การสังเคราะห์สารประกอบไดไนเตรทจากอัลเคนไดออล เพื่อใช้เป็นสารเพิ่มค่าซีเทน

นางสาวแสงโสม ศิรประภากิจ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2543

ISBN 974-347-152-9

SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKANE DIOLS AS CETANE IMPROVERS

Miss Sangsom Siraprapakit

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 974-347-152-9

Thesis Title SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKANE DIOLS AS CETANE IMPROVERS

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Field of Study **Petrochemistry and Polymer Science**

Thesis Advisor **Assistant Professor Somchai Pengprecha, Ph.D.**

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การสังเคราะห์สารประกอบไดไนเตรทจากอัลเคนไดออลได้แก่ 1,6-เฮกเซนไดออล 1,8-ออกเทนไดออล 1,10-เดคเคนไดออล และ 2-เมทิล-2,4-เพนเทนไดออล สามารถเตรียมได้โดยตรงจากปฏิกิริยาไนเตรชัน โดยใช้ของผสมระหว่างกรดไนตริก และกรดซัลฟูริกเข้มข้นในตัวทำละลาย สารที่ได้ทำการพิสูจน์เอกลักษณ์โดยการวิเคราะห์ด้วยเทคนิคทางสเปกโทรสโคปีได้แก่ อินฟราเรดสเปกโทรสโคปี และนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโคปี

สารประกอบไดไนเตรทที่สังเคราะห์ได้สามารถละลายในน้ำมันดีเซลพื้นฐานได้ง่าย จากการตรวจสอบค่าดัชนีซีเทนพบว่า สารเหล่านี้ให้ค่าดัชนีซีเทนเพิ่มขึ้นประมาณ 3.9 และ 6.3 หน่วย ที่ความเข้มข้น 0.05% และ 0.10%โดยน้ำหนัก ตามลำดับ และจากการทำนายค่าซีเทนพบว่า สารเหล่านี้ให้ผลที่ดีมากกว่าสารเพิ่มค่าซีเทนที่มีจำหน่ายในเชิงพาณิชย์ทั้งที่ระดับความเข้มข้น 0.05% และ 0.10%โดยน้ำหนัก โดยเฉพาะ 1,10-เดคเคน ไดไนเตรท สารประกอบไดไนเตรทเหล่านี้มีแนวโน้มที่สามารถนำมาใช้สำหรับเพิ่มค่าซีเทนในน้ำมันดีเซลพื้นฐานได้ดี

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ **ลายมือชื่อนิสิต**..

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ **ลายมือชื่ออาจารย์ที่ปรึกษา**................................

ปีการศึกษา 2543 **ลายมือชื่ออาจารย์ที่ปรึกษาร่วม**...........................

4172520023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORD: CETANE NUMBER / NITRATION / DIESEL FUEL / DIESEL ADDITIVE / CETANE IMPROVER / DINITRATE COMPOUNDS

SANGSOM SIRAPRAPAKIT : SYNTHESIS OF DINITRATE COMPOUNDS FROM ALKANE DIOLS AS CETANE IMPROVERS. THESIS ADVISOR : ASSIST. PROF. SOMCHAI PENGPRECHA, Ph.D., THESIS CO-ADVISOR : Mrs. RATANAVALEE IN-OCHANON, 85 pp. ISBN 974-347-152-9.

Synthesis of dinitrate compounds from alkane diols, such as 1,6-hexane diol, 1,8-octane diol, 1,10-decane diol, and 2-methyl-2,4-pentane diol could be prepared by direct nitration reaction. The nitration took place by using mixed acid containing concentrated nitric acid and concentrated sulfuric acid in the presense of solvent. The dinitrate compounds obtained were identified by spectroscopic techniques, such as Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy.

They could be easily blended with base diesel fuel. From the determination of cetane index, they could increase cetane index about 3.9 and 6.3 units at the concentration of 0.05% and 0.10% by weight, respectively. From the prediction of cetane number, they were more effective than commercial cetane improver at both concentrations of 0.05% and 0.10% by weight, especially 1,10-decane dinitrate. These dinitrate compounds had potential to be used for improving cetane number of base diesel fuel.

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 wish to express my sincere thank to my advisor, Assisant Professor Dr. Somchai Pengprecha and co-advisor, Mrs. Ratanavalee In-ochanon, for their generous guidance and encouragement throughout this research. I am also grateful to Associate Professor Dr. Supawan Tantayanon, Associate Professor Dr. Sophon Roengsumran, and Associate Professor Dr.Wimonrat Trakarnpruk, for serving as chairman and members of thesis committee, respectively, whose comments have been specially valuable.

I also thank for the research financial supports from Chulalongkorn University and the Petroleum Authority of Thailand for their assistance in determining the physical properties and cetane index of the blended diesel fuel and the special thanks for base diesel fuel from Thai Oil Refinery.

Lastly, I would like to thank everyone who has contributed suggestions and supports throughout this research.

CONTENTS

PAGE

CONTENTS (continued)

PAGE

CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Scientific Rationale

In the present, the diesel engines are the most important engines because they have extended over a much wider range of applications than any other engines currently in use. They are used for driving small and large electric power generating and pumping units such as the main propulsion of ships and their auxiliaries, in large and small road vehicles. The furthermore they are used for off road agricultural, civil engineering vehicles, machinery and also for mailway locomotives [1]. Therefore, the demand for diesel fuel has been increased. The consumptions of diesel fuel are being continuously increased as shown in Figure 1.1 [2].

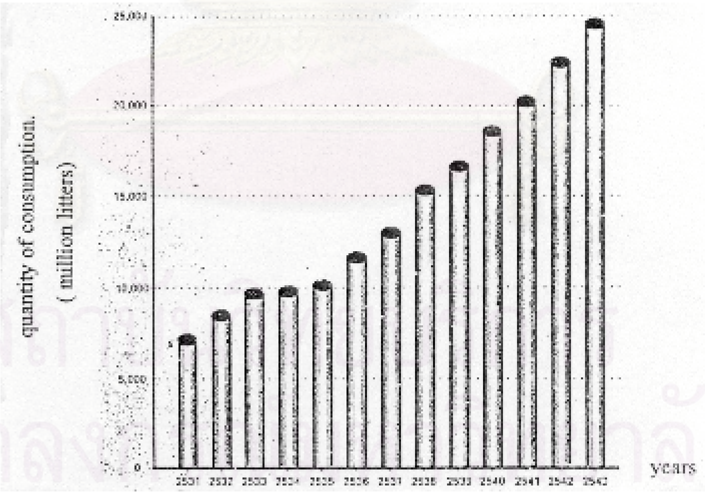


Figure 1.1 The quantity of high-speed diesel consumption in Thailand.

Because of the increased using of diesel engine, the demanding of diesel fuel is also increased. Diesel fuel contains hydrocarbons having higher boiling points than those of gasoline. Diesel fuel generally has a distillation range between 150 - 360 °C (300-700° F). Gasoline generally distills below this temperature range between about 40-205°C (100-400° F). Moreover, gasoline is designed to resist burning when compressed in the absence of a spark. Such burning is undesired because it causes knocking. Diesel fuel is the opposite. Diesel fuel must be ignited spontaneously and quickly without a spark [3]. Low-speed diesel engine may be ran by heavy kerosene or bunker oil. Modern high-speed diesel engine must be uses with better quality and clearer fuel or mixed fuel.

The using of diesel fuel must regards to ignition quality and other standard quality or appropriates that engines. If using low quality fuel, the engines will have the following problems:

1. The first start is difficult, especially when the engine is cool.
2. The power is down.
3. The fuel consumption is increased.
4. More smoke and soot are occurred.
5. The lubricant is dirty easily, etc.

The important target of fuel selection is to improve cold starting, have viscosity appropriate for lubrication of the fuel pump and injector nozzle, and have no excess mixer [4]. Then the additives are added in fuel to develop quality. Ignition quality of fuel is the most important quality of diesel fuel.

Cetane number indicates good or bad ignition quality which number has been developed on a basis very similar to that adapted for measuring the ignition quality of gasoline in the term of octane number. Cetane number is related to ignition delay after the fuel is injected into the combustion chamber. If ignition delays are too long, the amount fuel in the chamber is increased and upon ignition results in a rough running engine and results of smoke. In the other hand, a short ignition delay results to smooth engine operation and less smoke. In the present, high-speed diesel engine has ignition delay of about 0.0012-0.030 seconds [4]. Diesel fuel generally has a cetane number of about 40-55. Good ignition quality or high cetane number diesel tends to result in easier starting, although in cold weather, smooth quiet running engine, faster warm-up, high combustion efficiency and save fuel oil. If ignition quality is low, the engine is hard to start, rough operation and knock.

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

Cetane improvers are special chemicals which improve cetane number of diesel fuel similar to ethanol and MTBE improve the octane rating of gasoline. At concentrations less than 0.15%, cetane improvers can reduce ignition delay times of diesel fuels. Fundamentally, the cetane improver concentration is another degree of freedom in designing a diesel fuel. In practice, this degree of freedom is often capable of simultaneously decreasing NO_x, hydrocarbon and particular emissions [7]. The use of cetane improvers is increasing due to the increased demand for diesel fuel.

Through the years, many types of additives have been used to raise the cetane number of diesel fuel. These include peroxides, nitrates, nitrites, nitrosocarbonates and the like. Alkyl nitrate and mixed octyl nitrates have been used commercially with good results [8].

1.2 Objective and Scope of the Research Work

Objective

1. To synthesize dinitrate compounds from alkane diols for using as cetane improvers in diesel fuel.
2. To study the properties and cetane number of the blends of dinitrate products in base diesel fuel.

Scope of the Investigation

The investigation procedures were carried out as follows:

1. Literature survey and study of the research work.
2. Preparation of apparatus and chemical substance.
3. Synthesis of dinitrate compounds from alkane diols by nitration reaction. The alkane diols were :
   - 1,6-hexanediol
   - 1,8-octanediol
   - 1,10-decanediol
   - 2-methyl-2,4-pentanediol
4. Characterization of the dinitrate compounds by Fourier-Transform Infrared Spectrophotometer and Fourier-Transform NMR Spectrometer.
5. Determination of the physical properties of blended base diesel fuel containing dinitrate compouds.
   - Mid-Boiling Point by ASTM D86
   - API Gravity by ASTM D1298

- Pour Point by ASTM D97
- Flash Point by ASTM D93
- Viscosity by ASTM D445
- Cetane Index by ASTM D976
- Cetane Number by using nomograph

6. Conclusion.

CHAPTER 2

THEORETICAL CONSIDERATION

2.1 Diesel Engines

Diesel engines are known as compression ignition engines. Gasoline engines are known as spark ignition engines. Both engines are of the internal-combustion design because they burn the fuel within the engine. The major components of both engines are the same. However, the components of a diesel engine with the same horsepower as a gasoline engine are heavier because they must withstand greater dynamic force and more concentrated stress and load put on them due to the greater pressure. These two types of engines differ greatly in ignition and power control. Usually the diesel engine draws a full charge of air into the combustion chamber during the engine's intake stroke. Then the air is compressed to a compression ratio between 12:1 and 20:1 during a compression stroke depending on cylinder size, combustion system and whether the engine is turbocharged. This one factor contributes to the high efficiency of diesel engine. This high compression ratio typically raises the temperature of the air to 540°C (about 1000°F). Just before the top center of the compression stroke, fuel is sprayed into the combustion chamber. The high air temperature quickly ignites the fuel to produce combustion products. The combustion products expand to produce power and exhaust to complete the cycle [3].

Diesel engines are not self-speed limiting. Engine air intake for combustion is not limited. The cylinders always have more air than is needed to support combustion. A diesel engine required a speed limiter (the governor) because the amount of fuel injected into the cylinder controls the engine speed. A manual control would be near impossible because a diesel engine can accelerate at a rate of more than 2000 revolutions per second [9]. Furthermore the diesel engine requires no ignition system because the fuel is injected as the piston is near the top of its stroke. The injection pump and governor of a diesel engine control the quantity of fuel inject of by the fuel nozzle

2.1.1 The Diesel Combustion Process

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

Fuel will burn only when it is in a vaporized state (attained through addition of heat) and intimately mixed with a supply of oxygen. All these conditions are present in the cylinder. When the first minute droplet of fuel enters the combustion chamber, it is quickly surrounded by its own vapor because the compression temperature at this point is about 343°C (650°F). Heat is withdrawn from the air surrounding the droplet causing it to vaporize. It takes time for the heat to build up again and cause the vapor to ignite since the core of the droplet is still liquid and relatively cold. One ignition has started and a flame is present, the heat required for continuous vaporizing is supplied from that released by combustion and the higher compression temperature. The liquid droplet, surrounded by its own vapor, burns as fast as fresh oxygen is supplied. This process continues unchanged until the fuel oil is burned or the oxygen is used up [1] [10].

2.1.2 Combustion of Diesel Fuel Oils

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

2.1.3 General Outline of Combustion in the Diesel Engine

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

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

In the diesel engine, these requirements are met as indicated diagrammatically in Fig.2.1 [10].

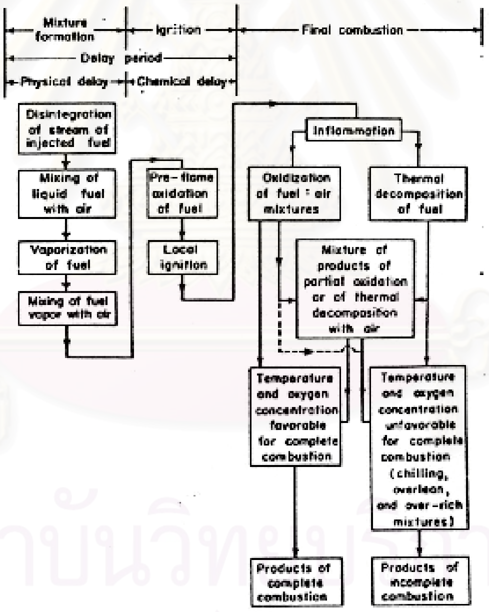


Figure 2.1 Outline of combustion process in the diesel engine.

Ignition in the diesel engine occurs as the result of auto-ignition of the fuel. This is accomplished by the direct oxidation of the fuel, the rate of which is comparatively slow at first and accelerates rapidly until ignition occurs. After ignition, the mixture inflames and combustion may proceed as indicated in Fig. 2.1, either by rapid oxidation of mixtures of fuel and air or by rapid oxidation of products of thermal decomposition of the fuel. If mixing is complete under conditions favorable for combustion, then combustion is complete. If mixing is inadequate or if combustion reactions or thermal decomposition reactions are chilled, products of incomplete combustion will result.

2.2 Diesel Fuel

Fuel for diesel engine is obtained from fractional distillation of the crude oil to separate it into ractions with boiling ranges appropriate to the major fuel application.

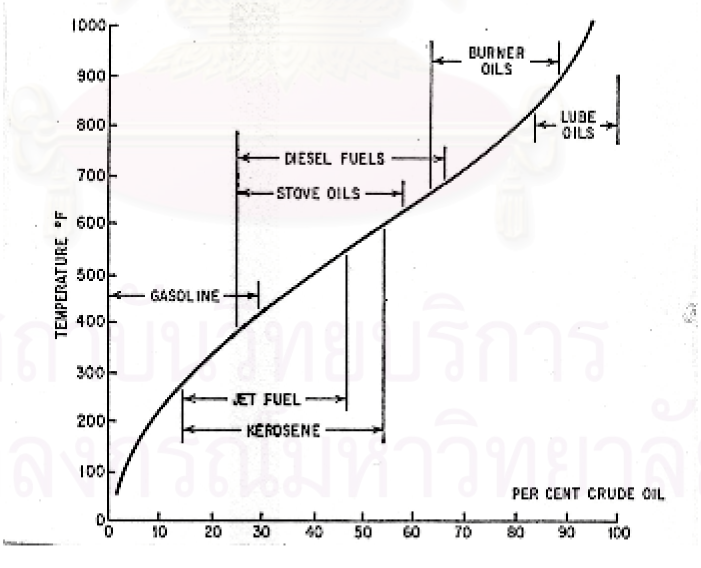


Figure 2.2 Proportion of diesel fuel and other petroleum products processed from crude petroleum.

