การสังเคราะห์สารประกอบไดไนเตรท
จากอัลคิลลีนไกลคอลเพื่อใช้เป็นสารเพิ่มค่าซีเทน

นางสาวจันทิมา สุทธิพิทักษ์วงศ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2543

ISBN 974-347-206-1

SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKYLENE GLYCOLS AS CETANE IMPROVERS

Miss Chantima Suttipitakwong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2000

ISBN 974-347-206-1

Thesis Title SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKYLENE GLYCOLS AS CETANE IMPROVERS

By Miss Chantima Suttipitakwong

Field of study Petrochemistry and Polymer Science

Thesis Advisor Assistant Professor Somchai Pengprecha, Ph.D.

Thesis Co-advisor Mrs. Ratanavalee In-ochanon

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

……………………………………………...Dean of Faculty of Science

(Associate Professor Wanchai Phothiphichitr, Ph.D.)

Thesis Committee

……………………………………………...Chairman

(Associate Professor Supawan Tantayanon, Ph.D.)

………………………………………………Thesis Advisor

(Assistant Professor Somchai Pengprecha, Ph.D.)

………………………………………………Thesis Co-advisor

(Mrs. Ratanavalee In-ochanon)

………………………………………………Member

(Associate Professor Sophon Roengsumran, Ph.D.)

………………………………………………Member

(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

จันทิมา สุทธิพิทักษ์วงศ์ : การสังเคราะห์สารประกอบไดไนเตรทจากอัลคิลลีนไกลคอลเพื่อเป็นสารเพิ่มค่าซีเทน. (SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKYLENE GLYCOLS AS CETANE IMPROVERS) อ.ที่ปรึกษา : ผศ.ดร.สมใจ เพ็งปรีชา, อ.ที่ปรึกษาร่วม : คุณรัตนาวลี อินโอชานนท์, 89 หน้า. ISBN 974-347-206-1.

สารประกอบอัลคิลีนไกลคอลไดไนเตรทสามารถสังเคราะห์ได้โดยวิธีไนเทรชันโดยตรงของ สารประกอบอัลคิลีนไกลคอล เช่น ไดเอทิลีนไกลคอล, ไดโพรพิลีนไกลคอล, ไตรโพรพิลีนไกลคอล และเอทิลเฮกซิลีนไกลคอล เป็นต้น ด้วยกรดไนตริกและกรดซัลฟุริกเข้มข้น โดยมีไดคลอโรมีเทนเป็นตัวทำละลาย การพิสูจน์เอกลักษณ์ของสารประกอบอัลคิลีนไกลคอลไดไนเตรท ทำได้โดยเทคนิคทางสเปคโทรสโกปี ได้แก่ อินฟราเรดสเปคโทรสโกปี และนิวเคลียร์แมกเนติกเรโซแนนซ์สเปคโทรสโกปี สารประกอบอัลคิลีนไกลคอลไดไนเตรทที่สังเคราะห์ได้ สามารถนำไปผสมกับน้ำมันดีเซลพื้นฐานได้ง่าย สารเหล่านี้เพิ่มค่าดัชนีซีเทน 3.9 หน่วย และ 6.3 หน่วย เมื่อใช้ที่ความเข้มข้น 0.05 เปอร์เซ็นต์ และ 0.10 เปอร์เซ็นต์ โดยน้ำหนักตามลำดับ ดังนั้นสารประกอบไดไนเตรทที่สังเคราะห์ได้มีแนวโน้มที่ให้ค่าซีเทนเพิ่มขึ้นมากกว่าน้ำมันดีเซลพื้นฐานและเอทิลเฮกซิลไนเตรทที่เป็นสารเพิ่มค่าซีเทนที่จำหน่ายในเชิงพาณิชย์ โดยเฉพาะไตรโพรพิลีนไกลคอลไดไนเตรทมีแนวโน้มเพิ่มค่าซีเทนมากที่สุด ดังนั้นสารเหล่านี้มีแนวโน้มที่จะเพิ่มค่าซีเทนได้ดีกว่าเมื่อเปรียบเทียบกับสารเพิ่มค่าซีเทนในปัจจุบัน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา...........................
ปีการศึกษา 2543 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.......................

4172246123 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: CETANE NUMBER / CETANE IMPROVER / DIESEL FUEL / DIESEL ADDITIVE / DINITRATE COMPOUNDS

CHANTIMA SUTTIPITAKWONG : SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKYLENE GLYCOLS AS CETANE IMPROVERS. THESIS ADVISOR : ASSIST. PROF. SOMCHAI PENGPRECHA, Ph.D., THESIS CO-ADVISOR : Mrs. RATANAVALEE IN-OCHANON, 89 pp. ISBN 974-347-206-1.

Alkylene glycol dinitrate compounds could be synthesized by direct nitration of glycols such as diethylene glycol, dipropylene glycol, tripropylene glycol and ethylhexylene glycol in the presence of concentrated nitric acid and concentrated sulfuric acid with dichloromethane as a solvent. The alkylene glycol dinitrate compounds thus obtained were identified by spectroscopic techniques such as Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy. The alkylene glycol dinitrate compounds could be easily blended with base diesel fuel. They were effective in increasing cetane index to 3.9 units and 6.3 units at the concentrations of 0.05% and 0.10%wt, respectively. It was found that these alkylene glycol dinitrate compounds gave higher cetane improvement than of base diesel fuel and the commercial ethylhexyl nitrate. Especially, tripropylene glycol dinitrate gave the highest cetane improvement. So these compounds had potential to be used to improve cetane number of base diesel fuel more than the commercial cetane improver.

Field of study Petrochemistry and Polymer Science Student's signature……………………...
Program........ Petrochemistry and Polymer Science Advisor's signature……………………..
Academic year………… 2000 ……………... Co-advisor's signature………………….

ACKNOWLEDGEMENT

I would like to express my sincerest gratitude to my advisor, Assistant Professor Dr. Somchai Pengprecha, and co-advisor, Mrs. Ratanavalee In-ochanon, for their generous guidance and encouragement throughout this research. Moreover, I am very grateful to Associate Professor Dr. Supawan Tantayanon, chairman of thesis committee, whose comments have been special valuable. In addition, I wish to thank the thesis committee for their valuable comments.

I also thank for the research financial from the Petroleum Authority of Thailand for their assistance in determining the cetane index and particularly to the Thai Oil Refinery for their assistance in base diesel fuel.

Finally, I would like to express my warmest thanks to my family for their care and supports to make my study successful. Thanks are also due to everyone who has contributed suggestions and supports throughout my research.

CONTENTS

Page

CHAPTER I INTRODUCTION

CHAPTER II THEORETICAL CONSIDERATIONS

CONTENTS (continued)

Page

CHAPTER III EXPERIMENTAL

CHAPTER IV RESULTS AND DISCUSSION

CONTENTS (continued)

LIST OF TABLES

TABLE Page

LIST OF TABLES (continued)

TABLE Page

LIST OF FIGURES

FIGURE Page

LIST OF FIGURES (continued)

FIGURE Page

LIST OF FIGURES (continued)

FIGURE Page

ABBREVIATIONS

ASTM = American Society for Testing and Materials

CCI = Calculated Cetane Index

^{13}C-NMR = Carbon-13 Nuclear Magnetic Resonance

cSt = Centistroke

CFR = Cooperative Fuel Research Council

°C = Degree Celsius

°F = Degree Fahrenheit

MPa = Mega Pascal

ml = Milliliter

^{1}H-NMR = Proton Nuclear Magnetic Resonance

rpm = Round per minute

cm^{-1} = Unit of wave number

%wt = Weight percent

%yield = Yield percent

CHAPTER I

INTRODUCTION

1.1 Introduction

In present, humans get many profits from petroleum. They include transportation, energy, food, medicine and daily equipment. Therefore, the living of human necessarily associates with using of petroleum. Thus, there are always searching, exploration and drilling the new petroleum sources. However, if humans don’t know well about petroleum and use it incorrectly, it will be disadvantage. In this research, it says about one product from petroleum. It is “Diesel Fuel”. It has also important properties and additives for it [1].

Diesel fuels originally were straight-run products from the distillation of crude oil. The boiling range of distillate fuel is approximately 300 to 750°F (149-399°C). Diesel fuels were used with diesel engines, which are well known for being highly durable and fuel efficient. Owing to this durability and fuel efficiency, diesel engines have long been used in heavy-duty motor vehicles, such as trucks, buses and locomotives [4].

Despite many years of work and billions of dollars spent by both government and industry in fighting air pollution, air quality problems remain a major problem. Motor vehicles powered by diesel combustion engines are a contributing factor to many of these problems.

So diesel fuel additives are more important today than they have ever been. The need for these additives has been growing for many years. This is because there has been a very significant change in the composition of diesel fuel over the past ten years resulting from the depression of the fuel oil market. Diesel fuel now contains more cracked components than in the past, which means that the olefin content of diesel fuel has increased. Olefins are less stable to oxidation and hence more likely to form deposits in a vehicle fuel system than are the paraffinic and aromatic components. They are also poorer in cetane quality. The fuels therefore need additives in order to overcome these deficiencies.

Another factor, which has increased the importance of additives, is the pressure on vehicle manufacturers to improve exhaust gas quality and fuel economy. Deposit formation can steadily worsen an engine's performance in these respects, and many new models are particularly sensitive to deposits in the inlet system. Additives can help to maintain engine performance by preventing deposit build-up.

A third factor is the wish for product differentiation on the part of oil companies, who need to demonstrate that their diesel fuel has special features that makes it more desirable than competitive materials. The widespread practice of exchanging fuels between companies to minimize distribution costs means that the use of additives is often the only way that a company can achieve this product differentiation, since such additives can be injected into the road tanker during loading prior to delivery to the service station.

A fourth factor is crude oil price changes. Although crude oil prices have been rather volatile in recent years it is generally accepted that, in the longer term, because of the limited nature of crude oil reserves, they must increase very significantly. After the first oil crisis in 1973, prices rose rapidly for several years, and this had the effect of considerably reducing the use of fuel oil in power stations, steelwork, shipping, etc. in favor of other energy sources such as coal, hydroelectric and nuclear [3].

Finally, requirement to improve fuel consumption. Fuel economy is an extremely important marketing aspect for motor vehicles. The amount of fuel consumption control required by governments varies throughout the world [2]. Diesel fuel consumption is being continuously increased as shown in Figure 1.1.

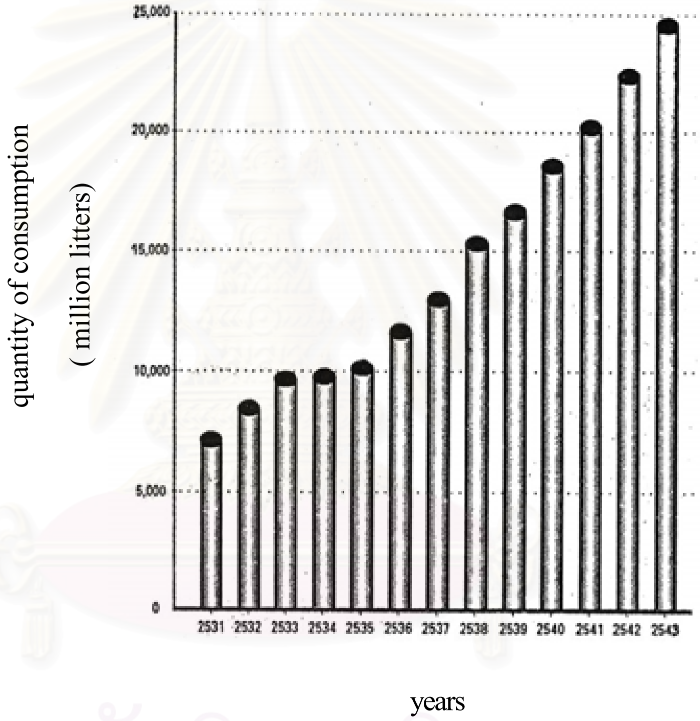


Figure 1.1 The quantity of high speed diesel consumption in Thailand.

For diesel fuel, ignition quality is important operational parameter. It is expressed in term of cetane number, which number has been developed on a basis very similar to that adopted for measuring the ignition quality of gasoline in term of octane number. If ignition delays too long, the amount of fuel in the chamber increases and upon ignition results in a rough running engine and increases smoke. A short ignition delay results in smooth engine operation and decreases smoke. So a high cetane number indicates a low ignition delay period, and hence better performance as a diesel fuel.

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

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

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

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

To the some extent, cetane improvers have been used for many years to increase the cetane number of diesel fuels. Higher cetane value leads to faster engine start especially in cold weather, quieter engine operation, less smoke and possibly less injector coking. Recently, use of cetane improvers has greatly increased due to increased demand for diesel fuel and the lower natural cetane number of diesel base stocks caused by more severe refining of crude oil to make unleaded gasoline of acceptable octane number.

From studies by Vasaruchtragul, J. [21], he revealed that cetane number of diesel fuel was increased by addition of a small amount of triethylene glycol dinitrate, in comparison with the addition of the commercial cetane improver, 2-ethylhexyl nitrate.

From the previous work, it is obvious that there is need for further investigation of the cetane improvers containing nitrogen and/or oxygen in straight chain molecular structure and they would be polynitrates which get more cetane number value than mononitrate. These compounds trend to get the high cetane number. Accordingly, in this research, it is anticipated that these compounds can effectively increase the cetane number.

1.2 Objectives and scope of the research

1.2.1 Objectives

1. To synthesize alkylene glycol dinitrate compounds.
2. To study the properties of alkylene glycol dinitrate compounds blended with base diesel as cetane improvers.

1.2.2 Scope of the research

1. Literature survey of the relevant research works
2. Providing of chemicals and equipments
3. Synthesizing of alkylene glycol dinitrate compounds
4. Characterizing of alkylene glycol dinitrate compounds by spectroscopic methods
5. Determination of cetane index, cetane number and important physical properties of diesel fuel blended with alkylene glycol dinitrate compounds
6. Summarizing of the results

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Diesel engines

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

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

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

In general, two combustion chamber forms are principally used in automotive diesel engine applications. These are the direct injection system as illustrated in Figure 2.1 and the pre-chamber, indirect injection system shown in Figure 2.2 [2].

Figure 2.1 Direct injection combustion system.

Figure 2.2 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 [5].

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.

2.2 Diesel fuel

Distilling crude oil, which is a mixture of heavy and light hydrocarbons requires different degrees of heat to produce different products. Lighter hydrocarbons have lower boiling points and can be separated using relatively little heat. For instance, gasoline components are lighter than those of diesel. The boiling range of gasoline currently in use is between 30°C and 210°C, while that of kerosene is between 150°C and 300°C. Diesel fuel is a distillate boiling between 150°C and 300°C, but this is not a unique description: other fractions boiling within this range, but meeting different secondary specifications comprise naphtha, jet fuel, kerosene, and so on [6]. An approximate classification is shown in Table 2.1.

Table 2.1 Classification of distillate fuels.

Classification	**Approximate boiling range (°C)**
Gas	< 30
Straight run gasoline	30 - 200
Light naphtha	30 - 110
Heavy naphtha	80 - 200
Middle distillate fuels	135 - 360
Kerosene and jet fuel	145 - 280
Diesel fuel	160 - 330
Light fuel oil	215 - 360
Heavy fuel oil	290 - 400

Within certain narrow limits, the relative amounts of gasoline, diesel and/or jet fuel and of heavier (heating) oils, that can be obtained by fractional distillation, are fixed and if there is a mismatch between this and what the market demands, then either shortages will ensure, or the legislated standards will not be met. To compensate for this, refinery processes have been developed whereby heavier gas oil fractions are subjected to catalytic cracking and hydrogenation to give more gasoline and distillate, but these cracked materials tend to be aromatic in nature; consequently, they make good gasoline, but poor diesel fuels. Mass- spectrometer analysis shows that they are much richer in alkylbenzenes, as well as in 2- and 3-ring aromatic compounds; it requires much more severe hydrogenation conditions to saturate aromatic rings. At the same time, some countries have under taken massive projects to extract oils from shale and tar-sands deposits: typically, bitumen is separated from the rock or sand and cracked at high temperature to form lighter materials; hydrogenation is then used to reduce both the nitrogen and sulfur content and to help to stabilize the cracked products. Again, these materials process much more aromatic character than does diesel fuel from conventional sources [7]; typical assays are shown in Table 2.2.

