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CATALYTIC CRACKING OF USED LUBRICATING OIL ON Fe/Al_2O_3 AND Fe/SiO_2-Al_2O_3

Miss Waraporn Makvisai

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จุดมุ่งหมายหลักของงานวิจัยนี้คือศึกษาถึงกระบวนการแตกตัวของน้ำมันหล่อลื่นใช้แล้วด้วยตัวเร่งปฏิกิริยาเหล็กบนซิลิกา-อะลูมินา เหล็กบนอะลูมินา และนิกเกิลบนอะลูมินา ทำการทดลองในเครื่องปฏิกรณ์ขนาดเล็กซึ่งมีปริมาตร 70 มิลลิลิตร โดยมีการเตรียมตัวเร่งปฏิกิริยา 0.5-5% ของเหล็กบนซิลิกา-อะลูมินา 5% ของเหล็กบนอะลูมินา และ 5% ของนิกเกิลบนอะลูมินา กระบวนการแตกตัวกระทำ ณ อุณหภูมิ 390-470 องศาเซลเซียส เวลาที่ใช้ในการทำปฏิกิริยาระหว่าง 45-90 นาที ความดันก๊าซไฮโดรเจนเริ่มต้น 0-200 ปอนด์ต่อตารางนิ้ว และปริมาณตัวเร่งปฏิกิริยา 0-6.0% โดยน้ำหนัก

ผลิตภัณฑ์น้ำมันที่ได้เมื่อนำไปวิเคราะห์หาองค์ประกอบโดยใช้เทคนิคก๊าซโครมาโตรกราฟี ด้วยวิธี Simulated Distillation Gas Chromatography (DGC) พบว่า 5% ของเหล็กบนซิลิกา-อะลูมินาเป็นตัวเร่งปฏิกิริยาให้ปริมาณแนฟทามากที่สุด ได้ภาวะที่เหมาะสมในการทำปฏิกิริยาของตัวเร่งปฏิกิริยา 5% ของเหล็กบนซิลิกา-อะลูมินา คือ อุณหภูมิของปฏิกิริยา 450 องศาเซลเซียส เวลาที่ใช้ทำปฏิกิริยา 75 นาที ความดันก๊าซไฮโดรเจนเริ่มต้น 100 ปอนด์ต่อตารางนิ้ว และปริมาณตัวเร่งปฏิกิริยา 4.0% โดยน้ำหนัก ให้ปริมาณน้ำมัน 76.24% ซึ่งประกอบด้วยแนฟทา 45.35%, เคโรซีน 15.71%, ก๊าซออยล์ชนิดเบา 22.83%, ก๊าซออยล์ชนิดหนัก 3.70% และไฮโดรคาร์บอนสายโซ่ยาว 12.41% ในส่วนของตัวเร่งปฏิกิริยา 5% ของเหล็กบนอะลูมินาที่สภาวะการทดลองเดียวกัน พบว่า ให้ปริมาณน้ำมัน 80.38% ซึ่งประกอบด้วยแนฟทา 35.14%, เคโรซีน 14.47%, ก๊าซออยล์ชนิดเบา 24.16%, ก๊าซออยล์ชนิดหนัก 5.53% และไฮโดรคาร์บอนสายโซ่ยาว 20.70% ในส่วนของตัวเร่งปฏิกิริยา 5% ของนิกเกิลบนอะลูมินา ให้ปริมาณน้ำมัน 77.20% ซึ่งประกอบด้วยแนฟทา 38.24%, เคโรซีน 15.67%, ก๊าซออยล์ชนิดเบา 25.44%, ก๊าซออยล์ชนิดหนัก 3.38% และไฮโดรคาร์บอนสายโซ่ยาว 16.94% ตามลำดับ

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์..ลายมือชื่อนิสิต....วราภรณ์ มากวิสัย....................
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The main objective of this research was aimed to study the catalytic cracking of used lubricating oil with Fe/SiO_2-Al_2O_3, Fe/Al_2O_3 and Ni/Al_2O_3 catalysts. The catalytic reaction was carried out in 70 ml micro-reactor volume. The 0.5-5 wt.% of iron on SiO_2-Al_2O_3, 5 wt.% of iron on Al_2O_3 and 5 wt.% of nickel on Al_2O_3 catalysts were prepared. The cracking process was performed at reaction temperature range from 390 to 470°C, reaction time range from 30 to 90 minutes, initial hydrogen pressure of 0 to 200 psi and mass of catalyst was varied between 0 to 6.0 %by wt.

Liquid products were analyzed by Simulated Distillation Gas Chromatography, (DGC). The experimental result was found that 5% Fe/SiO_2-Al_2O_3 gave highest % naphtha. The optimum condition of 5% Fe/SiO_2-Al_2O_3 was 450°C of reaction temperature, 75 minutes of reaction time, 100 psi of initial hydrogen pressure and 4.0% by wt. of Fe/SiO_2-Al_2O_3. The liquid product yield in case of using 5% Fe/SiO_2-Al_2O_3 was 76.24%, the liquid composition were consist of 45.35% of naphtha, 15.71% of kerosene, 22.83% of light gas oil, 3.70% of heavy gas oil and 12.41% of long residue. The liquid product yield in case of using 5% Fe/Al_2O_3 was 80.38%, the liquid composition were consist of 35.14% of naphtha, 14.47% of kerosene, 24.16% of light gas oil, 5.53% of heavy gas oil and 20.70% of long residue. The liquid product yield in case of using 5% Ni/Al_2O_3 was 77.20%, the liquid composition were consist of 38.24% of naphtha, 15.67% of kerosene, 25.44% of light gas oil, 3.38% of heavy gas oil and 16.94% of long residue.

Field of study:..Petrochemistry and Polymer Science...Student's signature..WARAPORN MAKVISAI
Academic year.....................2005.........................Advisor's signature T. Vitidsant

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ABBREVATIONS

%wt : percent by weight

°C : Degree of Celsius

VI : Viscosity Index

cSt : Centistokes unit

psi : pounds-force per square inch

ASTM D 2887 : American Standard Test Method for Boiling Range distribution of Petroleum Fraction Gas Chromatography

rpm : rounds per minute

DGC : Simulated Distillation Gas Chromatography

FT-IR : Fourier Transform Infrared Spectroscopy

Fe/SiO_2-Al_2O_3 : Iron impregnated on silica-alumina

Fe/Al_2O_3 : Iron impregnated on alumina

Ni/Al_2O_3 : Nickel impregnated on alumina

CHAPTER I

INTRODUCTION

1.1 Background

One of the most important lubricants of today use is lubricating oil. It is used in industrial machines, automobiles and all mechanical equipments, in order to operate them for a longer period and be done efficiently and nowadays, Thailand used 3.8 million vehicles. Quality of used lubricating oil assumed to be at 45 million liters per year, excluding other engine. Although used lubricating oil must be wasted in enormous residue chemical waste, if it has not managed. So that idea to recycle the used lubricating oil by uses in heavy industrial such as fuel for smelt industry, cement industry. And reprocess for new grade lubricant return to industrial again. But recycle processes are little points of method to get rid of used lubricating oil waste. High portion of lubricant waste must effect to environment. Now have law to control lubricating oil. Factory must to have responsible about management residue, by product, waste, for not effect to environment.

Generally, the used lubricating oil was drained into ground and channels or distributed cheaply to customers. These are causes of many problems, especially in the considerations of environmental and low-grade lubricating oil distribution.

In order to perform properly, used lubricating oils were usually disposed in three ways: [1]

(1) Disposal as toxic/hazardous waste

(2) Re-refining to produce base oils

(3) Used as fuel

Due to the rapid growth in Thailand's industrial sector, lubricating oils are in great demand. Nevertheless, Thailand has to import the oils from several countries such as Taiwan, China, Singapore, England, Korea, Hong Kong, Malaysia, Australia, Kuwait, etc.,. Thus, to minimize the trade deficit, recycling of used lubricating oil is one of the choices to be considered.

There are many researches which have the same objective to improve or to recycle the use oils. In following contents, the recycling processes were described.

In 1972, Brownawell, Darrell W., Renard, Remi H. [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. After the treatment, the viscosity and the color decreased.

In 1972, Biswas A. *et al.* [3], had regenerated used lubricating oil by setting and decantation used motor oils at 60-70°C, dehydration at 120-150°C followed by acid treatment, clay treatment and blending with additives.

In 1974, M.L., Whisman, *et al.* [4], worked in improving the used oil quality by the following processes:

- acid/clay treatment
- caustic treatment
- aliphatic alcohol- acid treatment
- caustic/peroxide/aluminium chloride treatment

In 1976, Khaltaeve T.S. [5], studied the hydrogenation of an asphalt-free lubricating oil at 400°C, 40 atm, liquid space velocity 1.5 hr^{-1} in the presence of a catalyst. After hydrotreating, they reported that a viscosity index of the oil increased from 55 to 104 and 65%wt of sulfur was removed.

In 1979, Salusinszky A.L. [6], had recycled used lubricating oils by mixed used oils with aqueous treating solution then passed through a self-cleaning centrifuge, separated and stripped of light hydrocarbons and brought the pretreated oils charged to refinery stream.

In 1981, Tirtaatmadja V., Agnew J.B. [7], had refined used lubricating oils by treated used oils with MEK followed by acid treating and separation.

In 1981, Marvin M. Johnson *et al.* [8], they reclaimed used motor oil by reacted with aq. Ammonium salt followed by separation and filtration step.

In 1982, Fletcher Laired C. [9], had refined used lubricating oil by distillation to remove a volatile forecourt and distillation to obtain the lubricating oil fractions.

In 1983, Fletcher Laired C. *et al.* [10], had refined used lubricating oils by distillation into light and heavy fractions followed by extraction with tetrahydrofurfuryl alcohol and separation.

In 1983, Wood William E. *et al.* [11], had reclaimed used lubricating oils by treated used oils with aqueous ammonium salt followed by dehydration, filtration and vacuum distillation.

In 1984, Mead Theodore C. *et al*. [12], studied the process for 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.

In 1985, Tabler Donald C. [13], had reclaimed used lubricating oils by filtration, acid treatment and clay treatment.

In 1986, Bhan O.K. *et al.* [14], who tested activity of several commercial catalysts in hydrotreating of used lubricating oil. Light and heavy hydrocarbon compounds were removed from feedstock by vacuum distillation. A viscosity at 38°C a ASTM color, a sulfur content of distillation oil were 29.18 cst, 8.0 and 0.3%wt respectively.

In 1986, Strahorn David A. [15], had purified used lubricating oil by distillation and mixing with NH_4OH followed by setting and separation.

In 1989, Langhoff Josef *et al.* [16], had improved used oil by solid content separation and hydrogenation.

In 1994, Charles W. Harrison, Arthur G. Gorneau, Robert M. Steinberg, Bruce R. Bond [17], had reclaimed zinc dithiophosphate from used lubricating oil by vacuum distillation.

In 1994, Edward C. and Shurtleff R.R. [18], had reclaimed waste oil by evaporation and condensation.

In 1994, Somsak Sriwanichanichapoom [19], studied the catalytic hydrotreatment of used lubricating oil by Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 catalysts.

In 1995, Kanite Rongsawad [20], had reclaimed used industrial oil by acid/clay treatment and hydrogenation.

In 1996, Rangsun Chaosuwannakij [21], studied the 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 pressures 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.

In 1998, Jirasak Tscheikuna and Sasithorn Boon-Long [22], had regenerated of used lubricating oil by $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and NiW/Al_2O_3 catalytic hydrotreatment.

In 1999, Prawpring Chaiprasert [23], studied the one-step catalytic hydrotreatment of used automotive lubricating oil by hydrotreating catalysts.

In 2003, Flight Lieutenant Atsadayut Kaewsaiyoy [24], studied the catalytic hydrotreatment of used lubricating oil by $Ni\text{-}Mo/Al_2O_3$ and HZSM-5 catalysts.

In 2004, Siwathida Insuk [25], studied the catalytic hydrotreatment of acrylonitrile-butadiene-styrene used lubricating oil with Fe/activated carbon catalyst.

In 2004, Pracharat Taepakdee [26], studied the catalytic hydrotreatment of polypropylene, polystyrene and used lubricating oil with Fe/activated carbon catalyst.

The cracking process was selected to convert waste of use lubricating oil to the value chemical and fuel. Thermal cracking was used high temperature consequently high cost and energy. More researches have interested in catalytic cracking reaction by using acid catalyst [19-26] due to high selectivity of products while low cost and temperature. Catalysts are more interesting to study such as acid catalysts and non-acid catalysts i.e. metal supported. The SiO_2-Al_2O_3 and Al_2O_3 are support due to cheap and commonly used industrially [27]. The metal loaded on SiO_2-Al_2O_3 and Al_2O_3 were the catalysts used in catalytic cracking process.

Apparatus used in this research is small reactor capacity 70 ml that able to reacts at high pressure and high temperature In order to investigate the effects of the conditions on catalytic cracking reaction, depend on parameter of reaction temperature, initial hydrogen pressure, reaction time, and the ratio of the percentage catalyst by weight of used lubricating oil were varied. The main product yield is liquid oil with high naphtha composition. Therefore, this research to investigate the performance of the tested Fe/SiO_2-Al_2O_3, Fe/Al_2O_3 and Ni/Al_2O_3 catalysts on used lubricating oil.

1.2 Objectives

1.2.1 To prepared and characterization of the 0.5-5% Fe/SiO_2-Al_2O_3, 5% Fe/Al_2O_3 and 5% Ni/Al_2O_3 catalysts.

1.2.2 To convert used lubricating oil to light oil with Fe/SiO_2-Al_2O_3, Fe/Al_2O_3 and Ni/Al_2O_3 catalysts.

1.2.3 To investigate the effects of the variables on % yield and % composition of oil products.

1.2.4 To found the optimum conditions of catalytic conversion used lubricating oil to light oil products.

1.3 Scopes of research

1.3.1 Prepare the 0.5-5% Fe/SiO_2-Al_2O_3, 5% Fe/Al_2O_3 and 5% Ni/Al_2O_3 catalysts then characterization by XRF, XRD and N_2-BET analyzer.

1.3.2 Investigate the catalytic cracking of used lubricating oil on 0.5-5% Fe/SiO_2-Al_2O_3 catalyst under the following conditions:

- Reaction temperature range of 390-470°C.
- Reaction time range of 45-90 minutes.
- Initial hydrogen pressure range of 0-200 psi.
- Mass of catalysts range of 0-6.0% by wt.

1.3.3 Analyze composition of oil products by GC Simulated Distillation.

1.3.4 Analyze the functional group of oil product by Fourier Transform Infrared Spectroscopy (FT-IR).

1.3.5 To compare efficiency of 3 types of catalysts in hydrocracking.

CHAPTE II

THEORY AND LITERATURE REVIEW

2.1 Lubricating oil [28]

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

2.1.1 Petroleum Crude Oil and Its Components

Crude oil was formed 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 blank, nearly solid asphalts. This crude is a 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.

2.1.1.1 Hydrocarbons

(a) Alkanes (paraffins): These have saturated linear or branched chain structures. They have high viscosity index and low pour point.

(b) Alkenes (olefins): These are unsaturated molecules. Certain reining processes, however, do produce large amounts of alkenes by cracking or dehydrogenation. They are more chemically active than the other three classes and subject to oxidation or polymerization forming gums.

(c) Alicyclics (naphthenes): These are saturated cyclic structures based on five- and six-membered rings. They are extremely stable compounds.

(d) Aromatics: These are cyclic structures with conjugated double bonds, based on the six-membered benzene ring. They have a low viscosity index and low pour point.

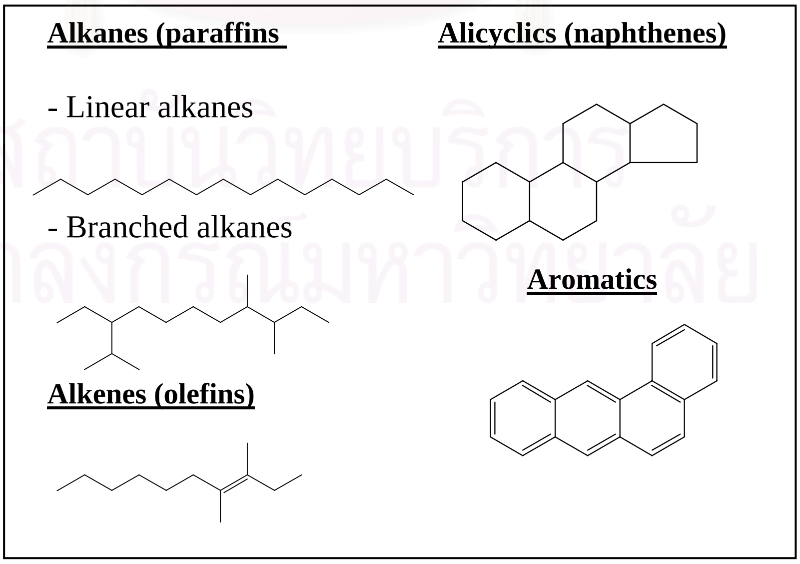


Figure 2.1 Examples of hydrocarbons [28].

2.1.1.2 Non-hydrocarbons

Many organic compounds in crude oil incorporate other elements sometimes within ring structures or as functional groups attached to a hydrocarbon structure. Organosulphur compounds are generally much more prevalent than nitrogen- or oxygen-containing molecules, while organometallics are usually present as traces.

Within the boiling range appropriate to lubricant base oils, almost all of the organosulfur and organonitrogen compounds are heterocyclic molecules (see Figure 2.2 for examples). In contrast, the principal oxygen-containing molecules are carboxylic acids; either saturated aliphatic acids or cycloalkanoic acids (naphthenic acids). Traces of phenols and furans may also occur.

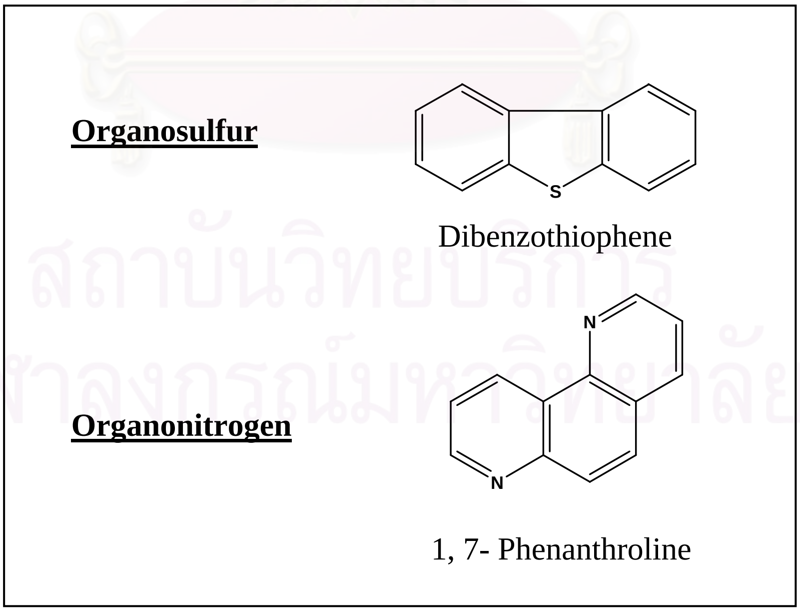


Figure 2.2 Non-hydrocarbon examples [28].

Finally, there are very high molecular weight resins and asphaltenes which contain a variety of aromatic and heterocyclic structures. Resins are the lower molecular weight (<1000) species while asphaltenes are the result of the linking together of many other structures and have exceptionally high molecular weights.

2.1.2 Source of Lubricating Base Oil

2.1.2.1 Refining of Petroleum Crude Oils

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 process is shown Figure 2.3. Essentially five steps are involved.