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

With reference to Fig. 2.2 [11], the more common designation is that portion of the distillation curve from 25 to 65 percent of the crude-oil barrel, or within the temperature ranges of 300-700 °F. Other properties are evaluated and characteristics are determined which influence the fuel performance value in a specific application. In the diesel fuel classification many properties are considered significant by the American Society for Testing Materials, such as cetane number, viscosity, carbon residue, sulfur content, flash point, pour point, ash, and copper-strip corrosion.

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

2.2.1 Composition of Fuels Derived from Petroleum

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

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

Class I Components

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

1. Paraffins, both straight chain and moderately branched. Generally, one may consider that for diesel fuels, in the formula varies from 9 to 20 carbon atoms.
2. Olefins structurally undefined.
3. Naphthenes consisting of major proportions of five and six carbon rings with multiple and short paraffinic side chains.
4. Aromatics consisting of major proportions of mononuclear compounds and multiple and short paraffinic side chains.

Class II Components

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

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

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

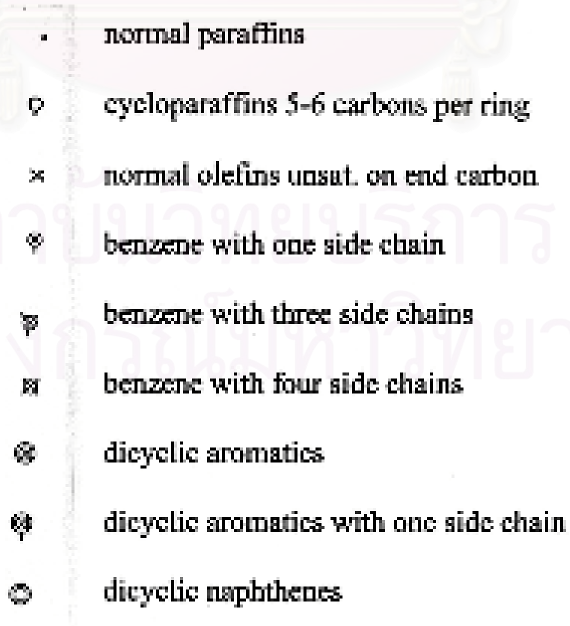
Oxygen derivatives – Hydrocarbon derivatives containing oxygen are also present in some crudes such as naphthenic acids.

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

2.2.2 Specifications for Diesel Fuel

Although hydrocarbons contained in the diesel fuel boiling range are complex and consist of a large number of individual compounds, it is possible to characterize these hydrocarbons in their respective groups as paraffins, olefins, naphthenes, aromatics and di-cycle compounds. It has been considered that gravity, net heat of combustion, melting point, and viscosity are the main properties of hydrocarbons which have significance in the study of the characteristics of diesel fuels

The symbols are used to represent the several types of hydrocarbons in the plots of the physical data in Figs. 2.3 through 2.6 [10].



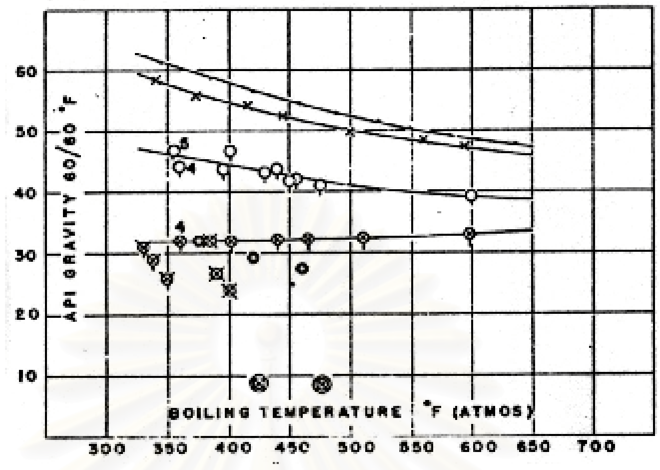


Figure 2.3 API gravity vs. boiling temperature range, for typical hydrocarbons.

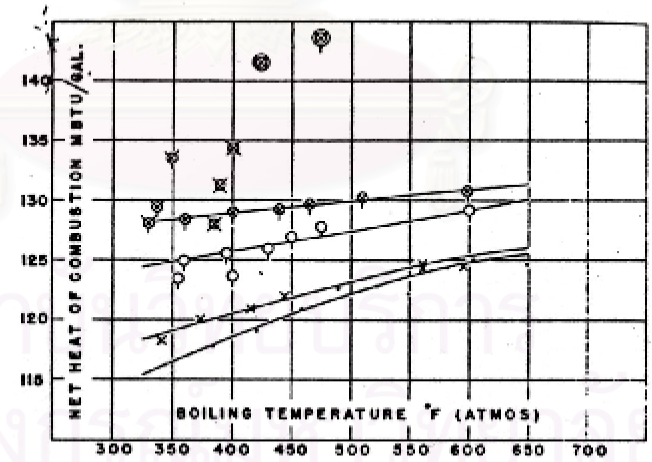


Figure 2.4 Net heat of combustion vs. boiling temperature range, for typical hydrocarbons.

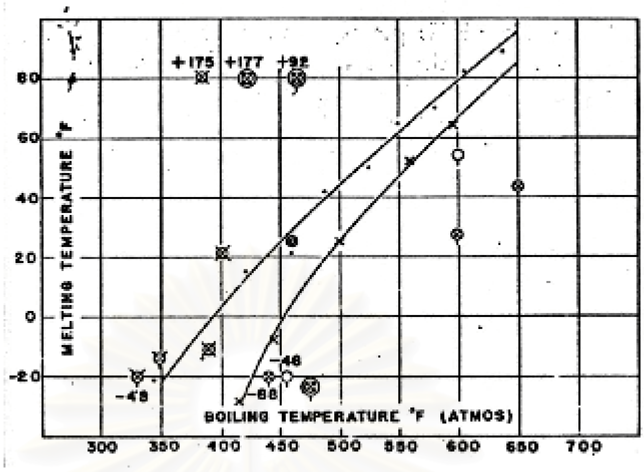


Figure 2.5 Melting point vs. boiling temperature range, for typical hydrocarbons.

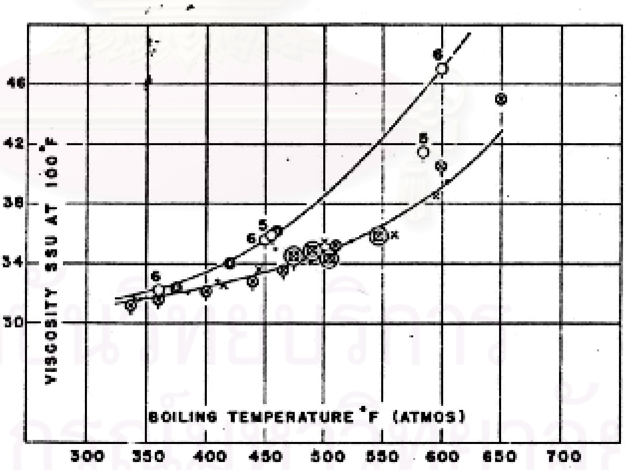


Figure 2.6 Viscosity, SSU at 100°F., vs. boiling temperature range, for typical hydrocarbons.

The trends in the physical properties of the individual hydrocarbons as a function of hydrocarbon type and boiling point can be used to indicate similar properties of mixtures. In order to obtain the most desirable quality for one property of the fuel, there frequently arises are incompatibility between certain other properties.

When this is not possible it means that one must resort to a change in the manufacturing steps either through blending of various other available components or through the addition of some processing step to convert the hydrocarbon mixture to a product having more favorable characteristics. Characterization tests considered from this standpoint are:

Distillation Range – Distillation range indicates the volatility characteristics of the fuel, and is reported in terms of the temperature at which successive percentages of the fuel have been distilled in a standardized apparatus. For example, high 90% temperatures indicate low quality for complete vaporization of the fuel, and conversely, low 90% temperatures indicate a favorable quality for complete vaporization.

Gravity – Gravity is usually given in terms of degrees API, the numerical value of which varier inversely as specific gravity. For example, a 10° API gravity is equivalent to a specific gravity of unity, and as the API gravity increases in numerical value the specific gravity decreases. The heat of combust of hydrocarbon mixtures is almost a direct function of the gravity. A lower gravity fuel increases power output and reduces fuel consumption in Fig.2.7 [10].

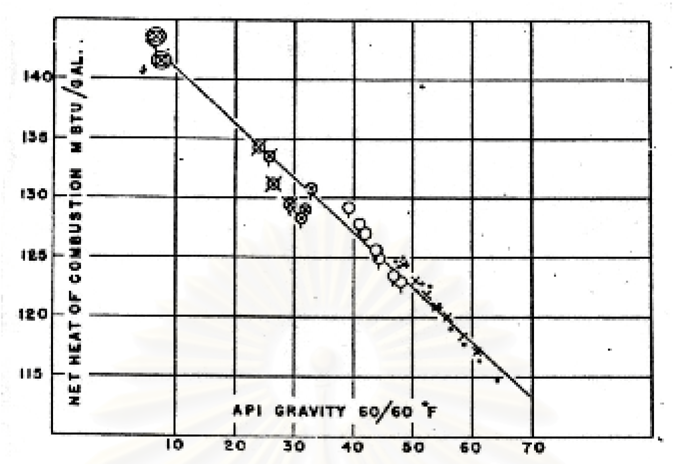


Figure 2.7 Net heat of combustion vs. API gravity.

Viscosity – The viscosity of diesel fuels is usually expressed in terms of Saybolt Universal seconds at 100°F. Control of viscosity appears to be a function only of the average boiling point of the fuel mixture and the concentration of naphthalene hydrocarbons.

Pour point – The pour point of a fuel can be broadly defined as a measure of the percentage of high-melting point components in the mixture. In order to reduce pour points for any particular stock mixture a reduction in paraffin content is usually required, inasmuch as paraffin hydrocarbons have higher melting points than all other hydrocarbons boiling at the same temperature. Another method to reduce pour point is through the use of pour depressors. Since paraffins are preponderantly high in cetane number, reduction in pour point through elimination of paraffinic fuels obviously is incompatible with cetane number. This points toward making a selection of which is the more important, cetane number or pour point. The pour point of diesel fuels should be at least 10°F below the lowest operating temperature of the engine [9].

Flash point – Flash point is considered as having no significance in diesel-engine performance. It is used primarily as a safety measure since it represents temperatures at which the fuel will flash in the presence of some igniting hot spot or flame.

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. It is quite easy to suspend water in hydrocarbon mixtures boiling in the range of diesel fuels, and it should be emphasized that in the handling of such fuels, where agitation is involved, potential contact with water and rust must be kept at a minimum.

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.

Carbon residue – Carbon residue reflects the presence of high-boiling or rather extremely low-volatility components present in a fuel. The components causing high carbon residues may be expected to increase engine deposits due to their inability to vaporize.

Sulfur content – The sulfur content is associated with the corrosion and deposit-forming tendencies of the fuel, usually specifying 0.75% maximum content [11].

The properties of commercial fuel oils depend on the refining practices employed and the nature of the crude oils from which they are produced[10].

Table 2.1 Properties of various hydrocarbon groups with respect to their suitability as diesel fuels.

Hydrocarbon groups	**Properties**
Paraffins	high cetane number, low combustion heat per gallon, high pour point, and low mixed fuel-air combustion characteristics.
Olefins	low combustion heat per gallon and low pour point. The cetane characteristics are not too well defined.
Naphthenes	intermediate cetane number, intermediate combustion heat per gallon, and low pour point.
Aromatics	Low cetane number and pour point, with high combustion heat per gallon and high mixed fuel-air combustion characteristics.

The ASTM Classification D975 of diesel fuel oils is intended as a statement of permissible limits of significant fuel properties used for classifying the wide variety of commercially available diesel fuel oils. These grades and their general applicability for use in diesel engines are broadly indicated as follows [11]:

Grade No. 1-D comprises the class of volatile fuel oils from kerosine to the intermediate distillates. Fuels within this classification are used in high-speed engines in services involving frequent and relatively wide variations in loads and speeds and also for use where abnormally low fuel temperatures are encountered.

Grade No. 2-D includes the class of distillate gas oils of lower volatility. These fuels are applicable for use in high-speed engines in services involving relatively high loads and uniform speeds, or in engines not requiring fuels having the higher volatility or other properties specified for No. 1-D.

Grade No. 4-D covers the class of more viscous distillates and blend of these distillates with residual fuel oils. These fuels are applicable for use in low- and medium-speed engines employed in services involving sustained loads at substantially constant speed.

Table 2.2 Properties of ASTM grades of diesel fuels [9].

Grade[a]	**Flash point, °F [°C]**	**Pour point, °F [°C]**	**Water and sediment vol %**	**Carbon residue on 10% residuum,%**	**Ash, wt%**	**Distillation temperatures, F[,°C] –90% point**		**Sulfur, wt%**	**Coppor strip corrosion**	**Cetane number**[e]
	Min.	Max.	Max.	Max.	Max.	Min.	Max.	Max.	Max.	Min.
1D	100 or Legal [37.8]	b	Trace	0.15	0.01		550 [287.8]	0.50	No.3	40[f]
2D	125 or Legal [51.7]	B	0.10	0.35	0.02	540[c] [282.2]	640 [338]	0.7[d]	No.3	40[f]
3D	130 or Logal [54.5]	B	0.50		0.10			2.0		30[f]

[a] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and supplier.

[b] For cold weather operation, the pour point should be specified 10°F [5.6°C] below the ambient temperature at which the engine is to be operated except where fuel oil heating facilities are provided.

[c] When pour point less than 0°F[-17.8°C] is specified, the minimum viscosity shall be 1.8 cSt (32.0 SSU) and the minimum 90 percent point shall be waived.

[d] For all products outside the United States, the maximum sulfur limit shall be 1.0 wt%.

[e] Where cetane number by Method D613 (Test for Ignition Quality of Diesel Fuels by the Cetane Method) is not available. ASTM Method D976 (Calculated Cetane Index of Distillate Fuels) may be used as an approximation. Where there is disagreement, Method D 613 shall be the referee method.

[f] Low-atmospheric temperatures as well as engine operation at high altitudes may require use of fuels with high cetane ratings.

Source : Chevron Research Company

2.3 Ignition Quality

Ignition quality is the most important property of diesel fuel. It is generally recognized that ignition quality is of considerable importance in cold-starting of diesel engines.

Fuel ignition in diesel engines is achieved through the heat generated by air compression, as a piston in the cylinder moves to reduce the cylinder volume during the compression stroke. In the engine, the air is first compressed, then the fuel is injected into the cylinder; as the fuel contacts the heated air, it vaporizes and finally begins to burn as the self-ignition temperature is reached. Additional fuel is injected during the compression stroke and the fuel burns almost instantaneously, once the initial flame has been established. Thus, a period of time elapses between the beginning of fuel injection and appearance of a flame in the cylinder. This period is commonly called " ignition delay " and must be relatively short in order to avoid " diesel knock "[5].

Fuels that have poor ignition characteristic, that is, relatively high spontaneous ignition temperature will exhibit an unduly large ignition lag between the time the fuel is injected into a zone of combustion and the time when the fuel ignites. In diesel engines, for example, a large ignition lag will result in combustion of the fuel and the development of pressure over an improper portion of the crank angle period and piston stroke, resulting in knocking, rough engine operation, incomplete combustion in the combustion zone, power loses, and ultimately detriment to the engine [6].

2.3.1 Physical Chemical Factors Affecting Ignition Delay

The magnitude of ignition delay is affected by significant physical and chemical factors, such as;

Effect of Temperature

It will be observed that ignition delay decreases as the temperature increases on this are shown in Fig. 2.8 [10].

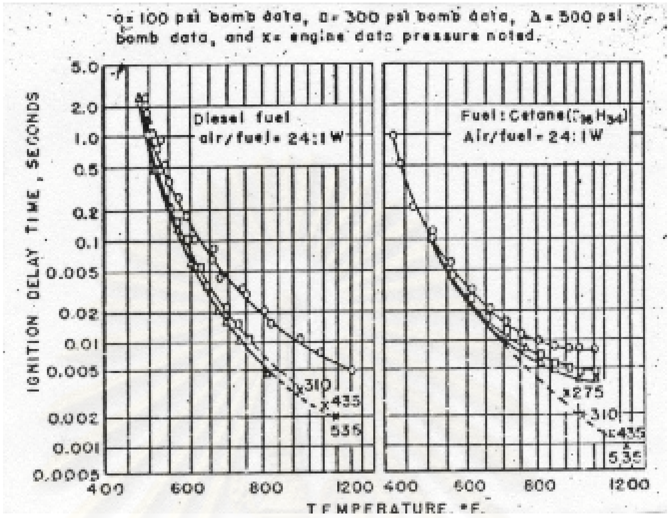


Figure 2.8 Effect of temperature on ignition delay of diesel fuel and cetane in a CFR engine and in a bomb (data of Starkman).