Table 2.2 Comparison of composition (in %wt.) of conventional diesel fuel with those of synthetic materials.

Fraction	Conventional diesel fuel	Cracked gas oil	Synthetic diesel fuel
Paraffins	39	19	17
Naphthenes	34	16	37
Alkylbenzenes	18	34	36
2-Ring Aromatics	8	28	8
3-Ring Aromatics	1	3	2

Furthermore, ^{1}H and ^{13}C NMR studies on the alkylbenzenes show that, for the same molecular weight, those found in conventional fuel have relatively few (1-3) longer aliphatic side-chains, whereas those from synthetic sources have many (4-6) shorter side-chains, several of them perhaps are methyl groups. Thus, it is this preponderance of short side-chains, rather than the increase in the lower cetane numbers for synthetic diesel fuels; also, the high content of naphthalenic compounds in the cracked oil fractions makes them unsuitable for augmenting the diesel fuel and jet fuel supply.

Under the broad definition of diesel fuel, there are many possible combinations of various characteristics such as volatility, ignition quality, viscosity, gravity, stability, and other properties. To characterize the diesel fuels and thereby establish a framework of definition and reference, various classifications are used.

The entire range of diesel engines can be divided into the three broad classification groups indicated in Table 2.3.

Table 2.3 Classification groups of diesel fuel.

Classification	Speed range	Conditions	Typing applications
Low speed	Below 300 rpm	Sustained heavy load, constant speed	Marine main propulsion; electric power generation
Medium speed	300 to 1000 rpm	Fairly high load and relatively constant speed	Marine auxiliaries; stationary power generators; pumping units
High speed	1000 rpm or above	Frequent and wide variation in load and speed	Road transport vehicles; diesel locomotives

2.3 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 [8].

Performance Feature Desired	*Indicated By*
1. Safety in handling	Flash point
2. Pumpability at low temperatures	Pour or cloud point, viscosity
3. Freedom from all suspended matter	Storage stability, suspended sediment tests
4. Readily atomized	Viscosity
5. Readily ignitable	Cetane No.
6. Clean burning	Volatility, Cetane No
7. Good fuel economy	°API Gravity
8. Major effect on engine wear and deposits	Sulfur

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

Cetane number

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

Volatility

A simple laboratory distillation test indicates the volatility or boiling range of a fuel. Important distillation points for determining fuel volatility are the 10%, 50%, 90%, and Final boiling point. The higher than 50% and/or Final boiling points, the more difficult it is to vaporize the fuel completely. High speed engines in particular require volatile fuels high boiling products cannot be vaporized in the short time available for combustion, and sooty, incomplete burning results. It is very important in high speed engines to have volatile, readily vaporized fuels; the importance of fuel volatility decreases as speed decreases or, stated another way, as the time available for combustion increases.

Viscosity

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

Gravity

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

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

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

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 [9].

2.4 Diesel ignition improvers

2.4.1 Cetane number

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

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

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (Cetane No. = 100) in a blend with heptamethylnonane (Cetane No. 15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number [5]:

$$\text{Cetane No.} \quad = \quad \%\ \text{n-cetane} + 0.15\ (\%\ \text{heptamethylnonane}) \qquad (1)$$

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 a 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 [11]. 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 2.3.

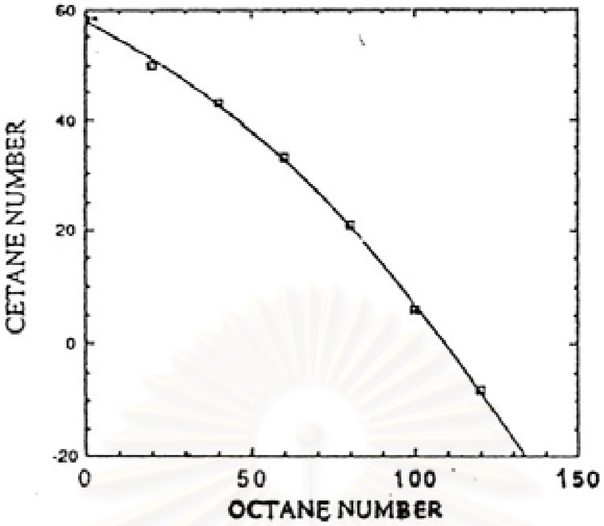


Figure 2.3 The inverse relationship between cetane and octane numbers.

The cetane numbers of a variety of compounds are shown in Table 2.4. 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 [7].

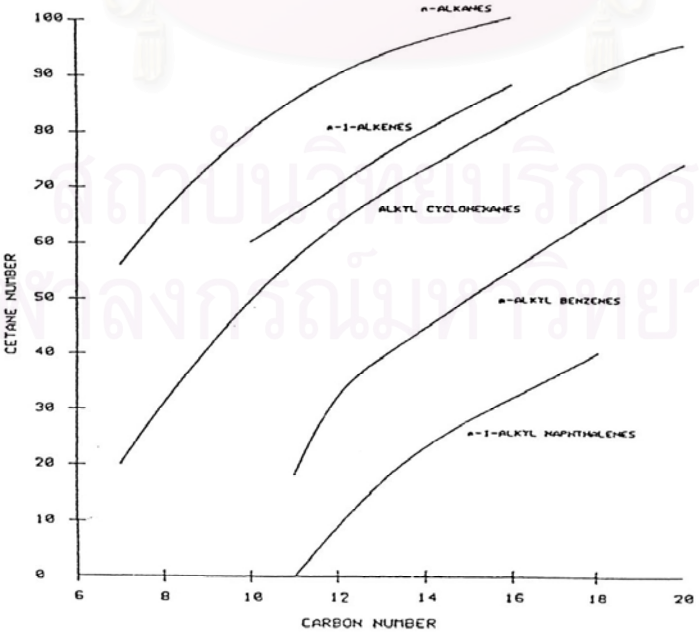


Figure 2.4 Cetane number of pure hydrocarbons.

Table 2.4 Cetane number for pure organic compounds.

Normal Paraffins		**Olefins**	
Heptane	56.3	1-Octene	40.5
Octane	63.8	1-Decene	60.2
Decane	76.9	1-Dodecene	71.3
Dodecane	87.6	1-Tetradecene	82.7
Tetradecane	96.1	1-Hexadecene	84.2
Hexadecane	100.0	1-Octadecene	90.0
Octadecane	103.0		
Naphthenes		**Aromatics**	
Methylcyclohexane	20.0	n-Amylbenzene	8
Dicyclohexyl	47.4	n-Hexylbenzene	26
Decalin	42.1	n-Nonylbenzene	50
		n-Diisopropylbenzene	-12

2.4.2 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 [6]. 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 2.5.

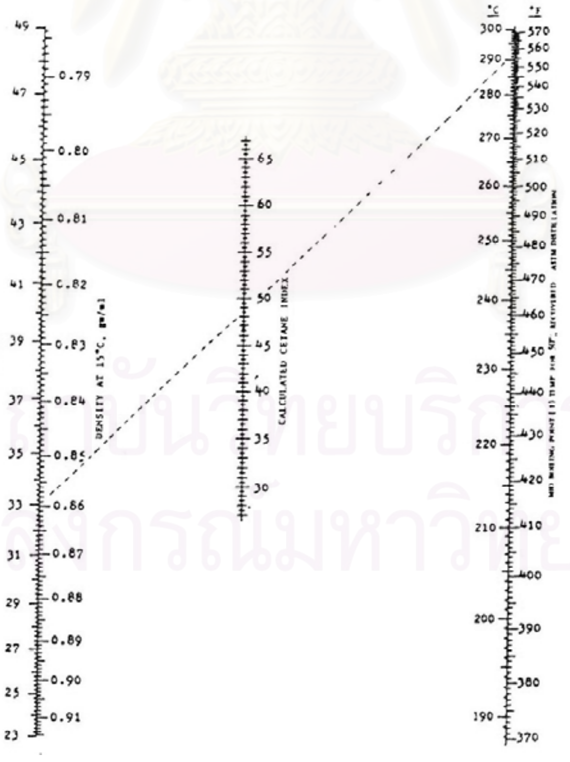


Figure 2.5 Nomograph for Calculated Cetane Index.

2. It is determined from the following formula [12]:

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

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

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.

$$\text{Improver value} = 0.1742 (0.1G)^{1.4444} (0.01M)^{1.0052} \{\ln (1+17.5534D)\} \quad (3)$$

Where:

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

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

D = Percent weight of cetane improver, %weight.

Therefore;

$$\text{CCI improved} = \text{CCI} + \text{Improver value} \quad (4)$$

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. Correlation is best for straight-run and catalytically-cracked distillates and blends of the two and least satisfactory for blends containing substantial proportions of thermally cracked stocks.

2.4.3 The cetane quality of diesel fuels and diesel fuel components.

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

1. Improved cold starting
2. Reduced smoke emission during warm-up
3. Reduced noise
4. Reduced fuel consumption and exhaust emissions
5. Improved engine durability

The scope of refiners to produce diesel fuel of high cetane quality varies significantly with the types of crude oil processed and the process units available within the refinery. In general, throughout the world the conversion refinery utilizing catalytic cracking predominates, and the diesel fuel blending components typically available are shown in Table 2.5 and 2.6, the effect of crude source on light gas oil quality being illustrated by the data in Table 2.5 and the effect of component type by the data in Table 2.6.

Table 2.5 Effect of crude source on diesel fuel blending component quality.

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

Table 2.6 Effect of component type on diesel fuel blending component quality.

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

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

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

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

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

3. Upgrade diesel fuel quality to give the premium grade products now being marketed by many oil companies in certain markets throughout the world [5].

2.4.4 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 speciality chemicals which, when added to diesel, improve diesel's cetane number similar to the way ethanol and ETBE improve the octane rating of gasoline [16]. At concentrations less than 0.15%, cetane improvers can reduce ignition delay times of diesel fuel. Fundamentally, the cetane improver concentration is another degree of freedom in designing a diesel fuel. In practice, this degree of freedom is often capable of simultaneously decreasing NO_x, hydrocarbon and particulate emissions. Cetane improvers are considered a key technology to provide cleaner burning diesel fuel. They are key additives for making premium diesel. Chemical compounds such as alkyl nitrates, ether nitrates, dinitrates of polyethylene glycols and certain peroxides are known cetane improvers [17].

The isooctyl nitrate product, in view of its good response and low production costs, is the most cost-effective additive and is now almost exclusively used in all commercial applications with hydrocarbon-based fuels. The weak RO-NO_2 bond in isooctyl nitrate provides the available source of the free radicals required to enhance diesel combustion [5].

However, polynitrates are more effective than the commercial mononitrates, such as octyl nitrates commercially used, because of their higher potential for generating reactive species, RO and NO_2 to ignite oxidation. The polynitrates are generally more effective than mononitrates by a factor of 2 to 5, i.e., the dosage requirement for polynitrates for similar cetane number improvement is 0.5 to 0.2 that required for mononitrates [13].

2.5 Fuel properties affecting ignition delay

2.5.1 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 2.6, 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.

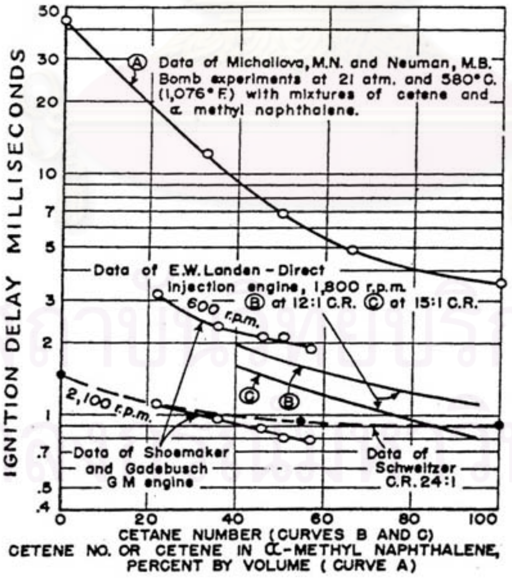


Figure 2.6 Relation between ignition delay and cetane number in tests in engines and bombs.

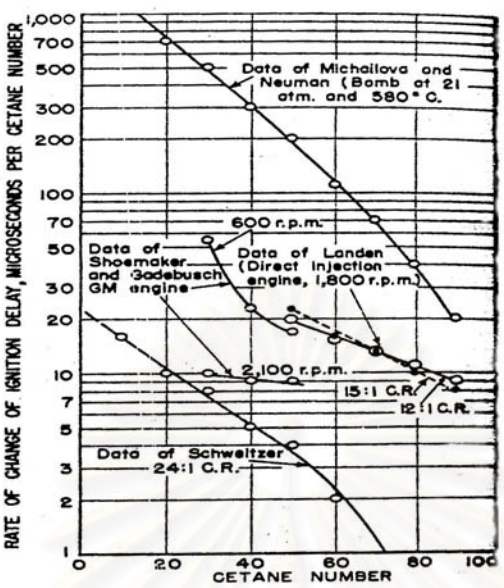


Figure 2.7 Variation of rate of change of ignition delay with cetane number.

Closer study of Figure 2.6 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 2.7, 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 [14].

2.5.2 Effect of chemical structure

The effect on cetane number of adding one side chain to a normal paraffin hydrocarbon is shown in Figure 2.8. The data were obtained by Petrov in a bomb which had been calibrated against a CFR engine. Figure 2.8 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 2.8 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.

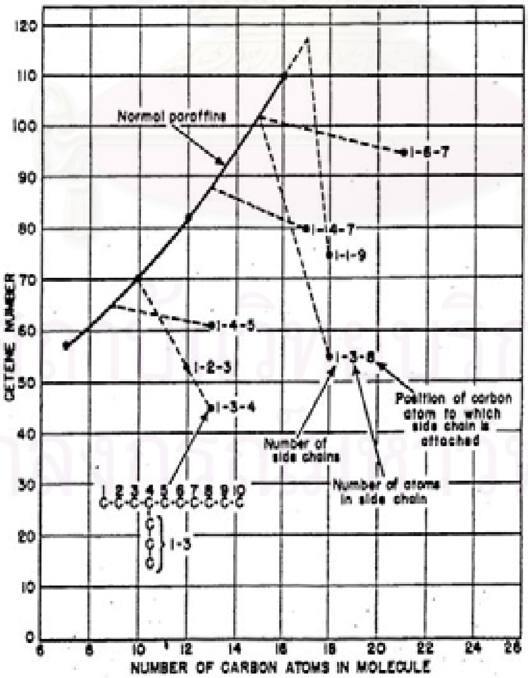


Figure 2.8 Cetane number of n-alkyl paraffin hydrocarbons (data of Petrov).

In order to overcome this difficulty, the results have been plotted as shown in Figure 2.9. 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 2.8 for interpolation and slight extrapolation.

