-108.

19. Society of Automative Engineers (SAE), *SAE Fuels and Lubricants Standards Manual*. (**1995**), pp. 49-63.

20. Suppes, G. J.; Goff, M.; Burkhart, M. L.; Bockwinkel, K.; Botts, J. B.; Mason, M. H.; Heppert, J. A. "Multifunctional Diesel Fuel Additives From Triglycerides" *Energy Fuels*. (**2001**), 15 (1), 151.

21. Liotta, Jr., Soaranko, J.A. "Diesel Fuel Composition" *US. Patent No. 5,258,049*, Nov. 2, (**1993**).

22. Siraprapakit, S. "Synthesis of Dinitrate Compounds from Alkane Diols as Cetane Improver" Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, (**2000**).

23. Suttipitakwong, C. "Synthesis of Dinitrate Compounds from Alkylene Glycols as Cetane Improver" Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, (**2000**).

24. Vasaruchtragul, J. "Synthesis of Dinitrate Compounds as Cetane Number Improver" Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, (**1997**).

25. Khankasikham, T. "Synthesis of Cycloalkyl Nitrate Compounds from Cycloaliphatic Monoalcohol as Cetane Improvers" Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, (**2001**).
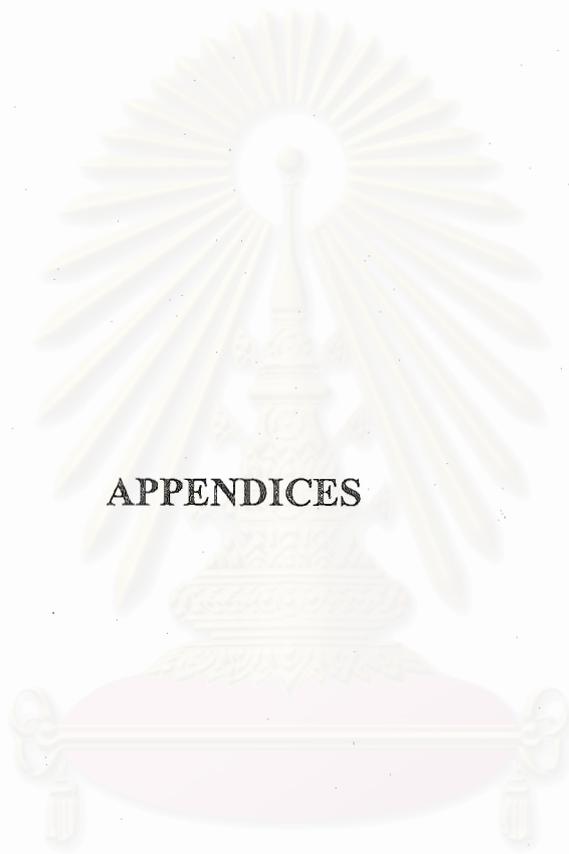
APPENDICES

