

การสังเคราะห์สารประกอบไนเตรตจากน้ำมันมะพร้าว
เพื่อเป็นสารเพิ่มค่าซีเทน



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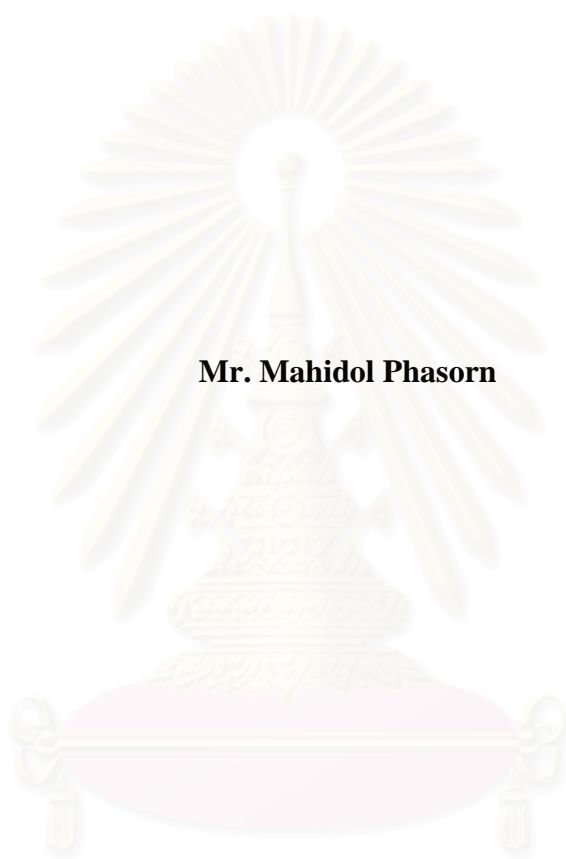
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SYNTHESIS OF NITRATE COMPOUNDS FROM COCONUT OIL

AS CETANE IMPROVERS



Mr. Mahidol Phasorn

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for the Degree of Master of Science in Petrochemistry and Polymer Science**

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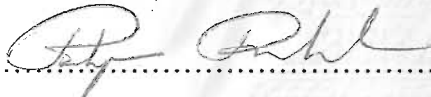
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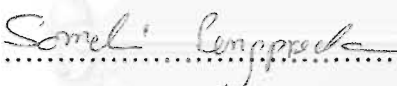
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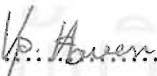
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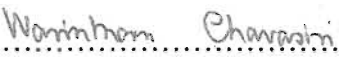
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สารประกอบไนเตรตจากน้ำมันมะพร้าวสามารถสังเคราะห์ได้โดยวิธีไนเตรชันของสารประกอบโมโนกลีเซอไรด์และไดกลีเซอไรด์ของน้ำมันมะพร้าวด้วยกรดไนตริกเข้มข้นและซัลฟูริกเข้มข้น โดยมีไดคลอโรมีเทนเป็นตัวทำละลาย สารประกอบโมโนกลีเซอไรด์และไดกลีเซอไรด์ของน้ำมันมะพร้าวสังเคราะห์ได้โดยวิธีทรานส์เอสเทอริฟิเคชันของน้ำมันมะพร้าวกับกลีเซอรอลโดยมีเลดออกไซด์เป็นตัวเร่งปฏิกิริยา การพิสูจน์เอกลักษณ์สารประกอบไนเตรตที่ได้โดยการวิเคราะห์ด้วยเทคนิคทางสเปกโทรสโกปี ได้แก่ อินฟราเรดสเปกโทรสโกปี และนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี สารประกอบไนเตรตที่สังเคราะห์ได้สามารถละลายในน้ำมันดีเซลพื้นฐานได้ง่าย การตรวจสอบค่าซีเทนพบว่า ไดกลีเซอไรด์โมโนไนเตรต, โมโนกลีเซอไรด์ไดไนเตรต และ สารผสมไนเตรตของสารไดกลีเซอไรด์โมโนไนเตรตและโมโนกลีเซอไรด์ไดไนเตรตในอัตราส่วน 1:1 โดยโมล สามารถเพิ่มค่าซีเทนเป็น 3.2, 3.9 และ 3.7 หน่วย ตามลำดับ เมื่อใช้ความเข้มข้น 2.5 เปอร์เซ็นต์โดยน้ำหนัก ที่สุดอย่างไรก็ตามสารประกอบไนเตรตที่สังเคราะห์ได้มีประสิทธิภาพในการเพิ่มค่าซีเทนได้ไม่ดีเท่ากับ 2-เอทิลเฮกซิลไนเตรตซึ่งเป็นสารเพิ่มค่าซีเทนที่จำหน่ายในเชิงพาณิชย์ พบว่า 2-เอทิลเฮกซิลไนเตรตใช้ความเข้มข้นเพียง 0.1 เปอร์เซ็นต์โดยน้ำหนัก สามารถเพิ่มค่าซีเทนของน้ำมันดีเซลได้ 3.3 หน่วย



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จุฬาลงกรณ์มหาวิทยาลัย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...
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ลายมือชื่ออาจารย์ที่ปรึกษา.....
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Nitrate compounds from coconut oil could be synthesized by nitration of coconut fatty acid diglyceride and coconut fatty acid monoglyceride in the presence of concentrated nitric acid and concentrated sulfuric acid using dichloromethane as a solvent. They were synthesized by transesterification of coconut oil with glycerol along with lead oxide catalyst. The nitrate compounds obtained (diglyceride mononitrate, monoglyceride dinitrate and mixed nitrate; diglyceride mononitrate and monoglyceride dinitrate in ratio 1:1 by mol, of coconut oil) 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 3.2, 3.9 and 3.7 units at the concentration of 2.5 % wt, respectively. These synthesized nitrate compounds are not as effective in improving the cetane number in comparison with 2-ethylhexylnitrate. The cetane numbers of base diesel fuel were increased by 3.3 units at concentrations of 0.1% by weight.

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จุฬาลงกรณ์มหาวิทยาลัย

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ABBREVIATIONS

ASTM	=	American Standard 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
¹ H-NMR	=	Proton Nuclear Magnetic Resonance
Sp.Gr.	=	Specific Gravity
cm ⁻¹	=	Unit of wave number
%wt	=	Percent by weight
%yield	=	Percentage yield
CFD	=	Coconut fatty acid diglyceride
CFM	=	Coconut fatty acid monoglyceride
CFDM	=	Coconut fatty acid diglyceride mononitrate
CFMD	=	Coconut fatty acid monoglyceride dinitrate
CFMI	=	Mixed nitrate of coconut
EHN	=	2-ethylhexyl nitrate

CHAPTER I

INTRODUCTION

1.1 Introduction

The diesel engine has been around for a long time. Within the past eighty years diesel engines have been used wherever engine power has been required. Diesel engines have been used for power generators that produce electricity; trucks, boats, trains, and aircraft that transport goods. The diesel engine's efficient use of fuel and its high torque output have established it as one of the major power sources of our energy hungry society [1].

The demand for diesel fuel has been increased. The consumption of diesel fuel continuously increases as shown in Figure 1.1 [2].

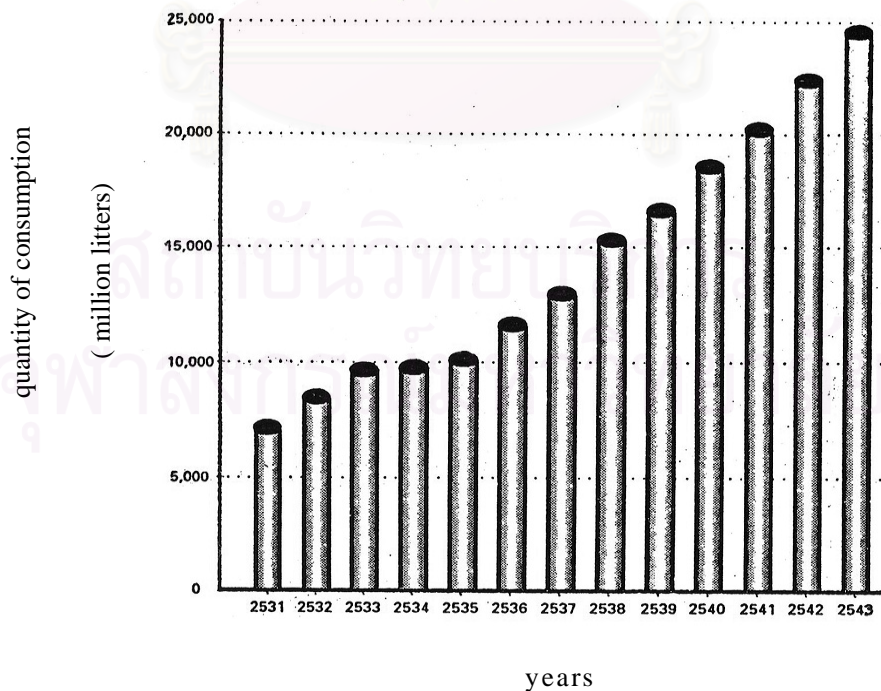


Figure 1.1 The quantity of high speed diesel consumption in Thailand.

Diesel fuel is obtained from crude oil, which is also known as petroleum. The major classes of hydrocarbons in crude oils including paraffins, olefins, aromatics and naphthenes. Other hydrocarbons such as alkenes and alkynes. Diesel fuels are middle distillates which are hydrocarbons containing 12 to 20 carbon atoms, generally boiling within the range of 482 to 662 degrees Fahrenheit / 250 to 350 degree Celsius.

Diesel fuel now contains more cracked components than in the past, which means that the olefins content of diesel fuel is increased. Olefins are less stable to oxidation and hence more likely to form deposits in a vehicle fuel system than are paraffinic and aromatic components. They are also poorer in cetane quality. The fuels therefore need additives in order to overcome these deficiencies.

For diesel fuel, ignition quality is important operational parameter. It is expressed in term of cetane number, which 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 which can be achieved by two methods.

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

2. Addition of cetane improver, which decreases ignition delay period so that engines can 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 and tetrazoles.

Refer to the two methods as above, it was found that the cracking of diesel fuel process is high in cost and cannot result in the sufficiently high cetane number. Being more cost effective than cracking of diesel fuel and being able to increase cetane number, addition of cetane improver is considered as a more effective method.

Cetane improvers have been used for many years to improve the ignition quality of diesel fuels [3]. 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 .

In a diesel engine, ignition quality and its direct and indirect impacts on fuel performance are some of the most important properties of a diesel fuel. When a diesel fuel has deficient ignition quality, cetane improvers (CI) are commonly added to improve the ignition. Improved ignition is detected as a decrease in the ignition delay times. The ignition delay times being measured as the time between start of fuel injection and detectable ignition. Fuel with short ignition delay times characteristically has high cetane number. Fundamentally, the cetane improver is often capable of simultaneously decreasing NO_x , hydrocarbon and particulate emissions [4].

There are many patents covering a variety of compounds that function as effective cetane improvers. The most common additives are alkyl nitrates and peroxides. The exact mechanisms of action for these additives are subject to debate. Many investigators believe nitrates are effective cetane improvers, because they

readily decompose to generate nitrogen dioxide radicals, which is believed to catalyze the initiation of combustion [5].

Triglycerides are renewable chemical feed stocks available from a variety of resources, including vegetable oils, tall oil and beef or pork fat. In this research, synthetic method, reaction conversions and performances of nitrates of coconut oil were investigated to evaluate the viability of converting triglycerides into nitrates for use as cetane improvers. Chemical synthesis included lithium catalyst esterification of coconut oil with glycerine followed by nitration of the terminal alcohol group to form nitrate compounds [6,7], it is anticipated that these compounds can effectively increase the cetane number.

1.2 Objectives

1. To synthesize nitrate compounds from coconut oil for using as cetane improvers in diesel fuel.
2. To study the properties of synthesized nitrate compounds blended with based diesel as cetane improvers.

1.3 Scope of the Research

1. Literature survey of the relevant research works.
2. Providing of chemicals and equipments.
3. Synthesis of nitrate compounds from coconut oil by esterification reaction following by nitration reaction.
4. Characterizing of synthesized nitrate compounds by spectroscopic methods such as FT-IR and FT-NMR.
5. Determination of cetane number of diesel fuel blended with synthesized nitrate compounds.

6. Summarizing the results.



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CHAPTER II

THEORETICAL CONSIDERATION

2.1 Diesel Engine

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 overning) thus leading to a very lean fuel-air mixture.

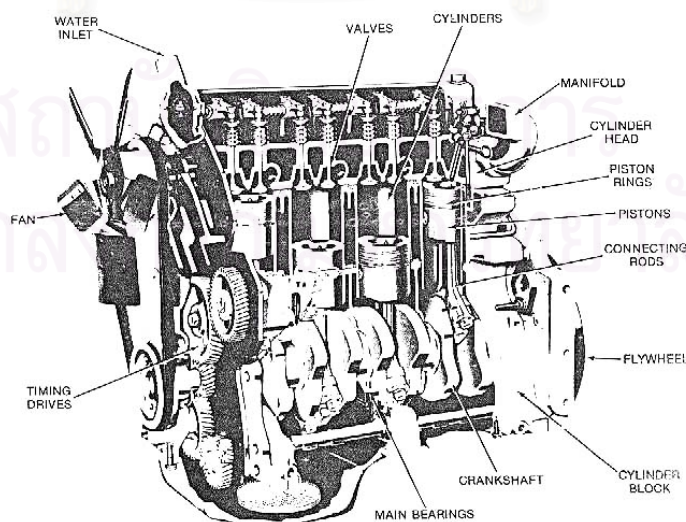


Figure 2.1 Basic parts of diesel engine.

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 2.2 and the pre-chamber, indirect injection system shown in Figure 2.3 [1].

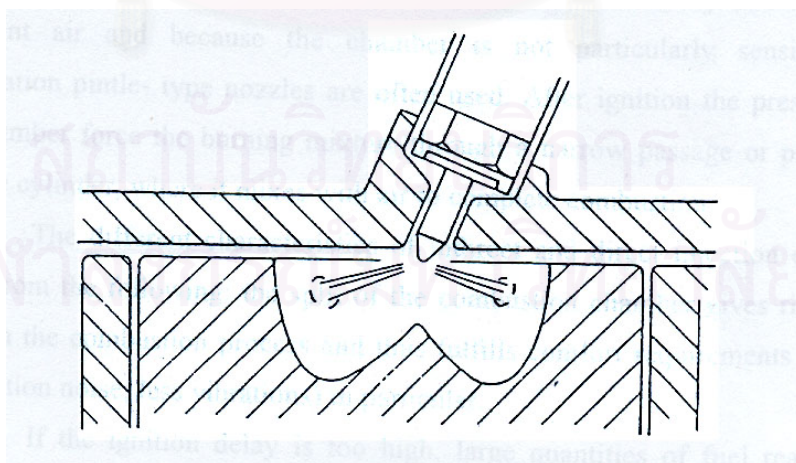


Figure 2.2 Direct injection combustion system.

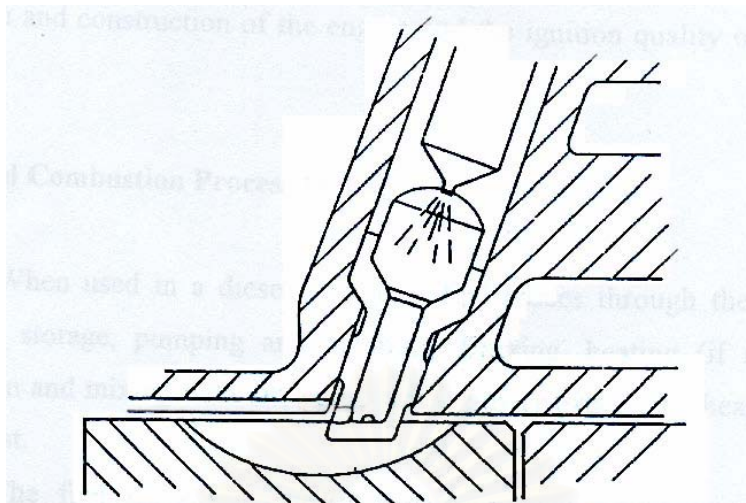


Figure 2.3 Indirect injection combustion system.

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 [8].

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. Once ignition has started and a flame is present, the heat required for continuous 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 [9].

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 Figure 2.4

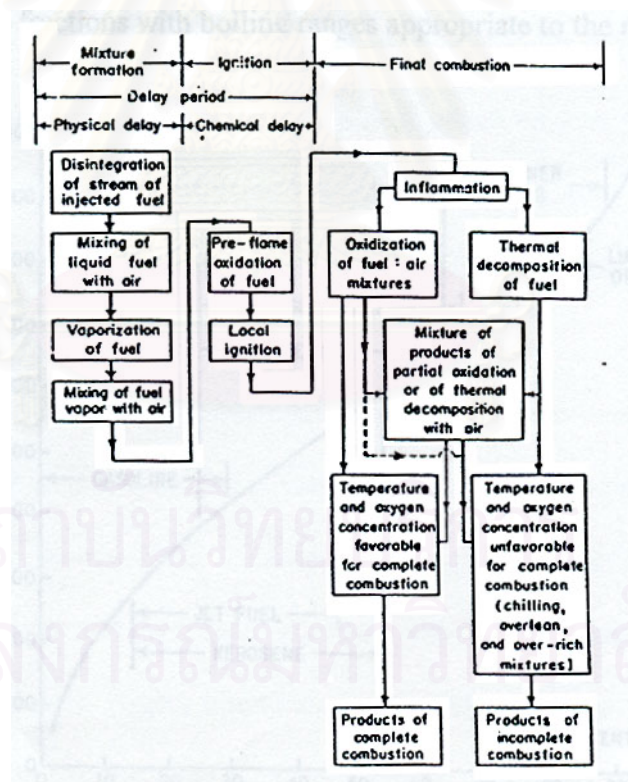


Figure 2.4 Outline of combustion process in the diesel engine.

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 Figure 2.4, 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 or if combustion reactions or thermal decomposition reactions are chilled, products of incomplete combustion will result.

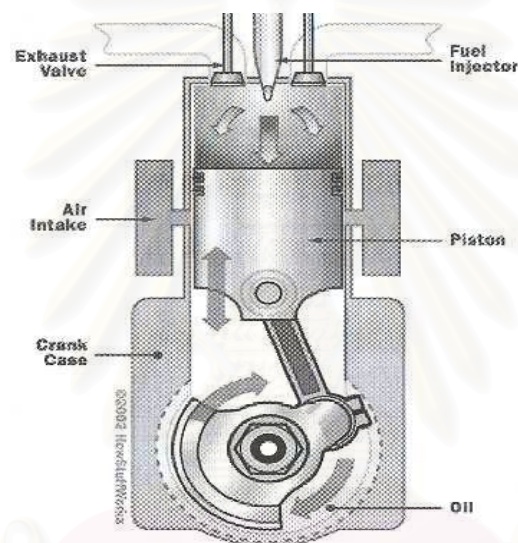


Figure 2.5 Fuel combustion.

