การบำบัดด้วยไฮโดรเจนแบบใช้ตัวเร่งปฏิกิริยาในขั้นตอนเดียวของน้ำมันหล่อลื่นเครื่องยนต์ใช้แล้ว

นางสาว เพราะพริ้ง ชัยประเสริฐ

ONE-STEP CATALYTIC HYDROTREATMENT OF USED AUTOMOTIVE LUBRICATING OIL

Miss Prawpring Chaiprasert

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

Graduate School

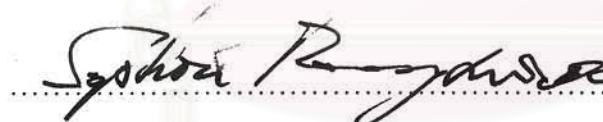Chulalongkorn University

Academic Year 1999

ISBN 974-333-134-4

Thesis Title	ONE-STEP CATALYTIC HYDROTREATMENT OF USED AUTOMOTIVE LUBRICATING OIL
By	Miss Prawpring Chaiprasert
Department	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Sophon Roengsumran, Ph.D.
Thesis Co-advisor	Mrs. Ratanavalee In-Ochanon

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of Graduate School

(Associate Professor Suchada Kiranandana, Ph.D.)

Thesis Committee

....Chairman

(Associate Professor Supawan Tantayanon, Ph.D.)

....Thesis Advisor

(Associate Professor Sophon Roengsumran, Ph.D.)

....Thesis Co-Advisor

(Mrs. Ratanavalee In-Ochanon)

....Member

(Associate Professor Amorn Petsom, Ph.D.)

....Member

(Assistant Professor Preecha Lertpratchya, Ph.D.)

เพราะพริ้ง ชัยประเสริฐ : การบำบัดด้วยไฮโครเจนแบบใช้ตัวเร่งปฏิกิริยาในขั้นตอนเดียวของน้ำมันหล่อลื่นเครื่องยนต์ ใช้แล้ว (ONE-STEP CATALYTIC HYDROTREATMENT OF USED AUTOMOTIVE LUBRICATING OIL) อ. ที่ปรึกษา : รศ. ดร. โสภณ เริงสำราญ; อ. ที่ปรึกษาร่วม : นางรัตนาวลี อินโอชานนท์; 103 หน้า. ISBN 974-333-134-4.

งานวิจัยนี้เป็นการศึกษาถึงการบำบัดตัวเร่งปฏิกิริยาในขั้นตอนเดียวของน้ำมันหล่อลื่นเครื่องยนต์ใช้แล้วโดยใช้ ตัวเร่งปฏิกิริยาคือ   นิกเกิลออกไซด์ทังสเตนไตรออกไซด์ฟลูออไรด์บนตัวรองรับอลูมินา   และนิกเกิลออกไซด์โมลิบดินัมไตร ออกไซด์ฟลูออไรด์บนตัวรองรับอลูมินา โดยทำการศึกษาถึงผลของอุณหภูมิ, ความดัน, เวลาที่ใช้ในการเกิดปฏิกิริยา และความ เข้มข้นของตัวเร่งปฏิกิริยา

จากการศึกษาพบว่า   การบำบัดด้วยไฮโดรเจนแบบใช้ตัวเร่งปฏิกิริยาชนิดนิกเกิลออกไซด์ทังสเตนไตรออกไซด์ ฟลูออไรด์บนตัวรองรับอลูมินา พบภาวะที่เหมาะสมคือ อุณหภูมิ 350 องศาเซลเซียส ความดัน 500 ปอนด์ต่อตารางนิ้ว เวลา 2.50 ชั่วโมง ปริมาณ 30 เปอร์เซ็นต์ น้ำมันผลิตภัณฑ์ที่ได้มีสมบัติที่ดีโดยเฉพาะสี, ดัชนีความหนืด, ค่าความเป็นกรด, ปริมาณซัลเฟอร์และ โลหะ   ภาวะที่เหมาะสมสำหรับตัวเร่งปฏิกิริยานิกเกิลออกไซด์โมลิบดินัมไตรออกไซด์ฟลูออไรด์บนตัวรองรับอลูมินา คือ อุณหภูมิ 350 องศาเซลเซียส ความดัน 500 ปอนด์ต่อตารางนิ้ว เวลา 2.50 ชั่วโมง ปริมาณ 30 เปอร์เซ็นต์ น้ำมันผลิตภัณฑ์ที่ได้มีสมบัติ ที่ดีโดยเฉพาะสี, ความเป็นกรด, ปริมาณซัลเฟอร์ และโลหะ

น้ำมันผลิตภัณฑ์ที่ได้จากการบำบัดด้วยไฮโดรเจนแบบใช้ตัวเร่งปฏิกิริยาทั้งสองชนิดมี   สมบัติเป็นน้ำมันหล่อลื่น พื้นฐานซึ่งให้สมบัติที่ดี โดยมีค่าดัชนีความหนืดสูง, ค่าความเป็นกรด, ปริมาณซัลเฟอร์และโลหะน้อย

ภาควิชา... ลายมือชื่อนิสิต..

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.......... ลายมือชื่ออาจารย์ที่ปรึกษา..

ปีการศึกษา...2542.. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม...................................

A one-step catalytic hydrotreatment of used automotive lubricating oil was developed. The catalysts were $NiO/WO_3/F$ and $NiO/MoO_3/F$ on alumina. The operating conditions were studied in temperature, hydrogen pressure, reaction time and catalyst concentration.

It was found that the suitable conditions for the $NiO/WO_3/F$ on alumina catalyst were at 350°C, hydrogen pressure of 500 psig, reaction time of 2.50 hours and catalyst concentration of 30%wt. The hydrotreated oil obtained from these conditions had good properties especially color, viscosity index, acidity, sulfur and metal content. The suitable conditions for the $NiO/MoO_3/F$ on alumina catalyst were at 350°C, hydrogen pressure of 500 psi, reaction time of 2.50 hours, and concentration of 30% wt. The hydrotreated oil obtained from these conditions had good properties especially color, acidity, sulfur and metal content.

The hydrotreated oil which was obtained from using two types of catalyst had good properties and it could be used as lube base oil. It had high viscosity index, low acidity, sulfur and metal content.

ภาควิชา _-_____ ลายมือชื่อนิสิต _____

สาขาวิชา ปิโตร เคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา _____

ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม _____

ACKNOWLEDGEMENTS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

สถาบันวิทยบริการ

จุฬาลงกรณ์มหาวิทยาลัย

ABBREVIATIONS

VI	=	Viscosity Index
Cst	=	Centistoke Unit
TG	=	Thermal Gravimetry
rpm	=	Revolution per minute
%wt	=	percent by weight
°C	=	Degree of Celsius
Al_2O_3	=	Alumina
psi	=	pound per square inch
TAN	=	Total acid number
ppm	=	part per million

CHAPTER I

INTRODUCTION

The petroleum shortages increased the oil price. The demand of oil products also increased because of the economic expansion and the rapid industrial growth in Thailand. Consequently, the consumption of lubricating base oil increased. However, almost all of the base oil is imported from several foreign countries such as Taiwan, Singapore, China, Australia [1]. It could be estimated that the consumption is more continuously increasing, therefore there is much interest in developing a method to conserve the valuable energy and resource content of these products. The lubricating oil is one of the highest valued products derived from petroleum. It is used in industrial machines, automobiles and is applied to lubricate and prevent wear of moving surfaces. After the lubricating oil is used, it is contaminated by dust, metal particles, oxidation products, unburned fuel and by product of combustion. The used oil deteriorates until it can no longer be used to lubricate the engine. The used or contaminated oil is usually considered a waste and is disposed of in many ways including incineration, landspreading and dumping on the ground and into water. All used oil creates environmental hazard later. There is interested in developing ways to utilize the used oil such as burning as fuel, road oiling or re-refining to produce base oil. There are many effective processes to improve or recycle used lubricating oil, which is aimed at removing contaminants from used oil and producing oil products

which have a quality similar to base lube oil. Several processes have been developed as the following:

Brownawell et al. (1972) [2] studied the process for recycling used lubricating oils by a preliminary treatment with C_4-C_5 aliphatic alcohol to separate oxidation products. The desludged oil was then subject to conventional refining steps with sulfuric acid, clay, solvent extraction, distillation and hydrogenation. The hydrogenation treatment was operated at a temperature of 300 °C and hydrogen pressures of 1500-2000 psia for 18 hours by using a nickel catalyst (Ni-0104T). After the treatment, the viscosity and the color decreased.

Cutler et al. (1975) [4] studied the process for re-refining waste automotive lubricating oil, which employed sequence steps of propane extraction, vacuum distillation and catalytic hydrogenation. The reaction was operated over cobalt-molybdenum catalyst, at temperatures of 600-700 °F and hydrogen pressures of 600-700 psi.

Whisman et al. (1978) [5] studied the process for recycling used oils by vacuum distillation and dissolved it in a solvent mixture. The oil-solvent mixture was separated and the solvent was recovered. The separated oil was distilled and hydrotreated. The reaction was operated at a temperature of 316 °C and hydrogen pressure of 650 psig. Typical catalysts were cobalt-molybdenum and nickel-molybdenum on alumina support. The product oil was suitable for blending with other base stocks and additives.

Mead et al. (1984) [6] studied the process for recycling used lubricating oils, which contained metal compounds, sludge and other undesirable components by vacuum distillation and catalytic hydrogenation, producing base stock suitable for blending. The reaction was operated at temperatures of 250-370 °C, hydrogen pressures of 200-400 psig, using commercial hydrogenation catalyst (American Cyanamid HDS-3A®).

Reid et al. (1985) [7] studied the process for re-refining waste oil, which used many steps to remove contaminants and additives. The steps were filtering, heat soaking, distillation and hydrotreating. The reaction was operated over a conventional Ni/Mo catalyst, at temperatures of 200-300 °C and hydrogen pressures of 3-5 Mpa. The oil product had good physical and chemical properties.

Rongsawad (1993) [8] studied a process for the recycling of used industrial oil by acid / clay treatment and hydrogenation.

Chaosuwannakij (1996) [9] studied a process for the recycling of used marine lubricating oil by one– step catalytic hydrogenation. The reaction was operated at a 350 °C, under 500 psig hydrogen pressure for 10 minutes and using commercial catalysts such as $NiO/WO_3/Al_2O_3$, $NiO/MoO_3/Al_2O_3$ and Raney nickel. The oil product had desirable properties, especially in terms of viscosity index, color and sulfur content.

Objective and Scope of the Research

The efforts to recycle used lubricating oil by studying new processes or new catalysts was to upgrade used oil until it is acceptable quality similar to base lube oil. Previous re-refining processes have had serious difficulties, for example treatment with sulfuric acid created a considerable volume of acid sludge which was difficult to properly dispose of, treatment with any caustic soda, slaked lime and created amount of noxious sludge containing significant amounts of oil. Re-refining with distillation process created severe equipment maintenance problems, oil loss and high cost. Today one of the effective processes to reuse used lube oil is direct catalytic hydrogenation. It is a process that removes contaminants from used oil and produces high quality lube base oil. So to improve used oil quality, this research comprises only one-process to recycle used lube oil by catalytic hydrotreatment.

The goals of this research are to improve the quality of used automotive lubricating oil and to simplify the process by using one-step catalytic hydrotreatment process. In addition, this research has more objective on the investigation of catalysts that are more effective and cheaper by using hydrotreating catalysts such as nickel, tungsten, molybdenum. Furthermore, this research aims to find optimum conditions by the variation of temperature, pressure, reaction time and concentration.

CHAPTER II

THEORETICAL CONSIDERATIONS

Lubricating Base Oil

The lubricating oil is usually a mixture of lubricating base oil and additives. There are essentially two sources from which the base lubricant fluids are obtained. There are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties, which are suitable for lubricant purposes.

Petroleum Crude Oil and Its Components [11-14]

Crude oil was formed many millions of years ago, and it is believed that it originated from the remains of tiny aquatic animals and plants that settled with mud and silt to the bottle of ancient seas. As successive layers built up, those deposits were subjected to high pressures and temperatures and as a result underwent chemical transformations leading to the formation of the hydrocarbon and other constituents of crude oil. They are found in a variety of types ranging from light colored oils, consisting mainly of gasoline, to black, nearly solid asphalts. These crudes are very complex mixtures ranging from methane with one carbon atom to compounds containing 50 or more carbon atoms. Crude oil consists of a very complex mixture of saturated and unsaturated hydrocarbons with minor amounts of non-hydrocarbons

consisting chiefly of sulfur, nitrogen and oxygen. There are typical of hydrocarbons in crude oil.

1) **Hydrocarbons**

    (a) Paraffinic hydrocarbons: These have saturated straight and branched-chain structures. The paraffinic hydrocarbons have high viscosity index and low pour point.

    (b) Aromatic hydrocarbons: These are both mono and polynuclear hydrocarbons based on the six-membered benzene ring. They have a low viscosity index and low pour point.

    (c) Naphthenic hydrocarbons: These are polycyclic and fused–ring saturated hydrocarbons based on five or six-member rings. They are extremely stable compounds.

    (d) Olefinic hydrocarbons: These are unsaturated molecules. They are more chemically active than the other three classes. They are subject to oxidation or polymerization forming gums
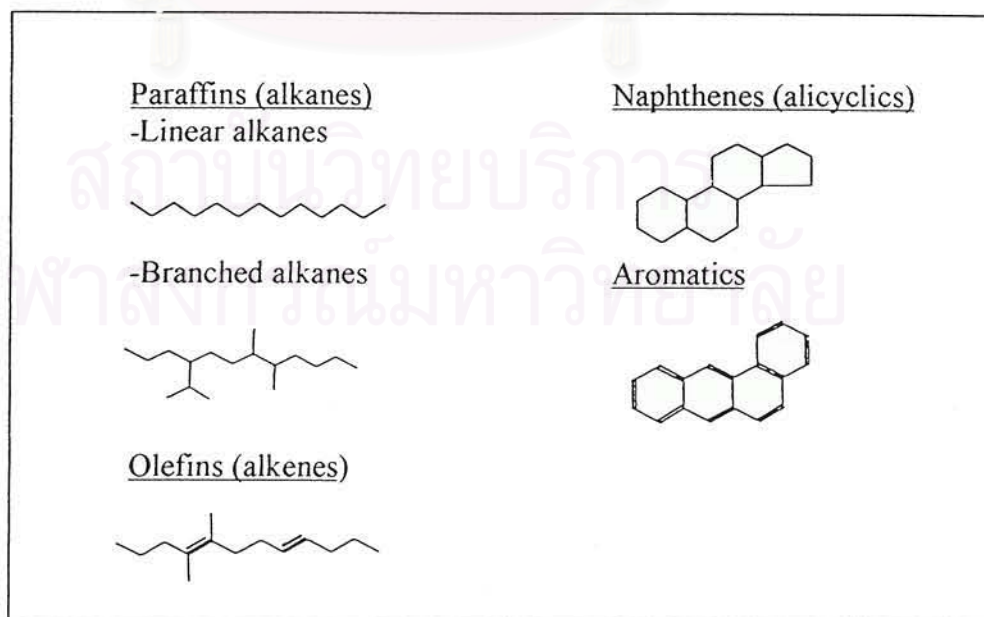
Figure 2.1 Examples of hydrocarbons

2) Non – hydrocarbons

Crude oils also contain varying amounts of compounds of sulfur, nitrogen, oxygen, varying metals such as vanadium, nickel, water and salts. Almost all of sulfur and nitrogen are heterocyclic molecules. In the production of lube oil, these compounds, including olefin and aromatic are removed. All of these materials can cause problems in refining or in subsequent products applications.
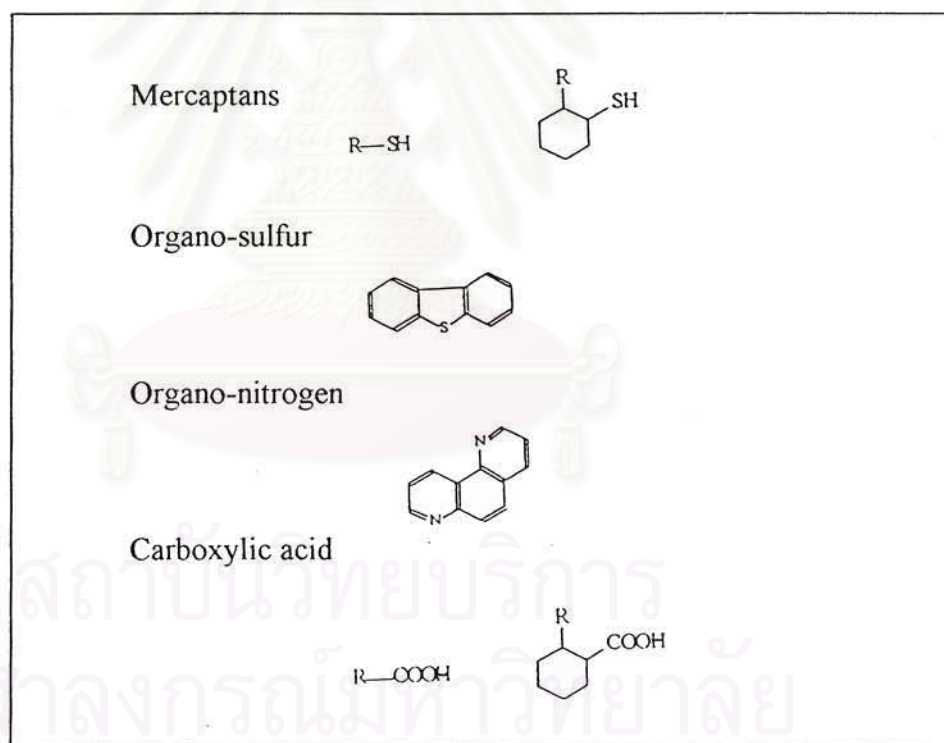
Figure 2.2 Examples of non-hydrocarbons

Source of Lubricating Base Oil

Refining of Petroleum Crude Oils [11,14,16]

The manufacture of lubricating base stocks consist of a series of separation or subtractive processes which remove undesirable components from the feedstock leaving a lubricating base stock that meets performance requirements. A simplified diagram of such a process is shown in Figure 2.3 Essentially five steps are involved.
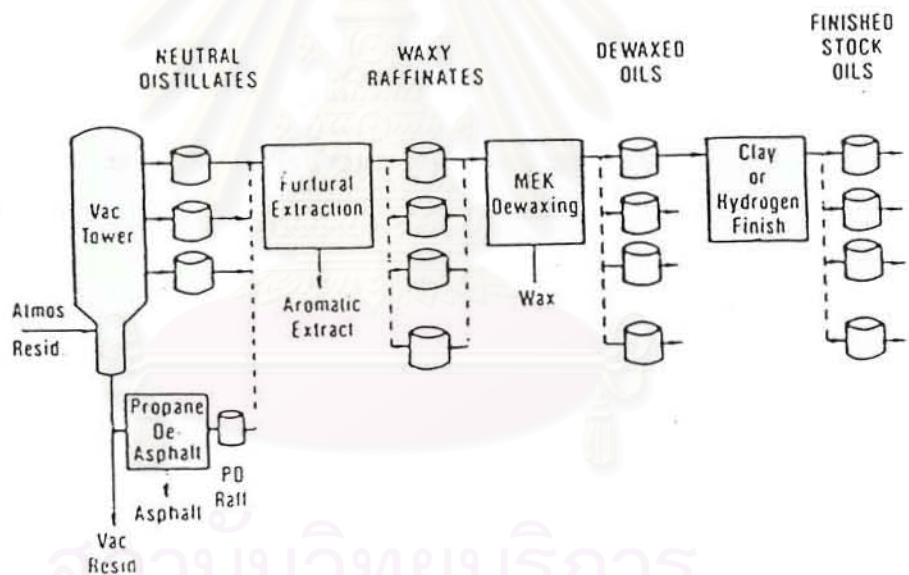
Figure 2.3 Lube processing

1. Vacuum distillation

This process which separates the atmospheric residue mixture into a series of fractions representing different molecular weight ranges or viscosity ranges from the

90-100 neutrals to the 500 neutrals. The residue contains the heavier base oils such as the bright stocks.

2. Propane deasphalting

The highest boiling portions of most crude oils contain resins and asphaltenes. These materials must be separated prior to introduction into the extraction process.

3. Furfural extraction

Solvent extraction (Furfural in this case) separates aromatic compounds from nonaromatic compounds. The resultant product shows an increase in thermal and oxidative stability as well as an improvement in viscosity and temperature characteristics, as measured by a higher viscosity index (VI).

4. MEK dewaxing

This process is to remove wax to reduce the pour point of the base stock. In this case illustrated, methyl ethyl ketone (MEK) is mixed with the waxy oil. The mixture is then cooled to a temperature between 10 °F (-12 °C) and 20 °F (-6 °C) below the desired pour point. The wax crystals which form are then removed from the oil by filtration.

5. Hydrofinishing

Some base stocks, particularly premium stocks, require a finishing process to improve the color, oxidation, or thermal stability of the base stock. The hydrofinishing process consists of a bed of catalyst through which heated oil and hydrogen are

passed. This process removes some of the color and unstable component such as nitrogen and sulfur in the oil.

Base Oil Composition, Properties and Structure Relationship [9,18]

The petroleum fraction used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating base oil fraction is a complex mixture consisting primarily of five characteristic classes:-paraffin naphthenes, condensed naphthenes, aromatic naphthenes, naphthalenes (two ring aromatics) and multi-ring aromatics. It also contains small amounts of heterocyclic compounds containing sulfur and nitrogen atoms (e.g. thionaphthene, indole, quinoline and carbazoled) and various oxygen containing compounds, including naphthenic acids, which account for most of the chemically bound oxygen in petroleum fractions.

Alkanes, alicyclics and aromatics of the same molecular weight have markedly different physical and chemical properties. Physical characteristics will affect the viscometrics of the lubricant. The chemical stability of each class to oxidation and degradation while in use will also be very important. The effect of different types of compounds on a lubricating oil's properties can be seen in Table 2.1
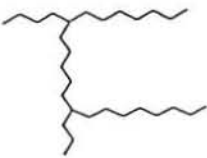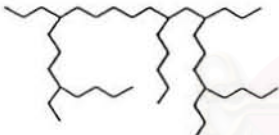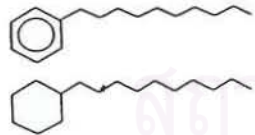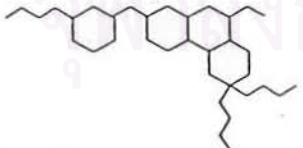
Table 2.1 shows qualitatively that the highly desirable structures for lubricant base oils are the highly branched isoparaffin and monocyclic hydrocarbons, saturated or unsaturated, with long aliphatic chains and preferably five carbon atoms in the ring.

The linear alkanes (normal paraffins) have good viscosity/ temperature characteristics. They are wax-like and therefore their concentrations must be minimized, especially in those oils for application at low temperature. On the other hand, branched-chain paraffins can be very desired constituents in a lubricant because of their good stability and viscosity/ temperature properties. Alicyclics and aromatics have rather higher density and viscosity for their molecular weight compared to the alkanes. However, their viscosity/ temperature characteristics and oxidation stability are in general rather poor. Single ring alicyclics or single ring aromatics with long alkyl side chains, in contrast, share many properties with branched alkanes and can in fact be very desirable base oil components.

Table 2.1 Lubricating oil properties of some typical hydrocarbon structures.

Structure	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin	Very high	High	Good	Nil
Isoparaffin with linear chains	High	Medium	Good	Medium
Isoparaffin with isomerized chain	High	Low	Good	High
Highly substituted isoparaffin	Medium	Low	Good	Medium
Single ring with long aliphatic chain	High	Low	Good	High
Polycondensed naphthenes	Low	Low	Medium	Nil
Polycondensed aromatics	Very low(<0)	Low	Weak	Nil

Lubricating Oil Additives [15,16-17]

Lubricating oils are produced by blending base lubricating oil and additives. The lube oil base stocks are prepared from crude oils by distillation and special processing to meet the desired qualification. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improved existing properties. Additives can be classified as materials which either impart or enhance a desirable property of the lubricant into which they may be incorporated.

A. Dispersants-Metallic Types

These compounds have been described in the literature as "detergent". Since their function appears to be one of affecting a dispersion of particulate matter rather than one of "cleaning up" any existing dirt and debris, it is more appropriate to categorize them as dispersants.

Materials of this type are generally molecules having a large hydrocarbon "tail" and a polar group head. The tail section, oleophilic group, serves as a solubilizer in the base fluid while the polar group serves as the element which is attracted to particulate contaminants in the lubricant.

These additives such as petroleum sulfonates, synthetic sulfonates, thiophosphonates, phenates, and phenol sulfide salts.

B. Dispersants-Ashless Types

A development of major importance in the additive field has been the discovery and use of ashless dispersants. These materials may be categorized into two

broad types: high molecular weight polymeric dispersants for the formulation of multigrade oils and lower molecular weight additives for use where viscosity improvement is not necessary.