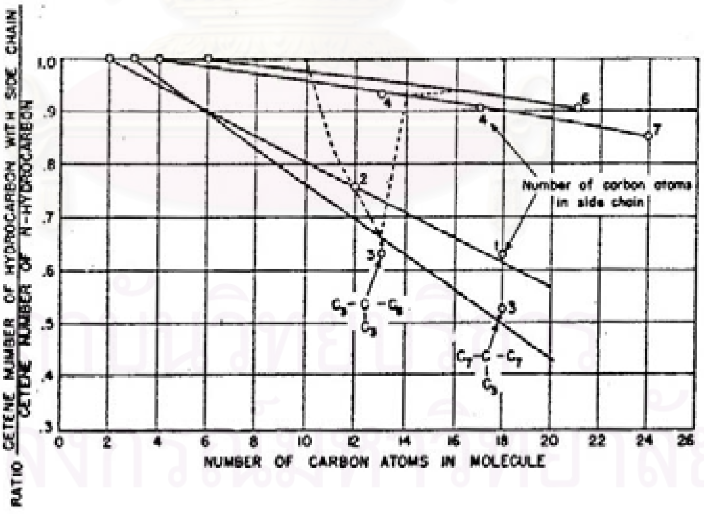


Figure 2.9 Effect of adding n-alkyl side chains on cetane number of paraffin hydrocarbons (derived from data of Petrov).

By interpolation, using Figures 2.8 and 2.9, 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 2.10 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 [14].

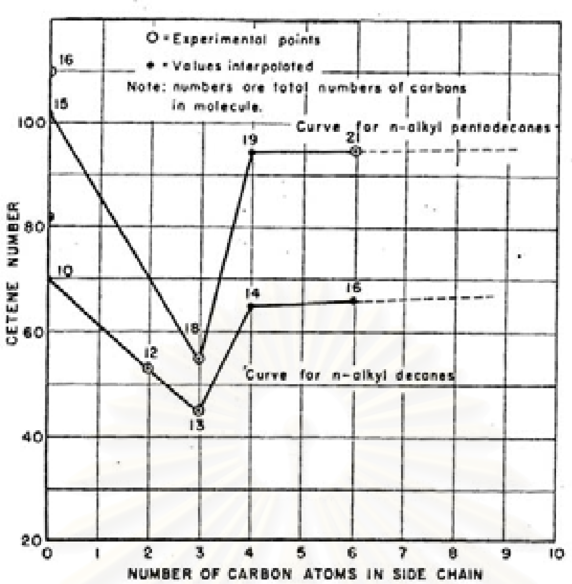


Figure 2.10 Relation between cetane number and number of carbon atoms in a single side chain in n-alkyl paraffin hydrocarbons (derived from data of Petrov).

2.5.3 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 2.11, 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.

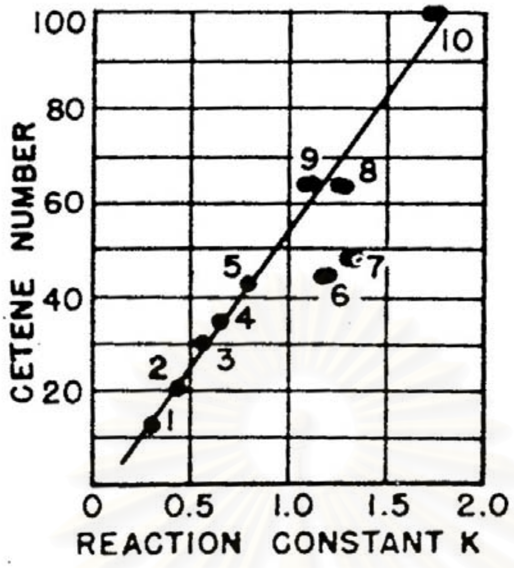


Figure 2.11 Reaction constant K in relation to cetane number. (cracking temperature 635°C). (Data of Boerlage and Van Dyck.)

2.5.4 Ignition accelerators

The rate of the chemical reactions preceding the auto-ignition of a fuel may be increased by the addition of ignition accelerators. Numerous compounds have been proposed as ignition accelerators, but probably the most effective, reasonably stable accelerator is acetone peroxide, and the most effective semi-commercially available accelerator is amyl nitrate. The average increase in cetane number obtained in tests of nine different fuels in shown in Figure 2.12, in relation to the concentration of ignition accelerator. It will be observed that significant improvement is obtained with comparatively small additions of accelerator.

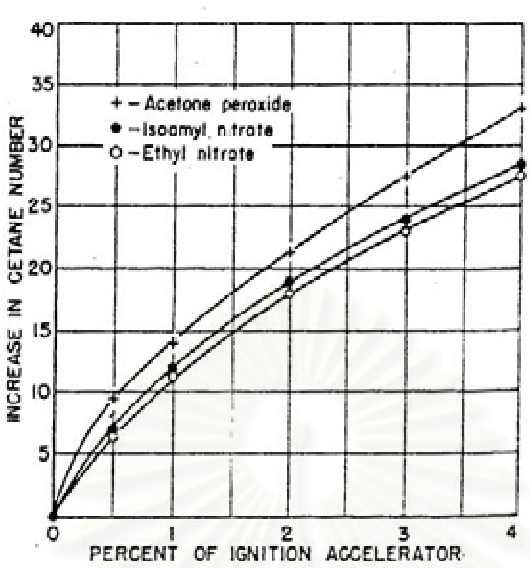


Figure 2.12 Average increase in cetane number of 9 test fuels in relation to concentration of ignition accelerator (data of Bogen and Wilson).

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.

2.5.5 Effect of physical properties of fuel

The interrelation between the physical properties of a fuel and cetane number is shown in Figure 2.13, 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.

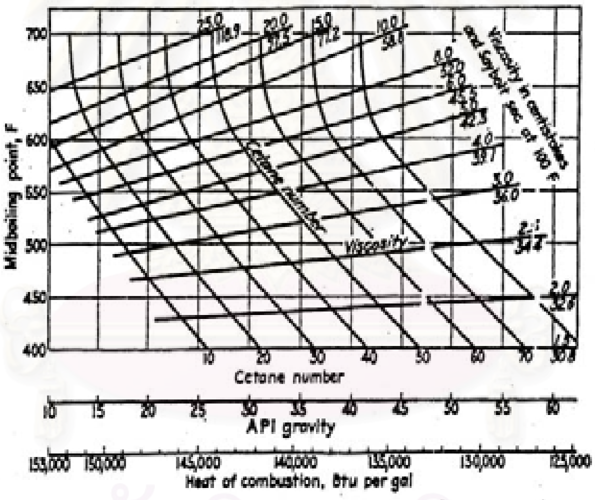


Figure 2.13 Interrelated properties of diesel fuels (according to Blackwood and Cloud).

2.6 Additives for diesel fuels

Apart from a few exceptions treatment of diesel fuel with additives has only recently become important. For this relatively late development in diesel fuels, compared with gasoline, two main reasons exist; First a significant progress occurred in diesel engine technology from about the mid-1970s, which made improved diesel fuel quality seem desirable, especially with respect to lower exhaust emissions. Second an anticipated change in the middle distillate quality became apparent at the same time and made the use of additives very attractive [15]. Additives for diesel fuel have many type which was shown in Table 2.7 [2].

Table 2.7 Additives for diesel fuels.

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

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

2.7 Literature reviews

Filbey, A.H. **[17]**, in U.S. Pat. No. 4,406,665, reported that cetane number of diesel fuel, both hydrocarbon and alcohol, was increased by adding a small amount of a tetrahydrofuranol nitrate. The Results of cetane increment which caused by the present additives was measured in comparison with that caused by a commercial cetane improver, 2-ethylhexyl nitrate, indicated that tetrahydrofuranol nitrate was more effective at very low concentration and it gave a cetane number increase that was almost linear with concentrations.

Seemuth, P.D. **[18]**, in U.S. Pat. No. 4,457,763, discovered that the cetane rating of diesel fuel could be substantially increased by the addition of a small amount of a dioxan nitrate such as m-dioxan-5-ol nitrate and 1,3-dioxolane-4-methanol nitrate. The results were directly compared to the response obtained with a commercial octyl nitrate cetane improver. At the same concentration, the dioxan nitrates gave a substantially higher cetane increase compared to a commercial alkyl nitrate.

Liotta, Jr. et al. **[19]**, in U.S. Pat. No. 5,258,049, described an improvement in the cetane rating of diesel fuel by the addition of a small but effective amount of the nitric acid ester of 1-phenyl ethanol herein called methyl benzyl alcohol nitrate (MBAN). In addition to the blends containing MBAN, blends were prepared using the same concentrations of the commercial cetane improver, 2-ethylhexyl nitrate. The results were obtained that MBAN was slightly less effective than the commercial material while it had a cost advantage over the currently commercial material. The cost advantage was due to the comparably lower cost of starting alcohol, 1-phenyl ethanol.

Waller et al. **[20]**, in U.S. Pat. No. 5,858,030, disclosed that the diesel fuel composition consisted of moderate amounts of dimethoxy propane (DMPP), dimethoxy ethane (DMET) and their mixture blended into a conventional diesel fuel. The cetane number of the resulting blends were significantly improved above 25 volume% and slightly improved below 25 volume%.

Vasaruchtragul, J. **[21]** revealed that a diesel fuel containing a small amount of alkane dinitrate such as 1,5-pentane dinitrate and triethylene 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 triethylene glycol dinitrate gave higher increased cetane number than commercial cetane improver but 1,5-pentane dinitrate gave lesser cetane number than the others.

Morever, Nontaganok, S. **[22]** and Rattanatawonkiti, W. **[23]** revealed that a diesel fuel containing a tetrazole derivatives such as 5-propyltetrazole and 5-(4′-nitrophenyl)tetrazole slightly increased cetane number, except the tetrazole derivatives containing many benzene rings.

CHAPTER III

EXPERIMENTAL

3.1 Apparatus

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

Table 3.1 Apparatus used in the experiment.

Apparatus	Model	Manufacturer
Fourier-Transform NMR Spectrometer	AC-F200 (200 MHz)	Bruker Spectrospin
Fourier-Transform Infrared Spectrophotometer	Impact 410	Nicolet
Automatic Distillation Apparatus	MP626	Herzog
Pensky-Martens Closed Flash Tester	ISL(PMFP93)	Perzoo
Automatic Pour Point Tester	ISL(CPP97-6)	
Automatic Viscometer		Cannon
Apparatus for API Gravity		

3.2 Chemicals

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

Table 3.2 Source of chemicals

No.	Materials	Company
1	Diethylene glycol, laboratory grade	BDH
2	Dipropylene glycol, analytical grade	MERCK
3	Tripropylene glycol, analytical grade	FLUKA
4	2-Ethyl-1,3-hexane diol, analytical grade	FLUKA
5	Methylene chloride, analytical grade	FLUKA
6	96% Sulfuric acid, analytical grade	MERCK
7	65% Nitric acid, analytical grade	LAB-SCAN
8	28-30% Ammonium hydroxide, analytical grade	J.T.BAKER
9	Chloroform-d, analytical grade	MERCK
10	Anhydrous sodium sulfate, analytical grade	MERCK
11	2-Ethylhexyl nitrate	OCTEL
12	Base diesel fuels	THAIOIL REFINERY

3.3 Synthesis of alkylene glycol dinitrate compounds.

3.3.1 Synthesis of diethylene glycol dinitrate

To 50 ml dichloromethane were added 20.45g of 96%H_2SO_4 (0.20 moles) and 9.70g of 65%HNO_3 (0.10 moles). 5.40g of diethylene glycol (0.05 moles) were then slowly added to the well-stirred mixture whilst maintaining a temperature of 0-2°C, over 1 hour. After the completion of addition, agitation was stopped, and the phases were allowed to separate. The organic layer was washed three times with 20 ml of deionized water, then the mixture was neutralized with 28-30%ammonia solution. The mixture was dried over anhydrous sodium sulfate and then filtered. Solvent was removed on a rotary evaporator at 60°C to give 9.08g of diethylene glycol dinitrate (90.98% yield) as a colorless liquid [24].

3.3.2 Synthesis of dipropylene glycol dinitrate

To 50 ml dichloromethane were added 20.61g of 96%H_2SO_4 (0.20 moles) and 9.70g of 65%HNO_3 (0.10 moles). 3.35g of dipropylene glycol (0.025 moles) were then slowly added to the well-stirred mixture whilst maintaining a temperature of 0-2°C, over 1 hour. After the completion of addition, agitation was stopped, and the phases were allowed to separate. The organic layer was washed three times with 20 ml of deionized water, then the mixture was neutralized with 28-30%ammonia solution. The mixture was dried over anhydrous sodium sulfate and then filtered. Solvent was removed on a rotary evaporator at 60°C to give 4.84g of dipropylene glycol dinitrate (86.48% yield) as a colorless liquid.

3.3.3 Synthesis of tripropylene glycol dinitrate

To 50 ml dichloromethane were added 20.50g of 96%H_2SO_4 (0.20 moles) and 9.70g of 65%HNO_3 (0.10 moles). 4.81g of tripropylene glycol (0.025 moles) were then slowly added to the well-stirred mixture whilst maintaining a temperature of .0-2°C, over 1 hour. After the completion of addition, agitation was stopped, and the phases were allowed to separate. The organic layer was washed three times with 20 ml of deionized water, then the mixture was neutralized with 28-30%ammonia solution. The mixture was dried over anhydrous sodium sulfate and then filtered. Solvent was removed on a rotary evaporator at 60°C to give 6.26g of tripropylene glycol dinitrate (88.65% yield) as colorless to a pale yellow liquid.

3.3.4 Synthesis of ethylhexylene glycol dinitrate

To 50 ml dichloromethane were added 20.50g of 96%H_2SO_4 (0.20 moles) and 9.70g of 65%HNO_3 (0.10 moles). 3.67g of 2-ethyl-1,3-hexane diol (0.025 moles) were then slowly added to the well-stirred mixture whilst maintaining a temperature of 0-2°C, over 1 hour. After the completion of addition, agitation was stopped, and the phases were allowed to separate. The organic layer was washed three times with 20 ml of deionized water, then the mixture was neutralized with 28-30%ammonia solution.

The mixture was dried over anhydrous sodium sulfate and then filtered. Solvent was removed on a rotary evaporator at 60°C to give 5.44g of ethylhexylene glycol dinitrate (91.76% yield) as a colorless liquid.

3.4 Determination of properties of alkylene glycol dinitrate compounds.

3.4.1 Characterization of the synthesized compounds by using instruments as follows:

1. Fourier-Transform Infrared Spectrophotometer
2. Fourier-Transform NMR Spectrometer

3.4.2 Determination of properties and cetane index of base diesel fuel blended with alkylene glycol dinitrate compounds and 2-ethylhexyl nitrate (0.05% and 0.10% by weight).

1. The blended base diesel fuels were obtained by blending base diesel fuels (500g) with each of alkylene glycol dinitrate compounds (0.25g and 0.50g).

These alkylene glycol dinitrate compounds were:

1) Diethylene glycol dinitrate

2) Dipropylene glycol dinitrate

3) Tripropylene glycol dinitrate

4) Ethylhexylene glycol dinitrate

5) 2-Ethylhexyl nitrate (commercial cetane improver)

2. The physical properties of these blended base diesel fuels were determined as follows:

1) Mid-boiling point	by ASTM D86
2) API Gravity	by ASTM D1298
3) Flash point	by ASTM D93
4) Pour point	by ASTM D97
5) Viscosity	by ASTM D445
6) Cetane index	by ASTM D976

3.4.3 Determination of cetane improvement of alkylene glycol dinitrate compounds and 2-ethylhexyl nitrate (0.05% and 0.10% by weight) in base diesel fuel.

Apart from cetane number testing according to ASTM D613 CFR engine technique, there is the other method for prediction of cetane number of diesel fuel. It is the calculation of cetane improvement from the alignment chart of the Associated Octel Company Ltd. [5], as follows:

1. The blended base diesel fuels were obtained by blending base diesel fuels with each of alkylene glycol dinitrate compounds (0.05% and 0.10% by weight).

These alkylene glycol dinitrate compounds were:

1) Diethylene glycol dinitrate

2) Dipropylene glycol dinitrate

3) Tripropylene glycol dinitrate

4) Ethylhexylene glycol dinitrate

5) 2-Ethylhexyl nitrate (commercial cetane improver)

2. Density @ 15°C (which correlated with API gravity @ 60°C) of blended base diesel fuels were measured at 0.05% and 0.10% concentrations.