APPENDIX A

SPECTRA OF SYNTHESIZED NITRATE COMPOUNDS
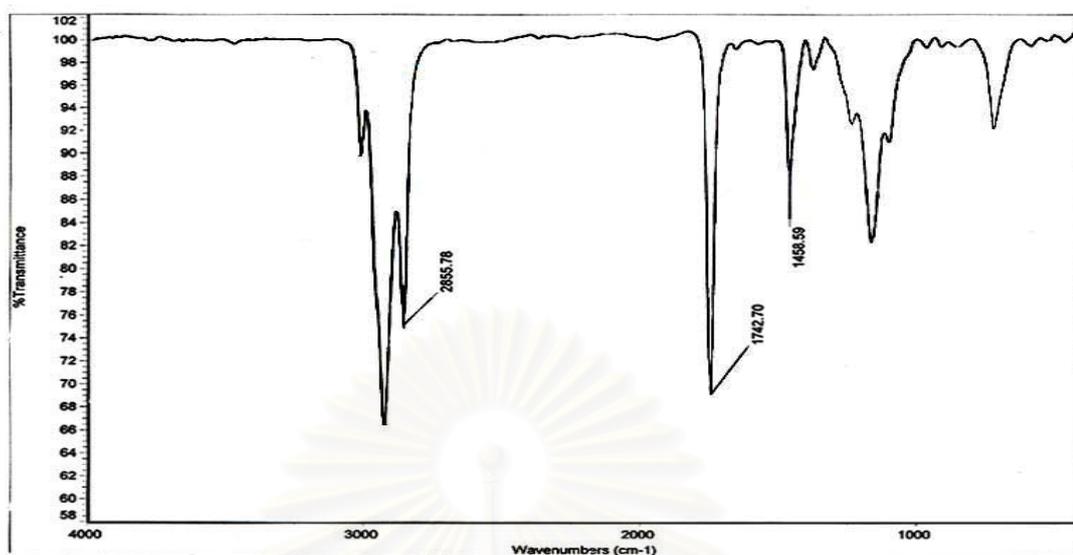
Figure A1 FTIR Spectrum of Soybean Fatty Acid Waste (NaCl)
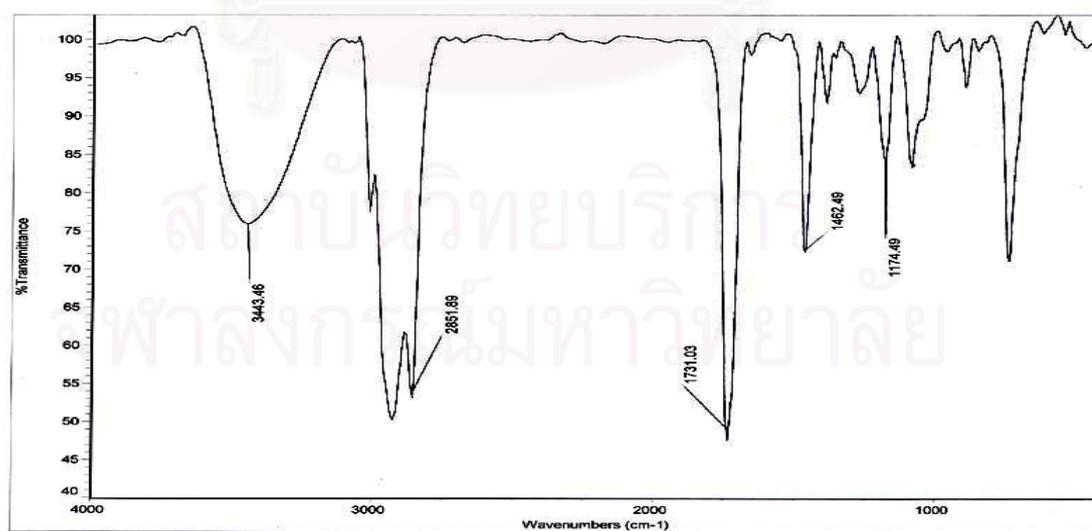
Figure A2 FTIR Spectrum of Soybean Fatty Acid Ethylene Glycol Ester (NaCl)
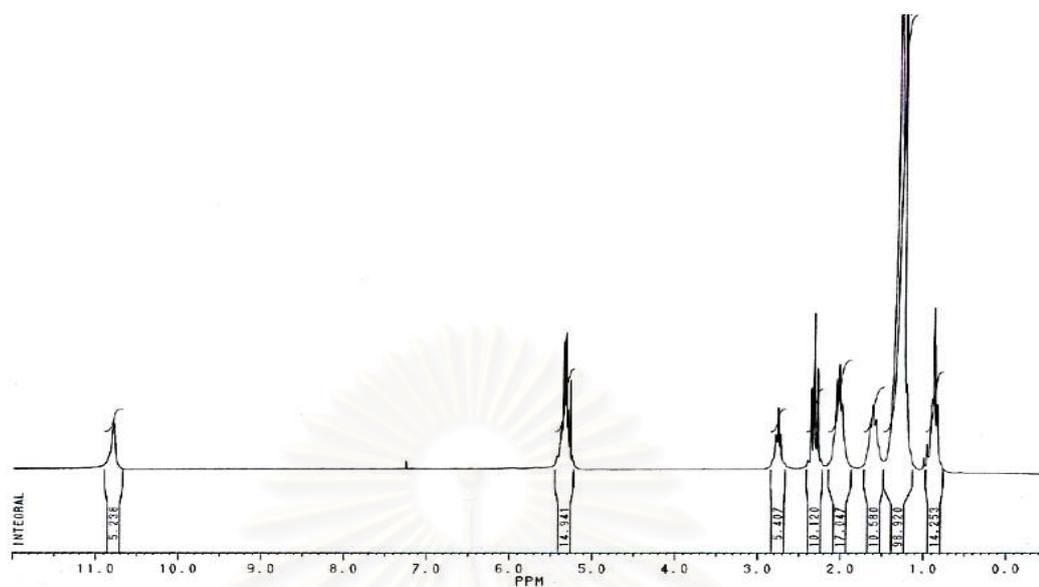
Figure A3 ^{1}H-NMR Spectrum of Soybean Fatty Acid Waste (CDCl$_3$)
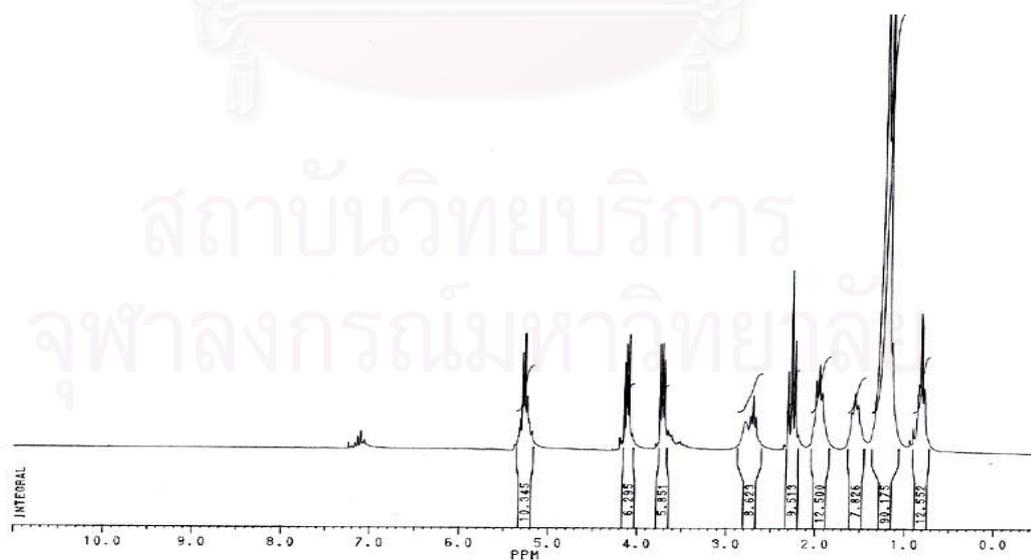
Figure A4 ^{1}H-NMR Spectrum of Soybean Fatty Acid Ethylene Glycol Ester (CDCl$_3$)
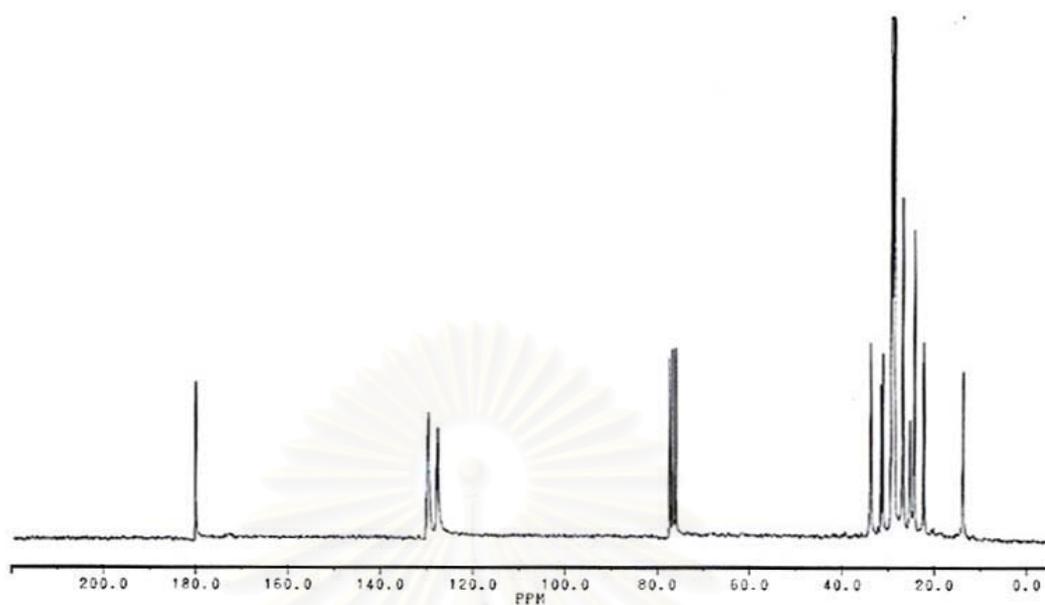
Figure A5 ^{13}C-NMR Spectrum of Soybean Fatty Acid Waste (CDCl$_3$)