These additives are much more effective than the metallic dispersants in controlling sludge and varnish deposits which are involved in intermittent and low-temperature gasoline engine operation. The compounds useful for these purpose are again characterized by a "polar" group attached to a relatively high molecular weight hydrocarbon chain. These compounds are N-substituted long chain alkenyl succinimide, high molecular weight esters for examples.

C. Polymeric Dispersant Additives

These ashless dispersants may serve a dual function. They can be both a viscosity index improver and a dispersant and consist of two general types of molecular configuration, i.e., those whose structure is similar to the ones employed as viscosity index improvers to insure oil solubility, and those containing "polar" compounds to impart the dispersancy characteristic.

D. Oxidation and Bearing Corrosion Inhibitors

The function of an oxidation inhibitor is prevention of deterioration associated with oxygen attack on the lubricant base fluid. These inhibitors function either to destroy free radicals (chain breaking) or to interact with peroxides which are involved in the oxidation mechanism. These compounds are phenolic inhibitors, zinc dithiophosphates for examples.

E. Anti- Wear Additives

Wear is loss of metal with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in engine malfunction. Amount the principal factors causing wear are metal to metal contact, presence of abrasive particulate matter, and attack of corrosive acids. Metal to metal contact can be prevented by addition of film-forming compounds which protect the surface either by physical absorption or by chemical reaction. Abrasive wear can be prevented by effective removal of particulate matter by filtration of both the air entering the engine and the lubricant during operation. Corrosive wear by acidic blow-by products, can be controlled by the use of alkaline additives.

F. Viscosity Improvers

Viscosity improvers or viscosity index improver, as they are quite often referred to, comprise a class of materials which improve the viscosity- temperature characteristics of the lubricating oil. This modification of the rheological property results in an increase in viscosity at all temperatures which significantly improves the viscosity index of the lubricating oil.

G. Pour Point Depressants

Pour point depressants prevent the congelation of the oil at low temperature. This phenomenon is associated with the crystallization of the paraffin wax which is most often present in the mineral oil fractions. The pour point depressants do not prevent wax from crystallizing from the oil, but amount of oil occluded on the crystal. The reduction in volume of the crystal permits flow of the lubricating oil.

Basic Function of Lubricating Oil [11]

The basic functions of a lubricating oil are :

A) Friction reduction

Simply stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage.

B) Heat removal

In heat removal, lubricating acts as coolant, removing heat generated either by friction or other sources such as via combustion process or by transfer from contact with substances at a higher temperature. In performing this function, it is important that the lubricating oil remains in a relatively unchanged condition. Changes in thermal and oxidative stability which materially decrease its efficiency in this respect. Additives are generally employed for the solution of such problems.

C) Containment of contaminants

Another function of lubricating oil is to remain effective in the presence of outside contaminants. These contaminants are water, acid combustion products, particulate matter, ect., which generally find their way into lubricating oils employed in various applications.

Necessary Properties of a Lubricant [15]

Lubricants are formulated by blending base oils and additives to meet a series of performance specifications. These specifications relate to the physical and chemical properties of the oil. Base oils have a range of properties that can be measured and used to predict performance. Analysis and testing of lubricants and related products are based on standards [International Organization for Standardisation (ISO), American Society for Testing and Materials(ASTM), Institute of Petroleum (IP), etc.] which are often identical.

A. Physical Properties [15-17]

1. Viscosity

Viscosity is the most significant property of a lubricating oil. The primary purpose of a lubricant is to reduce friction and minimize wear by separating lubricate surfaces with an oil film. Viscosity is a measure of resistance to flow. It decreases with increasing temperature and increases with large increasing pressure. The extend of the viscosity change depends on the crude source of the oil and the molecular weights of the constituent components.

The instrument used to determine the viscosity of an oil is called a viscometer. In general two types are used: the Saybolt and kinematic viscometers. Kinematic viscosity is the more common and is measured by the time required for a given volume of an oil at a specified temperature to flow through a capillary tube under

gravitational force. Test temperatures are usually at 40 and 100 °C for centistokes unit.

2. Viscosity Index (VI)

Viscosity index is a reflection of an oil's resistance to viscosity change with fluctuation in temperature. The higher the viscosity index of an oil, the more resistant it is to a viscosity change caused by temperature fluctuation. All lubricating oils thin out or have lower viscosity as the temperature is increased. Likewise, oils become thicker or more viscous as the temperature is reduced. However, not all oils respond to the same degree to temperature changes.

Lubricating oils are subjected to wide variations of temperature in service. At high temperatures the viscosity can drop to a point where the oil is so thin that the oil film may break, allowing metal surfaces to touch, resulting in excessive wear. At the other extreme, the temperature can be so low that the oil becomes viscous and does not allow proper circulation to the parts being lubricated.

Take an automobile, for example. During startup the oil can be quite cold, particularly during winter. But the oil must not be so viscous that the drag on the engine makes starting difficult. During warm-up the oil must be able to flow to all the moving parts. Finally, after the engine has reached its normal operating temperature, the oil must not be so thin that oil consumption is high or the lubricating film can no longer carry the load. Most motor oils have a viscosity index of 100 or higher. Where temperature variations are less or for continuous operation at constant temperature, Viscosity index is less critical.

3. Pour Point

As a lubricating oil is chilled, it eventually reaches a point where it will no longer flow under the influence of gravity. This condition is brought about either by the thickening (more viscous) that always accompanies a reduction in temperature or by crystallization of wax dissolved in the oil, restricting the flow of the liquid portion. The lowest temperature to which an oil can be chilled and still be poured from a container is called the "pour point".

The pour point is related to the ability of the oil to start lubricating when a cold machine is placed into operation. Engines that are stopped and started under low-temperature conditions require an oil that will flow readily when cold.

4. Flash Point

The flash point is a measurement of the flammability of a petroleum product. The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire.

Flash point is also useful in evaluating used oils. A drop in flash point indicates contamination by dilution of the motor oil with unburned fuel. An increase indicates evaporation of the oil. This property is determined by the open-cup method, usually called the Cleveland Open Cup method and abbreviated COC.

5. Color (ASTM D 1500)

The color test was performed by following the ASTM D 1500 method. The oil's color is normally not an indication of its lubricating properties. It is, however, a guide to the presence of contaminants or to the degree of deterioration in storage. It is also an indication of the intensity of refining. Absence of color (water white) is important in certain applications such as in textile machinery lubrication to avoid indelible staining of the textile. Absence of color is also important to users of waxes, and white oils where extremely high purity is required.

6. Sulfur Content

Sulfur content in lubricating oil will vary to some extent the instrumentation used and the nature of the oils. Sulfur content is measured by using x-ray fluorescence spectrometric method.

7. Neutralization Number

The neutralization number measures the organic acid content of base oils and the acids produced by oxidation in storage or service. The acid numbers are expressed in milligrams of potassium hydroxide (KOH) needed to neutralize a gram of sample. The neutralization number is important in oils of critical service, such as turbine oils and insulating oils. With new oils, neutralization test results serve as a guide to mechanical condition, change in operating conditions, or product deterioration due to oxidation.

8. Sulfated Ash

The sulfated ash of a lubricating oil is the residue, in percent by weight, remaining after burning the oil, treating the initial residue with sulfuric acid, and burning the treated residue. It is a measure of the noncombustible constituents (usually metallic materials) contained in the oil.

New, straight mineral lubricating oils contain essentially no ash forming materials. Many of the additives used in lubricating oils contain metallo organic components, which will form a residue in the sulfated ash test, so the concentration of such materials in an oil is roughly indicated by the test. Thus, during manufacture, the test gives a simple method of checking to ensure that the additives have been incorporated in approximately the correct amounts. However, since the test combines all metallic elements are in the oil in the correct proportions. With used oils, an increase in ash content usually indicates a buildup of contaminants such as dust and dirt, wear debris, and possibly other contamination such as lead salts, which are derived from the combustion of leaded gasolines in internal combustion engines.

9. Water Content

The removal of water is necessary to prevent condensation of the water and the formation of ice or gas hydrates. Water in liquid phase causes corrosion problems in equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas. The water content of petroleum products is important in the refining, purchase, sale, and transfer of products. The simplest method covers the determination of water in petroleum products by distillation method.

10. Metal Content

The heavier oils contain relatively high proportions of metals either in the form of salts or as organometallic constituents, which are extremely difficult to remove. A variety of tests have been designated for the determination of metals on petroleum products. Inductively coupled plasma (ICP) spectrometry has made the determination of metals very easy and used oil can be scanned for 22 elements in a few minutes.

B. Chemical Properties [9,17]

All petroleum products are subject to chemical attack by oxygen. Attack is promoted by high temperatures, catalysts, and the presence of water or acids. Oil oxidation results in two general classes of degradation products:

1. Oil-insoluble materials, i.e., resins, varnish, or sludge

2. Oil-soluble products, primarily acids and peroxides

Resistance to oxidation is important in the performance of a lubricant. Acids formed may be corrosive to metals. Varnish may deposit on sliding surfaces, causing them to·stick or wear. Sludge may plug screens or passages or the rings on cylinders, causing them to be ineffective. Resistance to oxidation is extremely important for a steam-turbine oil because of the serious consequences of a bearing failure. Transformer oils, gear oils, hydraulic fluids, heat transfer oils, and crankcase oils also require a high degree of oxidation stability to ensure a satisfactory service life.

There are several accelerated tests to measure an oil 's resistance to oxidation which are designed to correlate with field performance.

Oxidation Stability

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and a marked increase in viscosity of the lubricant, all which seriously impair the efficiency of the lubricant.

The thermogravimetric balance (TG) is one of recently technique developed to evaluate thermal behavior of different chemical component. Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300 °C. Higher than 300 °C, the sample weight begins a rapid and continuous loss. In the presence of oxygen, that decomposition reaction occurred, the reaction observed at temperature around 350 °C or higher which leads to retard decreasing in weight loss. These temperatures can be named oxidation points.

- oxidation points; i.e., temperature at which the rate of weight loss decreases due to the formation of high molecular weight oxygenated compounds.
- Oxidative compounds; i.e., weight of oxygenated compounds which remains in the pan of balance at the oxidation point. Higher than that point, the oxidative compounds state to carbonize and finally evaporate as CO_2.

Catalytic Hydrotreatment [18,19]

Catalytic Hydrotreating

Catalytic hydrotreating is a process to catalytically stabilize lubricating oils remove objectionable elements from the used oil or product by reacting them with hydrogen. Stabilization involves converting unsaturated hydrocarbon such as olefins and gum-forming unstable diolefins to saturated materials such as paraffins. Objectionable elements that are removed by the process include sulfur, nitrogen, oxygen, halides and trace metals. Generally, in practices, to treated used lubricating oils with the catalytic hydrogenation process, usually need the specific reaction as called hydrotreating process. In the main hydrotreating reaction is that of desulfurization but many others take place to a degree proportional to the severity of the operation. Typical reactions are:

- ring- opening, especially of multi- ring molecules

- cracking to lower molecular weight products

- isomerization of alkanes and alkyl side- chains

- desulfurization

- denitrogenation

- reorganization of reactive intermediates, e.g. to form traces of stable polycyclic aromatics.

The extend to which each of these reaction types occurs is determined by the types of catalyst used, the process conditions and base stock composition. In general,

to handle catalyst in use, more comfortable, and can be recycled well, the supported catalyst should be considered.

Hydrotreating is applied to a wide range of feedstocks from naphtha to reduced crude. When the process was employed specifically for sulfur removal it is usually called hydrodesulfurization or HDS.

Hydrodesulfurization [20-22]

Desulfurization is the removal of sulfur or sulfur compounds from hydrocarbons. Catalytic hydrodesulfurization involves the reaction of sulfur compounds with hydrogen in the presence of a catalyst, resulting in their decomposition into hydrogen sulfide and hydrocarbon remnants of the original sulfur compound. Both hydrogen sulfide and sulfur are found dissolved in oil. These materials cause corrosion problems, it is necessary to pretreat the feedstocks to sulfur contents of a few parts per million or lower to avoid catalyst deactivation. Desulfurization is accomplished by the cleavage of carbon-sulfur bonds. These bonds are replaced by C-H and S-H bonds. The step of the Co/Mo/alumina desulfurization catalyst consists of : The first step is the cleavage of the sulfur hydrogen bond. This step occurs very rapidly and is favored because both sulfur and hydrogen form strong bonds to the molybdenum surface. In subsequent steps, the carbon-sulfur bond must break, and one carbon-hydrogen bond is either formed or broken to yield the hydrocarbon products from the thiol. For example, ethanethiol bonds to the catalyst breaking the sulfur-hydrogen bond and becoming ethyl thiolate (CH_3CH_2S). The carbon-sulfur bond is broken next. Finally, the formation of a carbon-hydrogen bond yields ethane, whereas the breaking of such a bond leads to ethene. Sulfur atoms of

the molybdenum sulfide phase are rearranged and may be rejected into the gas phase as hydrogen sulfide.
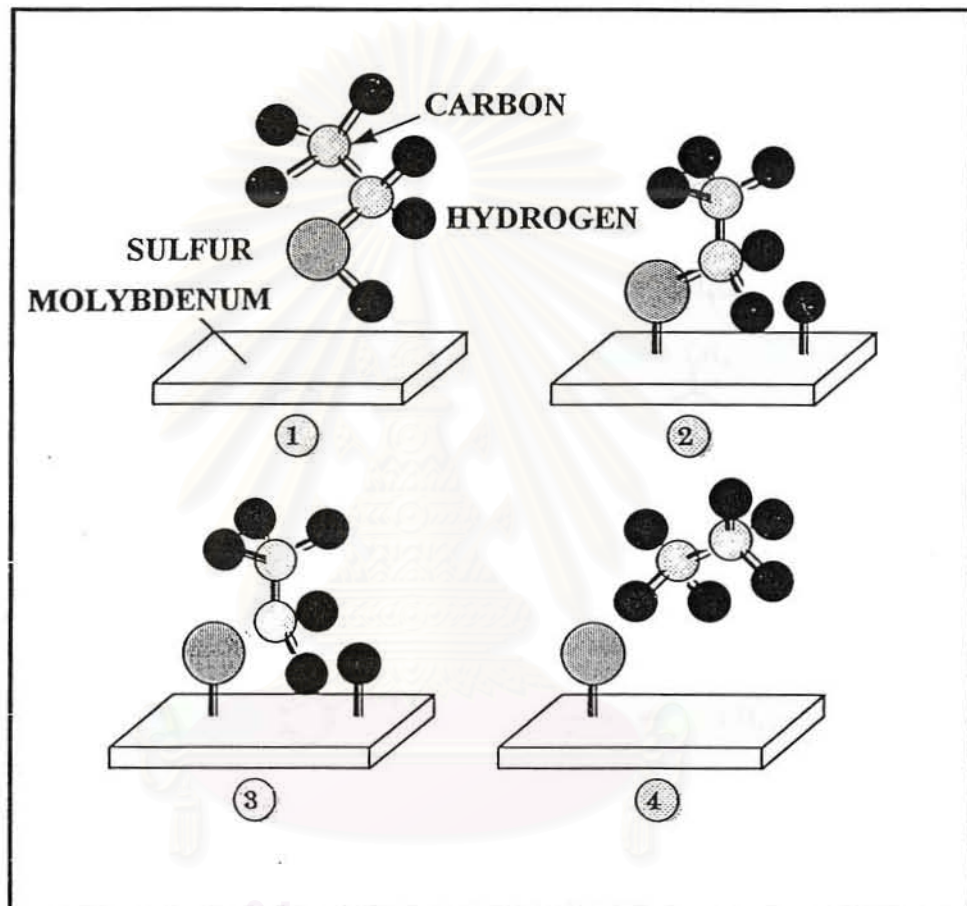
Figure 2.4 The steps of the desulfurization of thiol on molybdenum

Hydrotreating Reactions [11]

The main hydrotreating reaction is that of desulfurization but many others take place to a degree proportional to the severity of the operation. Typical reactions are:
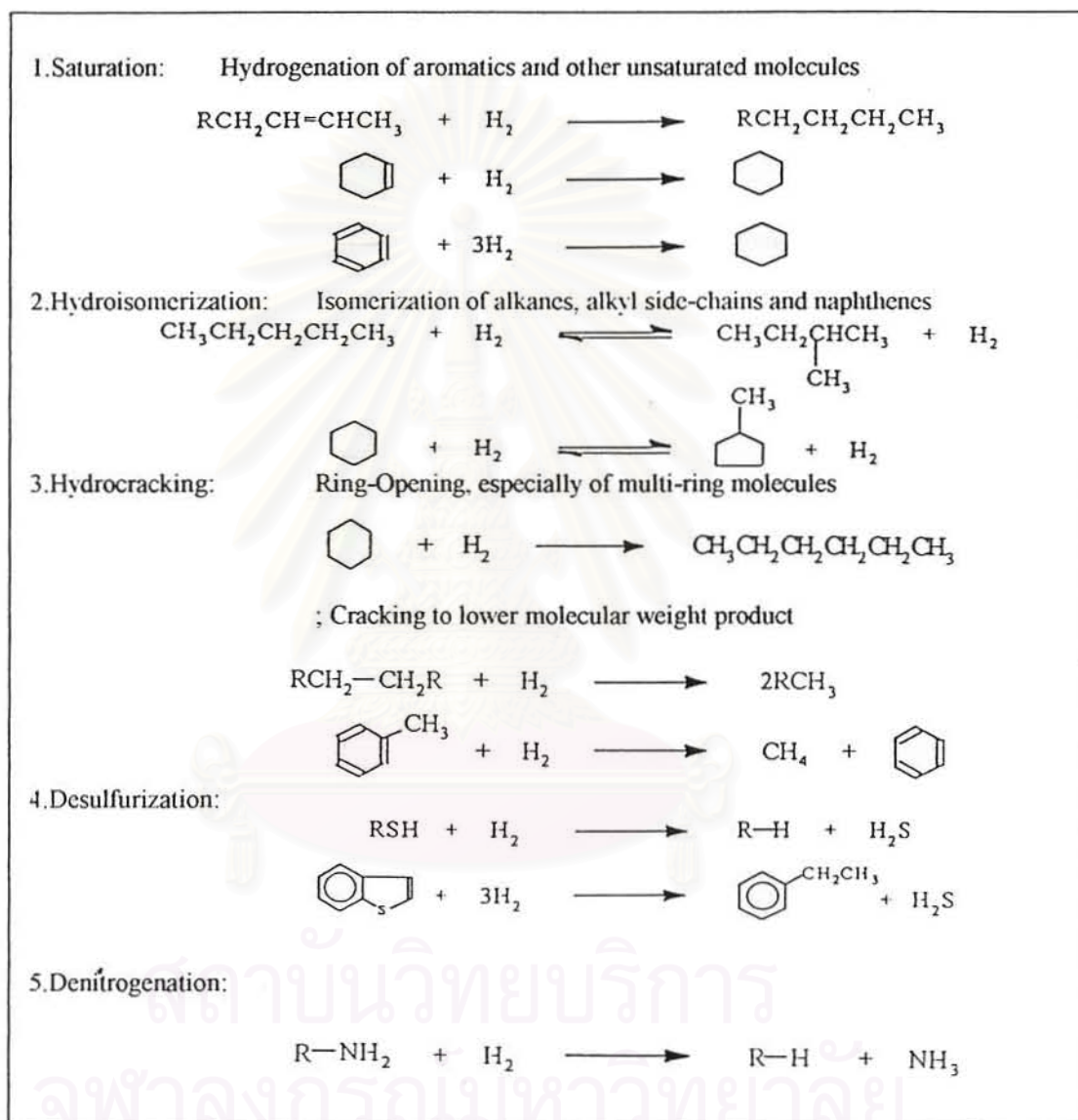
Figure 2.5 Typical hydrotreating reactions

The Preferred Reactions [9]

The preferred lubricating oil molecular structures were isoparaffins, single ring aromatics with long aliphatic chains, and naphthene with single ring, preferable having five carbon atoms on which aliphatic long chains are branched. The desired reactions are generally as follow:

- hydrogenation of polycondensed aromatics into polycondensed naphthenes:

VI = −60	VI = 20
Freezing point > +50 ^{0}C	Freezing point > +20 ^{0}C
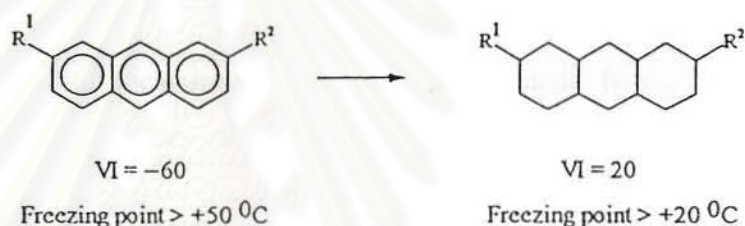
- Partial hydrogenation of polycondensed naphthenes

VI = 20	VI = 110−140
Freezing point > +20 ^{0}C	Freezing point < 0 ^{0}C
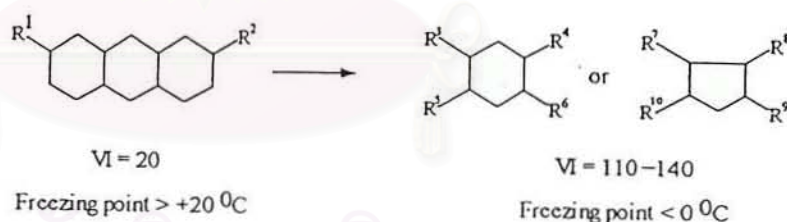
- hydroisomerization of normal or slightly branched paraffins into highly branched isoparaffins.

VI = 25	VI = 119
Freezing point = 19 ^{0}C	Freezing point = −40 ^{0}C
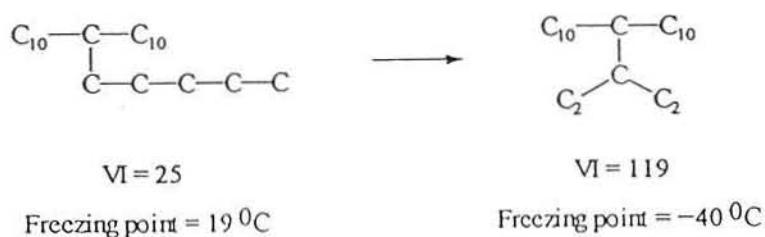
In general, the reactions to avoid are cracking reactions such as paraffin and isoparaffin hydrocracking and acid hydrodealkylation of alkylaromatics and alkylnaphthenes. These reactions lead to lower yields of lubricating base oils, lower viscosity and higher consumption of hydrogen.

The desired reaction indicate that the catalyst should simultaneously activate:

a) hydrogenation of aromatics

b) hydrodecyclization of naphthenes plus hydroisomerization of paraffins and naphthenes.

A combination of reactions require a bifunctional mechanism (Figure 2.5) consisting of a hydrogenating, dehydrogenating function and acidic function.
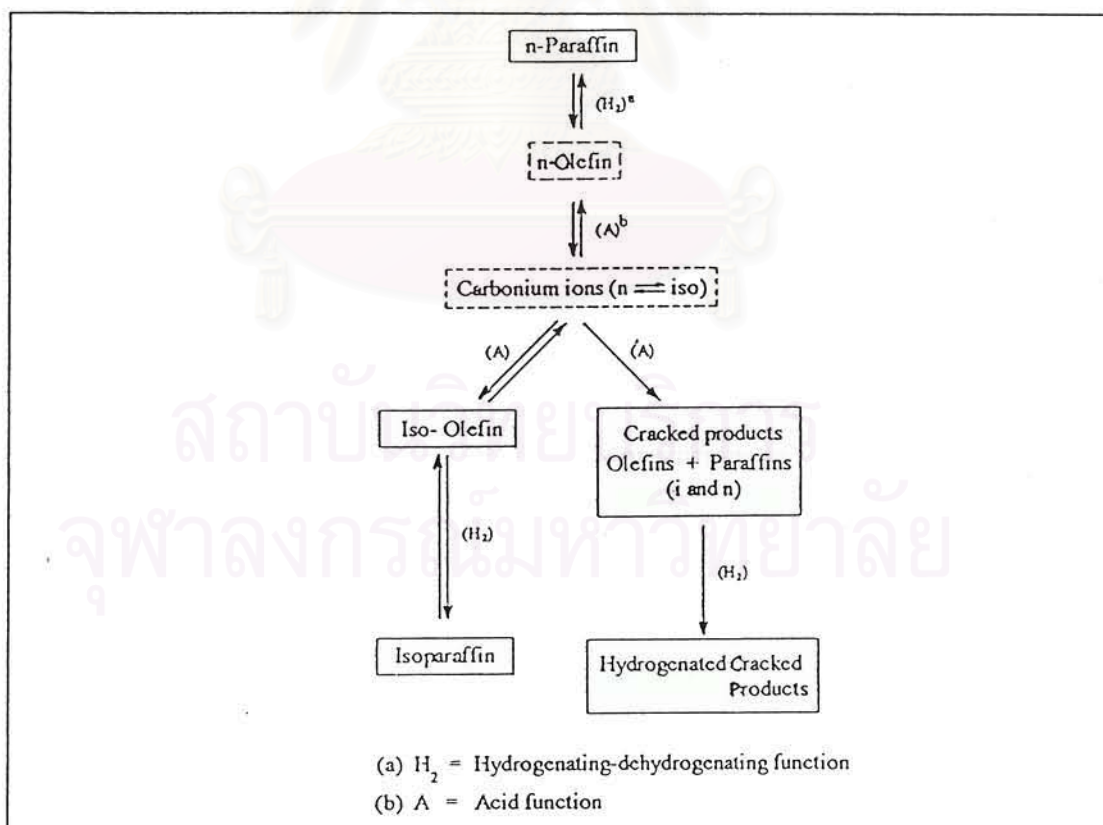
Figure 2.6 Reaction mechanism for bifunctional catalysts

Hydrotreating Catalysts [20-27]

Catalysts developed for hydrotreating, especially hydrotreating catalysts which can be suitable applied for production of lubricating oil comprise at least one more metal, metal oxide or metal sulfide or group VIB and VIII on a carrier support which comprises one or more oxide of elements of groups III, III and IV.