Effect of Pressure

The effect of pressure on ignition delay determined by Wolfer is show in Fig. 2.9 [10], which shows that ignition lag is reduced by increasing the pressure, the dependence on pressure being much greater at the lower pressure.

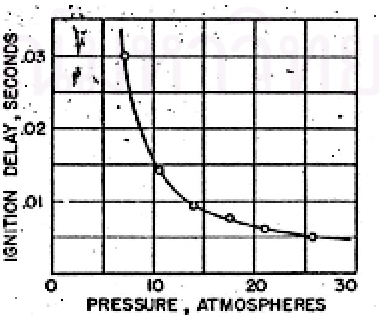


Figure 2.9 Effect of pressure on ignition delay of diesel fuel (data of Wolfer).

Concentration of Fuel

Under the heterogeneous conditions in the diesel engine at the time of ignition, we probably have in the combustion chamber local fuel-air ratios ranging from zero to infinity. Ignition takes place in some region where the fuel-air ratio is optimum. The determination of this optimum fuel-air ratio should be done under conditions such that all the fuel is vaporized and completely mixed with air. This minimum fuel-air ratio is analogous to the lower limit of inflammability. It is important in diesel-engine combustion because, under the heterogeneous conditions existing during combustion, local regions will be present in which the concentration of fuel is less than the minimum or lower limit. Partial oxidation will occur in these regions, but because of the low fuel concentration and low temperatures, the regions will not ignite or inflame. Consequently, products of partial oxidation giving rise to odor and possibly deposits will appear in the exhaust.

Effect of Turbulence

The effect of turbulence on ignition delay should be mentioned, although it is very difficult to establish a satisfactory criterion of turbulence. Data available indicate that, in some instances, turbulence reduced delay and, in other instances, the delay is increased by turbulence. In an engine, turbulence has a marked effect on increasing the rate of inflammation and combustion, and this effect probably far outweighs any effect on ignition delay.

Effect of Fuel Properties

Since both physical and chemical processes take place during the ignition delay, the effects of changes in the physical and chemical properties of fuel on the delay period have been studied. The chemical characteristics of the fuel are much the more important. The dependence of ignition delay on fuel molecular structure is as follows. Straight-chain paraffinic compounds (normal alkanes) have the highest ignition quality, which improves as the chain length increases. Aromatic compounds have poor ignition quality as do the alcohols (hence, the difficulties associated with using methanol and ethanol, possible alternative fuels, in compression-ignition engines). Fig. 2.10 [12] illustrates these effects.

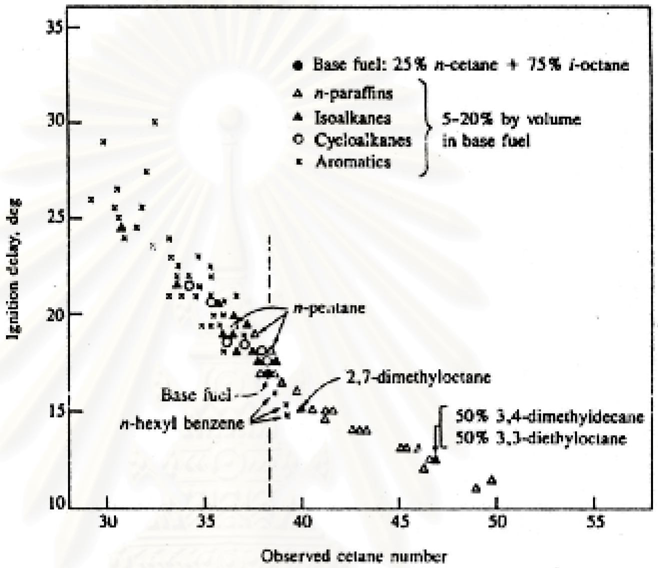


Figure 2.10 Effect of type of hydrocarbon structure on ignition quality of fuels DI diesel combustion process at constant compression ratio and engine operating conditions.

A base fuel was blended with pure paraffinic (normal, iso-, and cycloalkanes), aromatic, and olefinic hydrocarbons of various carbon numbers, by up to 20 percent by volume. The base fuel, a blend of 25 percent n-hexadecane and 75 percent isooctane, had a cetane number of 38.3. The figure shows that the resulting ignition delays correlate well as a function of cetane number at constant compression ratio and engine operating conditions. Addition of normal alkanes (excluding n-pentane and lower carbon number alkanes) improves the ignition quality. As the chain length of the added paraffin gets longer (higher carbon number) the cetane number improvement increases. Isoalkanes, depending on the degree of branching, degrade ignition quality (unless the branching is concentrated at one end of the molecule, when these types of isoalkanes improve ignition quality). Cycloalkanes and aromatics generally reduce the cetane number, unless they have a long n-alkane chain attached to the ring [12].

2.4 Cetane Number Improver

2.4.1 Cetane Number

A major contributing factor to diesel fuel performance and the avoidance of “diesel knock” is the cetane number of the diesel fuel. Cetane number is a test designed to measure ignition quality. Diesel fuels of higher cetane number exhibit a shorter ignition delay than do diesel fuels of a lower cetane number. Therefore, higher cetane number diesel fuels are desirable to avoid diesel knock. Most diesel fuels possess cetane numbers in the range of about 40 to 55 and a sulfur content of about 500 ppm and less [5].

In general, diesel fuel which was derived from petroleum products by distillation process has low cetane number, so it isn’t used as fuel for diesel engines. It must be improved quality for increasing cetane number before application. Two methods can be used for increasing cetane number [13];

1. Cracking of diesel fuel having low cetane number, such as by thermal cracking, catalytic cracking and hydrocracking.
   - Thermally cracked gas oil

     Thermally cracked gas oil originates from their visbreaking or the coking process and tends to have a lower cetane number and higher density than distillate gas oil. Thermally cracked gas oil usually goes through a subsequent hydrogenation step because of the formation of unstable olefinic components during the cracking process. After hydrogenation, it represents a useable diesel fuel component.

- Catalytically cracked gas oil

  Catalytically cracked gas oil is generally characterized by a very low cetane number and high density.

- Hydrocracked gas oil

  Hydrocracked gas oil is a very valuable diesel fuel component. The ignition performance is good and the smoking tendency is low.

These methods needed high cost and had not obtained the sufficient cetane number.

2. Adding 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 prepared and evaluated to raise the cetane number of diesel fuel. The additives for improving the cetane number, called pro-cetane, are particularly unstable oxidants, the decomposition of which generates free radicals and favors auto-ignition. Such additives include peroxides, nitrates, nitrites, azo compounds and the like [5]. The nitrates are practically the most ones being used, because of a better compromise between coat-effectiveness and ease of utilization.

Alkyl nitrates such as amyl nitrate, hexyl nitrate and mixed octyl nitrates have been used commercially with good results. However, it is generally accepted that organic nitrates, more specificially the commercial 2-ethylhexyl nitrate, are the most cost-effective additives to improve cetane number of diesels. Because of its relatively low cost, and environmentally friendly nature (ashless), there has been limited work done in this area to replace the 2-ethylhexyl nitrate.

The average increase in cetane number obtained in tests of nine different fuels is shown in Fig. 2.11 [10], in relation to the concentration of ignition accelerator. It will be observed that significant improvement is obtained with comparatively small additions of accelerator.

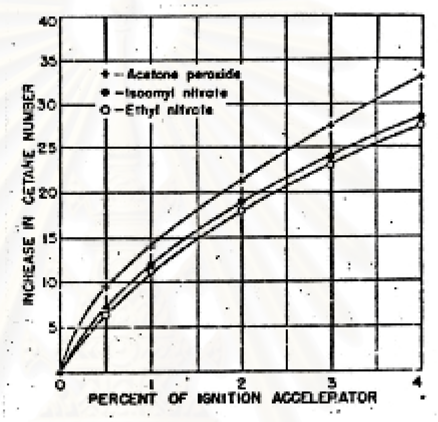


Figure 2.11 Average increase in cetane number of 9 test fuels in relation to concentration of ignition accelerator (data of Bogen and Wilson).

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.

We have just seen that the cetane number is used as an index of the auto-ignition or self-ignition property of the fuel. In general, the higher the cetane number, the more easily a fuel ignites under a given set of conditions. We also have another index for rating the ignitability of fuels, namely, the octane number. However, the octane number is used as an index of the resistance of a fuel to self-ignition. Those fuels that self-ignite most readily under a given set of conditions have a low octane number, those resistant to self-ignition have a high octane number [10]. From this, it is evident that we should expect an inverse relation between cetane number and octane number. Fig. 2.12 [13] shows that this reasoning is valid and that the relation can be expressed quantitatively.

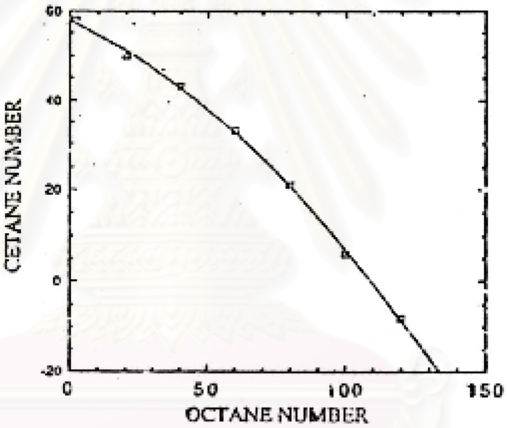


Figure 2.12 The inverse relationship between cetane and octane number.

The cetane numbers of compounds are in Table 2.3 [13]. 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.

Table 2.3 Cetane number for pure organic compounds.

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

The ignition quality of a diesel fuel is defined by its cetane number. The method used to determine the ignition quality in terms of cetane number is analogous to that used for determining the antiknock quality of gasoline in terms of octane number. The cetane number scale is defined by blends of two pure hydrocarbon reference fuels. Cetane (n-hexadecane, $C_{16}H_{34}$), a hydrocarbon with high ignition quality, represents the top of the scale with a cetane number of 100. An isocetane, heptamethylnonane (HMN), which has a very low ignition quality, represents the bottom of the scale with a cetane number of 15.* Thus, cetane number (CN) is given by [12]

$$CN = \text{percent n-cetane} + 0.15 \times \text{percent HMN}$$

The engine used in cetane number determination is a standardized single cylinder, variable compression ratio engine with special loading and accessory equipment and instrumentation. The engine, the operating conditions, and the test procedure are specified by ASTM Method D613. The operating requirements include: engine speed 900 rev/min; coolant temperature 100°C; intake air temperature 65.6°C (150°F); injection timing 13° BTC; injection pressure 10.3 MPa (1500 lb/in^2). With the engine operating under these conditions, on the fuel whose cetane number is to be determined, the compression ratio is varied until combustion starts at TC: i.e., an ignition delay period of 13° (2.4 ms at 900 rev/min) is produced. The above procedure is then repeated using reference fuel blends. Each time a reference fuel is tried, the compression ratio is adjusted to give the same 13° ignition delay [12]. When the compression ratio required by the actual fuel is bracketed by the values required by two reference blends differing by less than five cetane numbers, the cetane number of the fuel is determined by interpolation between the compression ratios required by the two reference blends.

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*In the original procedure $\propto$–methylnapthalene ($C_{11}H_{10}$) with a cetane number of zero represented the bottom of scale. Heptamethylnonane, a more stable compound, has replaced it.

2.4.2 Cetane Index

Because of the expense of the cetane number test and its complexity, many correlations which predict ignition quality based on the physical properties of diesel fuels have been developed. A calculated cetane index (CCI) is often used to estimate ignition quality of diesel fuels (ASTM D976). It is based on API gravity and the mid-boiling point (temperature 50 percent evaporated). Its use is suitable for most diesel fuels and gives numbers that correspond quite closely to cetane number [12]. The calculated cetane index is a useful tool for estimating ASTM cetane number where a test engine is not available for determining this property. 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. It is applicable to straight-run fuels, catalytically cracked stocks, blends of the two [11].

Formula for Calculated Cetane Index [14]

(*a*). Calculated Cetane Index is determined from the following equation:

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

$$\text{Calculated Cetane Index (CCI)} = -420.34 + 0.016G^2 + 0.192G \log M + 65.01 (\log M)^2 - 0.0001809 M^2 \qquad \mathbf{(1)}$$

2. When it is applicable to fuels containing additives for raising cetane number. The calculated cetane index improver is determined from the equation (1) plus equation (2)

$$\text{Improver value} = 0.1742(0.1G)^{1.4444} (0.01M)^{1.0052} [\text{In}(1+17.5534D)] \qquad \mathbf{(2)}$$

where G = API gravity, determined by Test Method D287 or D 1298,

M = mid-boiling temperature, °F, determined by Test Method D86 and corrected to standard barometric pressure,

D = percent weight of cetane improver, % wt.

Therefore;

$$\text{CCI improver} = \text{CCI} + \text{Improver value} \qquad \textbf{(3)}$$

(*b*). Calculated Cetane Index values for distillate fuels may be conveniently determined by means of the alignment chart in Fig. 2.13 [14] rather than by direct application of the formula. The method of using this chart is indicated by the illustrative example thereon.

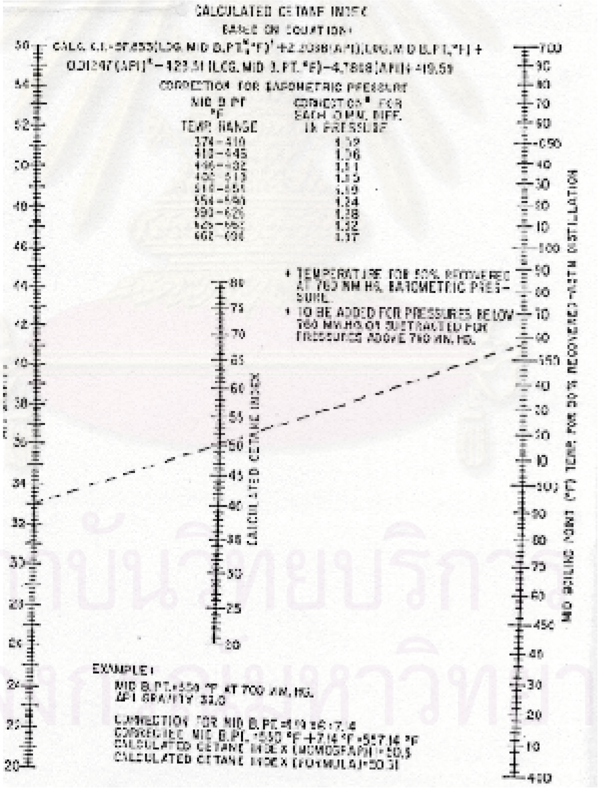


Figure 2.13 Nomograph for calculated cetane index.(From Appendix II, Tentative Classification of Diesel Fuel Oils, ASTM D975-53T.)

The differences between the measured cetane numbers and the cetane indices calculated by the above formula are relatively small for cetane indices between 40 and 55. Nevertheless, for diesel fuels containing a pro-cetane additive, the CCI will be much less than the actual value.

2.4.3 The Differences of High-Cetane and Low-Cetane Fuels

Diesel fuels of high cetane number differ from those of lower cetane number by having a shorter ignition lag when injected into the diesel-engine cylinder. High-cetane fuel also is ignited at a lower compressed-air temperature than low-cetane fuel. These characteristics result in the differences in the performance of high-cetane and low-cetane fuels in operating engines as described below [11]:

Starting. The higher the cetane number, the lower the temperature at which the engine can be started, but the range of the 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.