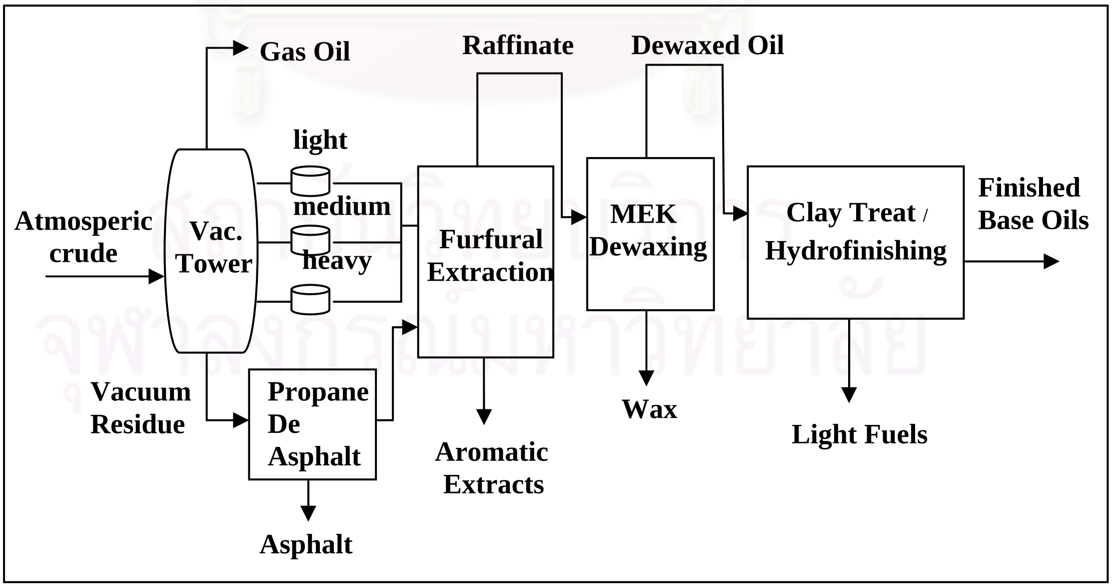


Figure 2.3 Lube processing.

(a) Vacuum distillation

The 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.

(b) Propane deasphlting

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

(c) 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).

(d) 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 cooled to a temperature between 100 °F (-12 °C) and 20 °F (-6 °C) below the desired pour point. The wax crystals which formed are then removed from the oil by filtration.

(e) Hyrofinishing

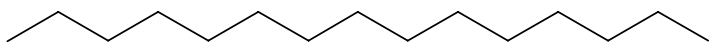
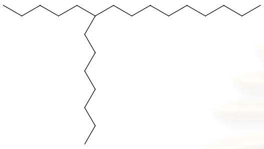
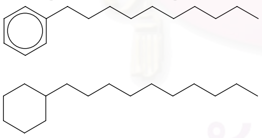
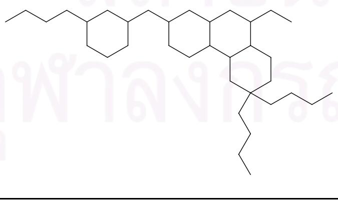
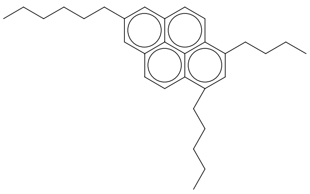
Some base stocks, particularly premium stocks, require a finishing process to improve the color, oxidation, or thermal stability of the base stock. The hydrofinishing process consists of a bed of catalyst through which heated oil and hydrogen are passed. This process removes some of the color and unstable component such as nitrogen and sulfur in the oil.

2.1.3 Base Oil Composition, Properties and Structure Relationship

The petroleum composition used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating composition is a complex mixture consisting primarily of five characteristic classes-paraffin naphthenes, condensed naphthenes, aromatic naphthenes, naphthalene (two ring aromatics) and multi-ring aromatics. It also contains small amounts of heterocyclic compounds containing sulfur and various oxygen containing small amounts of heterocyclic compounds containing sulfur and nitrogen atoms (e.g. thionaphthene, indole quinoline and carbazone) and various oxygen containing compound, including napthenic acids, which account for most of the chemically bond oxygen in petroleum compositions.

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 lubricating oil’s properties can be seen in Table 2.1.

Table 2.1 Lubricating oil properties of some typical hydrocarbon structures [23].

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 linear chains 	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

That 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 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.

2.1.4 Lubricating Oil Additives

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

2.1.4.1 Dispersants-Metallic Types

These compounds were used as detergent. Their function appears to be the factor of a dispersion of the particulate matter rather than one of cleaning up any existing dirt and debris, they are appropriate to categorize them as dispersant. Materials of this type are generally molecules having a large hydrocarbon tail and a polar group head. The tail section, olephilic 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 are such as petroleum sulfonates, Synthetic sulfonates, thiophosphonates and phenol sulfide salts.

2.1.4.2 Dispersants-Ashless Types

A development of major importance in the additive field has been discovered and used of ashless dispersants. These materials may be categorized into two types: high molecule weight polymeric dispersants for formulation of multi-grade oils and lower molecule weight additive 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 purposes are again characterized by a polar group attached a relatively high molecular weight hydrocarbon chain. These compounds are N-substituted long chain alkenyl succinimide, high molecular weight esters for examples.

2.1.4.3 Polymeric Dispersants Additives

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

2.1.4.4 Oxidation and Bearing Corrosion Inhibitors

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

2.1.4.5 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 of 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 protected 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 by products; can be controlled by use the alkaline additive.

2.1.4.6 Viscosity Improvers

Viscosity improvers or viscosity index improvers, 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 temperature which significantly improves the viscosity index of lubricating oil.

2.1.5 Basic Function of Lubricating Oil

The basic functions of lubricating oil are:

2.1.5.1 Friction reduction

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

2.1.5.2 Heat Removal

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

2.1.5.3 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, particulatematter, etc., which generally find their way into lubricating oil employed in various applications.

2.1.6 Necessary Properties of Lubricant

Lubricants are formulated by blending base oil and additives to meet a series of performance specifications. These are 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 standard [International Organization for Standardization (ISO), American Society for Testing and Material (ASTM), Institute of Petroleum (IP), etc.] which are often identical.

2.1.6.1 Physical Properties

(a) Viscosity

Viscosity is the most significant property of lubricant. The primary purpose of a lubricant is to reduce friction and minimize wear by separating surfaces with an oil film. Viscosity is a measure of resistance to flow. It decreases with 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 Say bolt and kinematics viscometer. Kinematics 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.

(b) Viscosity Index

Viscosity index is a reflection of an oil’s resistance to viscosity charge with fluctuation in temperature. The higher the viscosity index of and 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 reduced, not all oils respond to the same degree to temperature changes.

Lubricating oils are subjected to wide variation of temperature in service. At high temperature the viscosity can drop to a point where the oil is so thin that the oil film may break, allowing metal surface 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 start up the oil can be 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 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 oil has a viscosity index of 100 or higher where temperature variations are less or for continuous operation at constant temperature at constant temperature. Viscosity index is less critical.

(c) Pour Point

As 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 thickening 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 oil can be chilled and still be poured from a constrainer is called the “pour point”.

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

(d) 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 product 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 temperature and the type of storage that will preclude the possibility of a fire.

Flash point is also in evaluating used oils. A drop in flash point indicates contamination by dilution on the motor oil with burned fuel. An increased indicates evaporation of the oil. This property is determined by the open-cup method; usually called the Cleveland Open metrof and abbreviated COC.

(e) Color (ASTM D 1500)

The color test was performed by following the ASTM D 1500 method. The oil's color is normally not an indicating 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 application such as in textile machinery lubrication avoid indelible standing of the textile. Absence of color is also important to users of waxes, and white oils where extremely high purity is required.

(f) Sulfur Content

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

(g) Neutralization number

The neutralization number measures the organic acid content of base oils and the acid produced by oxidation in storage or service. The acid number 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 a guide to mechanical condition.

(h) Sulfated Ash

The sulfated ash of a lubricating oil is the residue, in present by weight after burning, treating the initial residue with sulfuric acid, and burning the treated residue. It is measure of the non-combustible (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 sulfur ash test so the concentration of such materials in 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 amount. However, since the test combines all metallic elements are in the oil in the correct amount. 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 gasoline in internal combustion engines.

(i) 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 the carbon dioxide and hydrogen sulfide are present in gas. The water content of petroleum products is important in the refining, purchase, sale, and transfer of products. The simplest method cover the determination of water in petroleum products by distillation method.

2.1.6.2 Chemical Properties

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

A. Oil-insoluble materials, *i.e.*, resin, varnish, or sludge

B. Oil-soluble products, primary acid and peroxide

Resistance to oxidation is important in performance of a lubricant.

Acids formed may be corrosive to metals. Varnish may be deposit on sliding surfaces, causing them to stick or wear. Sludge may plug screens or passages or the rings or cylinders, causing them to be in effective. Resistance to oxidation is extremely important for steam-turbine oil because of the serious consequences of a bearing failure. Transformer oils, gear oils, hydraulic fluid, 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 to oxidation which are designed to correlated with field performance.

C. Oxidation Stability

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricant 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 thermo gravimetric balance (TG) is one of recently technique developed to evaluate thermal behavior of different chemical component. Lose 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 point; *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 oxidative compounds state to carbonize and finally evaporate as CO_2.

2.1.7 Environmental consideration of used lubricating oil [29]

There are three basic disposal methods for used lubricating oil;

(a) Disposal as toxic/hazardous waste

(b) Re-refining to produce base oil

(c) Use as fuel

Of the three basic method of disposal or recycling of used oil, the most efficient in term energy conservation, in that is displaces an equivalent amount of oil, is the use of the material as a fuel. The fuel gas components of principal environmental concern are PCBs PAHs, dioxin and heavy metals. Some pretreatment of the oil will be required to ensure that emission standards for these materials are not exceeded when waste oil is used are fuel. Should this not be possible, the oil must be considered a hazardous waste and treatedaccordingly. Disposal waste oil as hazardous waste requires that it be incinerated at high temperature to ensure complete oxidation of PCBs, PAHs, PCTs. With regard to re-fining, the process is able to generate a product of sufficiently high quality; the principal environmental consideration concerns the disposal of the by products of the refinery process.

2.1.8 Economic aspects of used lubricating oil need of Thailand

As the growth of industries in Thailand, lubricating oil is a choice of demand for a necessary chemical used in the production processes. The more productions, the quantity of oil is needed. Thailand's economic data can be shown in the following Table 2.2

Table 2.2 Important of petroleum crude oil in Thailand [30].

Year	Quantity (million liters)
1993	16,148
1994	18,794
1995	21,336
1996	26,558
1997	36,844
1998	42,348
1999	39,446
2000	40,535
2001	39,242
2002	41,368
2003	42,279

From Table 2.3 shows that the more growth in industrial productions, more demand of lubricating oil in Thailand. Then, if some used lubricating oil can be recycled to the new process, we can save some quantities of oil in use.

2.2 Cracking reaction

2.2.1 Thermal Cracking [24]

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species and cracked by a β-scission mechanism. The most successful present explanation of thermal cracking of hydrocarbon is Rice free radical theory as modified by Kossiakoff and Rick. This will be called the “RK-theory” as follows to explain in the cracking of normal paraffin.

The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom closely approach each other. Radical isomerization is a change of the position of hydrogen atom usually to yields a more stable radical in order of tertiary> secondary> primary free radical.

Cracking of either the original or isomerized radical then takes place at carbon-carbon bond located in the β position to the carbon lacking one of hydrogen atom. Cracking at the β position gives directly an alpha olefin and primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position of any hydrogen atom with respect to the carbon skeleton.

The primary radical derived from this step may immediately recrack at the β bone to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radical are derived from cracking reaction of normal paraffin primary radical thus give only ethylene as the olefin product. Radical isomerization reduced the amount of ethylene, but it still remains the major product. By successive recracking, the radical ultimately are reduced to methyl or ethyl fragments. These radical then react with feedstock molecules to produce new free radicals and themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction.

A schematic representation of polyethylene cracking is as follow;

1. Initiation Step

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \xrightarrow{\text{heat, h}\upsilon} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + R^{\bullet}_2$$

2. Propagation Step

β-fission

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + CH_2{=}CH_2$$

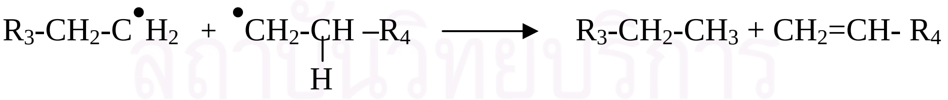
$$R_1\text{-}CH_2\text{-}\overset{H}{\overset{|}{C}}H\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH{=}CH_2 + H^{\bullet}$$

Chain transfer

$$R_1\text{-}CH_2\text{-}(CH_2)_4\text{-}CH_3 + H^{\bullet} \longrightarrow {}^{\bullet}R_1\text{-}CH\text{-}(CH_2)_4\text{-}CH_3$$

3. Termination Step

$$R_1^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}R_2$$



$$R_3\text{-}CH_2\text{-}C^{\bullet}H_2 + {}^{\bullet}CH_2\text{-}\underset{H}{\underset{|}{C}}H\text{-}R_4 \longrightarrow R_3\text{-}CH_2\text{-}CH_3 + CH_2{=}CH\text{-}R_4$$

2.2.2. Catalytic Cracking [24]

Catalytic cracking is the most important and widely used refinery process for converting heavy oil more valuable gasoline and light oil product. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because of more gasoline having a higher octane and less heavy oil and unsaturated gases are product.

Commercial cracking catalysts can be divided into three classes:

1. Acid-treated natural aluminosilicates
2. Amorphous synthetic silica-alumina
3. Crystalline synthetic silica-alumina catalysts (zeolites or molecular sieves).

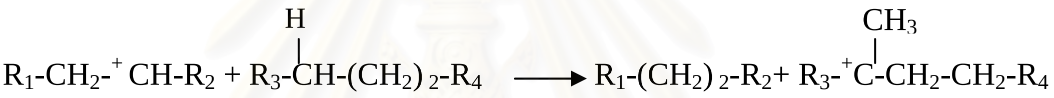
Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate. Compared to the free radical intermediate in thermal cracking. Carbonium ions are longer lived and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbonium ions. There are two possibilities for the initial step in the catalytic cracking of polyolefins. The first involves the simultaneous loss of a hydride ion from the polyolefins molecule and of a proton from the acidic catalyst surface. This produced a carbonmium ion in combination with acid anion and molecule hydrogen:

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 + H^+A^- \longrightarrow R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 + H_2 + A^-$$

Alternatively a small amount of olefin, create by thermal cracking could initiate the reaction;

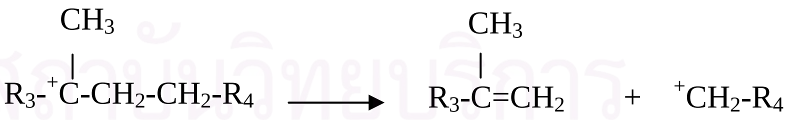
$$R_1\text{-}CH{=}CH\text{-}R_2 \quad + \quad H^{+}A^{-} \longrightarrow R_1\text{-}CH_2\text{-}^{+}CH\text{-}R_2 \quad + \quad A^{-}$$

Chain propagation involves an exchange reaction in which a carbonium ion react with a polyolefins to give a new hydrocarbon and a carbonium ion of the polyolefins to be cracked (hydride transfer).



$$R_1\text{-}CH_2\text{-}^{+}CH\text{-}R_2 + R_3\text{-}\overset{H}{\overset{|}{C}}H\text{-}(CH_2)_2\text{-}R_4 \longrightarrow R_1\text{-}(CH_2)_2\text{-}R_2 + R_3\text{-}^{+}\overset{CH_3}{\overset{|}{C}}\text{-}CH_2\text{-}CH_2\text{-}R_4$$

The next step is the decomposition of the activated molecule. The primary rule involved is that the carbon-carbon cleavage occurs at the position one carbon atom away from the carbonium ion, i.e. β-scission.



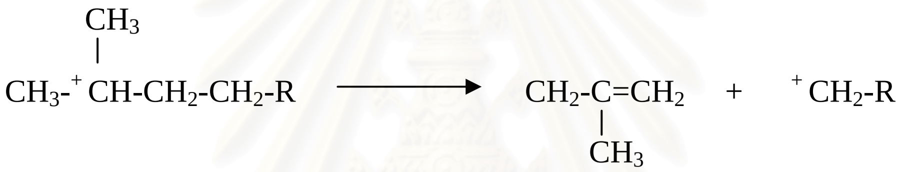
$$R_3\text{-}^{+}\overset{CH_3}{\overset{|}{C}}\text{-}CH_2\text{-}CH_2\text{-}R_4 \longrightarrow R_3\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 \quad + \quad ^{+}CH_2\text{-}R_4$$

A hydride shift then converts the primary carbonium ion formed into a secondary carbonium ion;

$$^{+}CH_2\text{-}R_4 \longrightarrow CH_3\text{-}\,^{+}CH_2\text{-}R_4$$

Subsequent step involve further β-scission and hydride transfer and proceed unit the chain becomes so short that cracking at the β-scission is no longer a rapid reaction. Large amounts of iso-compounds are formed in catalytic cracking. This is readily explained by the rearrangement of the secondary carbonium ion:

$$CH_3\text{-}CH_2\text{-}{}^{+}CH\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow {}^{+}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_2\text{-}R$$



$$CH_3\text{-}{}^{+}\overset{\overset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow CH_2\text{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2 \; + \; {}^{+}CH_2\text{-}R$$

The reaction model of hydrocarbon cracking on activated carbon was shown is figure 2.4

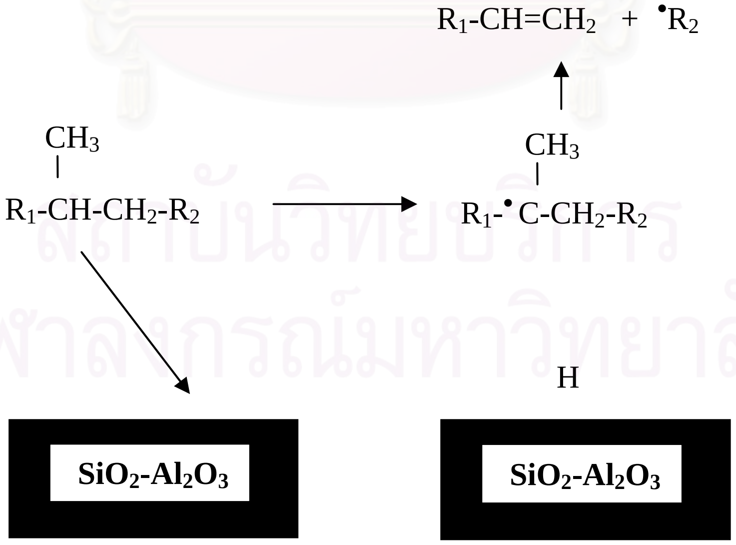
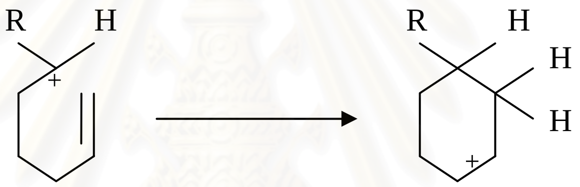


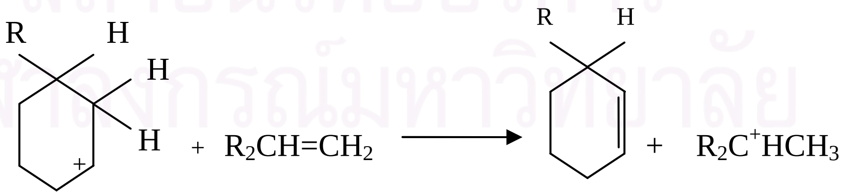
Figure 2.4 Reaction model of hydrocarbon cracking on $SiO_2\text{-}Al_2O_3$ [25].

Aromatization of paraffins can occur through a dehydrocyclization reaction. Oliefinic compounds formed by the beta scission can form a carbonium ion intermediate with the configuration conductive to cyclization. For example, if a carbonium ion such as that how below is formed (by any of the methods mentioned earlier), cyclization is likely to occur.