Generally, the metals employed will be chromium (Cr), molybdenum (Mo) or tungsten (W) metals of Group VI and iron (Fe), cobalt (Co) or nickel (Ni) metals of Group VIII. Mo is generally regarded as the active desulfurization component, with Co or Ni acting as a promoter which increases catalytic activity. CoMo catalysts are by far the most popular choice for desulfurization, particularly for straight–run petroleum fractions. NiMo is often chosen instead of CoMo when higher activity for polyaromatics saturation or nitrogen removal is required or when more refractory sulfur compounds such as those in cracked stocks must be desulfurized. NiW is usually chosen only when very high activity for aromatics saturation is required along with activity for sulfur and nitrogen removal. The metallic component can be employed either as the metals or as the oxides or sulfides of such metal.

These catalysts are in most general used today because they have proven to be highly selective, easy to regenerate, and resistant to poisons.

Metallic Component

The critical factor for catalytic activity is that transition metals have valency (i.e. outer) electrons in their atoms which are d-orbitals. These electrons are available for sharing into chemisorption bonds. The general predictions for chemisorption on transition metals are summarized as follows:

(a) the strength of the M-H bond decreases with increase in atomic number of the metal (M) along a particular transition series in the periodic table.

(b) the number of M-H bonds per unit area of metal surface at maximum surface coverage increases with increasing atomic number.

Alumina Support

The term alumina is used to describe various hydrated and anhydrous aluminium oxides. Most commercially available aluminas are prepared from the mineral bauxite (a mixture of hydrated aluminas and several non-alumina impurities) by the Bayer process, and are available at >99% purity. Thermally stable high-surface-area forms of alumina can be prepared, with acidic or basic surfaces. These may be used as acid or base catalysts or supports for other catalytic materials (e.g. metals, oxides, sulphides, etc.)

Alumina (Al_2O_3), the acidic component in dual function catalyst, exists in several distinct forms: the gamma form or the alpha form, depending on the method of preparation and subsequent treatment. Surface acidity can be increased by impregnation with promoters (e.g. Cl^- and F^-). Activated aluminas are amphoteric,

containing either acidic or basic sites of varying strength. As shown in Figure 2.7, if γ-alumina is heated above 800K, the residual water is driven off to generate a catalytically inactive form known as α-alumina. Activated aluminas are often used as supports, where they provide a large surface area on which catalysts (metal) can be highly despersed.
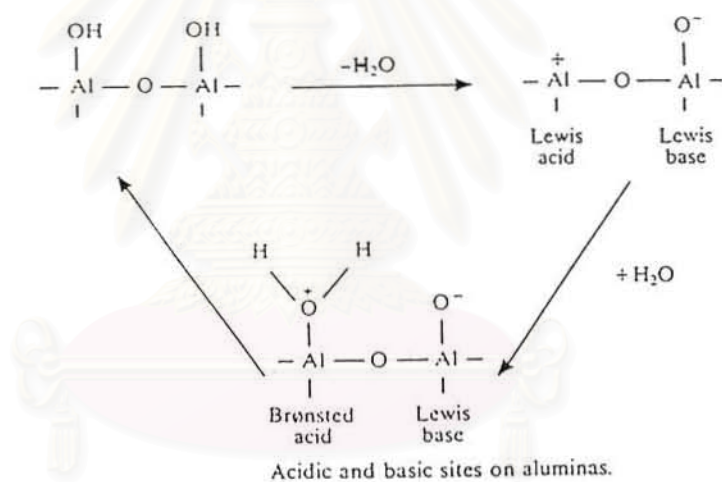
Acidic and basic sites on aluminas.

Figure2.7   Acidic and basic sites on aluminas

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Used lubricating oil was obtained from automotive service stations.

3.1.2 Industrial hydrogen gas was obtained from TIG Trading Ltd.

3.1.3 Nickel Chloride ($NiCl_2.6H_2O$) was obtained from Siam Science Co., Ltd.

3.1.4 Sodium Tungstate ($Na_2WO_4.2H_2O$) was obtained from BDH chemicals.

3.1.5 Ammonium Molybdate $(NH_4)_6 Mo_7O_{24}.4H_2O$ was obtained from J.T. Baker Inc.

3.1.6 Ammonium Fluoride (NH_4F) was obtained from Merck.

3.1.7 Haxane (C_6H_{14}) was obtained from Merck.

3.1.8 Raney Nickel catalyst was available from Merck.

3.1.9 Heterogeneous commercial catalyst was obtained from United Catalyst Inc., USA.

3.1.10 Alumina Support (CS331-3 1/16" Extrudated) was obtained from United Catalyst Inc., USA.

3.2 Apparatus and Instruments

3.2.1 Micro Pore Sizer for measuring pore volume of alumina support.

The Micromeritics model ASAP 2000 was used.

3.2.2 Calcinator

The apparatus model GSM from Carbolite Furnaces was used.

3.2.3 High Pressure Reactor

All experiments for the hydrotreating study of used lubricating oils were carried out in the hydrogenation apparatus which consisted of four parts at follows:

3.2.3.1 Reactor (Figure 3.1)

The hydrogenation floor stand reactor was a high pressure batch stirred autoclave model 4551 from Parr Instrument Company with a 3750 cubic centimeter stainless steel 316 cylindrical bomb, split ring closures and a bomb heater. The reactor could work in a pressure range from 0 - 2000 psig and a temperature range of 0– 400 °C.

4551
1 gal. Reactor with 4842 Controller
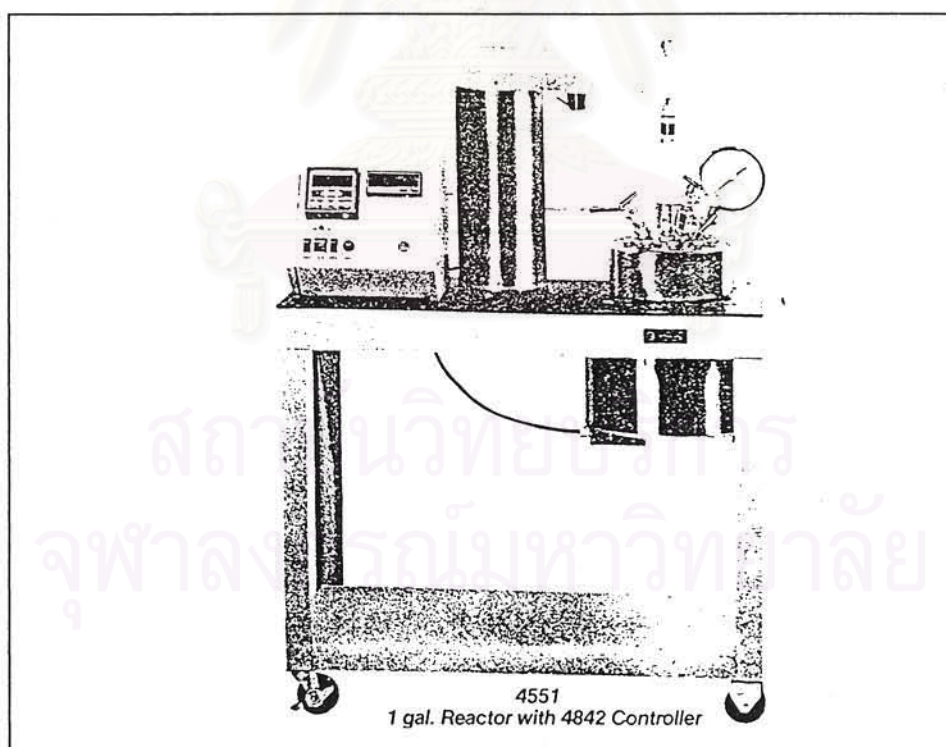
Figure 3.1 Floor stand reactor

3.2.3.2 Reactor Fitting (Figure 3.2)

The stirred unit of reactor was equipped with convenient valves and fittings for handling the various functions. The parts were indicated with the following number.

1. a pressure gauge

2. a safety rupture disc

3. a gas inlet valve

4. a liquid sampling valve

5. a gas release valve

6. a stirrer magnetic drive system

7. a water cooling channel

8. a thermocouple

9. a dip tube

10. a stirring shaft with 6-blade turbine type impeller
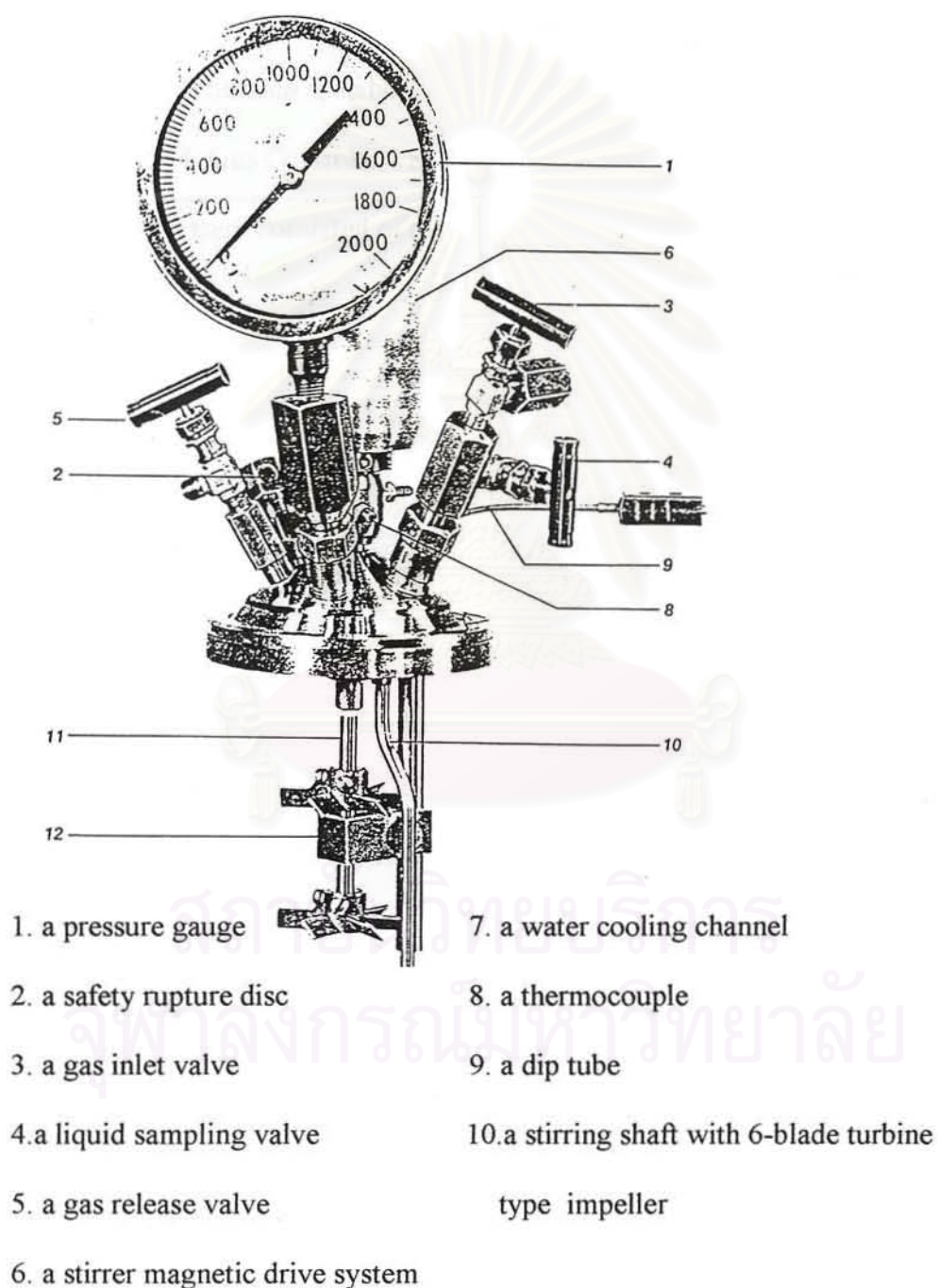
Figure 3.2 Reactor Fitting

3.2.3.3 Automatic Temperature Controller

The controller used was model 4842 PID controller from the Parr Instrument Company. It was operated in conjunction with a dual thermocouple. There were various enhancement modules to assist in monitoring and controlling the temperature, pressure and stirring speed. Stirring speed could be adjusted in the range of 0-1000 rpm.

3.2.3.4 Gas Controllers System

The system consisted of a hydrogen tank with a pressure regulator (0-2000 psig).

3.2.4 Viscometer

The apparatus Cannon Automatic Viscometer model CAV-3 was used.

3.2.5 Pour Point Tester

The Automatic Cloud and Pour Point Tester model CPP97 was used.

3.2.6 Sulfer Analyzer

The X – ray fluorescence was used.

3.2.7 Colorimeter

The Fisher ASTM D-1500 was used.

3.2.8 Flash Point Tester

The Automatic Flash Point Tester (COC) was used.

3.2.9 Thermogravimetric Analyzer

The Thermogravimetric Analyzer model NETZSCH STA 409 C was used.

3.2.10 ^{13}C – NMR Spectrometer

The NMR Spectrometer model AC- F 200 from Bruker was used.

3.3 Procedure

3.3.1 Measuring Pore Volume of Support

The pore volume and surface area of alumina support were measured by the Micro Pore Sizer according to Brunauer Emmett Teller (BET) method.

3.3.2 Preparation of Catalysts

3.3.2.1 Hydrotreating catalyst : containing 5% Ni/10%W/1% F on alumina support

Step 1: Nickel (II) chloride dihydrate (24.3 g) was dissolved in water (70ml). The solution was poured onto alumina (120 g) which was previously dried at 120 °C for 16 hours. The mixture was left at room temperature for 2 hours, dried at 120 °C for 16 hours, then calcined at 520 °C for 2 hours to obtain the calcined solid.

Step 2: The calcined solid was reimpregnated with a solution of sodium tungstate dihydrate (21.52 g) in water (70 ml), left at room temperature for 2 hours, dried at 120 °C for 16 hours and then calcined at 520 °C for 2 hours.

Step 3: The calcined solid was reimpregnated with a solution of ammonium fluoride(2.34 g) in water (70 ml), left at room temperature for 2 hours, dried at 120 °C for 16 hours and then calcined under the following conditions : held at 150 °C for 1 hour, the temperature was raised by 50 °C every 15 minutes to 400 °C, then held at 400 °C for 1 hour to obtain the $NiO/WO_3/F$ on alumina catalyst.

3.3.2.2 Hydrotreating catalyst: containing 5%Ni/10%Mo/1%F on alumina support

The procedure of 3.3.2.2 were repeated except in step 2, sodium molybdate dihydrate (30.26 g) was used in place of sodium tungstate dihydrate.

3.3.2.3 Activation of catalysts

The catalysts were activated before use by reduction with 400 psig hydrogen pressure in a stainless steel reactor. Then the high pressure reactor was heated at 400 °C for 6 hours to obtain the activated catalyst.

3.3.2.4 Regeneration of catalysts

The used catalyst was washed four times with hexane in a ratio of catalyst to hexane 1:2 by volume. The washed catalyst was dried at 120 °C for 16 hours, calcined at 500 °C for 4 hours and then activated following the procedure 3.3.2.3 to obtain the reusable catalyst.

3.3.2.5 Characterization of catalysts

The catalysts were characterized by X-fluorescence.

3.3.3 Hydrotreating Process

3.3.3.1 The Effect of Catalyst Type on Hydrotreating Process

The used lubricating oil (300 g) was charged into the reactor and the required quantity of catalysts $NiO/WO_3/F$ on alumina (120 g) were added. The reactor was closed. After a thermocouple was inserted into a sturdy thermowell, the stirring motor was connected, and water was passed into the cooling channel. Before running the process, all

oxygen gas in the reactor was removed by purging the system with some partial pressure of hydrogen gas. Then, the reactor was charged with hydrogen gas until the desired pressure was obtained. The reactor was operated at 350 °C, under 500 psig hydrogen pressure, 100 rpm stirring speed, and 30% catalyst concentration for 4 hours. After the reaction took place, heating was stopped and the reaction mixture was stirred until the mixture cooled to room temperature. The pressure was released and the catalyst was separated by filtration to give hydrotreated oil.

The experiment was repeated according to the procedure described above for the commercial United catalyst, commercial Raney nickel catalyst, $NiO/WO_3/F$ and $NiO/MoO_3/F$ on alumina. For each experiment the reaction mixture was worked up in the same manner as above to give the desired products. The physical and chemical properties of the hydrotreated oils were measured and listed in section 3.3.4.

3.3.3.2 The Effect of Temperature on Hydrotreating Process

The same procedure was followed as described in experiment 3.3.3.1 except that the reaction was operated at various temperatures (250, 300, 350 and 380 °C) using the $NiO/WO_3/F$ on alumina catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

3.3.3.3 The Effect of Hydrogen Pressure on Hydrotreating Process

The procedure was conducted similar to that in experiment 3.3.3.1 except that the reaction was operated at various hydrogen pressures (400, 500 and 600 psig) at the optimum temperature of 350 °C obtained from 3.3.3.2. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

3.3.3.4 The Effect of Reaction Time on Hydrotreating Process

The same procedure was followed as described in experiment 3.3.3.1 except that that the reaction was operated at various reaction times (4, 3, 2.5 and 2 hours) with optimum temperature of 350 °C, hydrogen pressure of 500 psig. by using Ni(5%)/W (10%)/F(1%) catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

3.3.3.5 The Effect of Catalyst Concentration on Hydrotreating Process

The same procedure was followed as described in experiment 3.3.3.1 except that the reaction was operated at various catalyst concentrations (40, 35, 30 and 25% by weight of oil) for the optimum reaction time of 2.50 hours obtained from 3.3.3.4. After the reaction was stopped, the mixture was worked up in the same manner described in 3.3.3.1 to give desirable products.

3.3.3.6 The Effect of Reaction Time on Hydrotreating Process

The same procedure was followed as described in experiment 3.3.3.1 except that the reaction was operated at 350 °C, 500 psig hydrogen pressure and various times from 4, 3, 2.5 and 2 hours using Ni(5%)/Mo(10%)/F(1%) on alumina catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

3.3.3.7 The Effect of Catalyst Concentration on Hydrotreating Process

The same procedure was followed as described in experiment 3.3.3.1 except that the reaction was operated at various catalyst concentrations from 40, 35, 30 and 20% by weight of oil at the optimum reaction time (2.50 hours) obtained from 3.3.3.6. After the reaction was stopped, the mixture was worked up in the same manner described in 3.3.3.1 to give desired products.

3.3.4   Determination of Physical and Chemical Properties of Hydrotreated Oils

The physical and chemical properties of hydrotreated oils were determined using the following standard procedure as follow:

Physical properties:

1. Kinematic Viscosity   by   ASTM D-445

    40 °C

    100 °C

2. Viscosity Index(VI)   by   ASTM D-2270

3. Colour,visual   by   ASTM D-1500

4. Pour Point   by   ASTM D-97

5. Flash Point   by   ASTM D-92

6. Sulfur Content   by   ASTM D-129

7. Ash Content   by   ASTM D-482

8. Total Acid Number   by   ASTM D-974

9. Metal Content   by   ASTM D-5185

10. Water Content   by   ASTM D-95

Chemical properties:

1. The percentages of oxidation components and oxidation point were determined by TGA.

2. The compositions of oil products were determined by ^{13}C-NMR and FTIR method.

CHAPTER IV

RESULTS AND DISCUSSION

This research aimed to upgrade the quality of used automotive lubricating oil in order to produce improved lubricating oils or base lube oil by the means of one–step catalytic hydrogenation. The experiment was performed under elevated temperature and pressure in the presence of hydrotreating catalyst. The hydrotreating catalyst was made up of a combination of hydrogenation metals from Group VI metal and Group VIII metal and a halogen on alumina support.

The goal of this research was to investigate catalysts that were more effective to improve properties of the used lubricating oil by using hydrotreating catalysts such as nickel, tungsten, and molybdenum in the production of lube base oil. The suitable hydrotreating process was varied to find optimum condition: temperature, pressure, reaction time, and concentration of catalyst in order to make it possible to be used in the industrial way.

4.1 Hydrotreating process

The aim of this study was to determine the suitable condition and effective catalyst for one-step catalytic hydrotreatment process of used automotive lubricating oils obtained from several service stations. The original used oil was characterized as shown in Table 4.1.

Table4.1 Properties of the used automotive lubricating oil

Properties	Test Method	Results
Color	ASTM D-1500	>8
Viscosity	ASTM D-445	
40 °C , cSt		114.80
100 °C , cSt		16.610
Viscosity Index	ASTM D-2270	123
Flash Point (°C)	ASTM D-92	216
Pour Point (°C)	ASTM D-97	-32
Total acid number (mgKOH/g)	ASTM D-664	2.30
Ash Content (%wt)	ASTM D-874	1.024
Sulfur Content (%wt)	ASTM D-4294	1.016
Water Content (%Vol)	ASTM D-95	0.1
Oxidation point(°C)		450
Oxidative compound (%wt)		10.10

Table 4.1 demonstrates that the viscosity and flash point of the used oil decrease while the color, acidity and sulfur content increase. An oil oxidation promotes the formation of sludge and gummy residue. The acidity is increased by acidic materials which are produced in a combustion process. The color of the oil becomes darker by contamination with soot carbon and oxidation products. Fuel usually contains small amounts of sulfur compounds. An increasing sulfur content in the used oil is expected to come from sulfur compounds in fuel. When fuel burns in combustion process by product gas including hydrogen sulfide is produced. An increase in ash content indicates the non-combustible constituents such as dust, dirt and metallic materials contained in the oil.

Catalytic hydrotreatment process is a modern method for stabilization of petroleum products or removal of sulfur, nitrogen, oxygen, halides and metallic compounds from products. In order to upgrade the quality of the used oil, therefore the hydrotreatment process was incorporated in this study for the removal of these contaminants.

4.1.1 Effect of Catalyst Type on Hydrotreating Process

The effect of catalyst types on catalytic hydrotreatment of used lubricating oil was studied using four types of catalysts. The first two types of catalysts were commercial United catalyst and commercial Raney nickel. The second two types of catalysts were Nickel oxide/Tungsten oxide/Fluoride and Nickel oxide/Molybdenum oxide/Fluoride. The hydrotreating catalysts were prepared by impregnation of alumina support type CS331-3 having a pore volume of 0.64 ml/g with solution of nickel and tungsten salts and solution of nickel and molybdenum salts. The impregnated catalysts were mixed with an aqueous solution of ammonium fluoride to improve the hydrogenation activity and the catalysts were dried and calcined to obtain 5%Ni/10%W/1%F and 5%Ni/10%Mo/1%F.

The four types of catalysts were employed to treat the used automotive lubricating oil. The operating condition produced at temperature of 350 °C, hydrogen pressure of 500 psig, reaction time of 4 hours, catalyst concentration of 30% by weight of oil and agitation speed 100 rpm in a stirred autoclave reactor. The properties of hydrotreated oils are shown in Table 4.2.

Table 4.2 The physical and chemical properties of hydrotreated oil produced at various catalyst types.