3. Cetane improvement was calculated by nomograph for the calculation of cetane improvement which given in Figure 3.1 by using density data and the cetane number of the known base diesel fuel.

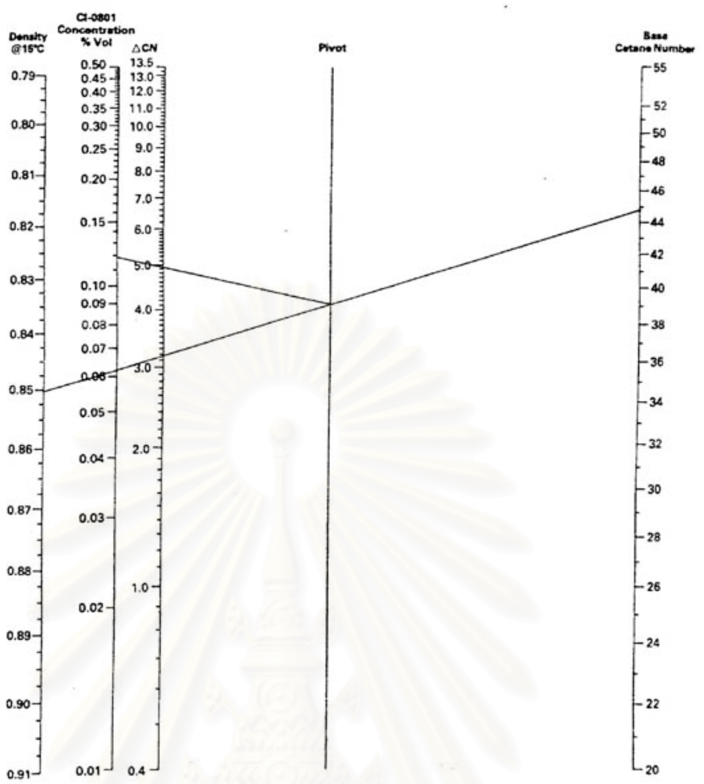


Figure 3.1 Nomograph for the calculation of cetane improvement from cetane improver additions. (Source: The Associated Octel Company Ltd.)

Note: Method of using nomograph in Figure 3.1.

1. Identify the base fuel cetane number and density on the appropriate axes and draw a line joining these two points.

2. Where this line intersects the pivot line, either

a) Connect the pivot point to the cetane number increase (ΔCN) that is desired and extend the line to the cetane improver axis to predict the additive concentration, or

b) Connect the pivot point to the chosen cetane improver concentration and read back along the line to the predicted cetane number increase.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of alkylene glycol dinitrate compounds

Dinitrate compounds could be prepared by direct nitration of organic hydroxy compounds with concentrated nitric acid and concentrated sulfuric acid, while maintaining the temperature of the reaction at 0-2°C.

In this study, all products were obtained in high yield. Moreover, the products were substantially pure which was the benefit of this process.

4.2 Characteristics of alklylene glycol dinitrate compounds

4.2.1 Diethylene glycol dinitrate

This compound was a colorless liquid. It was obtained at 90.92% yield. FTIR data of diethylene glycol dinitrate was shown in Table 4.1 and Figure A-2.

Table 4.1 FTIR data of diethylene glycol dinitrate.

Wave number (cm^{-1})	Assignment
2897	C-H stretching, aliphatic
1635	NO_2 asymmetric stretching
1437, 1388	C-H bending, aliphatic
1282	NO_2 symmetric stretching
1142	C-O stretching
861	O-N stretching vibration

From Table 4.1, IR spectrum of diethylene glycol dinitrate (Figure A-2) indicated important absorption bands of NO_2 (asymmetric stretching and symmetric stretching) at

1635 cm^{-1} and 1282 cm^{-1}. As compared with Figure A-1, it showed that there was no absorption band of OH stretching group of diethylene glycol, which was a starting material at 3400 cm^{-1}. It confirmed that hydroxy groups were completely substituted by nitronium ions.

To confirm the structure of diethylene glycol dinitrate, ^{1}H-NMR and ^{13}C-NMR were performed, as shown in Table 4.2 and Table 4.3, respectively.

Table 4.2 ^{1}H-NMR data of diethylene glycol dinitrate.

Chemical shift (δ, ppm)	Multiplicity	Position of proton	Number of proton
4.58	*t*	a, d	4
3.74	*t*	b, c	4

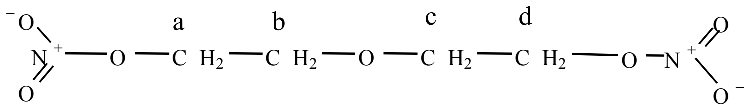
The ^{1}H-NMR spectrum of diethylene glycol dinitrate was shown in Figure A-4 which indicated 2 signals at 4.58 and 3.74 ppm.

Table 4.3 ^{13}C-NMR data of diethylene glycol dinitrate (in deuterated chloroform).

Chemical shift (δ, ppm)	Carbon type	Position of carbon
71.94	CH_2	a, d
67.25	CH_2	b, c

The ^{13}C-NMR spectrum of diethylene glycol dinitrate was shown in Figure A-6 which indicated 2 signals at 71.94 and 67.25 ppm.

All of these results suggested that this compound was diethylene glycol dinitrate which has the structure shown below:



$$\underset{O}{\overset{^{-}O}{N^{+}}}-O-\overset{a}{C}H_2-\overset{b}{C}H_2-O-\overset{c}{C}H_2-\overset{d}{C}H_2-O-\underset{O^{-}}{\overset{O}{N^{+}}}$$

4.2.2 Dipropylene glycol dinitrate

This compound was a colorless liquid. It was obtained at 86.43% yield. FTIR data of dipropylene glycol dinitrate was shown in Table 4.4 and Figure A-8.

Table 4.4 FTIR data of dipropylene glycol dinitrate.

Wave number (cm^{-1})	Assignment
2989	C-H stretching, aliphatic
1635	NO_2 asymmetric stretching
1456, 1388	C-H bending, aliphatic
1282	NO_2 symmetric stretching
1117	C-O stretching
861	O-N stretching vibration

From Table 4.4, IR spectrum of dipropylene glycol dinitrate (Figure A-8) indicated important absorption bands of NO_2 (asymmetric stretching and symmetric stretching) at 1635 cm^{-1} and 1282 cm^{-1}. As compared with Figure A-7, it showed that there was no absorption band of OH stretching group of dipropylene glycol which was a starting material at 3400 cm^{-1}. It confirmed that hydroxy groups were completely substituted by nitronium ions.

To confirm the structure of dipropylene glycol dinitrate, ^1H-NMR and ^{13}C-NMR were performed, as shown in Table 4.5 and Table 4.6, respectively.

Table 4.5 ^{1}H-NMR data of dipropylene glycol dinitrate.

Chemical shift (δ, ppm)	Multiplicity	Position of proton	Number of proton
5.26-5.14	*m*	a	1
4.40, 4.37	*d*	d	2
3.77-3.63	*m*	c	1
3.61-3.50	*d*	b	2
1.33, 1.30	*d*	e	3
1.21, 1.17	*d*	f	3

The ^{1}H-NMR spectrum of dipropylene glycol dinitrate was shown in Figure A-10 which indicated 6 signals.

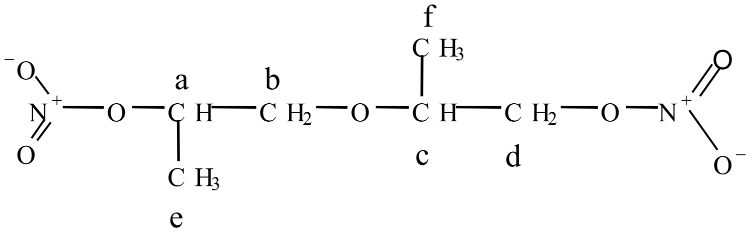
Table 4.6 ^{13}C-NMR data of dipropylene glycol dinitrate (in deuterated chloroform).

Chemical shift (δ, ppm)	Carbon type*	Position of carbon
79.12	CH	a
75.52	CH_2	d
72.07	CH	c
70.00	CH_2	b
16.38	CH_3	e
14.80	CH_3	f

* It was determined by DEPT spectra as shown in Figure A-25.

The ^{13}C-NMR spectrum of dipropylene glycol dinitrate was shown in Figure A-12 which indicated 6 signals.

All of these results suggested that this compound was dipropylene glycol dinitrate which has the structure shown below:



4.2.3 Tripropylene glycol dinitrate

This compound was a pale yellow liquid. It was obtained at 88.67% yield. FTIR data of tripropylene glycol dinitrate was shown in Table 4.7 and Figure A-14.

Table 4.7 FTIR data of tripropylene glycol dinitrate.

Wave number (cm^{-1})	Assignment
2984	C-H stretching, aliphatic
1630	NO_2 asymmetric stretching
1461	CH_2 methylene group
1383	CH_3 methyl group
1282	NO_2 symmetric stretching
1113	C-O stretching
861	O-N stretching vibration

From Table 4.7, IR spectrum of tripropylene glycol dinitrate (Figure A-14) indicated important absorption bands of NO_2 (asymmetric stretching and symmetric stretching) at 1630 cm^{-1} and 1282 cm^{-1}. As compared with Figure A-13, it showed that there was no absorption band of OH stretching group of tripropylene glycol, which was a starting material at 3400 cm^{-1}. It confirmed that hydroxy groups were completely substituted by nitronium ions.

To confirm the structure of tripropylene glycol dinitrate, ^{1}H-NMR and ^{13}C-NMR were performed, as shown in Table 4.8 and Table 4.9, respectively.

Table 4.8 ^{1}H-NMR data of tripropylene glycol dinitrate.

Chemical shift (δ, ppm)	Multiplicity	Position of proton	Number of proton
5.30-5.15	*m*	f	2
4.39-4.32	*m*	a	1
3.67, 3.59	*d*	b, d	4
3.44-3.34	*m*	c, e	2
1.31, 1.28	*d*	h, i	6
1.14, 1.09	*d*	g	3

The ^{1}H-NMR spectrum of tripropylene glycol dinitrate was shown in Figure A-16 which indicated 6 signals.

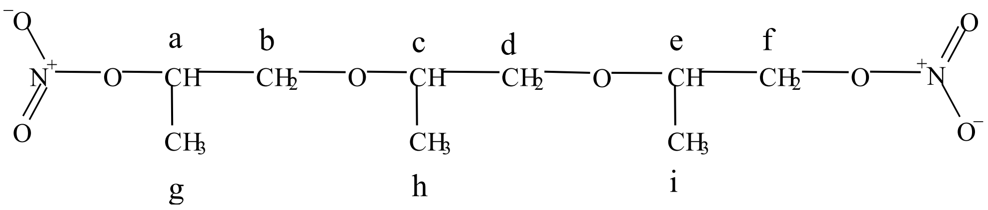
Table 4.9 ^{13}C-NMR data of tripropylene glycol dinitrate (in deuterated chloroform).

Chemical shift (δ, ppm)	Carbon type*	Position of carbon
79.79	CH_2	f
79.27	CH	a
75.73	CH_2	b
75.57	CH_2	d
70.34	CH	e
70.29	CH	c
16.51	CH_3	g
14.98	CH_3	h, i

*It was determined by DEPT spectra as shown in Figure A-26.

The ^{13}C-NMR spectrum of tripropylene glycol dinitrate was shown in Figure A-18 which indicated 8 signals.

All of these results suggested that this compound was tripropylene glycol dinitrate which has the structure shown below:



4.2.4 Ethylhexylene glycol dinitrate

This compound was a colorless liquid. It was obtained at 91.74% yield. FTIR data of ethylhexylene glycol dinitrate was shown in Table 4.10 and Figure A-20.

Table 4.10 FTIR data of ethylhexylene glycol dinitrate.

Wave number (cm^{-1})	Assignment
2965	C-H stretching, aliphatic
1635	NO_2 asymmetric stretching
1466	CH_2 methylene group
1282	NO_2 symmetric stretching
866	O-N stretching vibration

From Table 4.10, IR spectrum of ethylhexylene glycol dinitrate (Figure A-20) indicated important absorption bands of NO_2 (asymmetric stretching and symmetric stretching) at 1635 cm^{-1} and 1282 cm^{-1}. As compared with Figure A-19, it showed that there was no absorption band of OH stretching group of ethylhexylene glycol which was a starting material at 3400 cm^{-1}. It confirmed that hydroxy groups were completely substituted by nitronium ions.

To confirm the structure of ethylhexylene glycol dinitrate, ^{1}H-NMR and ^{13}C-NMR were performed, as shown in Table 4.11 and Table 4.12, respectively.

Table 4.11 ^{1}H-NMR data of ethylhexylene glycol dinitrate.

Chemical shift (δ, ppm)	Multiplicity	Position of proton	Number of proton
5.20-5.10	*m*	c	1
4.50, 4.46	*d*	a	2
2.06-2.02	*m*	b	1
1.64-1.36	*m*	d, e, g	6
0.98	*t*	f, h	6

The ^{1}H-NMR spectrum of ethylhexylene glycol dinitrate was shown in Figure A-22 which indicated 5 signals.

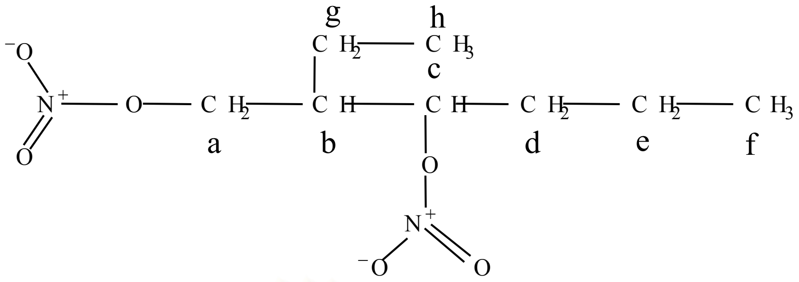
Table 4.12 ^{13}C-NMR data of ethylhexylene glycol dinitrate (in deuterated chloroform)

Chemical shift (δ, ppm)	Carbon type*	Position of carbon
83.39	CH	c
71.74	CH_2	a
40.91	CH	b
31.18	CH_2	d
19.89	CH_2	g
18.91	CH_2	e
13.62	CH_3	f
11.39	CH_3	h

*It was determined by DEPT spectra as shown in Figure A-27.

The ^{13}C-NMR spectrum of ethylhexylene glycol dinitrate was shown in Figure A-24 which indicated 8 signals. (Note: Ethylhexylene glycol, which was a starting alcohol, was a mixture of stereoisomer so ^{13}C-NMR spectrum of ethylhexylene glycol dinitrate was shown two sets.)

All of these results suggested that this compound was ethylhexylene glycol dinitrate which has the structure shown below:



4.3 Determination of cetane index of alkylene glycol dinitrate compounds and 2-ethylhexyl nitrate in base diesel fuel.

Table 4.13 provided mid-boiling point, API gravity and cetane index as the results of 0.05% and 0.10% by weight of diethylene glycol dinitrate, dipropylene glycol dinitrate, tripropylene glycol dinitrate, ethylhexylene glycol dinitrate and 2-ethylhexyl nitrate which were blended in base diesel fuel.

Table 4.13 Cetane index of the blend of alkylene glycol dinitrate compounds and 2-ethylhexyl nitrate with base diesel fuel.