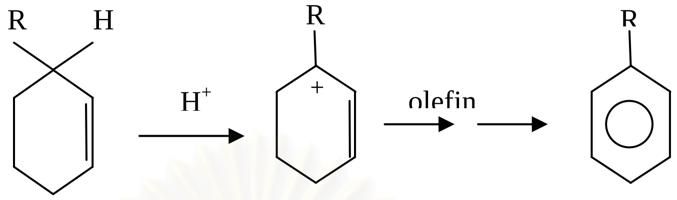
$$RCH_2CH_2CH_2CH_2CH_2{=}CH_2 \xrightarrow{\text{catalyst}} \overset{+}{R}CHCH_2CH_2CH_2CH{=}CH_2$$



Once cyclization has occurred, the formed carbonium ion can lose a proton, and a cyclohexene derivative is obtained. This reaction is acidic by the presence of an olefin in the vicinity (R-CH=CH_2).



The next step is the abstraction of a hydride ion by a lewis acid site from the catalyst surface to from the more stable allylic carbonium ion. This is again followed by a proton elimination to form a cyclohexadiene intermediate. The same sequence is followed until the ring is completely aromatized.



During the cracking process, fragmentation of complex polybnumlear cyclic compounds may occur, leading to formation of sample cycloparaffins. These compounds can be a source of C_6, C_7, and C_8 aromatics through isomerization and hydrogen transfer reactions.

Coke formed on the catalyst surface is thought to be due to polycondensation of aromatic nuclei. The reaction can also occur through a carbonium ion intermediate of the benzene ring. The polynuclear aromatic structure has a high C/H ratio.

2.2.3 Hydrocracking Processing [31]

Hydrocracking is essentially catalytic cracking the presence of hydrogen. It is one of the most versatile petroleum refining schemes adapted to process low value stocks. Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene. The process can also use feeds with high aromatic content. Products from hydrocracking process lack olefinic hydrocarbons. The product state ranges from light hydrocarbon gases to gasoline to residues.

Table 2.3 Analysis of products from hydrocracking process [31].

Yields: Typical from Various feeds: Feed	Naphtha	LCCO	VGO	VGO
Catalyst stages	1	2	2	2
Gravity, °API	72.5	24.6	25.8	21.6
Aniline pt, °F	145	92	180	180
ASTM 10% EP, °F	154/290	478/632	740/1,050	740/1,100
Sulfur, wt%	0.005	0.6	1.0	2.5
Nitrogen, ppm	0.1	500	1,000	900
Yields, vol.%				
Propane	55	3.4	-	-
Iso-Butane	29	9.1	3.0	2.5
n-Butane	19	4.5	3.0	2.5
Light naphtha	23	30.0	11.9	7.0
Heavy naphtha	-	78.7	14.2	7.0
Kerosene	-	-	86.8	48.0
Lt. Naphtha ROC cl	85	76	77	76
Hv. Naphtha ROC cl	-	65	61	61
Kerosene freeze pt, °F	-	-	-65	-75
Diesel pour pt, °F	-	-	-	-10

The dual-function catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites. Amorphous silica-alumina, zeolites, or mixture of them promote carbonium ion a high iso/normal ratios. The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements. As with catalytic cracking, the main reactions occur by carbonium ion and beta scission, yielding two fragments that could be hydrogenated on the catalyst surface. The main hydrocracking reaction could be illustrated by the first step formation of a carbonium ion over the catalyst surface:

$$\mathrm{R\ CH_2CH_2R'} \xrightarrow{\text{catalyst}} \mathrm{RCH_2CHR'} + \mathrm{H^+}$$

The carbonium ion may rearrange, eliminate a proton to produce an olefin, or crack at a beta position to yield to an olefin and a new carbonium ion. Under an atmosphere of hydrogen and in the presence of a catalyst with hydrogenation-dehydrogenation activity, the olefins are hydrogenated to paraffinic compounds. This reaction sequence could be represented as follows:

$$\mathrm{RCH_2\overset{+}{C}HR'} \xrightarrow{-\mathrm{H}^+} \mathrm{RCH{=}CHR'}$$

$$\mathrm{RCH_2\overset{+}{C}HHR'} \xrightarrow{\text{B scission}} \mathrm{R'CH{=}CH_2} + \mathrm{R^+}$$

$$\mathrm{R'CH{=}CH_2} + \mathrm{H_2} \xrightarrow{\text{Catalyst}} \mathrm{R'CH_2CH_3}$$

As can be anticipated, most products from hydrocracking are saturated. For this reason, gasoline from hydrocracking units have lower octane ratings than those produced by catalytic cracking units; they have a lower aromatic content due to high hydrogenation activity, products from hydrocracking units are suitable for jet fuel use. Hydrocracking also produces light hydrocarbon gases (LPG) suitable as petrochemical feedstock.

Other reactions that occur during hydrocracking are the fragmentation followed by hydrogenation (hydrogenolysis) of the complex asphaltenes and heterocyclic compounds normally present in the feeds. Hydroracking reaction conditions vary sidely, depending on the feed and the required products. Temperature and pressure range from 400 to 480°C and 35 to 170 atmospheres, respectively. Space velocities in the range of 0.5 to 2.0 hr^{-1} are applied.

2.3 Basic Principles of Catalysis [32]

In the study of reacting chemical system, two considerations are of importance. The first is chemical thermodynamics, the second is reaction kinetics. The thermodynamics of the system determines the maximum attainable yield of products under specified conditions. It is a fundamental principle of thermodynamics that changes in Gibbs free energy G, enthalpy H and entropy S depend only upon the initial and final states of the systems, and not upon the path taken to move from one to the other. The kinetic parameters, rate coefficient k, activation energy E, order of reaction. These parameters depend on the sensitivity on the path followed, and the introduction of a catalyzed pathway changes not only the values of these parameters, but also their significant. Classical kinetics based on collision theory is then really on little help, and theoretical discussion has necessarily to be based ion the absolute rate theory. It must first be emphasized, and this is another implication of our definition, that a catalyst can increase the rate only of a reaction that is already thermodynamics as are unanalyzed reactions. Catalyst decreases the activation energy of a reaction. This must mean that catalyzed reaction proceeds by a new and energetically more favorable partway.

It is possible to divide catalytic systems into two distinct categories, homogeneous catalysis and heterogeneous catalysis. With heterogeneous catalysis, concerns with the specific chemical properties of the surface of the chosen substance. These of course reflect the chemistry of the bulk solid, and some useful insight into the catalytic activities of surfaces is gained from knowledge of the bulk properties of the solid.

Table 2.4 presents a preliminary classification of solids into group. This table may be in part interpreted using the qualitative concept of compatibility between catalyst, reactants, and products.

Table 2.4 Classification of heterogeneous catalysts.

Class	**Functions**	**Examples**
Metals	Hydrogenation Dehydrogenation Hydrogenolysis	Fe, Ni, Pd, Pt, Ag
Semiconducting oxides and sulphides	Oxidation Dehydrogenation Desulphurization	NiO, ZnO, MnO_2, Cr_2O_3, Bi_2O_3-MoO_3, WS_2
Insulator oxides	Dehydration	Al_2O_3, SiO_2, MgO
Acids	Polymerization Isomerization Cracking Alkylation	H_3PO_4, H_2SO_4, SiO_2-Al_2O_3, zeolites

This table also shows that transition metals are especially good catalyst for reaction involving hydrogen and hydrocarbon. This is because these substances readily adsorb at the surfaces of metals, in a manner to be described in more detail below, and except in a few cases the reaction does not precede below the surface.

2.4 Metal Catalysts [33]

For a molecule to react catalytically as a metal surface, it must first be chemisorbed. When two molecules react, at least one and probably both must be chemisorbed. Chemisorption is an essential step in the preparation of a molecule for reaction: indeed a chemisorbed molecule sometimes resembles the product into which it will be transformed more than does the free molecule. The effect of chemisorption can also be very like that of raising a molecule it its first electronically excited state; physical adsorption on the other hand has little direct relevance to catalysis.

For metals, relationships have been sought between collective properties and catalytic behavior. The metallic state was generally described by the simple band model or the Pauling valence structure theory, in metal the valence shell is formed by s or d band. The main-group elements with their s bands are typical electron donors and form strong bonds with electron acceptors such as sulfur or oxygen; stable sulfides and oxides are formed. These metals are therefore not suitable as catalysts. In contrast the transition metals with their d bands are excellent catalysts. It is noted worthy that both hydrogenations and oxidations can be carried out with d-block elements.

Let us now describe the electronic structure of the transition metals with the aid of the band model. According to this model the metal is a collective source of electrons and electron holes (Figure 2.5). In a row of the periodic table, the metals on the left have fewer d electrons to fill the bands. There are two regions of energetic states, namely, the valence band and the conduction band with mobile electrons or position holes. The potential energy of the electrons is characterized by the Fermi level, which corresponds to the electrochemical potential of the electrons and electron holes.

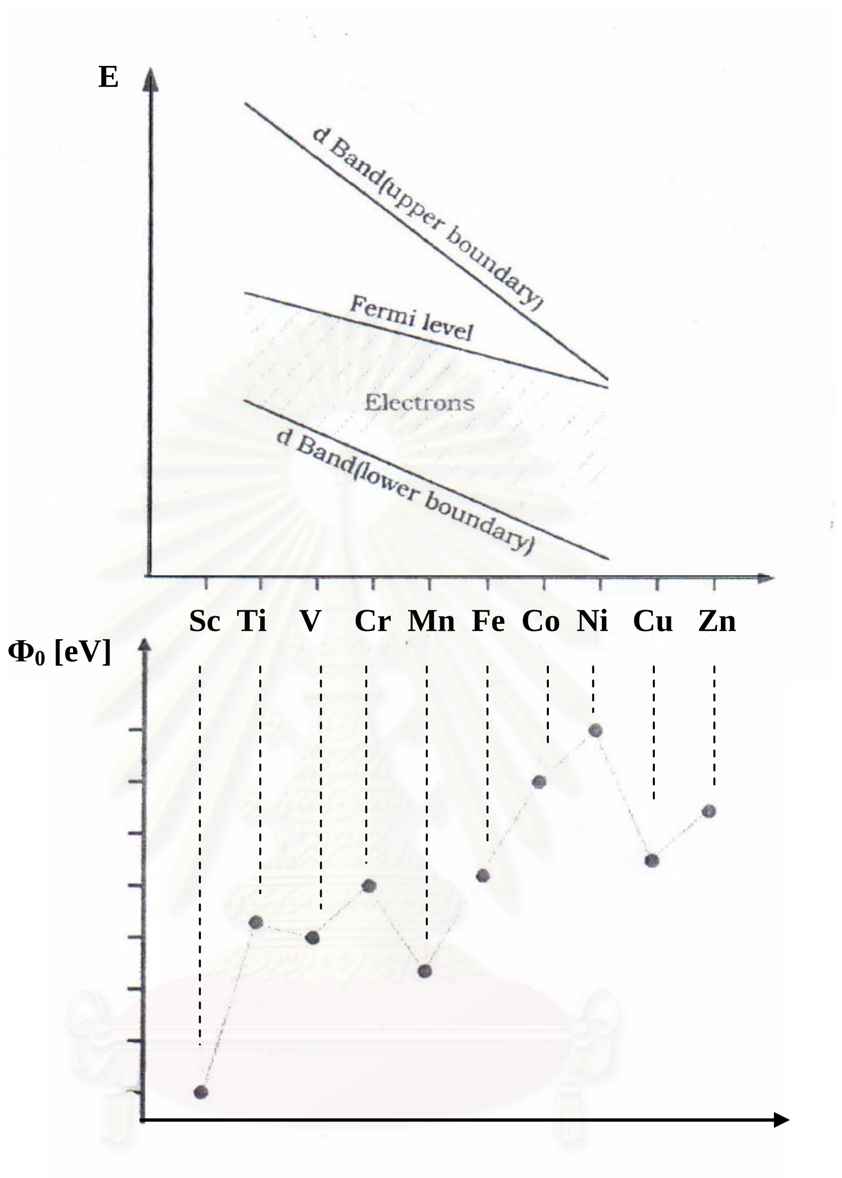


Figure 2.5 Electron density of the 3^{rd} band and work function ϕ of the transition metals of the fourth period [33].

The position of the Fermi level also indicates the number density of electrons in the band model. The energy required to transport an electron from the edge of the Fermi level into vacuum corresponds to the work function ϕ (Figure 2.6a). For the d-block metals, the work function is around 4 eV and therefore in the UV range.

A certain number of free levels or d-holes are available for bonding with adsorbates. The lower the Fermi level, the stronger the adsorption. How do donors and acceptors function in the band model. In the surface layer, the free electrons or holes allow molecules to be bound to the surface, whereby the strength of binding depends on the position of Fermi level. An acceptor removes electron density from the conduction band of the metal as a result of which the Fermi level drops to E_F and the work function $\Phi_A > \phi_O$ (Figure 2.6b). A donor donates electrons to the conduction band of the metal, and the work function becomes corresponding lower: $\Phi_A < \phi_O$ (Figure 2.6c).

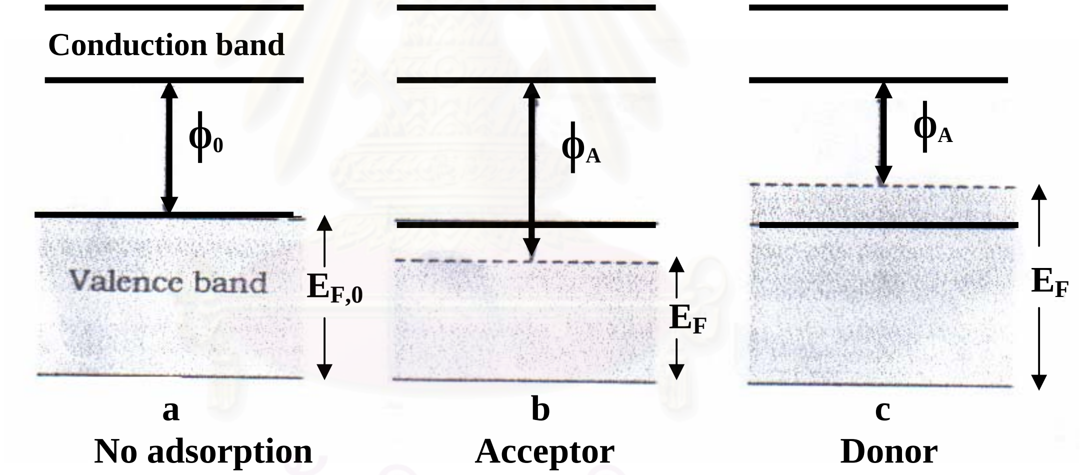


Figure 2.6 Acceptor and donor function according to the band model [33].

a) No adsorption ; b) Acceptor ; c) Donor

$E_{F,O}$ = Fermi level ; E_F = Fermi energy

Metals normally have a narrow d band. The catalyst properties are strongly influenced by the occupational density of the electrons in this band. In many cases a direct relationship has been found between the catalytic activity of transition metals and the electronic properties of the unfilled d bands. This is shown by the general trend of the rate of adsorption along the transition metal rows. For molecular species it was found that the rate of dissociative adsorption on the nobel metals increases from right to left as a function of the d-band occupation. Besides the electron occupation of the d bands, another description can be used for obtaining correlations, namely, the valence bond theory of metals. The bonding in transition metal is partially due to unpaired electrons in bonding d orbital. The contribution of these d electrons to the valence bonding was termed "percentage d character" of the metallic bonding by Pauling, who made a distinction between three types of d orbital in transition metals:

- Bonding d orbital involved in covalent d s p hybrid bonds
- Metallic (free) d orbital
- Atomic d orbital

2.4.1 Impregnation [27]

Two method of contacting may be distinguished. The support is sometimes dipped into an excess quantity of solution, where upon the uptake is the sum of solution occluded in the pore plus material adsorbed into the pore surfaces. If two or more compounds are present, they are frequent adsorbed on the support surface in a ration different from that the solution must take these effects into account. Moreover, material may be dissolved from the support into the treating solution. More precise control achieved by a technique termed dry impregnation or impregnation to incipient wetness, which is commonly used industrially. A batch of support is tumbled and sprayed with a solution of appropriate concentration, corresponding in quantity to the total known pore volume of the support, or slightly less. This allows accurate control of the amount of the active ingredient that will be incorporated into the catalyst, but the maximum loading obtainable in a single impregnation is limited by the solubility of the reagent. The resulting catalyst is then usually dried and calcined.

In the few cases, the active ingredient may be fixed inside by immersing the impregnated catalyst in a reagent to cause precipitation, occur oxide supports such as alumina and silica are readily wet by aqueous solutions. Capillary forces then ensure that liquid is sucked into the entire porous structure. Because of capillary pressure, even pore closed at on end are nearly filled, and the solution of gas in the liquid assist the process. If the support is not readily wetted, e.g., a carbon that is highly graphitized or without chemisorbed oxygen, an organic solvent may be used or the support may be impregnated under vacuum. These procedures are somewhat more costly to use in the plant incipient impregnation.

2.4.2 Catalyst support [27]

The early concept of a support or a carrier was of an inert substance that provided a means of spreading out an expensive catalyst ingredient such as platinum for its most effective use, or a means of improving the mechanical strength of the inherently weak catalyst. However, the carrier may actually contribute catalytic activity, depending on the reaction and reaction condition, and it may react to some extent with other catalyst ingredient during the manufacturing process. It can also help stabilize the catalytically active structure. The carrier may be used as pellets or powders to be impregnated, a powdered carrier may be incorporated into a mixture to be precipitated, or the carrier may itself be precipitated from the solution in manufacturing process.

Some substance such as colloidal alumina or silica may play a double role, acting as a binding agent in catalyst manufacturing and as a carrier in the ultimate product. Alumina in the gamma form is intrinsically weakly acidic, but such a substance may be a truly inert carrier for many reactions. In other cases it can be used by itself as a catalyst, as in dehydration of an alcohol. High area carrier is sometimes loosely referred to as active carrier in contrast to low area inert carrier, but this usage may be misleading.

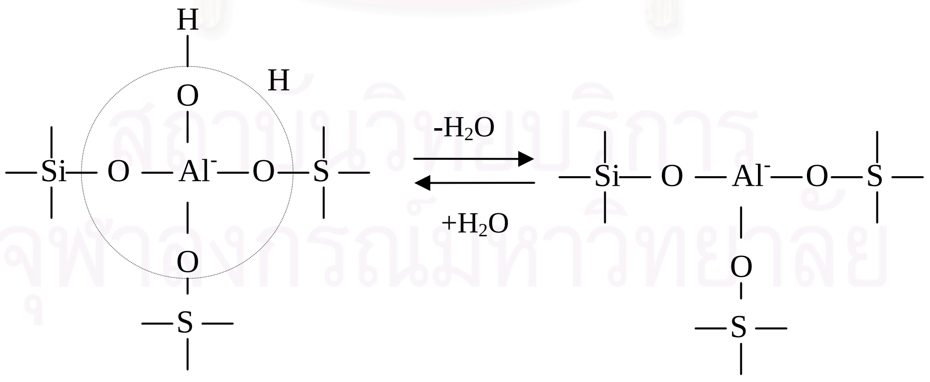
The selection of a carrier is based on its having certain desirable characteristics. In addition to possible chemical effects certain physical properties are importance:

1. Inertness to undesired reaction
2. Desirable mechanical properties, including attrition resistance, hardness, and compressive strength
3. Stability under reaction and regeneration conditions
4. Surface area (high surface area is usually, but not always, desirable)

5. Porosity, including average pore size and pore-size distribution (high area implied fine pores, but relatively small pores, such as less than 2 nm, may become plugged in catalyst preparation, especially if high loadings are sought.)
6. Low cost

2.4.3 SiO_2-Al_20_3 [27]

In the case of silica-alumina or similar mixed-oxide catalysts, the source of acidity may be rationalized in terms of a theory developed largely by Paul-ing. If an aluminum ion, which is trivalent, is substituted isomorphously for a silicon ion, which is quadrivalemt, in a silica lattice comprising silica tetrahedral, the net negative charge must be stabilized by a nearby positive ion such as a proton. This can be produced by the dissociation of water, forming a hydroxyl group on the aluminum atom. The resulting structure, in which the aluminum and the silicon are both tetrahedrally coordinated, is a Brönsted acid.