Properties	Used oil	Catalyst types			
		United catalyst	Raney nickel	NiO/WO$_3$ on Al$_2$O$_3$	NiO/MoO$_3$ on Al$_2$O$_3$
Color	>8	3	6	2	3
Viscosity					
40 °C, cSt	144.80	26.46	50.79	25.38	34.97
100 °C, cSt	16.610	5.24	7.989	5.201	6.271
Viscosity index	123	133	127	140	132
Flash point (°C)	216	144	176	144	158
Pour point(°C)	-32	-8	-10	-8	-8
Sulfur content (%wt)	1.016	0.249	0.564	0.091	0.103
TAN (mg KOH/g)	2.30	0.08	0.55	0.04	0.04
Yield (%)		77.1	81.6	75.7	76.3
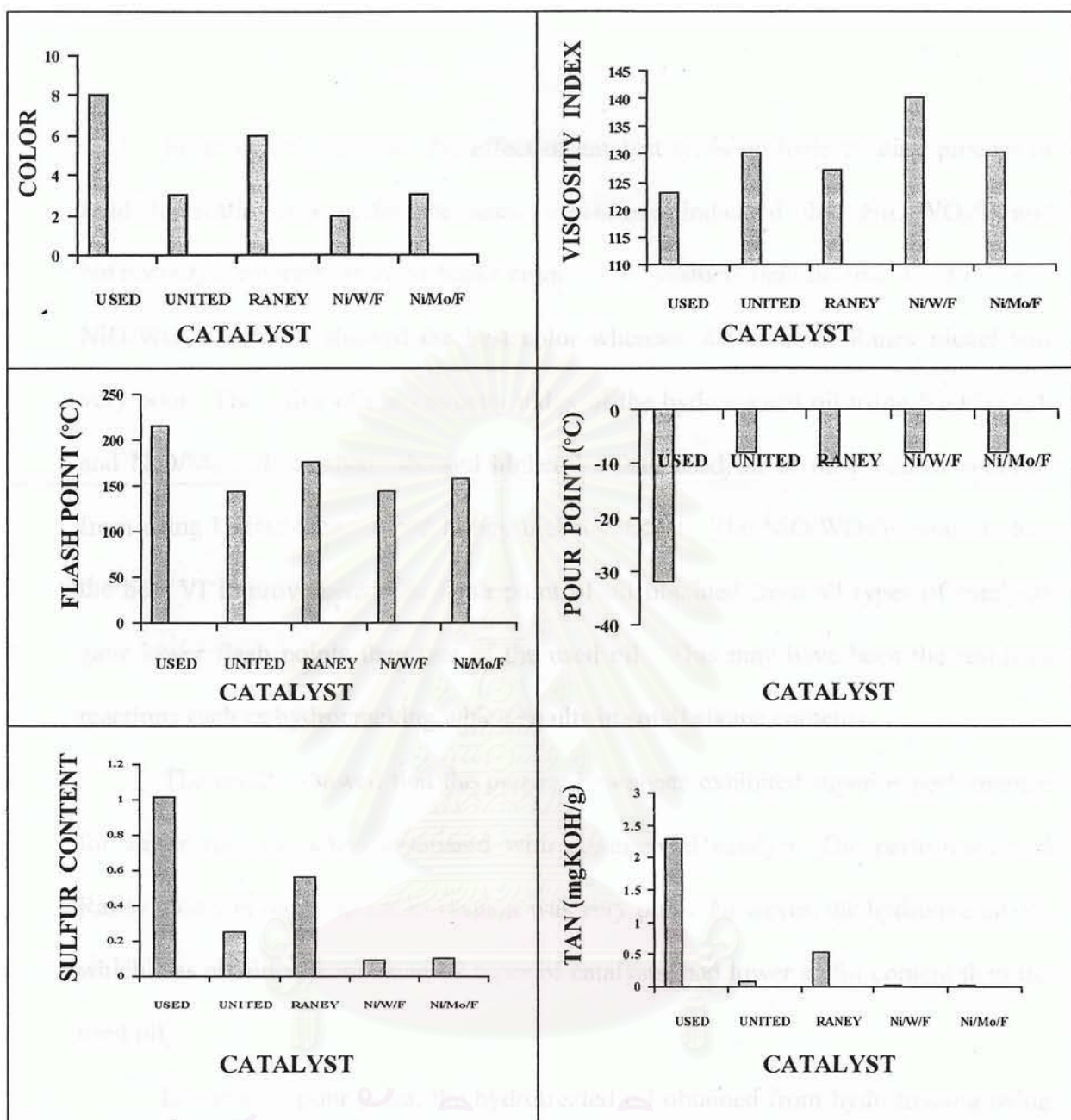
FIGURE 4.1 Effect of catalyst types on hydrotreated oil

From this experiment, the effect of catalyst types on hydrotreating process of used lubricating oil under the same conditions indicated that $NiO/WO_3/F$ and $NiO/MoO_3/F$ catalysts showed better color of oil products than original used oil. The $NiO/WO_3/F$ catalyst showed the best color whereas, the color of Raney nickel was very poor. The value of the viscosity index of the hydrotreated oil using $NiO/WO_3/F$ and $NiO/MoO_3/F$ catalysts showed higher VI than used oil or oil products obtained from using United catalyst and Raney nickel catalyst. The $NiO/WO_3/F$ catalyst gave the best VI improvement. The flash point of oil obtained from all types of catalysts gave lower flash points than that of the used oil. This may have been the result of reactions such as hydrocracking which results in small alkane contents.

The results showed that the prepared catalysts exhibited superior performance for sulfur removal when compared with commercial catalyst. The performance of Raney nickel in reducing sulfur content was very poor. However, the hydrotreated oil, which was obtained from using all types of catalysts, had lower sulfur content than the used oil.

In terms of pour point, the hydrotreated oil obtained from hydrotreating using these catalysts gave lower pour points than the used oil. This is a result from the deterioration of pour point depressant, which still remained in used oil when the reaction was operated at higher temperatures.

The comparison of catalytic activity on acidity of hydrotreated oil showed that the NiO/WO$_3$/F and NiO/MoO$_3$/F catalysts gave the best activity to reduce acidity of oil product.

From this study, it can be seen that NiO/WO$_3$/F catalyst gave better properties of hydrotreated oil than the used oil, especially the VI, color, acidity and sulfur removal. The NiO/MoO$_3$/F catalyst gave oil with better properties in terms of color, flash point and sulfur content. In comparison with commercial catalysts, the NiO/WO$_3$/F and NiO/MoO$_3$/F gave better properties of hydrotreated oil in terms of color, VI improvement, sulfur content and acidity. On the other hand, Raney nickel was poor in color, acidity and sulfur removal.

In the next experiment, NiO/WO$_3$/F and NiO/MoO$_3$/F would be studied in order to find the optimum condition by varying operation parameters such as reaction temperature, hydrogen pressure, reaction time, and catalyst concentration.

4.1.2. Effect of Temperature on Hydrotreating Process

The reaction was performed at 250, 300, 350 and 380 °C. The operating conditions were carried out at 500 psig hydrogen pressure, 4 hours reaction time, 30% by weight catalyst concentration using $NiO/WO_3/F/Al_2O_3$ catalyst. The properties of hydrotreated oils are shown in Table 4.3.

Table 4.3 Physical properties of hydrotreated oil obtained from various reaction temperatures.

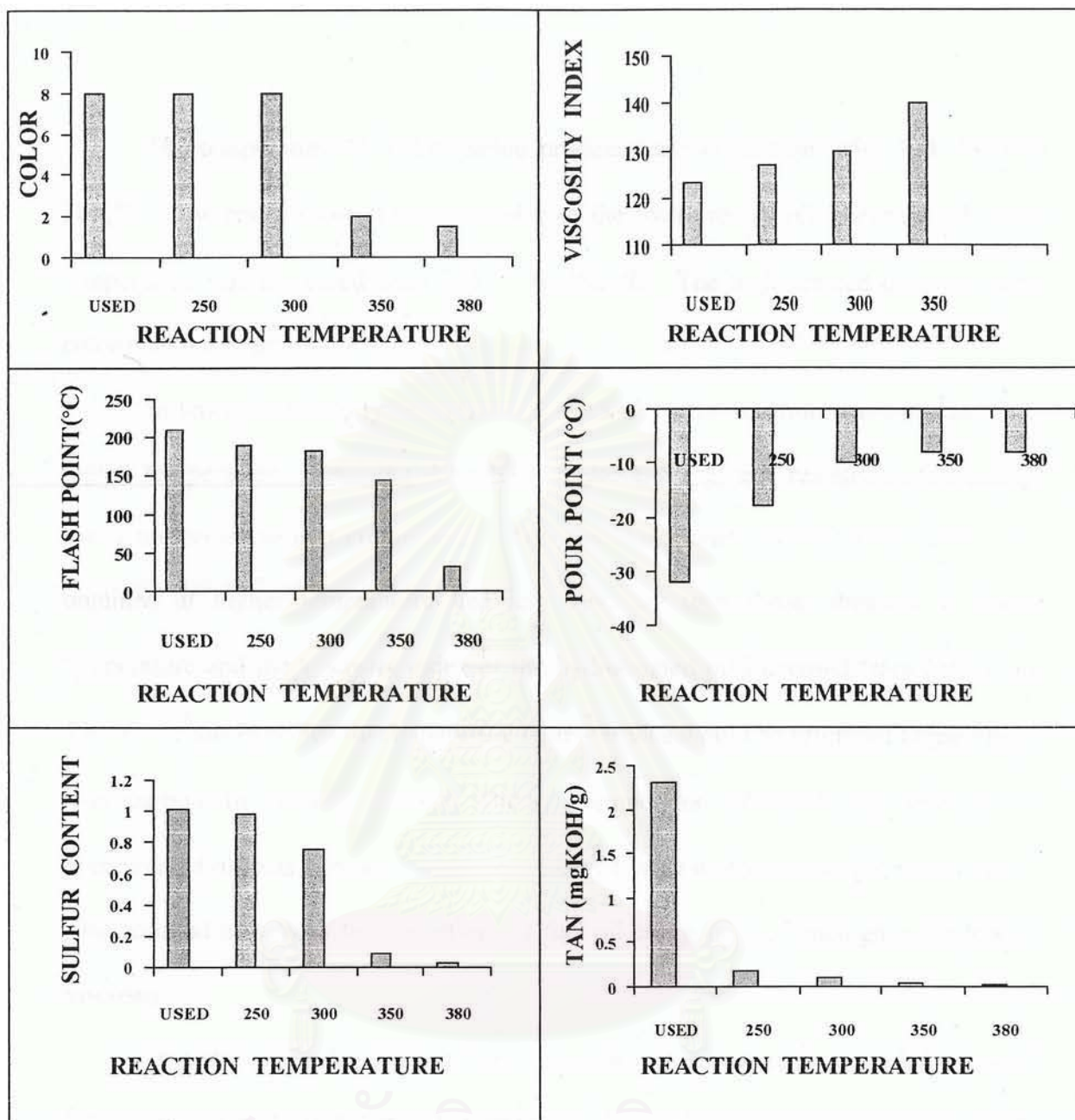| Properties	Used oil	Reaction Tempertures (°C)			
		250	300	350	380
Color	8	8	8	2	1.5
Viscosity					
40 °C, cSt	114.80	76.23	45.89	25.38	1.460
100 °C, cSt	16.610	10.68	7.544	5.201	-
Viscosity index	123	127	130	140	-
Flash point (°C)	216	190	182	144	32
Pour point(°C)	-32	-18	-10	-8	-8
Sulfur content (%wt)	1.016	0.985	0.749	0.091	0.027
TAN (mgKOH/g)	2.30	0.17	0.09	0.04	0.02
Yield (%)		83.6	80.2	75.7	70.8

FIGURE 4.2 Effect of reaction temperature on hydrotreated oil

The temperature of hydrotreating process was varied from 250, 300, 350 and 380 °C. The result showed that the color of the hydrotreated oil improved when the temperature was increased from 350 °C to 380 °C. The hydrotreated oil gave better color than the used oil

In terms of viscosity and viscosity index (VI), the reaction was operated at a higher temperature, increasing the rate of hydrocracking, and resulted in increasing lower molecular weight components. This result demonstrated that hydrotreated oil obtained at higher temperature had less viscosity than those obtained at lower temperature and the viscosity index of the hydrotreated oil increased from 250 °C to 350 °C. It was expected that naphthenic hydrocarbons would be reformed to paraffinic hydrocarbons by cracking process. But at a temperature of 380 °C, the viscosity of hydrotreated oil was very low, due to cracking of large molecular weight components. This resulted in increasing proportions of fuel oil components, which gave the lowest viscosity.

In terms of flash point, increasing reaction temperature increased the rate of hydrocracking and hydrogenation resulting in increasingly lower molecular weight hydrocarbon compounds. The hydrotreated oil obtained from higher temperatures had lower flash points than lower temperatures. From the experiment it showed that the pour point was increased with increasing temperature. This resulted from the deterioration of pore point depressant when the reaction was operated at high temperature.

Figure 4.2 showed that the sulfur content and acidity of the hydrotreated oil decreased with increasing operating temperature. It indicated that the hydrodesulfurization activity increased with increasing temperature. This was due to the acid compounds in the used oil was removed at a higher temperature. An increase in reaction temperature resulted in a slight decrease in yield from 83.6, 80.2, 75.7, and 70.8%, respectively.

From the results it can be concluded that the optimum temperature was 350 °C and it gave desirable properties of oil in terms of color, viscosity, sulfur content, VI, flash point and acidity.

4.1.3. Effect of Hydrogen Pressure on Hydrotreating Process

The reaction was performed at 400, 500 and 600 psig using $NiO/WO_3/F/Al_2O_3$ catalyst. The operating conditions were carried out at 350 °C, 4 hours reaction time, and 30% by weight catalyst concentration. The properties of oils are shown in Table 4.4.

Table 4.4 Physical properties of hydrotreated oil obtained from various hydrogen pressures using NiO/WO$_3$/F/Al$_2$O$_3$ catalyst.

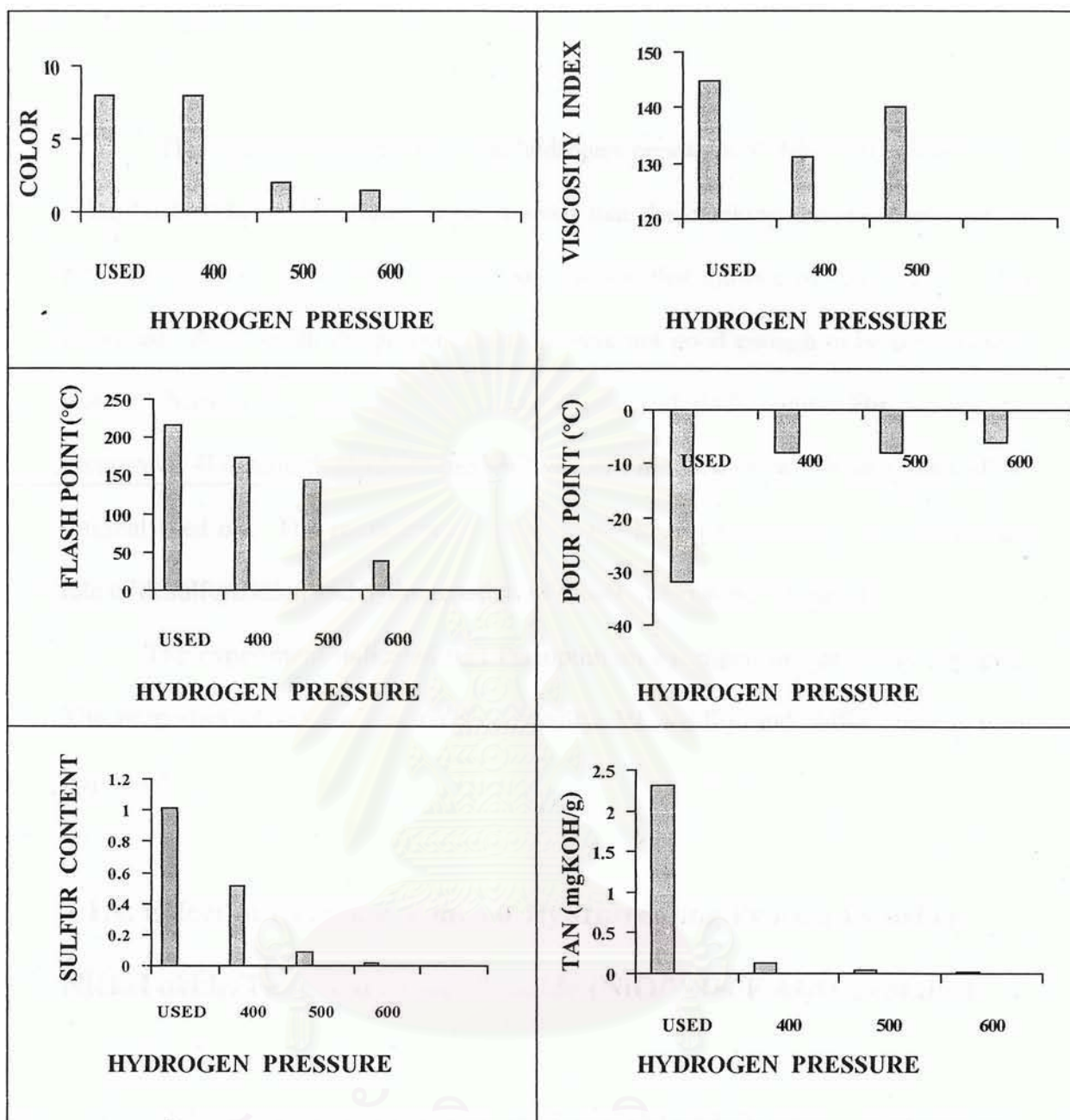| Properties	Used oil	Hydrogen Pressures (psig)		
		400	500	600
Color	8	8	2	1.5
Viscosity				
40 °C, cSt	144.8	34.73	25.38	1.571
100 °C, cSt	16.610	6.256	5.201	-
Viscosity index	123	131	140	-
Flash point (°C)	216	174	144	38
Pour point(°C)	-32	-8	-8	-6
Sulfur content (%wt)	1.016	0.520	0.103	0.024
TAN (mgKOH/g)	2.30	0.12	0.04	0.02
Yield (%)		77.9	75.7	67.9

FIGURE 4.3 Effect of hydrogen pressure on hydrotreated oil

The reaction was performed at hydrogen pressures of 400, 500 and 600 psig using $NiO/WO_3/F$. The flash points showed that the cracking process depended on hydrogen pressure. The result at 600 psig showed that the rate of cracking was also increased. As a result, the properties of oil were not good enough to be used as lube base oil because the oil gave low viscosity, VI and flash point. For a hydrogen pressure of 400 psig, the hydrotreated oil was still in black color similar to that of the original used oil. The result from increasing the hydrogen pressure showed that the rate of desulfurization and hydrogenation of unsaturation were increased.

The experiment indicated that the optimum hydrogen pressure was 500 psig. The properties of oil such as color, viscosity, VI, acidity and sulfur content were improved.

4.1.4. Effect of Reaction Time on Hydrotreating Process by using Nickel oxide/Tungsten oxide/Fluoride ($NiO/WO_3/F/Al_2O_3$) catalyst

The reaction was performed at 4, 3, 2.50 and 2 hours. The operating conditions were carried out at optimum temperature of 350 °C, optimum hydrogen pressure of 500 psig, catalyst concentration of 40% by weight. The properties of oils are shown in Table 4.5.

Table 4.5 Physical and chemical properties of hydrotreated oil obtained from various reaction times using NiO/WO$_3$/F.

| Properties	Base oil 150 SN	Reaction times (hour)			
		4.0	3.0	2.50	2.0
Color	max 1.5	1.5	2	2	8
Viscosity					
40 ° C, cSt	Report	17.86	21.01	23.20	n.a
100 °C, cSt	4.8-5.4	4.154	4.575	4.866	n.a
Viscosity index	min 95	140	137	136	n.a
Flash point (° C)	min 200	144	154	164	n.a
Pour point(° C)	max -9	-8	-8	-8	n.a
Sulfur content (%wt)	0.2-0.8	0.091	0.194	0.290	n.a
TAN (mgKOH/g)	max 0.05	0.031	0.039	0.042	n.a.
Ash content (%wt)	max 0.01	0.0028	0.0032	0.0037	n.a
Yield (%)		74.12	76.56	78.43	low

n.a. = not analyzed
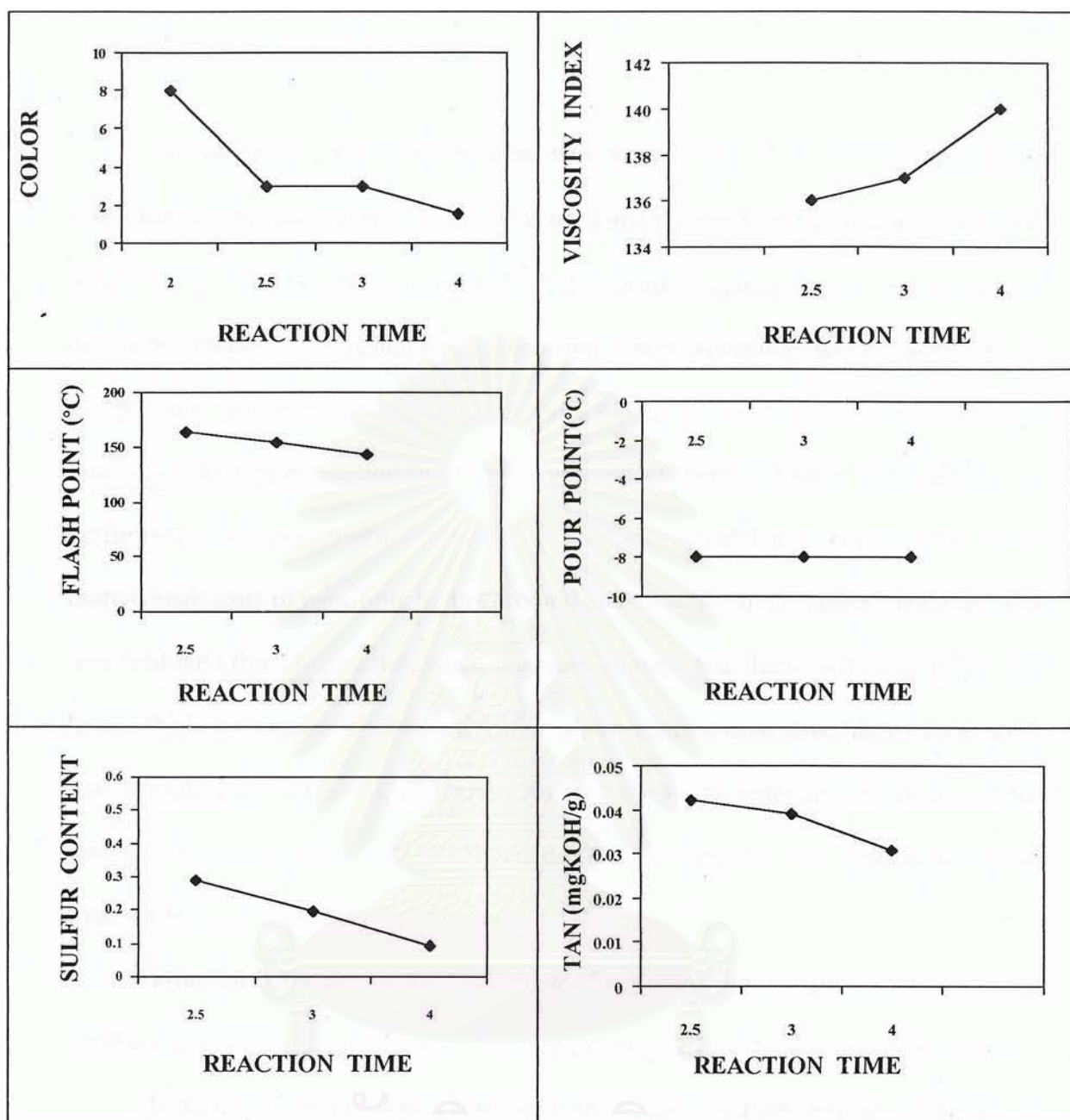
FIGURE 4.4 Effect of reaction time on hydrotreated oil using NiO/WO$_3$/F catalyst

In this study, the reaction time was varied from 4, 3, 2.5, and 2 hours, respectively. The $NiO/WO_3/F$ catalyst was used and the reaction was operated at 350°C and 500 psig. In terms of viscosity and VI, decreasing reaction time decreased the rate of hydrocracking. This resulted in decreasing lower molecular weight hydrocarbon components. Therefore, the hydrotreated oil operated at short reaction time had more viscosity than longer reaction time. The value of VI increased when the reaction was performed at a longer reaction time. It was expected that longer reaction time gave more constituents of paraffinic hydrocarbon than that of the hydrotreating reaction. The observed data from Figure 4.4, when the reaction time was decreased from 4, 3 to 2.5 hours, the hydrotreated oil obtained from a short reaction time gave higher flash point than operating at a long reaction time. An increase in the reaction time increased the rate of hydrocracking and hydrogenation. This resulted in increasing lower hydrocarbon components.

From this experiment, the decreasing of sulfur content occurred with increasing reaction time at 2.5, 3 and 4 hours. The sulfur content slightly increased after 4 hours.