The injector on a diesel engine is its most complex component and has been the subject of a great deal of experimentation – in any particular engine it may be located in a variety of places. The injector has to be able to withstand the temperature and pressure inside the cylinder and still deliver the fuel in a fine mist. Getting the mist circulated in the cylinder so that it is evenly distributed is also a problem, so some diesel engines employ special induction valves, pre-combustion chambers or other

devices to swirl the air in the combustion chamber or otherwise improve the ignition and combustion process.

One big difference between a diesel engine and a gas engine is in the injection process. Most car engines use port injection or a carburetor rather than direct injection. In a car engine, therefore, all of the fuel is loaded into the cylinder during the intake stroke and then compressed. The compression of the fuel/air mixture limits the compression ratio of the engine, if it compresses the air too much, the fuel/air mixture spontaneously ignites and causes knocking. A diesel compresses only air, so the compression ratio can be much higher. The higher the compression ratio, the more power is generated.

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.

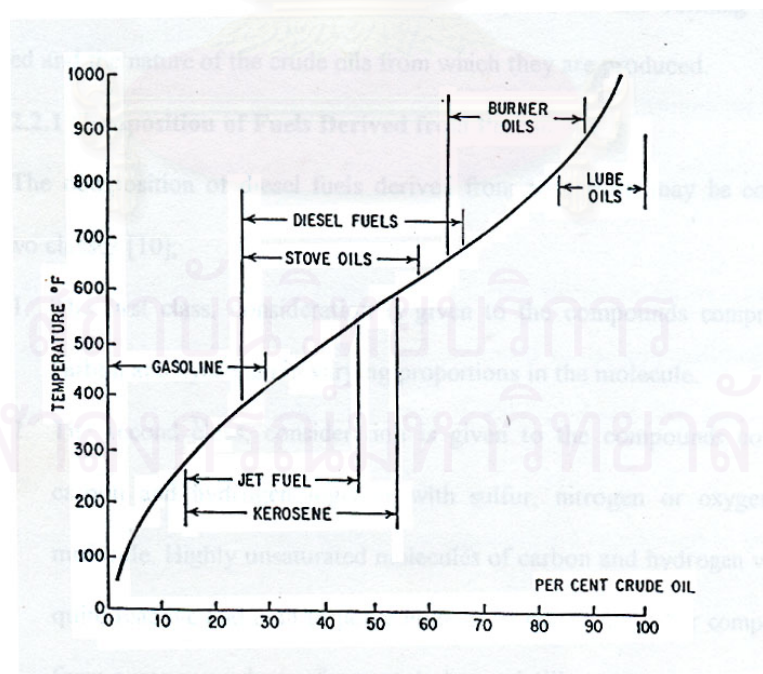


Figure 2.6 Proportion of diesel fuel and other petroleum products processed from crude petroleum.

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 Figure 2.6 [10], 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 [9];

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.

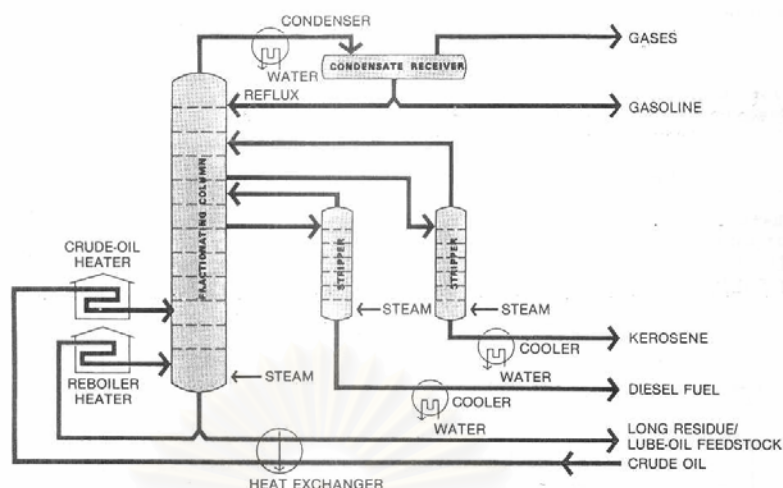


Figure 2.7 Catalytic cracking tower.

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: paraffins, 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 paraffinic 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 .

Sulfur derivatives – In the simplest 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 [11].

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

<u>Performance Feature Desired</u>	<u>Indicated By</u>
1. Safety in handling	Flash point
2. Pumpability at low temperature	Pour or cloud point, viscosity
3. Freedom from all suspended matter	Storage stability, Suspended sediment tests
4. Readily atomized	Viscosity
5. Readily ignitable	Cetane number
6. Clean burning	Volatility, Cetane number
7. Good fuel economy	°API gravity
8. Major effects on engine wear and deposit	Sulfur

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:

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

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 Diesel Ignition Improvers

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, alphas-methylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. In 1962, alphas-methylnaphthalene was replaced as a primary reference fuel by heptamethyl nonane, which has a cetane number of 15 as determined by use of the two original primary reference fuels.

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (Cetane No. = 100) in a blend with heptamethylnonane (Cetane No. 15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number [8]:

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

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

High speed diesel engines normally are supplied with fuels in the range of 45 to 55 cetane number. The actual cetane number required in any given service depend on

engine design and size, speed and load variations, and on starting and atmospheric conditions. Exhaust smoking and odor are affected only indirectly by cetane number.

Diesel fuels of high cetane number differ from those of lower cetane number by having a shorter ignition lag when injected into the diesel-engine cylinder. High-cetane fuel also is ignited at a lower compressed-air temperature than low-cetane fuel. These characteristics result in the differences in the performance of high-cetane and low-cetane fuels in operating engines as described below [10]:

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 [12]. 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 2.8.

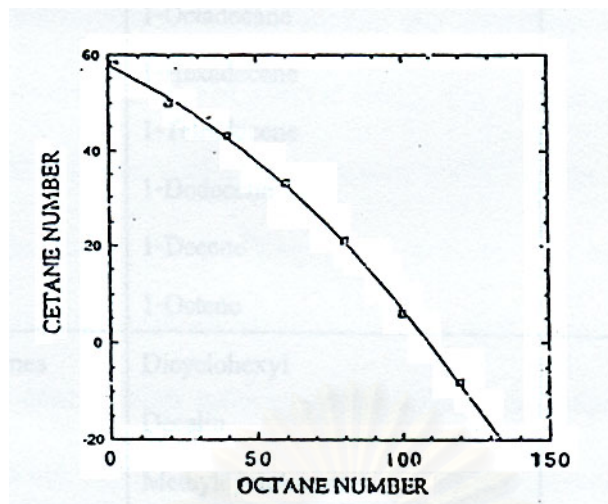


Figure 2.8 The inverse relationship between cetane and octane numbers.

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 [13].

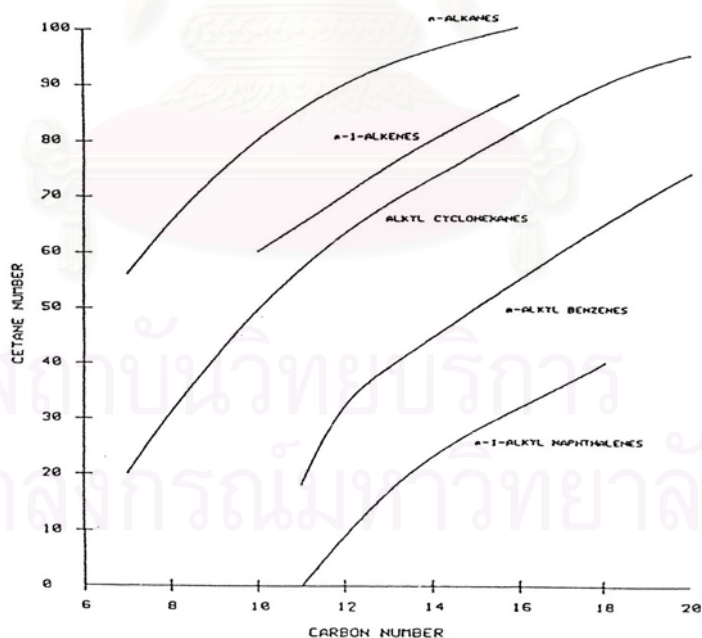


Figure 2.9 Cetane number of pure hydrocarbons.

Table 2.1 Cetane number for pure organic compounds.

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 [14]. 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 2.10.
2. It is determined from the following formula [15]:

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

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

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

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

Where:

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

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

D = Percent weight of cetane improver, % weight.

Therefore;

$$\text{CCI improved} = \text{CCI} + \text{Improver value} \tag{5}$$

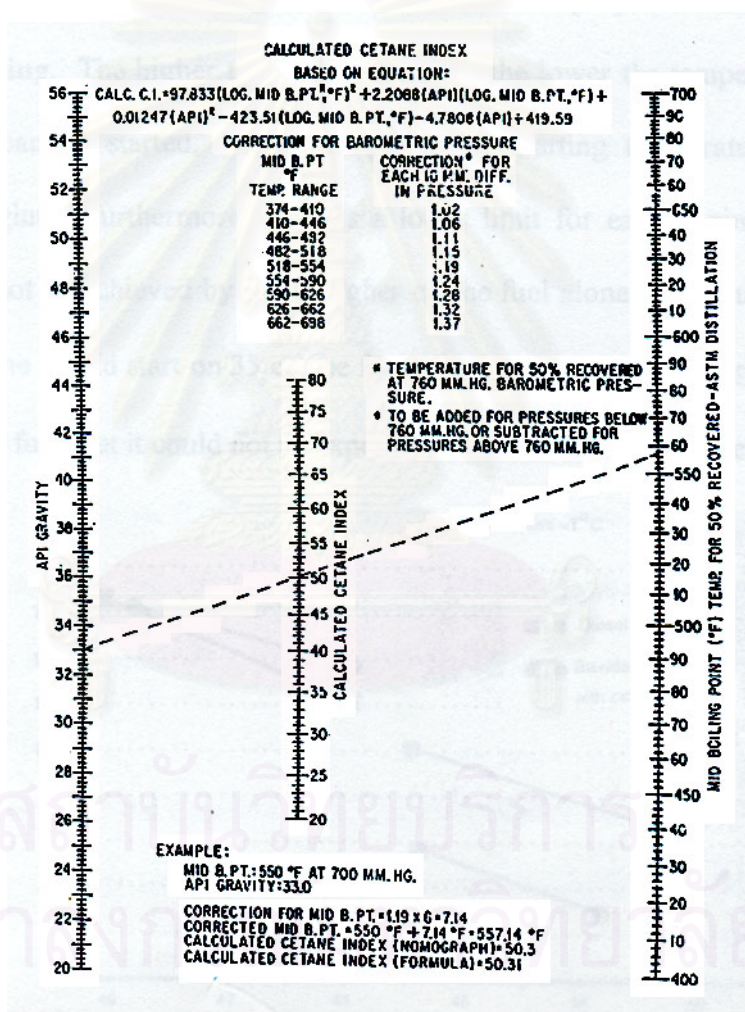


Figure 2.10 Nomograph for calculated cetane index.

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

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 [16].

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 [8].

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 2.11, 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.

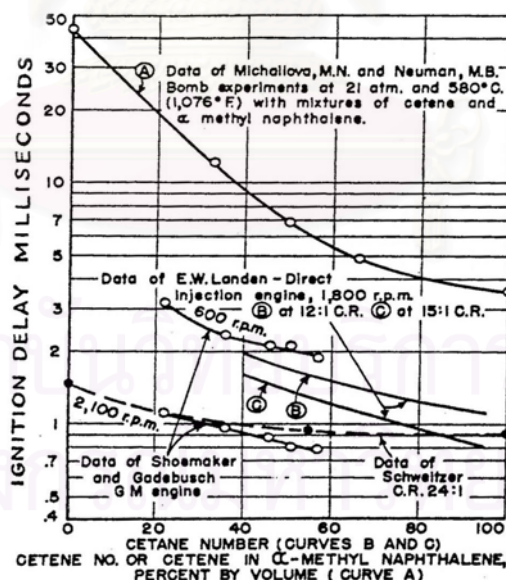


Figure 2.11 Relation between ignition delay and cetane number in tests in engines and bombs.

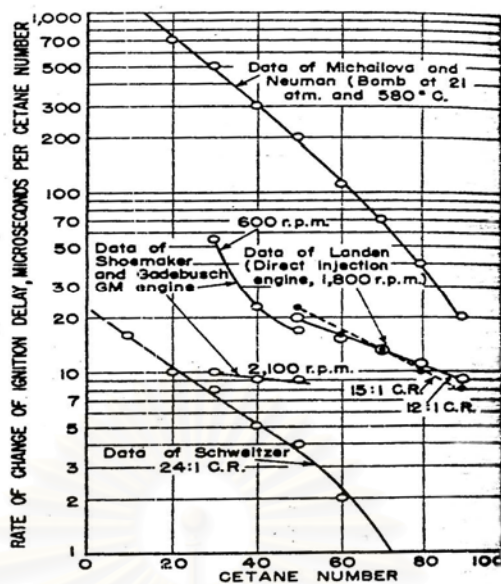


Figure 2.12 Variation of rate of change of ignition delay with cetane number.

Closer study of Figure 2.11 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 2.12, 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 [9].

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 2.13 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.

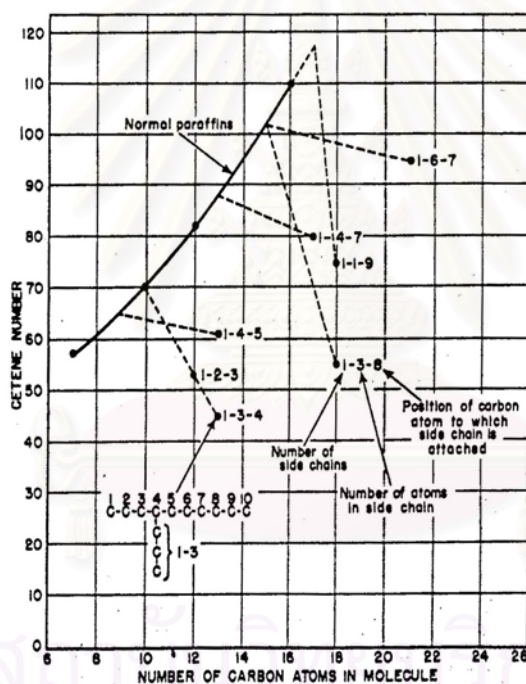


Figure 2.13 Cetane number of n-alkyl paraffin hydrocarbons .

In order to overcome this difficulty, the results have been plotted as shown in Figure 2.14. 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 2.13 for interpolation and slight extrapolation.

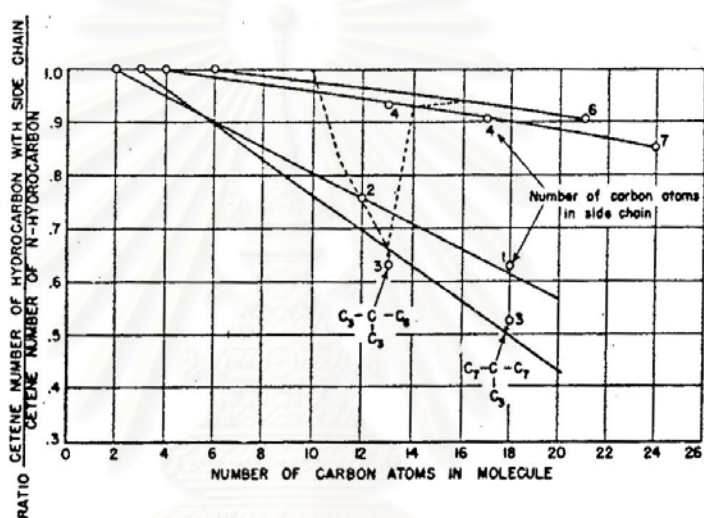


Figure 2.14 Effect of adding n-alkyl side chains on cetane number of paraffin hydrocarbons .

By interpolation, using Figures 2.13 and 2.14, 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 2.15 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 [9].

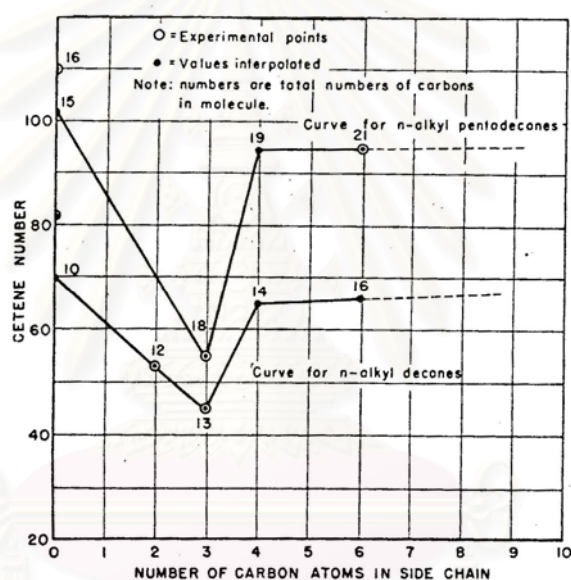


Figure 2.15 Relation between cetane number and number of carbon atoms in a single side chain in n-alkyl paraffin hydrocarbons .

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 2.16, 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.

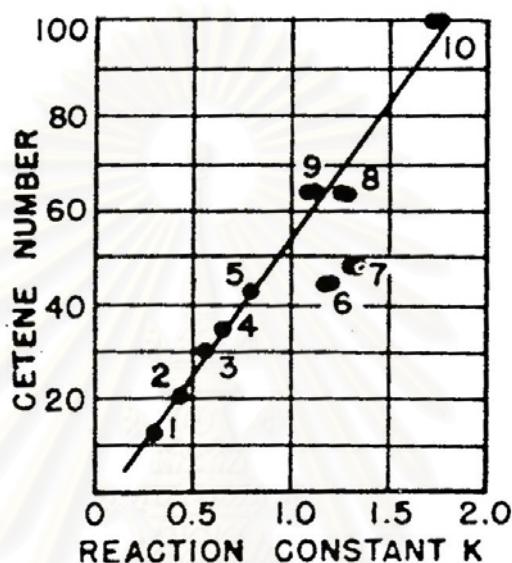


Figure 2.16 Reaction constant K in relation to cetane number. (cracking temperature 635°C).

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 is shown in Figure 2.17, in relation to the concentration of ignition

accelerator. It will be observed that significant improvement is obtained with comparatively small additions of accelerator.

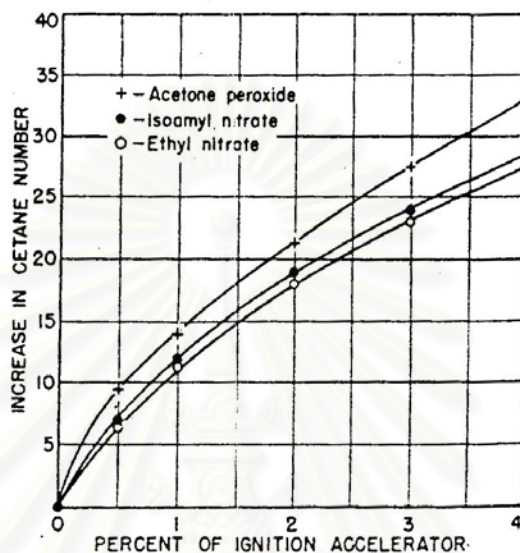


Figure 2.17 Average increase in cetane number of 9 test fuels in relation to concentration of ignition accelerator .