Brönsted acid

Lewis acid

Figure 2.7 Postulated structures of silica-alumina causing Brönsted and Lewis activity.

If this is heated, water of constitution is riven off and Brönsted acid sites are converted to Lewis acid sites as shown in scheme 2.1. Some metal atoms are now three-coordinated and some four-coordinated. The reverse can also occur.

The addition of water and heating can convert Lewis acid sites back to Bronsted acid sites. The aluminum atom is eletrophilic and can react with hydrocarbons to form an adsorbed carbonium ion, as illustrated below for the two kinds of sites.

Silica-alumina, which is amorphous, typically has a maximum degree of acidity and activity at an Al/Si atomic ratio of less than unity. This can be rationalized by the concept that –Al-O-Si- type of bonds are desired but not the –Al-O-Al- type and that formation of the former is enhanced by an excess of silica gel. This further implies that the detailed procedures used in manufacture may have a significant effect on activity at a specified Al/Si ratio. Alumina is more expensive than silica, so an excess of silica is also preferred for economic reasons. Pure silica of itself shows no acidic or basic properties, although commercial samples may exhibit a low amount of acidity because of the presence of impurities. A pure alumina may exhibit an acid concentration comparable to that of silica.

2.4.4 Al_20_3 [27]

The most important aluminas for use as a carrier are γ-Al_2O_3 or η-Al_2O_3, which have high area and are relatively stable over the temperature range of interest for most catalytic reactions. They are very similar in structure and indeed sometimes are not easily distinguishable. Both have a crystallographic from in which the oxygen atoms are arranged similarly to that in spinel ($MgAl_2O_4$), but the η form is more distorted than the γ form. The η form is inherently more acidic than the γ form, which makes it more active for many acid-catalyzed reactions such as olefin isomerization. All the oxygen ions in a spinel structure are equivalent, forming a close-packed cubic arrangement. The oxygen ions are much larger than the cations, and the latter fit into two kinds of gaps, octahedral (surrounded by six atoms) and tetrahedral (surrounded by four atoms), that exist between the oxygen ions in the structure. A large number of mixed oxides exist in the spinel structure, which is expressed in the general form $M^{II}M^{III}O_4$. Some single oxides also from this structure, for example, Mn_3O_4, Fe_3O_4 and Co_3O_4.

Aluminas are generally prepared by dehydration of various aluminium hydroxides, but even if the hydroxide is a gel, it is resdily converted to a crystalline from on aging and/or heating. The particular crystalline from obtained depends in a rather complicated way upon the time-temperature-environmental history to which the hydroxide is subjected, and this may be difficult to control, especially on a large scale. The aluminas contain water of constitution, which is slowly removed by heating, but it may amount to several tenths of a percent even at 1000°C. Aluminas may also contain various amounts of impurities, such as sodium and iron, as a result of the manufacturing process. For some catalyst uses these impurities are detrimental, and the catalyst manufactures or their suppliers may go to considerable pains to make their own active alumina by a special process starting with high-purity aluminium metal or aluminium compounds.

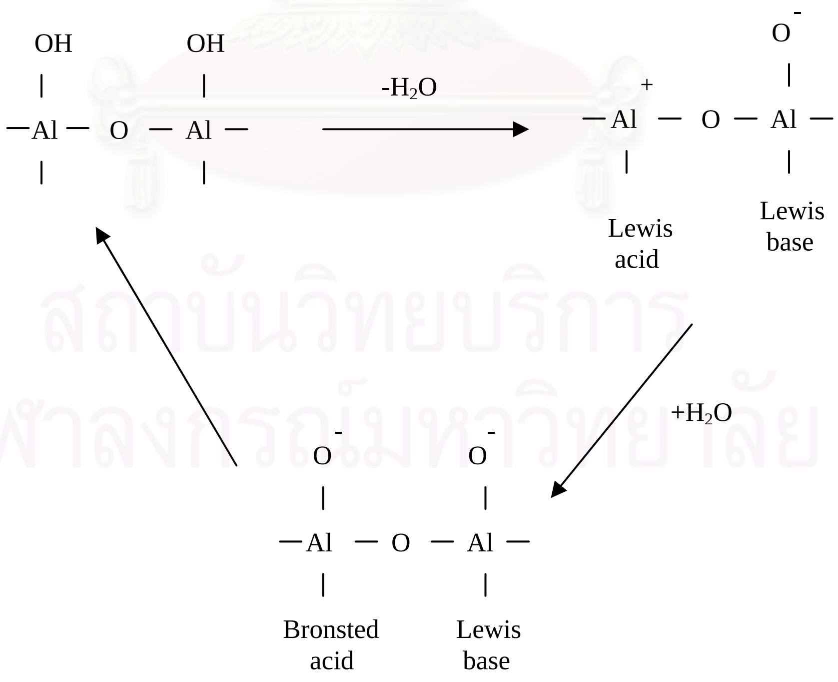
Crystallographically, the atomic ratio of total metal atoms is 3:4 for a spinel but only 2:3 for alumina. Hence for aluminas such as η and γ a portion of the gaps are vacant and there are varying degrees of disorder. This may be the principle reason for the greater solubility and compound formation between heavy metal cations and γ-alumina than between heavy metal cations and silica, which occur upon heating. In particular, aluminates and spinel-type structures may be formed between γ-alumina and a supported catalyst. These may have little catalytic activity. Aluminates in general are formed more readily than silicates. Aluminas react more readily with other species present during a phase change, a phenomenon that seems to be observed for solids in general and is sometimes termed the Hedvall effect.

A common manufacturing process for aluminas starts with sodium aluminate produced in conjunction with the Bayer process for purification of bauxites prior to their reduction to aluminum metal. Bauxite is dissolved in sodium hydroxide to form sodium aluminate. After separation of undissolved impurities, the solution is diluted with water to cause hydrolysis and precipitation of α-alumina trihydrate (gibbsite).

$$2NaAlO_2 + 4H_2O \longrightarrow Al_2O_3{\cdot}3H_2O + 2NaOH$$

Gibbsite can also be prepared by other procedures, but it always contains at least 0.2 to 0.3% Na2O, even after washing with hydrochloric acid.

Alumina (Al_2O_3), the acidic component in dual function catalyst, exist in several distinct forms: the gamma form or the alpha form, depending on the method of preparation and subsequent treatment. Surface acidity can be increase by impregnation with promoters (e.g. Cl^- and F^-). Activated aluminas are amphoteric, containing either acidic or basic sites of varying strength. As show in Fig 2.7, if γ-alumina is heated above 800K, the residual water is driven off to generate a catalytically inactive from know as α- alumina. Activated aluminas are often use as supports, where they provide a large surface area on which catalysts (metal) can be highly dispersed.



Acidic and basic sites on aluminas

Fig 2.8 Acidic and basic sites on aluminas.

The acid strength of alumina may be deliberately increased by incorporation of halogen ions such as chloride and fluoride. The effect is to increase the acid strength, although not the total number of acid sites. Direct treatment with an aqueous mineral acid may cause partial solution or other undesirable alterations in the alumina structure. Hence the alumina may instead be contacted with an organohalogen compound in the vapor phase at an elevated temperature. This decomposes to provide the acid vapor in a dilute form, which is adsorbed onto the alumina. Alternatively, alumina might be impregnated with, say, NH4F, and then calcined to incorporate up to several percent of fluoride into the structure. The halogen replaces a hydroxyl group and, having a higher electron affinity than a hydroxyl group, causes the residual hydrogen on the surface to be more acidic.

2.5 Literature Reviews

Lumberton J.L., Touzeyidio M., Guisnet M. [33], studied the reaction of catalytic hydroprocess simulated coal tars in activity of sulphided Ni-Mo/Al_2O_3 catalyst for the Hydroconversion of Model Compounds. The conversion of tars from coal pyrolysis into light aromatics, such as BTX (benzene-toluene-xylene) and naphthalene, requires the hydrocracking of heavy polyaromatics in the presence of nitrogen and oxygen containing compounds. The hydroconversion of phenenthrence, which occurs through bifunctional catalysis, was chosen as a model reaction. It was carried out over a sulphided Ni-Mo/Al_2O_3 catalyst in the presence of carbazole and 1-naphthol. Carbazole poisons slightly through coking both the hydrogenation and the acid sites of the catalyst. 1-naphthol has a more significant deactivating effect: the hydrogenation sites of the catalyst are poisoned by the water eliminated from 1-naphthol and the acid sites by coke generated by 1-naphthol. Lastly, the hydrogenation activity of the catalyst is not substantially affected in the presence of carbazole and 1-naphthol, but its cracking activity is much reduced, making it impossible for the catalyst to achieve the hydrocracking of phenanthrene into light aromatics.

Sriwanichanichapoom S. [19], studied the catalytic hydrotreatment of used lubricating oil by catalysts. The Co-Mo/Al_2O_3 catalyst can produced the product oils which had the best ASTM color, acidity and viscosity index. Ni-Mo/Al_2O_3 catalyst produced the product oils which had the lowest sulfur content while Ni-W/Al_2O_3 catalyst produced the product oils which had the best viscosity and flash point.

Nakamura *e al.* [34] studied the liquefaction of polypropylene using metal free active carbon, 5% Fe supported active carbon with and without adding CS_2 at low reaction temperature. The reaction was conducted in a batch apparatus using a conventional shaking autoclave with an inner volume of 75 ml. The reaction conditions were temperature; 380-400°C, reaction time; 1 h, initial hydrogen pressure; 3.0 Mpa, PP; 10 g, catalyst, 0.3 g, CS_2; 0.03 g.

In the Fe/A.C.-CS_2 system, little solid residue remained, yield of naphtha, kerosene and gas oil was very high (92 wt. %) and the product was colorless. At both of reaction temperature gave the same results that in three system of catalysts showed good activity for liquefaction of PP but yield of distillate such as naphtha, kerosene and gas oil was in order Fe/A.C.-CS_2 > Fe/A.C and A.C., respectively.

Sato Y. [35], studied how to improve heavy fraction of distillation oil from liquid Wondoan coal by catalyst Co-Mo and Ni-Mo on site of alumina. Found that temperature 390°C by product is amount of toluene and xylene, if temperature higher than by product amount of n-paraffins.

Ali M.A., Tatsumi T., Masuda T. [36], studied the hydrocracking of vacuum gas oil (VGO) with Ni-W and Ni-Mo were load on β-zeolite in combination with amorphous silica alumina (ASA) in fixed bed reactor. The reaction conditions for hydrocracking were 380°C and 14 h. Found that Ni-Mo/β-zeolite + ASA gave higher % yield of naphtha than Ni-W/β-zeolite + ASA and NiW/β-zeolite, respectively (23.4%, 20.6% and 20.2%). Because of β-zeolite alone and combination with the ASA, has a potential as a support for developing heavy oil hydrocracking catalysts. A balance of weak and strong acidities of β-zeolite provides control cracking, while high surface area of ASA may be useful for producing stable hydrocracking and hydrotreating catalysts.

Chang J., Fujimoto K., Tsubaki N. [37], studied the hydrothermal cracking of heavy oil with NiMo/Al_2O_3 in condition of hydrogen gas 5.0 MPa, temperature 430°C take 7.4% yield of naphtha. Addition 0.1 g of di-tert-butyl-peroxide (DTBP) into the feed with NiMo/Al_2O_3 found higher % yield of naphtha (9.6%) than NiMo/Al_2O_3 only. According to the reaction mechanism of hydrothermal cracking, some free radical initiators, such as DTBP was added into the feed to generate free radicals at lower temperature and might easily generate free radicals under the reaction temperature.

Bhaskar T., Uddin M.A., Muto A. [38], studied the recycling of waste lubricant oil from automobile industry with Fe/SiO_2-Al_2O_3, Fe/SiO_2 and Fe/Al_2O_3. The reaction conditions were 400°C at atmospheric pressure. Fe/SiO_2 catalyst decreased the sulfur content from 1640 to 90 ppm and produced low molecular weight hydrocarbons by cracking the high molecular weight hydrocarbons. Fe_2O_3 crystalline size was found to be smaller in Fe/SiO_2 catalyst than Fe/Al_2O_3 and Fe/SiO_2-Al_2O_3 catalysts. The Fe/SiO_2-Al_2O_3 (86%) and Fe/Al_2O_3 (90%) catalysts could decreased the sulfur content, with the increased the reaction time, the desulfurization activity was found to decrease because this might be due to the coke position on the catalysts.

CHAPTER III

EXPERIMENTAL

3.1 Raw material and Chemical

The used lubricating oil supplied from Bangsue train station. The SiO_2-Al_2O_3, grade 135 and Al_2O_3 were used as catalyst supported from Aldrich Company, Inc and AJAX respectively. Hydrogen gas (purity 99.5% minimum). Ferric nitrate nanohydrate was purchased from Fluka and Carbon disulfide (AR grade) was used as solvent for GC Simulate Distillation from Beck Thai Co., Ltd.

3.2 Apparatus and Instruments

3.2.1 The cracking unit

The reaction of used lubricating oil with Fe/SiO_2-Al_2O_3, Fe/Al_2O_3 and Ni/Al_2O_3 were carried out by using apparatus (shown in figure 3.1). The micro-reactor is a stainless steel tube (SS.316) with an inner volume of 70 cm^3, 30 mm inside diameter (shown in figure 3.2). It was heated by 450 watt electricity and temperature was measured by thermocouple type K having 1.6 mm diameter with and accuracy ±5°C by means of a programmable temperature controller. A speed motor was used to control the shaking rate of micro-reactor.

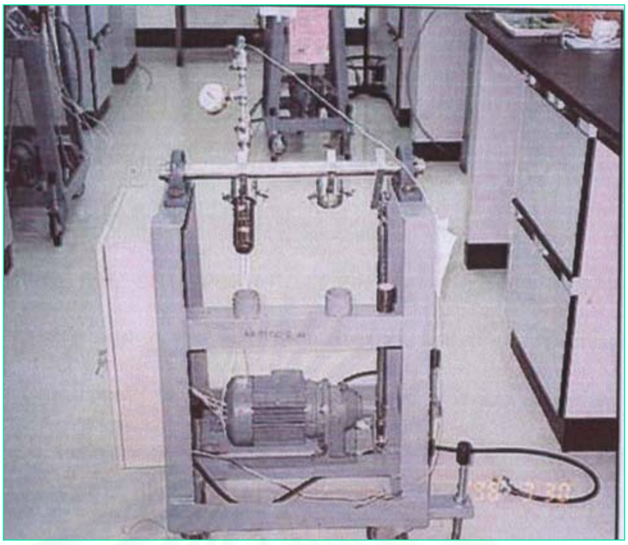


Figure 3.1 Apparatus for catalytic cracking reaction experimental**.**

Figure 3.2 Micro-reactor for reaction experimental.

3.2.2 Vacuum pump

The separation of liquid products from catalyst and residue by the vacuum filter pressure 1 kg/cm^2 show in figure 3.3

Figure 3.3 Vacuum Pump.

3.2.3 Simulated Distillation Gas Chromatography (DGC)

Agilent Technology model 7683 series as ASTM D 2887, analyzing the boiling distribution determination by distillation was simulated by the use of Simulate Distillation Gas chromatography at Fuels Research Center Chemical Technology, Chulalongkorn University. A non polar packed or open tubular (capillary) gas chromatographic column was used to elute the hydrocarbon components of the sample in the order of increasing boiling point. The column temperature was raised at a reproducible linear rate and area under the chromatogram was recorded through out the analysis. Boiling points were assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons converting the boiling range expected in the sample. The boiling range distribution was obtained. The apparatus was show in figure 3.4

Figure 3.4 Simulated Distillation Gas Chromatography (DGC).

3.2.4 Fourier-Transform Infrared Spectrometer (FT-IR)

FTIR, Thermo and model DF3C206 A, at Chemical Technology department, Chulalongkorn University was used to analyzed the functional group of oil products. The apparatus was show in figure 3.5

Figure 3.5 Fourier-Transform Infrared Spectrometer (FT-IR)

3.3 Experimental Procedure

3.3.1 The processes prepared for catalyst are as follows [33]:

3.3.1.1 A preparation of iron on SiO_2-Al_2O_3 catalyst (Fe/SiO_2-Al_2O_3) has been done through impregnation method with different percentage of iron at, 0.5, 1, 3 and 5%

3.3.1.2 About 100 g of each type of catalyst are prepared with the following steps:

- The 5% Fe supported on SiO_2-Al_2O_3 (5% Fe/ SiO_2-Al_2O_3) was prepared by wet impregnation method using excess water [33]. Ferric nitrate nanohydrate ($FeN_3O_9 \cdot 9H_2O$) was dissolved in deionized water to Fe concentration of 5% (calculation of Fe concentration was shown in Appendix C) and then loaded on to SiO_2-Al_2O_3 by wet impregnation under continuous agitation and heated at 80°C.

This slurry was dried at 120°C for 24 hrs. and thermally treated at 600°C to remove the nitrate or ammonium group. Finally, the sample was reduced in hydrogen gas at 400°C for 2 hrs. and keeping it cool at room temperature, catalyst usable for the intended purposes will be given.

3.3.2 The physical property analysis of 0.5, 1, 3 and 5% Fe/SiO_2-Al_2O_3

3.3.2.1 The contents of Fe impregnated on SiO_2-Al_2O_3 were determined by using a SISONA 9410 X-ray fluorescence spectrometer at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

3.3.2.2 BET surface area of catalysts were determined by using Micromeritics adsorptometer, model ASAP 2020, at Fuels Research Center Chemical Technology, Chulalongkorn University.

3.3.3 Catalytic cracking reaction procedure

Weighing 20 g of used lubricating oil and 0, 2.5, 4.0 and 6.0 wt. % of catalysts were fed in 70 ml micro-reactor under hydrogen pressure. Heating coil, insulator, and thermocouple were set up with reactor. The reactor was fixed with a shaker at 120 rpm for required reaction time. The parameters were reaction temperature, reaction time, initial hydrogen pressure and the mass of catalyst were investigated.

The raw material was converted under the following condition:

- Reaction temperature range from 390 to 470°C.
- Reaction time range from 45 to 90 minutes.
- Initial hydrogen pressure range from 0 to 200 psi.
- Mass of Fe/ SiO_2-Al_2O_3 catalyst range from 0.5 to 1.2 g.