In terms of acidity and ash content, the acidity of hydrotreated oil decreased with increasing reaction time. The result demonstrated that acidic compounds from oil oxidation was removed. The decreasing of ash content resulted in decreasing of the noncombustible constituents (usually metallic materials) in the oil. However, the sulfur content, acidity and ash content at 4, 3 and 2.50 hours reaction time were below the limit of base oil.

The results in Table 4.5 show that yield of hydrotreated oil was decreased from 78.43 %, 76.56 % to 74.12 % when the reaction was operated at longer time.

The goal of this study was to find the minimum reaction time that gave oil with desirable properties. These observations suggested that the optimum reaction time was 2.50 hours. At this reaction time, the hydrotreated oil had desirable properties in terms of color, VI, sulfur, ash content and acidity. Although the properties of oil (color, VI and sulfur content) were the best at a reaction time of 4 hours, it was not necessary to operate at a reaction time longer than 2.50 hours.

4.1.5. Effect of Catalyst Concentration on Hydrotreating Process by using Nickel oxide/Tungsten oxide/Fluoride (NiO/WO₃/F/Al₂O₃)

The reaction was performed at various catalyst concentrations of 40%, 35%, 30% and 25%. The operating conditions were carried out at 350 °C, 500 psig hydrogen pressure and 2.50 hours reaction time. The properties of hydrotreated oils are shown in Table 4.6.

Table 4.6 Physical and chemical properties of hydrotreated oil obtained from various catalyst concentrations using NiO/WO₃/F catalyst.

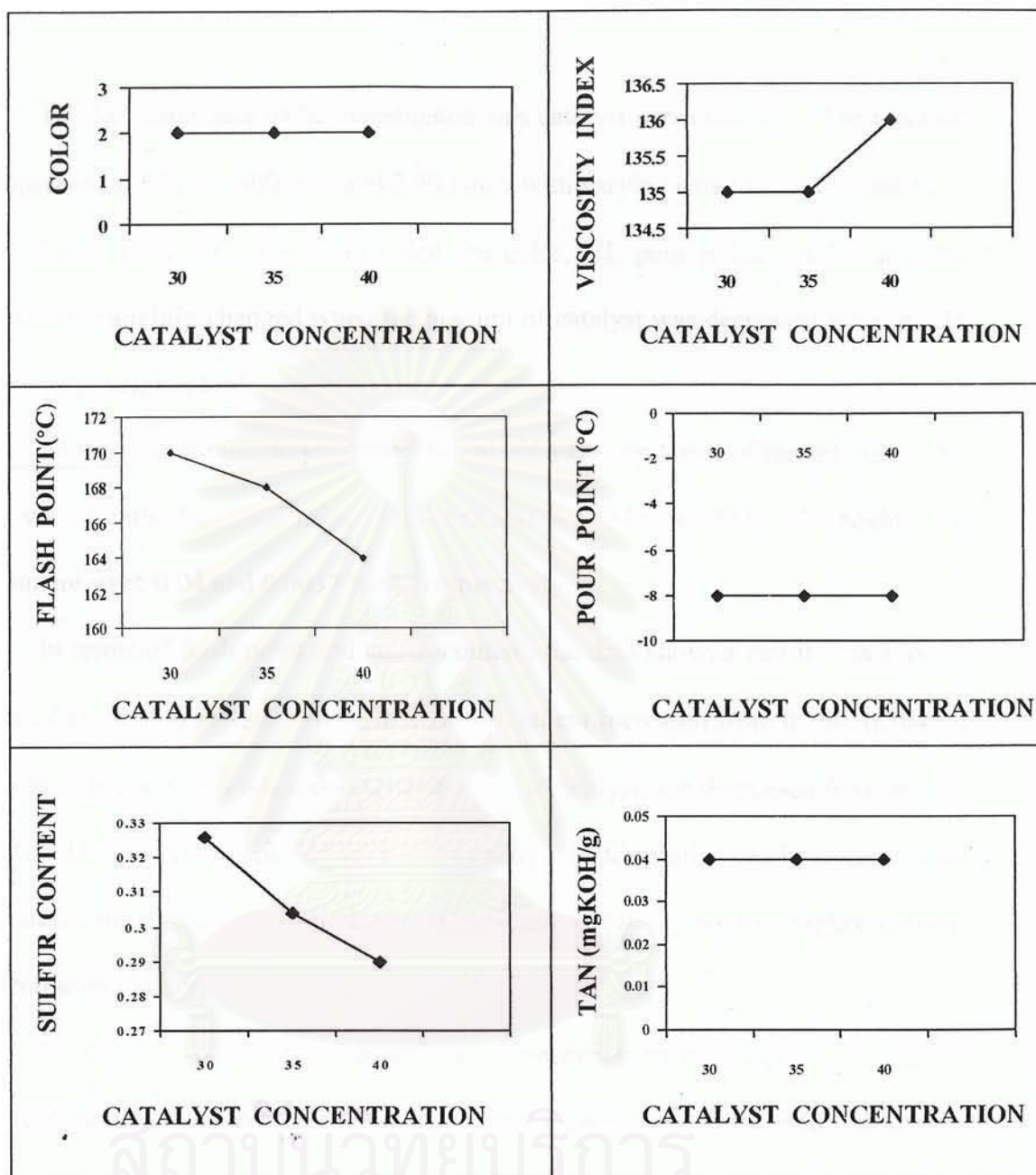| Properties	Catalyst concentrations (%)			
	40	35	30	25
Color	2	2	2	8
Viscosity				
40 ° C, cSt	23.20	24.84	27.72	n.a
100 ° C, cSt	4.866	5.056	5.429	n.a
Viscosity index	136	135	135	n.a
Flash point (°C)	164	168	170	n.a
Pour point(°C)	-8	-8	-8	n.a
Sulfur content (%wt)	0.290	0.304	0.326	n.a
TAN (mgKOH/g)	0.04	0.04	0.04	n.a.
Ash content (%wt)	0.0036	0.0037	0.0037	n.a.
Yield (%)	78.4	79.1	79.6	low

FIGURE 4.5 Effect of catalyst concentration on hydrotreated oil using NiO/WO$_3$/F catalyst

The last parameter to be investigated was catalyst concentration. The reaction was operated at 350 °C, 500 psig and 2.50 hours with varying catalyst concentrations

From Table 4.6, it is shown that the color, VI, pour point, acidity and ash content were slightly changed when the amount of catalyst was decreased from 40, 35 and 30% by weight of oil.

At the minimum catalyst concentration of 30%, the color of the oil was 2, VI value was slightly decreased from 136 to 135 and % yield was 79.6%. The acidity and ash content were 0.04 and 0.0037 %wt., respectively.

In terms of flash point and sulfur content, the data showed that the flash point increased from 164, 168, to 170 °C and sulfur content increased from 0.290, 0.304, to 0.326 %. This occurred when the concentration of catalyst was decreased from 40, 35, to 30%. This result indicated that at 30 % catalyst concentration the hydrotreated oil gave desirable properties. Therefore, it was not necessary to use higher catalyst concentration than this.

In summary, the optimum conditions (temperature, hydrogen pressure, reaction time and catalyst concentration) for the hydrotreating process of used automotive lubricating oil using 5%Ni-10%W-1%F on alumina support were 350 °C, 500 psig, 2.50 hours, 30% by weight, respectively. The hydrotreated oil obtained from these conditions gave better properties than the used oil, especially in color, VI, sulfur content, acidity and ash content.

4.1.6. Effect of Reaction Time on Hydrotreating Process by using Nickel oxide/Molybdenum oxide/Fluoride (NiO/MoO₃/F/Al₂O₃)

The reaction was performed at 4, 3, 2.50 and 2 hours. The operating conditions were carried out at 350 °C, 500 psig hydrogen pressure, 40% catalyst concentration. The properties of oils are shown in Table 4.7.

Table 4.7 Physical and chemical properties of hydrotreated oil obtained from various reaction times using NiO/MoO₃/F catalyst.

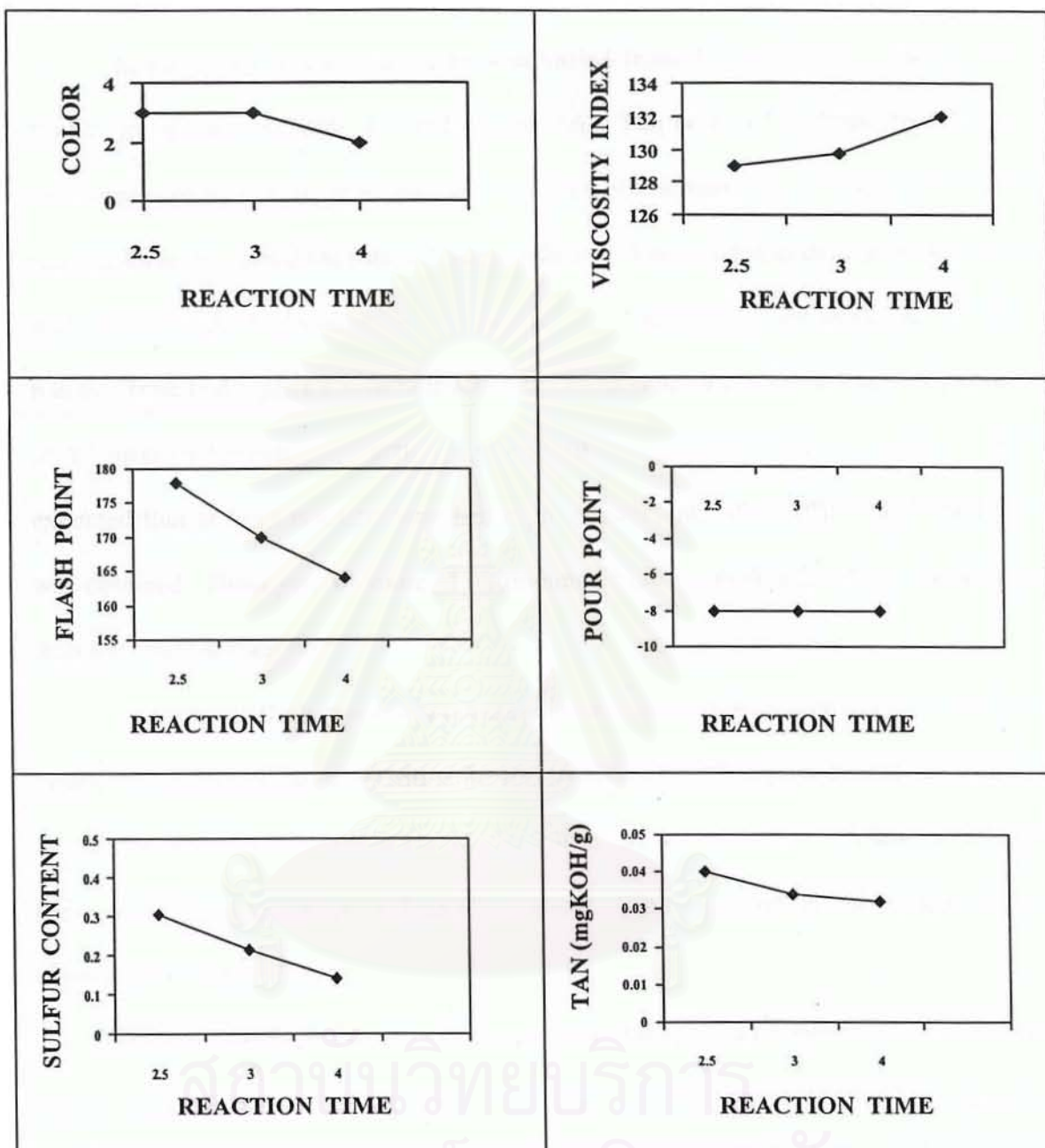| Properties	Reaction times (hour)			
	4.0	3.0	2.50	2.0
Color	2	3	3	8
Viscosity				
40 ° C , cSt	16.81	19.30	20.78	n.a
100 ° C , cSt	3.929	4.275	4.461	n.a
Viscosity index	132	130	129	n.a
Flash point (° C)	164	170	178	n.a
Pour point(° C)	-8	-8	-8	n.a
Sulfur content (%wt)	0.143	0.215	0.304	n.a
TAN (mgKOH/g)	0.03	0.03	0.04	n.a
Ash content (%wt)	0.0028	0.0031	0.0039	n.a
Yield (%)	74.86	77.20	80.16	low

FIGURE 4.6 Effect of reaction time on hydrotreated oil using NiO/MoO$_3$/F catalyst

In this study, the reaction time was varied from 4, 3, 2.50 and 2 hours. The results are shown in Table 4.7 and Figure 4.6. The color of hydrotreated oil was improved with increasing reaction time. In terms of viscosity and VI value, decreasing reaction time decreased the rate of hydrocracking. This resulted in decreasing of lower molecular weight hydrocarbons. Therefore, the hydrotreated oil obtained at short reaction time had higher viscosity than those obtained at long reaction time. The value of VI increased when the reaction was performed at a longer reaction time. It was expected that at long reaction time had more constituents of paraffinic hydrocarbons was obtained. However, VI value of oil obtained from every reaction time was higher than the original used oil.

In terms of flash point, when the reaction time was decreased from 4, 3 to 2.5 hours, the hydrotreated oil obtained from a short reaction time gave higher flash point than those obtained at longer reaction time. An increase in the reaction time increased the rate of hydrocracking and hydrogenation. This resulted in increasing lower hydrocarbon components.

From this experiment, the decreasing of sulfur content occurred with increasing reaction time from 2.5, 3 and 4 hours. The minimum sulfur content, after the reaction was performed for 4 hours, slightly increased. The acidity of hydrotreated oil decreased with increasing reaction time. The result demonstrated that the acidic compounds from oil oxidation was removed. The decrease in ash content indicated that metallo organic components from additives were also decreased.

The goal of this study was to find the minimum reaction time that gave oil with desirable properties. These observations suggested that the optimum reaction time was 2.50 hours. At this reaction time the hydrotreated oil showed desirable properties in terms of color, sulfur, ash content and acidity. Although the properties of oil (color, VI and sulfur content) were the best at a reaction time of 4 hours, it was not necessary to operate at a reaction time longer than 2.50 hours.

4.1.7. Effect of Catalyst Concentration on Hydrotreating Process by using Nickel oxide/Molybdenum oxide/Fluoride (NiO/MoO₃/F/Al₂O₃)

The reaction was performed at various catalyst concentrations of 40%, 35%, 30% and 25%. The operating conditions were carried out at 350°C, 500 psig hydrogen pressure and 2.50 hours reaction time. The properties of the oil products are shown in Table 4.8.

Table 4.8 Physical and chemical properties of hydrotreated oil obtained from various catalyst concentrations.

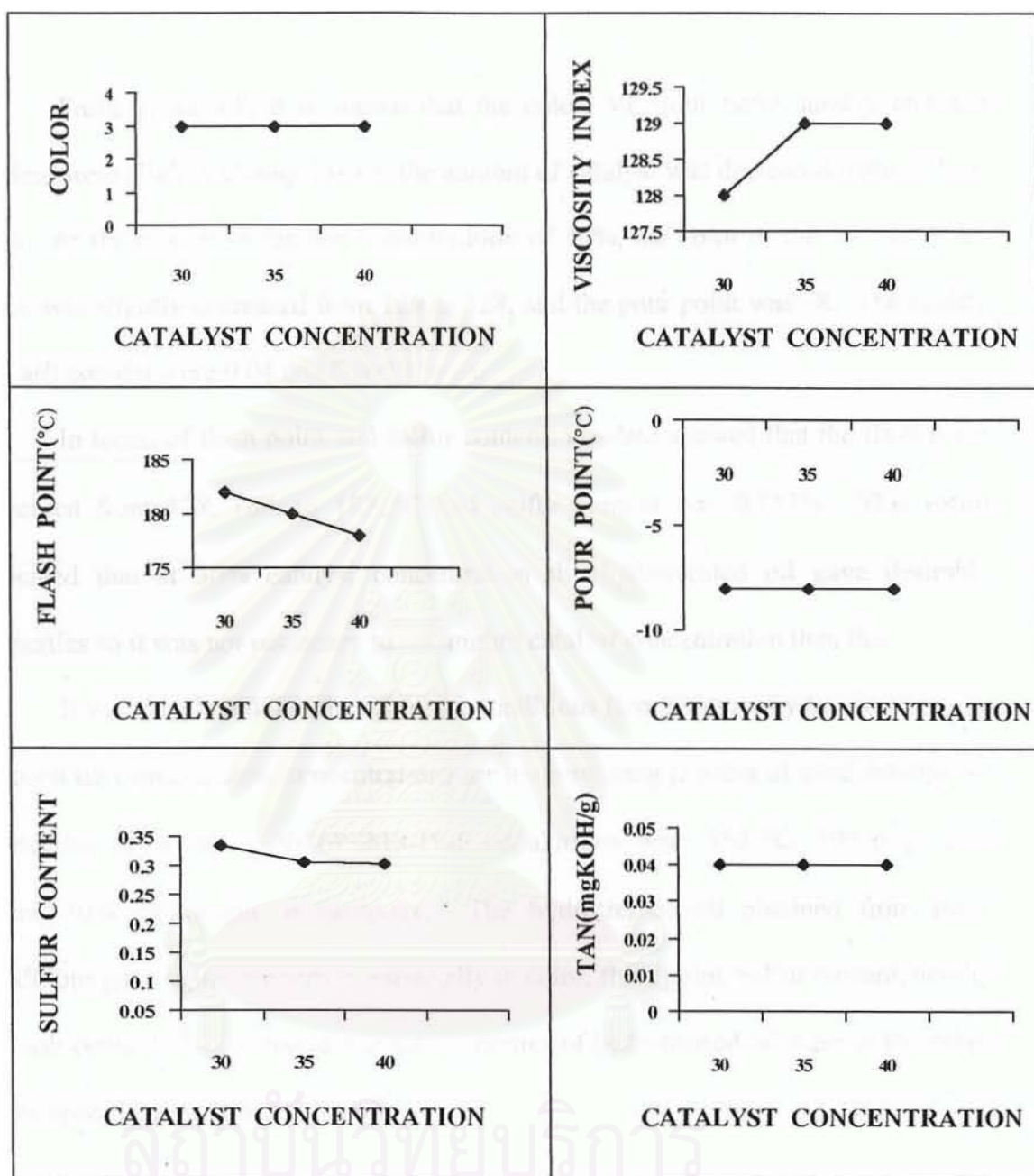| Properties	Catalyst concentrations (%)			
	40	35	30	25
Color	3	3	3	8
Viscosity				
40 °C, cSt	20.78	21.43	25.61	n.a
100 °C, cSt	4.461	4.551	5.059	n.a
Viscosity index	129	129	128	n.a
Flash point (°C)	178	180	182	n.a
Pour point (°C)	-8	-8	-8	n.a
Sulfur content (%wt)	0.304	0.307	0.333	n.a
TAN (mgKOH/g)	0.04	0.04	0.04	n.a.
Ash content (%wt)	0.0038	0.0038	0.0039	n.a.
Yield (%)	80.16	81.45	81.74	low

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

FIGURE 4.7 Effect of catalyst concentration on hydrotreated oil using NiO/MoO$_3$/F catalyst

From Table 4.8, it is shown that the color, VI, pour point, acidity and ash content were slightly changed when the amount of catalyst was decreased from 40% to 30%. At the minimum catalyst concentration of 30%, the color of the oil was 3, VI value was slightly decreased from 129 to 128, and the pour point was −8. The acidity and ash content were 0.04 and 0.0039 % wt.

In terms of flash point and sulfur content, the data showed that the flash point increased from 178, 180, to 182 °C and sulfur content was 0.333%. This result indicated that at 30% catalyst concentration the hydrotreated oil gave desirable properties so it was not necessary to use higher catalyst concentration than this.

It was concluded that the optimum conditions (temperature, hydrogen pressure, reaction time and catalyst concentration) for hydrotreating process of used automotive lubricating oil using 5%Ni-10%Mo-1%F on alumina were 350 °C, 500 psig, 2.50 hours, 30% by weight, respectively. The hydrotreated oil obtained from these conditions gave better properties, especially in color, flash point, sulfur content, acidity and ash content. It was found that the properties of hydrotreated oil were in the range of the specification of base lube oil.

4.1.8 Activity of Used Catalyst

This experiment studied the activity of used catalysts using NiO/WO$_3$/F and NiO/MoO$_3$/F under optimum conditions at 350 °C, 500 psig, 2.50 hours and 30% by weight. The properties of hydrotreated oils are shown in the Table 4.9.

Table 4.9 Properties of hydrotreated oil obtained from repeated used catalysts.

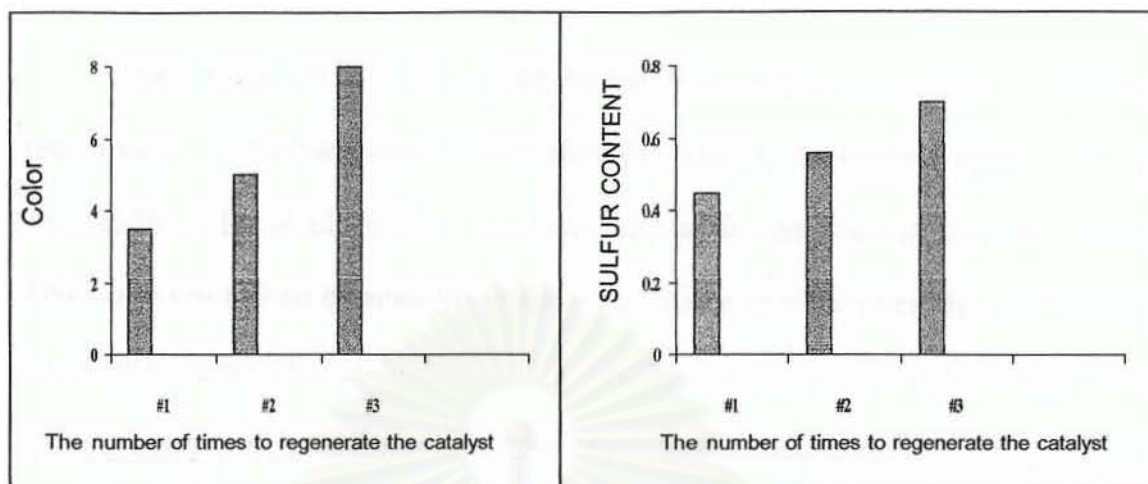| Properties	Catalyst Type					
	NiO/WO$_3$/F			NiO/MoO$_3$/F		
	# 1	# 2	#3	# 1	# 2	# 3
Color	3	5	8	3	6	8
Viscosity						
40 °C, cSt	25.84	42.25	50.07	41.75	48.06	63.92
100 °C, cSt	5.113	7.098	7.358	7.018	8.044	9.266
Viscosity index	130	129	128	128	127	127
Flash point (°C)	172	174	178	178	180	182
Pour point(°C)	-8	-8	-10	-8	-10	-10
Sulfur content (%wt)	0.447	0.560	0.698	0.308	0.425	0.745

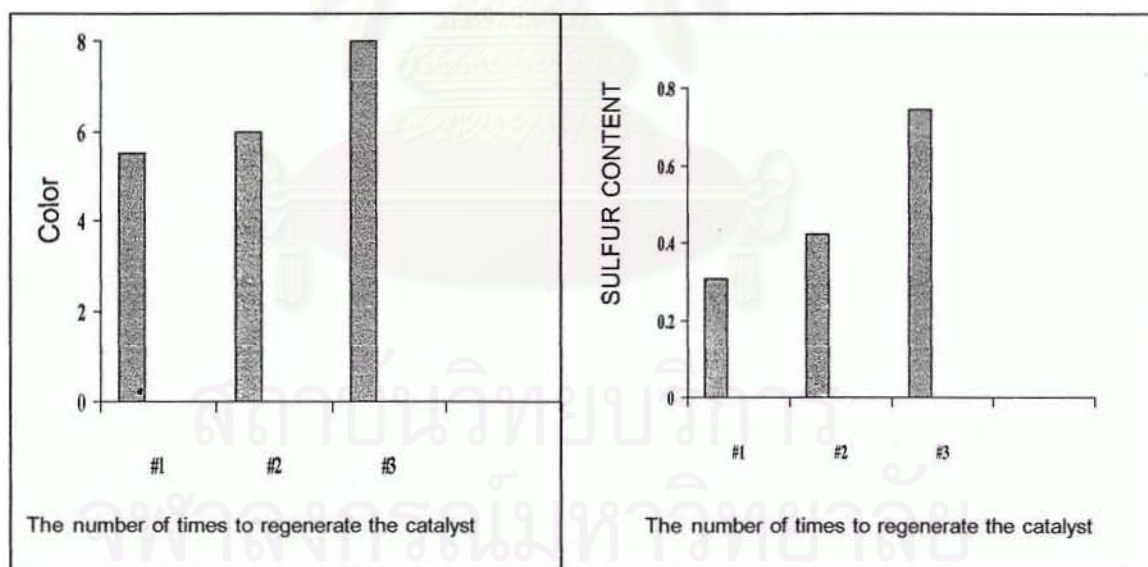FIGURE4.8 THE ACTIVITY OF USED NiO/WO$_3$/F CATALYST

FIGURE4.9 THE ACTIVITY OF USED NiO/MoO$_3$/FCATALYST

From Table 4.9, it is shown that the two types of preparing catalysts could be reused twice. After two times to regenerate the catalyst, the catalyst was less active because the color of oil product was black and sulfur removal had been decreased. This was a result from decreasing the surface area or active site of catalyst, which was due to the accumulated oil and by-products on the catalyst. The catalyst might have also been poisoned by sulfur, which was obtained from desulfurization. So the rate of hydrogenation and hydrodesulfurization were decreased too.
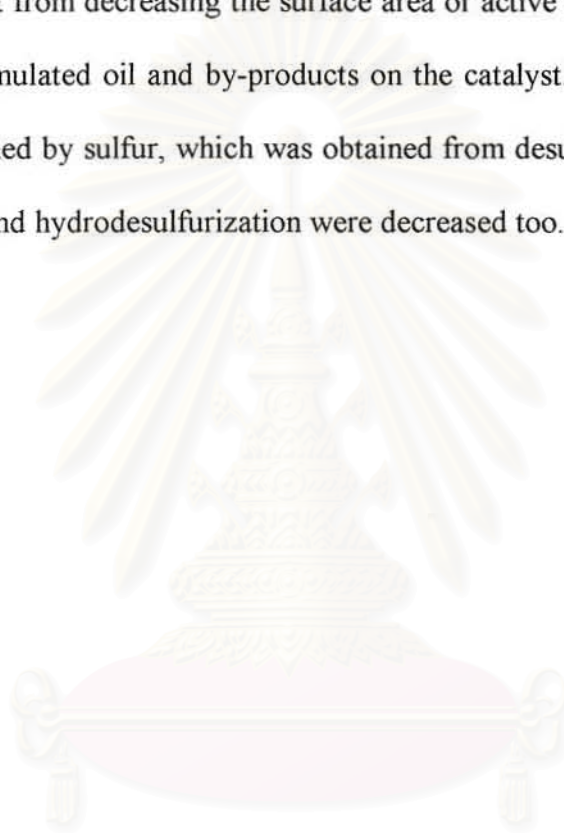
Table 4.10 The specification properties of base lubricating oil

Lubricating oil is formulated by blending base oil and additives to meet a series of performance specifications. Several types of base oil stocks are used in Thailand. Their properties depend on sources and companies who sell lubricating oil. Table 4.9 shows examples of base lube oil specifications normally used in Thailand.