Concentration (% weight)	Blended composition	Mid-boiling point (°F)	API gravity @ 60°F	CCI	Improver value	CCI improver
none	base	538.88	36.8	53.14	-	-
0.05	base + DEGN	539.24	36.8	53.17	3.92	57.09
	base + DPGN	539.42	36.8	53.19	3.92	57.11
	base + TPGN	539.96	36.8	53.24	3.92	57.16
	base + EHGN	539.02	36.8	53.15	3.92	57.07
	base + EHN	539.96	36.7	53.07	3.91	56.98
0.10	base + DEGN	537.44	36.8	53.00	6.28	59.28
	base + DPGN	537.96	36.8	53.05	6.29	59.34
	base + TPGN	538.16	36.8	53.07	6.29	59.36
	base + EHGN	537.08	36.8	52.96	6.28	59.24
	base + EHN	538.34	36.6	52.75	6.25	59.00

Note: DEGN = Diethylene glycol dinitrate

DPGN = Dipropylene glycol dinitrate

TPGN = Tripropylene glycol dinitrate

EHGN = Ethyhexylene glycol dinitrate

EHN = 2-Ethylhexyl nitrate

CCI = Calculated cetane index

CCI improver = CCI + Improver value

From Table 4.13 , it could be seen that mid-boiling point of all blended base diesel fuels at the concentrations of 0.05% and 0.10% by weight gave the values similar to base diesel fuel and there were the same API gravity values of 36.8. Therefore, it was found that calculated cetane index of these synthesized compounds did not give any change of these physical properties as compared to the value of base diesel fuel without cetane improver, on account of using only an equation according to the method of ASTM D976.

In fact, the calculated cetane index equation possesses certain inherent limitations which must be recognized in its application. There are:

1. It is not applicable to fuels containing additives for raising cetane number.

2. It is not applicable to pure hydrocarbons, synthetic fuels, such as certain products derived from shale oils, tar sands, alkylates, or coal-tar products.

Therefore, another equation having additional value was considered. It was found that the improved equation for considering the improver value could be calculated by the following equation [12]:

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

where: G = API gravity, determined by test method D1298

M = Mid-boiling temperature (°F), determined by test method D86

D = Percent weight of cetane improver, % wt.

By adding this equation to an equation in ASTM D976, the correct calculated cetane index of diesel fuel containing cetane improver could be determined as shown in Table 4.13. It could be seen that the calculated cetane index of all samples were increased by 3.9 units at the concentration of 0.05% by weight, and 6.3 units at the concentration of 0.10 % by weight, respectively, as compared with base diesel fuels.

From CCI improver values, it could be seen that the blended base diesel fuels with DEGN, DPGN, TPGN and EHGN gave higher CCI improver value than base diesel fuel and EHN at the concentrations of 0.05% and 0.10% by weight. According to both concentrations, TPGN gave the highest CCI improver value as compared with the others. These results were observed that the compound, which had incorporated oxygen atom in hydrocarbon chain, could be improved greater cetane number. This point out that oxygen atom in the hydrocarbon chain enhanced the oxidation, which resulted in increasing of cetane number. In addition, the polynitrates trended to be more effective than the commercial mono-nitrates, such as 2-ethylhexyl nitrate, because of their higher potential for generating reactive species, RO and NO_2 to ignited oxidation.

4.4 Determination of cetane improvement of alkylene glycol dinitrate compounds and 2-ethylhexyl nitrate in base diesel fuel.

In this study, there was another method for calculation of cetane improvement. Cetane improvement of blended base diesel fuels could be determined by nomograph of Octel Company and these results were shown in Table 4.14.

Table 4.14 Cetane improvement of blended base diesel fuels from nomograph of Octel Company.

Concentration (% weight)	Blended Composition	Density @ 15°C	Δ CN	CN
none	Base	0.8403	-	53.60
0.05	base + DEGN	0.8403	2.97	56.57
	base + DPGN	0.8403	2.97	56.57
	base + TPGN	0.8403	2.97	56.57
	base + EHGN	0.8403	2.97	56.57
	base + EHN	0.8408	2.95	56.55
0.10	base + DEGN	0.8403	4.84	58.44
	base + DPGN	0.8403	4.84	58.44
	base + TPGN	0.8403	4.84	58.44
	base + EHGN	0.8403	4.84	58.44
	base + EHN	0.8413	4.82	58.42

From Table 4.14, it could be seen that cetane improvements of all samples were increased by 2.97 units at the concentration of 0.05% by weight and 4.84 units at the concentration of 0.10% by weight, as compared with base diesel fuel. These results gave the similar trend of cetane improvement as Calculated Cetane Index. It could be concluded that the cetane number could be increased by adding the dinitrate compounds, such as these compounds of this study, to the base diesel fuel.

4.5 Some physical properties of alkylene glycol dinitrate compounds in base diesel fuel.

There were many properties which considered to be most indicative of diesel fuel quality. Some diesel fuel properties were presented in Table 4.15 except mid-boiling point, API gravity and cetane index which were shown in Table 4.13.

Table 4.15 Some physical properties of alkylene glycol dinitrate compounds in base diesel fuels.

Concentration (% by weight)	Blended composition	Properties		
		Flash point (°C)	Pour point (°C)	Viscosity (cSt)
none	base	72	-2	3.184
0.05	base + DEGN	71	-2	3.173
	base + DPGN	71	-5	3.174
	base + TPGN	71	-2	3.176
	base + EHGN	72	-2	3.186
	base + EHN	74	-2	3.186
0.10	base + DEGN	72	-2	3.176
	base + DPGN	72	-5	3.175
	base + TPGN	71	-5	3.180
	base + EHGN	72	-5	3.179
	base + EHN	71	-2	3.177

From the Table 4.15 , it could be seen that the dinitrate compounds did not make any change to the physical properties of the base diesel fuel and all of blended base diesel fuels gave the similar value as base diesel fuel.

If the dinitrate compounds did make any change to the physical properties of the base diesel fuel, these blended base diesel fuels could not be used according to the specification of diesel fuel.

CHAPTER V

CONCLUSION

Alkylene glycol dinitrate compounds could be prepared by direct nitration of alkylene glycols, such as diethylene glycol, dipropylene glycol, tripropylene glycol and ethylhexylene glycol with concentrated sulfuric acid and concentrated nitric acid in the presence of methylene chloride. These dinitrate compounds were diethylene glycol dinitrate, dipropylene glycol dinitrate, tripropylene glycol dinitrate, and ethylhexylene glycol dinitrate.

These compounds were easily soluble in base diesel fuel. When they were blended with base diesel fuel at the concentrations of 0.05% and 0.10% by weight, the calculated cetane index improver values were increased by 3.9 and 6.3 units, respectively, as compared with base diesel fuel. In addition, cetane improvement values from the nomograph of Octel Company, were increased by 2.97 and 4.84 units at the concentrations of 0.05% and 0.10% by weight, respectively, as compared with base diesel fuel. The calculated cetane index had been developed for estimating cetane number, so calculated cetane index could be represented the cetane number. Therefore, it could be concluded that the cetane number of base diesel fuels, which were blended with these dinitrate compounds, gave higher cetane number than the base diesel fuel and commercial cetane improver, 2-ethylhexyl nitrate. Particularly, tripropylene glycol dinitrate gave the highest cetane number as compared with the others.

Further study

Because of high cost for determining cetane number by ASTM D613, the future invention relates to a method for prediction of cetane number of a diesel fuel by correlation of its near-infra-red (N.I.R.) spectrum to the cetane number. The simple equation to calculate the cetane number should be proposed.

REFERENCES

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

2. การปิโตรเลียมแห่งประเทศไทย. ฝ่ายวิจัยเชื้อเพลิง ศูนย์วิจัยและพัฒนา. **หนังสือชุดปิโตรเลียมน่ารู้**. พิมพ์ครั้งที่ 1. สิงหาคม 2539.

3. Owen, K. **Gasoline and Diesel Fuel Additives**. Vol. 25. New York: John Wiley & Sons, 1989.

4. Nikanjam, M. **Low Emissions Diesel Fuel**. US. Patent No. 5,389,111, Feb. 14, 1995.

5. Russel, T.J. Additives influencing diesel fuel combustion. **Gasoline and Diesel Fuel Additives**. New York: John Wiley & Sons, 1989:65-88.

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

7. Schobert, H.H. **The Chemistry of Hydrocarbon Fuels**. 2nd ed. London: Buterwork-Heinemann, 1991:197-202.

8. Patberg, J.B. **Petroleum & Chemical Processes**. Exxon Research and Engineering Company, 1976.

9. Pinkerton, R.D. **Diesel Fuel Oils**. The American Society of Mechanical Engineers. New York, 1947.

10. Virgil, B.G. **Petroleum Products Handbook**. 1st ed. McGraw-Hill Book Company, 1960.

11. Popovich, M. **Fuels and Lubricants**. London: John Wiley & Sons, 1959:134-145.

12. Collins, J.M., and Unzelman, G.H. Better cetane prediction equations developed. **Oil & Gas Journal**. June 7, 1982:148-160.

13. Yan, T.Y. **Cetane Number of Diesel Fuel by Incorporating Polynitrate Esters and Stabilizers**. US. Patent No. 4,746,326, May. 24, 1988.

14. Elliott, M.A. **Diesel Fuel Oils**. The American Society of Mechanical Engineers. New York, 1947:81-90.

15. Clothier, P., Aguda, B., Moise, A., and Pritchard, H. How do diesel fuel ignition improvers works?. **Chemical Society Reviews**, 1993:101-108.

16. Suppes, G.J. et al. Synthesis and Cetane Improver Performance of Fatty Acid Glycol Nitrates. **Fuel** 1999;78:73-81.

17. Filbey, A.H. **Diesel Fuel Composition**. US. Patent No. 4,406,665, Sep. 27, 1983.

18. Seemuth, P.D. **Diesel Fuel Cetane Improver**. US. Patent No. 4,457,763, Jul. 3, 1984.

19. Liotta, Jr. et al. **Diesel Fuel Composition**. US. Patent No. 5,258,049, Nov. 2, 1993.

20. Waller et al. **Diesel Fuel Composition Comprising Dialkoxy Alkanes for Increased Cetane Number**. US. Patent No. 5,858,030, Jan. 12, 1999.

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

22. Nontakanok, S. **Synthesis of Tetrazole Derivatives as Cetane Improver**. Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 1991.

23. Rattanatawonkiti, W. **Preparation of Tetrazole Derivatives as Cetane Improver**._Master's Thesis, Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, 1996.