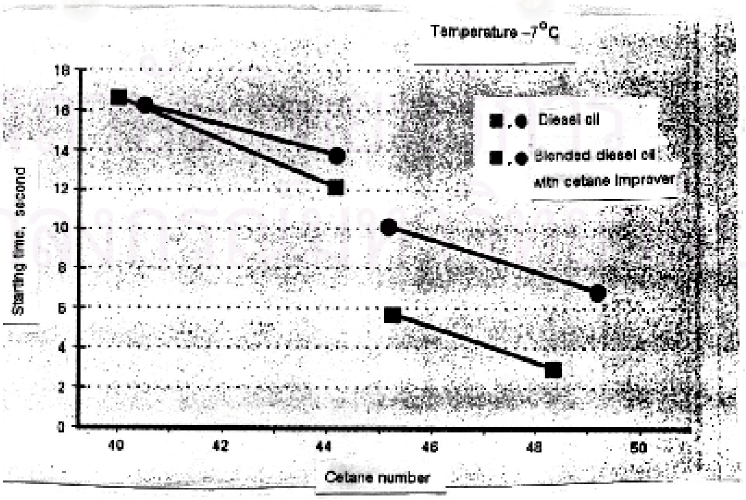


Figure 2.14 Effect of cetane number on starting of the engine [2].

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-low operation than high-cetane fuels of the same grade. Such deposits are probably the result of the fuel composition 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 condition; 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, contain more heat units per gallon [11].

The cetane number does not play the same essential role as does the octane number in the optimization of engines and motor fuels. In particular, it does not have a direct influence on the engine efficiency. However, a cetane number less than the required level could lead to operating problems: difficulties in starting, louder noise especially during idling while cold, and higher smoke emissions upon starting (refer to Fig. 2.15) [15].

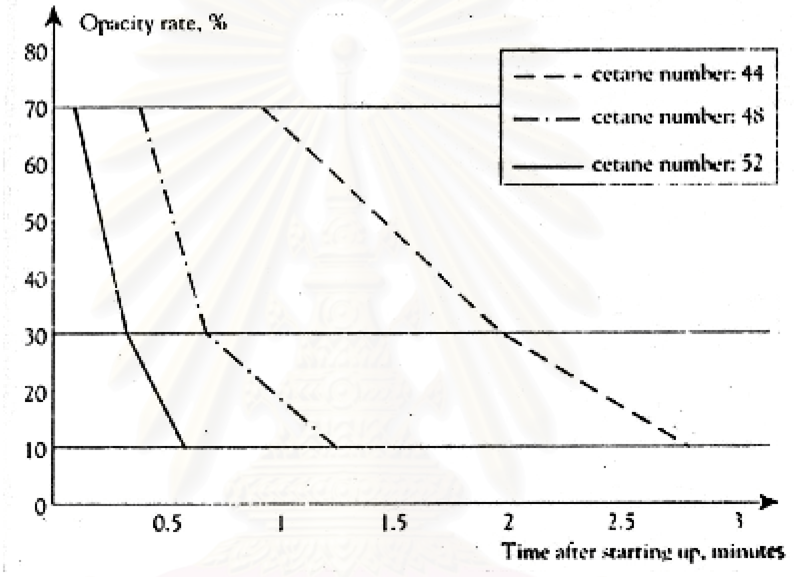


Figure 2.15 Influence of diesel fuel cetane number on exhaust smoke during cold starting. Source: VROM Program-Ricardo

High-cetane fuels will help reduce the engine’s pollutant emissions. Fig. 2.16 [15] gives a satisfactory correlation between emissions of CO, HC and particulates, and the cetane number.

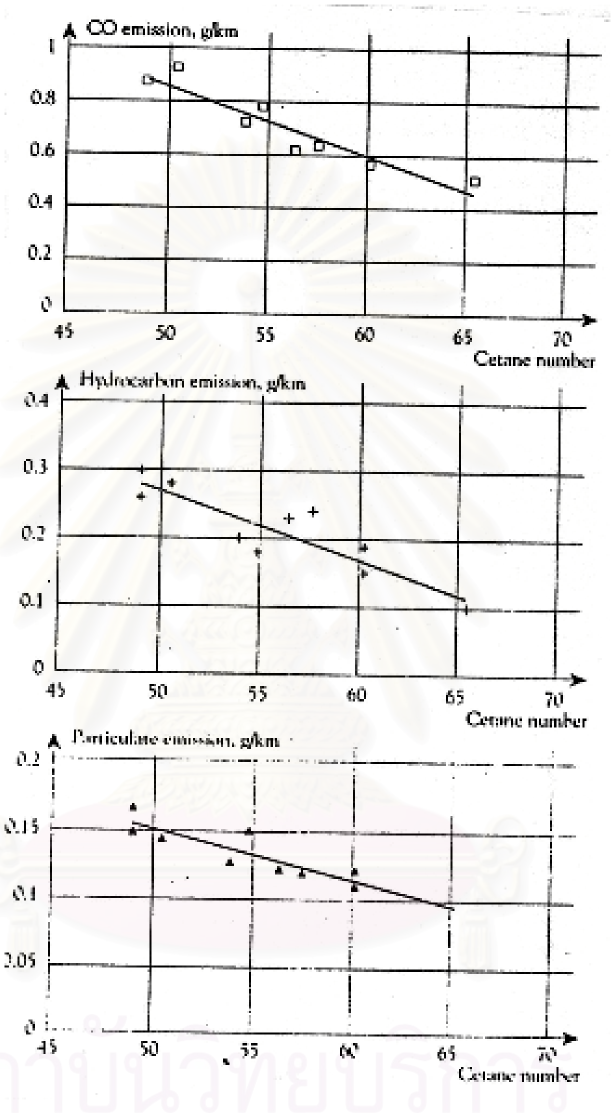


Figure 2.16 Effect of cetane number on the emissions of carbon monoxide, unburned hydrocarbons and particulates for a diesel passenger car.

These tendencies, incidentally, are more pronounced in passenger cars than in heavy trucks. It is highly desirable to produce a diesel fuel with sufficiently high cetane number in order to maintain or improve the diesel engine’s image for the customers.

2.5 Additives for Diesel Fuels

Additives are sometimes used to improve certain characteristics of diesel fuel. Additives for diesel fuel have many types which were shown in Table 2.4 [2]. The using of additives, which are mixed in diesel fuel, depends on the produced diesel and its quality demanding to appropriate with the applications. For example, from the production, it can produce diesel fuel which has only 52 cetane number but the engine wants 55 cetane fuel. Then the cetane improver is added for increasing cetane number from 52 to 55.

Table 2.4 Additives for diesel fuels.

Additives	**Functions**
❑ Ignition Quality Improvers, Cetane Improvers	Increase cetane number, start easily, reduce white smoke occurring from incompletely combustion in while engine is still cold, enhance completely combustion, and reduce exhaust
❑ Oxidation Inhibitors	Reduce sediment and gum occurring from reacting with oxygen in during storage
❑ Corrosion & Rust Inhibitors	Reduce corrosion and rust in fuel system throughout the storage
❑ Pour Point Depressants	Reduce pour point causing low temperature flowability
❑ Detergents - Dispersants	Keep clean the fuel system, wash and protect sooting on the fuel nozzle
❑ Demulsifiers	Help separate between water and oil rapidly
❑ Lubricating Agent	Lubricate pump system and nozzle
❑ Anti-foam	Brake foam occurring from addition of fuel

2.6 Literature Reviews

Purcell, R.F. et al.(1985) [6] examined the addition of nitrate ester cetane improvers in base diesel fuel. The nitrate esters were 3-methyl-3-nitro-2-butyl nitrate, 2-methyl-2-nitro-3-pentyl nitrate, and 5-methyl-5-nitro-3-oxo-1-hexanol. The diesel oils containing nitroalkyl nitrate, nitroalkoxy nitrate or octyl nitrate was tested for cetane number under standard test procedure ASTM D613. They had found that 3-methyl-3-nitro-2-butyl nitrate and 2-methyl-2-nitro-3-pentyl nitrate increased higher cetane number than octyl nitrate.

Liotta, F.J. et al.(1993) [8] studied on the improvement in cetane rating of diesel fuel by the addition of a small but effective amount of the nitric 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 result was obtained that while MBAN was slightly less effective than the commercial material 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.

Vasaruchtragul, J.(1997) [13] synthesized 1,2-ethane dinitrate, 1,4-butane dinitrate, 1,5-pentane dinitrate, and triethylene glycol for increasing cetane number in diesel fuels. These compounds were easily soluble in diesel fuel. They were in the blended composition at the concentration of 0.05 and 0.10% by weight. The cetane number would be increasing approximately 1.0 to 5.6 units.

From the above reports, they can be seen that the nitrate and dinitrate compounds gave cetane numbers at satisfactory level. Then synthesis of nitrate compound as cetane improver was interesting, particularly dinitrate compound containing both more nitrogen and oxygen than nitrate compound .

CHAPTER 3

EXPERIMENTAL

3.1 Instruments

1. Fourier-Transform Infrared Spectrophotometer

   Model Impact 410, Nicolet

2. Fourier-Transform NMR Spectrometer

   Model AC-F 200 (200 MHz), Bruker Spectrometer

3. Automatic Distillation Apparatus

   Herzog (MP 626)

4. Automatic Pour Point

   ISL (CPP 97-6)

5. Automatic Flash Point

   ISL (PMFP 93), Pensky-Martens

6. Cannon Automatic Viscometer

3.2 Chemicals

Reagents were obtained from various suppliers as shown in Table 3.1.

Table 3.1 Source of chemicals.

Materials	**Grade**	**Company**
1,6-Hexanediol	reagent	Fluka
1,8-Octanediol	reagent	Merck
1,10-Decanediol	reagent	Merck
2-Methyl-2,4-pentanediol	reagent	Fluka
Nitric acid, 65%	reagent	Labs-SCAN
Sulfuric acid, 96%	reagent	Merck
Urea	reagent	Fluka
Sodium chloride	reagent	Merck
Anhydrous sodium sulfate	reagent	Merck
Methylene chloride	reagent	Fluka
Chloroform	reagent	Fluka
Chloroform-d	analytical	Fluka
Isooctyl nitrate	reagent	OCTEL
Base diesel fuels	-	Thai Oil Refinery

3.3 Synthesis of Dinitrate Compounds

3.3.1 Synthesis of 1,6-Hexane Dinitrate

Mixture of 6.92 ml of 65% HNO_3, 12.13 ml of 96% H_2SO_4 and 6.79 ml of H_2O was well stirred and maintained the temperature at 23±2°C. 1.36 g of urea was added to the mixture and stirred for ½ hour. Then, the solution of 2.95 g of 1,6-hexanediol in 30 ml of $CHCl_3$ was added to the reactor slowly while maintaining the temperature at 23±2°C. After the addition was completed, the reaction mixture was held at 23±2°C for 1 hour at which time agitation was stopped. The mixture was allowed to warm to ambient temperature, and the organic phase separated. The organic phase was washed with an aqueous saturated sodium chloride solution. The washing procedure was repeated until the pH of the product was about 5-6, dried over anhydrous sodium sulphate and filtered to yield. 4.16 g (80%yield) of 1,6-hexane dinitrate as a colorless liquid.

3.3.2 Synthesis of 1,8-Octane Dinitrate

Mixture of 6.92 ml of 65% HNO_3 and 11.10 ml of 96% H_2SO_4 was well stirred and cooled to 2±2°C. 30 ml of CH_2Cl_2 was added to the mixture. Then, 3.64 g of 1,8-octanediol was added to the reactor slowly while maintaining the temperature at 2±2°C. After the addition was completed, the reaction mixture was held at 2±2°C for 1 hour at which time agitation was stopped The mixture was allowed to warm to ambient temperature, and the organic phase separated. The organic phase was washed with an aqueous saturated sodium chloride solution. The washing procedure was repeated until the pH of the product was about 5-6, dried over anhydrous sodium sulphate and filtered to yield. 5.13 g (86.9% yield) of 1,8-octane dinitrate as a colorless liquid.

3.3.3 Synthesis of 1,10-Decane Dinitrate

Mixture of 3.46 ml of 65% HNO_3 and 5.55 ml of 96% H_2SO_4 was well stirred and cooled to 2±2°C. 30 ml of CH_2Cl_2 was added to the mixture. Then, 2.18 g of 1,10-decanediol was added to the reactor slowly while maintaining the temperature at 2±2°C. After the addition was completed, the reaction mixture was held at 2±2°C for 1 hour at which time agitation was stopped. The mixture was allowed to warm to ambient temperature, and the organic phase separated. The organic phase was washed with an aqueous saturated sodium chloride solution. The washing procedure was repeated until the pH of the product was about 5-6, dried over anhydrous sodium sulphate and filtered to yield. 2.82 g (88.5% yield) of 1,10-decane dinitrate as a colorless liquid.

3.3.4 Synthesis of 2-Methyl-2,4-Pentane Dinitrate

Mixture of 3.46 ml of 65% HNO_3 and 5.55 ml of 96% H_2SO_4 was well stirred and cooled to 2±2°C. 30 ml of CH_2Cl_2 was added to the mixture. Then, 1.47g of 2-methyl-2,4-pentanediol was added to the reactor slowly while maintaining the temperature at 2±2°C. After the addition was completed, the reaction mixture was held at 2±2°C for 1 hour at which time agitation was stopped. The mixture was allowed to warm to ambient temperature, and the organic phase separated. The organic phase was washed with an aqueous saturated sodium chloride solution. The washing procedure was repeated until the pH of the product was about 5-6, dried over anhydrous sodium sulphate and filtered to yield. 1.37 g (53.2% yield) of 2-methyl-2,4-pentane dinitrate as a yellow liquid.

3.4 Characterization and Determination of the Synthesized Compounds

3.4.1 Characterization of the Synthesized Compounds

The synthesized compounds were characterized by using instruments as follow:

- Fourier-Transform Infrared Spectrophotometer
- Fourier-Transform NMR Spectrometer

3.4.2 Determination of Properties and Cetane index of Blended Base Diesel Fuel containing Dinitrate Compounds

Blended base diesel fuels containing with 0.05% and 0.10% by weight of dinitrate compounds were determined of their properties and cetane index.

1. The blended base diesel fuels were prepared by blending dinitrate compounds (0.5 and 1 g) in base diesel fuels (1000 g). The dinitrate compounds were as follow:
    - 1,6-hexane dinitrate
    - 1,8-octane dinitrate
    - 1,10-decane dinitrate
    - 2-methyl-2,4-pentane dinitrate
2. The properties of the blended base diesel fuels were determined as shown in Table 3.2 [14][16-19].

Table 3.2 Test method of the blended base diesel fuels

Properties	ASTM
1. Mid-boiling point	D86
2. API gravity	D1298
3. Pour point	D97
4. Flash point	D93
5. Viscosity	D445
6. Cetane index	D976

3.4.3 Prediction of Cetane Number of Blended Base Diesel Fuel containing Dinitrate Compounds by Using Nomograph

Blended base diesel fuels containing with 0.05% and 0.10% by weight of dinitrate compounds were determined for their cetane numbers. The cetane numbers of blended base diesel fuels were predicted by the nomograph for the calculation of cetane improvement. The nomograph given in Figure 3.1 [20] presented one of these equations in an easy to use form.

<u>*Method of use:*</u>

1. Identifying 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) connecting the pivot point to the Cetane Number increase (ΔCN) that is desired and extend the line to the concentration axis to perdict the additive concentration, or

b) connecting the pivot point to the chosen concentration and read back along the line to the predicted Cetane Number increase.