Properties	Type of Base oil		
	150 BS	150 SN	500 SN
Color	Max 6.0	Max 1.5	Max 3.5
Viscosity			
40 ° C, cSt	Report	Report	Report
100 °C, cSt	30.0-34.0	4.8-5.4	10.1-12.0
Viscosity index	min 95	min 95	min 95
Flash point (°C)	min 260	min 200	min 220
Pour point (°C)	max –6	max –9	max –6
Sulfur content (%wt)	0.5-1.7	0.2-0.8	0.2-0.8

Table 4.11 Properties of hydrotreated oil obtained from optimum conditions using NiO/WO$_3$/F and NiO/MoO$_3$/F compared with the specification of base oil (150 SN).

Properties	Base oil 150 SN	Hydrotreated oil (NiO/WO$_3$/F)	Hydrotreated oil (NiO/MoO$_3$/F)
Color	Max 1.5	2.0	3.0
Viscosity			
100 °C, cSt	4.8-5.4	5.429	5.059
Viscosity index	min 95	135	128
Flash point (°C)	min 200	170	182
Pour point(°C)	max –9	-8	-8
Sulfur content (%wt)	0.2-0.8	0.326	0.333
TAN (mg KOH/g)	max 0.05	0.04	0.04
Ash content (%wt)	max 0.01	0.0037	0.0039
Water content (%Vol)	Nil	Nil	Nil

Table 4.12   Metal analysis of hydrotreated oil obtained from optimum conditions.

Metal components (ppm)	Used oil	Base oil 150 SN	Hydrotreated oil (NiO/WO$_3$/F)	Hydrotreated oil (NiO/MoO$_3$/F)
Al	13.92	4.15	5.03	5.72
Si	15.54	-	-	-
Fe	37.40	2.29	-	-
Cr	0.72	-	-	-
Cu	13.19	3.34	-	-
Zn	963.98	6.79	-	-
Ca	1840.04	1.24	-	-
Mg	394.11	8.25	9.18	11.04
P	1056.61	3.59	3.82	6.42

Table 4.11 and Table 4.12 show the physical and chemical properties of oil products from the hydrotreating process under optimum conditions. The hydrotreated oil product from $NiO/WO_3/F/Al_2O_3$ was operated at temperature of 350 °C, hydrogen pressure of 500 psi, reaction time of 2.50 hours and catalyst concentration of 30% wt. The oil product from $NiO/MoO_3/F/Al_2O_3$ was operated under optimum conditions temperature of 350 °C, hydrogen pressure of 500 psig, reaction time of 2.50 hours, catalyst concentration of 30% wt. These two oils had similar properties when compared with the specifications of base oil (150 SN). On comparing the specifications of base oil (150 SN), it could be seen that hydrotreated oil had good properties especially for color, increased viscosity index, reduced sulfur, acidity and metal content.

In summary, hydrotreated oil from the two types of catalyst under optimum conditions can be used as lubricating base oil.

4.2 Characterization of the catalysts

Characterization of the catalysts by X-ray fluorescence were shown in Figure B2 and B3. Table B1 showed information about the amount of elemental composition of catalysts. The result indicated that the catalysts $NiO/WO_3/F$ and $NiO/MoO_3/F$ catalysts on alumina support contained metal as the following:

Nickel	$\cong$ 5 %
Tungsten	$\cong$ 10 %
Molybdenum	$\cong$ 10 %

The fluoride peak was not detected because the X-ray fluorescence condition was not suitable to detect in the range of light atoms.

4.3 Determination Spectroscopic Properties

The ^{13}C NMR spectrum of the oil product from optimum conditions were shown in Figures A4, A5 and A6. The NMR spectrum showed aliphatic carbon between 0-60 ppm and aromatic carbon from 110-160 ppm. The FTIR spectra of the oil product from optimum conditions were shown in Figures A13 and A14. The IR spectrum indicated C-H stretching of aliphatic hydrocarbon around 2,800-3,000 cm^{-1}. The signal of C-H bending vibration of $-CH_2$, $-CH_3$ were at 1450 and 1375 cm^{-1}.

CHAPTER V

CONCLUSION

This research aimed to improve the quality of used automotive lubricating oil from service stations, in order to produce oil product which has a quality similar to lube base oil by means of one–step catalytic hydrotreatment. To accomplish this objective, catalytic hydrotreatment was carried out by using effective hydrotreating catalyst $NiO/WO_3/F$ and $NiO/MoO_3/F$ on alumina support. The operating condition was studied by varying catalyst type, which had an effect on the properties of the oil product such as color, viscosity, flash point, pour point and sulfur removal. The optimum conditions from this study are summarized below:

1) The $NiO/WO_3/F$ catalyst was effective at temperature of 350 °C, hydrogen pressure of 500 psig, catalyst concentration of 30% by weight of oil and reaction time of 2.50 hours. This catalyst produced the hydrotreated oil with the best properties in terms of color, viscosity index, sulfur and acidity.

2) The $NiO/MoO_3/F$ catalyst was effective at temperature of 350 °C, hydrogen pressure of 500 psig, catalyst concentration of 30% by weight of oil and reaction time of 2.50 hours. The hydrotreated oil obtained from this condition had the best properties in terms of color, flash point, acidity and sulfur content.

As mentioned above, these optimum conditions were useful in the production of lube base oil from used automotive lubricating oil. Hydrotreating process using these catalysts resulted in the improvement of color, increasing of viscosity index, reducing sulfur, acidity and metal content of used oil.

In summary, it is suggested that hydrotreated oil can be used as lubricating base oil. However, the hydrotreated oil can be blended with suitable additives until it has an acceptable quality comparable to commercial lubricating oil by adding the suitable additives.

Suggestion for future work

Recommendation for future study is that a continuous process should be studied in order to better understanding of the reaction under dynamic conditions.

REFERENCES

1. กรมศุลกากร. <u>ข้อมูลสถิติการค้าระหว่างประเทศไทย</u> (2539).

2. Brownawell, D.K. Refining Used Lubricating Oils with Sulfuric Acid and Hydrogenation. <u>U.S. Patent 3,3346,483</u> (1967).

3. Biswas, A.K. Regeneration of Used Lubricating Oils. <u>CA156421t</u> (1972).

4. Cutler, L.E. Re-refining of Used Automotive Lubricating Oils. <u>U.S. Patent 3,919,076</u> (1975).

5. Mowack, P.G. Reclaiming Used Lubricating Oils. <u>U.S. Patent 4,151,072</u> (1979).

6. Mead, T.C. Reclaiming Used Lubricating Oils. <u>U.S. Patent 4,490,245</u> (1984).

7. Reid, L.D. Used Oil Re-refining. <u>U.S. Patent 4,512,878</u> (1985).

8. Rongsawad, K. <u>Recycle of Used Lubricating Oil</u>. Master' Thesis, Multidisciplinary Program of Petrochemistry-Polymer, Chulalongkorn University, (1993).

9. Chaosuwannakij, R.<u>Recycle of Used marine Lube Oil</u>. Master' Thesis, Multidisciplinary Program of Petrochemistry-Polymer, Chulalongkorn University, (1993).

10. Somogyi, R.M. Refining Used Lubricating Oils with Sulfuric acid and Hydrogenation. <u>U.S. Patent 3,346,483</u> (1967).

11. Asseff, D.A. <u>Lubrication Theory and Practice</u>. Ohio: The Lubrizol Co., 1988.

12. Hobson, G.D. <u>Modern Petroleun Technology</u>. London: John Willey & Son, 1984.

13. Matar, S.M., Mirbach, M., and Tayim, H.A. Catalysis in Petrochemistry Process. Netherlands: Kluwer Academic Publishers, 1989.

14. Mcketta, J.J. Encyclopedia of Chemical Processing and Design (vol.28), pp.335-351. New York: Marcel Dekker, 1988.

15. Elver, B. Ullmann's Encyclopedia of Industrial Chemistry (5 th ed.), pp.428-432. Germany: John Wiley & Son, 1990.

16. Wills, J.G. Lubrication Fundamentals. New York: Mobil Corporation, Marcel Dekker, 1990.

17. Aboul El Naga, H.H., and Salem, A.E.M. Lubrication Engineering. 42 (1986): 210-217.

18. Page, G.L. Applied Heterogeneous Catalysts Design Manufacture, pp.432-456. Paris: Technic, 1987.

19. Horne, W.A., and McAffe, J. Advance in Petroleum Chemistry and Refining (vol.3), pp.211-213. New York: Interscience, 1965.

20. Gates, B.C., Katzer, J.R., and Schuit, G.C.A. Chemistry of Catalytic Process. New York: McGraw-Hill, 1980.

21. Satterfield, C.N. Hetergeneous Catalysis in Practice. New York: McGraw-Hill, 1980.

22. Mcketta, J.J. Encyclopedia of Chemical Processing and Design.(vol.15), pp. 216-246 New York: Marcel Dekker, 1982.

23. Kembel, C. Catalysis (vol.1), pp.205-233. London: Billing & Son, 1977.

24. Nebesh, E., Plundo, R.A., and McMahon, S.L. Impregnated Alumina Containing Material. U.S. Patent NO. 4,831,004 (1989).

25. Gary, P.H. and Handwerk, G.E. Hydrotreating. <u>Petroleum Refining Technology and</u>
     <u>Economics</u>, pp.426-435. New York: Marcel Dekker, 1984.

26. Emmett, P.H. Catalysis (vol.5), pp.426-435. New York: Reinhold Pulishing, 1957.

27. Brandes, K., Kuhes, S.G. and Davis, T. Impregnated Alumina Containing Material.
     <u>U.S. Patent NO.4,831,004</u> (1989).