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 2.18, 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.

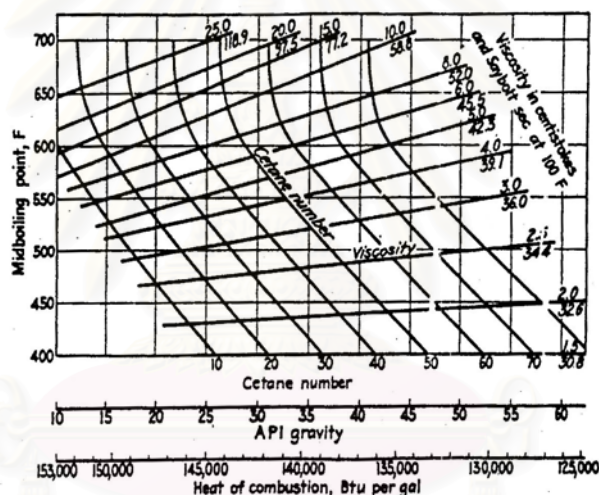


Figure 2.18 Interrelated properties of diesel fuels .

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 .

2.5 Composition of fatty acids in coconut oil

Most vegetable oils are a mixture of different triglycerides of fatty acid. Plant oils differ from animal fats because the vegetable fatty acids are predominately

unsaturated. It has been known that polysaturated molecules are also less prone to oxidation than polyunsaturated molecules.

This research chose coconut oil for synthesizing of nitrate compounds as cetane improvers. Due to about 50% of coconut oil consists of fatty acids of medium chain length (C6-C12) of which the major fatty acid is lauric acid (C12), it is also the most saturated compared with palm, soybean, and corn oils, and animal fat such as butter, tallow, and lard [18].

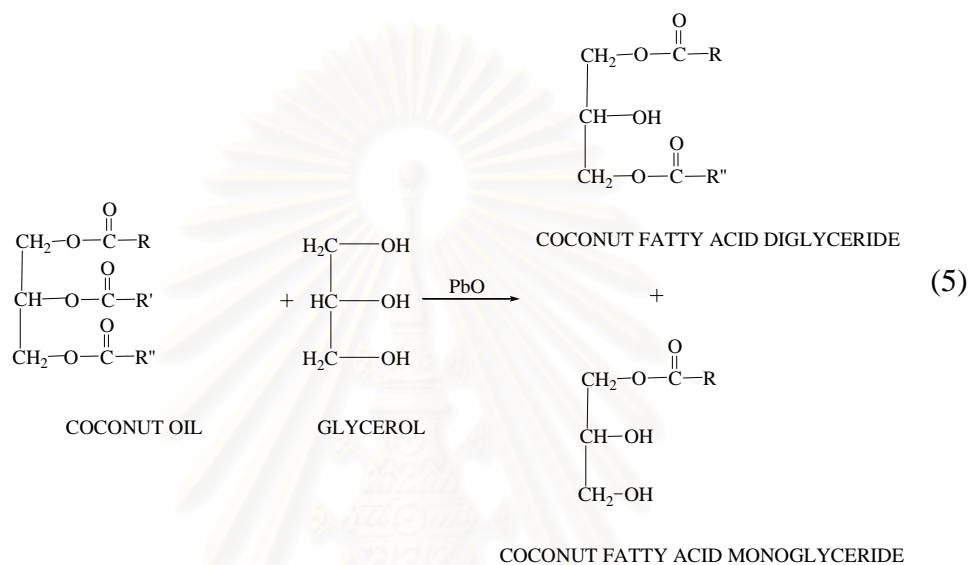
Table 2.2 Composition of fatty acids in coconut oil

Fatty acids (R, R' or R'')	Compositon
Caproic acid (C6:0)	tr.
Caprylic acid (C8:0)	10.4
Capric acid (C10:0)	7.6
Lauric acid (C12:0)	50.2
Myristic acid (C14:0)	17.3
Palmitic acid (C16:0)	7.1
Stearic acid (C18:0)	2.0
Total saturated fatty acid	94.6%
Oleic acid (C18:1)	4.4
Linoleic acid (C18:2)	1.0
Total unsaturated fatty acid	5.4%

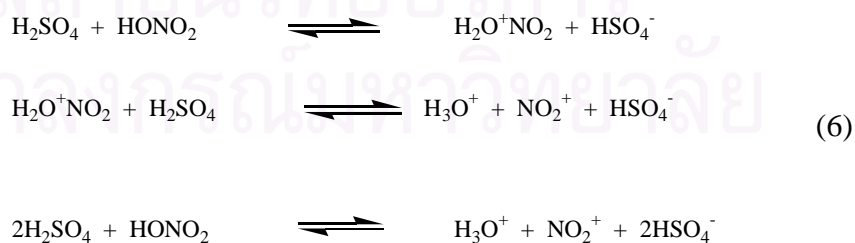
2.6 Synthesis of nitrate compounds from coconut oil as cetane improvers.

Synthesis of nitrate compounds from coconut oil as cetane improvers consists of two reactions; transesterification following by nitration reaction.

Transesterification coconut oil using glycerine; chemical synthesis included litharge catalyst transesterification of coconut oil with glycerine to yield terminal alcohol [6].



Nitration of coconut fatty acid diglyceride and coconut fatty acid monoglyceride of coconut oil; nitration with mixtures of nitric acids and sulfuric acids. Nitric acids react with sulfuric acids to form the nitronium ion (NO_2^+), a powerful electrophile.



The nitronium ion reacts with coconut fatty acid diglyceride and coconut fatty acid monoglyceride of coconut oil to form nitrate compounds [4].



2.7 Literature Reviews

Mark, H.M. *et al.* [5], synthesized nitrate compounds from fatty acid of methyl oleate and soybean oil as cetane improvers by epoxidation, hydrolysis and nitration reaction, respectively. The results revealed that nitrate of methyl oleate was slightly less ignition delay time than dinitrate of soybean oil. Due to soybean has on average 4.5-5 double bonds per mole of triglycerides; the unreacted π bonds may quench the radical cascade caused by thermal decomposition of these molecules during combustion. This would also lower the cetane improving capability of dinitrate of soybean oil.

Liotta, F.T. Jr. [19], had reported that improved cetane rating was achieved with a base diesel fuel having a cetane number of 43 by addition of a small amount of methyl benzyl nitrate (MBN). In addition to the blends containing MBN, blends were prepared using the same concentrations of the commercial cetane number improver, 2-ethylhexyl nitrate. The results exhibited 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 tend to decrease cetane number but MBAN are comprised of nitrate groups, which induce 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.

Suppes, G.J. *et al.* [7], synthesized fatty acid glycol nitrate as cetane improvers by acid catalyzed transesterification of organic acid ranging from C_6 to C_{18} with ethylene glycol followed by nitration of the terminal alcohol group to form fatty acid glycol nitartes. All the nitartes compounds provided good cetane improving capabilities, fatty acid glycol nitrates with carbon numbers between 8 and 14

exhibited the best performance, a balance between high carbon numbers and high nitrate group concentration.

Lucita, R. *et al.* [18], studied the fatty acid profiles and triglyceride composition of coconut oil using gas chromatography and high performance liquid chromatography. They have found that about 50% of coconut oil consists of fatty acids of medium chain length (C_6 - C_{12}) of which the major fatty acid is lauric acid (C_{12}). It is also the most saturated compared with palm, soybean and corn oils.

Prashantha, K. *et al.* [6], synthesized polyol modified castor oil by transesterification of castor oil with glycerol. The products were used for synthesizing polyurethane by reacting with the hexamethylene diisocyanate.

Moreover, several studies by Siraprapakit, S. [20], Suttipitakwong, C. [21] and Vasaruchtragul, J. [22] have 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 improver containing nitro, nitrate and oxygroup was an outstanding cetane improver, especially at very low concentrations and had many times as effective as the commercial additive. From what has been mentioned, the need for further research of these compounds is urgent.

CHAPTER III

EXPERIMENTAL

3.1 Apparatuses

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

Bruker Spectrospin

2. Fourier-Transform Infrared Spectrophotometer: Model Impact 410;

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. Diesel 2000 fuel analyzer

3.2 Chemicals

1. Coconut oil
2. Glycerine: laboratory grade; KH
3. Lead monoxide: analytical grade; Riedel-de Hean
4. 2-Ethyl-1-hexanol: analytical grade; Fluka
5. Dichloromethane: analytical grade; Lab-Scan
6. 96% Sulfuric acid: analytical grade; Merck
7. 65% Nitric acid: analytical grade; Lab-Scan
8. Sodium hydrogen carbonate: analytical grade; Merck
9. Anhydrous sodium sulfate: analytical grade; Merck
10. Chloroform-D1: NMR spectroscopy grade; Merck
11. Based diesel fuels; Petroleum Authority of Thailand

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

3.3 Synthesis of Coconut Fatty Acid Diglyceride and Coconut Fatty Acid Monoglyceride

500 mL 3-neck flask equipped with thermometer, stirrer and reflux condenser was charged with 150 g (0.24 mole) of coconut oil and an excess of glycerine along with catalyst litharge 0.03 g ($\text{PbO } 1.2 \times 10^{-4}$ mole). A reaction was carried out at 240 – 250 °C for 5 h. Progress of the reaction was monitored by thin layer chromatography (hexane and diethyl ether in ratio 4:1 by volume was used as a solvent). Then the solution was allowed to separate. The solution of coconut fatty acid diglyceride and coconut fatty acid monoglyceride in dichloromethane (200 mL) was washed with 300 mL of water for 5 times in a separatory funnel, dried over anhydrous sodium sulfate, and filtered. The solvent was removed in vacuo at 60 °C to give 148 g (98% yield) of mixture of coconut fatty acid diglyceride and coconut fatty acid monoglyceride as a dark color liquid.

The product was purified by silica gel column chromatography (glass tube, 2.5 cm in diameter and 70 cm in length) using hexane and diethyl ether in the ratio of 9:1 by volume as an eluent.

3.4 Synthesis of Nitrate Compounds of Coconut Oil

3.4.1 Synthesis of Coconut Fatty Acid Diglyceride Mononitrate

In 250 mL round bottom flask, 5.0 g of coconut fatty acid diglyceride was mixed with 50 mL of CH_2Cl_2 . The solution was added dropwise into a stirred mixture of 65% nitric acid (2.07 g) and 96% sulfuric acid (6.44 g) within 30 minutes and cooled in an icebath at $0 \pm 5^\circ\text{C}$. The solution was stirred for over 5 h. Then the solution was allowed to separate. The organic layer was neutralized with 20 mL of 10% aq sodium hydrogen carbonate, washed with 50 mL of water for 3 times, dried

over Na_2SO_4 and filtered. The solvent was removed in vacuo. at $60\text{ }^\circ\text{C}$ to give 4.4 g (88% yield) of coconut fatty acid diglyceride mononitrate as a pale yellow liquid.

3.4.2 Synthesis of Coconut Fatty Acid Monoglyceride Dinitrate

In 250 mL round bottom flask, 5.0 g of coconut fatty acid monoglyceride was mixed with 50 mL of CH_2Cl_2 . The solution was added dropwise into a stirred mixture of 65% nitric acid (4.59 g) and 96% sulfuric acid (14.31 g) within 30 minutes and cooled in an icebath at $0\pm 5^\circ\text{C}$. The solution was stirred for 6 h. Then the solution was allowed to separate. The organic layer was neutralized with 20 mL of 10% aq. sodium hydrogen carbonate, washed with 50 mL of water for 3 times, dried over Na_2SO_4 and filtered. The solvent was removed in vacuo. at $60\text{ }^\circ\text{C}$ to give 4.0 g (80% yield) of coconut fatty acid monoglyceride dinitrate as a pale yellow liquid.

3.4.3 Synthesis of Mixed Nitrate of Coconut

In 250 mL round bottom flask, 5.0 g of mixture of coconut fatty acid glyceride was mixed with 50 mL of CH_2Cl_2 . The solution was added dropwise into a stirred mixture of 65% nitric acid (4.59 g) and 96% sulfuric acid (14.31 g) within 30 minute and cooled in an icebath at $0\pm 5^\circ\text{C}$. The solution was stirred for over 6 h. Then the solution was allowed to separate. The organic layer was neutralized with 20 mL of 10% sodium hydrogen carbonate, washed with 50 mL of water for 3 times, dried over Na_2SO_4 and filtered. The solvent was removed in vacuo at $60\text{ }^\circ\text{C}$ to give 4.2 g (84% yield) of mixed nitrate of coconut fatty acid glyceride as a pale yellow liquid.

The reaction was allowed to proceed for the set reaction time and ratio of alcohol to acids.

3.5 Synthesis of 2-Ethylhexyl Nitrate

In 250 mL round bottom flask, 50 mL of dichloromethane was added to 96% sulfuric acid (6.13 g, 0.06 mole) and 65% nitric acid (3.88 g, 0.04 mole). 2-Ethyl-1-hexanol (2.6 g, 0.02 mole) was then slowly added to the well-agitated mixture whilst maintaining the temperature between 0 °C and 5 °C. The mixture was stirred for over one hour and allowed the mixture to separate. The lower spent acid (comprising mainly sulfuric acid) was removed. The organic layer was washed with water then washed with aq sodium hydrogen carbonate, after which it was neutralized. Solvent was removed on a rotary evaporator at 60 °C, to give 3.26 g of 2-ethylhexyl nitrate (93% yield) as a colorless liquid.

3.6 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.

The steps in deducing the structure of an organic compound, using the ^{13}C NMR spectrum are:

1. Count the number of signals in the spectrum; this is the number of nonequivalent carbon environments in the molecule. (Identify and discount the signal(s) from solvent; see table B1).

2. Use figure B1 to assign signals approximately to the regions δ 0-80, δ 80-150 and δ 160-220 (carbonyl carbons).

3. Note the intensities of the peaks: non-proton-bearing carbons give lower intensity signals, and groups of two or more equivalent carbons give higher intensity signals.

4. Taking into account of any multiplicity information (q, t, d or s).

5. Use the correlation tables (tables B2 and B3) to predict the chemical shifts of all carbons in each putative structure.

There are two principal predictable influences, which we can quantify in determining the chemical shift positions of any carbon atom:

1. The number of other carbon atoms attached to it (and whether these are CH₃, CH₂, CH or C groups).

2. The nature of all other substituents attached (or nearby along a chain of other carbon atoms).

It could be calculated by;

$$\text{Chemical shift } (\delta) = \text{constant} + \sum\alpha + \sum\beta + \sum\gamma$$

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

Blended base diesel fuels containing with 0.05% - 5% by weight of synthesized nitrate were determined of their cetane number.

The blended base diesel fuels were prepared by blending synthesized nitrate compounds (0.05-5 g) in base diesel fuel (100 g). The synthesized nitrate compounds were :

- 1) Coconut fatty acid diglyceride mononitrate
- 2) Coconut fatty acid monoglyceride dinitrate
- 3) Mixnitrate of coconut oil
- 4) 2-Ethylhexyl nitrate

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Coconut Fatty Acid Diglyceride and Coconut Fatty Acid Monoglyceride

Coconut fatty acid diglyceride and coconut fatty acid monoglyceride can be prepared by transesterification of coconut oil with glycerine along with a catalyst litharge (PbO) at 240-250 °C. Column chromatography was used to purify the products of transesterification.

4.2 Characteristics of Coconut Oil, Coconut Fatty Acid Diglyceride and Coconut Fatty Acid Monoglyceride

4.2.1 Coconut Oil and Coconut Fatty Acid Diglyceride

The IR spectrum of coconut oil and coconut fatty acid diglyceride is shown in Figures A1 and A5, respectively. The important absorption bands of coconut fatty acid diglyceride are listed in Table 4.1.

Table 4.1 The absorption assignments of coconut oil and coconut fatty acid diglyceride.

Wave number (cm ⁻¹)		Assignment
Coconut oil	Coconut fatty acid diglyceride	
-	3479	O-H Stretching
2850	2850	C-H Stretching, Aliphatic
1745	1753	C=O Stretching Vibration
1157	1172	C-O Stretching

From the IR spectrum of coconut fatty acid diglyceride (Figure A5) showed a characteristic absorption broad peak of OH stretching a $3200-3600\text{ cm}^{-1}$ which was not observed in spectrum of coconut oil (Figure A1). In addition, the strong C-O stretching absorption, showed a strong absorption in the range of $1,000-2,000\text{ cm}^{-1}$. The strong C=O stretching absorption was observed around $1,710\text{ cm}^{-1}$. A characteristic set of two C-H stretching frequencies was detected at 2850 cm^{-1} . All of these, both of coconut oil and coconut fatty acid diglyceride exhibited the same characteristic. The result was confirmed by using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis.

The $^1\text{H-NMR}$ spectrum of coconut oil and coconut fatty acid diglyceride is shown in Figures A2 and A7, respectively. The important signals of coconut fatty acid diglyceride are shown in Table 4.2.

Table 4.2 The assignments of $^1\text{H-NMR}$ spectrum of coconut oil and coconut fatty acid diglyceride.

Compound	Chemical Shift (δ ,ppm)	Multiplicity	Position of Proton	Number of Protons
Coconut Oil	4.09-4.31	<i>m</i>	a,c	4
	5.17	<i>t</i>	b	1
Coconut fatty acid diglyceride	4.03-2.28	<i>m</i>	d,e,f	5

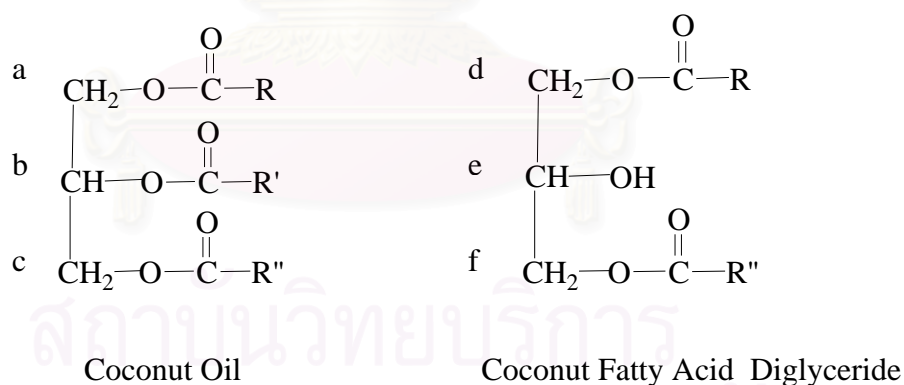
The $^{13}\text{C-NMR}$ spectrum of coconut oil and coconut fatty acid diglyceride is shown in Figures A3 and A9, respectively. The important signals of coconut fatty acid diglyceride are shown in Table 4.3.

Table 4.3 The assignments of ^{13}C -NMR spectrum of coconut oil and coconut fatty acid diglyceride.