24. Stiff, A.J. **Process for the Manufacture of Nitric Acid Esters**. US. Patent No. 4,853,157, Aug. 1, 1989.

APPENDICES

APPENDIX A

SPECTRA OF ALKYLENE GLYCOL DINITRATE COMPOUNDS

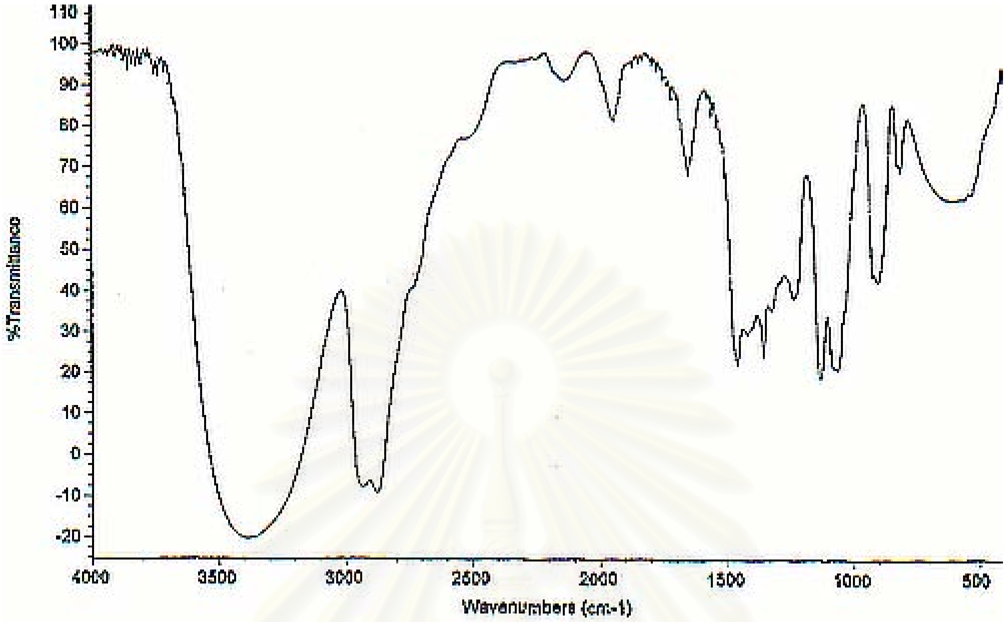


Figure A-1 FTIR spectrum of diethylene glycol

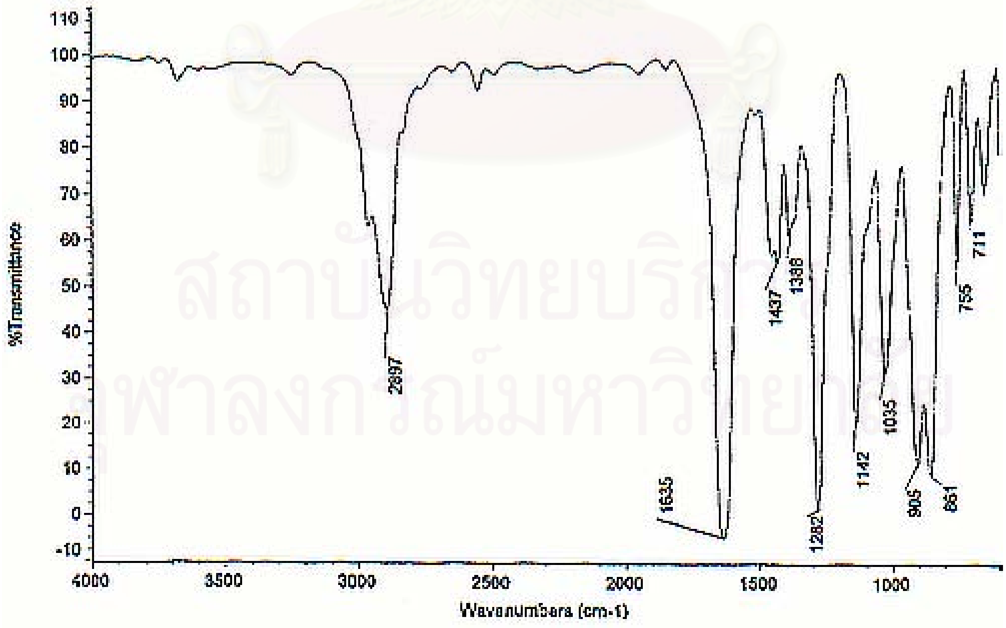


Figure A-2 FTIR spectrum of diethylene glycol dinitrate

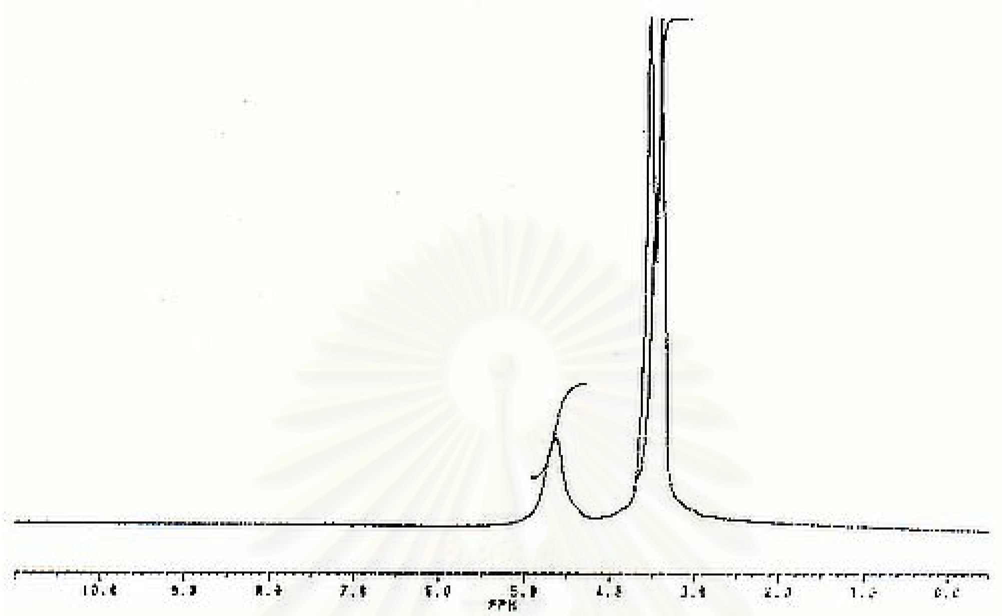


Figure A-3 ^{1}H-NMR spectrum of diethylene glycol

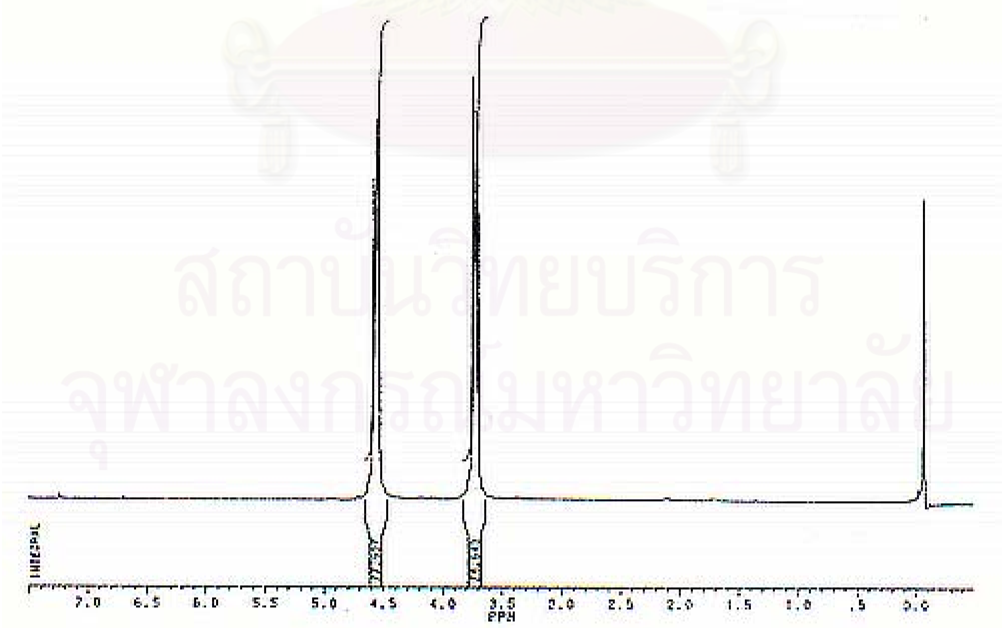


Figure A-4 ^{1}H-NMR spectrum of diethylene glycol dinitrate

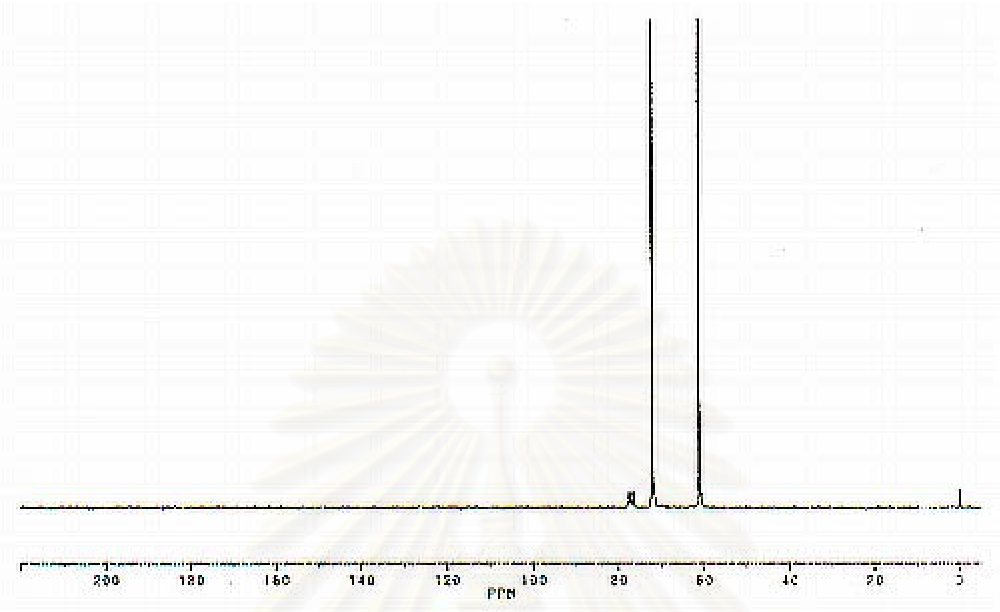


Figure A-5 ^{13}C-NMR spectrum of diethylene glycol

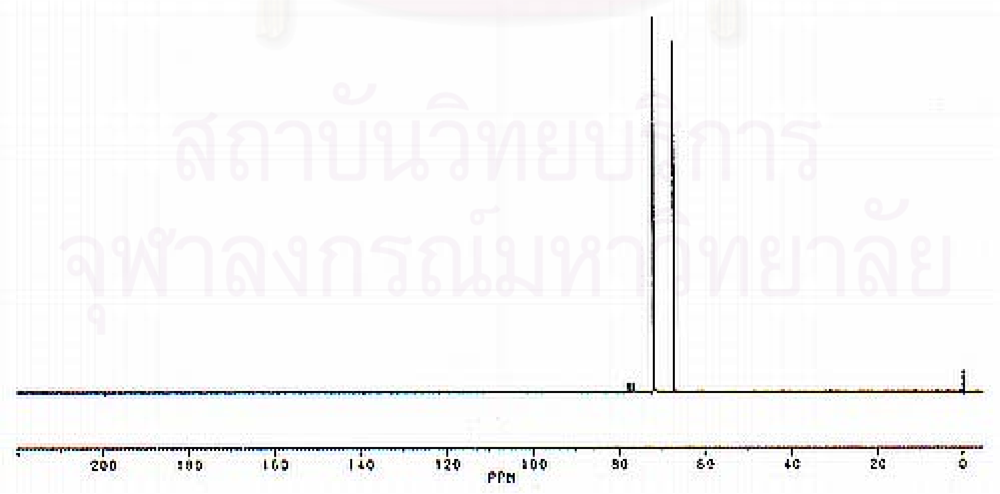


Figure A-6 ^{13}C-NMR spectrum of diethylene glycol dinitrate

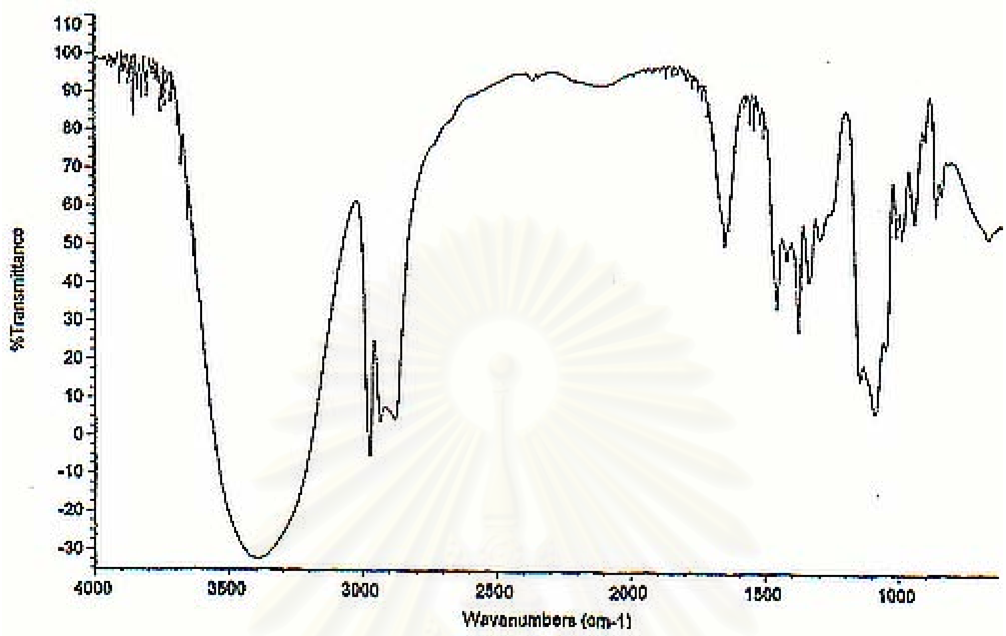


Figure A-7 FTIR spectrum of dipropylene glycol

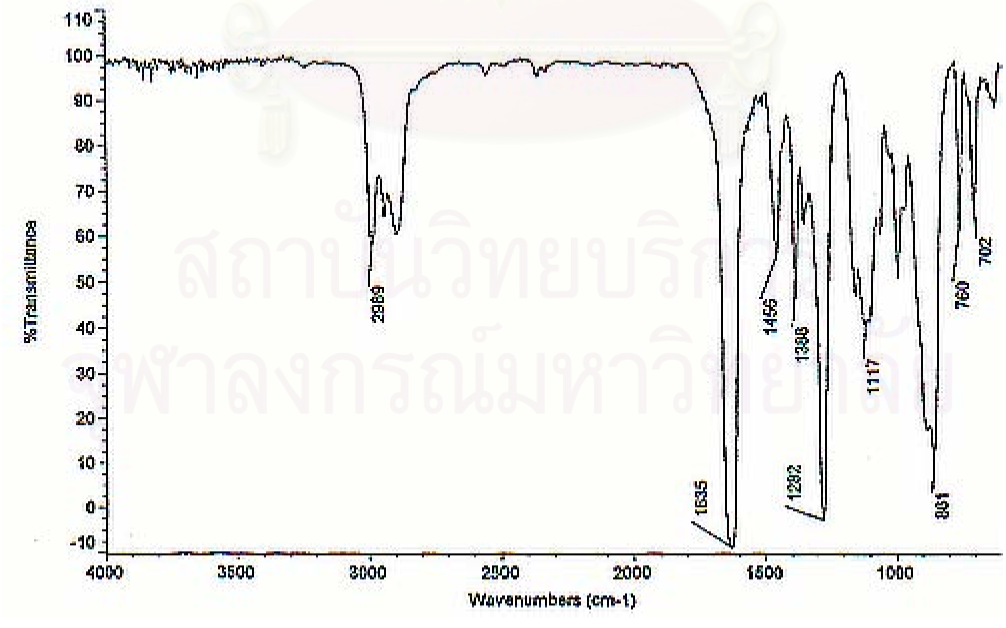


Figure A-8 FTIR spectrum of dipropylene glycol dinitrate

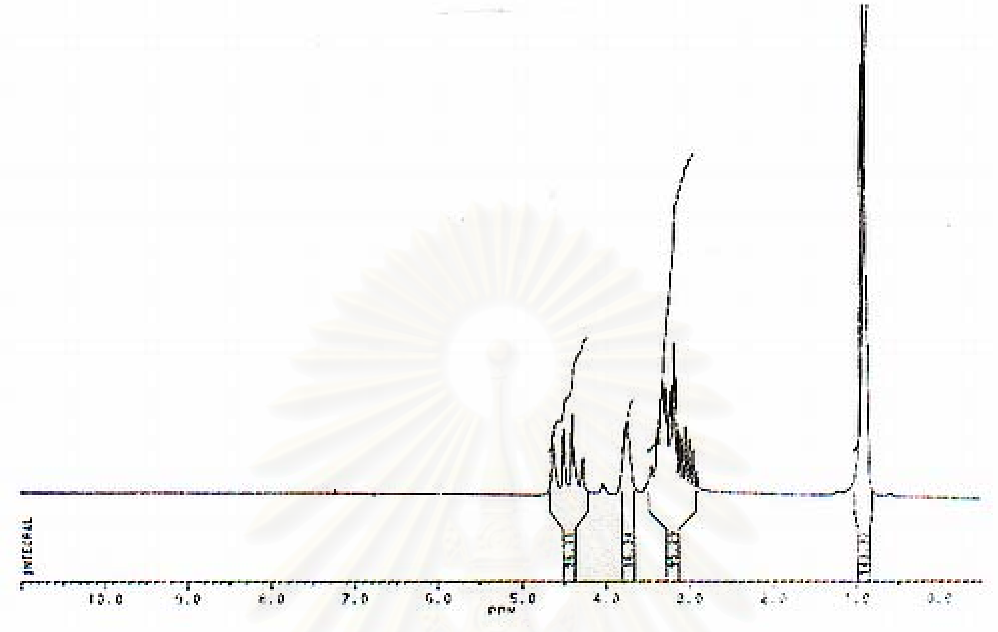


Figure A-9 ^{1}H-NMR spectrum of dipropylene glycol

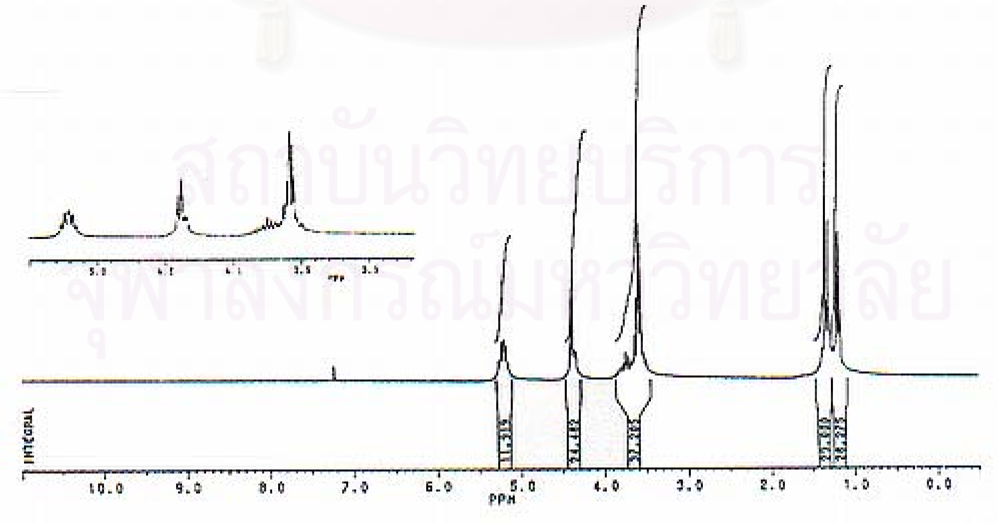


Figure A-10 ^{1}H-NMR spectrum of dipropylene glycol dinitrate

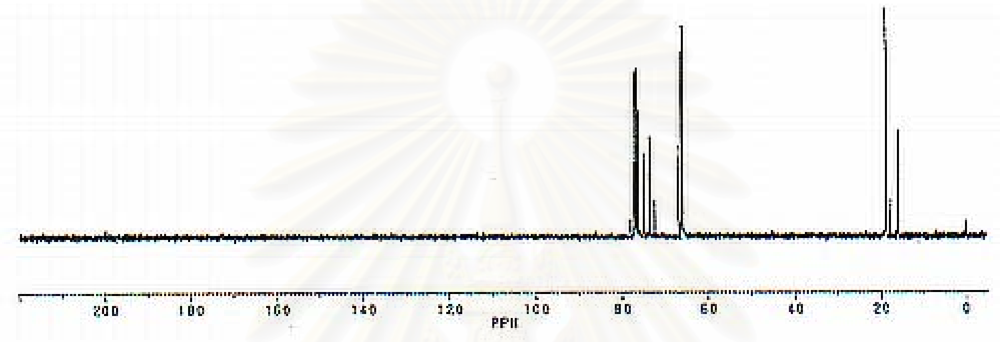


Figure A-11 ^{13}C-NMR spectrum of dipropylene glycol

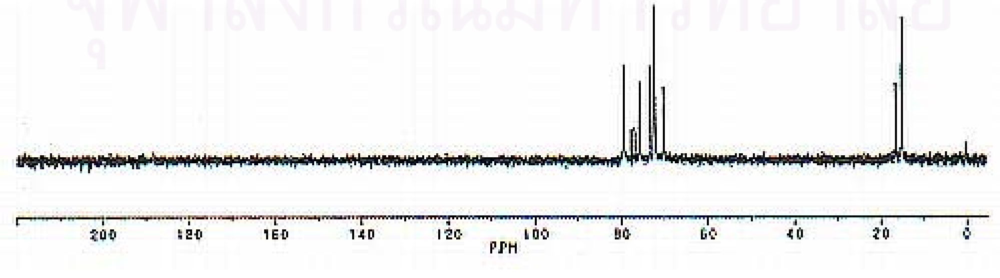


Figure A-12 ^{13}C-NMR spectrum of dipropylene glycol dinitrate

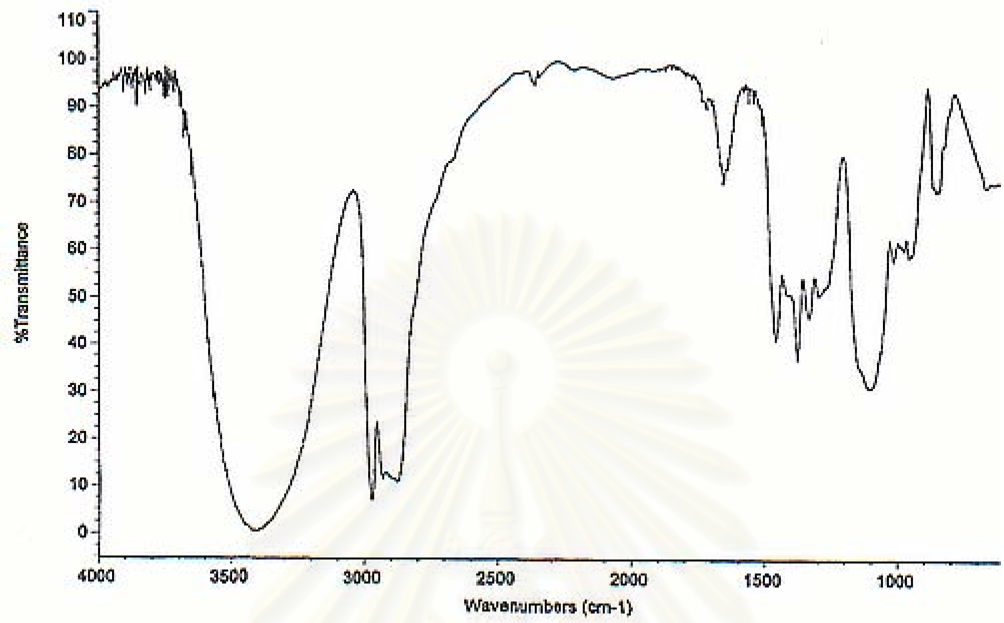


Figure A-13 FTIR spectrum of tripropylene glycol

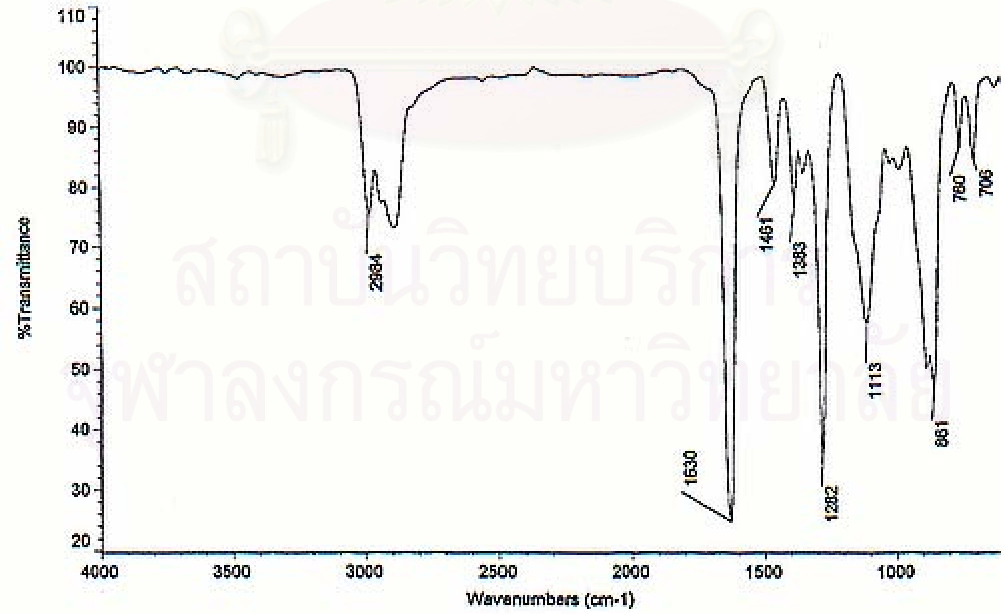


Figure A-14 FTIR spectrum of tripropylene glycol dinitrate

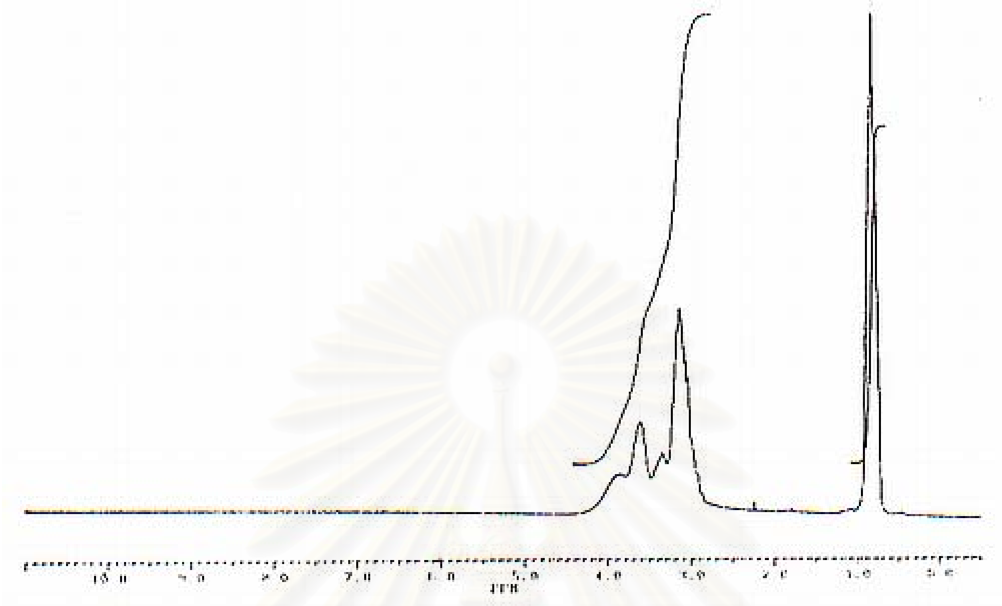


Figure A-15 ^{1}H-NMR spectrum of tripropylene glycol

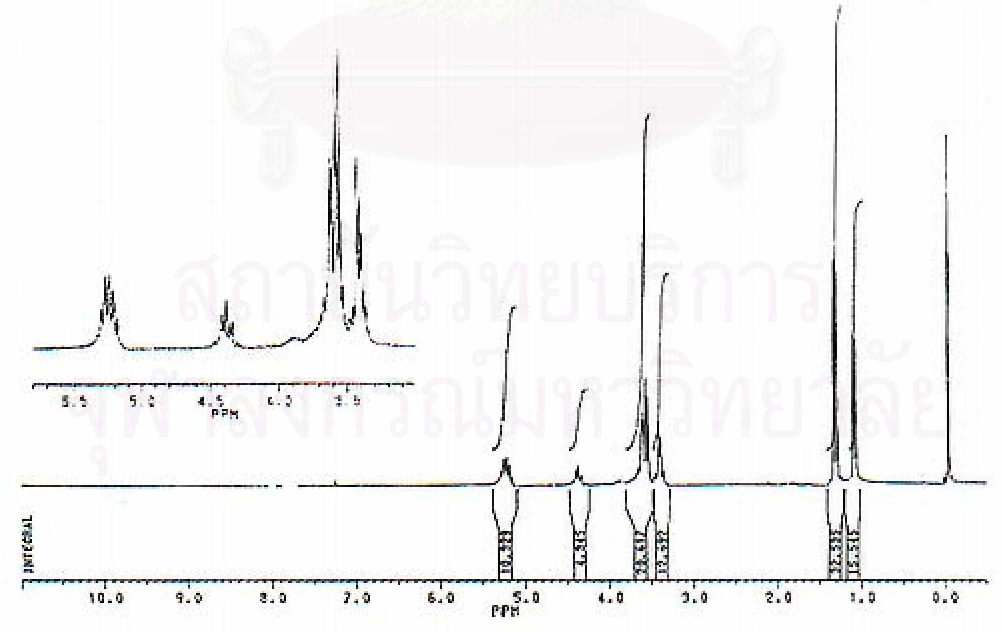


Figure A-16 ^{1}H-NMR spectrum of tripropylene glycol dinitrate

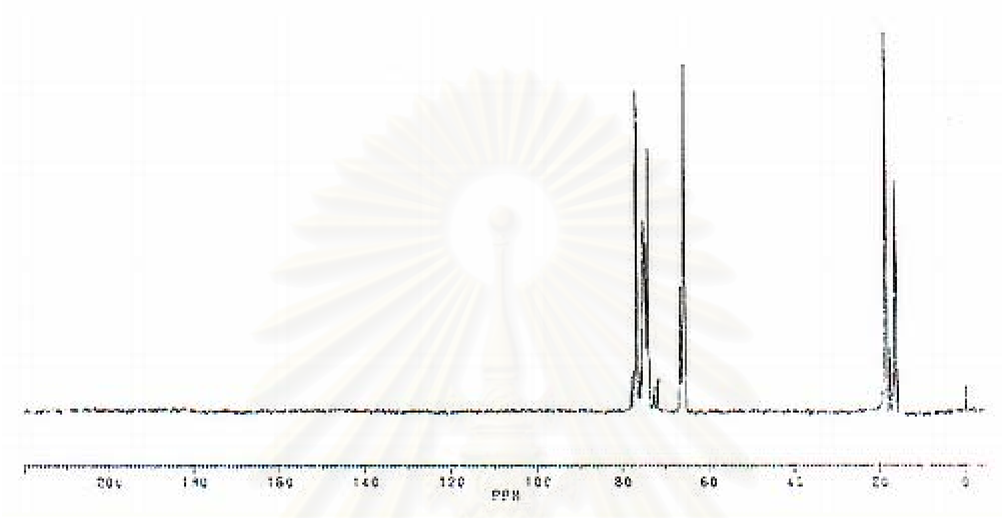