APPENDICES
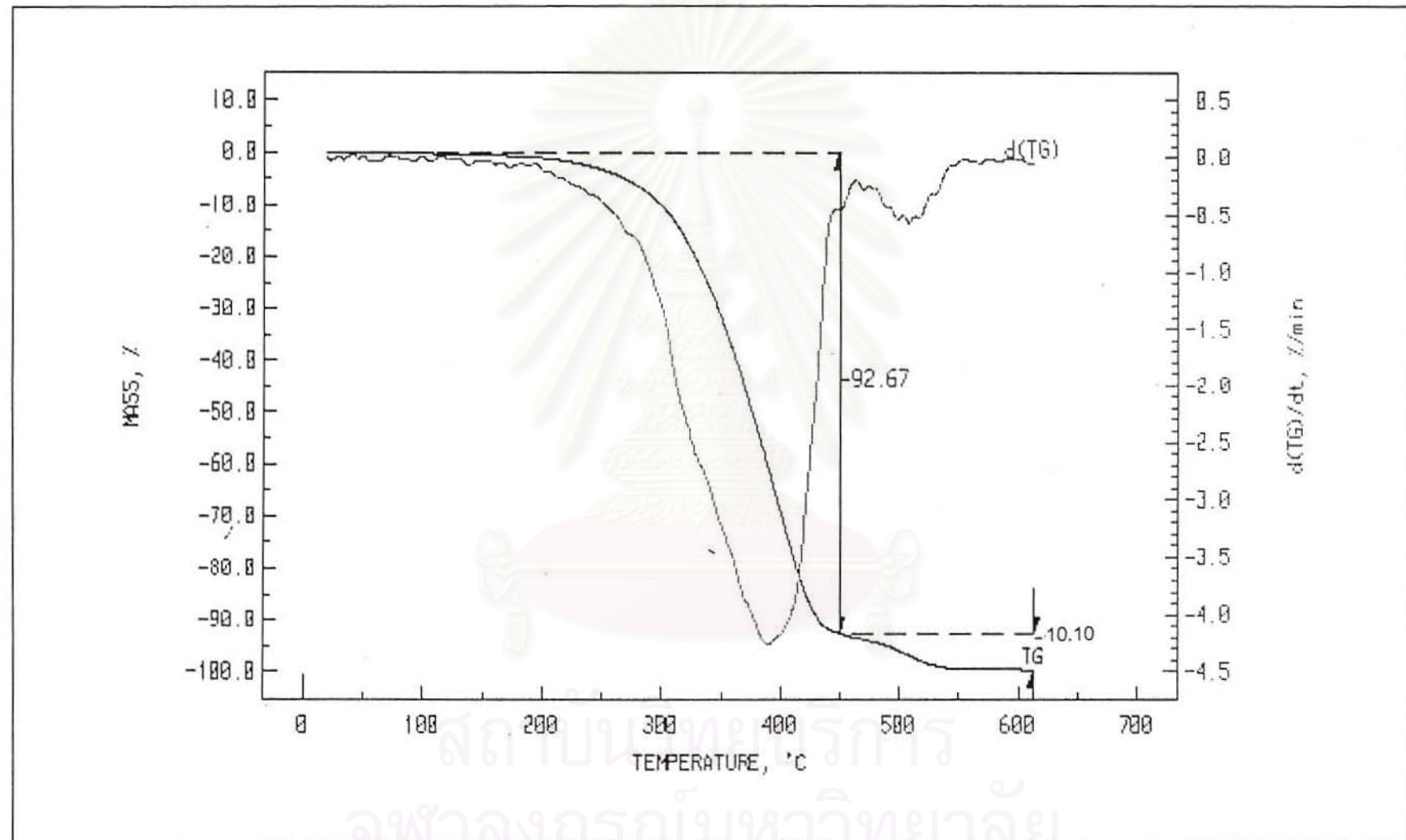
Figure A1 Thermogram of used automotive lubricating oil.
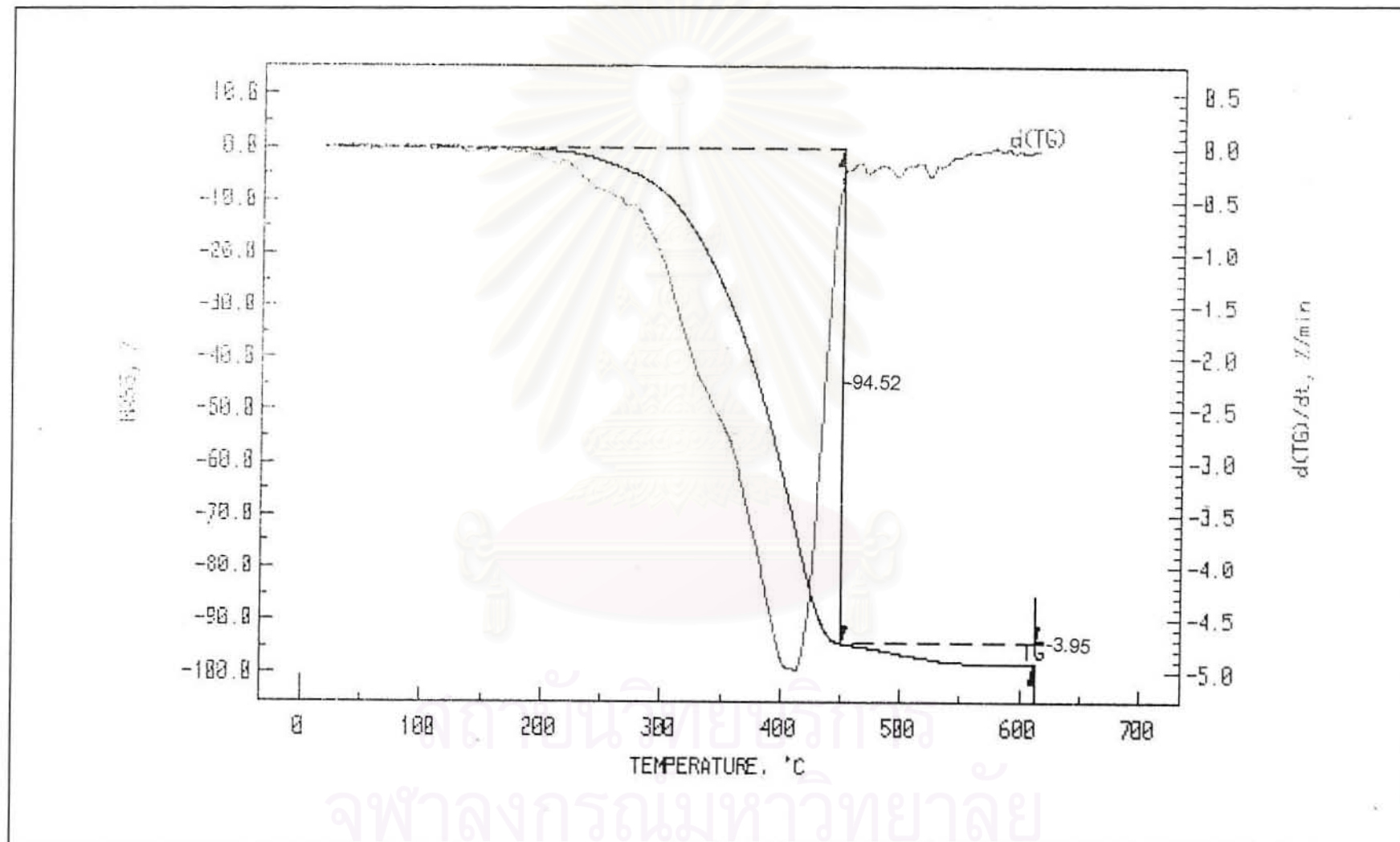
Figure A2 Thermogram of hydrotreated oil obtained from optimum condition using NiO/WO$_3$/F on alumina catalyst.
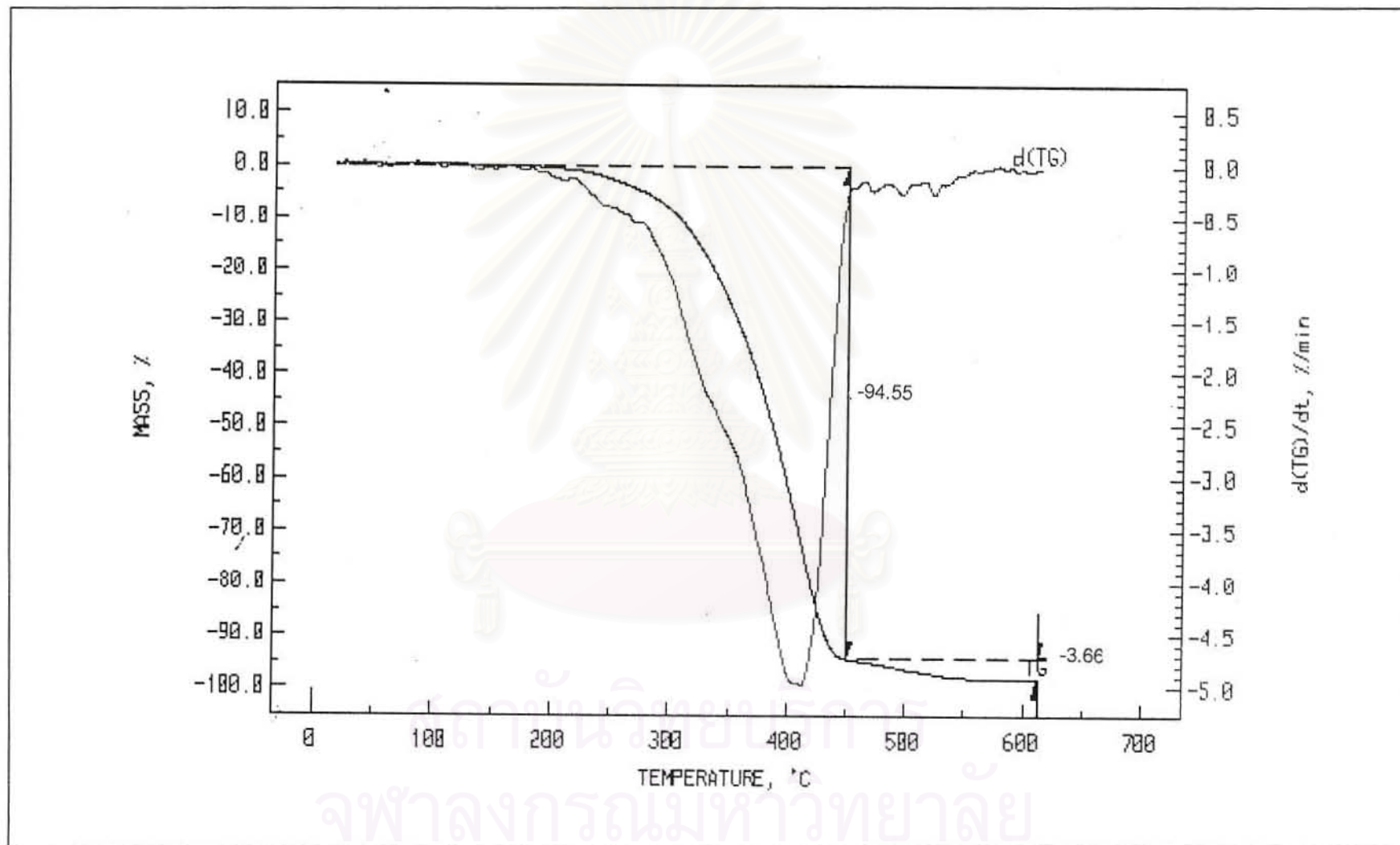
Figure A3 Thermogram of hydrotreated oil obtained from optimum condition using NiO/MoO$_3$/F on alumina catalyst.
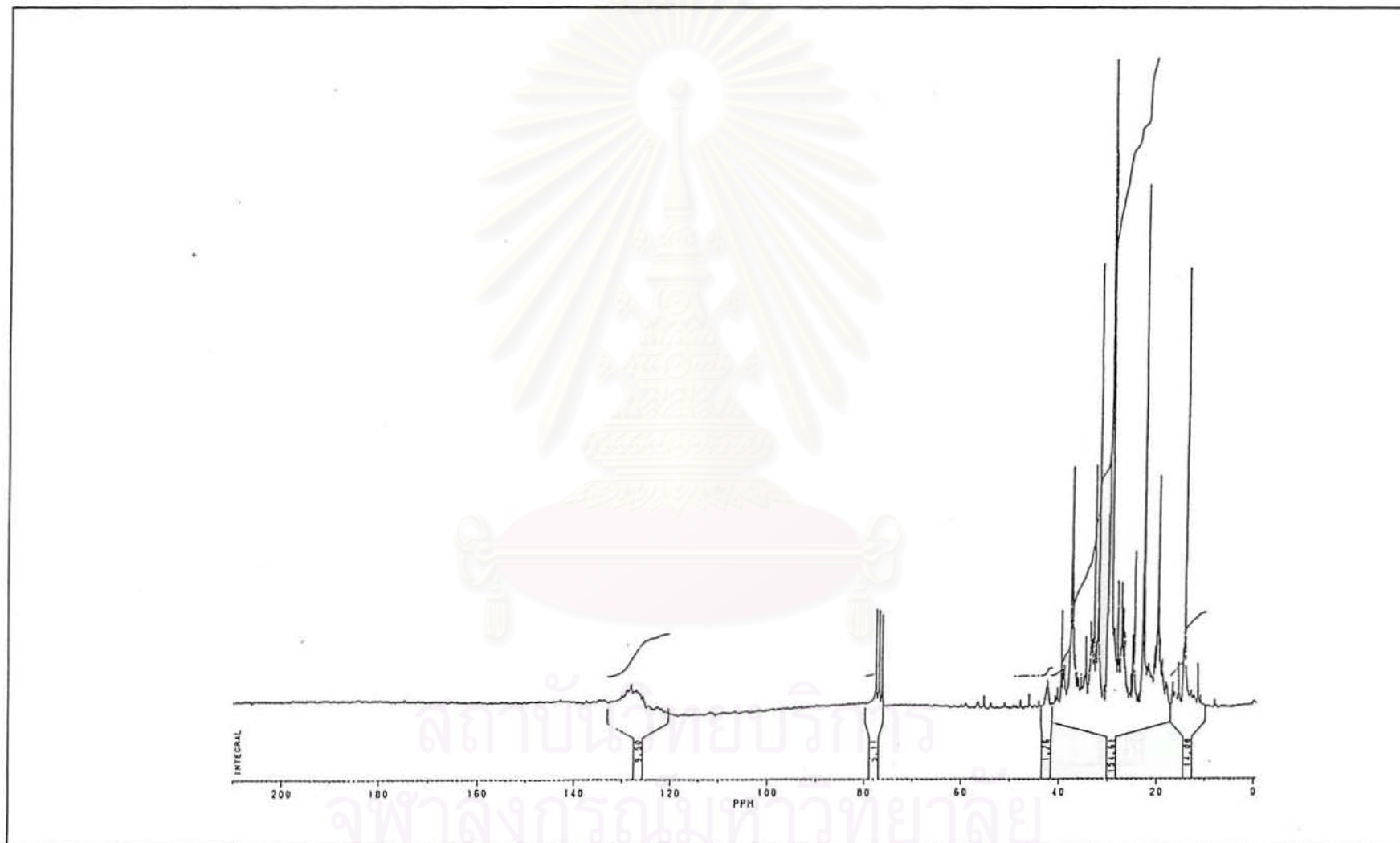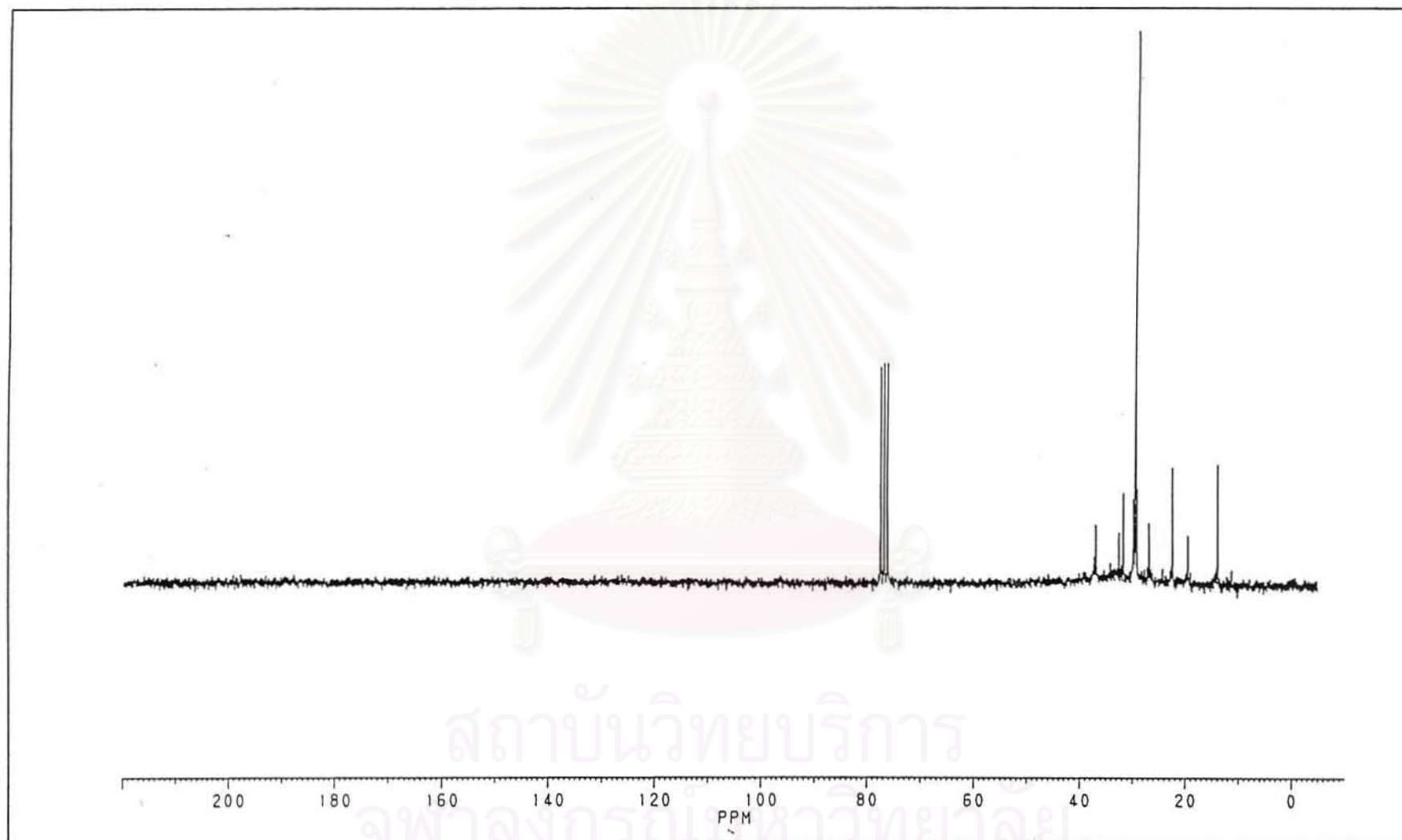
Figure A4 ^{13}C-NMR spectrum used automotive lubricating oil.
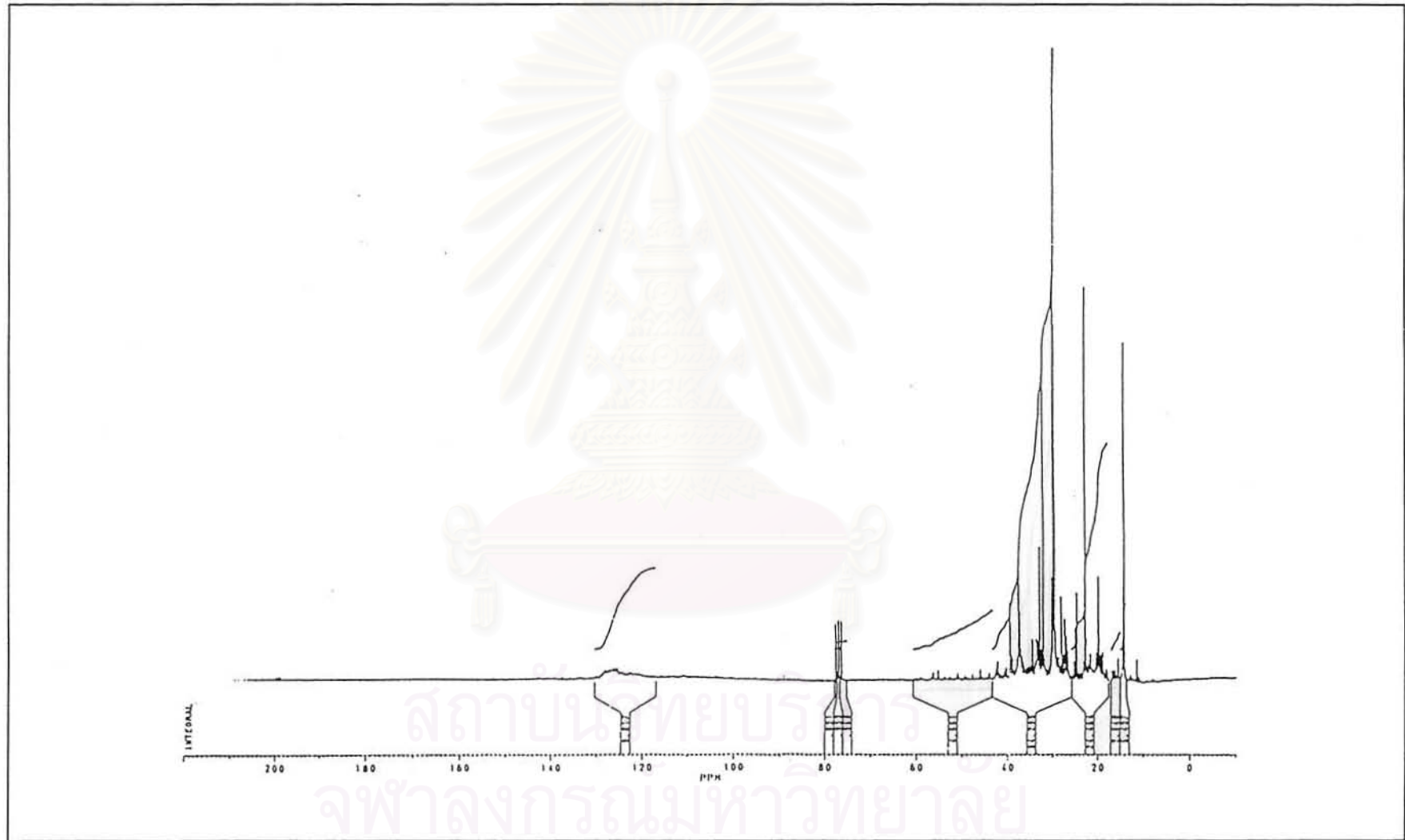
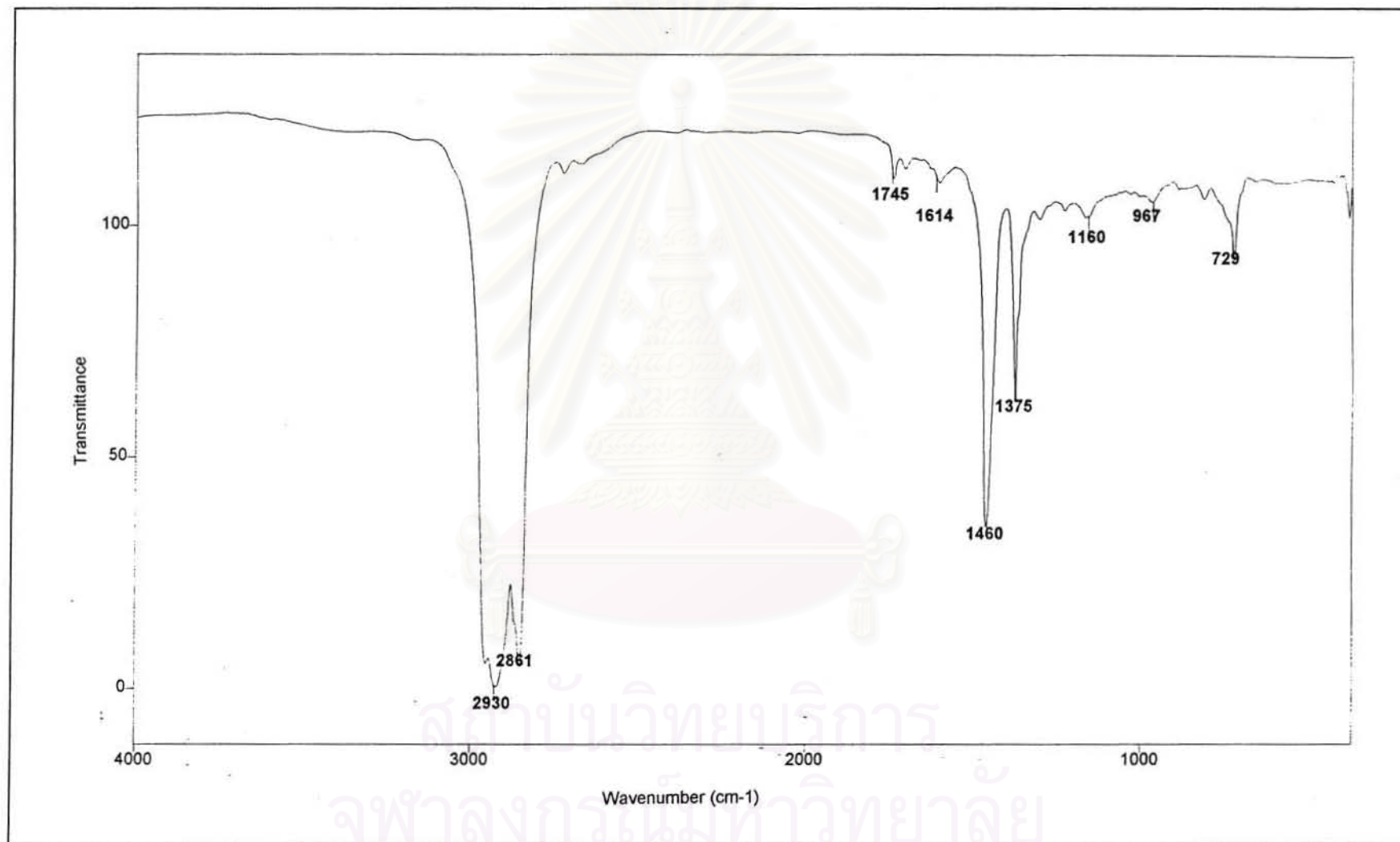**Figure A5** ^{13}C-NMR spectrum of hydrotreated oil obtained from optimum condition using NiO/WO$_3$/F on alumina catalyst.
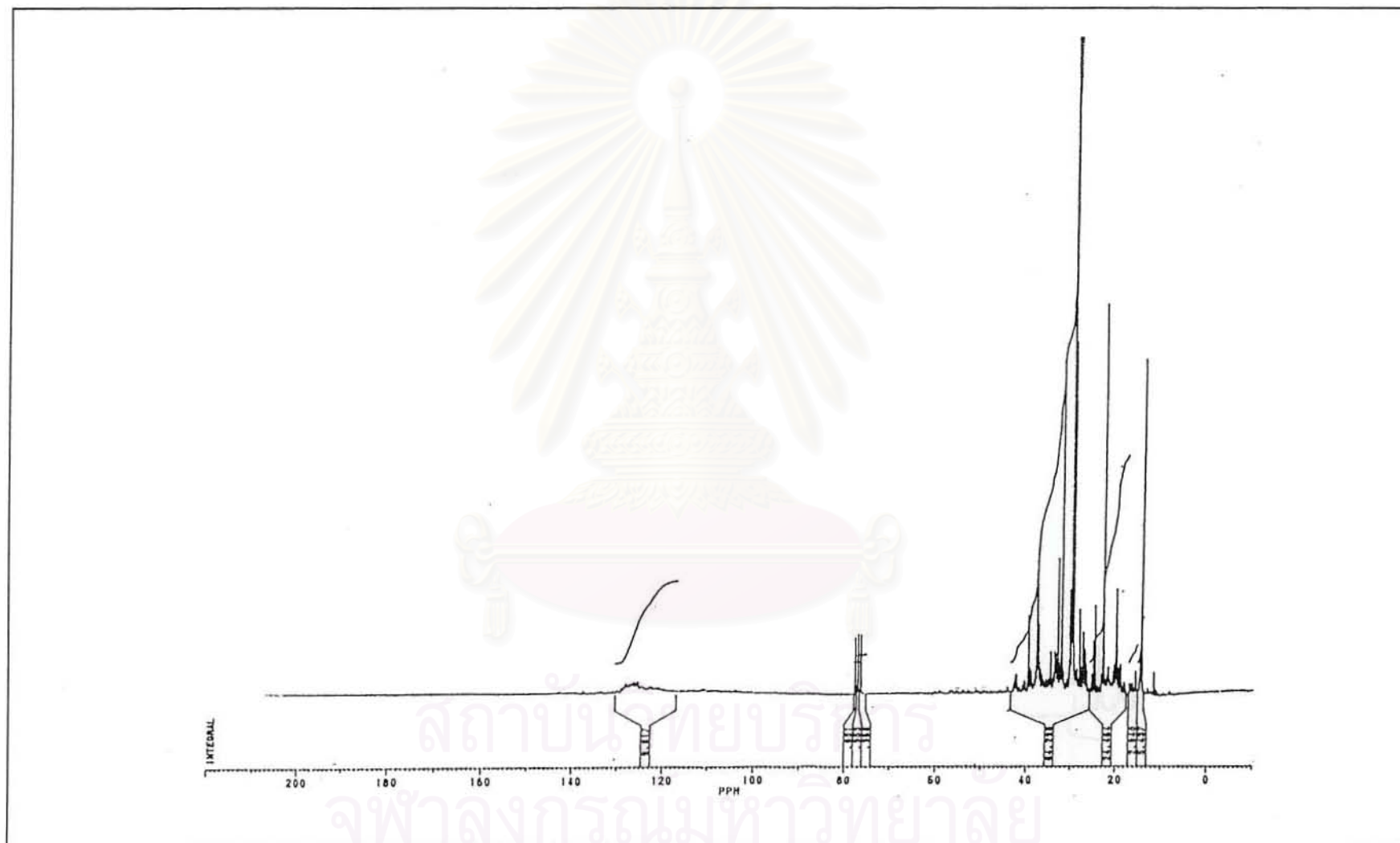
Figure A6 ^{13}C-NMR spectrum of hydrotreated oil obtained from optimum condition using NiO/MoO$_3$/F on alumina catalyst.
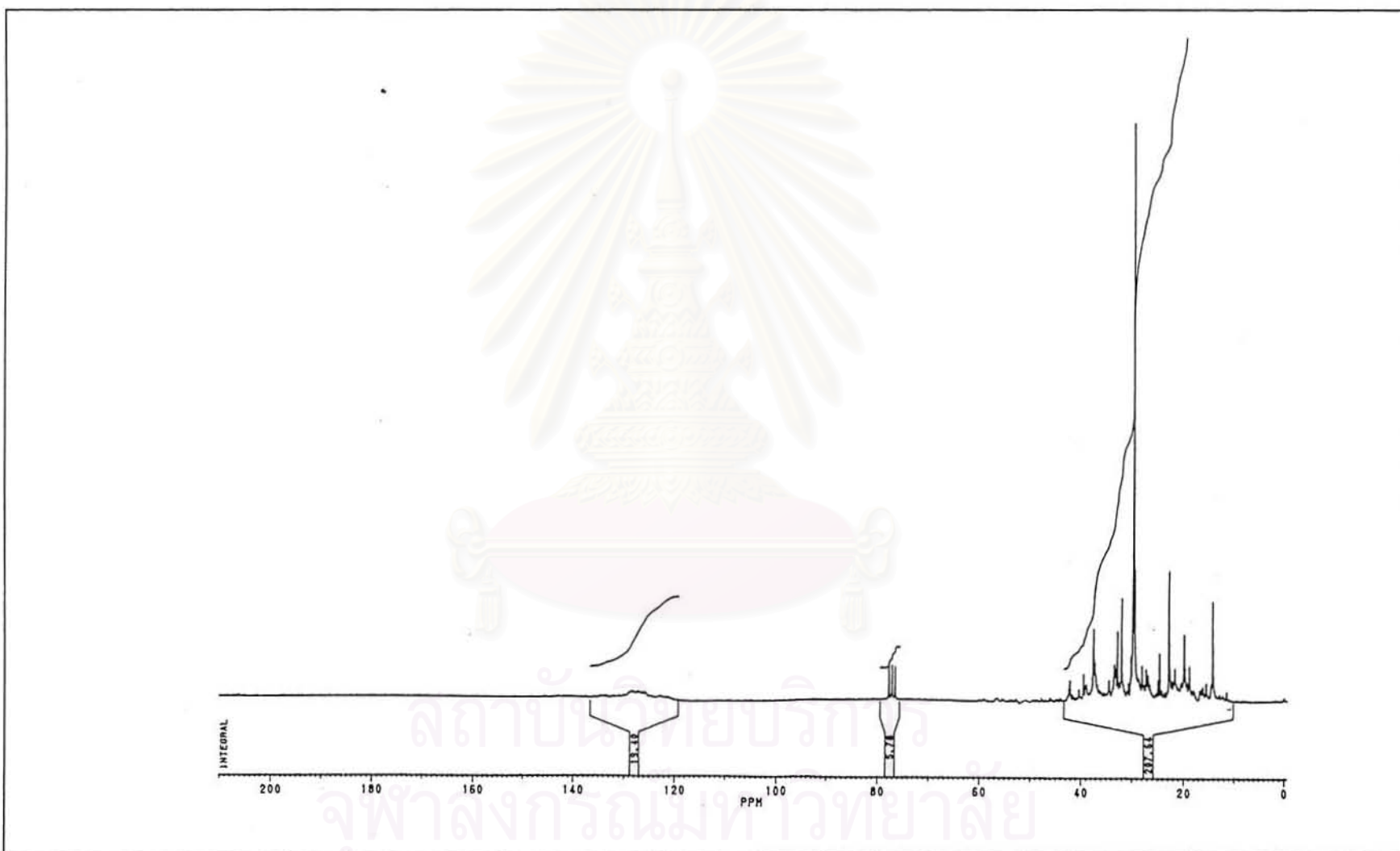
Figure A7 ^{13}C-NMR spectrum base lubricating oil (150SN).

Figure A8 ^{13}C-NMR spectrum of hydrotreated oil obtained from Raney nickel catalyst.
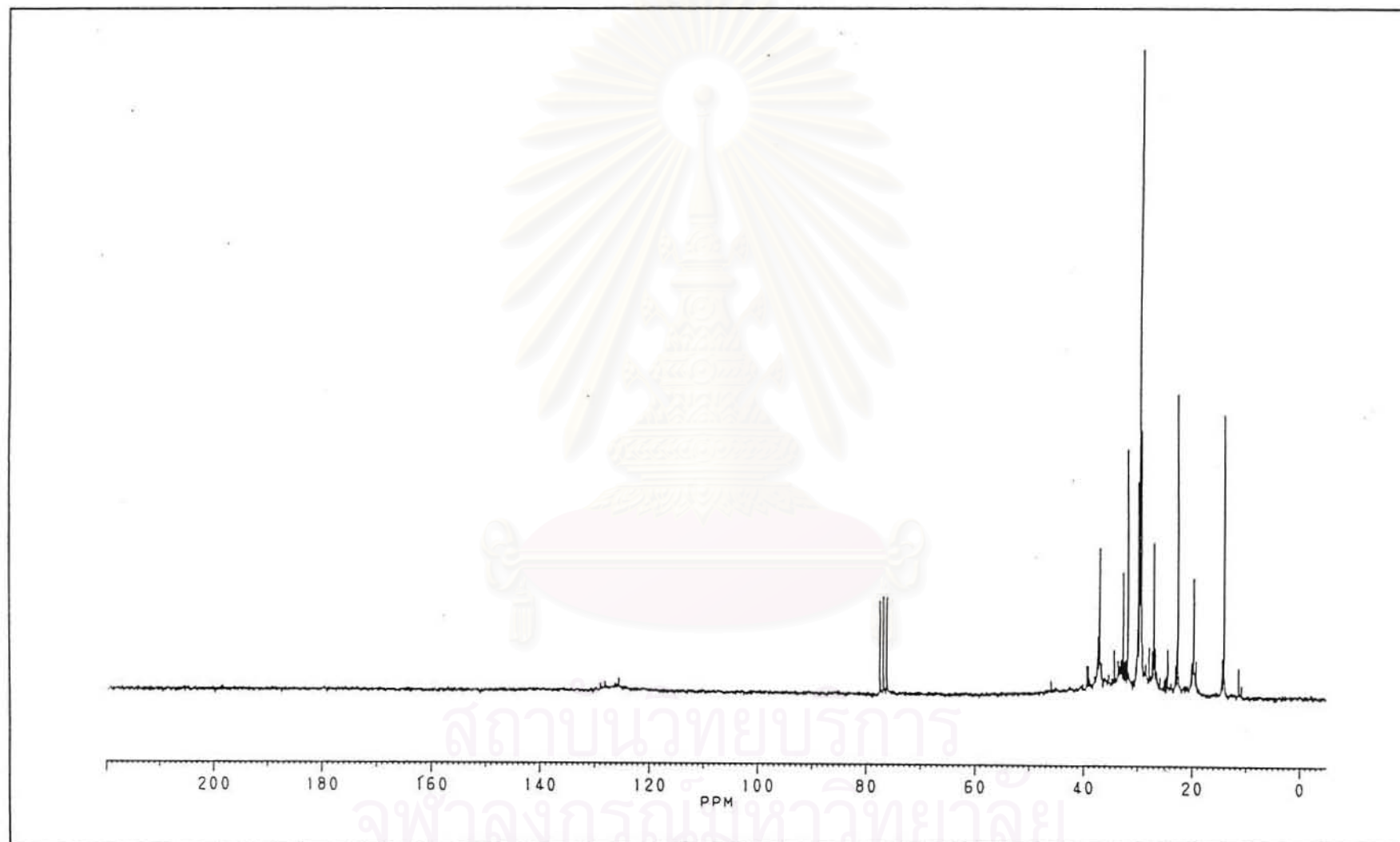
Figure A9 ^{13}C-NMR spectrum of hydrotreated oil obtained from United catalyst.

