การแตกตัวของอะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนและน้ำมันหล่อลื่นใช้แล้วด้วยตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์

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CATALYTIC CRACKING OF ACRYLONITRILE-BUTADIENE-STYRENE AND USED-LUBRICATING OIL WITH Fe/ACTIVATED CARBON

Miss Siwathida Insuk

A Thesis Submitted in Partial Fulfillment of the Requirements
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จุดมุ่งหมายหลักของงานวิจัยนี้คือศึกษาการแตกตัวของอะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนและน้ำมันหล่อลื่นใช้แล้วด้วยตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์ ในเครื่องปฏิกรณ์ขนาดเล็ก ซึ่งมีปริมาตร 70 มิลลิเมตร โดยมีการเตรียมตัวเร่งปฏิกิริยา 5% เหล็กบนถ่านกัมมันต์ การเปลี่ยนแปลงค่าตัวแปรในการแตกย่อยดังนี้ อัตราส่วนระหว่างอะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนและน้ำมันหล่อลื่นใช้แล้ว 1:9 ถึง 5:5 โดยน้ำหนักต่อน้ำหนัก อุณหภูมิของปฏิกิริยาระหว่าง 400-470 องศาเซลเซียส เวลาที่ใช้ทำปฏิกิริยา 45-120 นาที ปริมาณตัวเร่งปฏิกิริยา 0-5% โดยน้ำหนัก และความดันของแก๊ซไฮโดรเจนเริ่มต้น 0-200 psi

ผลิตภัณฑ์น้ำมันที่ได้วิเคราะห์โดยใช้เครื่องแก๊ซโครมาโตรกราฟีชนิดจำลองการกลั่น พบว่า 5% เหล็กบนถ่านกัมมันต์ เป็นตัวเร่งปฏิกิริยาที่เหมาะในการแตกตัวอะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนและน้ำมันหล่อลื่นใช้แล้ว โดยภาวะที่เหมาะสมในการทำปฏิกิริยามีดังนี้ อัตราส่วนระหว่างอะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนและน้ำมันหล่อลื่นใช้แล้ว 4 : 6 โดยน้ำหนักต่อน้ำหนัก อุณหภูมิของปฏิกิริยา 430-450 องศาเซลเซียส เวลาที่ใช้ทำปฏิกิริยา 90 นาที ปริมาณตัวเร่งปฏิกิริยา 2.5 %โดยน้ำหนัก และความดันของแก๊ซไฮโดรเจนเริ่มต้น 100 psi ผลิตภัณฑ์ที่ได้จากสภาวะที่เหมาะสมมีปริมาณแนฟทา 37.91-38.60%, เคโรซีน 7.14-7.64%, แก๊ซออยเบา 12.20-13.17%, แก๊ซออยหนัก 1.40-1.48% และโมเลกุลสายยาว 2.38-4.44% นอกจากนั้นจากอินฟราเรดสเปกตรัม พบหมู่ฟังก์ชันของสารประกอบแอโรมาติก เช่นเดียวกับสเปกตรัมของน้ำมันเบนซิน 95

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SIWATHIDA INSUK: CATALYTIC CRACKING OFACRYLONITRILE-BUTADIENE-STYRENE AND USED-LUBRICATING OIL WITH Fe/ACTIVATED CARBON. THESIS ADVISOR: ASSOC. PROF. THARAPONG VITIDSANT, Ph.D., 87 pp. ISBN: 974-17-6648-3

The main objective of this research was aimed to study the catalytic cracking of acrylonitrile-butadiene-styrene (ABS) and used lubricating oil with Fe/activated carbon catalyst. The 5 wt % Fe/activated carbon catalyst was prepared. The catalytic reaction was done in micro-reactor volume of 70 ml by varying operating conditions which were used-lubricating oil and ABS were from 6 : 4 to 9: 1, reaction temperature range of 400 to 470°C, reaction time range of 45 to 120 minutes, initial hydrogen pressure range of 0 to 200 psi, and mass of catalyst was varied between 0 to 5 % by wt respectively.

The analyzed oil product from gas chromatography (GC Simulated Distillation) was found that Fe/activated was suitable to crack ABS and used-lubricating oil. The optimum condition was the ratio of used lubricating oil and ABS 6 : 4, reaction temperature 430-450°C, initial hydrogen pressure 100 psi, 90 minutes of reaction time and 2.5 % by wt of Fe/activated carbon catalyst. The product from the optimum condition was 22.7-23.4 % of gas 62.6-63.8 % of oil and 13.5-13.9 % of solid. The oil products distribution were 37.9-38.6 % of gasoline, 7.14-7.64 % of kerosene, 12.2-13.2 % of light gas oil, 1.40-1.48 % of heavy gas oil, 2.38-4.44 % of long residue. Moreover, functional groups of product analyzed by FT-IR also show the same position as those of gasoline octane number 95.

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ABBREVATIONS

DGC : Simulated Distillation Gas Chromatography

ABS : Acrylonitrile-Butadiene-Styrene

psi : pound per square inchs

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

FT-IR : Fourier Transform Infrared Spectroscopy

Fe/activated carbon : Iron impregnated on activated carbon

CHAPTER I

INTRODUCTION

1.1 Background

In the past years, the increase in plastic materials consumption has led to a parallel rise in the generation of plastic wastes, About 88% of waste plastics disposed of in landfills or by combustion. Landfill and combustion are no longer acceptable for the disposal of plastics because of serious environmental concern [1]. The quantity of used lubricating oil assumed to 40 million liters per year, used lubricating oil must be waste in enormous residue chemical waste. These alternatives are unacceptable regarding the environmental damage that can be caused since the used lubricating oils contain numerous additives harmful to human health (metals, sulfur, PAH, etc.) [2]. Therefore, the recycling of waste plastics and used lubricating oil has significant worldwide attention. The cracking process was selected to convert waste of plastic and 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 [3-5] 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 [6]. The activated carbon is the one of the support due to high surface area, high porosity and cheap [7]. The metal loaded on activated carbon were the catalyst used in catalytic cracking process [8].

So, in this research was investigated the catalytic cracking process of the mixture used lubricating oil and acrylonitrile-butadiene-strylene (ABS) to light fuel oil using Fe/activated carbon catalyst. Because of the incorporation of the lubricating oil into the plastic leads to a significant decrease in its viscosity which favors the mixture flow through the reactor [9].

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 aims to investigate the performance of the tested Fe/activated carbon catalyst on used lubricating oil and acrylonitrile-butadiene-styrene (ABS) copolymer.

.

1.2 Objectives

1.2.1 To prepared and characterization of the 5 wt % Fe/activated carbon catalyst.

1.2.2 To convert acrylonitrile-butadiene-styrene (ABS) and used lubricating oil to light oil with Fe/Activated carbon catalyst.

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 of acrylonitrile-butadiene-styrene (ABS) and used lubricating oil to light oil products.

1.3 Scopes of research

1.3.1 Prepare the 5 wt % Fe/activated carbon catalyst and characterization by XRF and BET analyzer.

1.3.2 Investigate the catalytic cracking of acrylonitrile-butadiene-styrene (ABS) and used lubricating oil on Fe/activated carbon under the following conditions :

- Ratio of ABS and used-lubricating oil range of 1: 9 - 4: 6.
- Reaction temperature range of 400-470°C.
- Reaction time range of 45-120 minutes.
- Initial hydrogen pressure range of 0-200 psi.
- Mass of Fe/Activated carbon catalyst (5 wt%. Fe loading) range of 0-5 % 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).