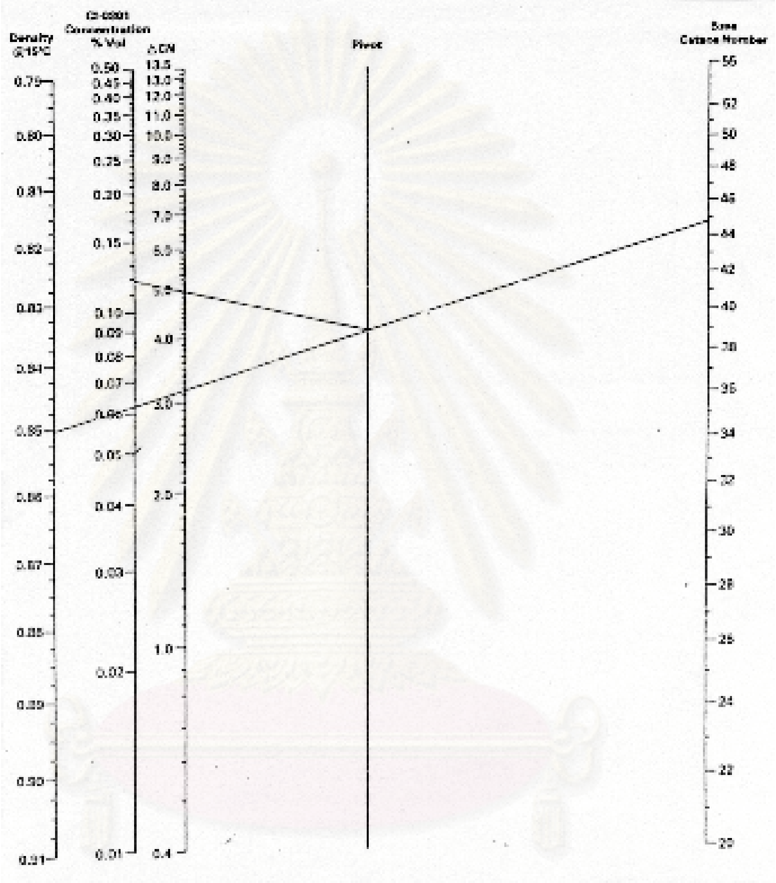


Figure 3.1 Nomograph for the calculation of cetane improvement.(Source: The Associated Octel Company Ltd.)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results of the Synthesis of Dinitrate Compounds

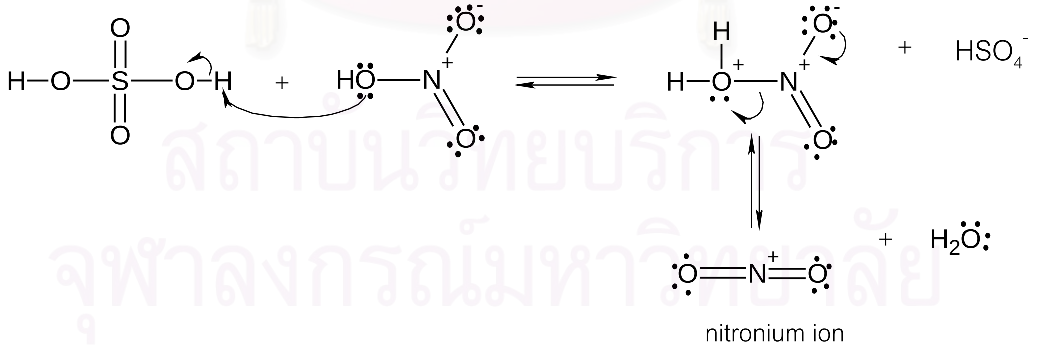
Dinitrate compounds could be prepared by nitration reaction using concentrated nitric acid and concentrated sulfuric acid.

In this study, four dinitrate compounds were synthesized from 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, and 2-methyl-2,4-pentanediol. The syntheses of these compounds can be simply represented by the reaction below:

$$\text{HO-R-OH} + H_2SO_4 + HNO_3 \longrightarrow O_2\text{NO-R-ONO}_2 + H_2SO_4 + H_2O$$

where HO-R-OH = 1,6-hexanediol,
1,8-octanediol,
1,10-decanediol, and
2-methyl-2,4-pentanediol

Mechanism :



$$HNO_3 + H_2SO_4 \longrightarrow NO_2^{+} + HSO_4^{-} + H_2O$$

$$\text{R-OH} + NO_2^{+} \longrightarrow \text{R-ONO}_2 + H^{+}$$

$$H^{+} + HSO_4^{-} \longrightarrow H_2SO_4$$

Most of products were obtained in high yield, except 2-methyl-2,4-pentane dinitrate because of its sensitivity to the autooxidation. In addition, the raw material, 2-methyl-2,4-pentanediol was hygroscopic and sensitive to air.

4.2 Results of the Characterization of Dinitrate Compounds

4.2.1 Characteristics of 1,6-Hexane Dinitrate

The IR spectra of 1,6-hexanediol and 1,6-hexane dinitrate were shown in Fig. A1 and A2, respectively. The important absorption bands of 1,6-hexane dinitrate were listed in Table 4.1.

Table 4.1 The absorption assignments of 1,6-hexane dinitrate.

Wave number (cm^{-1})	**Assignment**
2941,2878	C-H stretching, aliphatic
1630	NO_2 asymmetric stretching
1471,1393	C-H bending, aliphatic
1287	NO_2 symmetric stretching
967	C-O stretching
871	N-O stretching

From the IR spectrum of 1,6-hexane dinitrate (Fig.A2) comparing with of 1,6-hexanediol (Fig.A1), it could be observed that there was no the absorption band of OH stretching group at near 3500 cm^{-1}. There were the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching at 1630, 1287 and 871 cm^{-1}, respectively. It presented that 1,6-hexane dinitrate was completely synthesized from 1,6-hexanediol. The result was assured by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of 1,6-hexanediol and 1,6-hexane dinitrate were shown in Fig. A3 and A4, respectively. The important signals of 1,6-hexane dinitrate were shown in Table 4.2.

Table 4.2 The assignments of ^{1}H-NMR spectrum of 1,6-hexane dinitrate.

Chemical shift (δ,ppm)	**Multiplicity**	**Position of proton**	**Number of protons**
4.36	Triplet	1,6	4
1.65	Quintet	2,5	4
1.36	Triplet	3,4	4

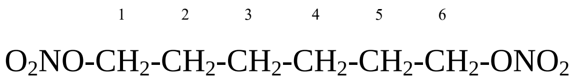
The ^{13}C-NMR spectra of 1,6-hexanediol and 1,6-hexane dinitrate were shown in Fig. A5 and A6, respectively. The important signals of 1,6-hexane dinitrate were shown in Table 4.3.

Table 4.3 The assignments of ^{13}C-NMR spectrum of 1,6-hexane dinitrate.

Position of carbon	**Carbon type**	**Chemical shift of dinitrate (δ,ppm)**	**Chemical shift of diol (δ,ppm)***
1,6	CH_2	73.36	62.61
3,4	CH_2	26.38	32.55
2,5	CH_2	25.08	25.59

*The position of carbon of diol was referred by Ref.[22].

From the results of the spectral data, the product was 1,6-hexane dinitrate and its structure was :



$$O_2NO-\overset{1}{CH_2}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_2}-ONO_2$$

4.2.2 Characteristics of 1,8-Octane Dinitrate

The IR spectra of 1,8-octanediol and 1,8-octane dinitrate were shown in Fig. A7 and A8, respectively. The important absorption bands of 1,8-octane dinitrate were shown in Table 4.4.

Table 4.4 The absorption assignments of 1,8-octane dinitrate.

Wave number (cm^{-1})	Assignment
2931,2859	C-H stretching, aliphatic
1625	NO_2 asymmetric stretching
1471,1383	C-H bending, aliphatic
1282	NO_2 symmetric stretching
982	C-O stretching
861	N-O stretching

From the IR spectrum of 1,8-octane dinitrate (Fig.A9) comparing with of 1,8-octanediol (Fig.A8), it could be observed that there was no the absorption band of OH stretching group at near 3500 cm^{-1}. There were the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching at 1625, 1282 and 861 cm^{-1}, respectively. It presented that 1,8-octane dinitrate was completely synthesized from 1,8-octanediol. The result was assured by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of 1,8-octanediol and 1,8-octane dinitrate were shown in Fig. A9 and A10, respectively. The important signals of 1,8-octane dinitrate were shown in Table 4.5.

Table 4.5 The assignments of ^{1}H-NMR spectrum of 1,8-octane dinitrate.

Chemical shift (δ,ppm)	**Multiplicity**	**Position of proton**	**Number of protons**
4.36	Triplet	1,8	4
1.61	Quintet	2,7	4
1.25-1.40	Multiplet	3,4,5,6	8

The ^{13}C-NMR spectra of 1,8-octanediol and 1,8-octane dinitrate were shown in Fig. A11 and A12, respectively. The important signals of 1,8-octane dinitrate were shown in Table 4.6.

Table 4.6 The assignments of ^{13}C-NMR spectrum of 1,8-octane dinitrate.

Position of carbon	**Carbon type**	**Chemical shift of dinitrate (δ,ppm)**	**Chemical shift of diol (δ,ppm)***
1,8	CH_2	73.40	62.77
2,7	CH_2	28.72	32.62
4,5	CH_2	26.48	29.29
3,6	CH_2	25.35	25.61

*The position of carbon of diol was referred by Ref [23].

From the results of the spectral data, the product was 1,8-octane dinitrate and its structure was :

$$O_2NO\text{-}\overset{1}{CH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{3}{CH_2}\text{-}\overset{4}{CH_2}\text{-}\overset{5}{CH_2}\text{-}\overset{6}{CH_2}\text{-}\overset{7}{CH_2}\text{-}\overset{8}{CH_2}\text{-}ONO_2$$

4.2.3 Characteristics of 1,10-Decane Dinitrate

The IR spectra of 1,10-decanediol and 1,10-decane dinitrate were shown in Fig. A13 and A14, respectively. The important absorption bands of 1,10-decane dinitrate were listed in Table 4.7.

Table 4.7 The absorption assignments of 1,10-decane dinitrate.

Wave number (cm^{-1})	**Assignment**
2936,2863	C-H stretching, aliphatic
1630	NO_2 asymmetric stretching
1471,1388	C-H bending, aliphatic
1287	NO_2 symmetric stretching
982	C-O stretching
861	N-O stretching

From the IR spectrum of 1,10-decane dinitrate (Fig.A14) comparing with of 1,10-decanediol (Fig.A13), it could be observed that there was no the absorption band of OH stretching group at near 3500 cm^{-1}. There were the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching at 1630, 1287 and 861 cm^{-1}, respectively. It presented that 1,10-decane dinitrate was completely synthesized from 1,10-decanediol. The result was assured by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of 1,10-decanediol and 1,10-decane dinitrate were shown in Fig. A15 and A16, respectively. The important signals of 1,10-decane dinitrate were shown in Table 4.8.

Table 4.8 The assignments of ^{1}H-NMR spectrum of 1,10-decane dinitrate.

Chemical shift (δ,ppm)	**Multiplicity**	**Position of proton**	**Number of protons**
4.36	Triplet	1,10	4
1.64	Quintet	2,9	4
1.25-1.37	Multiplet	3,4,5,6,7,8	12

The ^{13}C-NMR spectra of 1,10-decanediol and 1,10-decane dinitrate were shown in Fig. A17 and A18, respectively. The important signals of 1,10-decane dinitrate were shown in Table 4.9.

Table 4.9 The assignments of ^{13}C-NMR spectrum of 1,10-decane dinitrate.

Position of carbon	**Carbon type**	**Chemical shift of dinitrate (δ,ppm)**	**Chemical shift of diol (δ,ppm)***
1,10	CH_2	73.44	63.01
2,9	CH_2	29.14	32.74
3,8	CH_2	26.26	29.36
4,5,6,7	CH_2	25.52	25.69

*The positon of carbon of diol was referred by Ref [24].

From the results of the spectral data, the product was 1,10-decane dinitrate and its structure was :

$$O_2NO\text{-}\overset{1}{CH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{3}{CH_2}\text{-}\overset{4}{CH_2}\text{-}\overset{5}{CH_2}\text{-}\overset{6}{CH_2}\text{-}\overset{7}{CH_2}\text{-}\overset{8}{CH_2}\text{-}\overset{9}{CH_2}\text{-}\overset{10}{CH_2}\text{-}ONO_2$$

4.2.4 Characteristics of 2-Methyl-2,4-Pentane Dinitrate

The IR spectra of 2-methyl-2,4-pentanediol and 2-methyl-2,4-pentane dinitrate were shown in Fig. A19 and A20, respectively. The important absorption bands of 2-methyl-2,4-pentane dinitrate were shown in Table 4.10.

Table 4.10 The absorption assignments of 2-methyl-2,4-pentane dinitrate.

Wave number (cm^{-1})	**Assignment**
2991,2935	C-H stretching, aliphatic
1634	NO_2 asymmetric stretching
1460,1393	C-H bending, aliphatic
1280	NO_2 symmetric stretching
1132	C-O stretching
871	N-O stretching vibration

From the IR spectrum of 2-methyl-2,4-pentane dinitrate (Fig.A20) comparing with of 2-methyl-2,4-pentanediol (Fig.A19), it could be observed that there was no the absorption band of OH stretching group at near 3500 cm^{-1}. There were the absorption bands of NO_2 (asymmetric and symmetric) stretching and NO stretching at 1634, 1280 and 871 cm^{-1}, respectively. It presented that 2-methyl-2,4-pentane dinitrate was completely synthesized from 2-methyl-2,4-pentanediol. The result was assured by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of 2-methyl-2,4-pentanediol and 2-methyl-2,4-pentane dinitrate were shown in Fig. A21 and A22, respectively. The important signals of 2-methyl-2,4-pentane dinitrate were shown in Table 4.11.

Table 4.11 The assignments of ^{1}H-NMR spectrum of 2-methyl-2,4-pentane dinitrate.

Chemical shift (δ,ppm)	**Multiplicity**	**Position of proton**	**Number of protons**
4.80	Multiplet	4	1
2.14	Doublet	3	2
1.47	Singlet	1,2	6
1.28	Doublet	5	3

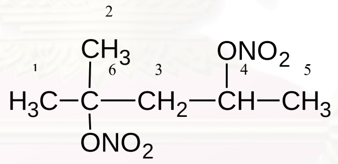
The ^{13}C-NMR spectra of 2-methyl-2,4-pentanediol and 2-methyl-2,4-pentane dinitrate were shown in Fig. A23 and A24, respectively. The important signals of 2-methyl-2,4-pentane dinitrate were shown in Table 4.12.

Table 4.12 The assignments of ^{13}C-NMR spectrum of 2-methyl-2,4-pentane dinitrate.

Position of carbon	**Carbon type**	**Chemical shift of dinitrate (δ,ppm)**	**Chemical shift of diol (δ,ppm)**
6	C	89.34	70.95
4	CH	77.08	65.00
3	CH_2	42.72	48.96
1	CH_3	25.73	31.12
2	CH_3	24.88	27.40
5	CH_3	19.97	23.93

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

From the results of the spectral data, the product was 2-methyl-2,4-pentane dinitrate and its structure was :



$$\overset{1}{H_3C}-\underset{ONO_2}{\overset{\overset{2}{CH_3}}{\overset{6}{C}}}-\overset{3}{CH_2}-\overset{ONO_2}{\overset{4}{CH}}-\overset{5}{CH_3}$$

4.3 Results of the Determination of the Properties of Blended Base Diesel Fuel containing Dinitrate Compounds.

The dinitrate compounds were blended with base diesel fuels. Each of 0.05% and 0.10% by weight of 1,6-hexane dinitrate, 1,8-octane dinitrate, 1,10-decane dinitrate, and 2-methyl-2,4-pentane dinitrate, respectively, were used and their properties were determined by comparing with iso-octylnitrate. The properties of these blended base diesel fuels were shown in Table 4.13.

Table 4.13 Physical properties of the blended base diesel fuels.

Concentration (% by wt.)	**Blended composition**	**API gravity @ 60°F**	**Mid-boiling point(°F)**	**Pour point (°C)**	**Flash point (°C)**	**Viscosity (cST)**
	Base	36.8	538.88	-2.0	72	3.184
0.05%	Base + HDN	36.8	538.70	-5.0	72	3.178
	Base + ODN	36.8	539.96	-2.0	71	3.184
	Base + DDN	36.9	539.96	-2.0	73	3.176
	Base + MPDN	36.8	538.88	-2.0	72	3.173
	Base + ION	36.7	539.96	-2.0	74	3.186
0.10%	Base + HDN	36.8	538.70	-2.0	72	3.175
	Base + ODN	36.8	539.06	-1.0	71	3.185
	Base + DDN	36.8	539.96	-2.0	71	3.177
	Base + MPDN	36.8	537.98	-5.0	72	3.172
	Base + ION	36.6	538.34	-2.0	71	3.177

Note : HDN = 1,6-hexane dinitrate
ODN = 1,8-octane dinitrate
DDN = 1,10-decane dinitrate
MPDN = 2-methyl-2,4-pentane dinitrate
ION = iso-octylnitrate

From these results, it could be seen that the dinitrate did not make any change to the physical properties of the base diesel fuel and all of blended base diesel fuels gave the similar figure as base diesel fuel. Then they could be used according to the specification of diesel fuel.

4.4 Results of the Determination of the Cetane Index of Blended Base Diesel Fuel containing Dinitrate Compounds.

The calculated cetane index of each of blended base diesel fuels (at of 0.05% and 0.10% by wt.) was determined by using Test Method of ASTM D976. The values of these CCI were shown in Table 4.14.