Compound	Position of Carbon	Carbon Type*	Chemical Shift of Carbon (δ ,ppm) (spectrum)	Chemical Shift of Carbon (δ ,ppm) (calculation)
Coconut oil	a	CH_2	62.00	68
	b	CH	68.87	80
	c	CH_2	62.00	68
Coconut fatty acid diglyceride	d	CH_2	62.27	70
	e	CH	64.86	75
	f	CH_2	62.27	70

* It was determined by DEPT spectrum as shown in Figure A17

From the spectroscopic data, it can be concluded that the products were coconut oil and coconut fatty acid diglyceride having the structures as follows:



4.2.2 Coconut Oil and Coconut Fatty Acid Monoglyceride

The IR spectrum of coconut fatty acid monoglyceride is shown in Figure A11. The important absorption bands of coconut fatty acid monoglyceride are listed in Table 4.4.

Table 4.4 The absorption assignments of coconut oil and coconut fatty acid monoglyceride.

Wave number (cm ⁻¹)		Assignment
Coconut oil	Coconut fatty acid monoglyceride	
-	3413	O-H Stretching
2850	2850	C-H Stretching, Aliphatic
1745	1735	C=O Stretching Vibration
1456	1464	C-H Bending ,Aliphatic
1157	1165	C-O Stretching

From the IR spectrum of coconut fatty acid monoglyceride (Figure A11) as comparing with of coconut oil (Figure A1), it was seen that coconut fatty acid monoglyceride showed a strong absorption broad peak of OH stretching in the range of 3200-3600 cm⁻¹ which did not appear in spectrum of coconut oil. The structure was confirmed by ¹H-NMR and ¹³C-NMR analysis.

The ¹H-NMR spectrum of coconut fatty acid monoglyceride is shown in Figures A13. The important signals of coconut fatty acid monoglyceride are shown in Table 4.5.

Table 4.5 The assignments of ^1H -NMR spectrum of coconut oil and coconut fatty acid monoglyceride.

Compound	Chemical Shift (δ ,ppm)	Multiplicity	Position of Proton	Number of Protons
Coconut Oil	4.09-4.31	<i>m</i>	a,c	4
	5.17	<i>t</i>	b	1
coconut fatty acid monoglyceride	4.07-4.16	<i>m</i>	d	2
	3.83-3.94	<i>m</i>	e	1
	3.50-3.70	<i>m</i>	f	2
	3.19	<i>s</i>	g,h	2

The ^{13}C -NMR spectrum of coconut fatty acid monoglyceride was shown in Figures A9. The important signals of coconut fatty acid monoglyceride were shown in Table 4.6.

Table 4.6 The assignments of ^{13}C -NMR spectrum of coconut oil and coconut fatty acid monoglyceride.

Compound	Position of Carbon	Carbon Type*	Chemical Shift of Carbon (δ ,ppm) (spectrum)	Chemical Shift of Carbon (δ ,ppm) (calculation)
Coconut oil	a	CH_2	62.00	68
	b	CH	68.87	80
	c	CH_2	62.00	68
coconut fatty acid monoglyceride	d	CH_2	65.06	73
	e	CH	70.22	80
	f	CH_2	61.96	68

* It was determined by DEPT spectrum as shown in Figure A19.

Note;	(*)	=	incomplete reaction
	(**)	=	complete reaction
	CFD	=	Coconut fatty acid diglyceride
	CFM	=	Coconut fatty acid monoglyceride

4.4 Characteristics of Synthesized Nitrate Compounds of Coconut Oil

4.4.1 Coconut Fatty Acid Diglyceride Mononitrate

The IR spectrum of coconut fatty acid diglyceride mononitrate is shown in Figure A6. The important absorption bands of coconut fatty acid diglyceride mononitrate are listed in Table 4.8.

Table 4.8 The absorption assignments of coconut fatty acid diglyceride mononitrate.

Wave Number (cm ⁻¹)	Assignment
2850	C-H Stretching, Aliphatic
1743	C=O Stretching Vibration
1642	NO ₂ Asymmetric Stretching
1456	C-H Bending, Aliphatic
1277	NO ₂ Symmetric Stretching
1172	C-O Stretching
850	O-N Stretching Vibration

From the IR spectrum of coconut fatty acid diglyceride mononitrate (Figure A6) as comparing with of coconut fatty acid diglyceride (Figure A5), it could be observed that there was no the absorption band of OH stretching in the range of 3200-3600 cm⁻¹ but the absorption bands of NO₂ (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1642, 1277 and 850 cm⁻¹, respectively. The result was confirmed by ¹H-NMR and ¹³C-NMR analysis.

The ^1H -NMR spectrum of coconut fatty acid diglyceride mononitrate is shown in Figure A8. The important signals of coconut fatty acid diglyceride mononitrate are shown in Table 4.9.

Table 4.9 The assignments of ^1H -NMR spectrum of coconut fatty acid diglyceride mononitrate

Chemical Shift (δ ,ppm)	Multiplicity	Position of Proton	Number of Protons
4.08-4.70	<i>m</i>	a,c,d,f	8
5.24-5.41	<i>m</i>	b,e	2

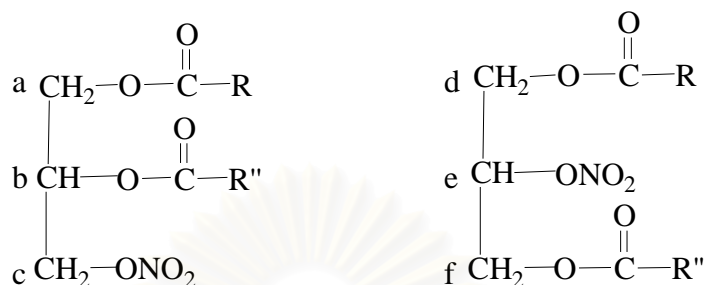
The ^{13}C -NMR spectrum of coconut fatty acid diglyceride mononitrate is shown in Figure A11. The important signals of coconut fatty acid monoglyceride are shown in Table 4.10.

Table 4.10 The assignments of ^{13}C -NMR spectrum of coconut fatty acid diglyceride mononitrate.

Position of Carbon	Carbon Type*	Chemical Shift of Carbon (δ ,ppm) (spectrum)	Chemical Shift of Carbon (δ ,ppm) (calculation)
a	CH_2	61.55	69
b	CH	67.40	78
c	CH_2	70.37	78
d	CH_2	60.64	64
e	CH	78.12	92
f	CH_2	60.64	64

* It was determined by DEPT spectrum as shown in Figure A18

From the results of the data, it could be concluded that the products were two structural isomers of coconut fatty acid diglyceride mononitrate. Their structures were as follows:



4.4.2 Coconut Fatty Acid Monoglyceride Dinitrate

The IR spectrum of coconut fatty acid monoglyceride dinitrate is shown in Figure A12. The important absorption bands of coconut fatty acid monoglyceride dinitrate are listed in Table 4.11.

Table 4.11 The absorption assignments of coconut fatty acid monoglyceride dinitrate.

Wave Number (cm ⁻¹)	Assignment
2846	C-H Stretching, Aliphatic
1739	C=O Stretching Vibration
1646	NO ₂ Asymmetric Stretching
1452	C-H Bending, Aliphatic
1273	NO ₂ Symmetric Stretching
1157	C-O Stretching
850	O-N Stretching Vibration

From the IR spectrum of coconut fatty acid monoglyceride dinitrate (Figure A12) in comparison with coconut fatty acid monoglyceride (Figure A11), it could be observed that there was no absorption band of OH stretching in the range of 3200-

3600 cm^{-1} but the absorption bands of NO_2 stretching was clearly observed at 1646 and 1273 cm^{-1} . The result was confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analysis.

The $^1\text{H-NMR}$ spectrum of coconut fatty acid monoglyceride dinitrate is shown in Figure A9. The important signals of coconut fatty acid monoglyceride dinitrate are shown in Table 4.12.

Table 4.12 The assignments of $^1\text{H-NMR}$ spectrum of coconut fatty acid monoglyceride dinitrate.

Chemical Shift (δ ,ppm)	Multiplicity	Position of Proton	Number of Protons
4.14-4.78	<i>m</i>	a,c,d,f	8
5.30-5.45	<i>m</i>	b, e	2

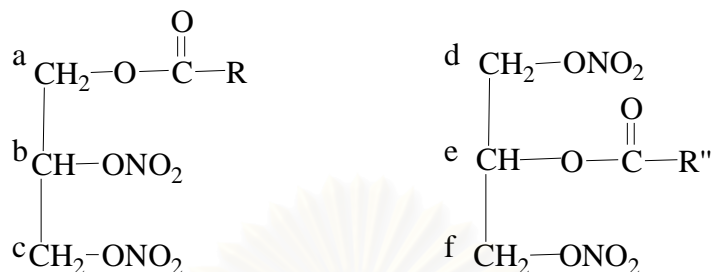
The $^{13}\text{C-NMR}$ spectrum of coconut fatty acid monoglyceride dinitrate is shown in Figure A16. The important signals of coconut fatty acid monoglyceride dinitrate are shown in Table 4.13.

Table 4.13 The assignments of $^{13}\text{C-NMR}$ spectrum of coconut fatty acid monoglyceride dinitrate.

Position of Carbon	Carbon Type*	Chemical Shift of Carbon (δ ,ppm) (spectrum)	Chemical Shift of Carbon (δ ,ppm) (calculation)
a	CH_2	60.28	65
b	CH	76.40	88
c	CH_2	68.70	74
d	CH_2	69.71	79
e	CH	66.03	74
f	CH_2	69.71	79

* It was determined by DEPT spectrum as shown in Figure A20.

It could be concluded that the products were two structural isomers of coconut fatty acid monoglyceride dinitrate having the structures as follows:



4.5 Characteristics of 2-Ethylhexyl Nitrate

The IR spectrum of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate are shown in Figures A21 and A22, respectively. The important absorption bands of 2-ethylhexyl nitrate are 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) in comparison with that of 2-ethyl-1-hexanol (Figure A21), it could be observed that there was no absorption band of OH stretching in the range of 3200-3500 cm⁻¹ but the absorption bands of NO₂ (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1634, 1280 and 866 cm⁻¹, respectively. The result was confirmed by using

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum. The $^1\text{H-NMR}$ spectrum of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate is shown in Figures A23 and A24, respectively. The important signals of 2-ethylhexyl nitrate are shown in Table 4.15.

Table 4.15 The assignments of $^1\text{H-NMR}$ spectrum of 2-ethylhexyl nitrate.

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

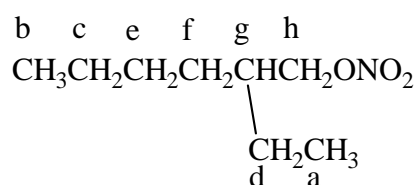
The $^{13}\text{C-NMR}$ spectrum of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate is shown in Figures A23 and A24, respectively. The important signals of 2-ethylhexyl nitrate are shown in Table 4.16.

Table 4.16 The assignments of $^{13}\text{C-NMR}$ 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	23.10	23.73
e	CH_2	28.34	29.58
f	CH_2	29.21	30.59
g	CH	41.21	42.31
h	CH_2	78.19	65.21

* The position of carbon of nitrate was referred by Ref. [25].

From the spectroscopic data, it can be concluded that the product was 2-ethylhexyl nitrate and its structure was as follow:



4.6 Determination of Cetane Number of Synthesized Nitrate Compounds in Base Diesel Fuel.

The physical properties of base diesel fuel and blend of synthesized nitrate compounds with base diesel fuel are shown in Table 4.17.

Table 4.17 Physical properties of base diesel fuel and blend of synthesized nitrate compounds with base diesel fuel.

Properties	Base	Base+CFDM	Base+CFMD	Base+CFMI
Mid-Boiling Point (°F)	554.78	556.24	556.13	556.11
API Gravity@ 60 °F	38.90	38.58	38.56	38.49
Viscosity	3.31	3.49	3.47	3.46
Pour Point	1 °C	3 °C	3 °C	2 °C
Cetane Index	58.24	56.56	56.44	56.40
Cetane Number	52.7	55.3	55.5	55.8

Physical properties of the synthesized nitrate compounds was not changed within the specification of diesel fuel.

Table 4.18 Cetane number of the blend of synthesized nitrate compounds with base diesel fuel.

wt%	Cetane Number				
	Base+Coconut oil	Base+CFDM	Base+CFMD	Base+CFMI	Base+EHN
0.05	52.7	52.7	52.8	52.7	54.2
0.10	52.6	52.8	53.1	52.9	56.0
0.15	-	-	-	-	57.0
0.20	-	-	-	-	58.3
0.25	52.3	53.3	53.5	53.4	-
0.50	52.3	53.5	53.7	53.7	-
0.75	52.2	53.7	54.1	54.0	-
1.00	52.1	53.9	54.6	54.2	-
2.00	51.4	55.3	55.8	55.5	-
2.50	51.1	55.9	56.6	56.4	-
3.00	50.9	56.5	57.5	57.1	-
4.00	50.4	57.6	60.0	58.4	-
5.00	50.2	58.9	62.9	60.0	-

Note: CFDM = Coconut fatty acid diglyceride mononitrate
 CFMD = Coconut fatty acid monoglyceride dinitrate
 CFMI = Mixed nitrate of coconut fatty acid glyceride
 EHN = 2-ethylhexyl nitrate

Table 4.18 exhibited cetane number as the results of 0.05% to 5% by weight of coconut fatty acid diglyceride mononitrate, coconut fatty acid monoglyceride dinitrate, mixed nitrate of coconut (CFDM and CFMD in ratio 1:1 by mol), and 2-ethylhexylnitrate which were blended in base diesel fuel.

From Figure 4.1, it showed the relationship between the cetane number with % wt of coconut oil and synthesized nitrate compounds in base diesel fuel.

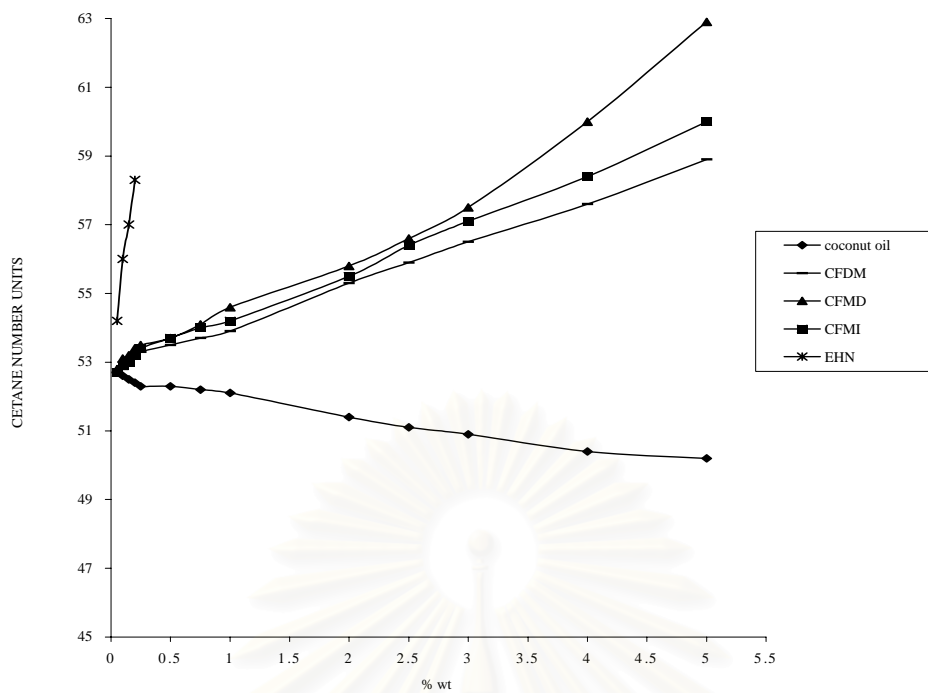


Figure 4.1 Cetane number of the synthesized compounds compared with coconut oil

From Figure 4.1, It could be seen that the synthesized nitrate compounds of coconut oil can increase the cetane number of base diesel fuel, but coconut oil itself give adversely effect to the cetane number of base diesel fuel.

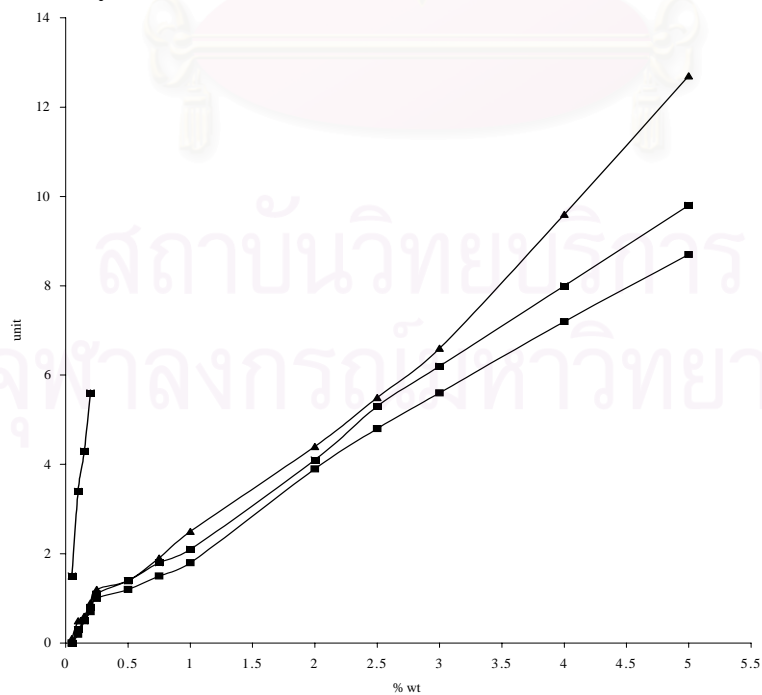


Figure 4.2 Increasing units of the synthesized compounds

From Figure 4.2, the cetane number of all samples were increased by 3 units using the concentration about 2.5% by weight as compared with base diesel fuel. It was also found that coconut fatty acid monoglyceride dinitrate can improve the cetane number more than others. The cetane number of base diesel was increased by 3.9 units at concentration of 2.5 % by weight. In addition, coconut fatty acid diglyceride mononitrate and mixed nitrate of coconut, the cetane number was increased by 3.2 and 3.7 units, respectively. Because coconut fatty acid monoglyceride dinitrate have more ratio of nitrate group to the number of carbon atoms than coconut fatty acid diglyceride mononitrate. These synthesized nitrate compounds are not as effective in improving the cetane number in comparison with 2-ethylhexylnitrate. The cetane numbers of base diesel fuel were increased by 3.3 units at concentrations of 0.10% by weight.



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CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

Nitrate compounds of coconut oil could be prepared by transesterification followed by nitration.

Firstly, transesterification of coconut oil with glycerine was conducted at 240-250°C. The esterified products are coconut fatty acid diglyceride and coconut fatty acid monoglyceride. Nitrate compounds could be prepared by nitration of coconut fatty acid diglyceride and coconut fatty acid monoglyceride with concentrated nitric acid and sulfuric acid maintaining the temperature of reaction at $0\pm 5^\circ\text{C}$ in the presence of dichloromethane. These synthesized nitrate compounds are coconut fatty acid diglyceride mononitrate, coconut fatty acid monoglyceride dinitrate.