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Acrylonitrile-Butadiene-Styrene Copolymer (ABS)

Acrylonitrile-Butadiene-Styrene Copolymer or ABS [10] is an ideal material wherever superlative surface quality, colorfastness and luster are required. ABS is a two phase polymer blend. ABS have three monomer which are acrylonitrile, butadiene and styrene. The toughness of ABS is the result of submicroscopically fine polybutadiene rubber particles uniformly distributed in the SAN matrix. Styrene acrylonitrile copolymers have been available since the 1940's and while its increased toughness over styrene made it suitable for many applications, its limitations led to the introduction of a rubber (butadiene) as a third monomer and hence was born the range of materials popularly referred to as ABS plastics. These became available in the 1950's and the variability of these copolymers and ease of processing has led to ABS becoming the most popular of the engineering polymers. The molecular structure of ABS was shown in **figure 2.1**

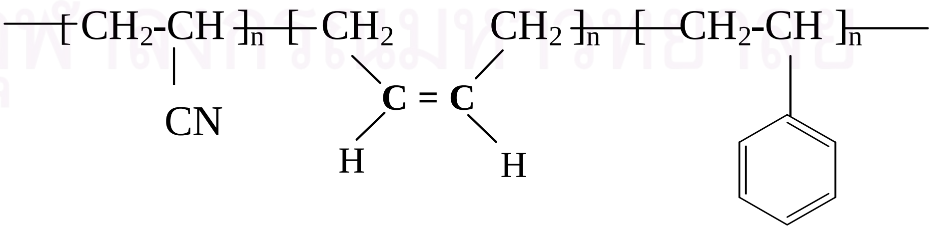


Figure 2.1 Molecular structure of ABS

ABS standard grades have been developed specifically to meet the requirements of major customers. ABS is readily modified both by the addition of additives and by variation of the ratio of the three monomers acrylonitrile, butadiene and styrene: hence grades available include high and medium impact, high heat resistance, and electroplatable. Fibre reinforcement can be incorporated to increase stiffness and dimensional stability. ABS is readily blended or alloyed with other polymers further increasing the range of properties available. Fire retardancy may be obtained either by the inclusion of fire retardant additives or by blending with PVC.

2.1.1 Physical and chemical properties of ABS

The physical properties and chemical properties of ABS were shown in **Table 2.1 and 2.1**

Table 2.1 Physical properties of ABS

Tensile Strength	40 - 50	Mpa
Notched Impact Strength	10 - 20	Kj/m^2
Thermal Coefficient of expansion	70 - 90	x 10^{-6}
Max Cont Use Temp	80 - 95	^{o}C
Density	1.0 - 1.05	g/cm^3

Table 2.2 Resistance to chemicals of ABS

Resistance to chemicals	
Dilute Acid	very good
Dilute Alkalis	very good
Oils and Greases	very good

2.1.2 Application of ABS

Because of its good balance of properties, toughness/strength/temperature resistance coupled with its ease of moulding and high quality surface finish, ABS has a very wide range of applications. These include domestic appliances, telephone handsets computer and other office equipment housings, lawn mower covers, safety helmets, luggage shells, pipes and fittings. Because of the ability to tailor grades to the property requirements of the application and the availability of electroplatable grades ABS is often found as automotive interior and exterior trim components.

Automotive construction places particularly high requirements on the materials used. Under extreme stresses they have to be dimensionally stable and must not warp, even when faced with great temperature variations.

Electrical and electronics industries increasingly require surfaces which are not only highly scratch- and wear-resistant but also decorative and easy to maintain. ABS's excellent antistatic performance is a particular advantage here.

Attractive products with elegant design and high quality create a feeling of well-being at home and in the office. ABS can create exciting and varied color schemes. Grades can also be electroplated, emboss-stamped or metallized. Depending on the molding equipment used. Surfaces can be matt, glossy or satin.

2.2 Lubricating oil [11]

2.2.1 Lubricating Base oil

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. There are the refining of petroleum crude oil and the synthesis of relatively pure compounds with are suitable for lubricant purposes.

2.2.2 Source of lubricating Base oil

The source of lubricating base oil were from

2.2.2.1 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.

2.2.2.2 Base Oil Composition

The petroleum composition used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating composition is a complex mixture consisting primary of five characteristic classes-paraffin naphthenes, condensed naphthenes, aromatic naphthenes, naphthalene 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.

2.2.3 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.

2.2.3.1 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.

2.2.3.2 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.

2.2.3.3 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.

2.2.3.4 Oxidation and Bearing Corrosion Inhibitors

The function of oxidation inhibitor is prevention of deterioration with oxygen attack on the lubricant base fluid. These 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.

2.2.3.5 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 an be controlled by use the alkaline additive.

2.2.3.6 Viscosity Improvers

Viscosity improvers or viscosity index improvers, as the 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.

2.2.4 Basic Function of Lubricating Oil

The basic function of lubricating oil are:

2.2.4.1 Friction reduction

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

2.2.4.2 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.

2.2.4.3 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, particulate matter. Etc., which generally find their way into lubricating oil employed in various applications.

2.2.5 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.

2.2.5.1 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 Saybolt 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 and 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 have 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 a lubricating oil is chilled, it eventually reaches a point where it will no longer flow under the influence of gravity. This condition is brought about either by 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 an 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 an 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 an oil is roughly indicated by the test. Thus, during manufacture, the test give 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.

2.2.5.2 Chemical Properties

All petroleum products are subject to chemical attack by oxygen. Attack is promoted by high temperature, catalysts ant 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 lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and a marked increase in viscosity of the lubricant, all which seriously impair the efficiency of the lubricant.

The 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.

2.2.6 Environmental consideration of used lubricating oil [12]

There are three basic disposal methods for used lubricating oil;

- Disposal as toxic/hazardous waste
- Re-fining to produce base oil
- Used 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 treated accordingly.

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.

2.2.7 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 2.3** and **Table 2.4**.

Table 2.3 Important of petroleum crude oil in 1992 to 2003 [13]

Year	Quantity (million liters)
1992	16,148
1994	18,794
1995	21,336
1996	26,558
1997	36,844
1998	42,348
1999	39,446
2000	41,386
2001	39,242
2002	41,386
2003	45,025

Table 2.4 Monthly import of lubricating oil in 1993 to 1994 [13]

	Quantity (million liters)	
Month	1993	1994
January	6.39	6.48
Febuary	4.79	7.86
March	12.45	7.54
April	10.5	14.17
May	5.79	10.85
June	8.34	8.4
July	10.19	4.2
August	8.89	5.8
September	2.67	11.44
October	8.15	16.64
November	7.2	6.75
December	10.05	13.27

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.

2.3 Cracking reaction

2.3.1 Thermal Cracking [14]

Thermal cracking, where free radical (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which 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 call 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 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 polyolefins cracking as follows;

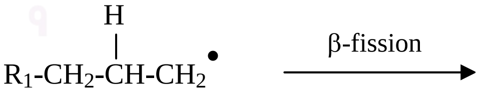
1. Initiation Step

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \xrightarrow{\text{heat},h\upsilon} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + R_2^{\bullet} \tag{2.1}$$

2. Propagation Step

2.1 **β-fission**

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2^{\bullet} + CH_2=CH_2 \tag{2.2}$$



$$R_1\text{-}CH_2\text{-}\overset{\overset{\displaystyle H}{|}}{C}H\text{-}CH_2^{\bullet} \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH=CH_2 + H^{\bullet} \tag{2.3}$$

2.2 **Chain transfer**

$$R_1\text{-}CH_2\text{-}(CH_2)_4\text{-}CH_3 + H^{\bullet} \longrightarrow R_1\text{-}\overset{\bullet}{C}H\text{-}(CH_2)_4\text{-}CH_3 + \overset{\bullet}{H} \tag{2.4}$$

3. Termination Step

$$R_1^{\bullet} + R_2^{\bullet} \longrightarrow R_1 - R_2 \qquad (2.5)$$

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

(2.6)

2.3.2 Catalytic Cracking [15]

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 produced.