Figure A-17 ^{13}C-NMR spectrum of tripropylene glycol

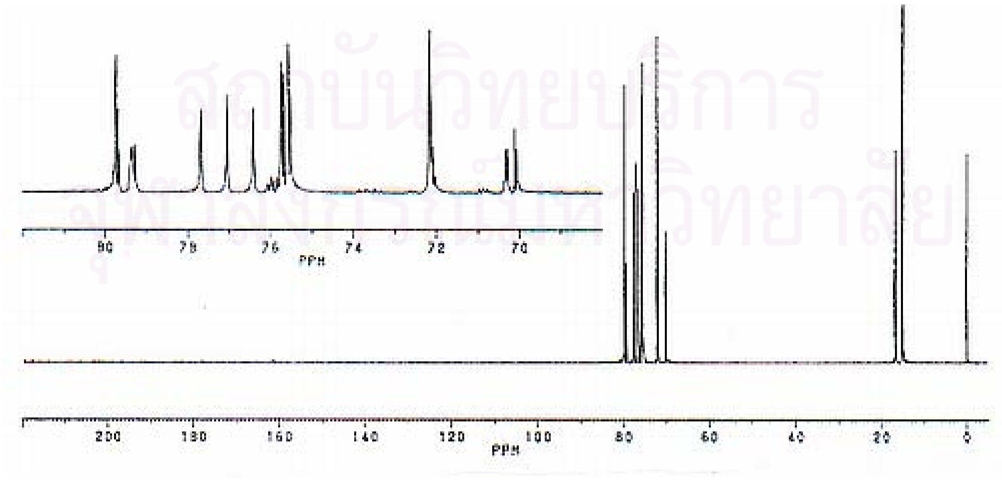


Figure A-18 ^{13}C-NMR spectrum of tripropylene glycol dinitrate

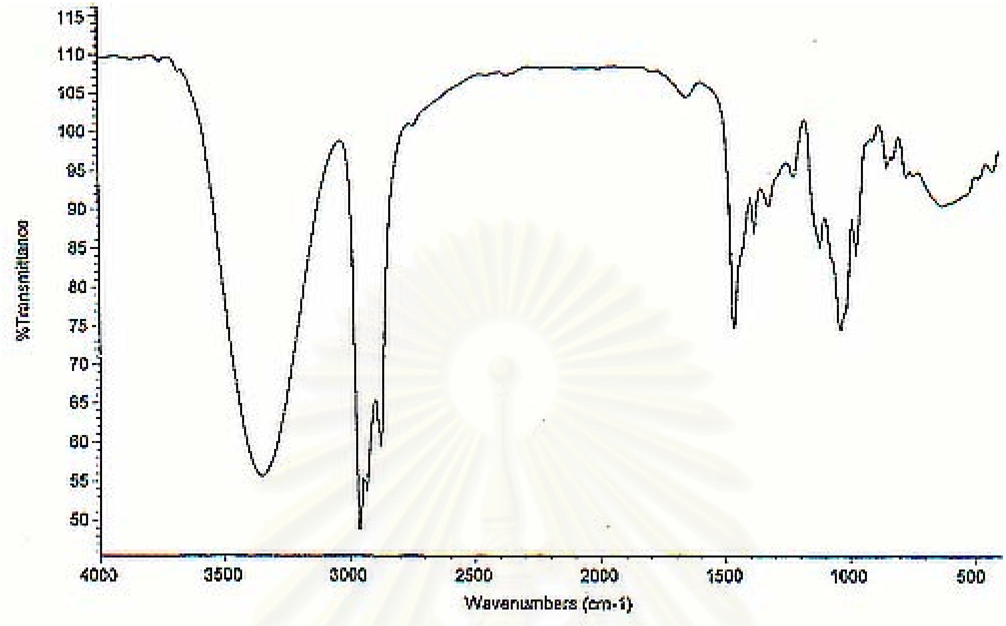


Figure A-19 FTIR spectrum of ethylhexylene glycol

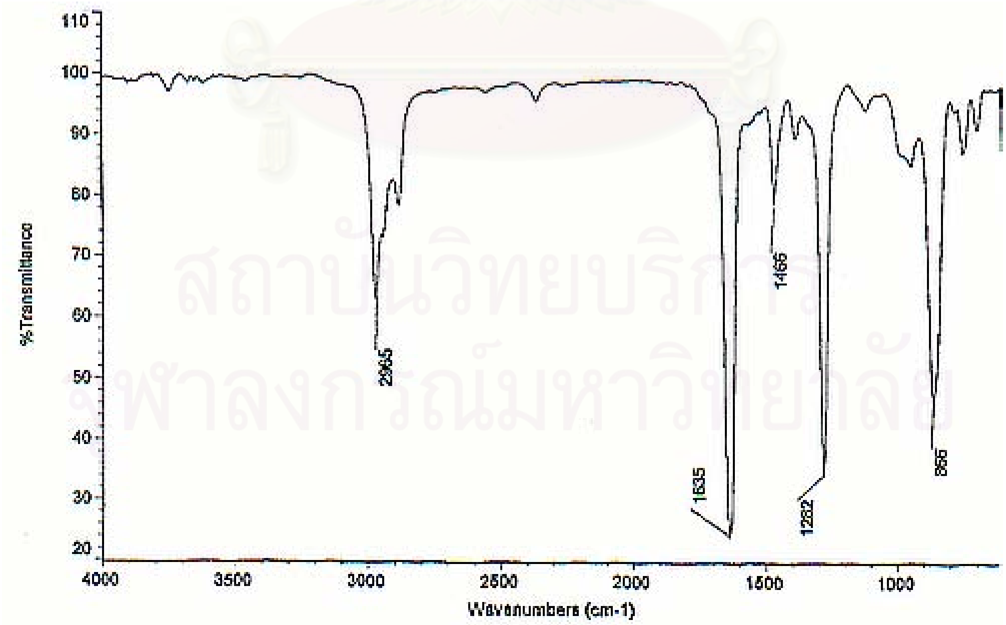


Figure A-20 FTIR spectrum of ethylhexylene glycol dinitrate

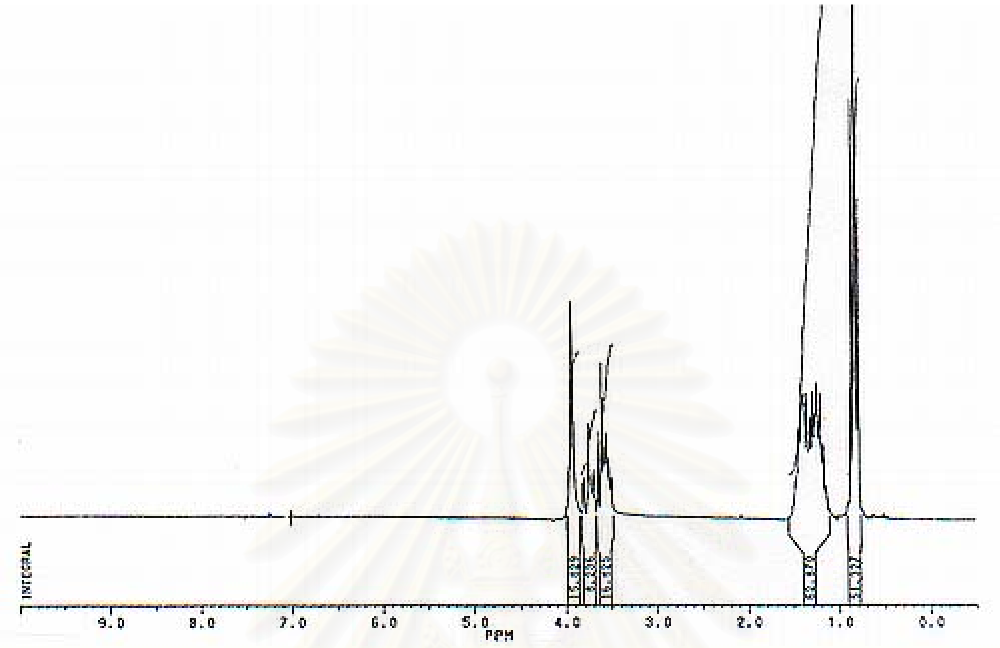


Figure A-21 ^{1}H-NMR spectrum of ethylhexylene glycol

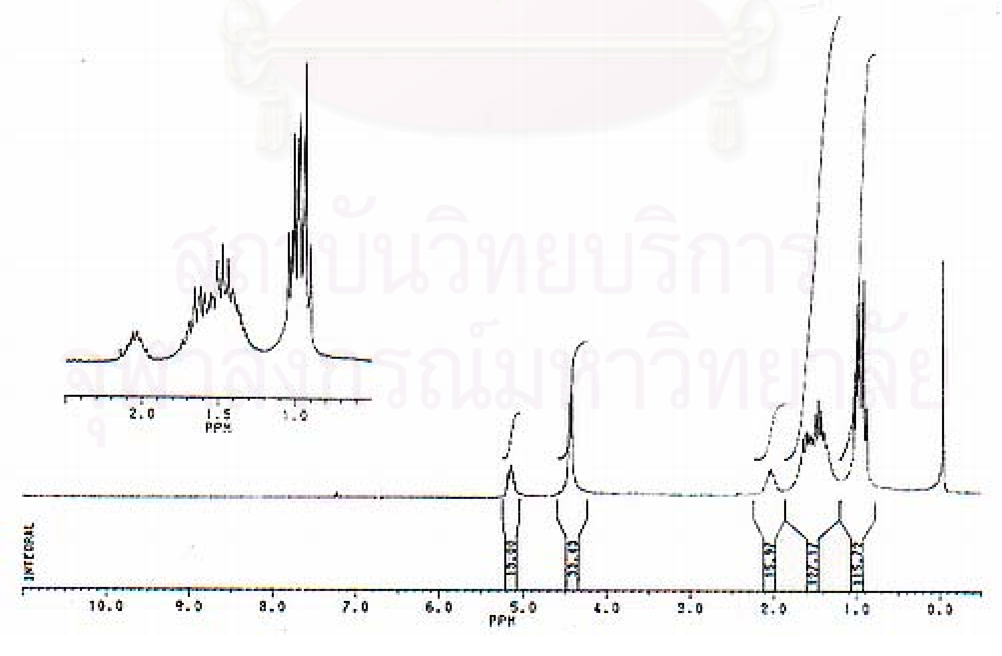


Figure A-22 ^{1}H-NMR spectrum of ethylhexylene glycol dinitrate

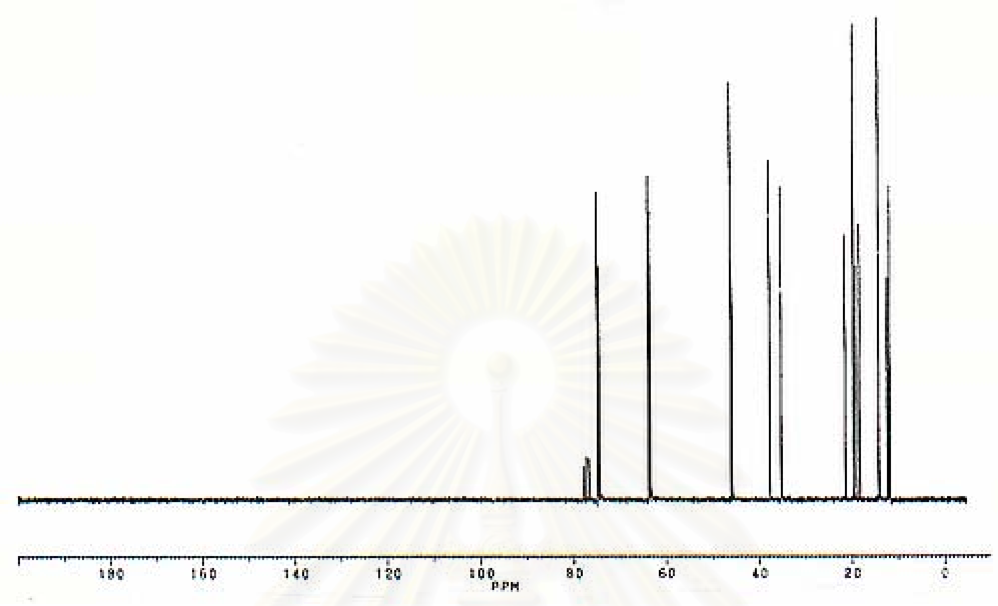


Figure A-23 ^{13}C-NMR spectrum of ethylhexylene glycol

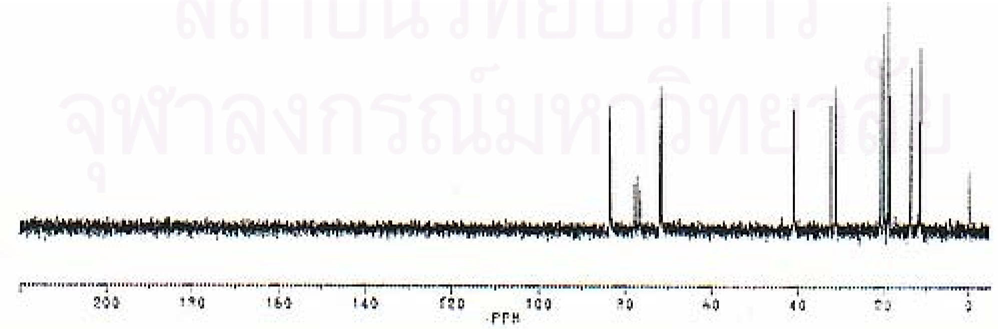


Figure A-24 ^{13}C-NMR spectrum of ethylhexylene glycol dinitrate

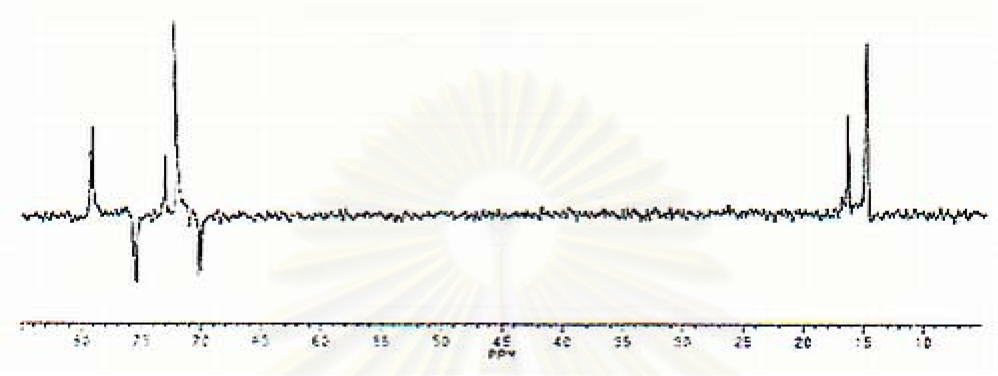


Figure A-25 DEPT 135 spectrum of dipropylene glycol dinitrate.

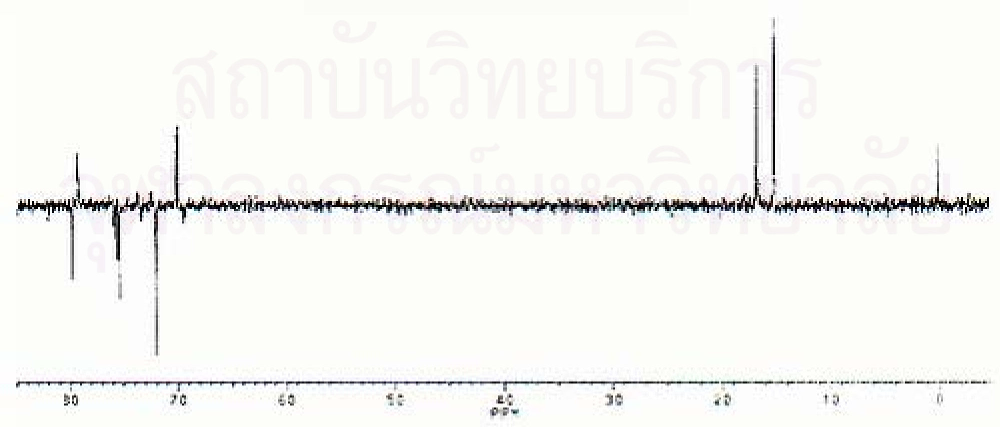


Figure A-26 DEPT 135 spectrum of tripropylene glycol dinitrate.

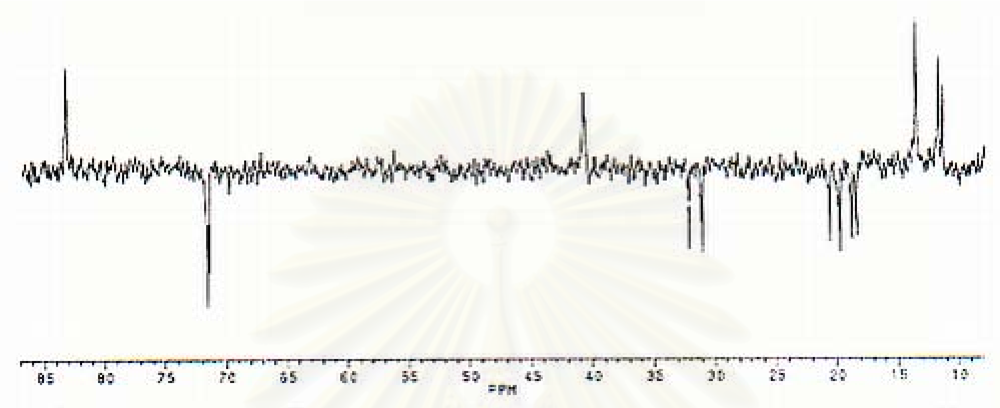


Figure A-27 DEPT 135 spectrum of ethylhexylene glycol dinitrate.

APPENDIX B

THE CALCULATION OF CETANE INDEX

The Calculated Cetane Index was determined from the following equation:

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

$$\text{Calculated Cetane Index} = -420.34 + 0.016G^2 + 0.192G(\log M) + 65.01(\log M)^2 - 0.0001809M^2 \quad \text{.........(C1)}$$

2. When it is applicable to fuels containing additives for raising cetane number. The Calculated Cetane Index is determined from the equation C1 plus equation C2.

$$\text{Improver value} = 0.1742(0.1G)^{1.4444}(0.01M)^{1.0052}\{\ln(1+17.5534D)\} \quad \text{.........(C2)}$$

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, %wt.

For example:

-Determine the cetane index of the blended diesel fuel with ethylhexylene glycol dinitrate when percent weight of cetane improver at 0.05%wt., mid-boiling point at 539.02 °F, API gravity = 36.8

Solution:

From the equation C1,

$$\begin{aligned} \text{CCI} &= -420.34 + 0.016(36.8)^2 + 0.192(36.8)\{\log(539.02)\} \\ &\quad + 65.01\{\log(539.02)\}^2 - 0.0001809(539.02)^2 \\ &= 53.15 \end{aligned}$$

And from the equation C2,

$$\begin{aligned} \text{Improver value} &= 0.1742\{0.1(36.8)\}^{1.4444}\ \{0.01(539.02)\}^{1.0052} \\ &\quad \{\ln(1+17.5534(0.05))\} \\ &= 3.92 \end{aligned}$$

Therefore;

$$\begin{aligned} \text{CCI Improver} &= \text{CCI} + \text{Improver value} \\ &= 53.15 + 3.92 \\ &= 57.07 \end{aligned}$$

APPENDIX C

GENERAL PHYSICAL PROPERTIES TEST OF DIESEL FUEL

Test items	Test Method	Limits
1. API Gravity @ 60°F	ASTM D1298	Report
2. Specific Gravity at 15.6/15.6°C	ASTM D1298	0.81-0.87
3. Cetane Number or	ASTM D613	47 min
Calculated Cetane Index	ASTM D976	47 min
4. Kinematic Viscosity at 40°C, cSt	ASTM D445	1.8-4.1
5. Pour Point, °C	ASTM D97	10 max
6. Flash Point, °C	ASTM D93	52 min
7. Sulphur Content, %wt.	ASTM D4294	0.05 max
8. Copper Strip Corrosion (3 hrs. @ 50°C)	ASTM D130	No. 1 max
9. Carbon Residue, %wt.	ASTM D189	0.05 max
10. Water & Sediment, %vol.	ASTM D2709	0.05 max
11. Ash, %wt.	ASTM D482	0.01 max
12. Distillation, °C	ASTM D86	
Initial boiling Point		Report
10%recovered		Report
50%recovered		Report
90%recovered		357 max
End Point		report
13. Color, ASTM	ASTM D1500	2.0 max

VITA

Chantima Suttipitakwong was born on May 25, 1976 in Chonburi, Thailand. She received her Bachelor's Degree of Science in Chemistry, Kasetsart University in 1998. She continued her Master's Degree of Science in Petrochemistry and Polymer Science, Faculty of Science at Chulalongkorn University in 1998 and finished in 2001.