The experimental scheme was shown in **figure 3.6**

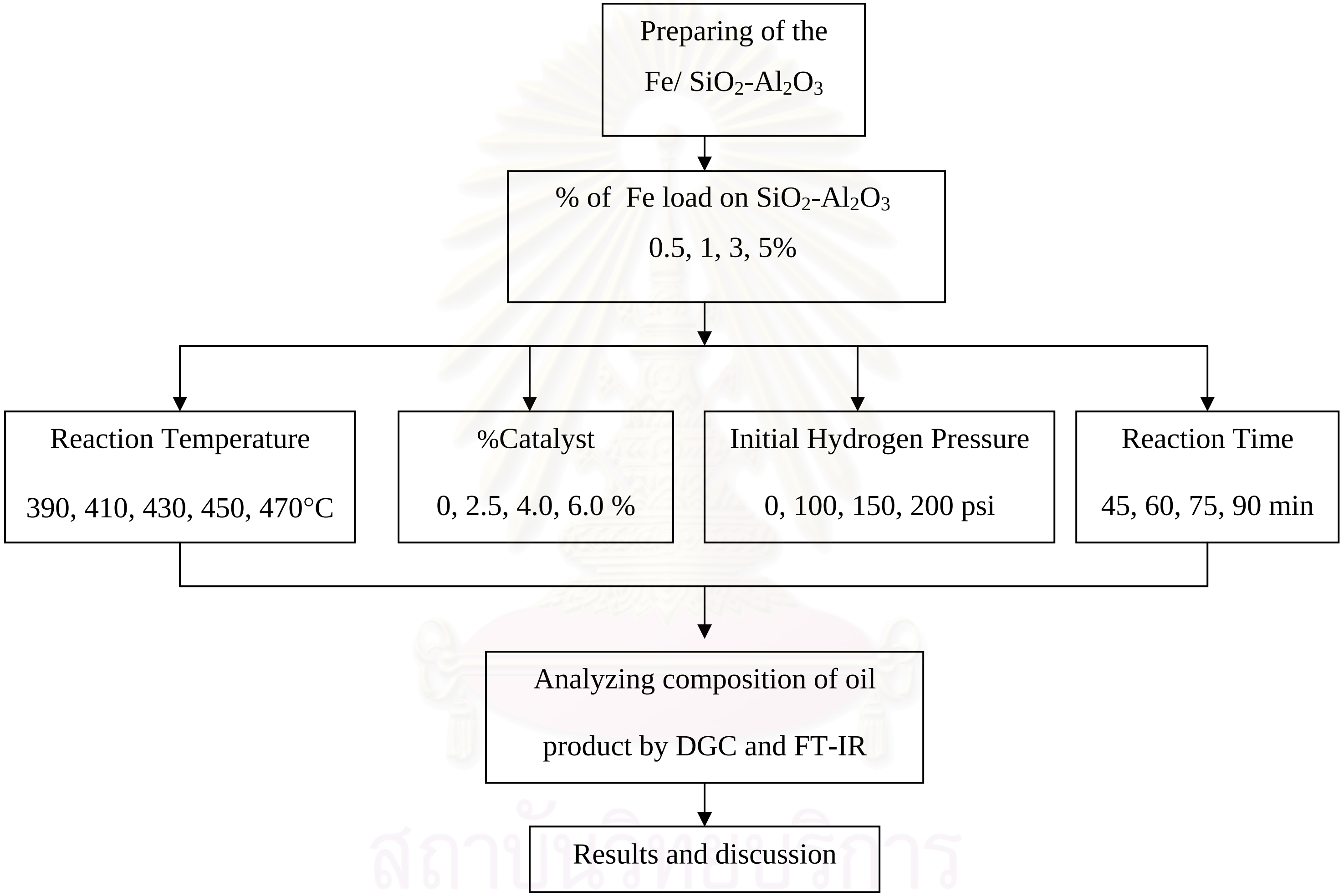


Figure 3.6 Experimental scheme of the hydrocracking of used lubricating oil by Fe/SiO_2-Al_2O_3 catalyst.

After the reaction, the gaseous product was determined by weighing the tubular micro-reactor before and after being released gaseous product; this fraction in the product distribution is called gas. The liquid were brought to filtration step. The catalyst and residue were separated from liquid products by vacuum filtration. The liquid products were analyzed by Simulated Distillation Analysis follow at the ASTM D 2887 method. After the entire set of the reactions were completed, the reactions were replicated. After the Simulated Distillation recovery was determined, the weight percentage of liquid products boiling in the range ibp-100 (where ibp is initial boiling point), <200, <300, <400, <500°C were calculated. Standard deviations for theses weight percentages were calculated by using standard deviations obtained in the product distributions and from Simulated Distillation recovery. The total product distribution of the reaction product was calculated by Simulated Distillation.

Table 3.1 Oil composition calculated by DGC based on ASTM D 2887

Boiling range(°C)	Oil composition
IBP-200	naphtha
201-250	kerosene
251-350	light gas oil
350-370	heavy gas oil
370-FBP	long residue

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Properties of raw material

4.1.1 Used lubricating oil

The composition of used lubricating oil was analyzed by DGC before cracking. The composition distribution was shown in Table 4.1.

Table 4.1 Composition of used lubricating oil.

Composition	% Recovered
naphtha	0.00
kerosene	0.50
light gas oil	3.72
heavy gas oil	8.48
long residue	87.25

From Table 4.1, the main composition of used lubricating oil is compound of 87.25% long residue, heavy gas oil 8.48% and light gas oil 3.72%.

4.1.2 Properties of Fe/SiO_2-Al_2O_3 catalyst

4.1.2.1 BET surface area

The 5% Fe/SiO_2-Al_2O_3 catalyst was prepared and compared the BET surface area with 0.5% Fe/SiO_2-Al_2O_3, 1% Fe/SiO_2-Al_2O_3 and 3% Fe/SiO_2-Al_2O_3. The surface area was obtained using BET analyzer. The BET surface area of catalysts of prepared were shown in Table 4.2.

Table 4.2 The BET surface area of Fe/SiO_2-Al_2O_3.

Sample	Surface area (m^2/g)
SiO_2-Al_2O_3	602
0.5% Fe/SiO_2-Al_2O_3	589
1% Fe/SiO_2-Al_2O_3	526
3% Fe/SiO_2-Al_2O_3	468
5% Fe/SiO_2-Al_2O_3	461

From Table 4.2, it showed that the BET surface area of SiO_2-Al_2O_3 was 602 m^2/g while that other sample loaded Fe on SiO_2-Al_2O_3 were decreased when % Fe was increased. It is because of the deposition in the pores SiO_2-Al_2O_3. However the 5% Fe/SiO_2-Al_2O_3 has 461 m^2/g which is reduced of 23% from SiO_2-Al_2O_3.

4.1.2.2 Chemical Analysis of impregnated Fe on SiO_2-Al_20_3

The composition of 0.5, 1, 3 and 5% Fe/SiO_2-Al_2O_3 was determined by XRF and presented in Table 4.3.

Table 4.3 % Concentration of metal in catalysts.

Element	**Concentration (%)**			
	0.5% Fe	**1% Fe**	**3% Fe**	**5% Fe**
Al	4.929	11.369	10.141	11.279
Si	94.279	87.133	86.432	84.022
S	0.107	0.125	0.119	0.161
P	0.097	0.087	0.086	0.064
Ca	0.05	0.099	0.096	0.085
Zn	0.008	0.013	0.009	0.013
Fe	**0.436**	**0.986**	**2.942**	**5.006**
Zr	0.004	0.007	0.007	0.008

From Table 4.3, it showed that the iron loading in catalysts from XRF is near the desired value. This can firmed the prepared iron loading catalysts. These catalysts could be used in the next experiments.

4.2 Catalytic cracking process

This experiment aims to search the optimum condition to convert used lubricating oil with Fe/SiO_2-Al_2O_3 to light oil. All parameters from catalytic cracking process of used lubricating oil with Fe/SiO_2-Al_2O_3 were investigated as a function of variables, *i.e*. the percentage of iron on SiO_2-Al_2O_3 support, reaction temperature, reaction time, initial hydrogen pressure and percentage of catalyst. The oil products were determined by Simulated Distillation Gas Chromatography, following the ASTM D-2887 method. The variable of % naphtha overall in the oil products as a function of the above variables allowed for the selection of suitable conditions. The optimum percentage of iron on SiO_2-Al_2O_3 was searched in the first step.

4.2.1 Effect of percentage of iron on SiO_2-Al_2O_3 on distribution of oil product

The variation of percentage loading of iron 0.5, 1, 3 and 5% on SiO_2-Al_2O_3 using as catalyst at a fixed condition of 20g of used lubricating oil, with initial hydrogen pressure of 100 psi, reaction time of 60 min, temperature at 430°C and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst and comparing with non using catalyst. The product distributions were shown in Table 4.4 and Figure 4.1.

Table 4.4 Effect of % Fe on product distribution at 430°C of reaction temperature, 100 psi of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst.

percentage	Gas product	Oil product	Solid	Oil products (% recovered)				
of Fe	(%yield)	(%yield)	(%yield)	naphtha	kerosene	light gas oil	heavy gas oil	long residue
thermal cracking	8.05	80.42	11.53	20.49	7.04	17.52	4.39	50.55
0.5% Fe	16.52	78.92	4.56	27.92	11.41	23.47	5.33	31.87
1% Fe	17.27	78.11	4.62	30.71	17.71	29.37	4.79	17.42
3% Fe	17.58	77.82	4.60	32.70	16.01	28.04	4.98	18.27
5% Fe	17.82	77.04	5.14	35.65	14.90	25.38	4.61	19.46

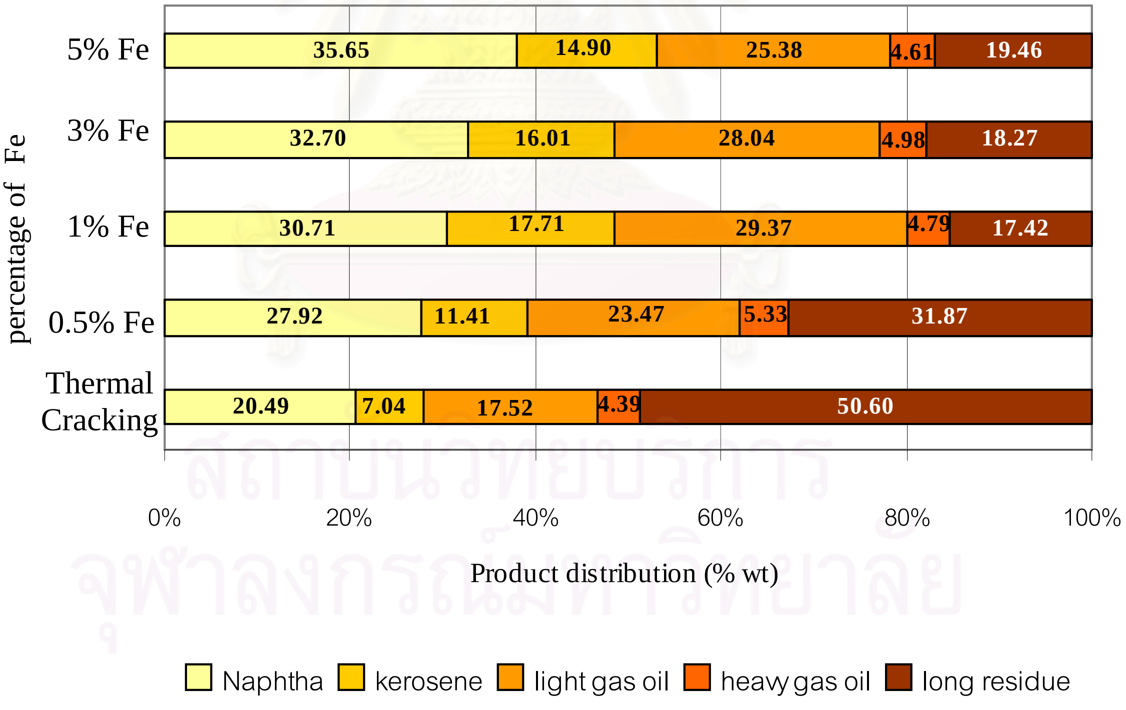


Figure 4.1 Effect % Fe on product distribution at 430°C of reaction temperature, 100 psi of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst.

The conversion of used lubricating oil in non using catalyst at 430°C, pressure of hydrogen gas of 100 psi, time of reaction of 60 minutes and 4.0% by wt. Fe/SiO_2-Al_2O_3 was about 80.42%, 8.05% and 11.53% in liquid product, gas product and solid, respectively. In addition, the liquid product gave the product distribution which determined from simulated distillation gas chromatograph about 20.49% of naphtha, 7.05% of kerosene, 17.52% of light gas oil, 4.39% of heavy gas oil and 50.55% of long residue. While the reaction was carried out without using catalyst, the percentage of oil composition was low quality from that using catalyst because only thermal cracking not enough because lubricating oil was complex structure and high molecular weight.

The reaction of catalytic cracking over Fe/SiO_2-Al_2O_3, the liquid yield was decreased with increased of %Fe whereas the yield of naphtha fraction increased. Found thermal cracking mechanism of long chain hydrocarbon from lubricating oil, firstly was broken down to a middle hydrocarbon molecule such as kerosene and gas oil. Thereafter kerosene, light gas oil and heavy gas oil were catalytically cracked at the surface of Fe/SiO_2-Al_2O_3, converting them into naphtha and gaseous (normally C_1-C_4). Whereas, the catalyst system was simultaneously preceded by thermal cracking and catalytic cracking, as a result the distribution of hydrocarbon molecules was obtained the higher naphtha and gases.

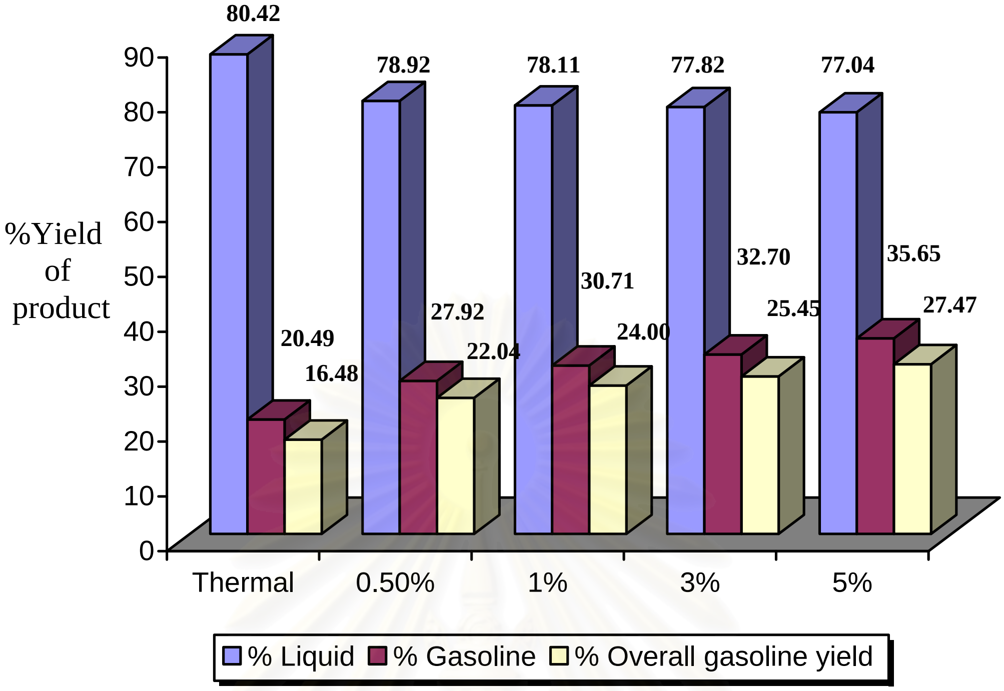


Figure 4.2 Effect of % Fe on product distribution at 430°C of reaction temperature, 100 psi of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst.

When the percentage of iron loading in catalysts increased to 5%, a large amount of gaseous products have been observed to increase substantially. It seemed that when higher percentage of iron was used, light hydrocarbon could be cracked more. The result of this effect showed that 5% of iron loading in catalyst gave the appropriate fraction of naphtha; the liquid yield of 77.04% was obtained with the composition of naphtha 35.65%, kerosene 14.90%, light oil 25.38%, heavy gas oil 4.61% and long residue 19.46% whereas the gas by product of 17.82% and solid of 5.14% were obtained, it decided to choose 5% loading of iron on SiO_2-Al_2O_3 using as catalyst for studying others variables because 5% loading of iron gave highest gasoline and overall gasoline.

4.2.2 Effect of reaction temperature on product distribution

The study of reaction temperature on the catalytic cracking of used lubricating with Fe/SiO_2-Al_2O_3 catalyst was performed by operating in various temperatures: 390, 410, 430, 450, 470°C. Mass of Fe/SiO_2-Al_2O_3 catalyst at 4.0% by wt., 100 psi of initial hydrogen pressure, reaction time 60 minutes. Generally, at reaction temperature lower 400°C the product was sticky like wax. At reaction temperature above 470°C, carbon was deposited on the surface of catalyst. Therefore, the experiment was carried out at temperature 390°C to 470°C only. The product distribution was shown in Table 4.5 and figure 4.3.

Table 4.5 Effect of reaction temperature on product composition at 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst, 100 psi of initial hydrogen pressure, 60 minutes of reaction.

Temperature (^oC)	Gas product (%yield)	Oil product (%yield)	Solid (%yield)	Oil products (% recovered)				
				naphtha	kerosene	light gas oil	heavy gas oil	long residue
390	3.24	89.11	8.55	5.91	2.51	9.67	3.01	78.90
410	10.28	82.59	7.13	23.59	7.61	16.71	4.63	47.47
430	12.82	82.04	5.14	35.65	14.90	25.38	4.61	19.46
450	18.60	75.79	5.61	44.29	16.57	24.34	3.92	10.88
470	23.58	71.19	5.24	39.02	15.62	24.80	3.63	16.93

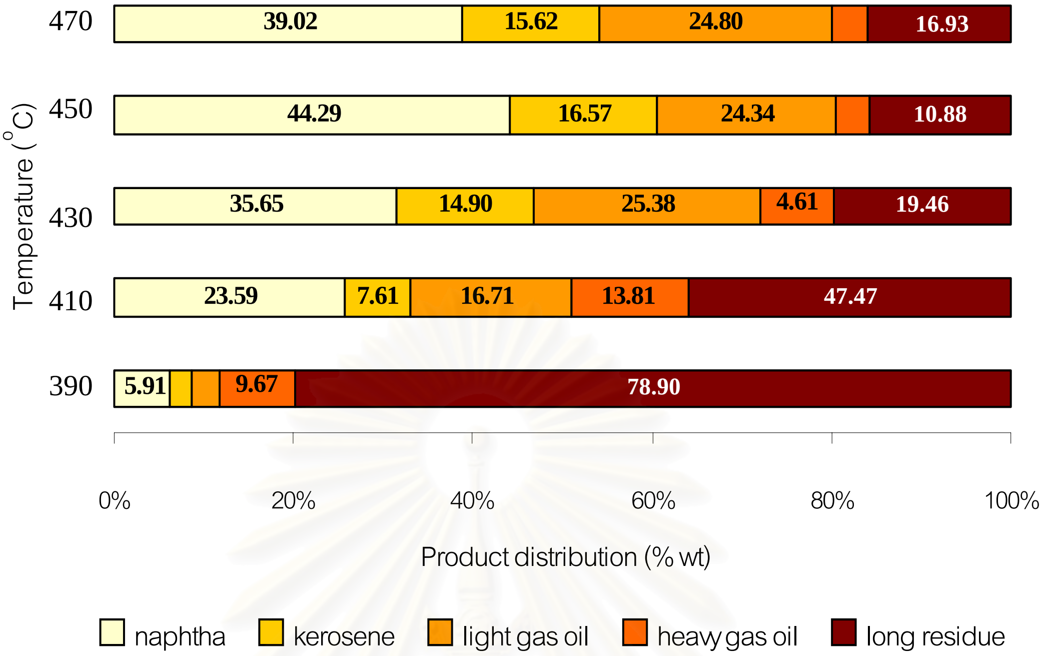


Figure 4.3 Effect of reaction temperature range of 390-470°C on product composition at 4.0% by wt. $Fe/SiO_2-Al_2O_3$ catalyst, 100 psi of initial hydrogen pressure, 60 minutes of reaction time.

From Table 4.5 and figure 4.3 show the reaction of catalytic cracking over 5% $Fe/SiO_2-Al_2O_3$, the liquid yield was decreased with increased of temperature whereas the yield of naphtha fraction increased with increased temperature. A possible reason for this behavior is that the higher temperature accelerated the thermal cracking into a middle hydrocarbon molecule such as kerosene and gas oil fraction. Thereafter kerosene, light gas oil and heavy gas oil were catalytically cracked at the surface of $Fe/SiO_2-Al_2O_3$, converting them into naphtha and gaseous (normally C_1-C_4). When the temperature was increased from 390°C to 450°C, % yield of naphtha increased from 5.91% to 44.29% because the high temperature (450°C) accelerating the thermal cracking which changed kerosene and gas oil. However, at temperature 470°C, it was that noticed the % yield of naphtha decreased from 44.29% to 39.02%, because catalytic cracking was dominated by thermal cracking. The gaseous product increased with increasing temperature which long chain hydrocarbon as broken into lower hydrocarbon (C_1-C_4). When the temperature reached 470°C, we observed the large decreasing of naphtha and kerosene from 44.29% to 39.02% and 16.57 to 15.62%, respectively. It seemed that when higher temperature was used, light hydrocarbon could be cracked more, as a result we found the % of gases increasing because thermal cracking was faster than catalytic cracking.