There are tow 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 produceds a carbonmium ion in combination with acid anion and molecule hydrogen:

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 + H^+A^- \longrightarrow R_1\text{-}CH_2\text{-}{}^{+}CH\text{-}R_2 + H_2 + A^- \qquad (2.7)$$

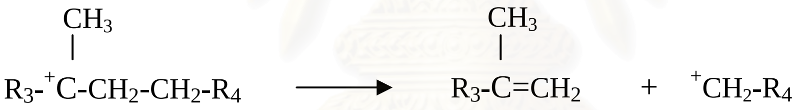
Alternatively a small amount of olefin, create by thermal cracking could initiate the reaction;

$$R_1\text{-}CH{=}CH\text{-}R_2 \;+\; H^+A^- \longrightarrow R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \;+\; A^- \qquad (2.8)$$

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).

$$R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 + R_3\text{-}\overset{\overset{H}{|}}{C}H\text{-}CH_2\text{-}CH_2\text{-}R_4 \longrightarrow R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 + R_3\text{-}{}^+\overset{\overset{CH_3}{|}}{C}\text{-}CH_2\text{-}CH_2\text{-}R_4 \qquad (2.9)$$

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

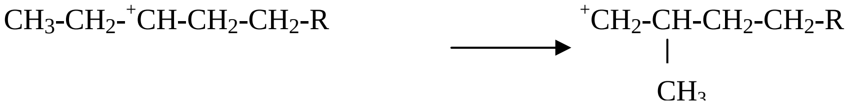


$$R_3\text{-}{}^+\overset{\overset{CH_3}{|}}{C}\text{-}CH_2\text{-}CH_2\text{-}R_4 \longrightarrow R_3\text{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \;+\; {}^+CH_2\text{-}R_4 \qquad (2.10)$$

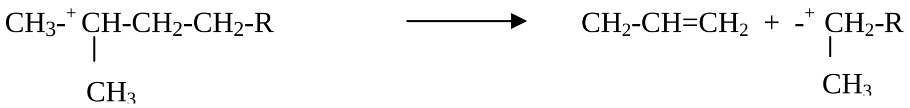
A hydride shift then converts the primary carbonium ion formed into a secondary carbonium ion;

$${}^+CH_2\text{-}R_4 \longrightarrow CH_3\text{-}\,{}^+CH_2\text{-}R_4 \qquad (2.11)$$

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:



$$CH_3\text{-}CH_2\text{-}{}^+CH\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow {}^+CH_2\text{-}\underset{\underset{CH_3}{|}}{C}H\text{-}CH_2\text{-}CH_2\text{-}R \qquad (2.12)$$



$$CH_3\text{-}^{+}\underset{CH_3}{\underset{|}{C}}H\text{-}CH_2\text{-}CH_2\text{-}R \longrightarrow CH_2\text{-}CH=CH_2 + \text{-}^{+}\underset{CH_3}{\underset{|}{C}}H_2\text{-}R \qquad (2.13)$$

The reaction model of hydrocarbon cracking on activated carbon was shown is **figure 2.2**

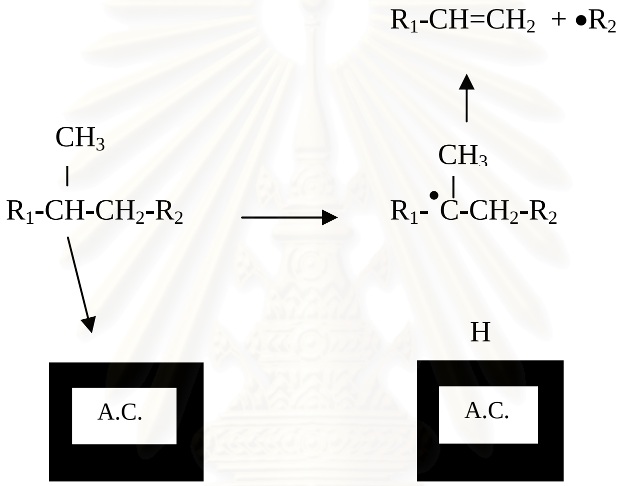


Figure 2.2 Reaction model of hydrocarbon cracking on activated carbon [8]

2.4 Metal Catalysts [16]

Metal catalysts are of particular interest for reaction involving hydrogen, such as hydrogenation, hydrocracking and catalytic reforming [17]. The use of iron for ammonia synthesis and for the Fisher-Tropsch reaction, and nickel for steam reforming and methanation. In many of these applications the metal is highly dispersed on a support, in aggregates so small that many or most of the atom of exposed metal (turn number) and, more importantly, the reaction rates of alloys; by kinks, steps and other crystal imperfections; and by the blockage of some of the sites by deliberately added poison or by accumulation of carbonaceous deposites. There is also a possible role of the support in influencing the properties of the metal.

2.4.1 Impregnation [18]

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. Most of active carbons, which have a layer of chemisorbed oxygen on them. 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 [19]

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 are 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 Activated carbon [20]

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area. If you take a look at a cross section structure of activated carbon particle, it looks like a beehive. It consist principally of carbon (87 to 97%) but also contains such element as hydrogen, oxygen, sulfur and nitrogen as well as various compound either originating from the raw material used in its production or during its manufacture. Activated carbon has the ability to adsorb various substance both from the gas and liquid phases.

The reason that activated carbon is such an effective support material is due to its large number of cavernous pores. These provide a large surface area relative to the size of the actual carbon particle and its visible exterior surface. An approximate ratio is 1 gram = 900 m^2 of surface area [21]. The scanning electron microscope images of activated carbon were shown in **figure 2.3**.

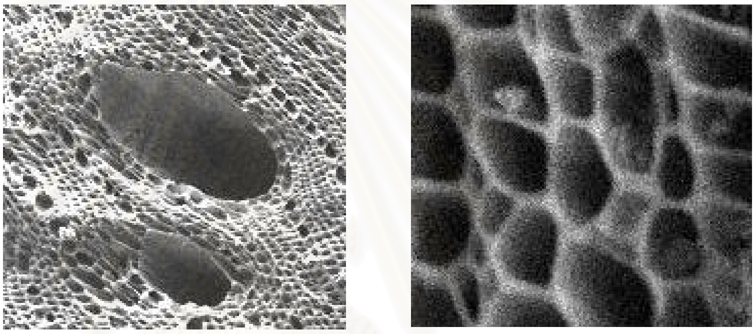


Figure 2.3 Scanning electron micrograph of Pores of activated carbon [21].