Table 4.14 The calculated cetane index of the blended base diesel fuels.

Concentration (%by wt.)	Blended composition	CCI	Improver value	CCI improved
	Base	53.14	-	-
0.05%	Base + HDN	53.12	3.92	57.04
	Base + ODN	53.24	3.93	57.17
	Base + DDN	53.41	3.94	57.35
	Base + MPDN	53.14	3.92	57.06
	Base + ION	53.07	3.91	56.98
0.10%	Base + HDN	53.12	6.30	59.42
	Base + ODN	53.16	6.30	59.46
	Base + DDN	53.24	6.31	59.55
	Base + MPDN	53.05	6.29	59.34
	Base + ION	52.75	6.25	59.00

Note : HDN = 1,6-hexane dinitrate
ODN = 1,8-octane dinitrate
DDN = 1,10-decane dinitrate
MPDN = 2-methyl-2,4-pentane dinitrate
ION = iso-octylnitrate
CCI = Calculated Cetane Index

From Table 4.14, it could be seen that the CCI of the blended base diesel fuel were increased as compared to the base diesel fuel. The increased CCI was about 3.9 at concentration of 0.05% by weight and about 6.3 at concentration of 0.10% by weight, respectively. The dinitrate compounds gave higher CCI than of iso-octylnitrate at both of concentrations, especially 1,10-decane dinitrate. It could be concluded that these compounds had 2 nitrate groups enhanced the ignited-oxidation which results in increasing of CCI. In the case of 1,10-decane dinitrate, the longer chain hydrocarbon could give the potential to increase higher cetane number. It could be concluded that the more CCI, the more CN could be received [12].

4.5 Results of the Prediction of the Cetane Number of Blended Base Diesel Fuel containing Dinitrate Compounds by Using Nomograph.

In addition to Test Method ASTM D976, the cetane numbers of blended base diesel fuels could be determined by using nomograph for the calculation of cetane improvement at the concentrations of 0.05% and 0.10% by weight by comparing its density as shown in Table 4.15.

Table 4.15 The cetane number of the blended base diesel fuels.

Concentration (% by wt.)	**Blended composition**	**Density @15°C**	**ΔCN**	**CN**
	Base		-	53.6
0.05%	Base + HDN	0.8403	2.97	56.57
	Base + ODN	0.8403	2.97	56.57
	Base + DDN	0.8398	3.00	56.60
	Base + MPDN	0.8403	2.97	56.57
	Base + ION	0.8408	2.92	56.52
0.10%	Base + HDN	0.8403	4.85	58.45
	Base + ODN	0.8403	4.85	58.45
	Base + DDN	0.8403	4.85	58.45
	Base + MPDN	0.8403	4.85	58.45
	Base + ION	0.8413	4.80	58.40

Note : HDN = 1,6-hexane dinitrate
ODN = 1,8-octane dinitrate
DDN = 1,10-decane dinitrate
MPDN = 2-methyl-2,4-pentane dinitrate
ION = iso-octylnitrate
CN = Cetane Number

From the results obtained from the nomograph, the blended base diesel fuels gave the cetane numbers higher than base diesel fuel. The cetane number was about 56 at concentration of 0.05% by weight and about 58 at concentration of 0.10% by weight, respectively. These results had the same trend as the results of the calculated cetane index. It could be concluded that the cetane numbers of base diesel fuels were increased by these dinitrate compounds.

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

The dinitrate compounds could be easily prepared by direct nitration reaction by reacting alkane diols such as1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 2-methyl-2,4-pentanediol, with a mixture of concentrated H_2SO_4 and concentrated HNO_3 in the presence of solvent. These dinitrate compounds were 1,6-hexane dinitrate, 1,8-octane dinitrate, 1,10-decane dinitrate, and 2-methyl-2,4-pentane dinitrate. They were obtained in high yield except 2-methyl-2,4-pentane dinitrate because of its sensitivity.

These dinitrate compounds were easily soluble in base diesel fuel which did not change their physical properties within the specification of diesel fuel at the concentrations of 0.05% and 0.10% by weight. The calculated cetane index of the blended base diesel fuel was increased approximately for 3.9 and 6.3 units at concentrations of 0.05% and 0.10% by weight, respectively. In case of the cetane number, the blending of dinitrate compounds gave higher cetane numbers as comparing with iso-octylnitrate, the commercial available cetane improver. Especially 1,10-decane dinitrate, the cetane number of this compound was increased more than the others. Then these dinitrate compounds had potential to be used for improving cetane number in base diesel fuel.

5.2 Suggestions for Future Work

1,10-Decane dinitrate is an effective compound in improving a cetane number. The future work should study dinitrate compound, which has carbon atoms more than this for improving cetane number.

Since the expense of the cetane number test and its complexity, other correlation which predict of ignition quality base on the physical properties of diesel fuel should be studied in the future. For example the calculation by using (Near) I.R., NMR and MS techniques.