In this study, all of products were obtained in high yield. These synthesized 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 0.05-2.5% by weight. The cetane number of the blended base diesel fuel was increased approximately for 3 units at concentrations of 2.5% by weight as compared with base diesel fuel. Coconut fatty acid monoglyceride dinitrate gave higher cetane number in comparison with coconut fatty acid diglyceride mononitrate and mixed nitrate of coconut oil, which increased cetane number by 3.9, 3.2 and 3.7 units, respectively. These synthesized nitrate compounds have potential to be used in based diesel fuel as cetane improvers. But these synthesized nitrate compounds are not as effective in improving the cetane number as compared with 2-ethylhexylnitrate. The cetane

numbers of base diesel fuel is increased by 3.3 units using concentration of 0.1% by weight, because the synthesized nitrate compounds have less ratio of nitrate group to the number of carbon atoms than 2-ethylhexylnitrate.

5.2 Suggestions for future work

The synthesized nitrate compounds of coconut oil can increase the cetane number of base diesel fuel. Therefore, future studies will probably use the other vegetable oils such as palm oil, olive oil, corn oil, and sunflower oil *etc.* for synthesizing the nitrate compounds. The synthesized nitrate compounds of coconut oil are ester compounds, which can be used as potential lubricating and biodiesel. Their properties in that aspect should be studied.



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REFERENCES

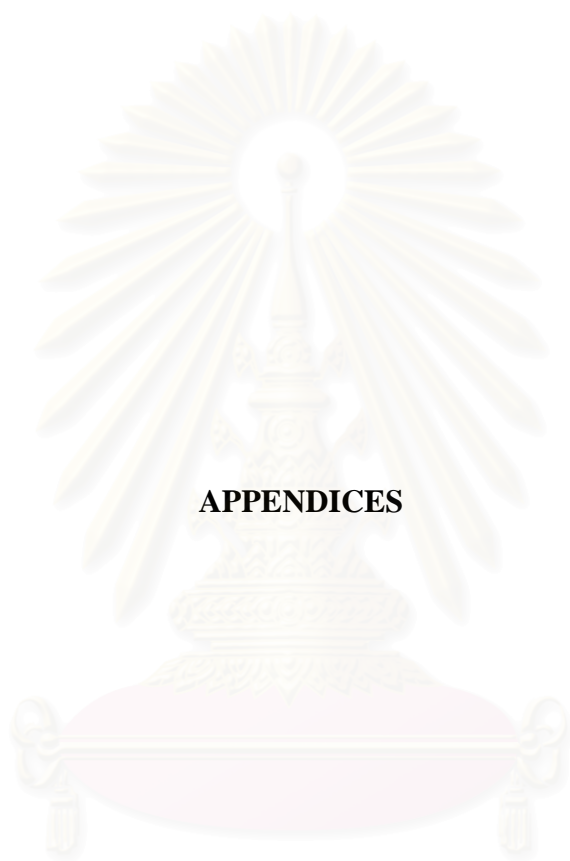
1. Richard, L. G., and Edmonton, C. *Diesel Mechanics an Introduction*, New York, 1982, 1-79.
2. Hobson, G. D. *Modern Petroleum Technology Part 2*, 5th ed, New York: John Wiley & Sons, 1984, 823-828.
3. Poirer, M. A., Steere, D. V., and Krogh, J. A. "Cetane Improver Compositions Comprising Nitrated Fatty Acid Derivatives" *US Patent 5, 454, 842*, 1995.
4. Suppes, G. T., Goff, M., and Bockwinkel, K. "Multifunctional Diesel Fuel Additives from Triglycerides" *Energy & Fuels* 2001, **15**, 151-157.
5. Mark, H. M., Cristopher, Y., Zhi, C., Joseph, A. H., and Galen, J. S. "Synthesis of Low Nitrogen Cetane Improvers from the Nitration of Renewable Feedstocks" *Chemistry of Diesel Fuels* 2000, **10**, 199-211.
6. Prashatha, K., Vasanth, K. P., Sherigara, B. S., and Prasannakuma, S. "Interpenetrating Polymer Networks Based on Polyol Modified Castor oil Polyurethane and Poly(2-hydroxyethylmethacrylate)" *Bulletin Material Science*, 2001, **24**, 335-538.
7. Suppes, G. J., Zhi, C., Ying, R., and Heppert, J. A. "Synthesis and Cetane Improver Performance of Fatty Acid Glycol Nitrates" *Fuel* 1999, **78**, 73-81.
8. Russel, T. J. Additives Influencing Diesel Fuel Combustion. *Gasoline and Diesel Fuel Additives*, New York: John Wiley & Sons, 1989, 65-88.
9. The American Society of Mechanical Engineers. *Diesel Fuel Oils Production, Characteristics, and Combustion*, New York: 1947, **59**, 78-89.
10. Virgil, B. G. *Petroleum Products Handbook*, 1st ed., New York: McGraw-Hill, 1960, 6-11.

11. Patberg, J. B. *Petroleum & Chemical Processes*. Exxon Research and Engineering Company, 1976.
12. Popovich, M. *Fuels and Lubricants*, London: John Wiley & Sons, 1959, 134-145.
13. Schobert, H. H. *The Chemistry of Hydrocarbon Fuels*, 2nd ed, London: Butterworth-Heinemann, 1991, 197-202.
14. Allinson, J. P. *Criteria for Quality of Petroleum Products*, 1st ed, Great Britain: Applied Science Publishers, 1975, 121-141.
15. Collins, J. M., and Unzelman, G.H. "Better Cetane Prediction Equations Developed". *Oil & Gas Journal*, 1982, 148-160.
16. Filbey, A. H. *Diesel Fuel Composition*. US Patent 4, 406, 665, 1983.
17. Clothier, P., Aguda, B., Moise, A., and Pritchard, H. "How do Diesel Fuel Ignition Improvers Works" *Chemical Society Reviews*, 1993, 101-108.
18. Lucita, R. L., Felicito, M. R., Consorcia, E. R., Antonio, C. L., and Evelyn, T. M. "Variability in Fatty Acid and Triacylglycerol Composition of the Oil of Coconut" *Journal of Agricultural and Food Chemistry*, 2002, **50**, 1581-1586.
19. Liotta, Jr., Soaranko, J. A. *Diesel Fuel Composition*. US Patent 5, 258, 049, 1993.
20. 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.
21. 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.

22. Vasaruchtragul, J. *Synthesis of Dinitrate Compounds as Cetane Number Improver*. Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 1997.
23. Khankasikham, T. *Synthesis of Cycloalkyl Nitrate Compounds from Cycloaliphatic Monoalcohols as Cetane Improvers*. Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 2001.



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APPENDICES

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APPENDIX A
SPECTRA OF SYNTHESIZED NITRATE COMPOUNDS

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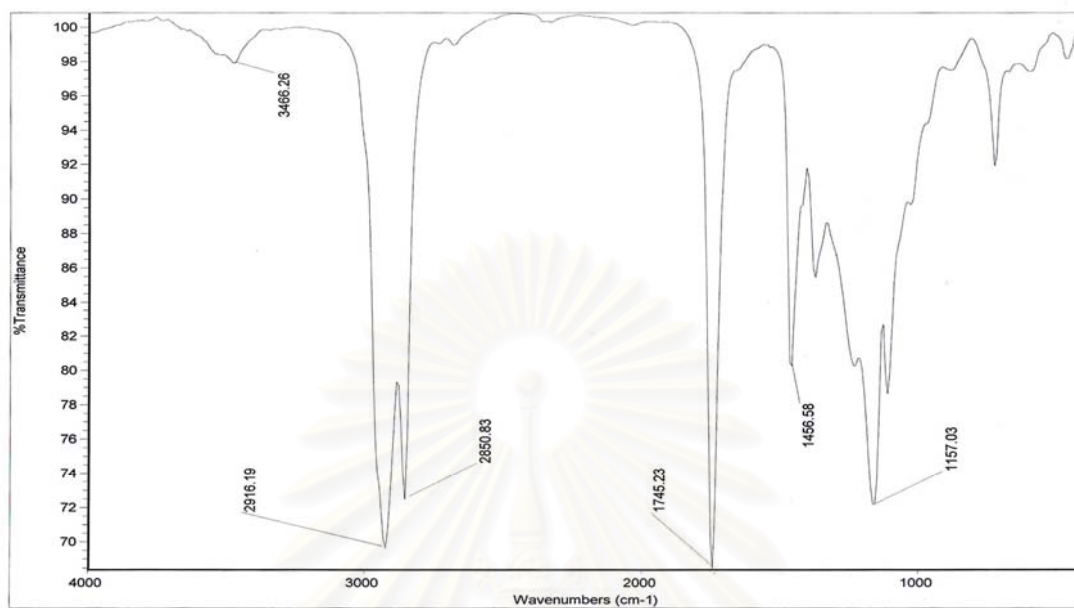


Figure A-1 FT-IR spectrum of coconut oil (NaCl)

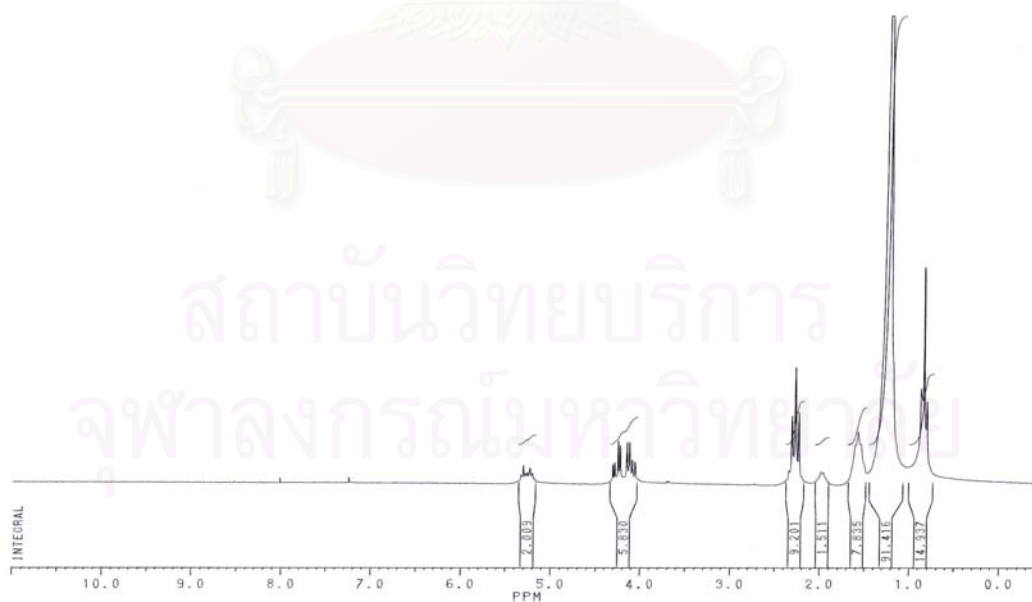


Figure A-2 ¹H-NMR spectrum of coconut oil (CDCl₃)

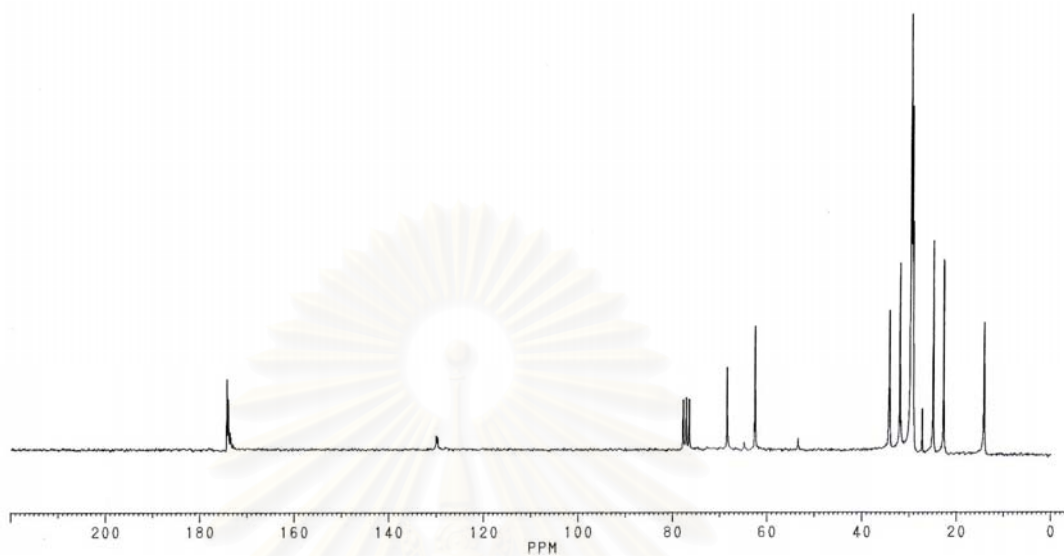


Figure A-3 ^{13}C -NMR spectrum of coconut oil (CDCl_3)

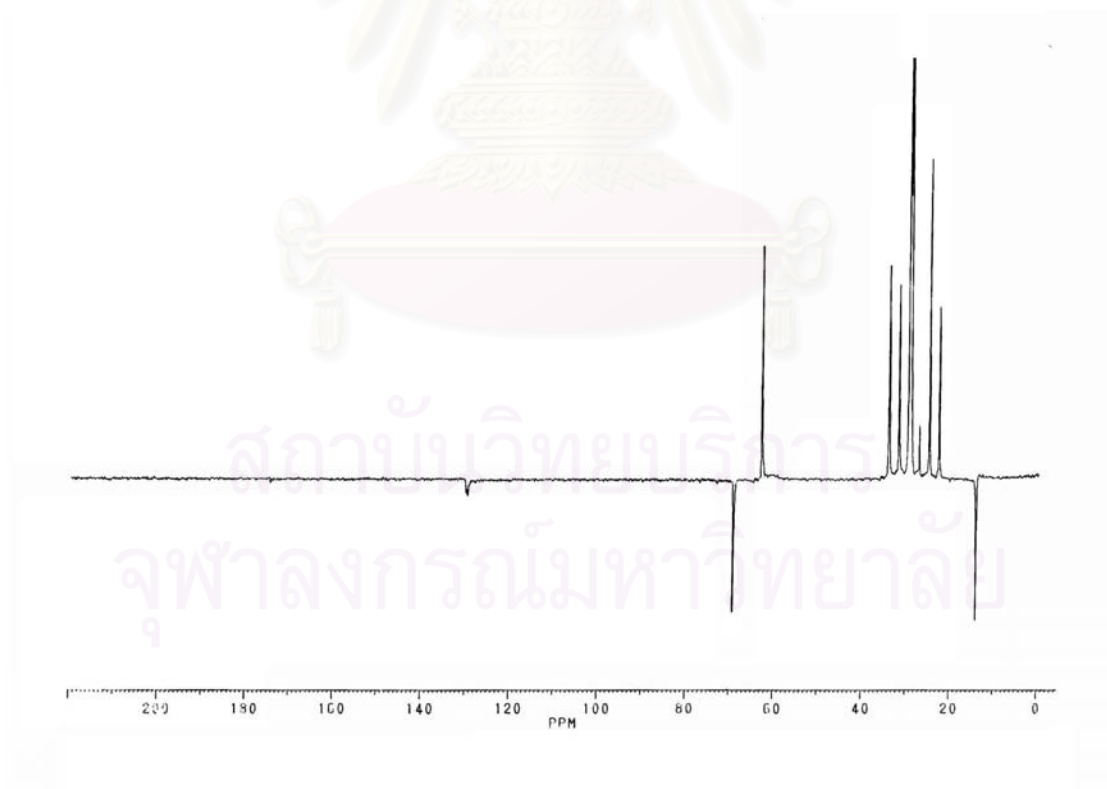


Figure A-4 DEPT 135 spectrum of coconut oil (CDCl_3)

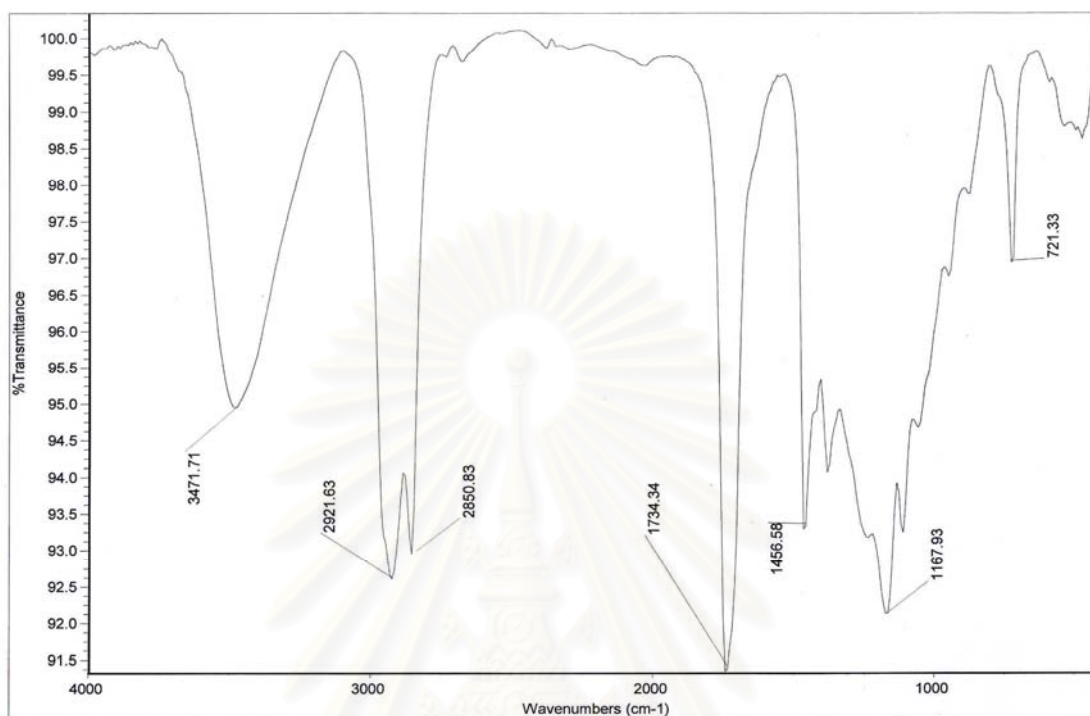


Figure A-5 FT-IR spectrum of coconut fatty acid diglyceride (NaCl)