2.4.3.1 Molecular, crystalline and porous structure of activated carbon

The graphite-like microcrystalline structure is the basic structural unit of activated carbon, as in the case of carbon black. The ordering of carbon atoms in an elementary microcrystallite indicates considerable similarity to the structure of pure graphite, the crystals of which consist of parallel layers of condensed regular hexagonal ring space 0.335 nm. apart. Such interlayer spacing is diagnostic of interaction by means of Van Der Waals forces. The length of the carbon-carbon bond in individual layers is 0.142 nm. Each carbon atom bonds with the three adjoining ones by means of covalent bonds, and the fourth delocalized π-electron may move freely in a system of conjugated double bonds of condensed aromatic ring. The formation of the crystalline structure of activated carbon beings early during the carbonization process of the starting material. Thus sets of condensed aromatic ring of various numbers, which are the nascent center of graphite-like microcrystallites, are formed. Although their structure resembles that of a crystal of graphite there exist some deviations from that structure. Thus, among other things, the interlayer distances are unequal in crystals of activated carbon and range from 0.34 to 0.35 nm. Again, the orientations of the respective layers generally display deviations, such deviations from the ordering characteristic of graphite, called a turbostratic structure. Disordering of the crystal lattice may be caused to a considerable degree both by its defects (vacant lattice sites) and by the presence of built-in heteroatoms. It is resulted from the kind of the raw material used, the nature and quantity of its impurities as well as the methods and conditions of the production processes of the active carbon. The average activated carbons have a strongly developed internal structure (the specific surface often exceeds 1000 and sometimes even 1500 m^2/g), and they are usually characterized by a polydisperse capillary structure, featuring pores of different shapes and sizes. Bearing in mind the values of the effective radii and the mechanism of adsorption of gases, Dubinin proposed three main types of pore, namely macropores, mesopores and micropores.

2.4.3.2 Chemical nature of the surface of activated carbon

The chemical nature of activated carbons significantly influences their adsorptive, electrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites and in intercrystalline spaces and even in defect zones of particular planes constituting the crystallites. Most heteroatomes are grouped at the surface of activated. Apart from their different locations, the heteroatoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as = OH or = COOH. Surface functional groups can originate from the starting material from which a particular activated carbon is produced. Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activated carbonaceous materials by oxidizing gases, such as water vapor and air. Activated carbon used predominantly for practical purposes generally includes some percentage by weight of chemically-bond oxygen and usually much smaller quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

2.4.3.3 Estimation of the properties of activated carbon

The commercial use of activated carbons, their transport, storage and sales require knowledge of the properties of these materials. The methods for estimating these properties are approved by the members of the activated carbons sector group of the European Council of Chemical Manufactures' Federations (CEFIC). The tests require highly professional laboratories and advanced equipment.

Most of the testing methods have been developed and by approved such organizations as the American Society for Testing Material (ASTM), the

American Water Works Association (AWWA), the Deutsches Institute fur Normung e.V. (DIN), or the International Organization for Standardization (ISO)

- **(a) B.E.T. Surface area**

To measure total surface area, nonspecific physical adsorption is required, but even with physical adsorption the isotherm varies somewhat with the nature of the adsorbent (the solid). Most physical adsorption isotherms may be grouped into five types, as originally proposed by Frunauer, Deming, Deming and Teller (BDDT). More recently, the grouping has generally been termed the *Bruneuer, Emmett, and Teller* (BET) *classification.* In all cases the amount of vapor adsorbed increase as its partial pressure is increased, becoming at some point equivalent to a monolayer, but then increasing to a multilayer, which eventually merges into a condensed phase as the relative pressure, P/Po approaches unity.

(b) Physical test

- *Bulk density.* The bulk density is defined as the mass per unit volume of the activated carbon sample in air including both the pore system and the void between the particles. The bulk density of activated carbon, depending on the shaped, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

(c) Adsorption tests

adsorption properties of activated carbons are generally estimated by determining the isotherms of adsorption from the liquid phase. The determination of the adsorption of one test substance from an aqueous solution is often insufficient for characterizing the adsorption properties of a carbon.

Thus the properties of activated carbons are estimated by comparing the result of measurements for different adsorbates, e.g. by comparing the adsorptions of fairly large molecules of methylene blue or iodine.

- *Iodine adsorption.* The study of the process of iodine adsorption and also the determination of the iodine number is a simple and quick test estimating the specific surface area of activated carbon. The iodine number is defined as the number of milligrams of iodine adsorbed by 1 g of activated carbon from an aqueous solution when the iodine concentration of the residual filtrate is 0.02 N. If the final values obtained are different from 0.02 N but lie in the range of 0.007-0.03 N, appropriate corrections are necessary. In this method it is assumed that iodine at the equilibrium concentration of 0.02 N is adsorbed on the carbon in the form of a monolayer, and this is the reason why there is a relationship between the iodine number of activated carbon and its specific surface area which may be determined, for example, by the BET method. The specific surface areas of activated carbons with highly developed microporous structures as determined by the iodine number method are too low. This is because iodine is adsorbed chiefly on the surface of pores much larger than 1 nm, while in activated carbons with large specific surface areas the proportion of vary fine pores inaccessible to iodine molecules is significant.

(d) Physico-chemical test

- *Volatile matter content.* The international standard used for determination of volatile matter in hard coal and coke is also applicable to activated carbon. A sample of powdered (<0.1 nm) activated carbon is heated at 950 ± 25 °C for 7 min ± 10 s.

Volatile matter content is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

- *Moisture content.* A simple method of determining the water content is drying activated carbon in a dryer. The sample of powdered (1-2 g) or granular (5-10 g) carbon is dried at 150 °C to constant weight (usually about 3 hr.) The weight loss is expressed as a percentage of the weight of the original sample.

- *Ash content.* The ash content in various types of activated carbon varies over a wide range, depending primarily on the type of raw material. The relative ash content also increases with increase in the degree burning of the coal during activation. Ash consists mainly of oxides and in smaller amounts, of sulfates, carbonates, and other compounds of iron, aluminium calcium, sodium, potassium, magnesium and many other metals. Depending upon the type of raw material, it may comprise different and often fairly large quantities of silicon. The commonly used method of removing ash is to leach activated carbon with acids. Due to the complex composition of ash, mixture of acids, e.g. hydrochloric or hydrofluoric acid, are often used if ash contains substantial quantities of silicon. The ash content of activated carbon can be determined by ignition of the crucible in an electric muffle furnace. Ignition is conducted at 650 ± 25 °C for 3 to 16 hr, depending on the type of activated carbon and dimensions of its particles, to constant mass. The weight of the ashes carbon is expressed as a percentage of the weight of the original carbon sample.

2.5 Literature Reviews

Nakamura *et al.* [7] studied the liquefaction of polypropylene using metal free active carbon, 5 % Fe supported coal derived 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.

Siauw [8] studied the thermal cracking and catalytic cracking of vacuum gas oil (VGO) and blends containing 5 and 10 wt% high density polyethylene, respectively, in the VGO in a fixed bed reactor at 510°C and 20 h^{-1} WHSV. The objective was to produce transportation fuels from direct cracking of polyethylene without prior pyrolysis at 450-500°C as reported previously. Thermal cracking resulted in low overall conversion to naphtha and its secondary products including coke, although polyethylene in the blend was substantially converted. In contrast, high conversion was obtained from catalytic cracking. However, the naphtha yield of polyethylene. depended on its concentration in the blend. At 5 wt. % polyethylene, the naphtha produced from primary cracking appeared to be completely decomposed to gas and coke through secondary cracking whereas at 10 wt. %, a substantial amount of naphtha was produced.