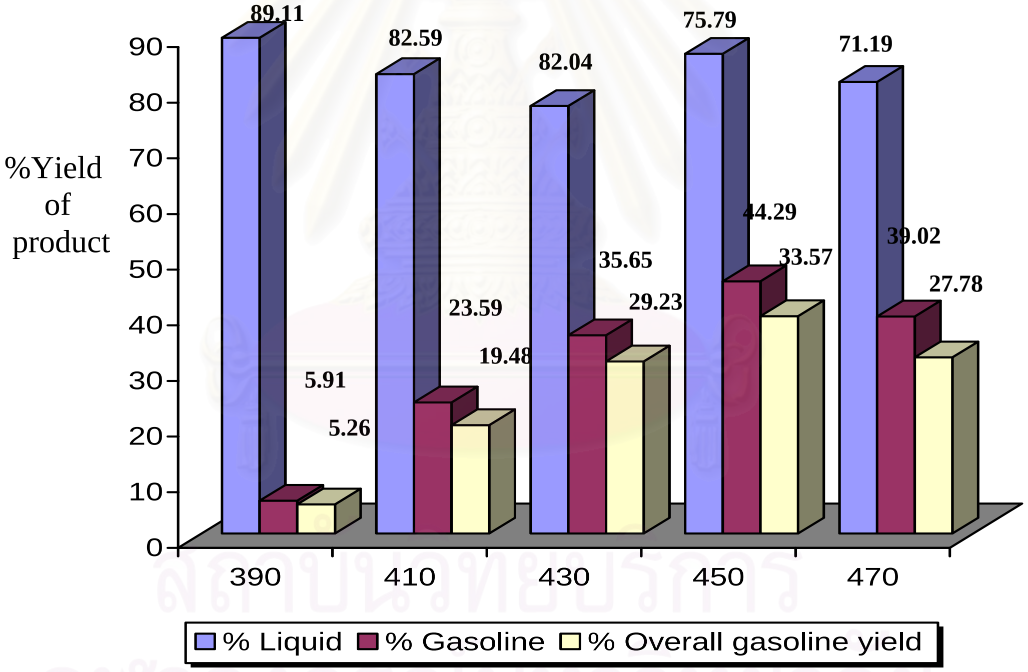


Figure 4.4 Effect of reaction temperature on product distribution 100 psi of initial hydrogen pressure, 60 minutes of reaction time and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst.

In conclusion, the optimum reaction temperature was 450°C because of highest % yield of liquid and % overall gasoline. The conversion of used lubricating oil was about 75.79%, 18.60% and 5.61% in liquid product, gas product and solid, respectively. In addition, the liquid product gave the product distribution which determined from simulated distillation gas chromatograph about 44.29% of naphtha, 16.57% of kerosene, 24.34% of light gas oil, 3.92% of heavy gas oil, 10.88% long residue and 33.57% of % overall gasoline.

4.2.3 Effect of reaction time on product distribution

The study of the reaction time on the catalytic cracking of used lubricating oil with Fe/SiO_2-Al_2O_3 catalyst was performed by operating with various reaction times: 45, 60, 75 and 90 minutes by using mass of Fe/SiO_2-Al_2O_3 catalyst at 4.0% by wt., 100 psi of initial hydrogen pressure and reaction temperature at 450°C. The product distribution was shown in Table 4.6 and figure 4.5.

Table 4.6 Effect of reaction time on product composition at 450°C of reaction temperature 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst and 100 psi of initial hydrogen pressure.

Reaction time (minutes)	Gas product (%yield)	Oil product (%yield)	Solid (%yield)	Oil products (% recovered)				
				naphtha	kerosene	light gas oil	heavy gas oil	long residue
45	9.60	86.00	4.40	27.29	7.85	16.02	4.65	44.19
60	18.60	75.79	5.61	44.29	16.57	24.34	3.92	10.88
75	18.94	76.25	4.82	45.35	15.71	22.83	3.70	12.41
90	19.10	74.53	6.37	43.71	15.67	20.98	3.87	15.77

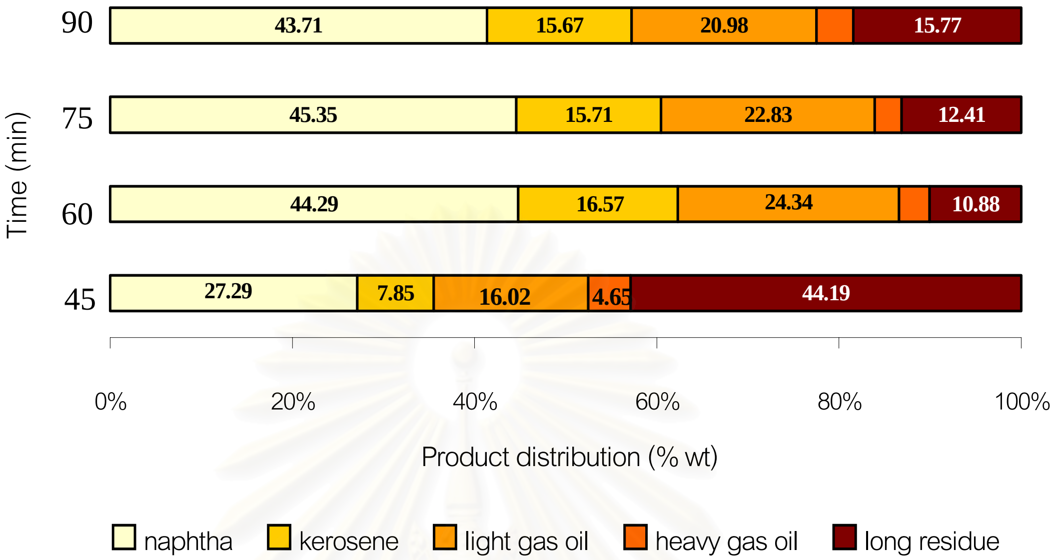


Figure 4.5 Effect of reaction time range of 45-90 minutes on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst.

Time of reaction contributed mainly to the liquid yield and product distribution, Table 4.6 shows that the yield of liquid was increased with increased reaction time from 45-75 minutes and decreased with increased reaction time from 75-90 minutes. It seems that in the first of reaction, used lubricating oil begins crack and undergoes more cracking when the reaction time is continues, and hence, the light hydrocarbon molecules were produced in greater from the effect of the thermal cracking. When the time of reaction is continued the liquid yield which consisted of the fraction of light hydrocarbon was continued cracking to the gaseous product. Hence, the gaseous product increased with increasing the time of reaction. The yield of liquid product was decreased from 86.00% to 74.53% in ranging of increased the reaction time of 45 to 90 minutes.

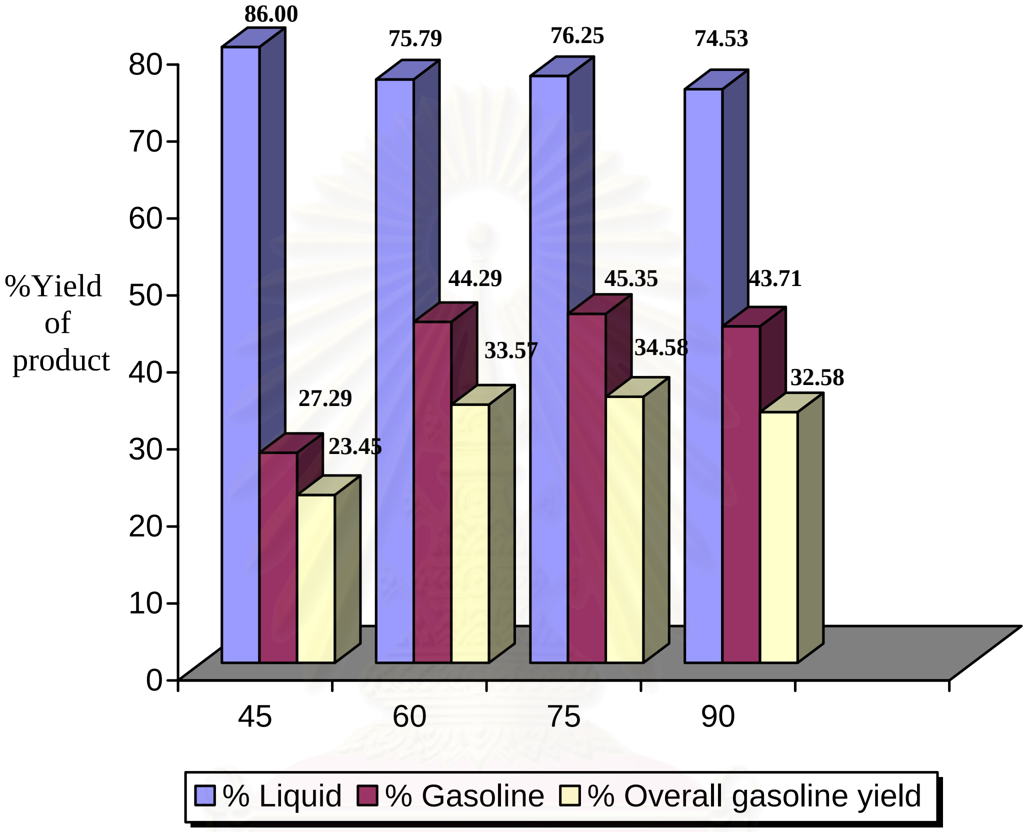


Figure 4.6 Effect of reaction time range of 45-90 minutes on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure and 4.0% by wt. Fe/SiO_2-Al_2O_3 catalyst.

Figure 4.5 and 4.6 show the effect of reaction time on the product distribution. It seemed that temperature was mainly affecting the thermal cracking of long chain hydrocarbon molecules into light molecules and continued cracking led to light hydrocarbon gaseous with increasing the reaction time. The result of increase reaction time shows that the gaseous products increased whereas the product distribution such as naphtha, kerosene, light gas oil and heavy gas oil decreased. The effect of reaction time shows the results in greater amount naphtha boiling range fraction also increased with increase in reaction temperature reached a maximum at 470°C and gave later decrease. Furthermore, the naphtha fraction represents the boiling range 0-200°C fraction which was increased with increase in the reaction of time from 45 to 75 minutes and was dropped at the time of reaction more than 75 minutes.

In conclusion, the optimum condition of reaction time was 75 minutes, reaction temperature 450°C and initial hydrogen pressure of 100 psi, the liquid yield of 76.24% was obtained with the composition of naphtha 45.35%, kerosene 15.71%, light gas oil 22.83%, heavy gas oil 3.70%, long chain hydrocarbon molecule 12.41% and 34.58% gasoline overall whereas the gaseous products of 18.94% and solid of 4.82% were obtained.

4.2.4 Effect of mass of catalyst on liquid product distribution

The study of mass of catalyst on the catalytic cracking process of used lubricating oil with $Fe/SiO_2-Al_2O_3$ catalyst was performed by operating in various mass of catalyst: 0, 2.5, 4.0 and 6.0% by wt. $Fe/SiO_2-Al_2O_3$ catalysts were treated under 100 psi of initial hydrogen pressure at reaction time 75 minutes, reaction temperature 450°C and 5% $Fe/SiO_2-Al_2O_3$. The product distribution was shown in Table 4.7 and figure 4.7.

Table 4.7 Effect of mass of Fe/SiO_2-Al_2O_3 catalyst on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure, 75 minutes of reaction time and 5% Fe/SiO_2-Al_2O_3.

% of catalyst	Gas product	Oil product	Solid	Oil products (% recovered)				
	(%yield)	(%yield)	(%yield)	naphtha	kerosene	light gas oil	heavy gas oil	long residue
0	15.05	79.42	5.53	20.86	5.71	11.77	3.37	58.30
2.5	15.84	79.81	4.35	31.90	9.64	14.21	3.15	41.10
4	18.94	76.24	4.82	45.35	15.71	22.83	3.70	12.41
6	13.13	76.14	10.74	42.14	13.47	23.16	3.53	18.70

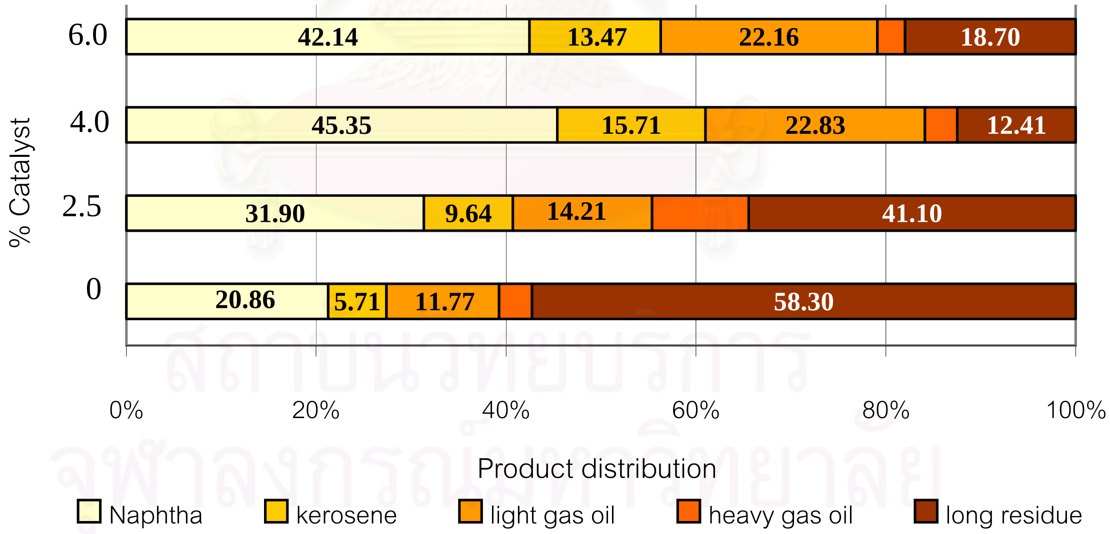


Figure 4.7 Effect of mass of Fe/SiO_2-Al_2O_3 catalyst on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure, 5% Fe/SiO_2-Al_2O_3 catalyst and 75 minutes of reaction time.

The investigate of catalytic cracking of used lubricating oil in non using catalyst at 450°C, pressure of hydrogen gas at of 100 psi and time of reaction of 75 minutes was about 79.42%, 15.05% and 5.53% in liquid product, gas product and solid, respectively. It seems that the effect of temperature mainly cracked long chain hydrocarbon to the middle molecule and continuously cracked to light hydrocarbon. Whereas using variation of the mass of Fe/SiO_2-Al_2O_3 shows the trend of gaseous yield increased with increasing the mass of ranging of 2.5-4.0 wt%. Hence, the mass of Fe/SiO_2-Al_2O_3 in the catalytic cracking was significant on the yield of gases is due to the acid sites in the catalyst promotes the cracking reactions responsible for the formation of gaseous product. In addition, the light hydrocarbon molecules from thermal and catalytic cracking were converted to light gases.

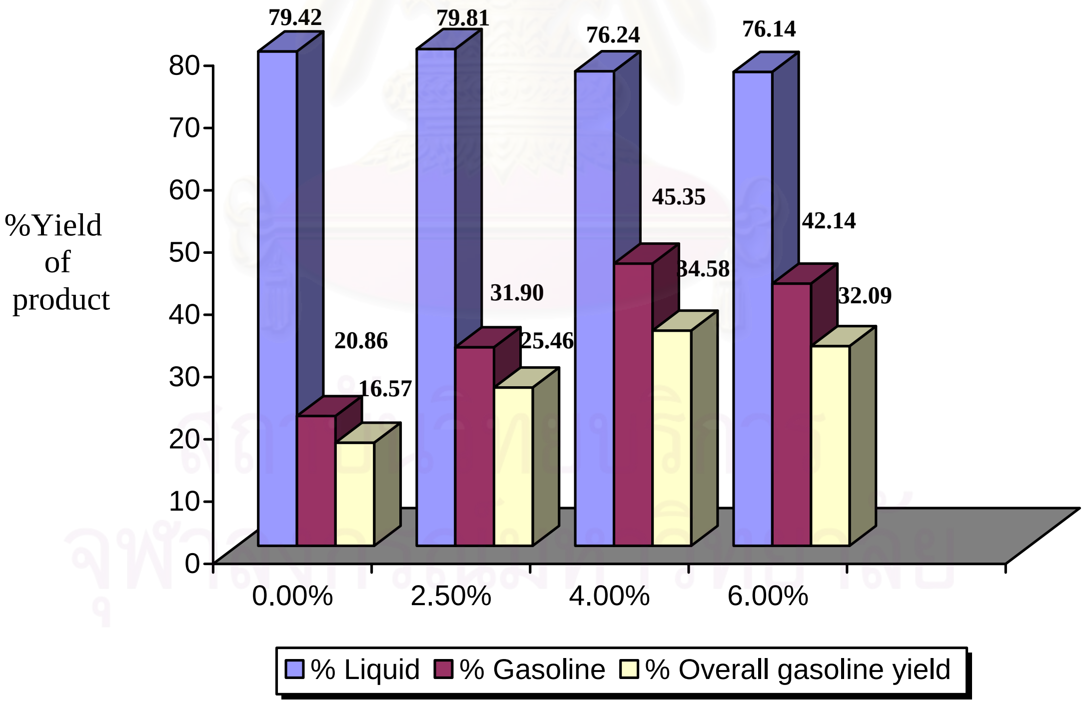


Figure 4.8 Effect of mass of Fe/SiO_2-Al_2O_3 catalyst on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure, 5% Fe/SiO_2-Al_2O_3 catalyst and 75 minutes of reaction time.

The effect of mass of catalyst from ranging of 2.5-6.0 %wt. shows the difference of fraction of naphtha, kerosene, light gas oil, heavy gas oil and long residue. A possible reason for this behavior is that the mass of Fe/SiO_2-Al_2O_3 may correlation to the Fe/SiO_2-Al_2O_3 concentration. Hence, Fe/SiO_2-Al_2O_3 concentration increases the selectivity to naphtha fraction increases while that of long residue decreases, with the exception of the light gas oil and heavy gas oil which presented a small increase in the selectivity. Therefore, an increase in the mass of Fe/SiO_2-Al_2O_3 increased the acid sites in the catalyst promotes the cracking reactions, and also responsible for the formation of gaseous products. High concentration of Fe/SiO_2-Al_2O_3 is in effect equivalent to an increase in the contact time of the reactants and products distribution with the acid sites and is therefore contrary to the liquid yield preservation. The selectivity increase toward the naphtha fraction at high Fe/SiO_2-Al_2O_3 contents can be due to the formation of these products, which is favored at high Fe/SiO_2-Al_2O_3 contents. Furthermore, this result relatively an increase acid site in the catalyst promotes the cracking reaction responsible for the formation of light hydrocarbon molecule. Therefore, the catalytic cracking of used lubricating oil at reaction temperature of 450°C, initial hydrogen pressure of 100 psi, time of reaction of 75 minutes over 4.0 wt.% of Fe/SiO_2-Al_2O_3 was gave the highest naphtha fraction amounting 45.35% while, kerosene 15.71%, light gas oil 22.83%, heavy gas oil 3.70% and long residue 12.41% were obtained.

4.2.5 Effect of initial hydrogen pressure on product distribution

The study of initial hydrogen pressure on the catalytic cracking process of used lubricating oil with Fe/SiO_2-Al_2O_3 catalyst was performed by operating in various initial hydrogen pressure; blank, 100, 150, and 200 psi, with 4.0% by wt. of catalyst, reaction time 75 minutes and reaction temperature 450°C.

Table 4.8 Effect of initial hydrogen pressure on product composition at 450°C of reaction temperature, 4.0% by wt. of catalyst and 75 minutes of reaction time.