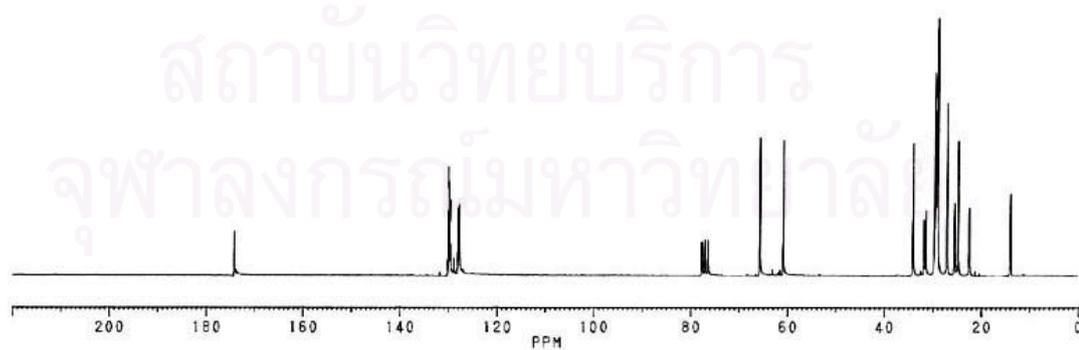
Figure A6 ^{13}C-NMR Spectrum of Soybean Fatty Acid Ethylene Glycol Ester (CDCl$_3$)
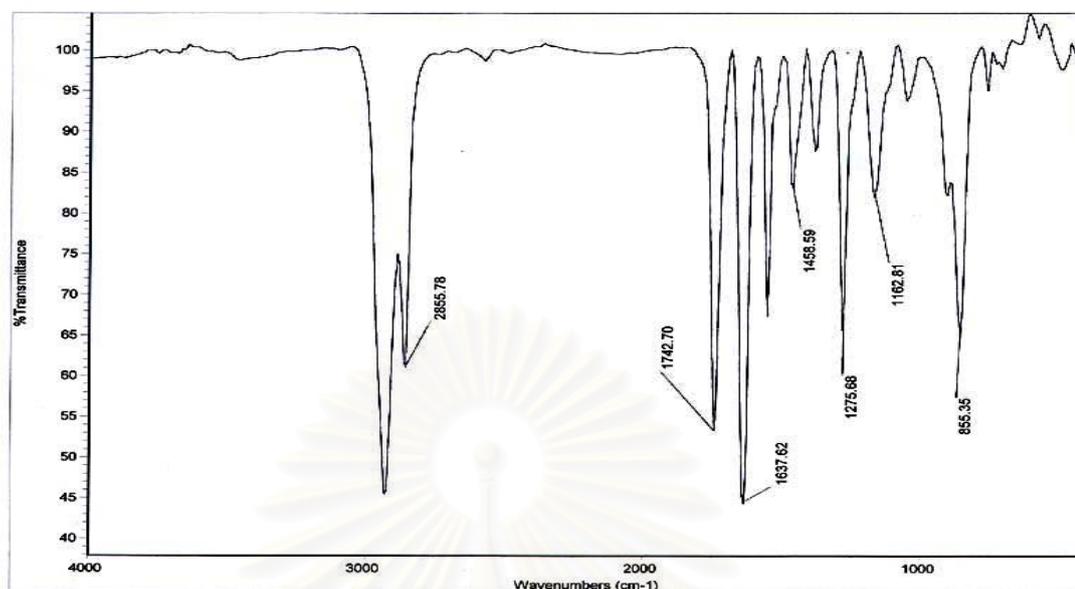
Figure A7 FTIR Spectrum of Soybean Fatty Acid Ethylene Glycol Nitrate (NaCl)
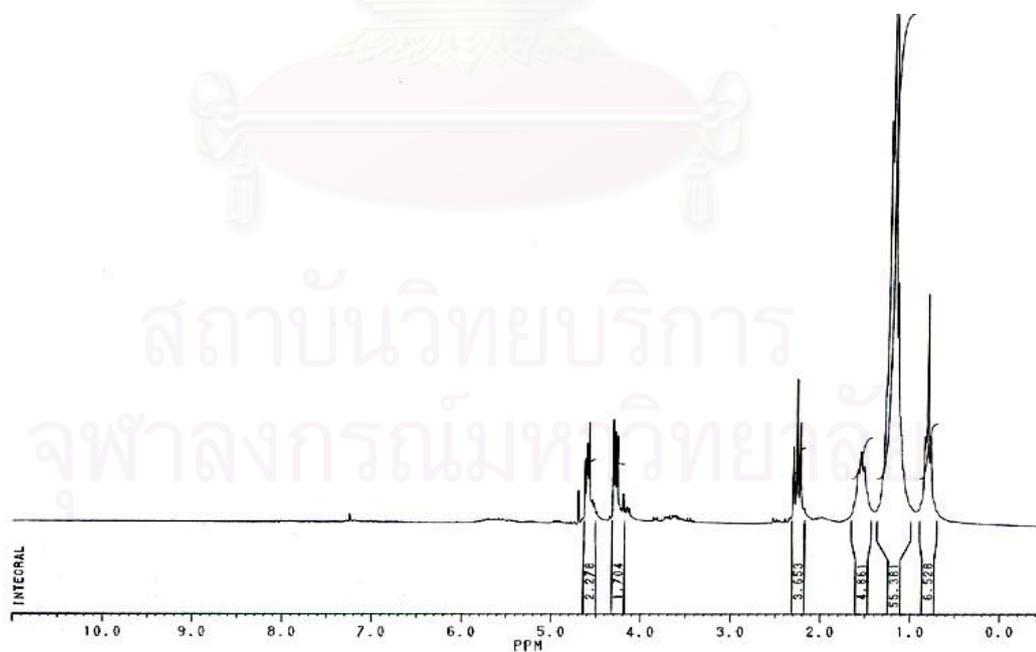
**Figure A8** ^{1}H-NMR Spectrum of Soybean Fatty Acid Ethylene Glycol Nitrate (CDCl$_3$)
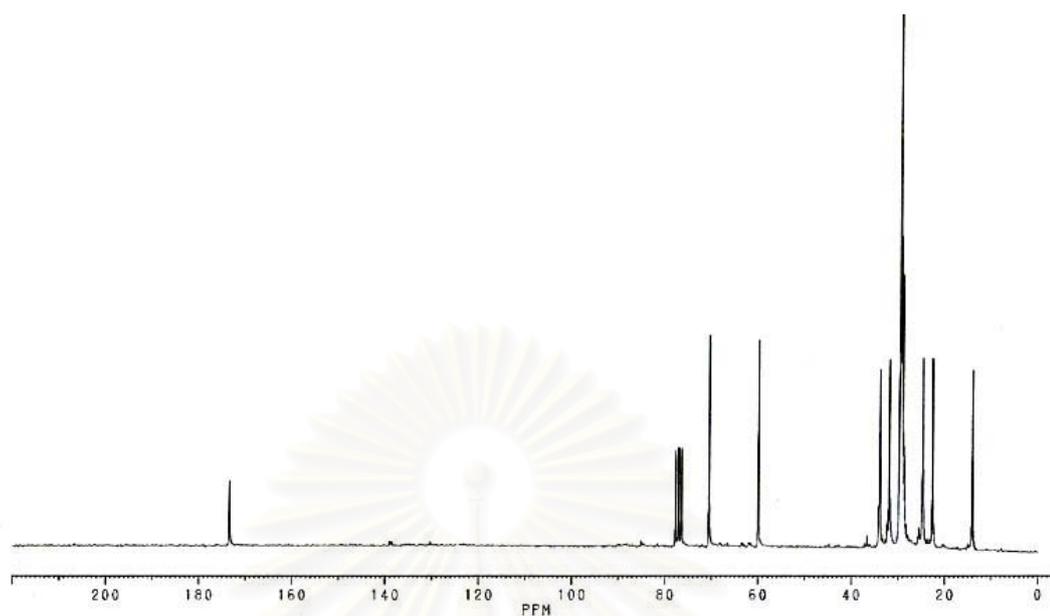
**Figure A9** ^{13}C-NMR Spectrum of Soybean Fatty Acid Ethylene Glycol Nitrate
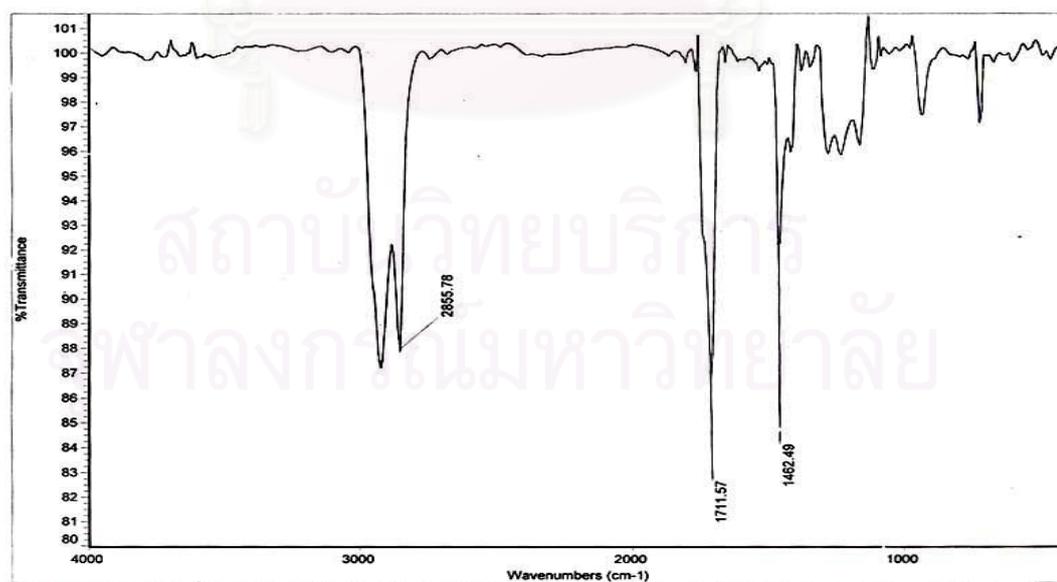
(CDCl$_3$)