Serrano *et al.* [9] investigated both thermal and catalytic cracking of mixtures consisting of low-density polyethylene (LDPE) and a lubricating oil base in a continuous screw kiln reactor, provided with two reaction zones operating at different temperatures (*T*1/*T*2). The incorporation of the lubricating oil into the plastic leads to a significant decrease in its viscosity which favors the mixture flow through the reactor. Thermal cracking at 450/500°C of LDPE–lubricating oil base mixtures with compositions ranging from 40/60–70/30 (%, w/w) led in all cases to their almost catalytic cracking of a 70/30 (%, w/w) LDPE–lubricating oil base mixture over mesoporous Al-MCM-41 catalysts at 400/450 ◦C proceeded with lower activity with regards to the pure LDPE catalytic cracking. Al-MCM-41 materials led mainly to C5–C12 products (65% selectivity) whereas lighter hydrocarbons were formed preferentially over n-HZSM-5 (63% selectivity towards C3–C5 compounds). complete conversion (~90%) towards a broad spectrum of C1–C40 hydrocarbons.

Tiganis *et al.* [22] studied the composition of nitrogen-containing compounds in oil obtained from acrylonitrile-butadiene-styrene(ABS) thermal degradation. The thermal degradation of the acrylonitrile-butadiene-styrene copolymer was carried out at different temperatures from 360 to 440°C in static and dynamic atmospheres of nitrogen, using semi-batch operation. Nitrogen-containing compounds were found in all three degradation composition: gases (as NH_3 and HCN), oil, and residue. The percentage of the oil composition increases with the degradation temperature At 440°C 63 wt.% of the initial ABS feed was recovered in the oil composition.

Wang *et al*. [23] investigated thermal cracking of mixture consisting polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), acrylonitrile –butandiene–styrene (ABS) and used-lubricating oil in a 70 ml of reactor. PE, PP, and PS gave the high yield but PET and ABS gave low yield. Especially the mixture of HDPE, LDPE and used lubricating oil gave the highest yield (99%) at 430°C and reaction time in 30 minutes. The mixture of PS and used lubricating oil gave the higher yield (95%) at 426°C and reaction time in 12 minutes.

Peuaknapo [18] studied the conversion of acrylonitrile –butandiene–styrene (ABS) into oil product using iron on activated carbon catalyst. Experiment was investigated in a micro-reactor width 30 mm inside diameter and volume of 70 ml by varied temperature between 390 and 450°C, hydrogen pressure at 20-40 kg/cm^2, amounts of catalyst and percentages loading of iron were varied between 30 and 90 minutes, 0 and 0.75 g and 1, 5, 10 % on activated carbon catalyst, respectively.

The analyzed oil product from Gas Chromatography Distillation was found that iron on activated carbon catalyst was suitable to crack ABS. The optimum condition was 430°C , hydrogen pressure at 40 kg/cm^2, reaction time 60 min, amount of catalyst 5% . The product distribution was 45 % naphtha, 4.8 % kerosene, 8.1 % gas oil and 9.1 % long residue. Moreover, the product showed aromatic functional group by mean of Fourier Transform Infrared Spectrometer, which indicated in the presence of high octane number and showed low intensity of N-containing.

CHAPTER III

EXPERIMENTAL

3.1 Raw material and Chemical

The acrylonitrile-butadiene-styrene (ABS) copolymer used in experiments is commercial grade supplied from Thai Petrochemical Industry Co., Ltd. It was virgin plastic of 3x3x2 mm size granules. The used lubricating oil supplied from Gasoline Station II Directorate of welfare, Royal Thai Air Force. The activated carbon was used as supported from CGS Co., Ltd. Hydrogen gas (purity 99.5 % minimum) and toluene (commercial grade; purity 80 % minimum) from Lab System Co., Ltd. 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

An apparatus for catalytic cracking reaction experimental (shown in **figure 3.1**) was used to carry out the reaction. The micro-reactor is stainless steel tube (SS.316) with an inner volume of 70 cm^3 (shown in **figure 3.2**). It was heated by 450-watt electricity. The 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.

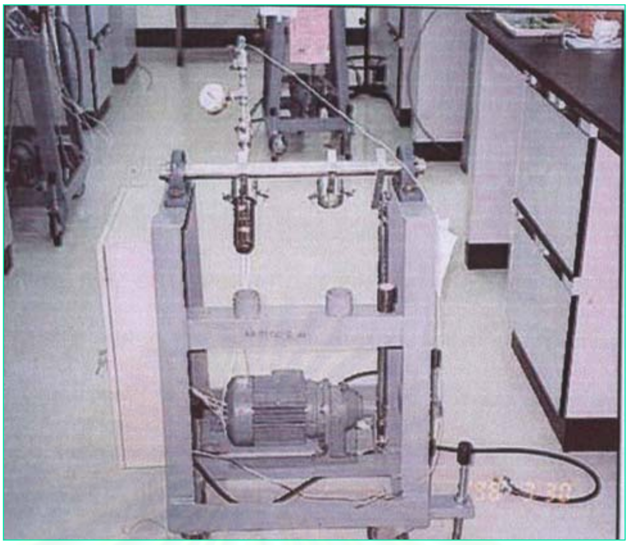


Figure 3.1 Apparatus for catalytic cracking reaction experimental.

Figure 3.2 Micro-reactor

3.2.2 Vacuum pump

The separation of liquid product from catalyst and residue by the vacuum filter pressure 1 kg/cm^2.

3.2.3 Gas chromatography (GC Simulated Distillation)

Perkin Elmer 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 were obtained.

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.

3.3 Experimental Procedure

3.3.1 Preparation of catalyst

The 5 wt % Fe supported on activated carbon (5 wt % Fe/Activated carbon) was prepared by wet impregnation method using excess water [19]. Ferric nitrate nanohydrate ($FeN_3O_9 . 9H_2O$) was dissolved in deionized water to Fe concentration of 5 wt %. (calculation of Fe concentration was shown in Appendix D) and then loaded onto activated carbon 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.

3.3.2 Catalyst Characterization

The contents of Fe impregnated on activated carbon were determine using a SISONA 9410 X-ray fluorescence spectrometer at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

BET surface area of a catalyst was determined using Micromeritics adsorptometer, model Flowsorb 2300, at Metallurgy and Materials Science Research Institute, Chulalongkorn University.

3.3.3 Catalytic cracking reaction procedure

An required mass of ABS, used-lubricating oil and catalyst were fed in 70 ml micro-reactor under hydrogen pressure. Heating coil, insulator, and thermocouple were covered the reactor. The reactor was fixed with a shaker at 120 rpm for required reaction time. The parameters were the ratio of mixed ABS and used lubricating oil, reaction temperature, reaction time, initial hydrogen pressure and the mass of catalyst (5 wt % Fe loading) were effected and investigated respectively,. Each experiment was used total 20 g of raw materials.

The raw materials were converted under the following condition:

- Ratio of used lubricating oil and ABS range from 5 : 5 to 9 : 1
- Reaction temperature range from 400 to 470°C.
- Reaction time range from 45 to 120 minutes.
- Initial hydrogen pressure range from 0 to 200 psi.
- Mass of Fe/Activated carbon catalyst (5 wt % Fe loading) range from 0 to 5 % by wt.

The experimental scheme was shown in **figure 3.3**.