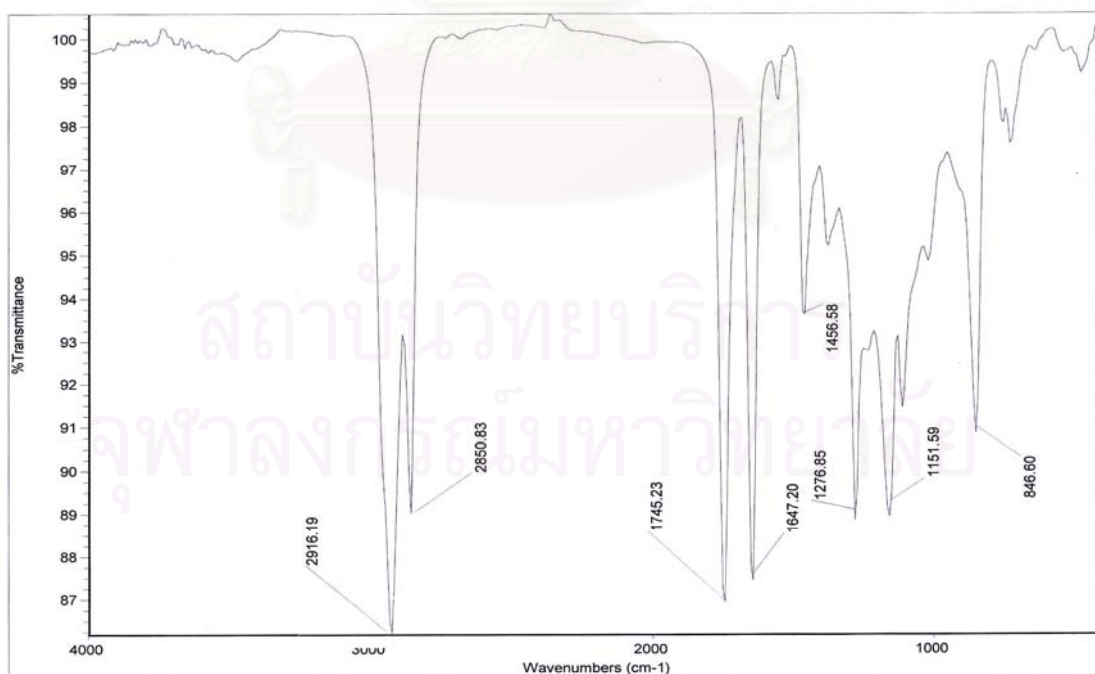


Figure A-6 FT-IR spectrum of coconut fatty acid diglyceride mononitrate (NaCl)

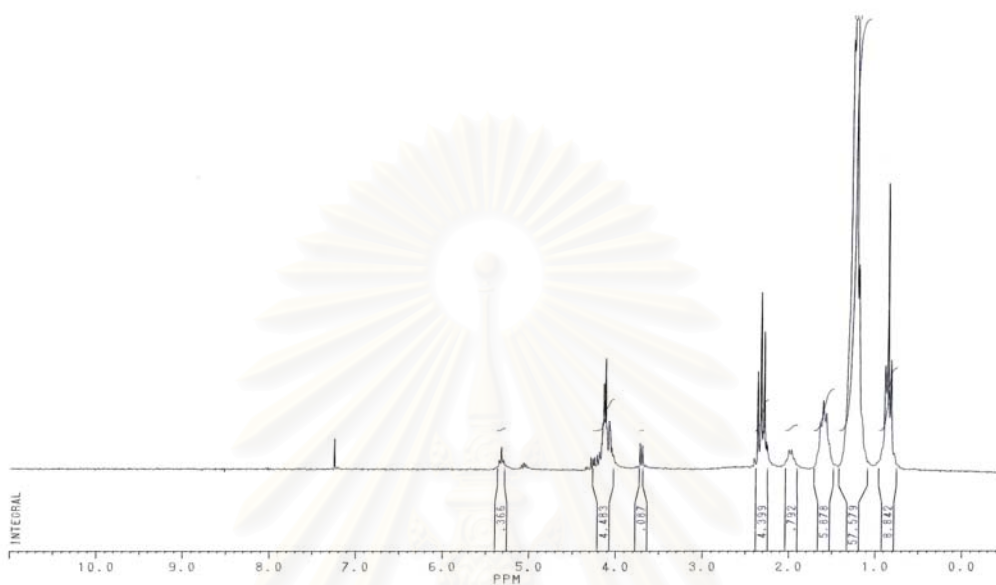


Figure A-7 ¹H-NMR spectrum of coconut fatty acid diglyceride (CDCl₃)

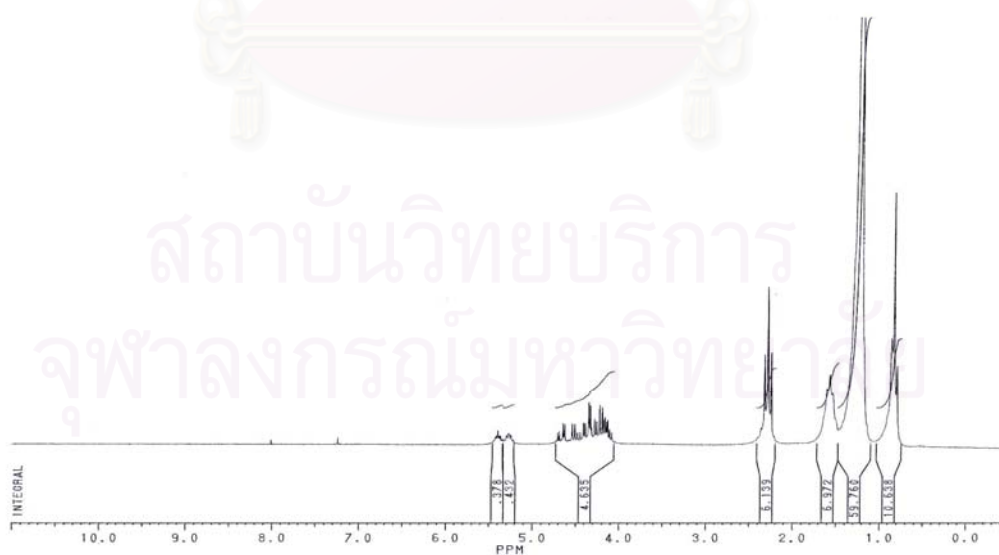


Figure A-8 ¹H-NMR spectrum of coconut fatty acid diglyceride mononitrate (CDCl₃)

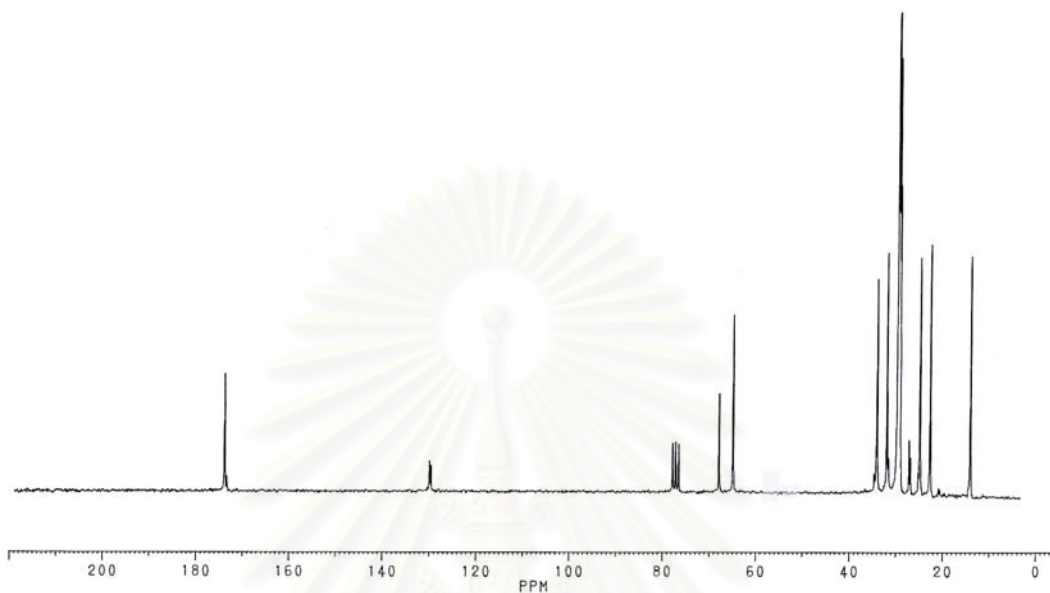


Figure A-9 ^{13}C -NMR spectrum of coconut fatty acid diglyceride (CDCl_3)

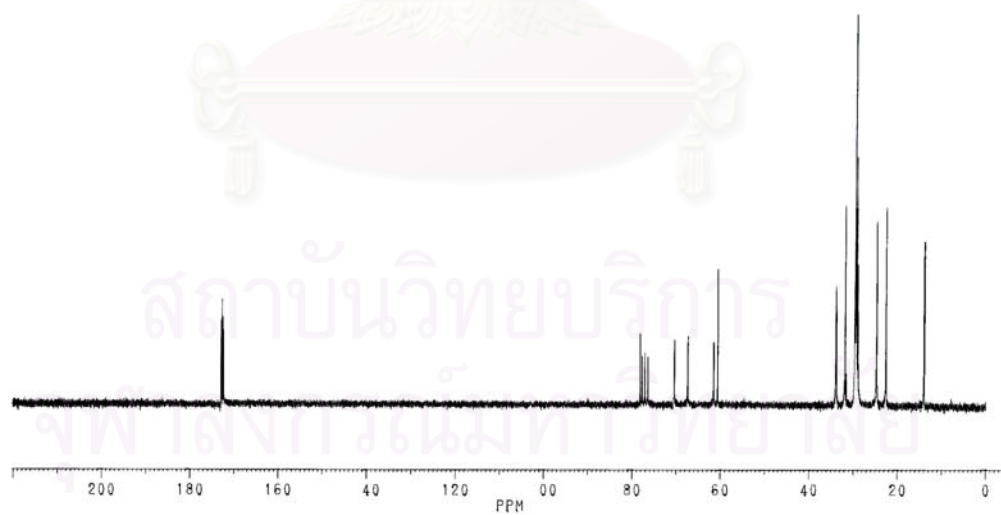


Figure A-10 ^{13}C -NMR spectrum of coconut fatty acid diglyceride mononitrate (CDCl_3)

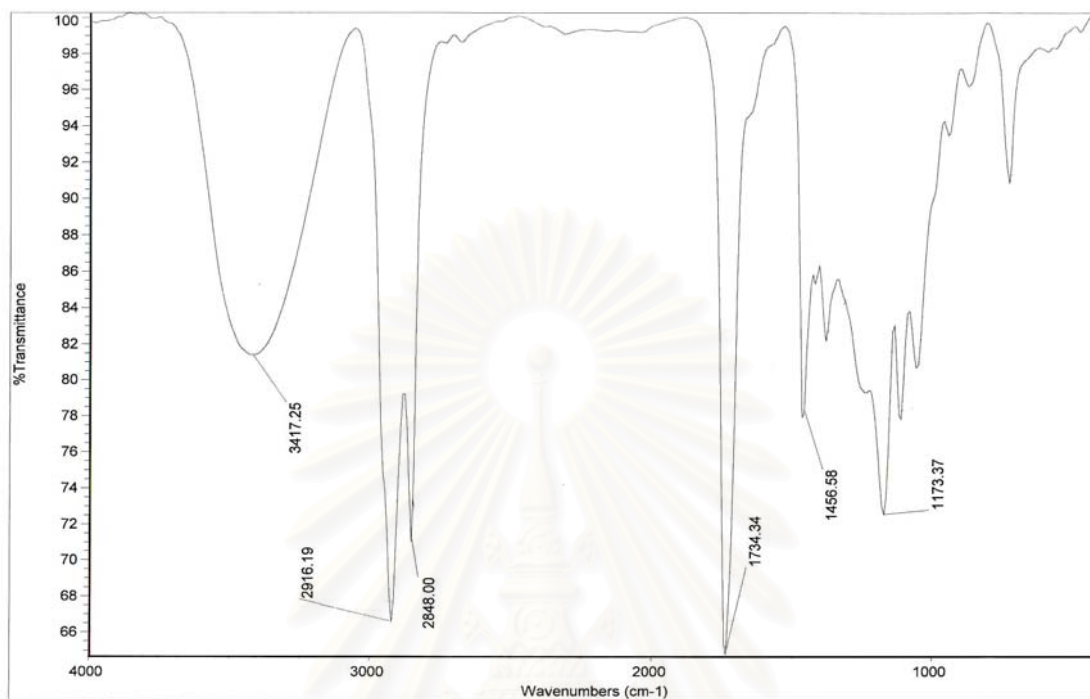


Figure A-11 FT-IR spectrum of coconut fatty acid monoglyceride (NaCl)

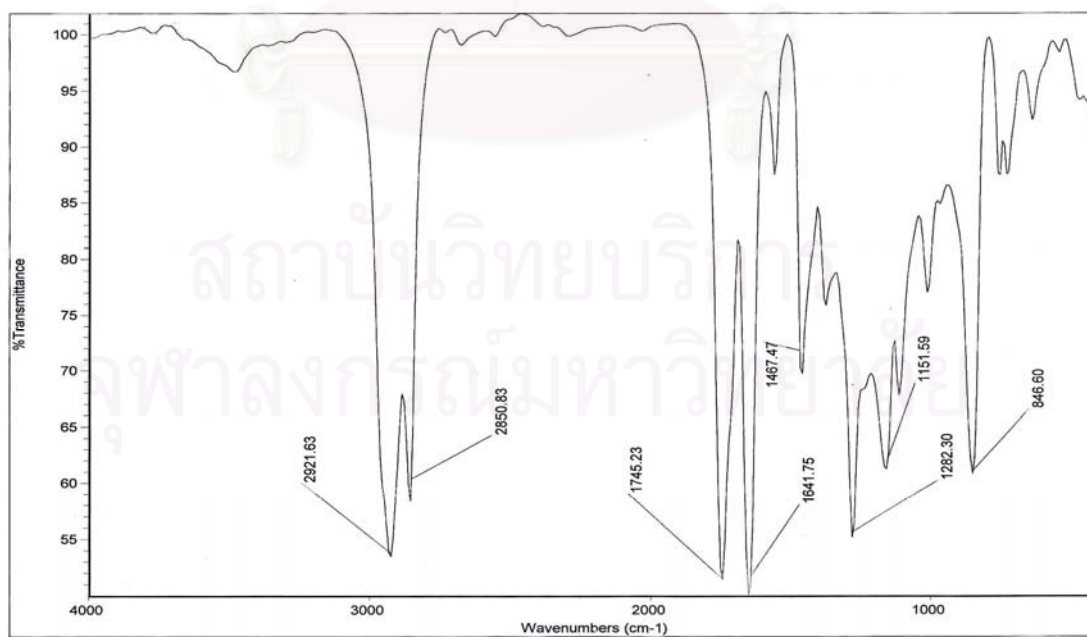


Figure A-12 FT-IR spectrum of coconut fatty acid monoglyceride dinitrate (NaCl)

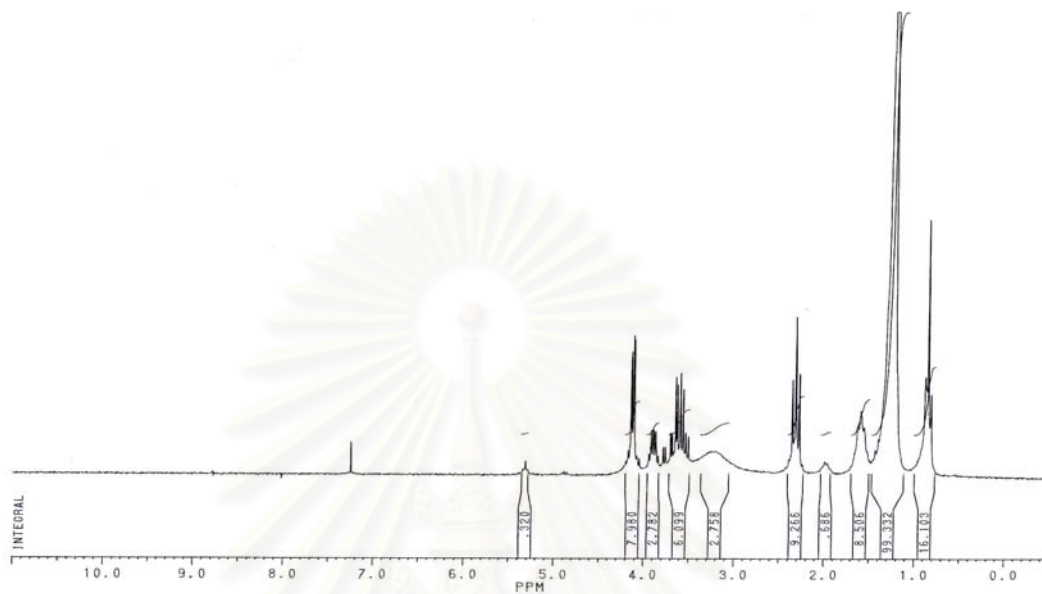


Figure A-13 ¹H-NMR spectrum of coconut fatty acid monoglyceride (CDCl₃)

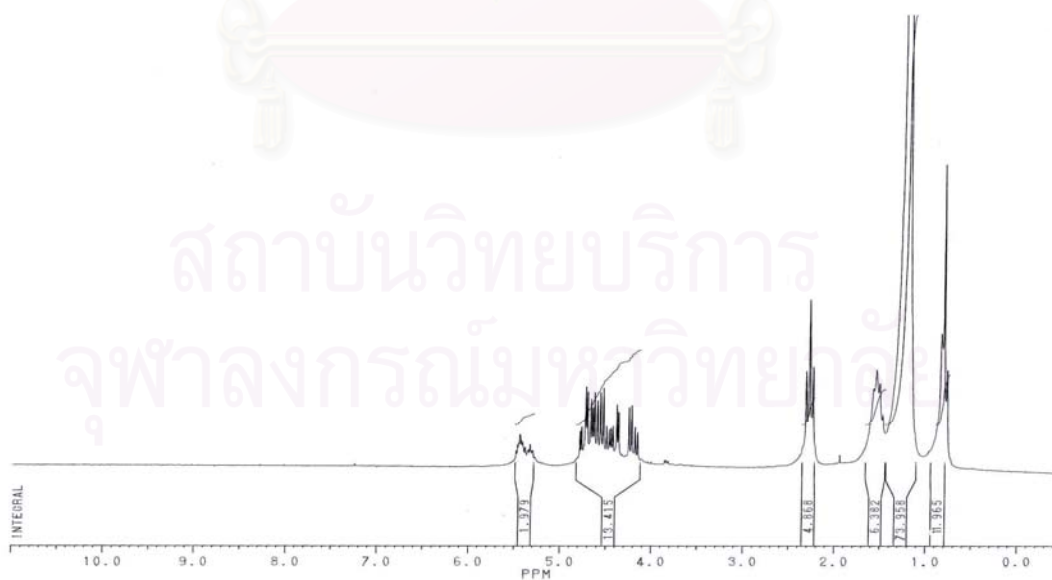


Figure A-14 ¹H-NMR spectrum of coconut fatty acid monoglyceride dinitrate (CDCl₃)