Figure A10 FTIR Spectrum of Coconut Fatty Acid Waste (NaCl)
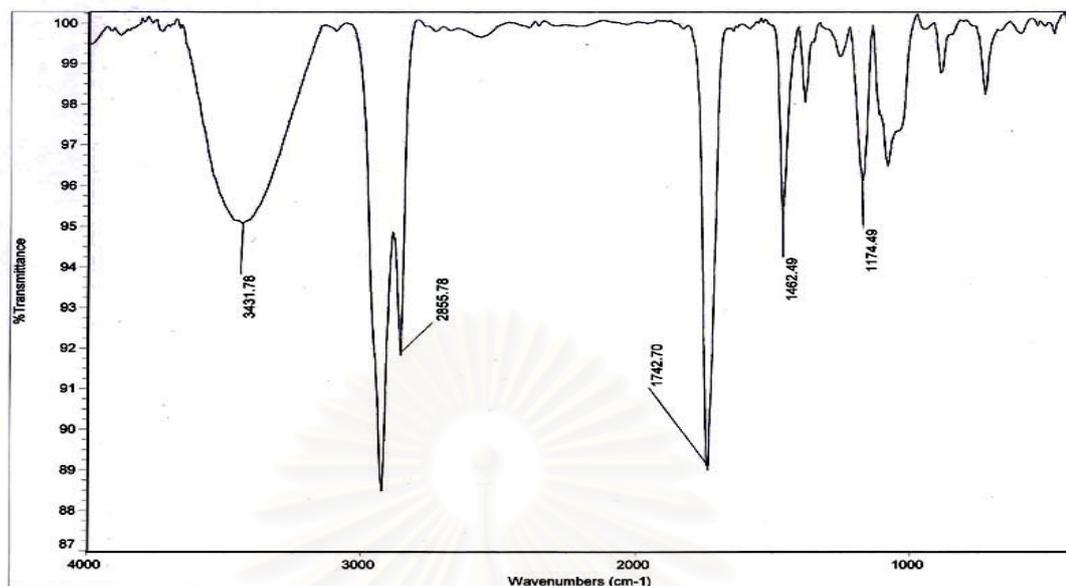
Figure A11 FTIR Spectrum of Coconut Fatty Acid Ethylene Glycol Ester (NaCl)
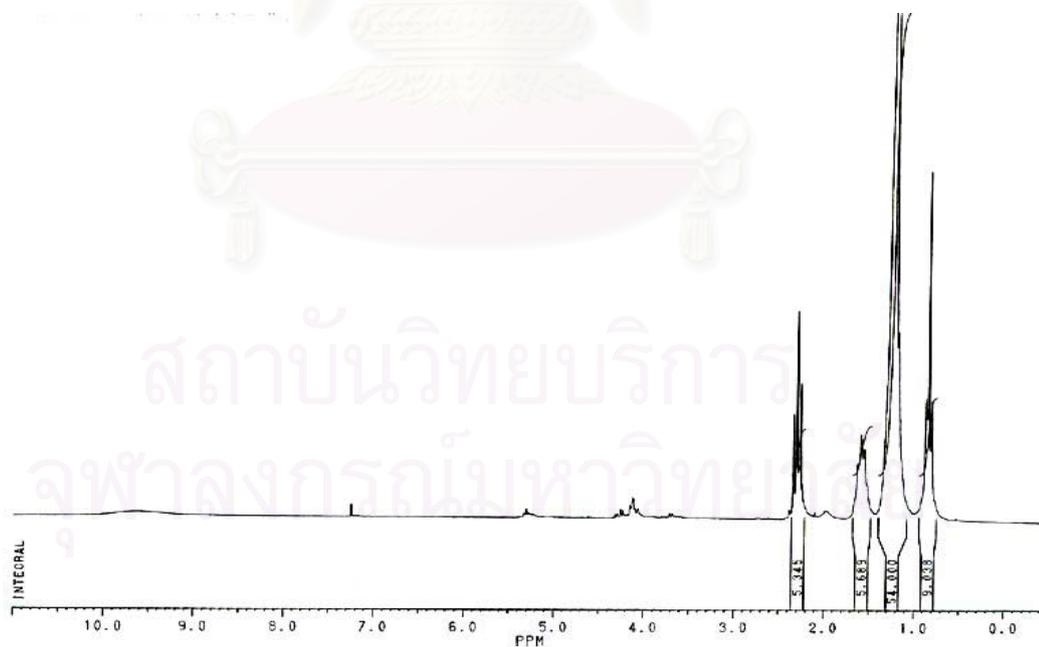
Figure A12 ^{1}H-NMR Spectrum of Coconut Fatty Acid Waste (CDCl$_3$)
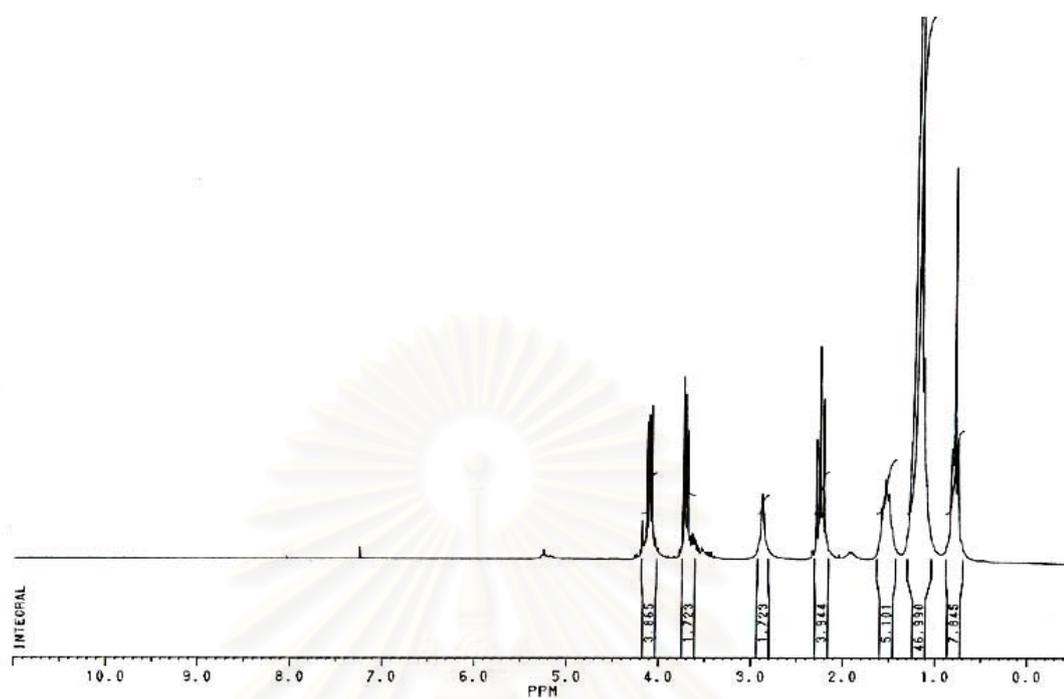