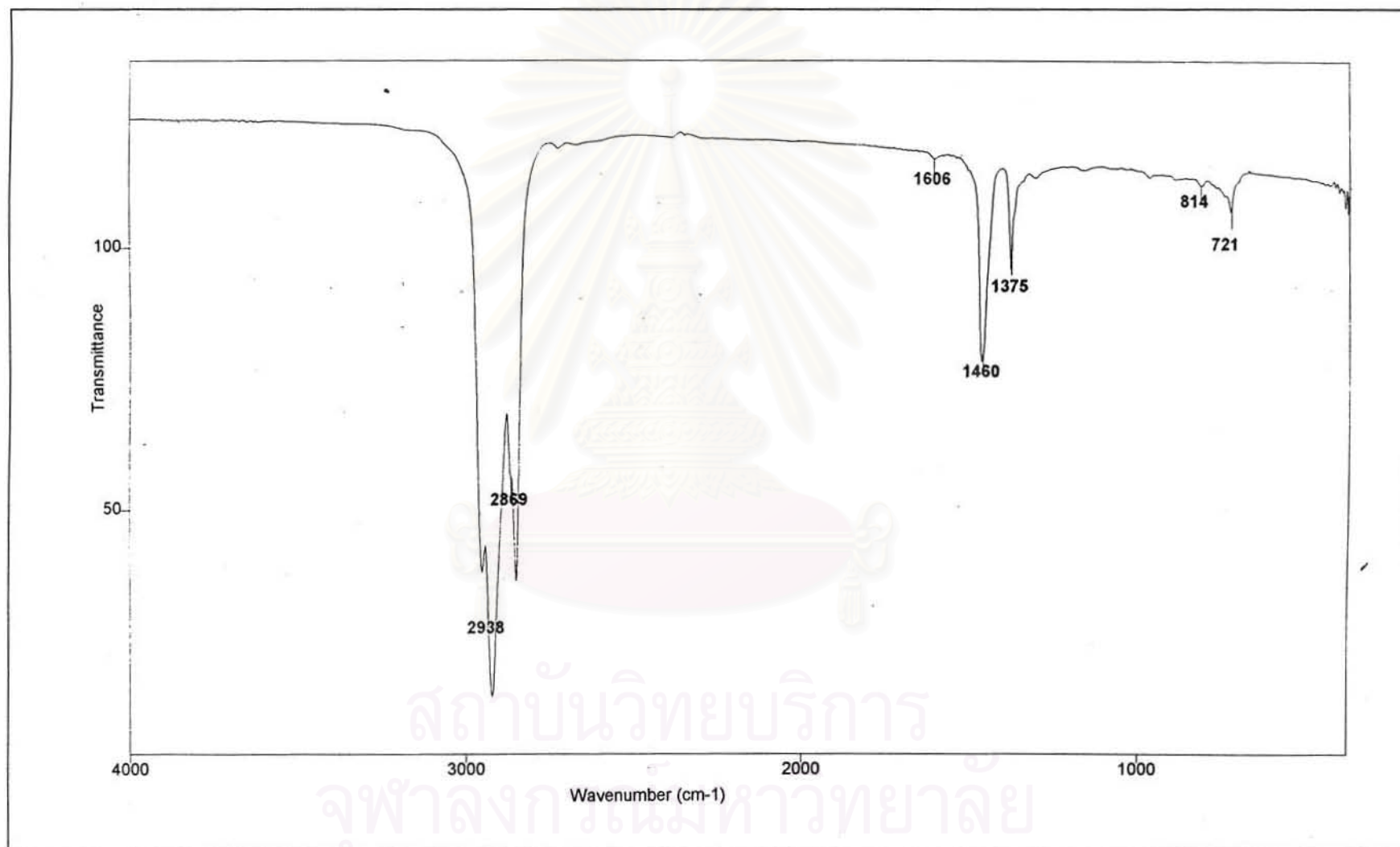**Figure A10** FTIR spectrum of used automotive lubricating oil.

Figure A11 FTIR spectrum of hydrotreated oil obtained from optimum condition using NiO/WO$_3$/F on alumina.
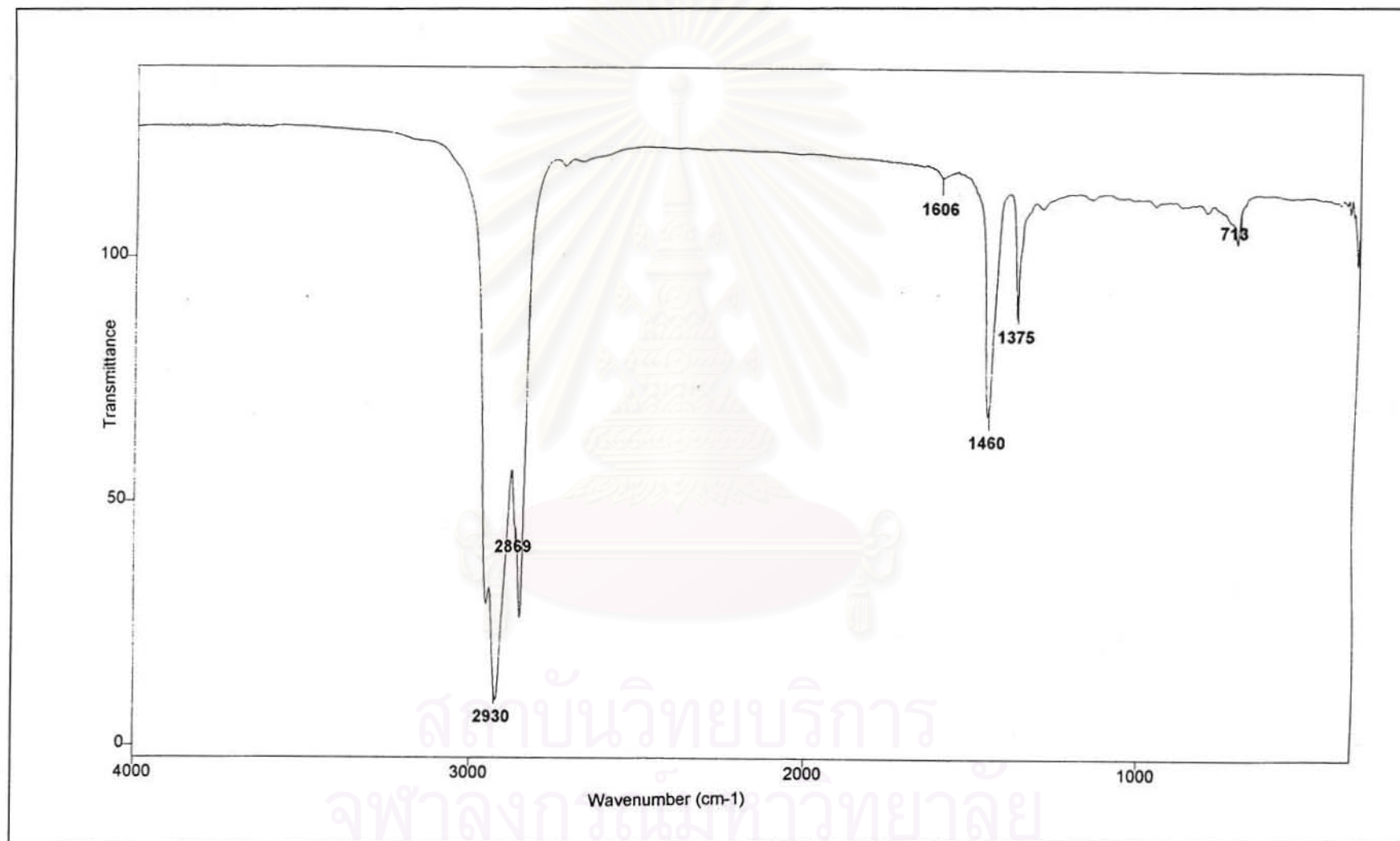
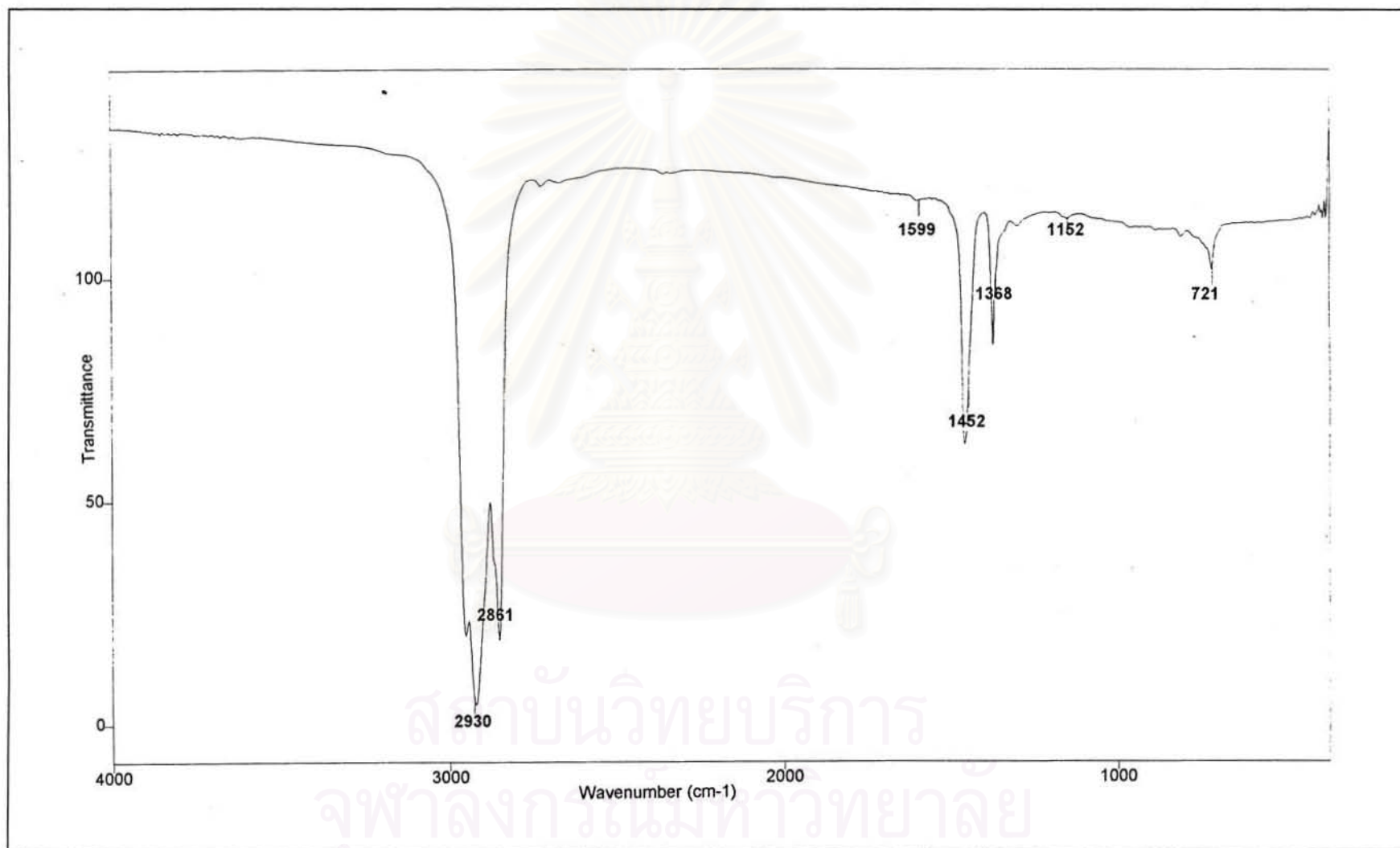**Figure A12** FTIR spectrum of hydrotreated oil obtained from optimum condition using NiO/MoO$_3$/F on alumina.

Figure A13 FTIR spectrum of base lubricating oil (150SN).

TableB₁ Characterization of catalyst

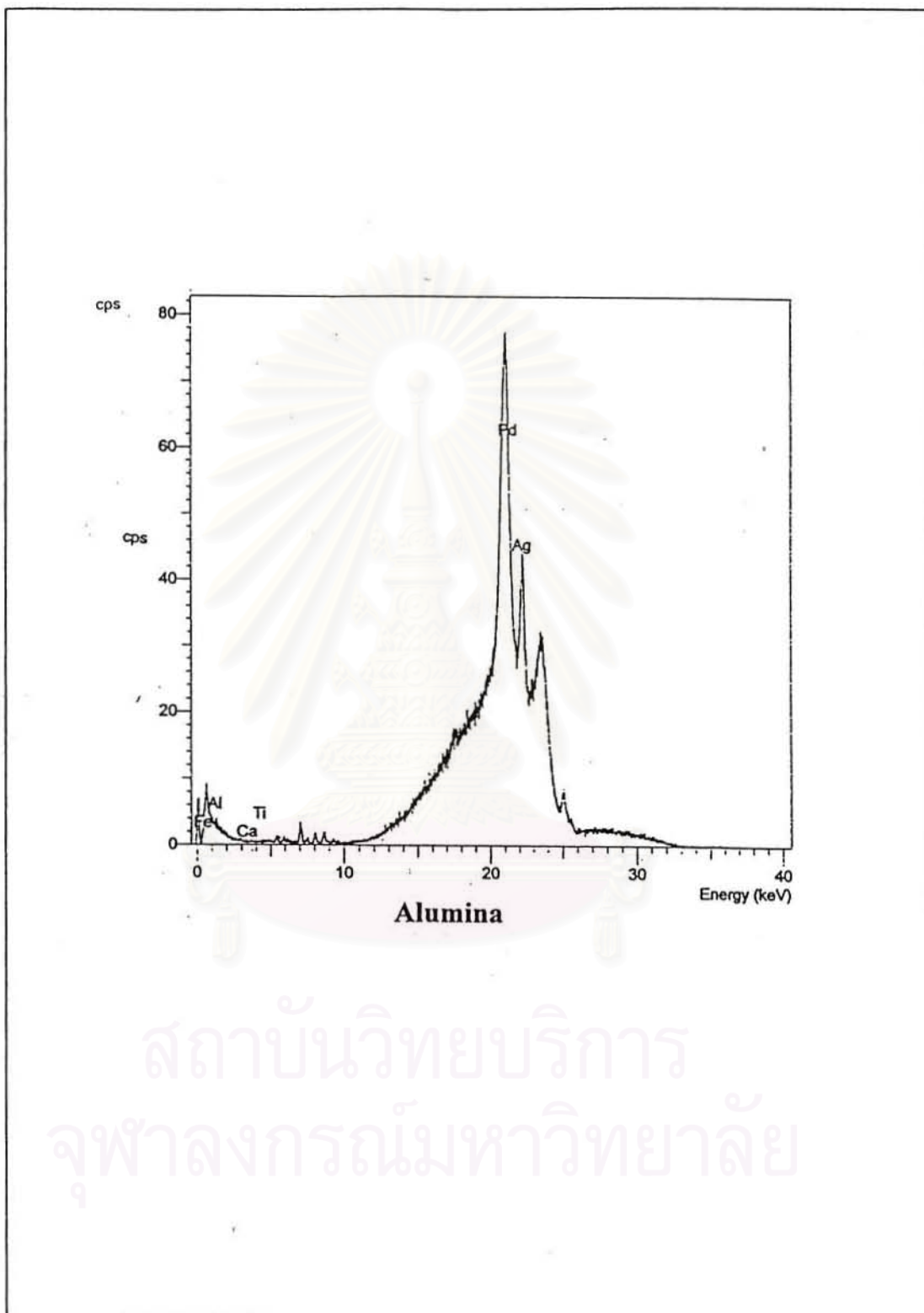| Catalyst	Composition of catalyst (%wt)									
	F	Cl	Al	Mn	Fe	Ca	Zn	Ni	Mo	W
United catalyst	D	0.15	15.8	D	D	0.26	0.30	3.23	-	22.5
Raney nickel	D	0.16	10.1	D	2.97	1.28	0.01	70.20	-	-
Ni/W	1.0	10.80	18.6	D	0.12	1.10	0.21	5.41	-	10.97
Ni/Mo	1.1	10.2	18.0	D	0.10	1.21	0.26	5.22	9.8	-

D = XRFS detect in ppm unit

Figure B₁ A plot of X-ray fluorescence data of alumina support.
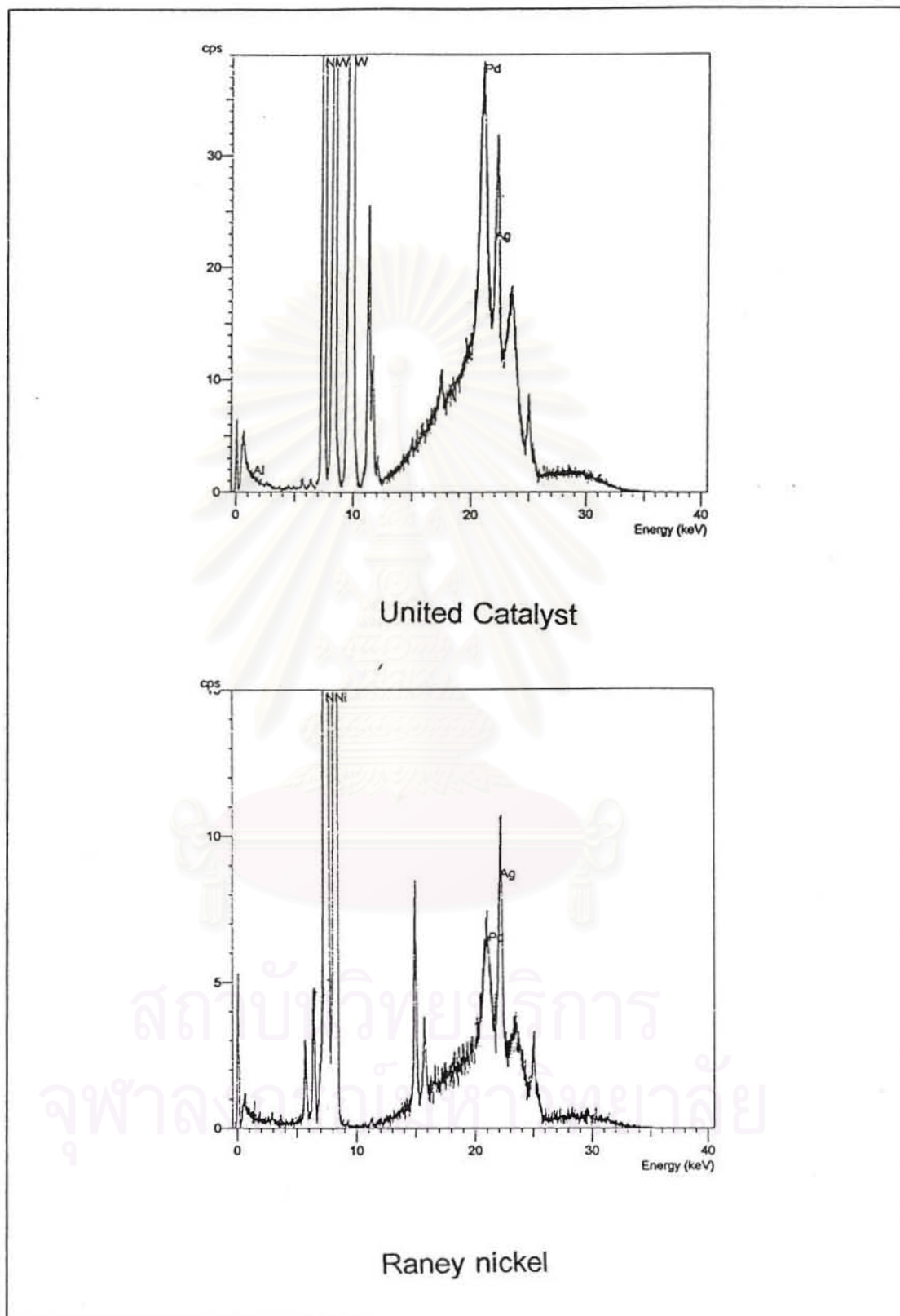
Figure B2 Plots of X-ray fluorescence data of commercial catalysts.

NiO / MoO$_3$ / F on Alumina
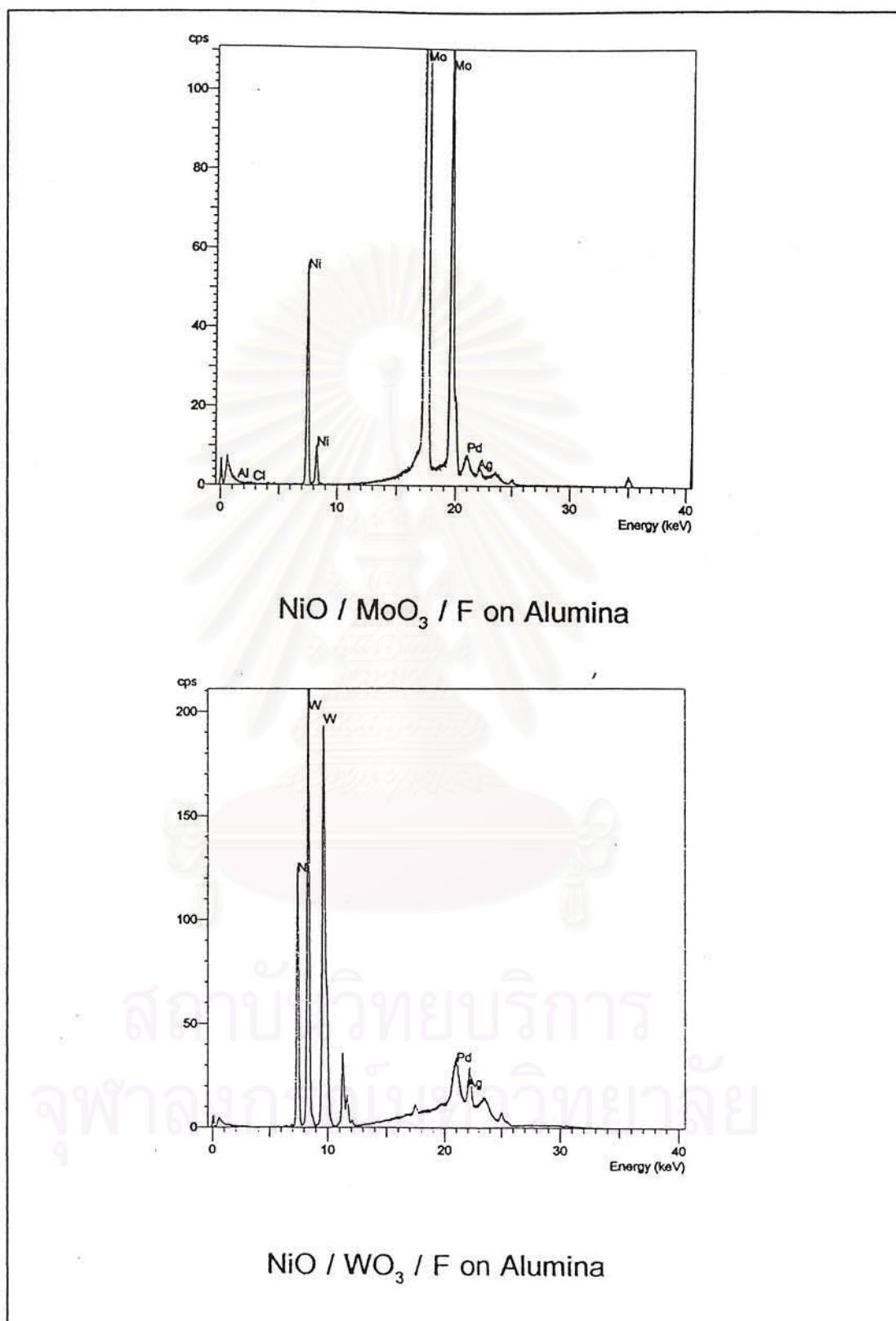

NiO / WO$_3$ / F on Alumina

Figure B3 Plots of X-ray fluorescence data of prepared catalysts.

VITA

Miss Prawpring Chaiprasert was born on May 4, 1974 in Udornthani. She received a Bachelor 's Degree of Science in Chemistry from Mahidol University in 1996. She continued her Master 's Degree in the Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University in 1996 and completed the program in 1999.