H_2 pressure (psi)	Gas Product (%yield)	Oil Product (%yield)	Solid (%yield)	Oil products (% recovered)				
				naphatha	kerosene	light gas oil	heavy gas oil	long residue
Blank	7.03	81.83	11.15	22.30	8.66	15.76	3.56	49.72
100	12.94	76.24	10.82	45.35	15.71	22.83	3.70	12.41
150	17.50	74.33	8.17	36.55	17.12	28.09	4.39	13.85
200	25.03	62.30	12.67	31.73	12.79	21.54	4.06	29.88

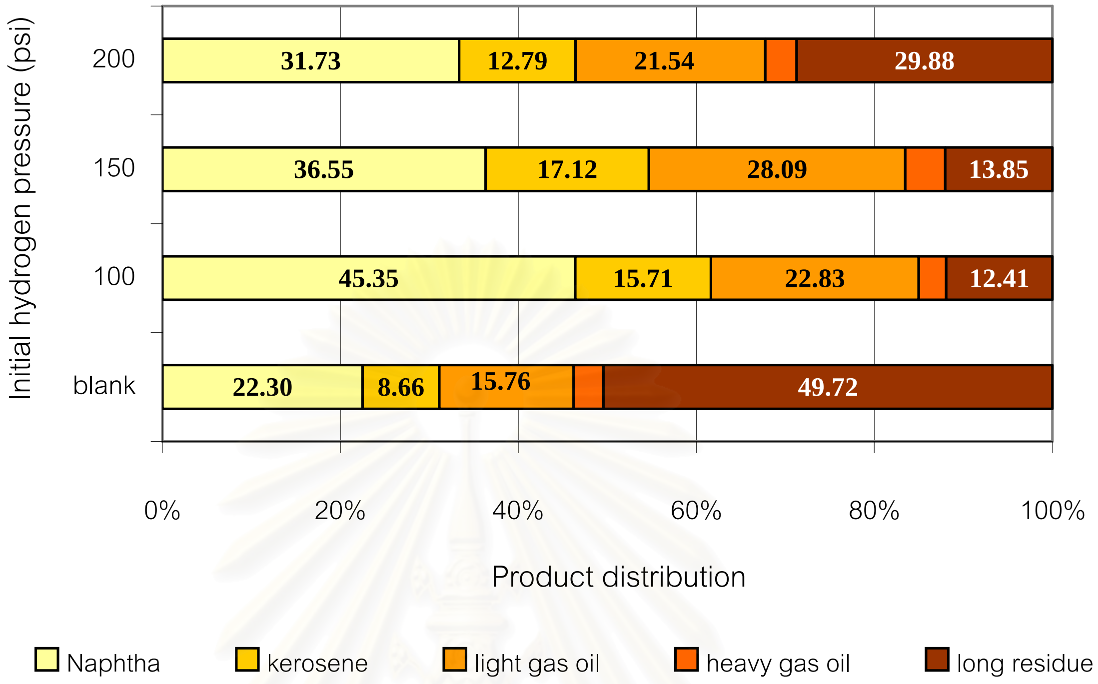


Figure 4.9 Effect of initial hydrogen pressure range of blank-200 psi on product distribution at 450°C of reaction temperature 4.0% by wt. of catalyst, 75 minutes of reaction time and 5% Fe/ SiO_2-Al_2O_3 catalyst.

Effect of variation of initial hydrogen pressure show in table 4.8 and figure 4.9, when the initial hydrogen pressure was increased from 100 psi to 200 psi on the hydrocracking process of used lubricating oil with 5%Fe/SiO_2-Al_2O_3 catalyst at reaction time 75 minutes, 4.0% by wt. of catalyst and reaction temperature at 450°C. It noticed that the pressure increased from 0 to 100 psi, the % of naphtha increased from 22.30% to 45.35%. It was observed the difference between using and without using initial hydrogen pressure. When hydrogen concentration increased, it would promote the catalytic reaction by increasing more hydrogen free radical. Thus catalytic cracking could be occurred than thermal cracking at 100 psi of initial hydrogen pressure as a result. When the initial hydrogen pressure increased from 100 to 200 psi, the % yield of liquid and % naphtha was decreased from 76.24% to 62.30% and 45.35% to 31.73%, respectively. But the gases and solids were slightly increased from 18.94% to 25.03% and 4.82% to 12.67%, respectively. It seemed that the pressure at 100 psi was the best condition.

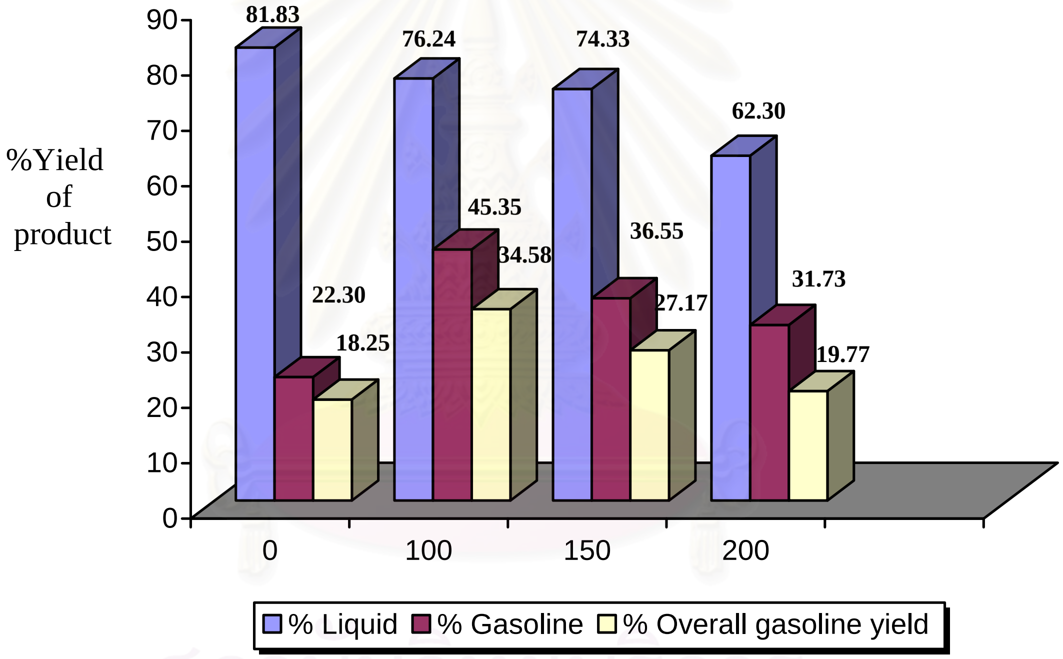


Figure 4.10 Effect of initial hydrogen pressure range of blank-200 psi on product distribution at 450°C of reaction temperature, 4.0% by wt. of catalyst, 75 minutes of reaction time and 5% Fe/SiO_2-Al_2O_3 catalyst.

In conclusion, the initial hydrogen pressure condition was 100 psi, this pressure gave the highest % yield of overall gasoline and % yield of kerosene were 34.58% and 15.71%, respectively. Thus, catalytic cracking could be occurred at 100 psi of initial hydrogen pressure as a result.

4.3 Comparison of type of catalyst on product distribution

The comparison of the efficiency of 3 types of catalyst of 5% $Fe/SiO_2-Al_2O_3$, 5% Fe/Al_2O_3, 5% Ni/Al_2O_3 and thermal cracking reaction. The condition was fixed at 4.0% by wt. of each catalyst, reaction time 75 minutes, reaction temperature 450°C and 100 psi of initial hydrogen pressure. The product distribution were shown in Table 4.9 and figure 4.11.

Table 4.9 Effect of type of catalyst on product composition at 450°C of reaction temperature, 4.0% by wt. of each catalyst, 100 psi of initial hydrogen pressure and 75 minutes of reaction time.

Type of catalyst	Gas product (%yield)	Oil product (%yield)	Solid (%yield)	Oil products (% recovered)				
				naphtha	kerosene	light gas oil	heavy gas oil	long residue
Thermal cracking	8.05	80.42	11.53	20.86	5.71	11.77	3.37	58.30
$Fe/SiO_2-Al_2O_3$	12.94	76.24	10.82	45.35	15.71	22.83	3.70	12.41
Fe/Al_2O_3	11.62	80.38	8.00	35.14	14.47	24.16	5.53	20.70
Ni/Al_2O_3	12.00	77.20	10.80	38.24	15.67	25.44	3.38	16.94

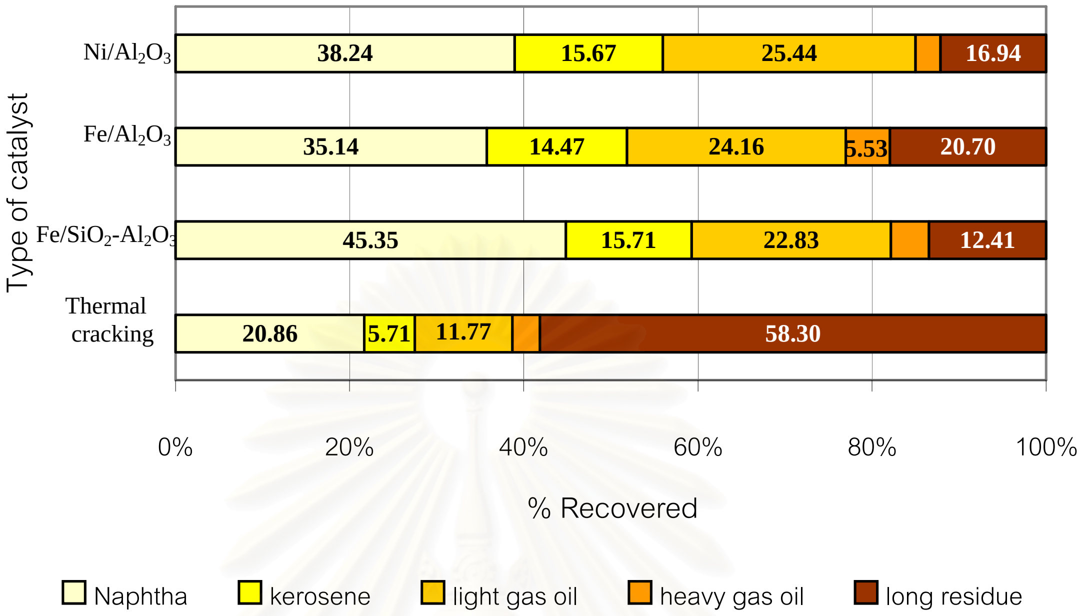


Figure 4.11 Effect of type of catalyst on product composition at 450°C of reaction temperature, 4.0% by wt. of each catalyst, 100 psi of initial hydrogen pressure, 75 minutes of reaction time and 5% of metal load on support.

From Table 4.9 and figure 4.11 showed that all of catalyst gives nearly % yield of oil product. The Fe/SiO_2-Al_2O_3 gave highest light oil *i.e.*, % naphtha, kerosene and light gas oil. The Fe/Al_2O_3 gave the highest heavy hydrocarbon product while and low naphtha composition. It was obviously noticed that, the role of catalyst to convert of used lubricating oil was very important. When Fe/SiO_2-Al_2O_3 gave high gaseous product more than other catalysts because of its acidic catalyst and high surface area. The mechanism was investigated *via* the carbonium ion consequence to crack the long chain hydrocarbon to short chain (C_1-C_5) while the other catalysts.

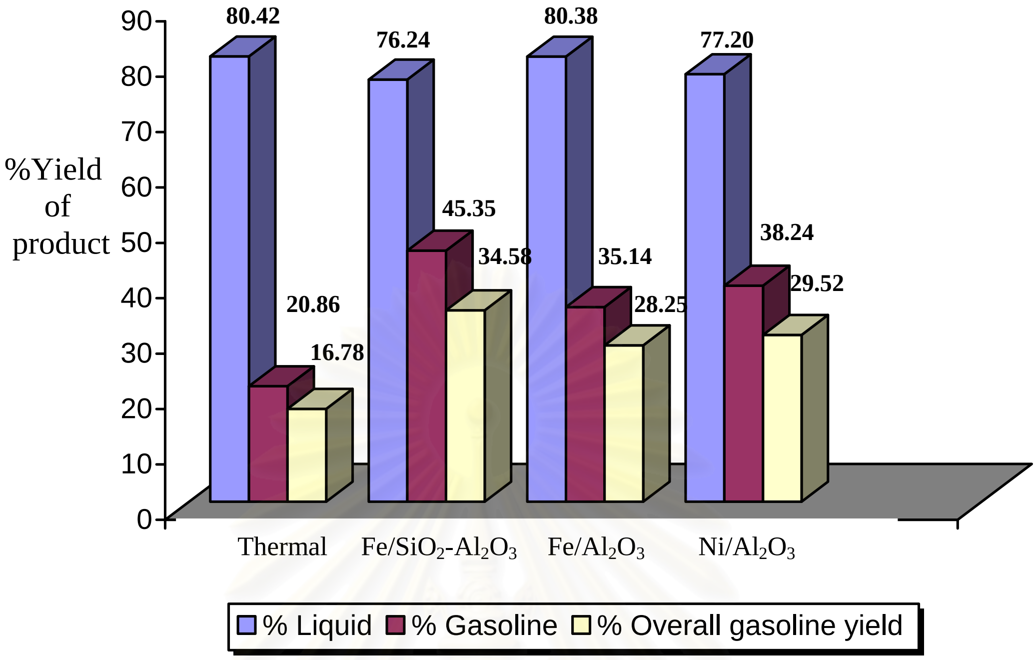


Figure 4.12 Effect of type of catalyst on product composition at 450°C of reaction temperature, 4.0% by wt. of each catalyst, 100 psi of initial hydrogen pressure, 75 minutes of reaction time and 5% of metal load on support.

In conclusion, to comparison of catalyst Fe/SiO_2-Al_2O_3, Fe/Al_2O_3 and Ni/Al_2O_3 using to convert used lubricating oil to light oil by hydrocracking process was found that Fe/SiO_2-Al_2O_3 shows better efficiency catalyst than Ni/Al_2O_3 and Fe/Al_2O_3.

When the catalyst was not used in the reaction, the thermal cracking reaction was developed. The long chain hydrocarbon of reactant was cracked into medium chain hydrocarbon (light gas oil and heavy gas oil). When the long reaction time, the medium chain hydrocarbon was cracked continuingly into short chain hydrocarbon such as naphtha composition and gaseous product (C_1-C_4). On the contrast, the Fe/SiO_2-Al_2O_3 catalyst was used in the reaction. The long chain hydrocarbon was cracked into medium chain hydrocarbon (light gas oil and heavy gas oil) and then the catalyst produced hydrogen radical to develop catalytic cracking reaction. The medium chain hydrocarbon was cracked into short chain hydrocarbon such as naphtha more than without using catalyst. Thus, when the catalyst was used, it showed the good efficiency for produced naphtha more quantity than without using catalyst. That is the reason that when thermal cracking was carried out only, it gave less quantity of naphtha when compare with catalytic cracking. The model of the thermal and catalytic reaction was shown in figure 4.12.

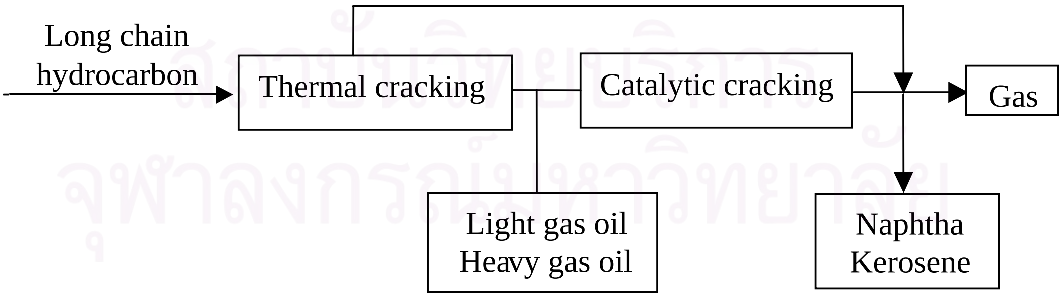


Figure 4.13 The model of the thermal and catalytic reaction.

The mechanism of Fe/SiO_2-Al_2O_3 catalyst was developed by free radical as shown in figure 4.13.

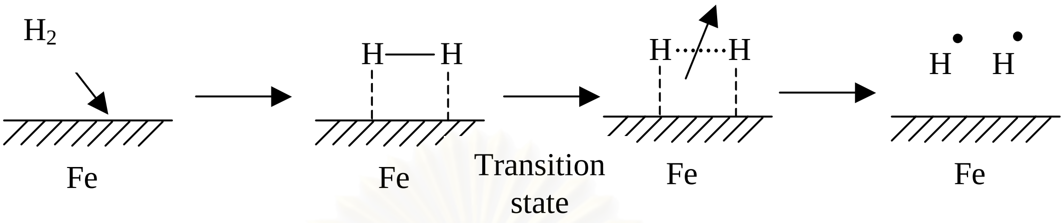
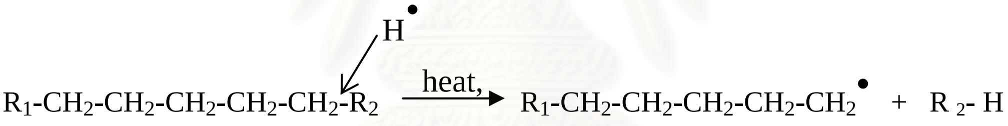


Figure 4.14 The mechanism on surface of Fe/SiO_2-Al_2O_3 catalyst.

The hydrogen radical was produced and attacked the long chained hydrocarbon. The mechanism was shown in follow:

1. **Initial step**



$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{H^{\bullet}}{R_2} \xrightarrow{\text{heat,}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + R_2\text{-}H$$

2. **Propagation Step**

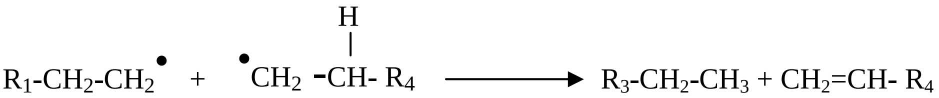
β-fission

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + CH_2=CH_2$$

$$R_1\text{-}CH_2\text{-}\overset{H}{\overset{|}{C}}H\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH=CH_2 + H^{\bullet}$$

3. **Termination Step**

$$R_1^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}R_2$$



$$R_1\text{-}CH_2\text{-}CH_2^{\bullet} + {}^{\bullet}CH_2\text{-}\overset{H}{\overset{|}{C}}H\text{-}R_4 \longrightarrow R_3\text{-}CH_2\text{-}CH_3 + CH_2=CH\text{-}R_4$$

4.4 Characterization of functional groups of oil product by Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 4.15 shows the functional group compositional analysis of the oil derived from catalytic reaction of 20 g of used lubricating oil, 450°C of reaction temperature, 5% Fe/SiO_2-Al_2O_3, 100 psi of hydrogen pressure, 75 minutes of reaction time and 4.0% by wt. of Fe/SiO_2-Al_2O_3 catalyst by Fourier transform infrared (FT-IR) spectrometry. The oil product showed a strong spectrum presence of both aromatic and aliphatic functional group. The strong peak at 1600 cm^{-1}, 1495 cm^{-1} and 1454 cm^{-1} were indication of the presence of C=C stretching of aromatic. In addition, there are weak peak between 3000 and 3100 cm^{-1} shows the presence of C-H stretching and the very strong peaks present at 700 cm^{-1} indicated the substituted aromatic ring.

Figure 4.16 shows the functional group of gasoline octane number 95 by Fourier transform infrared (FT-IR) spectrometry. It showed a strong spectrum of both aromatic and aliphatic functional group same functional group of oil product. Compared the functional groups of oil product with functional group of gasoline octane number 95 that the aromatic group presents show that some of the functional groups are similar which show that oil products obtained from hydrocracking process can be used as fuel oil effectively.