Figure A13 ^{1}H-NMR Spectrum of Coconut Fatty Acid Ethylene Glycol Ester (CDCl$_3$)
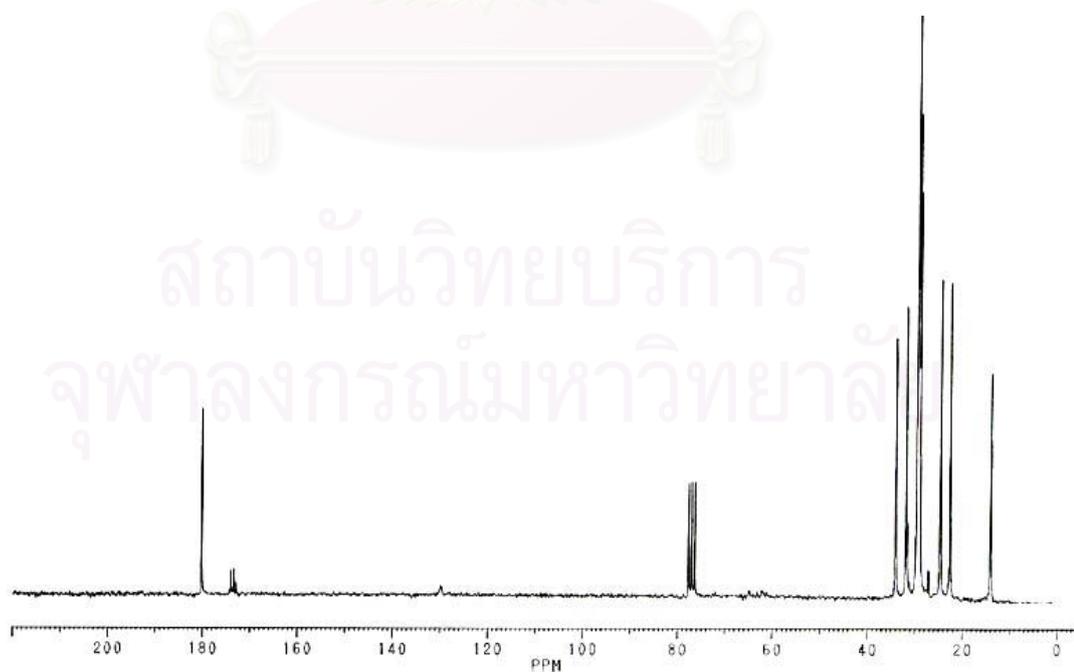
Figure A14 ^{13}C-NMR Spectrum of Coconut Fatty Acid Waste (CDCl$_3$)
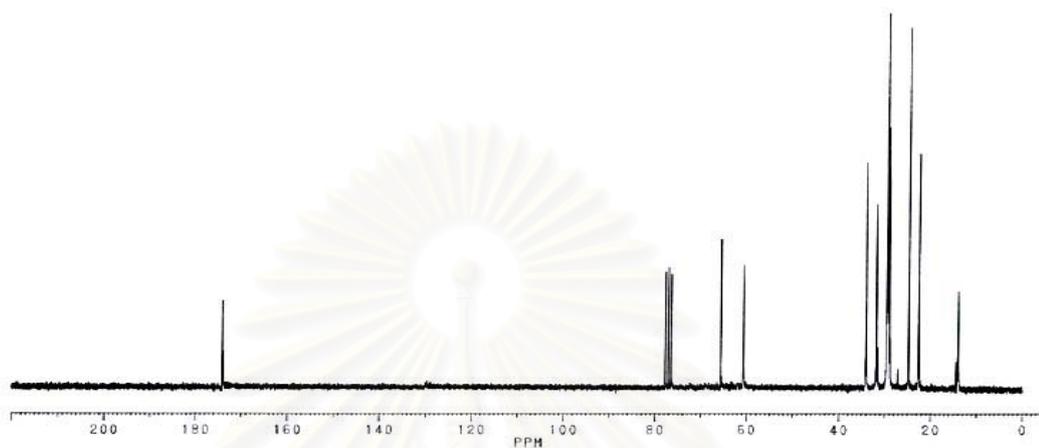
Figure A15 ^{13}C-NMR Spectrum of Coconut Fatty Acid Ethylene Glycol Ester
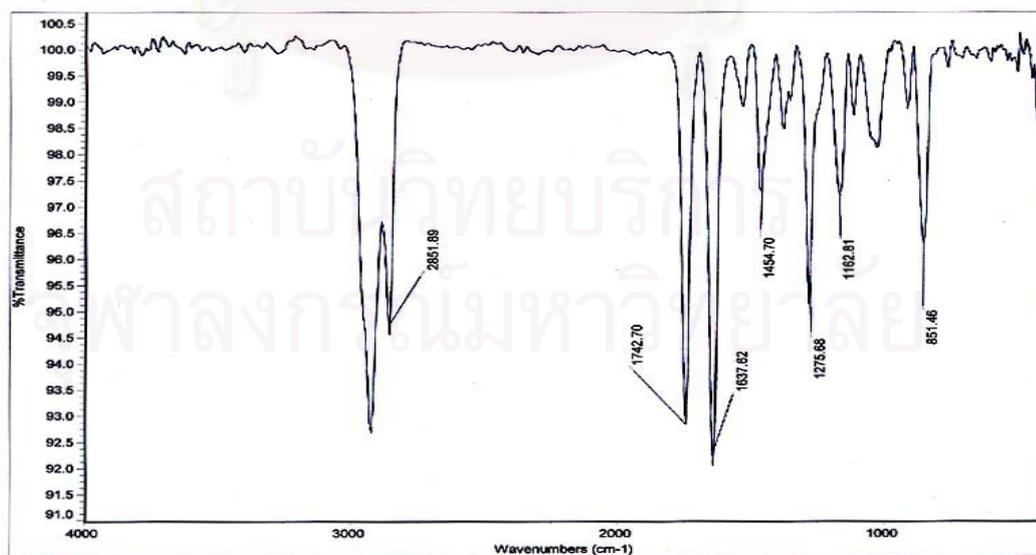
(CDCl$_3$)