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APPENDICES

APPENDIX A

SPECTRA OF DINITRATE COMPOUNDS

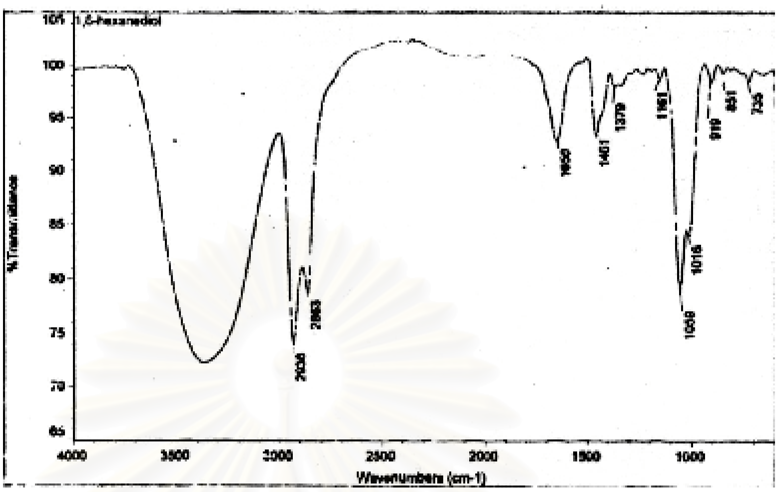


Figure A1 FTIR spectrum of 1,6-hexane diol

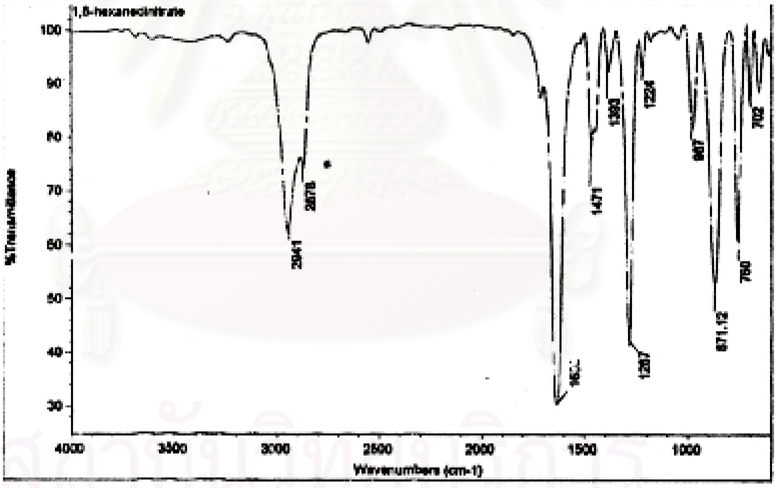


Figure A2 FTIR spectrum of 1,6-hexane dinitrate

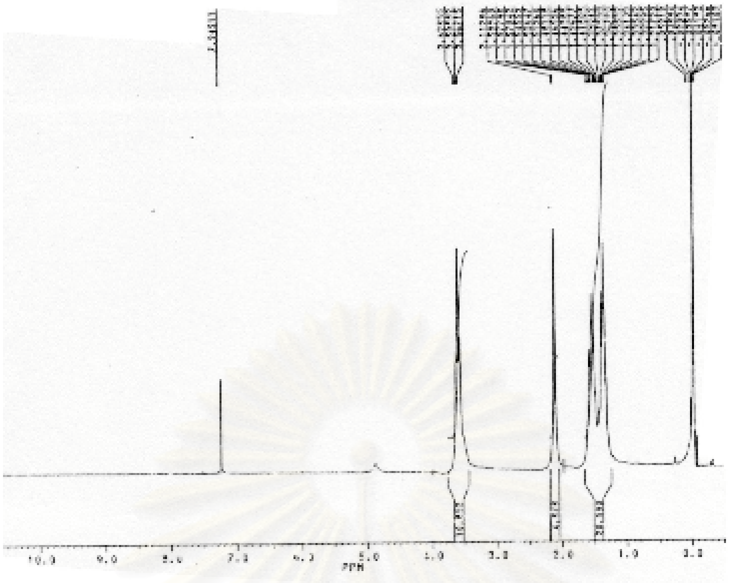


Figure A3 ^{1}H-NMR spectrum of 1,6-hexanediol

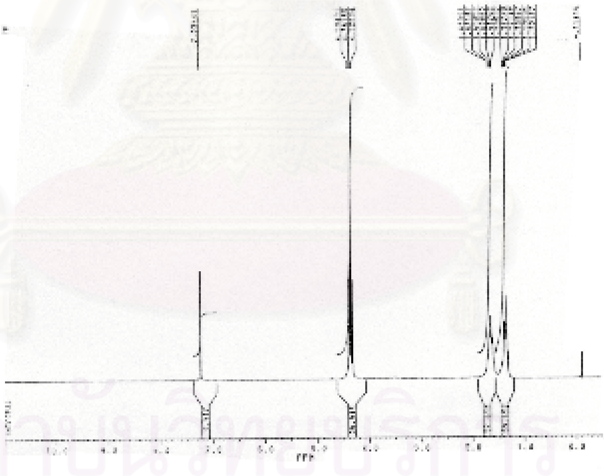


Figure A4 ^{1}H-NMR spectrum of 1,6-hexane dinitrate

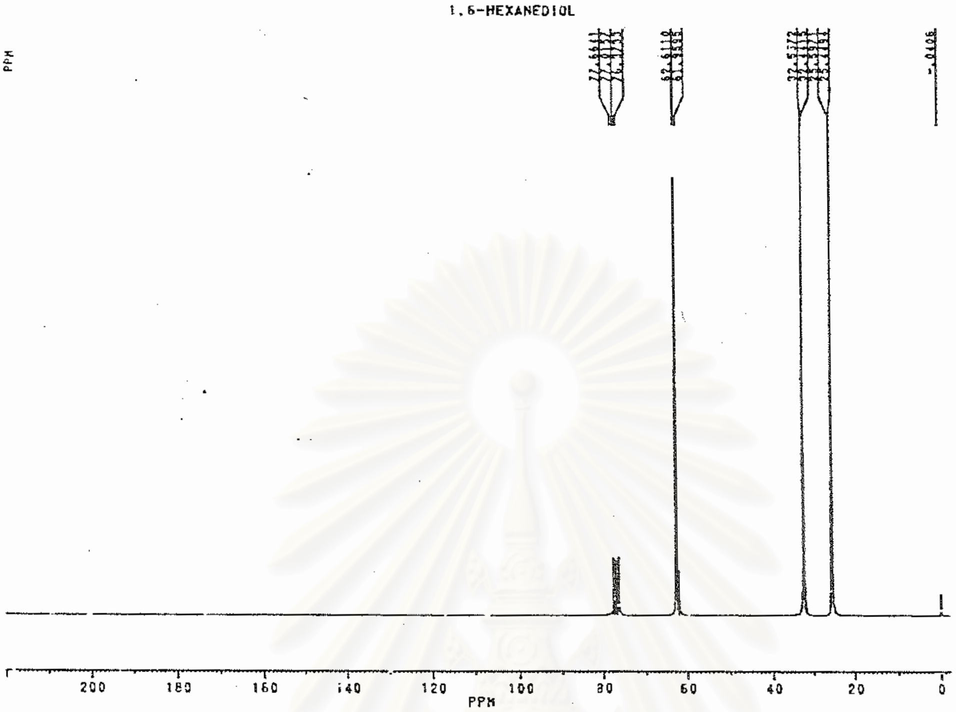


Figure A5 ^{13}C-NMR spectrum of 1,6-hexane diol

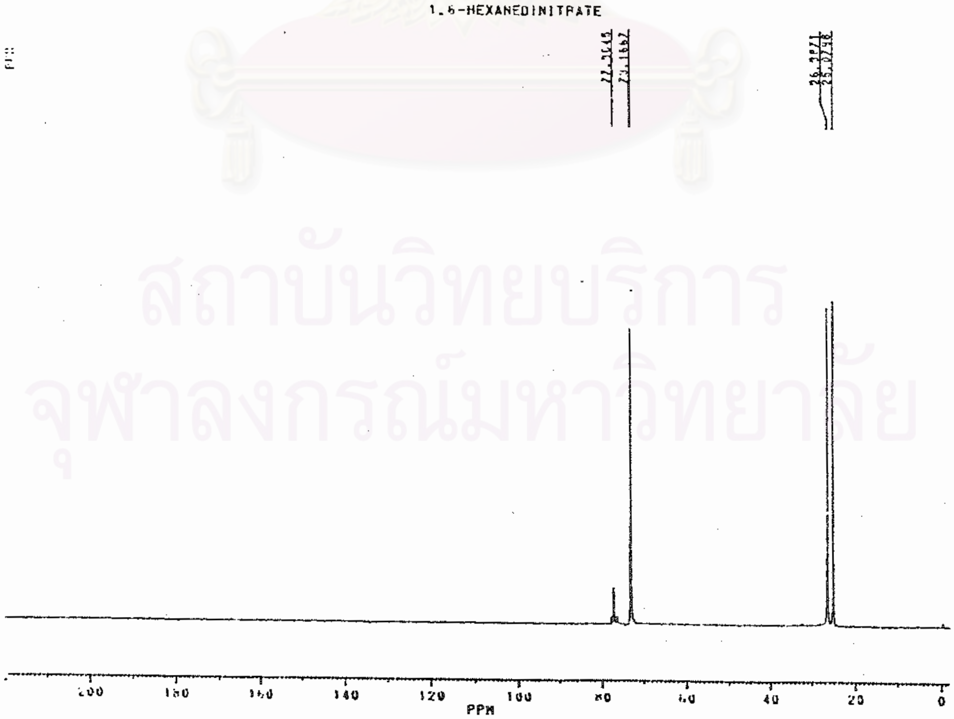


Figure A6 ^{13}C-NMR spectrum of 1,6-hexane dinitrate

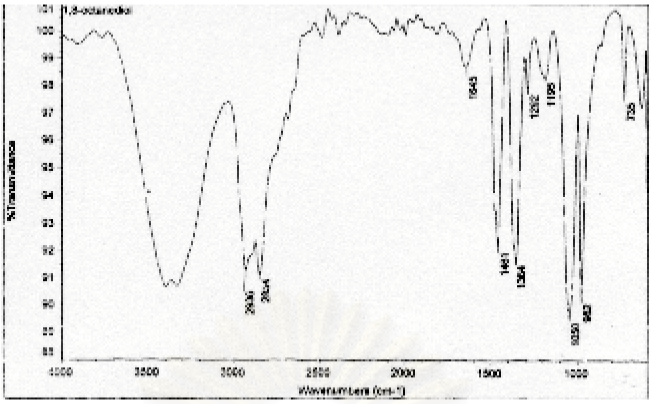


Figure A7 FTIR spectrum of 1,8-octane diol

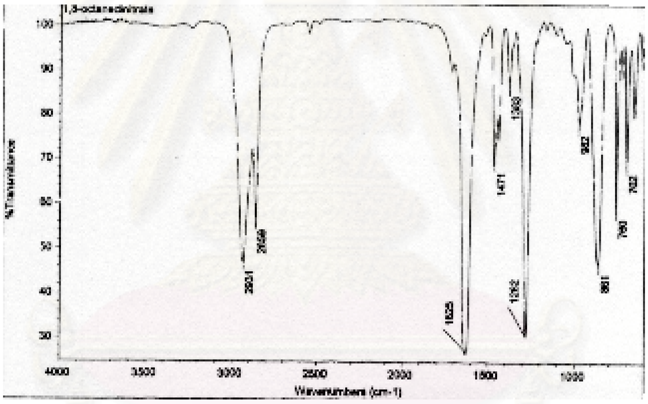


Figure A8 FTIR spectrum of 1,8-octane dinitrate

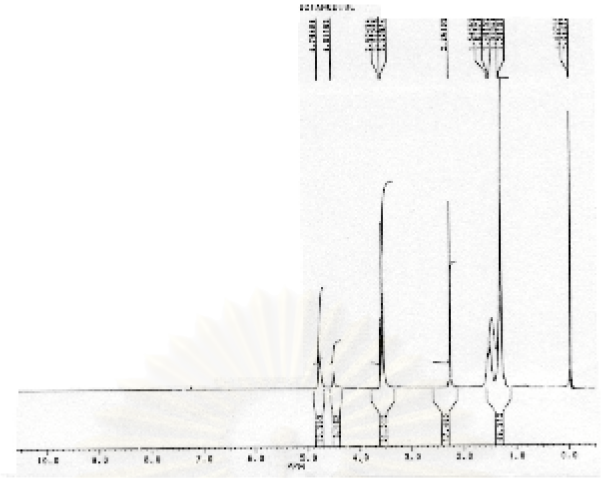


Figure A9 ^{1}H-NMR spectrum of 1,8-octane diol

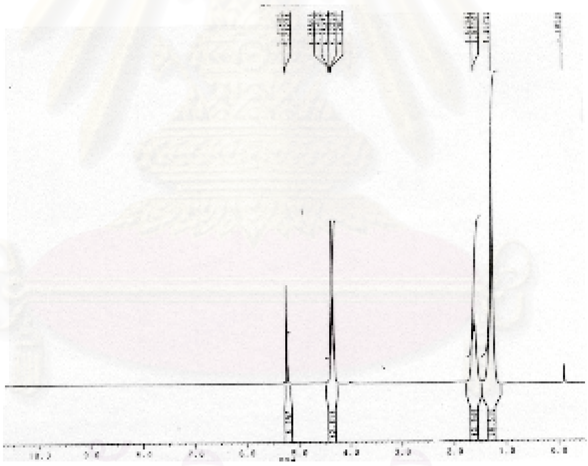


Figure A10 ^{1}H-NMR spectrum of 1,8-octane dinitrate

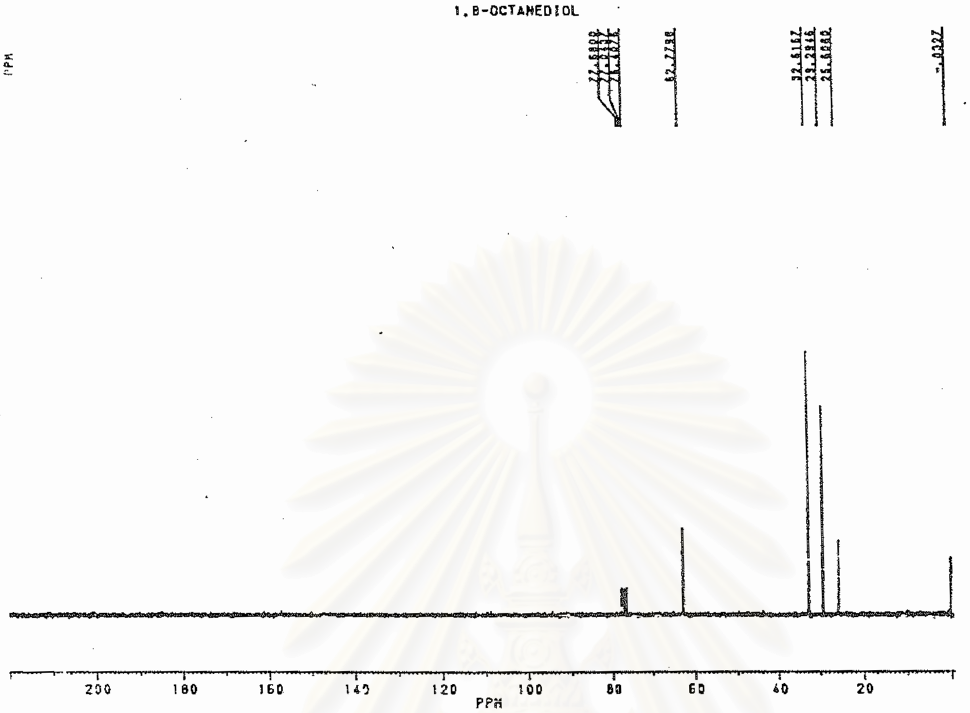


Figure A11 ^{13}C-NMR spectrum of 1,8-octane diol

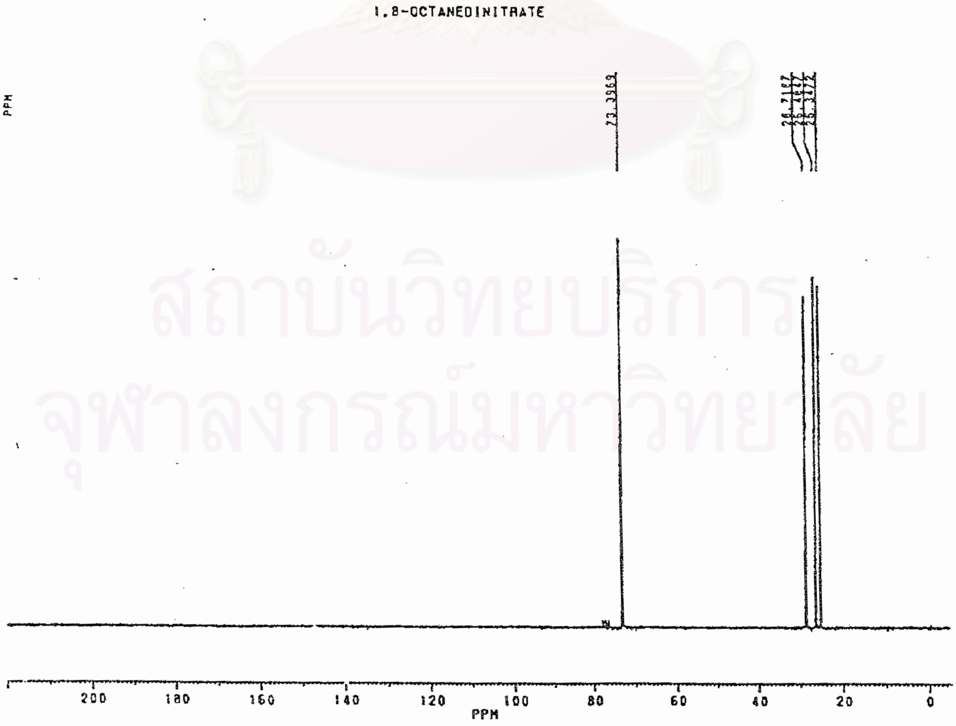


Figure A12 ^{13}C-NMR spectrum of 1,8-octane dinitrate

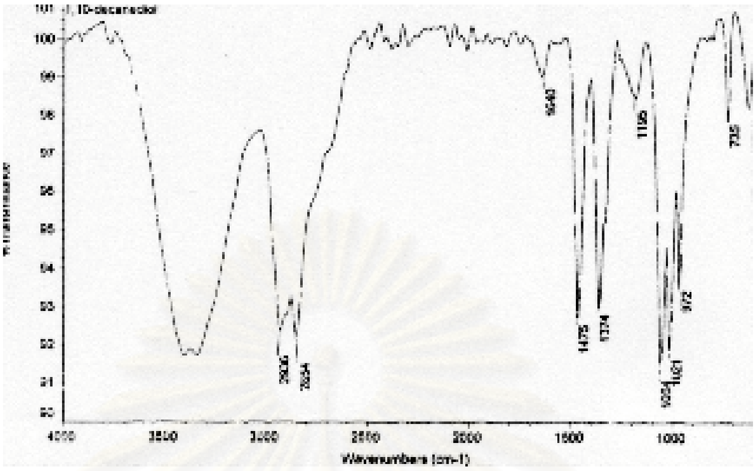


Figure A13 FTIR spectrum of 1,10-decane diol

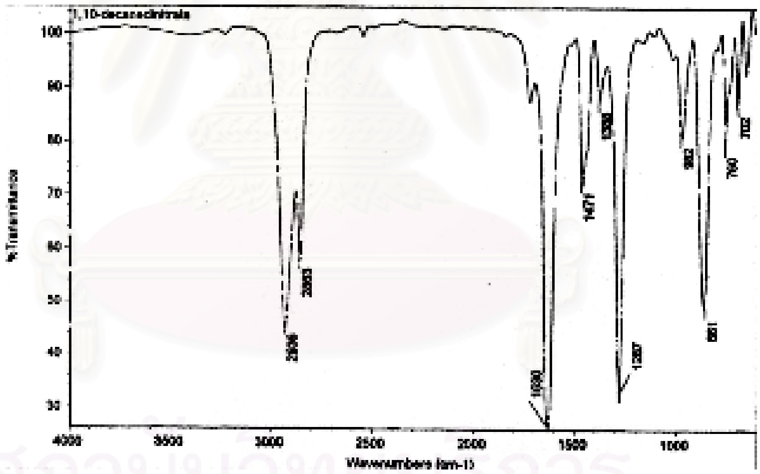


Figure A14 FTIR spectrum of 1,10-decane dinitrate

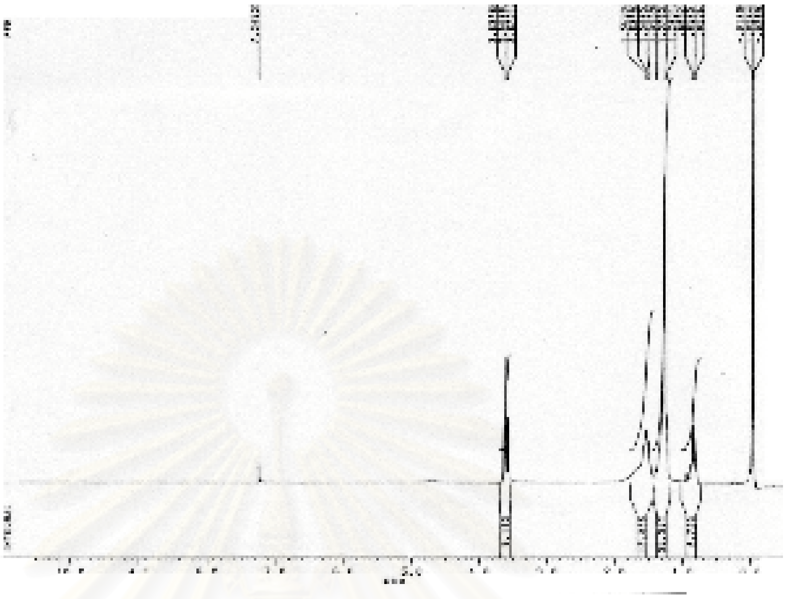


Figure A15 ^{1}H-NMR spectrum of 1,10-decane diol

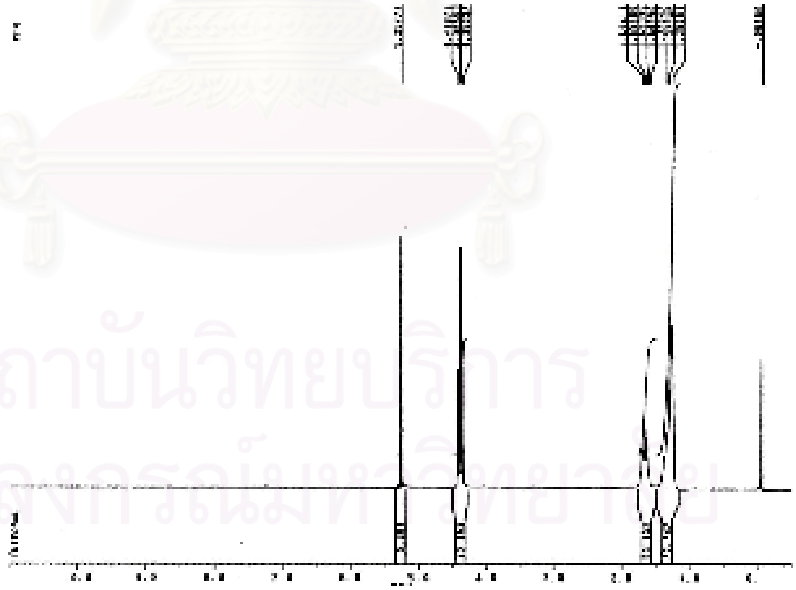


Figure A16 ^{1}H-NMR spectrum of 1,10-decane dinitrate

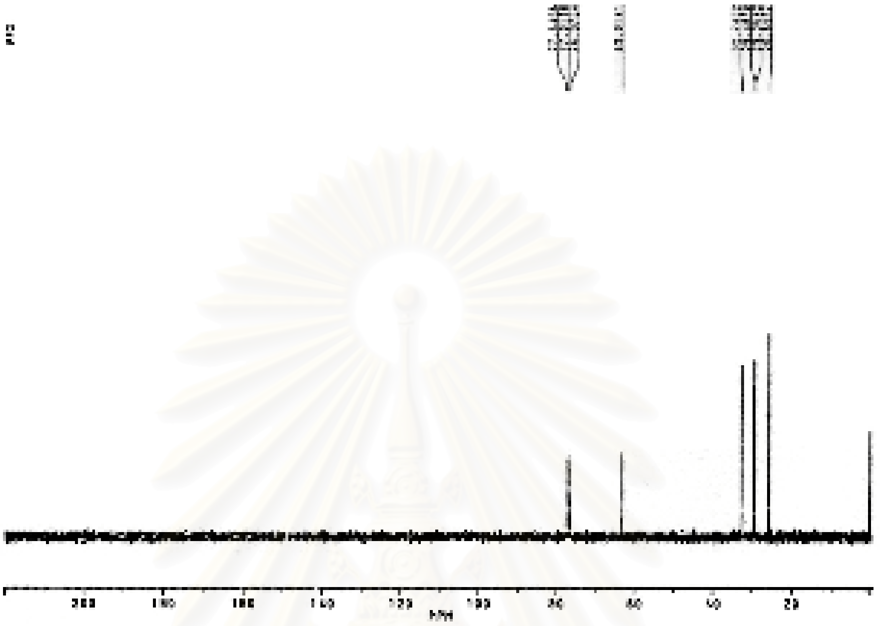


Figure A17 ^{13}C-NMR spectrum of 1,10-decane diol

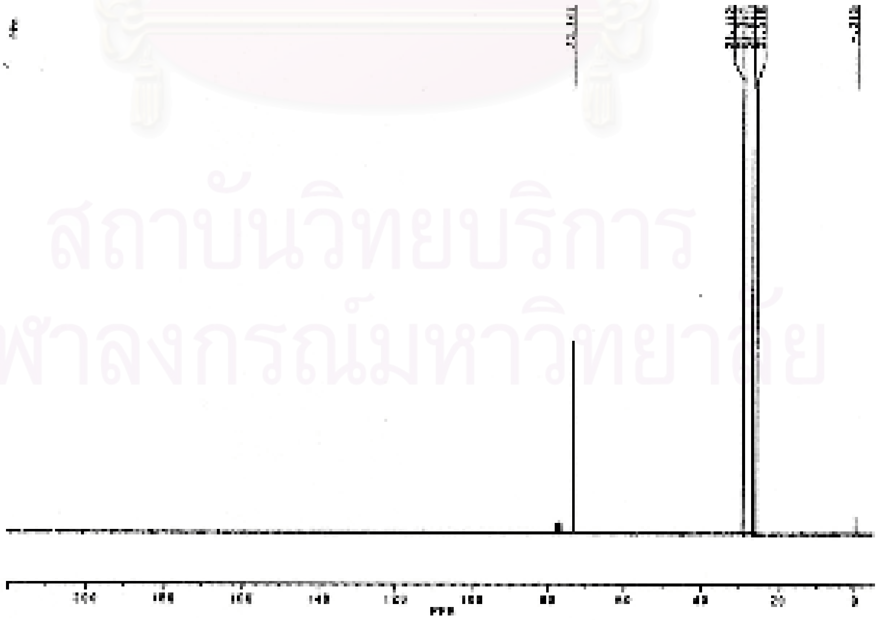


Figure A18 ^{13}C-NMR spectrum of 1,10-decane dinitrate

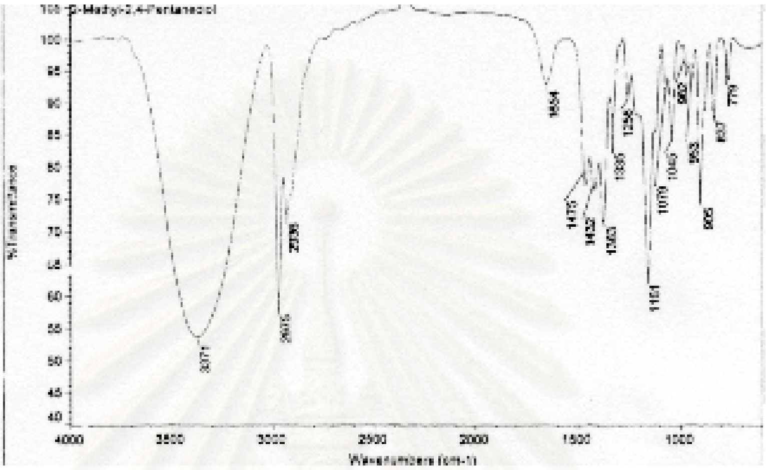


Figure A19 FTIR spectrum of 2-methyl-2,4-pentane diol

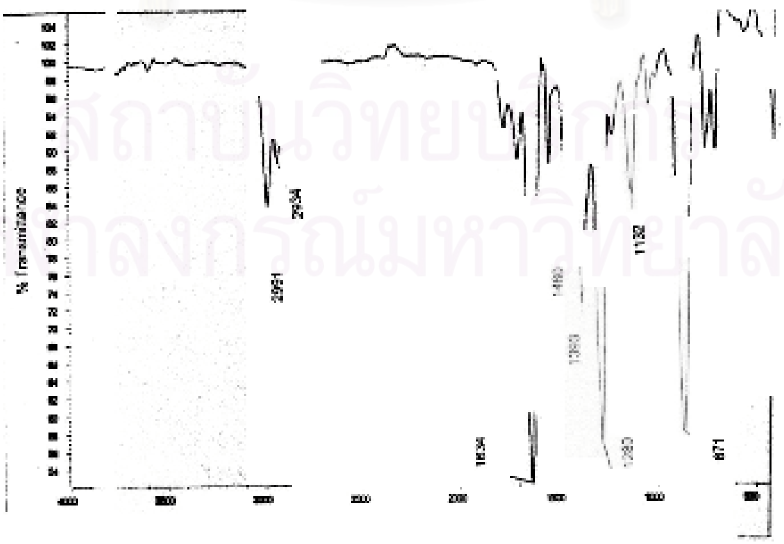


Figure A20 FTIR spectrum of 2-methyl-2,4-pentane dinitrate

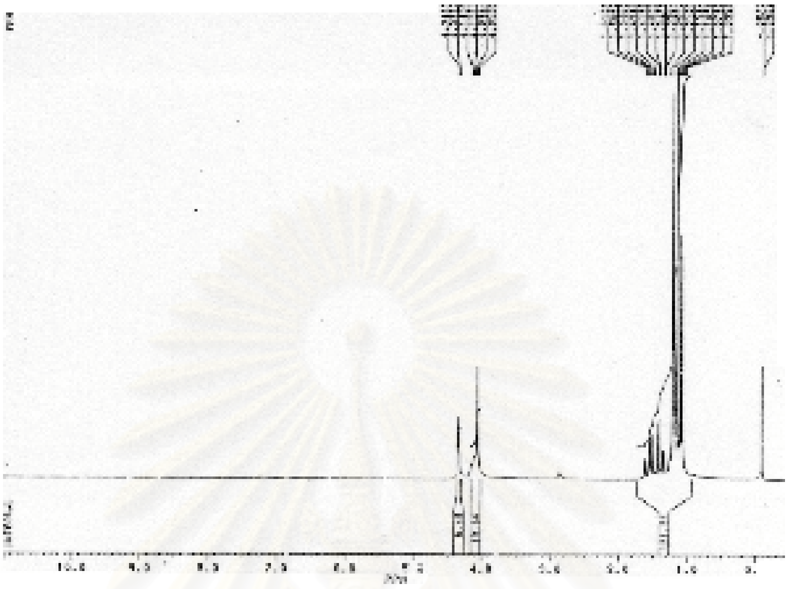


Figure A21 ^{1}H-NMR spectrum of 2-methyl-2,4-pentane diol

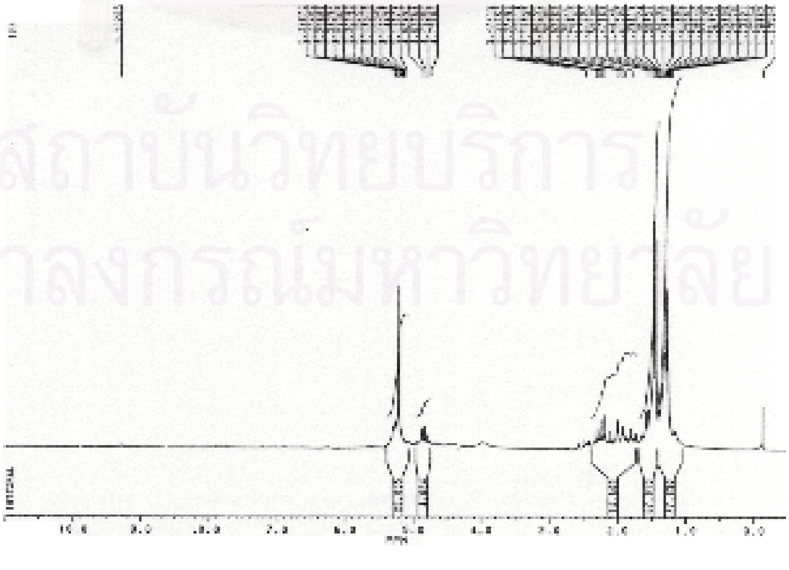


Figure A22 ^{1}H-NMR spectrum of 2-methyl-2,4-pentane dinitrate

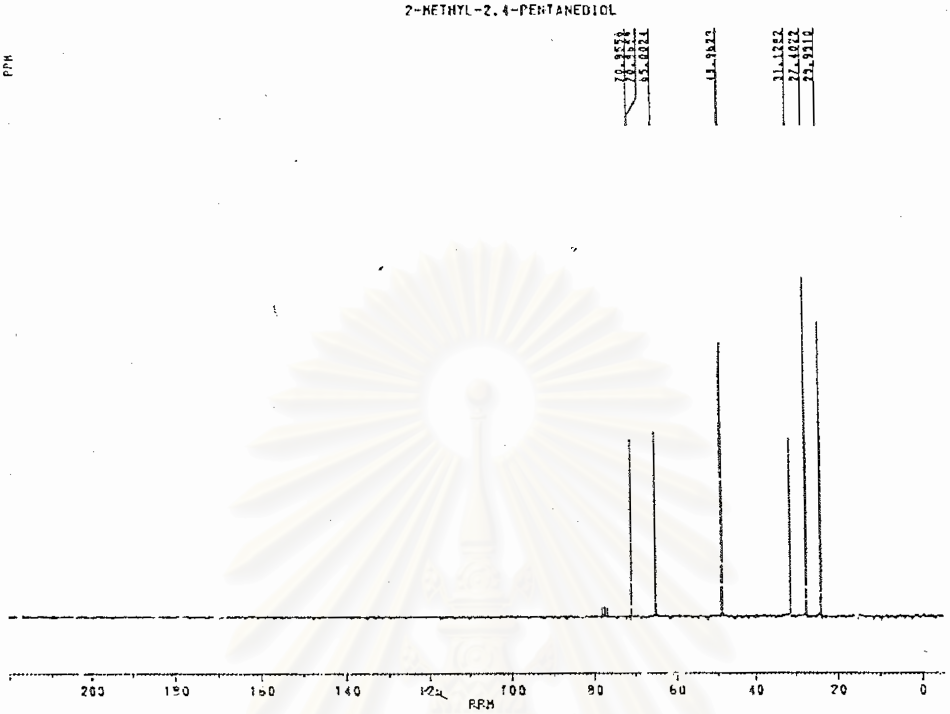


Figure A23 ^{13}C-NMR spectrum of 2-methyl-2,4-pentane diol

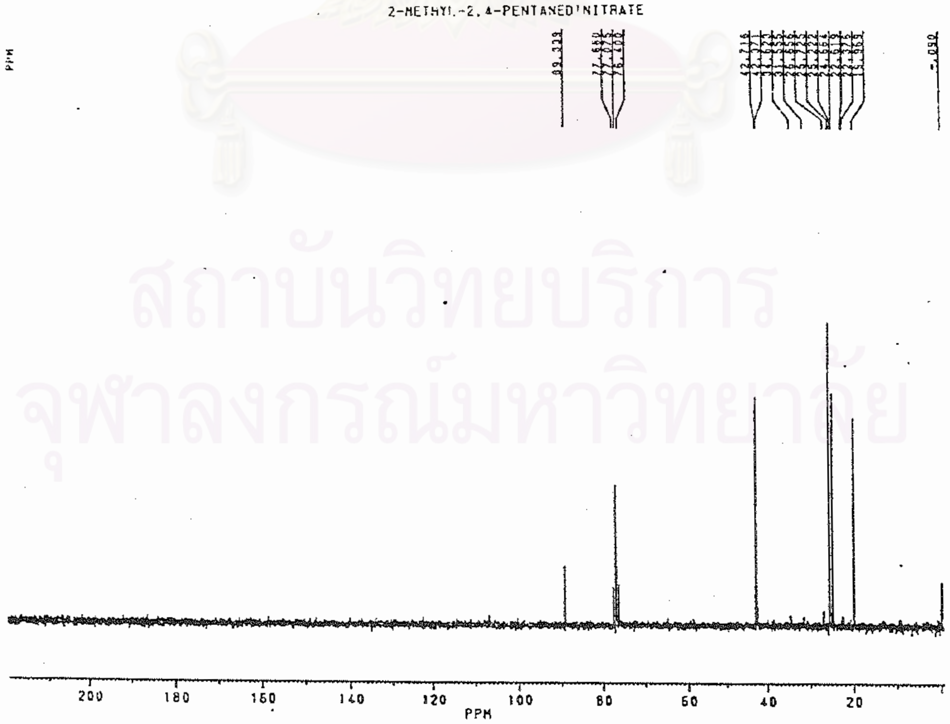


Figure A24 ^{13}C-NMR spectrum of 2-methyl-2,4-pentane dinitrate

APPENDIX B

THE CALCULATION OF CETANE INDEX

The Calculated Cetane Index is determined from the following equation:

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

$$\textbf{Cetane Cetane Index} = -420.34 + 0.016G^2 + 0.192G \log M + 65.01(\log M)^2 - 0.0001809M^2 \qquad \textbf{[B1]}$$

2. When it is applicable to fuels containing additives for raising cetane nymber. The Calculated Cetane Index is determined from the equation B1 plus equation B2.