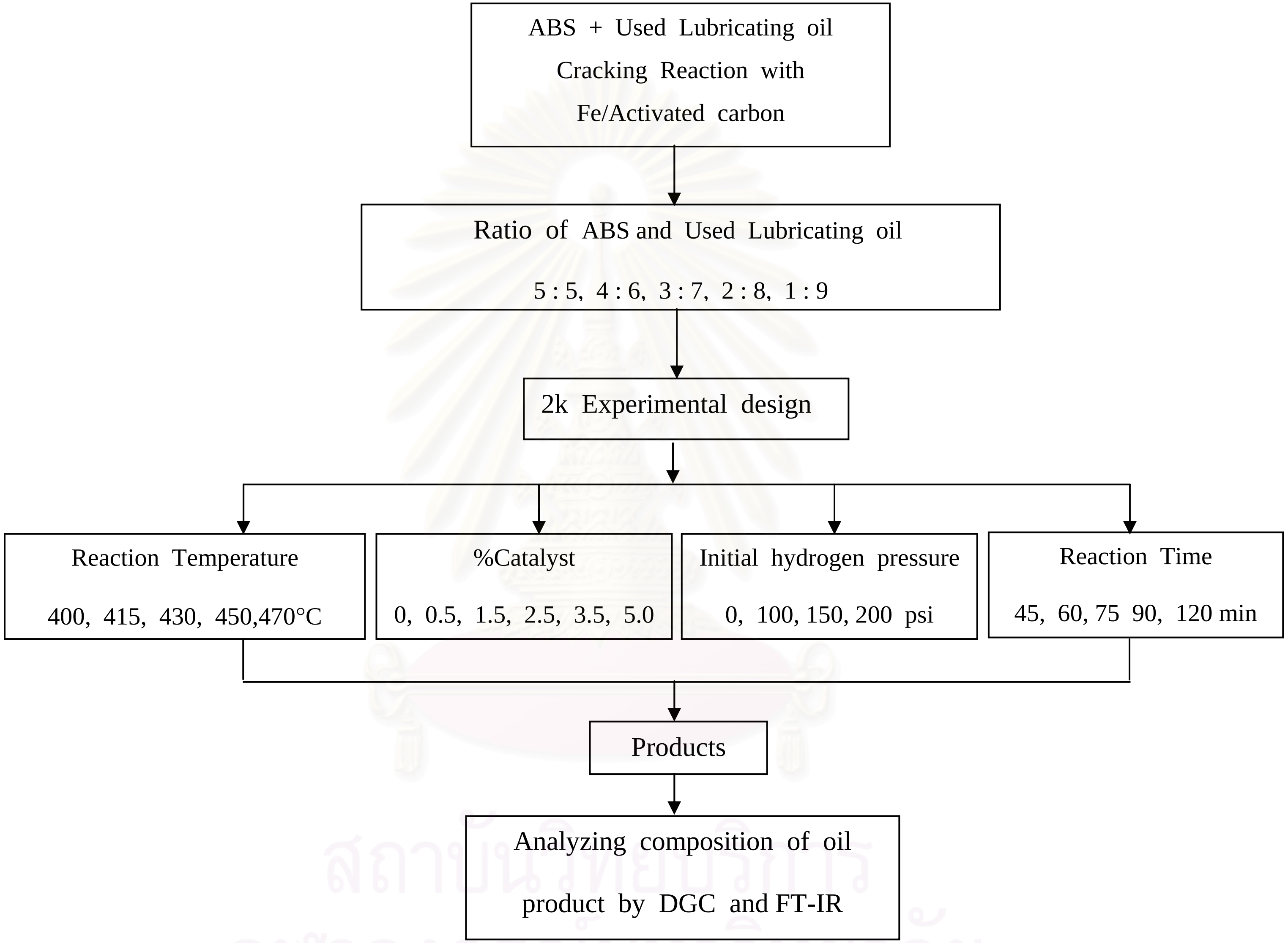


Figure 3.3 The scheme of experiment in this research

After the reaction, the gaseous product were determined by weighing the tubular micro-reactor before and after 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 product by vacuum filtration. The liquid products were analyzed by Simulated Distillation Analysis. The boiling point range of the liquid from the different reactions Simulated Distillation follow as 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 were calculated by Simulated Distillation.

Table 3.1 Oil composition calculated by Simulated Distillation 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 Fe/activated carbon catalyst

4.1.1 BET surface area

The 5 wt % Fe/activated carbon catalyst was prepared and compared the BET surface area with 1 wt % Fe/activated carbon and 10 wt % Fe/activated carbon (data from Rujasiri, W.). The surface area was obtained using BET analyzer. The surface area was shown in Table 4.1.

Table 4.1 The BET surface area of activated carbon

Sample	Surface area (m^2/g)
Activated carbon	950
1 wt % Fe/activated carbon	790
5 wt % Fe/activated carbon	774
10 wt % Fe/activated carbon	529

From Table 4.1, it showed that the BET surface area of activated carbon was 950 m^2/g while that other samples loaded Fe on activated carbon were decreased when % Fe was increased. It is because of the substitution of metal distributed on surface area of activated carbon. The 5 % Fe/activated carbon has 774 m^2/g which still high surface area.

4.1.2 Chemical Analysis of impregnated Fe on activated carbon

The Fe/activated carbon catalyst was prepared by impregnating on activated carbon with Fe concentration of 5 wt %. The XRF was used to determine the metal in catalyst as shown in Table 4.2.

Table 4.2 % Concentration of metal in catalyst

Element	Concentration (%)
Al	0.02
Si	0.06
S	0.06
K	0.95
Ca	0.10
Zn	0.10
Fe	**4.63**
C	94.1

From Table 4.2, it showed that many elements were in catalyst. The % concentration of Fe was 4.63 that slightly decreased from the calculation of Fe for synthesis.

4.2 Properties of raw materials

4.2.1 Used lubricating oil

The composition of used lubricating oil was analyzed by DGC before used. The composition distribution was shown in **Table 4.3.**

Table 4.3 Composition of used lubricating oil

Composition	% Selectivity
naphtha	0.00
kerosene	0.50
light gas oil	3.72
heavy gas oil	8.48
long residue	87.3

From Table 4.3, the main composition of used lubricating oil is long residue and no composition of naphtha because of its high molecular weight hydrocarbon.

4.2.2 Acrylonitrile-Butadiene-Styrene (ABS)

Commercial acrylonitrile-butadiene-styrene (ABS) copolymer typically contains approximately 35 % acrylonitrile, 25 % butadiene and 40 % styrene.

4.3 Catalytic cracking process

This experiment aim to search the optimum conditions to convert used lubricating oil and ABS with Fe/activated carbon to light oil (main in naphtha composition). All parameters from catalytic cracking process of used lubricating oil and ABS with Fe/activated carbon were studied as a function of processing variable, *i.e.* the ratio of used lubricating oil to ABS, reaction temperature, reaction time, initial hydrogen pressure and percentage of catalyst. The oil product were determined by Simulated Distillation Gas Chromatography, following the ASTM D-2887 method. The variable of % naphtha overall in the oil product as a function of the above variables allowed for the selection of suitable conditions.

The optimum ratios between used lubricating oil and ABS were searched in the first step. The experiment was investigated using the 2^k factorial experimental design before searching the optimum conditions.

4.3.1 Effect of ratio of used lubricating oil and ABS on product distribution

The study of ratio of used lubricating oil and ABS on the catalytic cracking was performed based on condition from Kaewsaiyoy A. [10] by operating in various ratios: 5: 5, 6 : 4, 7 : 3, 8 : 2 and 9 : 1, respectively at 5 % by wt of Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure, 450°C of reaction temperature and 90 minutes of reaction time. The product distribution were shown in **Table 4.4** and **figure 4.1.**

Table 4.4 Effect of ratio of used lubricating oil and ABS on product composition at 450°C of reaction temperature, 5 % by wt Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure and 90 minutes reaction time.