Figure A16 FTIR Spectrum of Coconut Glycol Fatty Acid Ethylene Glycol Nitrate

(NaCl)
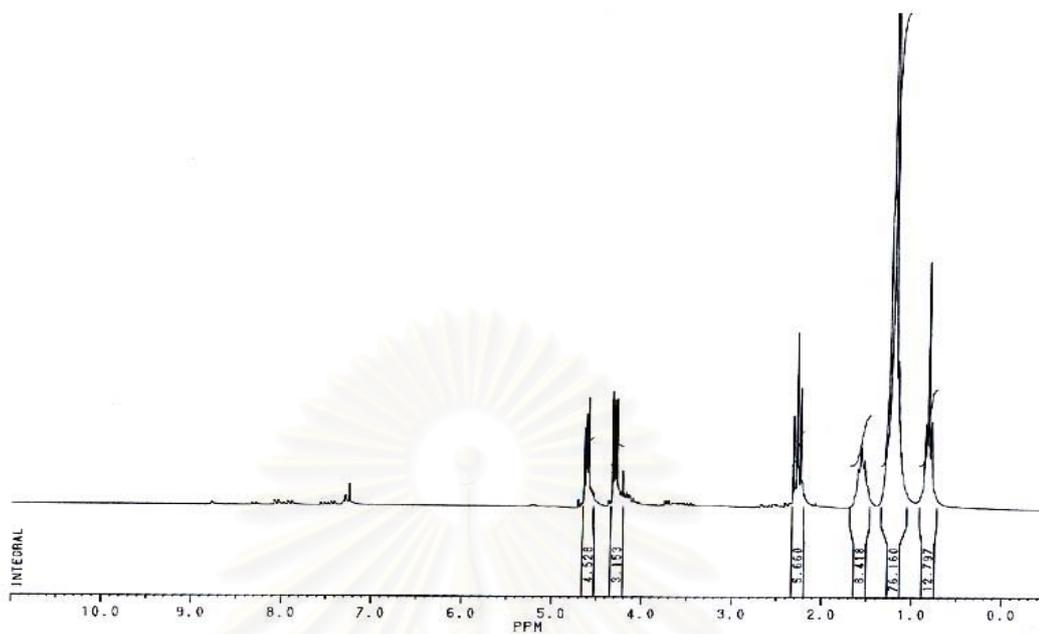
Figure A17 ^{1}H-NMR Spectrum of Coconut Fatty Acid Ethylene Glycol Nitrate (CDCl₃)
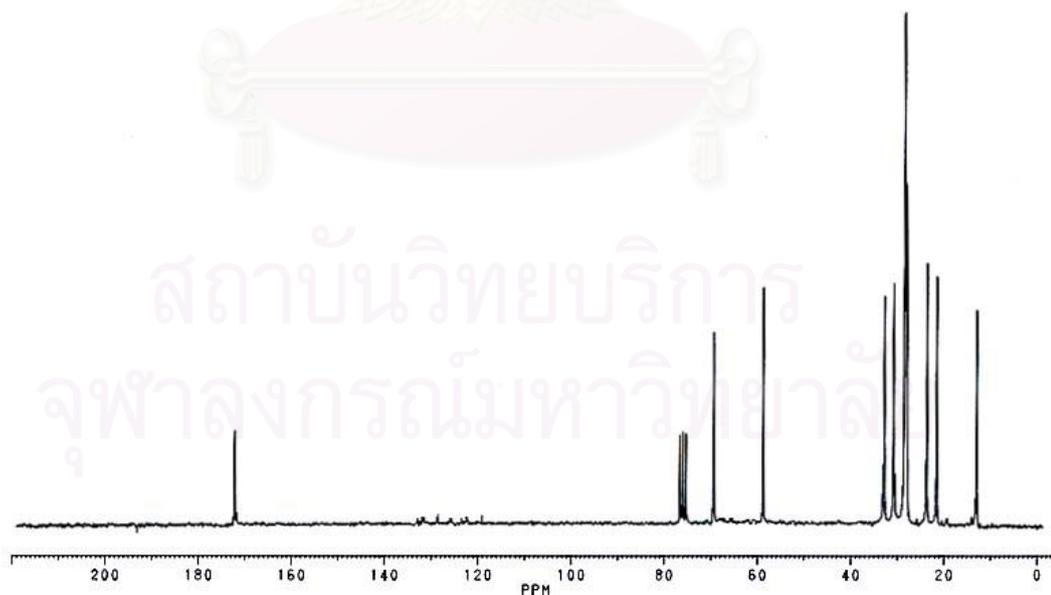
Figure A18 ^{13}C-NMR Spectrum of Coconut Fatty Acid Ethylene Glycol Nitrate (CDCl₃)
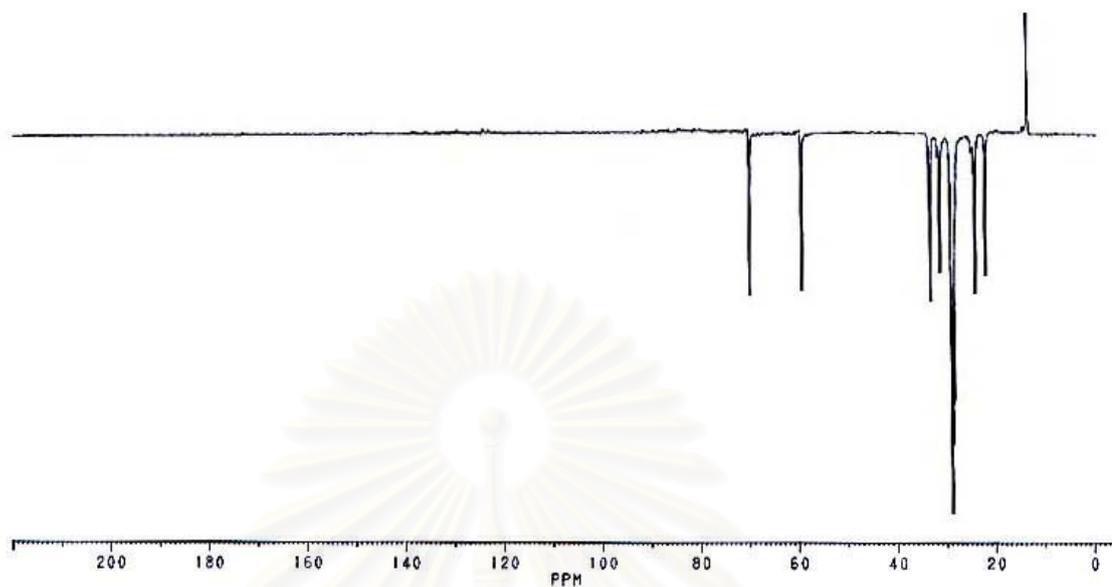
**Figure A19** DEPT 135 Spectrum of Soybean Fatty Acid Ethylene Glycol Nitrate
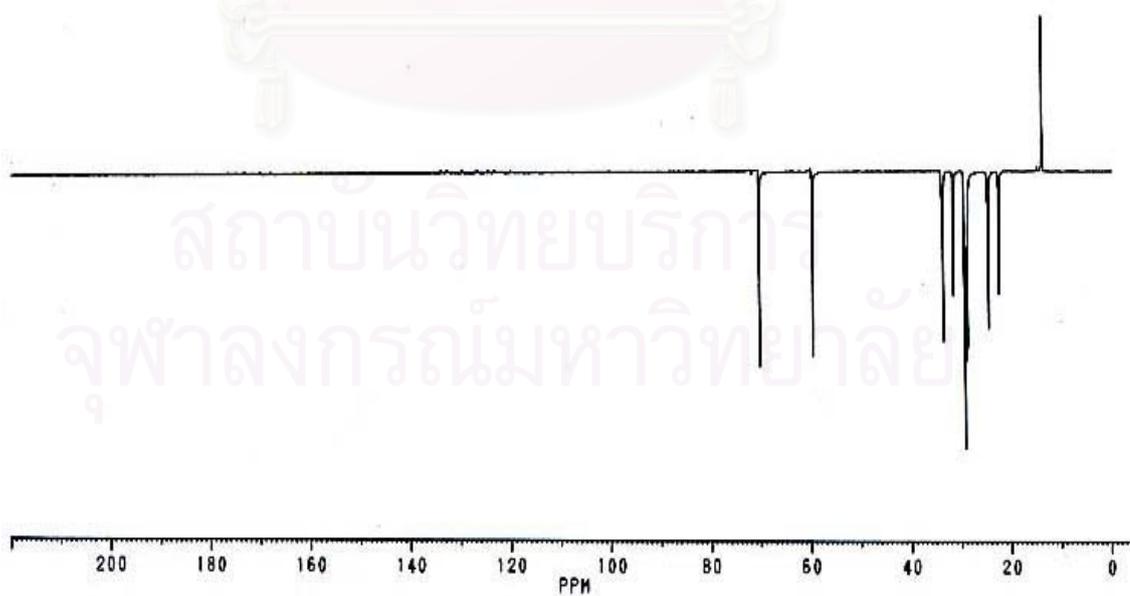
(CDCl$_3$)

Figure A20 DEPT 135 Spectrum of Coconut Fatty Acid Ethylene Glycol Nitrate
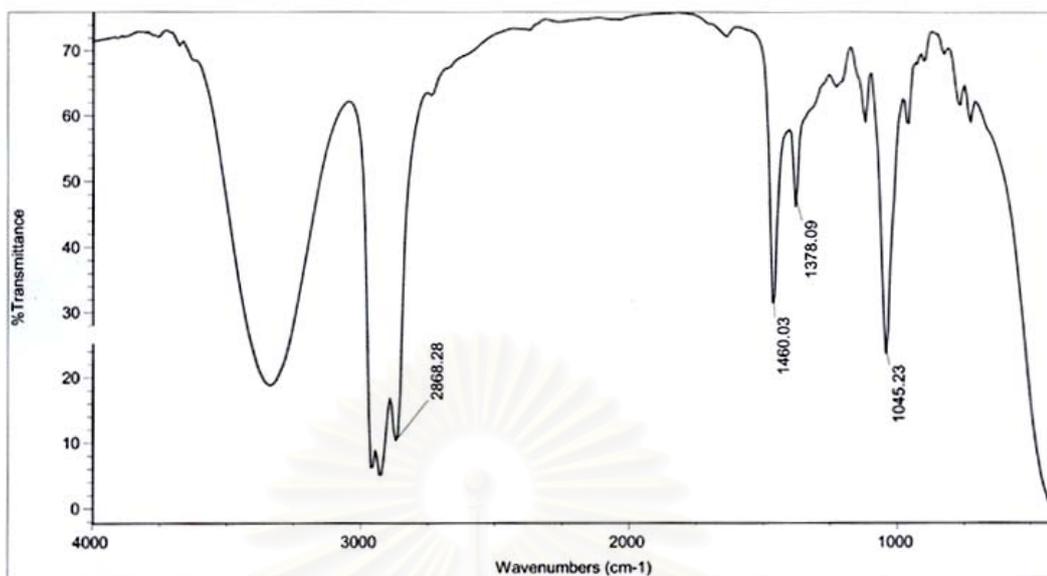
(CDCl$_3$)