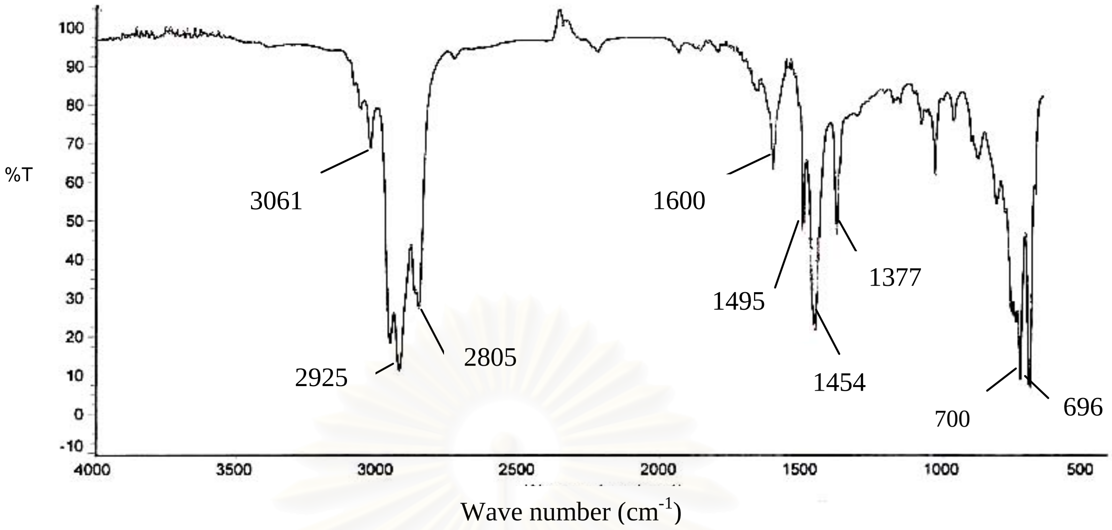


Figure 4.15 FT-IR spectrum of oil product derived from catalytic reaction of 20 g of used lubricating oil, 450°C of reaction temperature, 100 psi of initial hydrogen pressure, 5% Fe/SiO_2-Al_2O_3, 75 minutes of reaction time and 4.0% by wt. of catalyst.

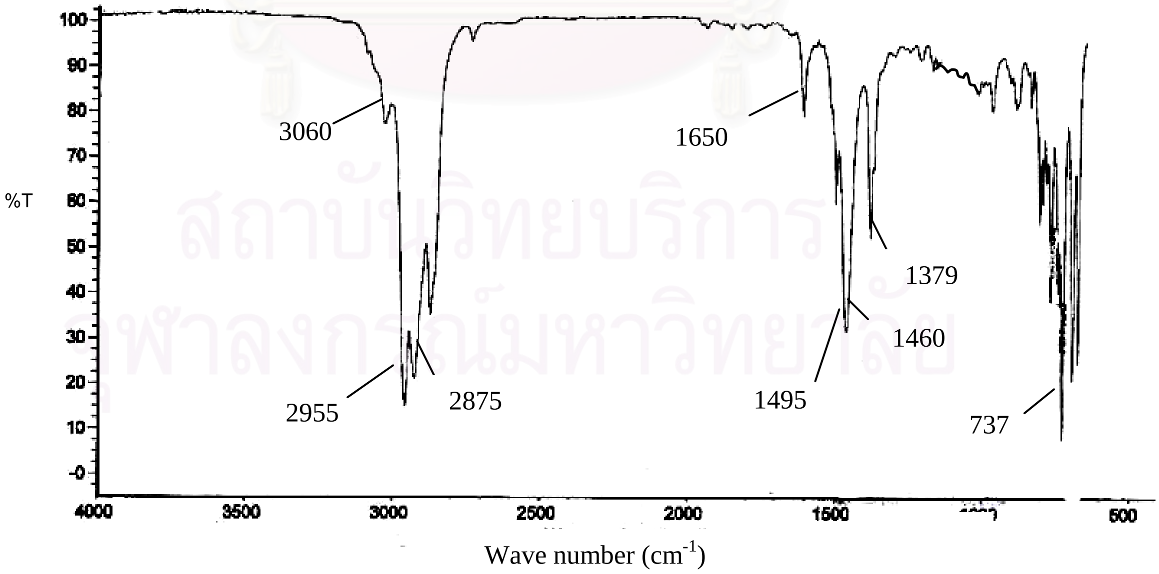


Figure 4.16 FT-IR spectrum of gasoline octane number 95.

4.5 Comparison of this work with other works

The comparison of this work with Kaewsaiyoy, A. (2003) with the reaction condition, % yield of product and product distribution was shown in Table 4.10.

Kaewsaiyoy, A. studied hydrocracking of used lubricating oil to fuel oil on HZSM-5 catalyst and Taepukdee, P. studied the conversion of polypropylene, polystyrene and used lubricating oil to fuel oil on Fe/activated carbon.

From Table 4.10, at 450^{o}C, 60 min, HZSM-5 catalyst Kaewsaiyoy, A. obtained 85.46% of oil yield, naphtha 34.87%, kerosene 11.03%, gas oil 20.22%, and long residue 19.34%. At 430^{o}C, 60 min, 5% by wt. of Fe/activated carbon catalyst Taepukdee, P. obtained 76.56% of oil yield, naphtha 46.34%, kerosene 13.25%, gas oil 19.49%, and long residue 6.01%. Whereas this work obtained 76.24% of oil yield, naphtha 34.58 %, kerosene 15.71%, gas oil 26.54%, and long residue 12.41%. This result showed same yield of naphtha that of Kaewsaiyoy’s but lower than Taepukdee, P. because his work mixed plastic into used lubricating oil which caused to give short chain hydrocarbon (light oil) more than only used lubricating oil which was large molecule. But this work still show high yield of oil and high yield of light oil composition.

Table 4.10 Comparison of this work with other works.

Description	Kaewsaiyoy, A.	Taepukdee, P.	This work
Condition			
Feed	Used lubricating oil	PP +PS + Used lubricating oil	Used lubricating oil
Catalyst	HZSM-5	5% Fe/AC	5% Fe/SiO_2-Al_2O_3
Reaction Temperature (°C)	450	430	450
Initial Hydrogen Pressure (psi)	100	100	100
Reaction Time (minutes)	60	75	75
Percentage of Catalyst (wt. %)	0.5	4.0	4.0
Results			
Oil Products (wt. %)	85.46	75.65	76.24
- Naphtha	40.80	61.25	45.35
- kerosene	11.03	13.25	15.71
- light gas oil	11.49	15.84	12.50
- heavy gas oil	8.73	3.65	14.04
- long residue	19.34	6.01	12.41
Gas Products (wt. %)	12.33	17.37	18.94
Solid Products (wt. %)	2.21	6.98	10.82
% overall naphtha	**34.87**	**46.34**	**34.58**

CHAPTER V

CONCLUSIONS

5.1 Conclusion

In this research, the used lubricating oil was used to convert to light oil product by catalytic cracking with Fe/SiO_2-Al_2O_3 catalyst. To achieve this objective, the reaction conditions were varied in terms of percentage of Fe load on SiO_2-Al_2O_3, reaction temperature, reaction time, initial hydrogen pressure and percentage of catalyst. The following conclusion from this study has been drawn:

The 0.5, 1, 3 and 5% Fe/SiO_2-Al_2O_3 catalysts were prepared. The analysis of percentage of Fe was determined using XRF. The 0.5, 1, 3 and 5% Fe/SiO_2-Al_2O_3 catalysts were 0.44%, 0.10%, 2.94% and 5.01%., respectively and BET surface area of catalysts were performed using BET analyzer have 589, 526, 468 and 461 m^2/g, respectively.

This work aims to study the catalytic cracking of used lubricating oil with Fe/SiO_2-Al_2O_3 catalysts in 70 ml micro-reactor, was used the percentage of iron load on SiO_2-Al_2O_3 from 0.5%-5%, 390-470°C of reaction temperature, 0-200 psi of initial hydrogen pressure, 45-90 minutes of reaction time and 0-6.0% by wt. of Fe/SiO_2-Al_2O_3 catalyst. Analysis of oil product was performed using DGC. It may be concluded that the optimum condition: 5% Fe/SiO_2-Al_2O_3, reaction temperature

450°C, initial hydrogen pressure100 psi, 75 minutes of reaction time and 4.0% by wt. of Fe/SiO_2-Al_2O_3 catalyst.

The products from the optimum condition were 18.94% of gas, 76.24% of oil and 10.82% of solid. The oil products distribution were 45.35% of naphtha, 15.71% of kerosene, 12.50% of light gas oil, 14.04 % of heavy gas oil, 12.41% of long residue and 34.58% overall gasoline.

To compare efficiency of Fe/Al_2O_3, Ni/Al_2O_3 and thermal cracking were compared with Fe/SiO_2-Al_2O_3 catalyst. It was found that Fe/SiO_2-Al_2O_3 catalyst shows better efficiency than other catalysts, while used same reaction time and percentage of catalyst because it gave high % light oil especially highest % overall gasoline.

From FT-IR, the oil product was showed strong presence of both aromatic and aliphatic functional group. There were very strong peaks of the substituted aromatic groups and the presence of C-H stretching of aromatic which same position of spectrums of gasoline octane number 95.

5.2 Recommendation

1. The type of used lubricating oil that used in this research can be change to another type such as Jet lube oil.

2. The type of metal used for impregnation or support can be changed to another type.

3. The type of reactor that used can be change to tubular flow reactor which develops to industrial process.

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APPENDICES

APPENDIC A

TABLE A. THE CONDITION REACTIONS OF ALL PARAMETERS OF HYDROCRACKING USED LUBRICATING OIL.

Table A.1 Effect of % Fe on product distribution from hydrocracking of lubricating oil with Fe/SiO_2-Al_2O_3**.**

%Fe	%Yield Solid	%Yield Gas product	%Yield Oil product	Oil products (%)					Gasoline overall
				Naphtha	kerosene	Light gas oil	heavy gas oil	long residue	
Thermal	11.53	8.05	80.42	20.49	7.05	17.52	4.39	50.55	16.48
0.5% Fe	4.56	16.52	78.92	27.92	11.41	23.47	5.33	31.87	22.04
1.0% Fe	4.62	17.27	78.11	30.71	17.71	29.37	4.79	17.42	24.00
3.0% Fe	4.60	17.58	77.82	32.70	16.01	28.04	4.98	18.27	25.46
5.0% Fe	5.14	17.82	77.04	35.65	14.90	25.38	4.61	19.46	27.47

Table A.2 Effect of reaction temperature on product distribution from hydrocracking of lubricating oil with 5% Fe/SiO_2-Al_2O_3**.**

Reaction Temp. (°C)	%Yield Solid	%Yield Gas product	%Yield Oil product	Oil products (%)					Gasoline overall
				Naphtha	kerosene	Light gas oil	heavy gas oil	long residue	
390	8.55	2.34	89.11	5.91	2.51	9.67	3.01	78.90	5.26
410	7.13	10.28	82.59	23.59	7.61	16.71	4.63	47.47	19.48
430	5.14	12.82	82.04	35.65	14.90	25.38	4.61	19.46	29.33
450	5.61	18.60	75.79	44.29	16.57	24.34	3.92	10.88	33.57
470	5.24	23.58	71.19	39.02	15.62	24.80	3.63	16.93	27.78

Table A.3 Effect of reaction time on product distribution from hydrocracking of lubricating oil with 5% Fe/SiO_2-Al_2O_3.

Reaction time. (min.)	%Yield Solid	%Yield Gas product	%Yield Oil product	Oil products (%)					Gasoline overall
				Naphtha	kerosene	Light gas oil	heavy gas oil	long residue	
45	4.40	9.60	86.00	27.29	7.85	16.02	4.65	44.19	23.45
60	5.61	18.60	75.79	44.29	16.57	24.34	3.92	10.88	33.57
75	4.82	18.94	76.24	45.35	15.71	22.83	3.70	12.41	34.58
90	6.37	19.10	74.53	43.71	15.67	20.98	3.87	15.77	32.58

Table A.4 Effect of mass of 5% Fe/SiO_2-Al_2O_3 on product distribution from hydrocracking of lubricating oil.

Mass of catalyst (g)	%Yield Solid	%Yield Gas product	%Yield Oil product	Oil products (%)					Gasoline overall
				Naphtha	kerosene	Light gas oil	heavy gas oil	long residue	
0	5.53	15.05	79.42	20.86	5.71	11.77	3.37	58.30	16.57
0.5	4.35	6.84	79.81	31.90	9.64	14.21	3.15	41.10	25.46
0.8	4.82	18.94	76.24	45.35	15.71	22.83	3.70	12.41	34.58
1.2	10.74	13.13	76.14	42.14	13.47	23.16	3.53	17.70	32.09

Table A.5 Effect of initial hydrogen pressure on product distribution from hydrocracking of lubricating oil with 5% Fe/SiO_2-Al_2O_3.

Initial H_2 pressure (psi)	%Yield Solid	%Yield Gas product	%Yield Oil product	Oil products (%)					Gasoline overall
				Naphtha	kerosene	Light gas oil	heavy gas oil	long residue	
blank	11.15	7.03	81.83	22.30	8.66	15.76	3.56	49.72	18.25
100	4.82	18.94	76.24	45.35	15.71	22.83	3.70	12.41	34.58
150	8.17	17.50	74.33	36.55	17.12	28.09	4.39	13.85	27.17
200	12.67	25.03	62.30	31.73	12.79	21.54	4.06	29.88	19.77

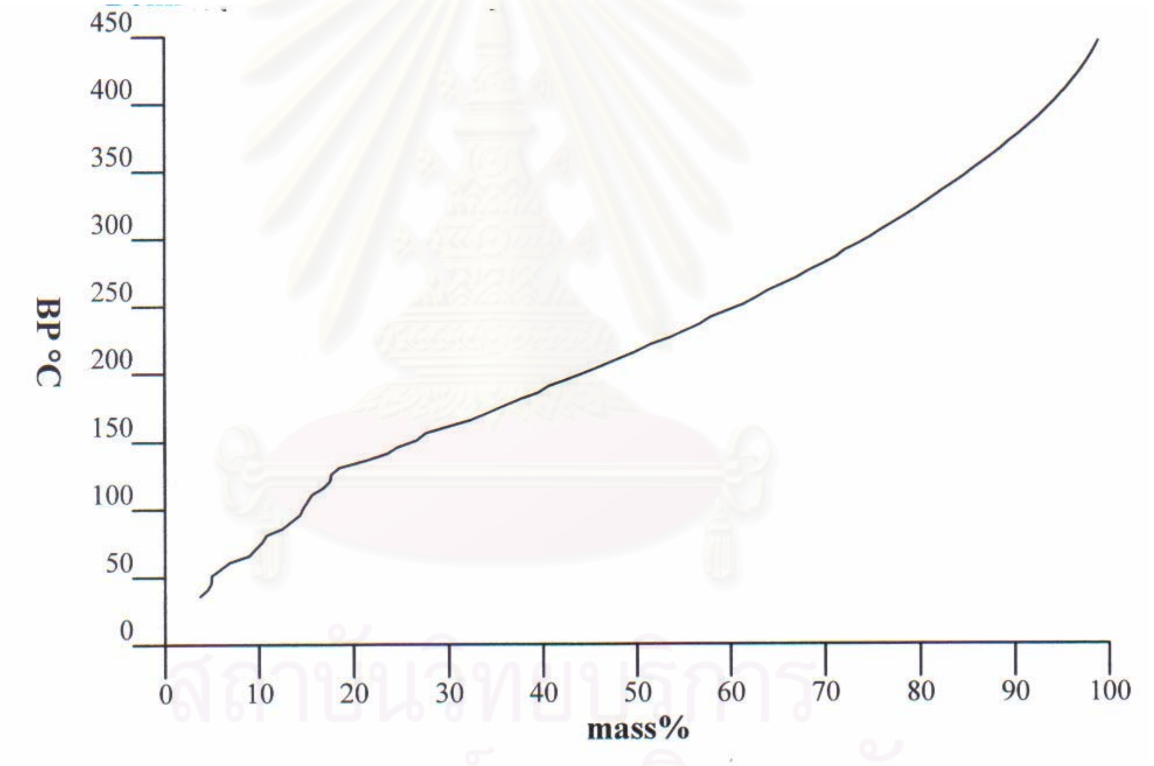
Table A.5 Effect of types of catalysts on product distribution from hydrocracking of lubricating oil with 5% Fe/SiO_2-Al_2O_3.

Type of catalyst	%Yield Solid	%Yield Gas product	%Yield Oil product	Oil products (%)					Gasoline overall
				Naphtha	kerosene	Light gas oil	heavy gas oil	long residue	
Thermal	11.53	8.05	80.42	20.86	5.71	11.77	3.37	58.29	16.78
Fe/SiO_2-Al_2O_3	10.82.	12.94	76.24	45.35	15.71	22.83	3.70	12.41	34.58
Fe/Al_2O_3	8.00	11.62	80.38	35.14	14.47	24.16	5.53	20.70	28.25
Ni/Al_2O_3	10.80	12.00	77.20	38.24	15.67	25.44	3.38	16.94	29.52

APPENDIC B

DGC CHROMATOGRAM OF OPTIMUM CONDITION PRODUCT

Unit	Boiling Range Distribution										
°C	36.0	71.5	135.0	160.0	188.0	220.0	256.0	304.5	340.0	398.0	455.0
%mass	IBP	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	FBP



Chromatogram of optimum condition product at 450°C of reaction temperature, 5% Fe/SiO_2- Al_2O_3, 100 psi of initial hydrogen pressure, 75 minutes of reaction time and 4.0% by wt. Fe/SiO_2-Al_2O_3.

APPENDIC C

CALCULATION OF IMPREGNATED Fe ON SILICA-ALUMINA

AND

CALCULATION OF % OVERALL NAPHTHA

1. Calculation of Fe impregnated on activated carbon

M.W. of $Fe(NO_3)_2.\ 9H_2O$ = 341.84

Atomic weight of Iron = 55.84

Prepare 100.0 g of 5 wt %. $Fe/SiO_2\text{-}Al_2O_3$

$$\text{Mass of } Fe(NO_3)_2{\cdot}9H_2O = \frac{\text{M.W. of } Fe(NO_3)_2.\ 9H_2O \times \text{required mass of catalyst}}{\text{Atomic weight of Fe}}$$

$$= \frac{341.84 \text{ g/mol} \times 2.5 \text{ g}}{55.84 \text{ g mol}}$$

$$= 15.31 \text{ g}$$

In conclusion, we must used $Fe(NO_3)_2.\ 9H_2O$ 15.31 g dissolved in excess water before impregnated on $Fe/SiO_2\text{-}Al_2O_3$ 100 g by wet impregnation process.

2. Calculation of % overall naphtha

$$\text{\% overall naphtha} = \frac{\text{\% off naphtha from DGC} \times 100}{\text{\% oil yield}}$$

APPENDIC D

UNITS AND CONVERSION FACTORS

UNITS AND CONVERSION FACTORS

Temperature: 1°C = 1.8°F

°C to °F 9/5 × (°C) + 32 = °F

°F to °C (°F – 32) × 5/9 = °C

Volume: 1 cubic inch = 16.39 cm^3 = 0.01639 litres

1 Imperial gallon = 4546 cm^3 = 1.201 U.S. gallons

1 U.S. gallons = 3785 cm^3 = 3.785 litres

1 cubic foot = 28.32 litres = 0.02832 m^3

1 cubic metre = 35.315 ft^3

Mass: 1 gram = 15.432 grains = 0.0022 lb

1 pound = 453.6 g = 7000 grains

1 ton = 1016 kg = 1.12 U.S. tons

1 U.S. ton = 907 kg = 0.907 tonnes = 0.893 tons

1 tonne = 1000 kg = 2204.6 lb

Pressure: 1 atmosphere = 760 mm Hg at 0°C

= 29.93 in. Hg

= 33.9 ft H_2O = 1.033 kg/cm^3

= 14.695 lb/in^2 (psi) = 2116 lb/ft^2

VITA

Miss Waraporn Makvisai was born on February, 19, 1982 in Bangkok. She received the B.Sc. Degree in Industrial Chemistry at King’s Mongkutt Institute of Technology North Bangkok in 2002. Since then, she has been a graduate student studying in the program of Petrochemistry and Polymer Science at Faculty of Science Chulalongkorn University. During her graduate studies towards her M.Sc. degree, the Graduate School, Chulalongkorn University awarded her a research grant.