Ratio of	Gas produc	Oil product	Solid	Oil products (% recovered)				
Lubricating oil: ABS	(%yield)	(%yield)	(%yield)	naphtha	kerosene	light gas oil	heavy gas oi	long residue
5 : 5	24.5	60.0	15.5	38.6	7.60	10.2	1.08	2.54
6 : 4	22.5	63.8	13.8	38.5	7.14	12.2	1.40	4.51
7 : 3	19.4	67.9	12.7	35.9	7.16	13.6	2.29	9.00
8 : 2	19.1	68.5	12.4	34.2	7.95	14.3	2.33	9.70
9 : 1	14.6	69.4	16.0	33.7	5.89	14.3	2.31	13.2

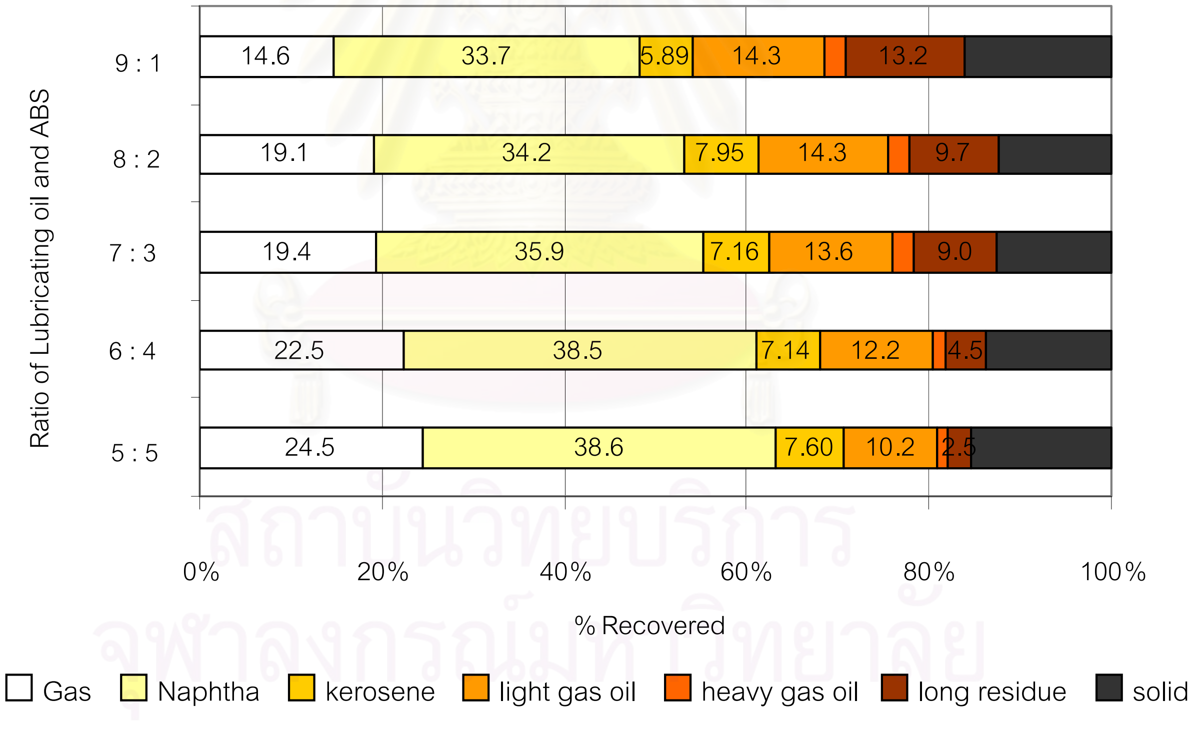


Figure 4.1 Effect of the ratio of used lubricating oil and ABS range of 5:5 - 9: 1 on product composition at 450°C of reaction temperature 5 % by wt Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure and 90 minutes of reaction time.

From Table 4.4 and figure 4.1 show that the percentage of naphtha quite increased from 33.7 % to 38.5 % when the ratio were increased from 9: 1 to 6: 4 (used lubricating oil : ABS) whereas it was slightly increased to 38.6 % with the ratio 5: 5. The gaseous product were increased when increased plastic ratio due to long chain hydrocarbon molecules were broken into lower hydrocarbon (C_1-C_5). When the ratio of used lubricating oil : ABS was 6: 4, it gave high % naphtha and % kerosene thus it was the optimum ratio.

In conclusion, the optimum ratio of used lubricating oil and ABS was 6 : 4. because it gave high naphtha 38.5 %, kerosene 7.14 %, low gas and residue. This ratio was used to study for other variables. After that, the 2^k experimental design was carried to study the variables effected in this process.

4.3.2 2^k Experimental design

The 2^k experimental design was carried out in this research work to study the factors to influence the yield of naphtha. The four process variables were % by weight of catalyst (A), initial hydrogen pressure (B), reaction time (C) and reaction temperature (D). To ensure that the assumptions of normality and constant variable were met, the response variable, yield of naphtha was calculate. The response variable was analyzed by constructing a normal probability plot of the effect estimates. The table of plus and minus for the 2^k experimental design was shown in **Table 4.5.**

From Table 4.5, the calculation of contrasts, estimate effects, and the summation of square were calculated. The normal probability plot of effect estimate on yield of naphtha was shown in **figure 4.2.**

All of the effects that lie along the line are negligible, whereas the large effects are far from the line. From figure 4.2, the important effects are C and D. The analysis of variance (ANOVA) of yield of naphtha was shown in **Table 4.6**. Table 4.6 shows the F test of effects of the process variables. The effect of variables which are significant with respect to yield of naphtha, can be identified. An “effect” is identified as the change in the response on changing the variable from the “-“ level to “+” level.

From the normal probability and the analysis of variance (ANOVA), the reaction temperature (D) and reaction time (C) effected on the catalytic cracking process while percentage of catalyst (A) and initial hydrogen pressure (B) was not effected.

Table 4.5 Design factor levels for factorial designed experiments

Batch No.	Design factor				Yield of gasoline (%)
	% catalyst	H_2 pressure	Temp.	Time	
1	-	-	-	-	24.3
2	+	-	-	-	20.8
3	-	+	-	-	19.6
4	+	+	-	-	22.2
5	-	-	+	-	22.6
6	+	-	+	-	26.3
7	-	+	+	-	20.7
8	+	+	+	-	25.0
9	-	-	-	+	31.7
10	+	-	-	+	31.8
11	-	+	-	+	31.4
12	+	+	-	+	37.1
13	-	-	+	+	31.4
14	+	-	+	+	41.0
15	-	+	+	+	41.1
16	+	+	+	+	40.6

% catalyst : - (0.5), + (5.0) H_2 pressure : - (100 psi), + (200 psi)

Time : - (45 min.), + (90 min.) Temp. : - (400 °C), + (450 °C)