Figure A21 FTIR Spectrum of 2-Ethyl-1-hexanol (NaCl)
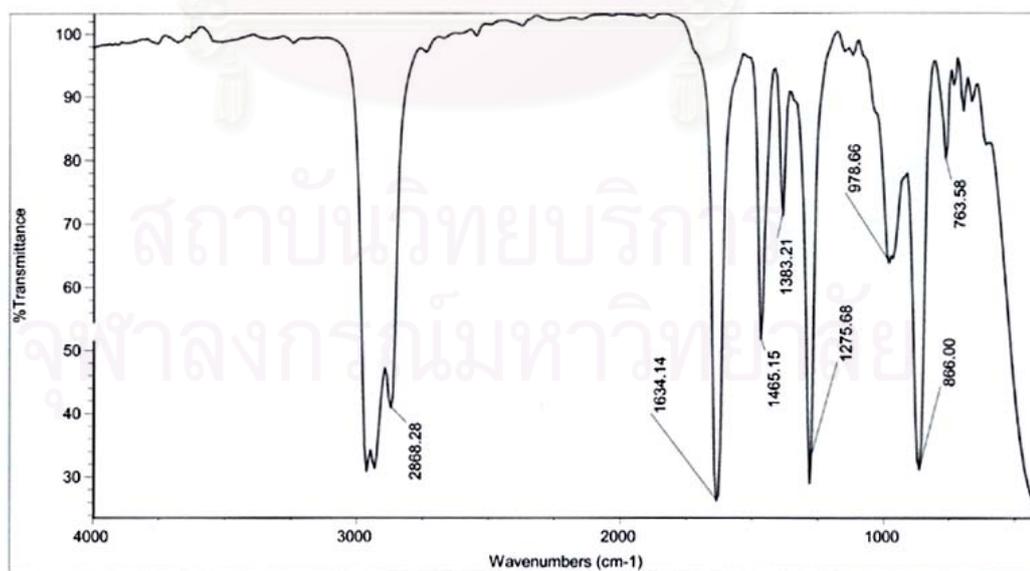
**Figure A22** FTIR Spectrum of 2-Ethylhexyl Nitrate (NaCl)
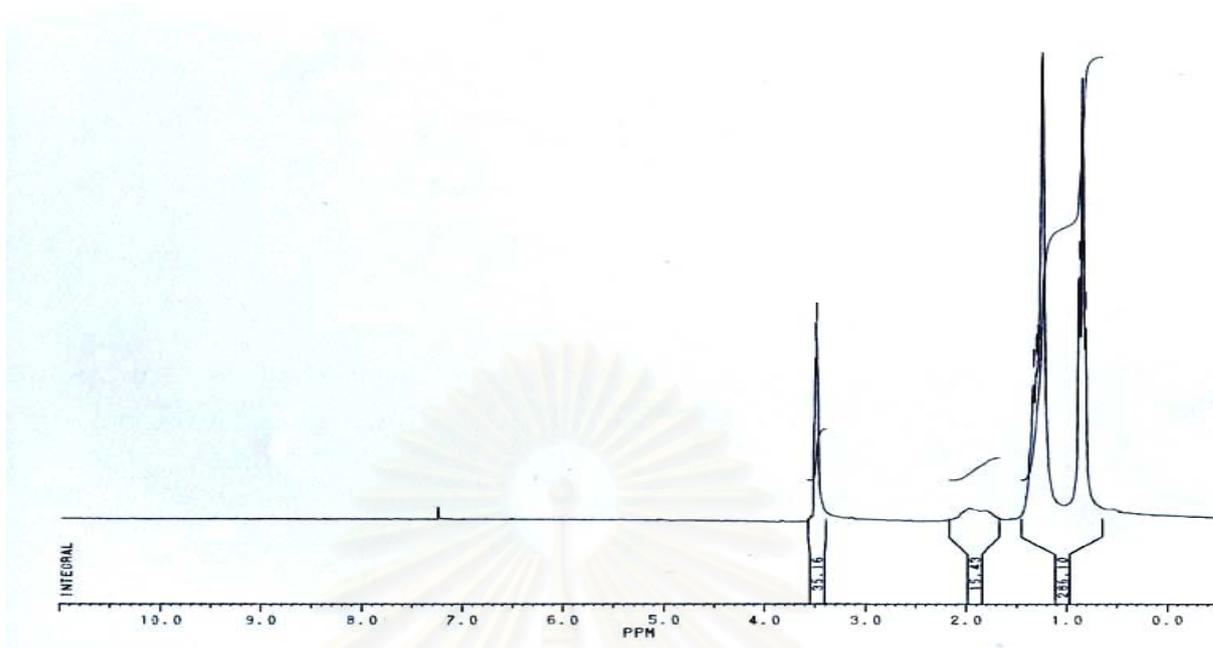
Figure A23 ^{1}H-NMR Spectrum of 2-Ethyl-1-hexanol (CDCl₃)
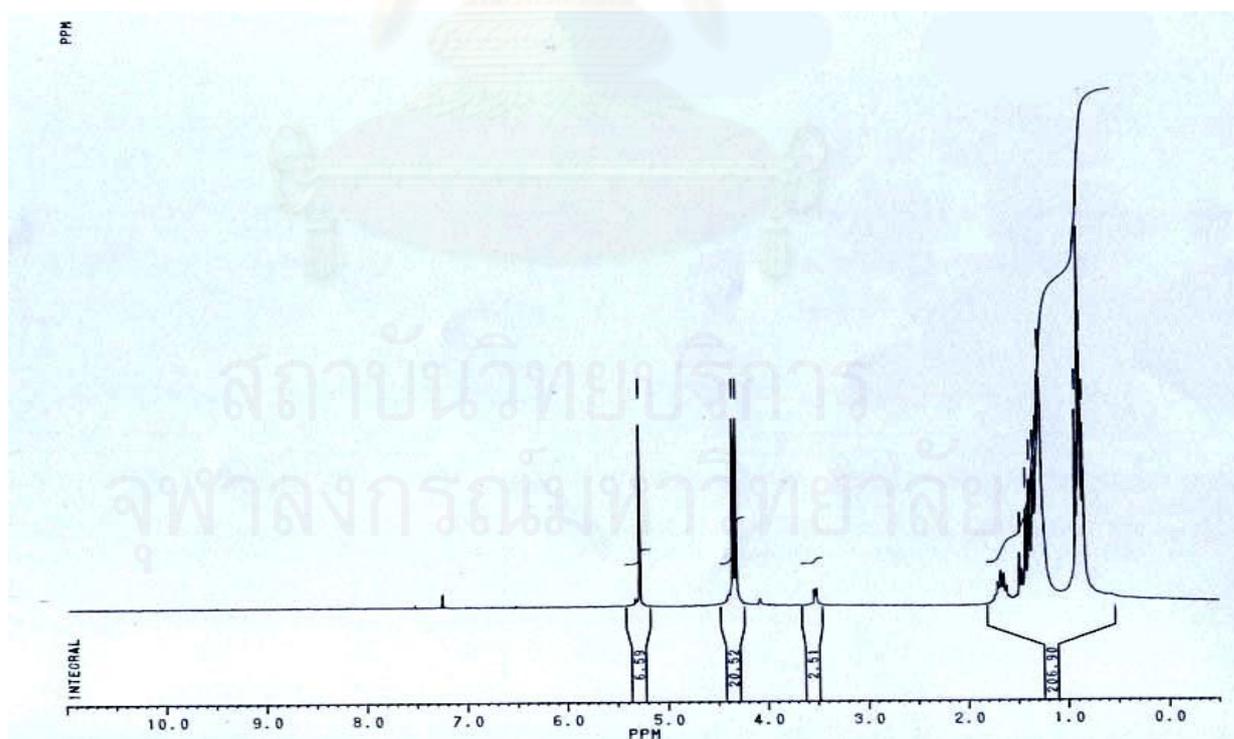
**Figure A24** ^{1}H-NMR Spectrum of 2-Ethylhexyl Nitrate (CDCl₃)
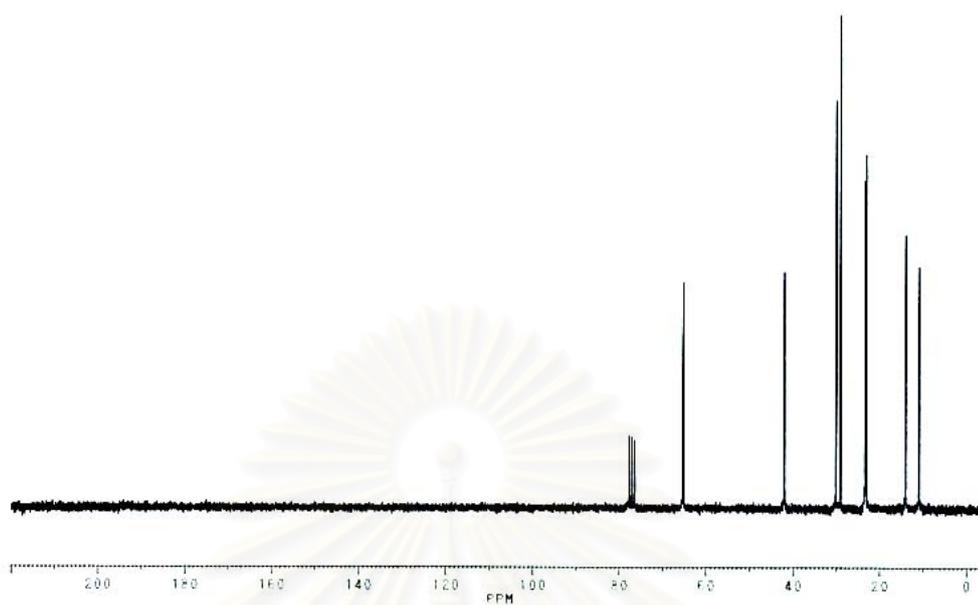
Figure A25 ^{13}C-NMR Spectrum of 2-Ethyl-1-hexanol (CDCl$_3$)
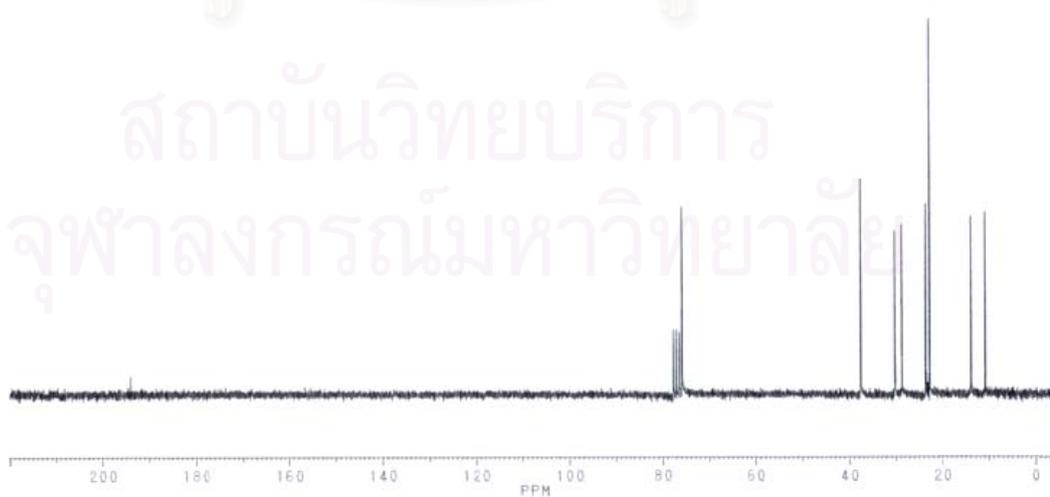
**Figure A26** ^{13}C-NMR Spectrum of 2-Ethylhexyl Nitrate (CDCl$_3$)
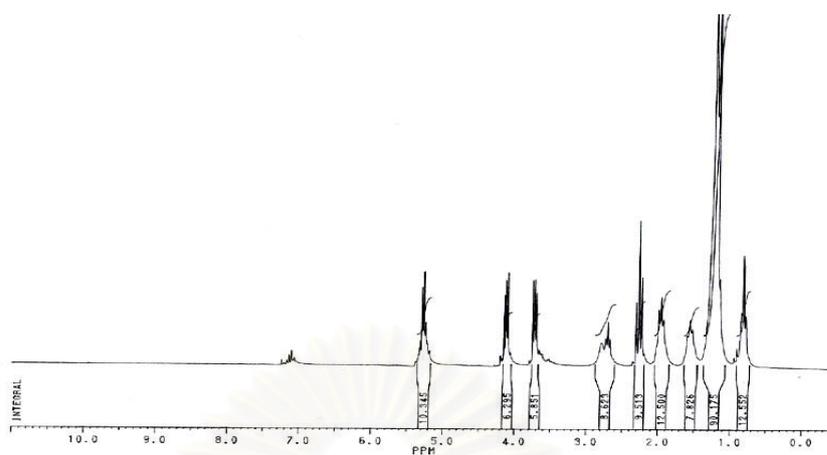
Figure A27 ^{1}H-NMR Spectrum of Fatty Acid Ethylene Glycol Ester (CDCl$_3$)