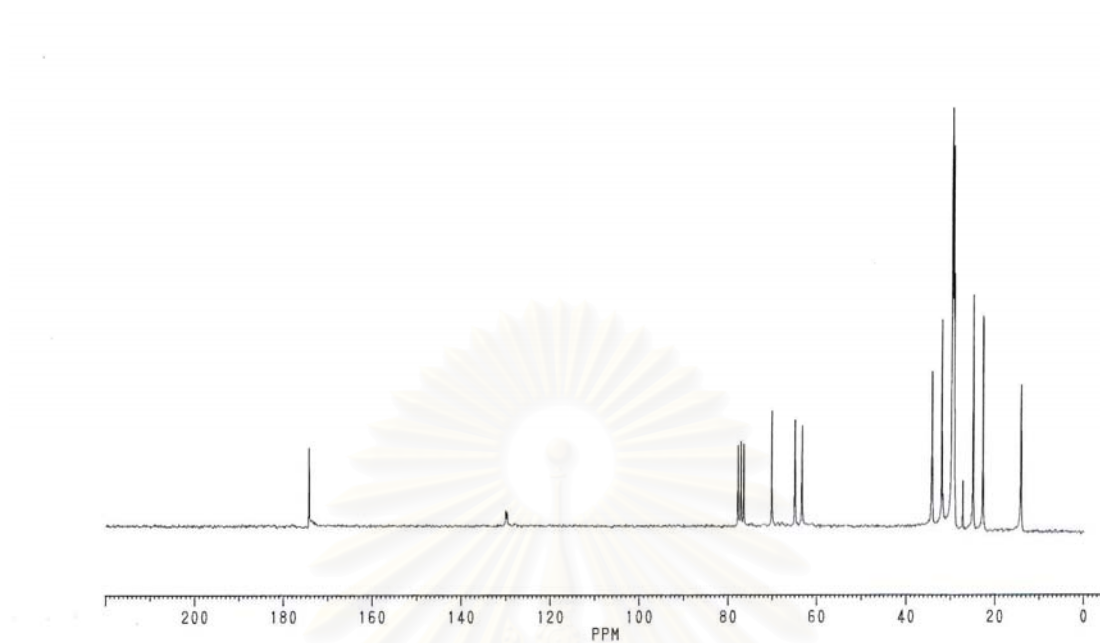


Figure A-15 ^{13}C -NMR spectrum of coconut fatty acid monoglyceride (CDCl_3)

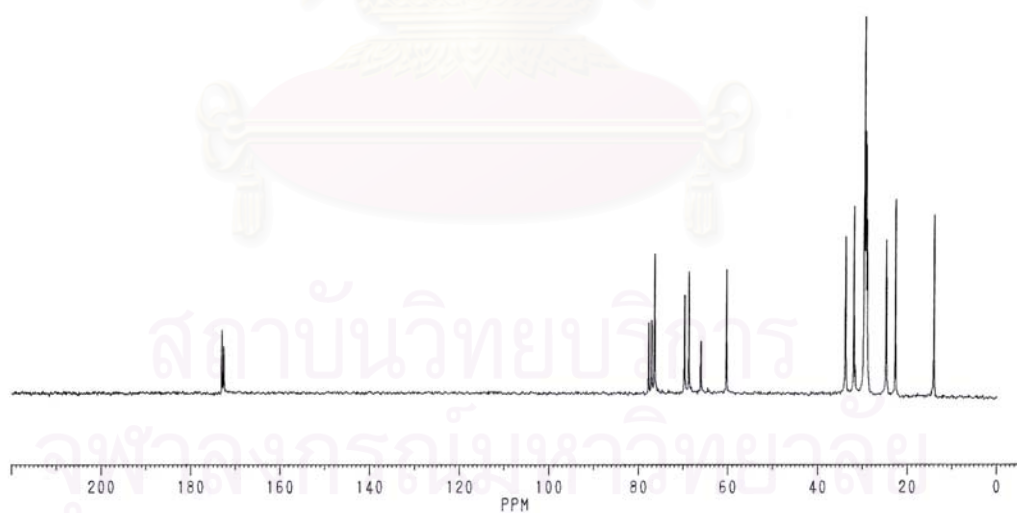


Figure A-16 ^{13}C -NMR spectrum of coconut fatty acid monoglyceride dinitrate (CDCl_3)

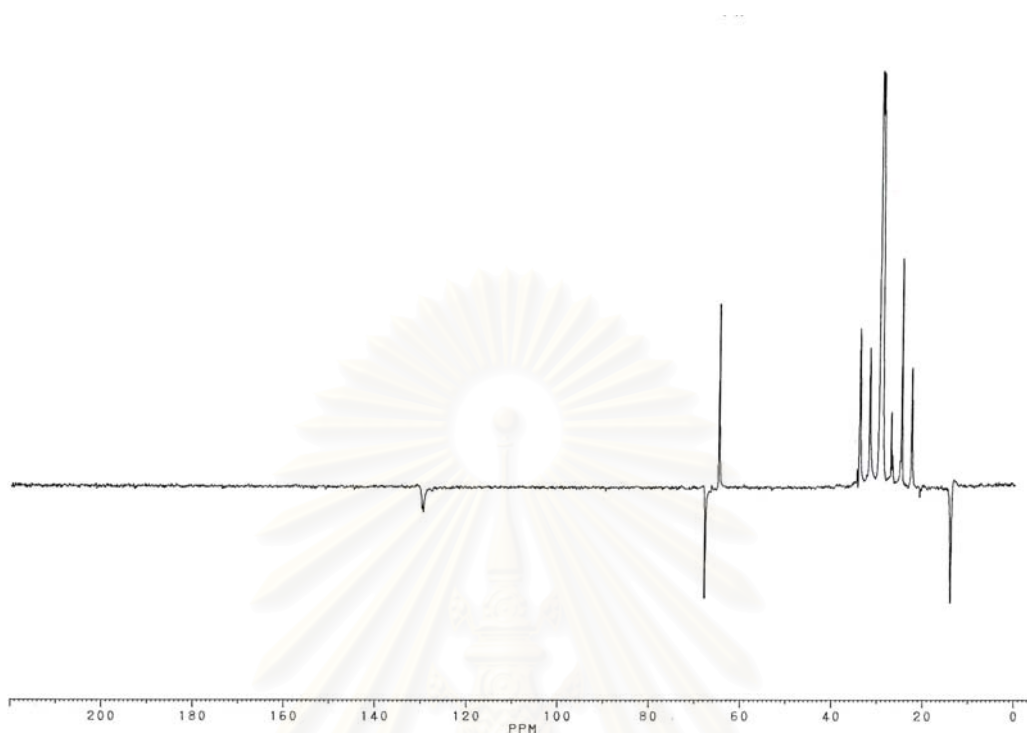


Figure A-17 DEPT 135 spectrum of coconut fatty acid diglyceride (CDCl_3)

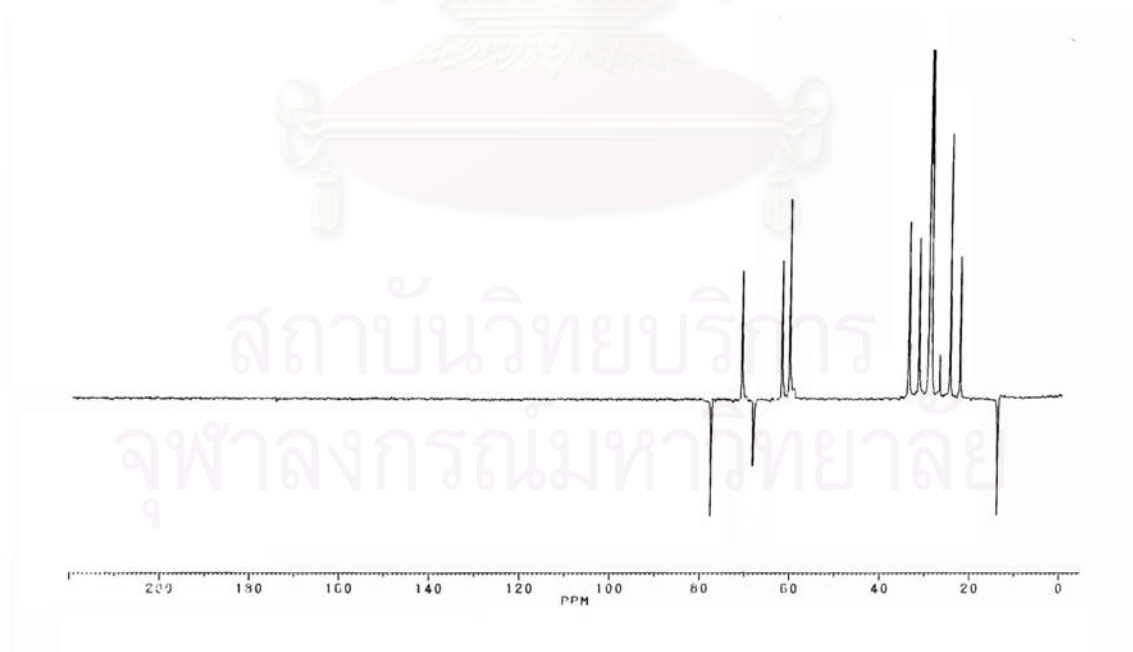


Figure A-18 DEPT 135 spectrum of coconut fatty acid diglyceride mononitrate (CDCl_3)

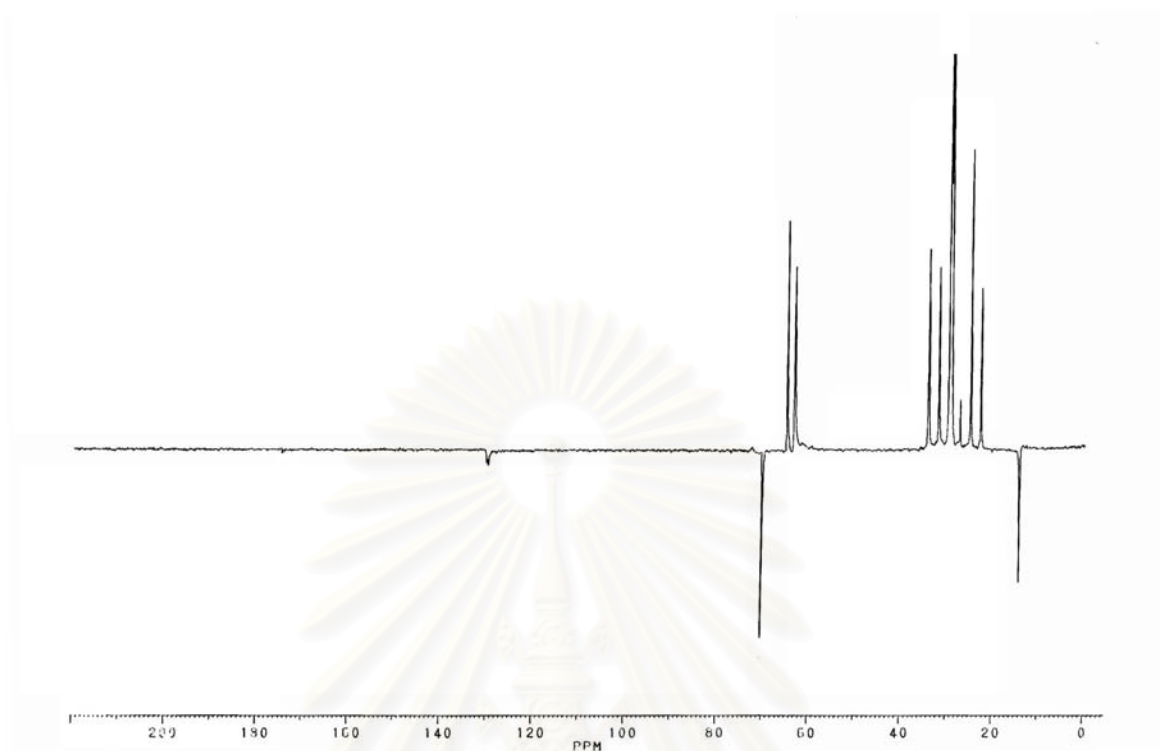


Figure A-19 DEPT 135 spectrum of coconut fatty acid monoglyceride (CDCl_3)

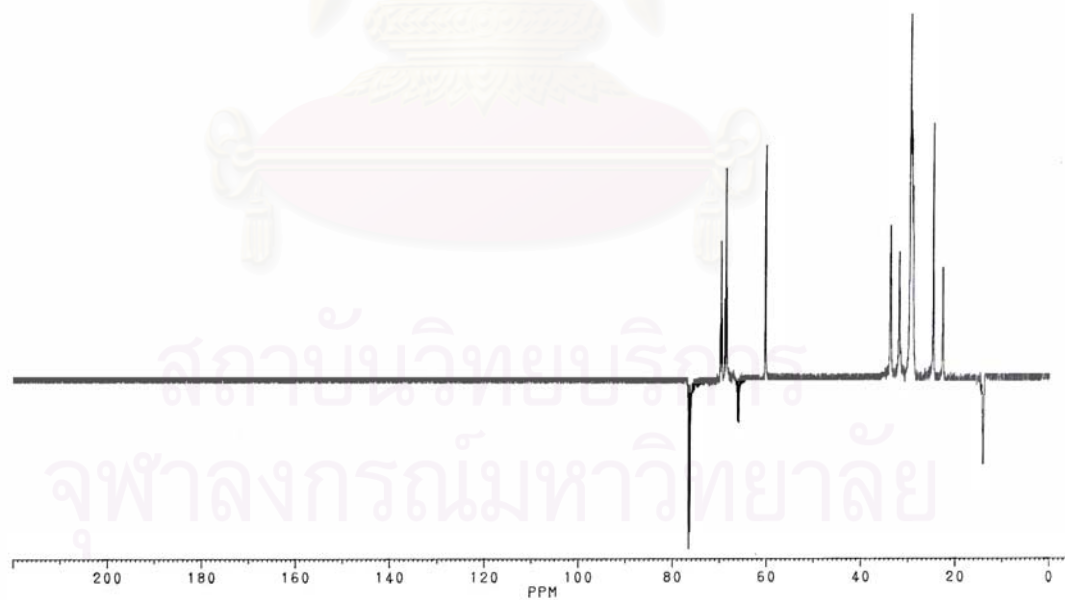


Figure A-20 DEPT 135 spectrum of coconut fatty acid monoglyceride dinitrate (CDCl_3)

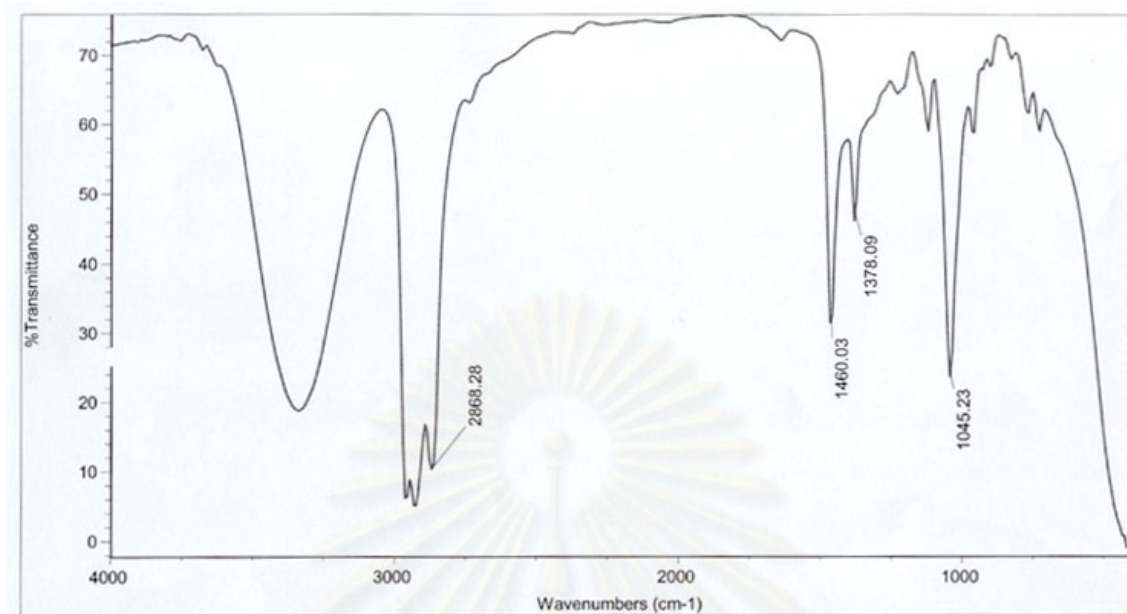


Figure A-21 FT-IR spectrum of 2-ethyl-1-hexanol (NaCl)

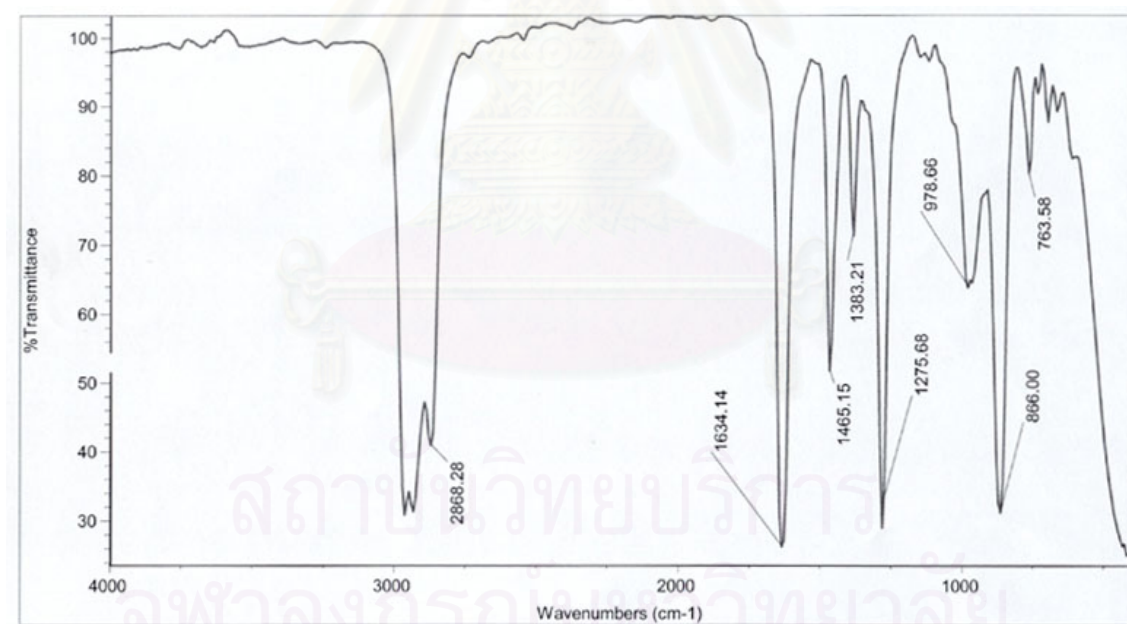


Figure A-22 FT-IR spectrum of 2-ethylhexyl nitrate (NaCl)