$$\textbf{Improver value} = 0.1742(0.1G)^{1.4444} (0.01M)^{1.0052}\{in(1+17.5534D)\} \qquad \textbf{[B2]}$$

where

G = API gravity, determined by Test Method D287 or D 1298.

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 1,6-hexane dinitrate when percent weight of cetane improver at 0.05% wt., mid-boiling point at 538.70 °F,and API gravity = 36.8.

Solution;

From the equation B1,

$$\begin{aligned} \text{CCI} = {} & -420.34 + 0.016(36.8)^2 + 0.192(36.8)\{\log(538.70)\} \\ & + 65.01\{\log(538.70)\}^2 - 0.0001809(538.70)^2 \\ = {} & 53.12 \end{aligned}$$

And from the equation B2,

$$\begin{aligned} \text{Improver value} = {} & 0.1742\{0.1(36.8)\}^{1.4444}\{0.01(538.70)\}^{1.0052} \\ & \{\mathrm{In}(1+17.5534(0.05))\} \\ = {} & 3.92 \end{aligned}$$

Therefore,

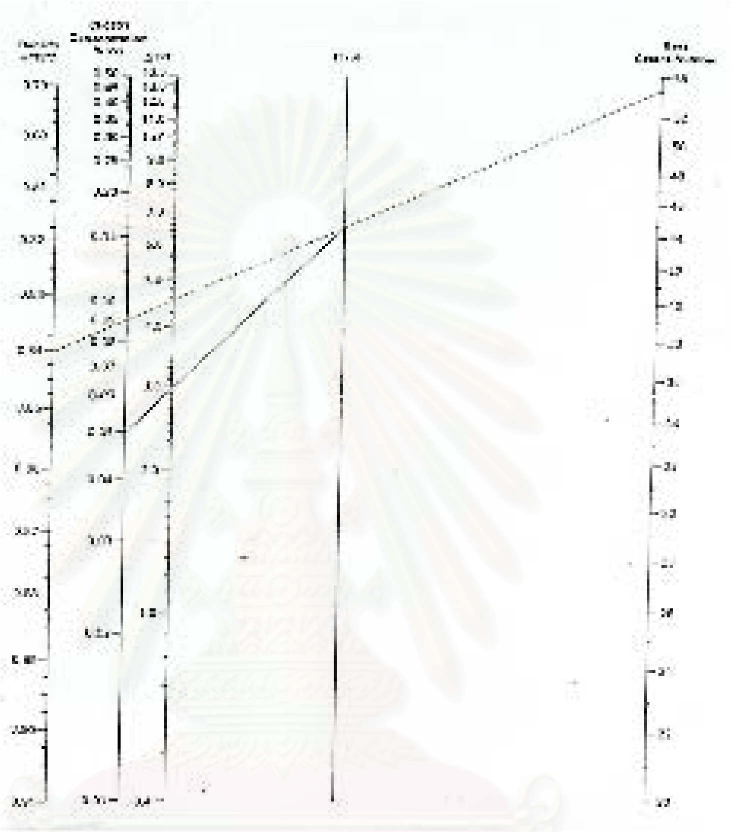
$$\begin{aligned} \text{CCI Improver} &= \text{CCI} + \text{Improver} \\ &= 53.12 + 3.92 \\ &= 57.04 \end{aligned}$$

APPENDIX C

THE CALCULATION OF CETANE NUMBER BY USING NOMOGRAPH

For example;

- Predict the cetane number of the blended diesel fuel with 1,6-hexane dinitrate when percent weight of cetane improver at 0.05% wt. and density @ 15°C at 0.8403. The base cetane number is 53.6.
- Identify the base fuel cetane number and density on the appropriate axes and draw a line joining these two points.
- Connect the pivot point to the concentration and read back along the line to the predicted cetane number increase.
- The increased cetane number is 2.97, so its cetane number is 56.57.



FigureC1 Example for the calculation of cetane number by using nomograph.

APPENDIX D

Specification and Test Methods for Diesel Fuel in Thailand

Characteristics	Specifications		
	High-speed engine	Low-speed engine	Methods
Density @ 15.6/15.6°C	0.81-0.87	0.92	ASTM D 1286
Cetane Number	min 47	min 45	ASTM D 613
or Calculated Cetane Index	min 47	min 45	ASTM D 976
Viscosity @ 40°C, cSt	1.8-4.1	max 8.0	ASTM D 445
or @ 50°C, cSt		max 6.0	
Pour Point, °C	max 10	max 16	ASTM D 97
Sulfur Content, % wt.	max 0.25	max 1.5	ASTM D 129
Copper Strip Corrosion, number	max 1	-	ASTM D 130
Carbon Residue, % wt.	max 0.05	-	ASTM D 189
Water and Sediment, % vol.	max 0.05	max 0.3	ASTM D 2709
Ash Content, % wt.	max 0.01	max 0.02	ASTM D 482
Flash Point, °C	min 52	min 52	ASTM D 93
Distillation (temperature of 90% distillation)	max 357	-	ASTM D 86
Color	max 4.0	4.5-7.5	ASTM D 1500
Detergent Additive	Test by the standard CUMMINS Tandem L-10 (Superior level)	-	-

VITA

Miss Sangsom Siraprapakit was born on January 10, 1977 in Bangkok, Thailand. She received her Bachelor’s degree of Science in Industrial Chemistry, from the Facylty of Science, King Mongkut’s Institute in 1997. Since she was interested in Petrochemistry, she has pursued Master’s degree of Science in Petrochemistry and Polymer Science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 1998 and finished her study in 2001.