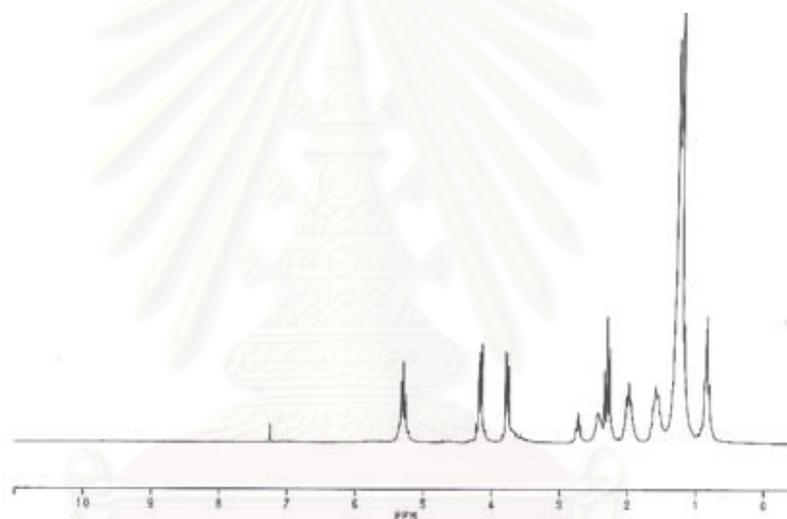
Figure A28 ^{1}H-NMR Spectrum of no reaction (CDCl$_3$)
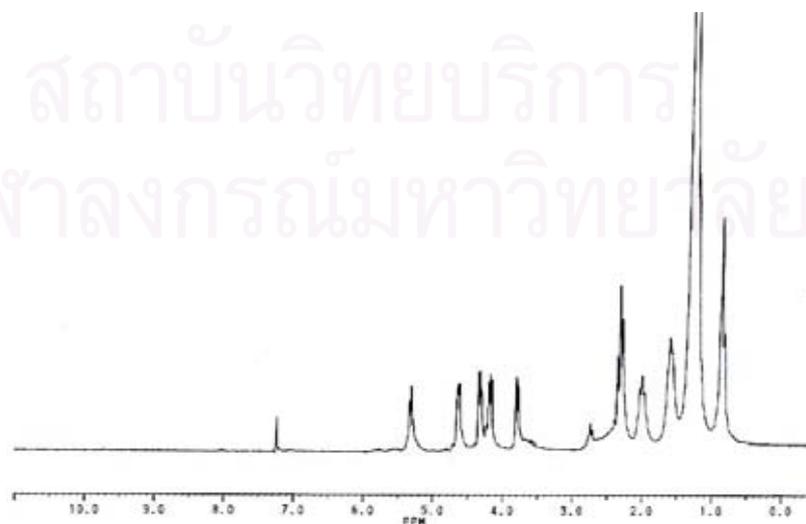
Figure A29 ^{1}H-NMR Spectrum of non complete reaction (CDCl$_3$)

APPENDIX B

SPECIFICATION AND TEST METHOD FOR DIESEL

FUEL IN THAILAND

Characteristics	Specification		Methods
	High-Speed Engine	Low-Speed Engine	
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 (temperature of 90% distillation)	max 357	-	ASTM D 86
Color	max 4.0	-	ASTM D 1500
Detergent Additive	Test by the Standard CUMMINS Tandem L-10 (Superior Level)	-	-

VITA

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