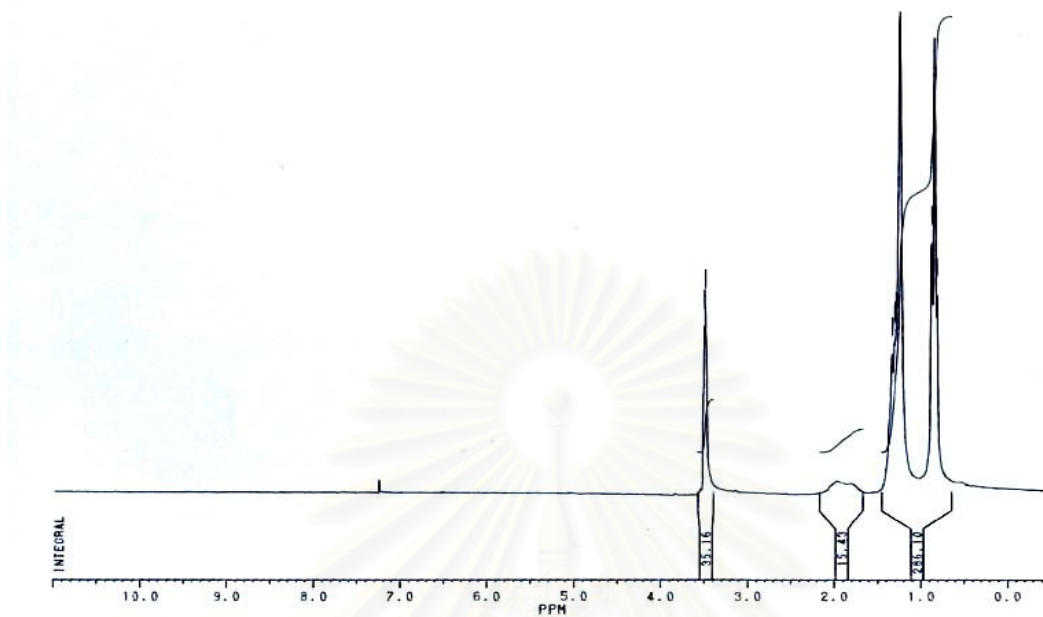


Figure A-23 ¹H-NMR spectrum of 2-ethyl-1-hexanol (CDCl₃)

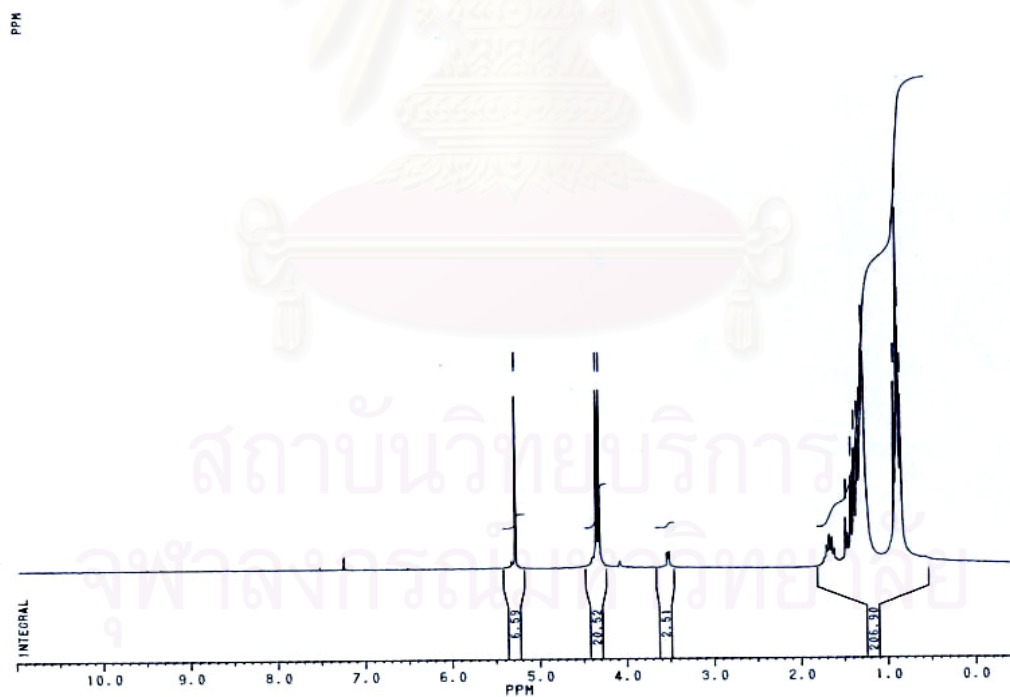


Figure A-24 ¹H-NMR spectrum of 2-ethylhexyl nitrate (CDCl₃)

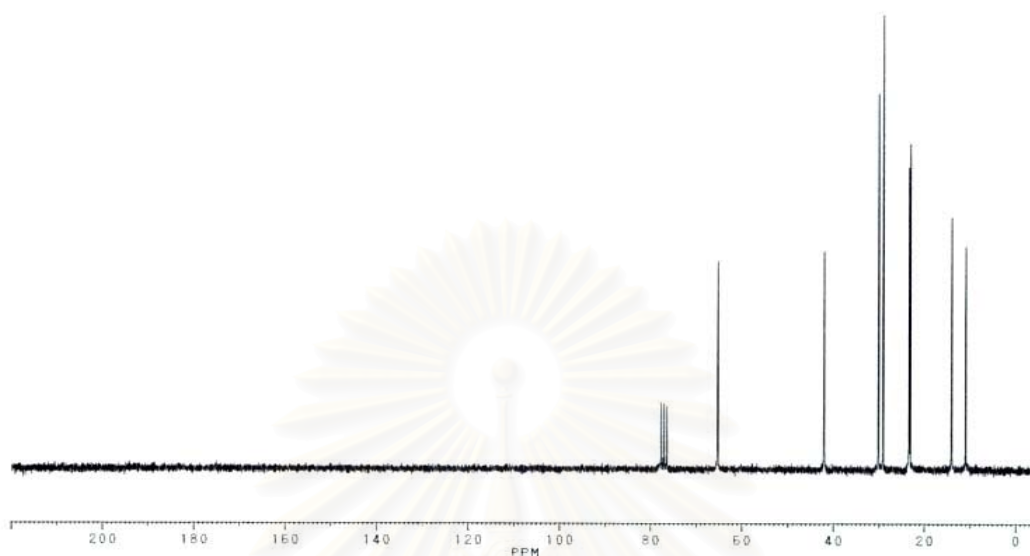


Figure A-25 ^{13}C -NMR spectrum of 2-ethyl-1-hexanol (CDCl_3)

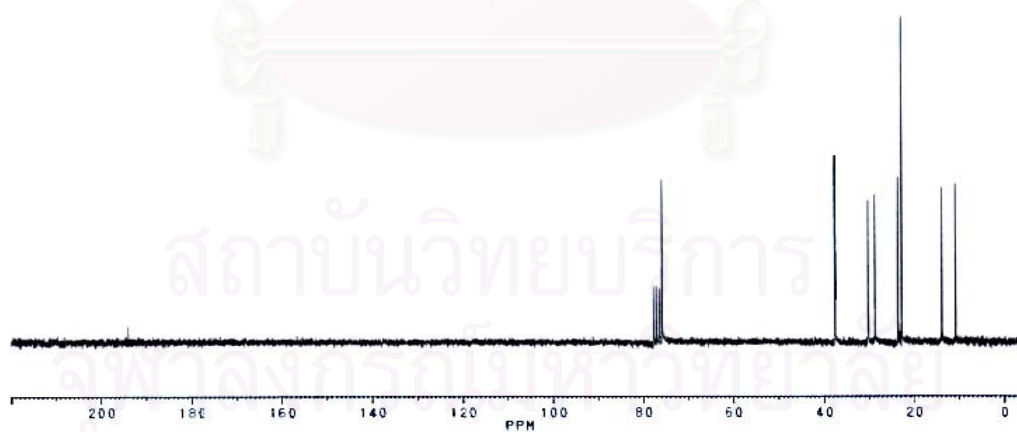


Figure A-26 ^{13}C -NMR spectrum of 2-ethylhexyl nitrate (CDCl_3)

APPENDIX B

THE PREDICTION OF THE CHEMICAL SHIFT

FOR THE CARBONS

The first steps in deducing the structure of an organic compound, using the ^{13}C NMR spectrum, are:

1.Count the number of signals in the spectrum; this is the number of nonequivalent carbon environments in the molecule. (Identify and discount the signal(s) from solvent; see table B1).

2.Use figure B1 to assign signals approximately to the regions δ 0-80, δ 80-150 and δ 160-220 (carbonyl carbons).

3.Note the intensities of the peaks: non-proton-bearing carbons give lower intensity signals, and groups of two or more equivalent carbons give higher intensity signals.

4.Take account of any multiplicity information (q, t, d or s).

5.Use the Correlation Tables (table B2 and B3) to predict the chemical shifts of all carbons in each putative structure.

There are two principal predictable influences, which we can quantify in determining the chemical shift positions of any carbon atom:

1.The number of other carbon atoms attached to it (and whether these are CH_3 , CH_2 , CH or C groups).

2.The nature of all other substituents attached (or nearby along a chain of other carbon atoms).

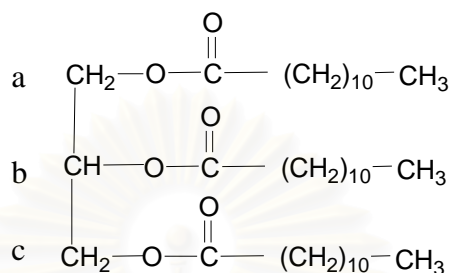
It could be calculated by;

$$\text{Chemical shift } (\delta) = \text{constant} + \sum\alpha + \sum\beta + \sum\gamma \dots\dots\dots(\text{B1})$$

α carbon – the increment varies for CH_2 , CH and C carbon

For example:

Predict the chemical shift positions for carbons in coconut oil (a,b,c).



Model answer:

- To do this, we must first know the δ values for propane, it is listed in table B2.
- C:a ; take the base value for the terminal carbons of propane (δ 15) and note from table B3 that an ester group, δ to it increases the values of the chemical shift by 52 ppm, β position increases the value by 7 ppm and γ decreases by 6 ppm. The predicted value is therefore δ 68.
- C:b ; take the base value for the middle carbon of propane (δ 16). δ ester group to it increases the chemical shift value by 50 ppm and two β ester groups increase the value by 14 (2 times of one ester group δ 7). The predicted values is therefore δ 80.

From the equation B1

$$\text{The chemical shift of carbons (a and c)} = 15 + 52 + 7 - 6 = 68$$

$$\text{The chemical shift of carbon (b)} = 16 + 50 + 7 + 7 = 80$$

Table B-1 Solvents used for NMR analysis.

<i>Solvent</i>	<i>Approximate δ for ^1H equivalent (as contaminant)</i>	^{13}C δ value(s)	<i>bpt</i> $^\circ\text{C}$	<i>fpt</i> $^\circ\text{C}$
acetic acid- d_4	13 and 2	21, 177	118	16.6
acetone- d_6	2	30, 205	56	-95
acetonitrile- d_3	2	0.3, 117	82	-44
benzene- d_6	7.3	128	80	5.5
carbon disulfide	—	1931	46	-108.5
carbon tetrachloride	—	97	77	-23
chloroform- d	7.3	77	61	-63
deuterium oxide	4.7-5	—	101.5	3.8
dimethylsulfoxide- d_6	2	43	189	18
methanol- d_4 (CD_3OD)	3.4	49	65	-98
hexachloroacetone	—	124, 126	203	-2
pyridine- d_5	7.5	124-150	115	-42
toluene- d_8	7.3 and 2.4	21, 125-138	110	-95
trifluoroacetic acid- d	13	115, 163 (quartets)	72	-15
dioxane	3.7	67	101	11.8

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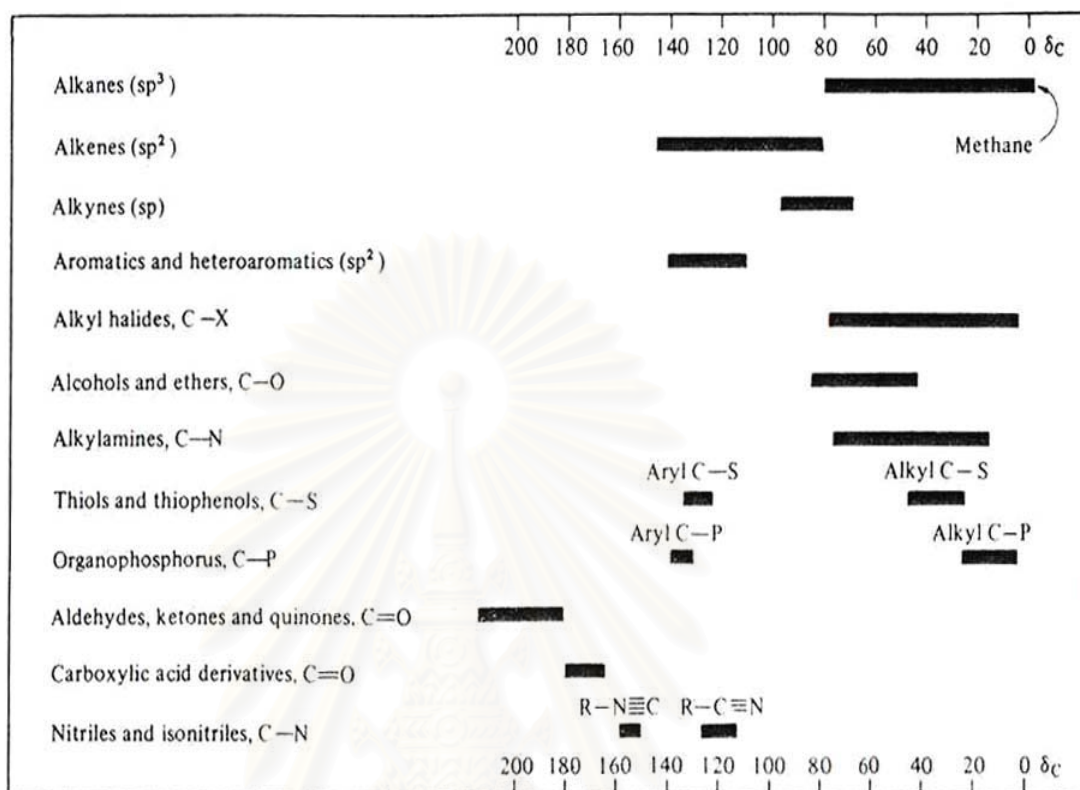


Figure B-1 ^{13}C chemical shift summary chart (δ values).

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Table B-2 Data for ^{13}C NMR spectra.

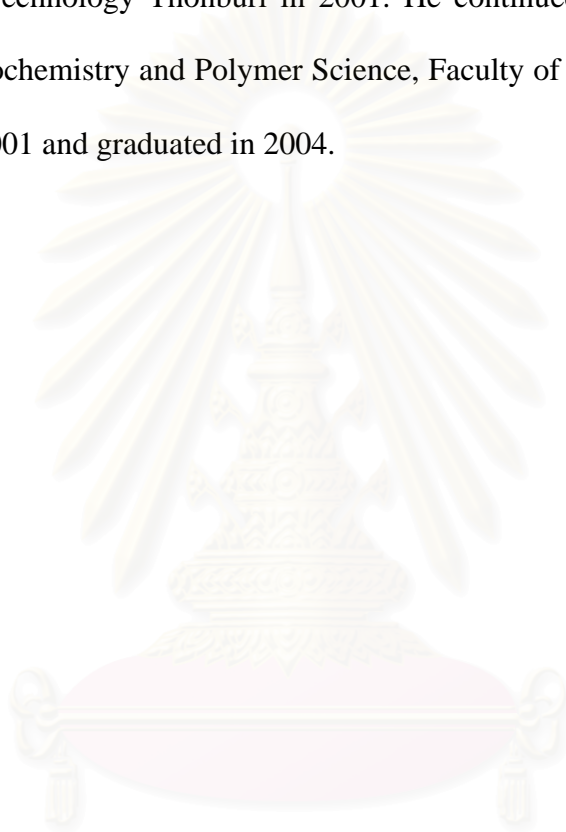
REPRESENTATIVE ALKANES AND CYCLOALKANES									
Methane	CH_4	$\delta -2.3$	ethane			CH_3CH_3	$\delta 5.7$		
propane			butane		isobutane		long alkyl chain		
Cycloalkanes									
Ring size	3	4	5	6	7	8	9	10	
Shift (δ)	-2.9	23.3	26.5	27.3	29	28	27	26	
Bicycloalkanes									
norbornane							bicyclo[2,2,2]octane		
EMPIRICAL PREDICTIONS FOR OTHER ALKANE CARBONS									
Chemical shift (δ) = constant + $\Sigma\alpha$ + $\Sigma\gamma$ + $\Sigma\delta$									
α carbons - the increment varies for CH_2 , CH and C carbons									
α CH_3 groups	} do not count these (the constant includes them)								
β carbons	}								
Constant	Increment for each carbon substituent α carbons			γ carbons	δ carbons				
	$-\text{CH}_2-$	$-\text{CH}-$	$-\text{C}-$						
$-\text{CH}_3$ carbons	6.80	9.56	17.83	25.48	-2.99	0.49			
$-\text{CH}_2-$ carbons	15.34	9.75	16.70	21.43	-2.69	0.25			
$-\text{CH}-$ carbons	23.46	6.60	11.14	14.70	-2.07	0			
$-\text{C}-$ carbons	27.77	2.26	3.96	7.35	0.68	0			

Table B-3 Influence of functional group X on the chemical shift position (δ).
$$X-C-\underset{\alpha}{C}-\underset{\beta}{C}-\underset{\gamma}{C}-C$$

X	α -shift			β -shift	γ -shift
	$X-CH_2-$ 1°	$X-\underset{\substack{ \\ R}}{CH}-$ or 2°	$X-\underset{\substack{ \\ R}}{C}-$ or 3°		
$-CH_3$	9	6	3	9	-3
$-R$: see table 3.11					
axial $-CH_3$	1	-	-	5	-6
equatorial $-CH_3$	6	-	-	9	0
(in cyclohexanes)					
$-CH=CH_2$	22	16	12	7	-2
$-C\equiv CH$	4	-	-	3	-3
$-C_6H_5, -Ar$	23	17	11	10	-3
$-F$	70	-	-	8	-7
$-Cl$	31	35	42	10	-5
$-Br$	19	28	37	11	-4
$-I$	-7 to 20	-	-	11	-2
$-NH_2, -NHR, -NR_2$	29	24	18	11	-4
$-NO_2$	62	-	-	3	-5
$-NHCOR, -NRCOR$	10	-	-	0	0
$-NH_3^+$	25	-	-	7	-3
$-CN$	3	4	-	2	-3
$-SH$	2	-	-	2	-2
$-OH$	50	45	40	9	-3
$-OR$	50	24	17	10	-6
$-OCOR$	52	50	45	7	-6
$-COOH, -COOR, -CON<$	20	16	13	2	-3
$-COR, -CHO$	30	24	17	2	-3
$-SO_3H, -SO_2N<$	50	-	-	3	0

VITA

Mr. Mahidol Phasorn was born on September 24, 1979 in Nongkhai, Thailand. He received his Bachelor's Degree of Science in Chemistry, King Mongkut's University of Technology Thonburi in 2001. He continued his Master's Degree of Science in Petrochemistry and Polymer Science, Faculty of Science at Chulalongkorn University in 2001 and graduated in 2004.



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