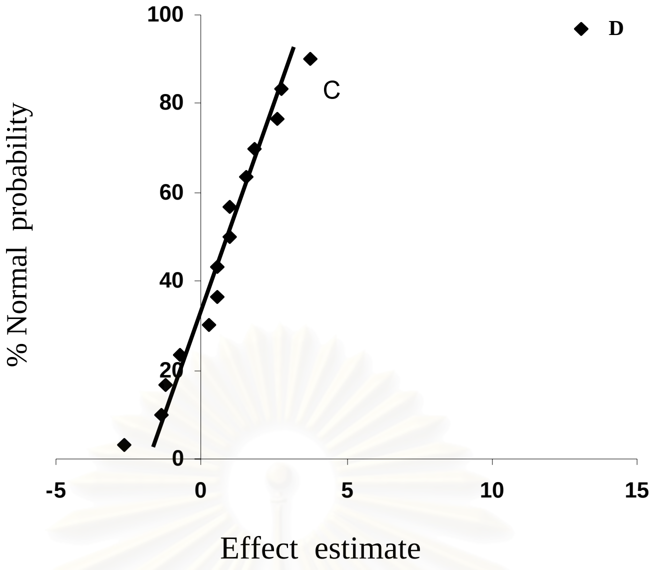


Figure 4.2 The normal probability plot of effect estimate on % yield of naphtha

Table 4.6 The analysis of variance (ANOVA) of yield of naphtha

Effect Name	Estimate Effect	Sum of Square	Degree of Freedom	Mean Square	F_0	F_c
C	3.72	55.4	1	55.4	5.37	4.67
D	13.1	683.8	1	683.8	66.2	4.67
Error		134.3	13	10.3		
Total		873.5	15			

4.3.3 Effect of reaction temperature on product distribution

The study of reaction temperature on the catalytic cracking of used lubricating oil and ABS with Fe/activated carbon catalyst was performed (based on 2^k experimental design) by operating in various temperatures: 400, 415, 430, 450, 470°C. Mass of Fe/activated carbon catalyst at 2.5 % by wt, 100 psi of initial hydrogen pressure, reaction time 90 minutes, and 6: 4 of used lubricating oil and ABS were fixed.

Generally, at reaction temperature lower 400°C the product were sticky like wax. At reaction temperature above 470°C, wax could be further cracked and carbon was deposited on the surface of catalyst. Therefore, the experiment was carried out at temperature 400°C to 470°C only. The product distribution was shown in **Table 4.7 and figure 4.3.**

Table 4.7 Effect of reaction temperature on product composition at 2.5 % by wt Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS.

Temperature (^{o}C)	Gas product (%yield)	Oil product (%yield)	Solid (%yield)	Oil products (% recovered)				
				naphtha	kerosene	light gas oil	heavy gas oil	long residue
400	23.0	71.5	5.49	28.1	7.97	15.1	2.17	18.2
415	23.0	70.0	7.01	34.2	8.41	13.7	1.50	12.2
430	23.5	62.6	13.9	37.9	7.64	13.2	1.48	2.38
450	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
470	24.8	58.3	16.9	34.7	5.62	10.5	1.11	6.33

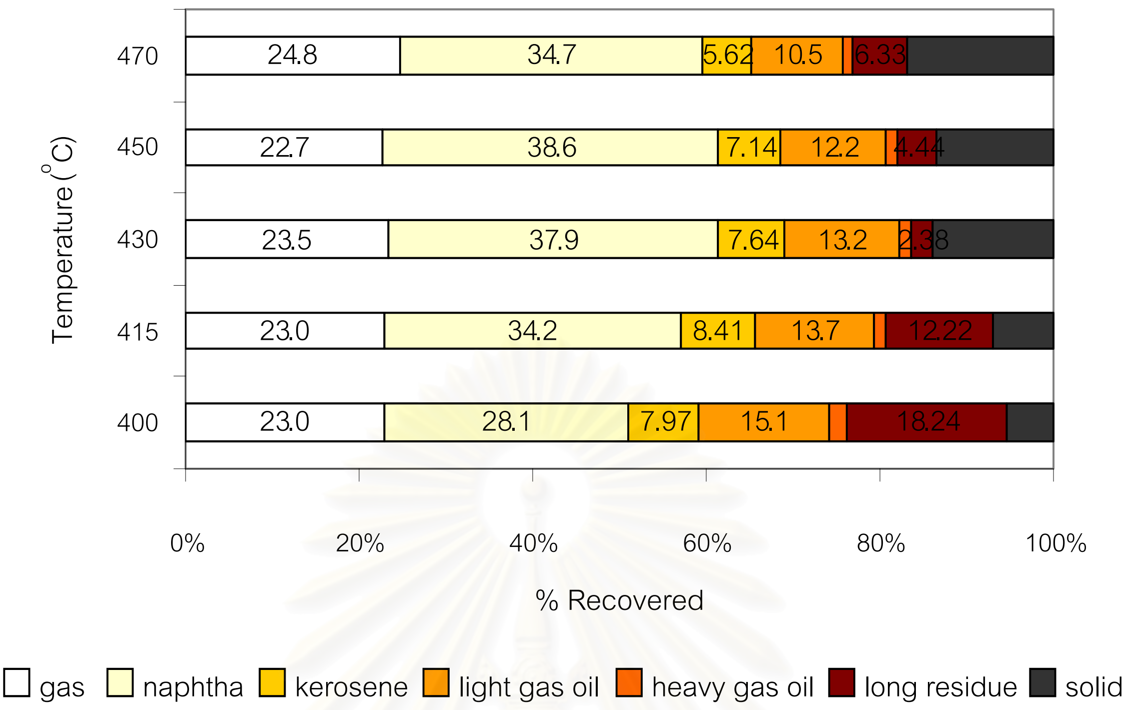


Figure 4.3 Effect of reaction temperature range of 400-470°C on product composition at 2.5 % by wt Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS.

Table 4.7 and figure 4.3 show % yield of naphtha increased from 28.1 % to 38.6 % when the temperature was increased from 400°C to 450°C. However, at temperature 470°C, it was that noticed the % yield of naphtha decreased from 38.6 % to 34.7 %, because catalytic cracking was dominated by thermal cracking. The gaseous product increased with increasing temperature which long chain hydrocarbon was broken into lower hydrocarbon (C_1-C_5). It was also observed that solid was increased from 5.49 % to 16.9 % when the temperature was increased from 400°C to 470°C. From result obtained, they noticed that at reaction temperature 430°C and 450°C gave the same compositions of all product composition at both of temperature showed high composition of light oil.

In conclusion, the optimum reaction temperature was 430-450°C because they gave high % naphtha range of 37.9-38.6 %, % kerosene range of 7.14-7.64%, % gas range of 22.7-23.4 % and low residue.

4.3.4 Effect of reaction time on product distribution

The study of the reaction time on the catalytic cracking of used lubricating oil and ABS with Fe/activated carbon catalyst was performed by operating with various reaction times: 45, 60, 75, 90, 120 minutes by using mass of Fe/activated carbon catalyst at 2.5 % by wt, 100 psi of initial hydrogen pressure, reaction temperature 450°C and 6 : 4 of used lubricating oil and ABS. The product distribution was shown in **Table 4.8** and **figure 4.4**.

Table 4.8 Effect of reaction time on product composition at 450°C of reaction temperature 2.5 % by wt Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure and 6 : 4 of used lubricating oil and ABS.

Reaction time (minutes)	Gas produc (%yield)	Oil product (%yield)	Solid (%yield)	Oil products(% recovered)				
				naphtha	kerosene	light gas oi	heavy gas oi	long residu
45	19.3	70.1	10.7	36.1	9.59	11.2	2.10	11.1
60	16.3	64.4	19.3	37.0	8.66	12.1	2.20	4.55
75	22.7	64.0	13.3	37.0	8.02	12.0	2.10	4.86
90	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
120	26.5	54.0	19.5	33.8	7.15	9.98	2.00	1.08

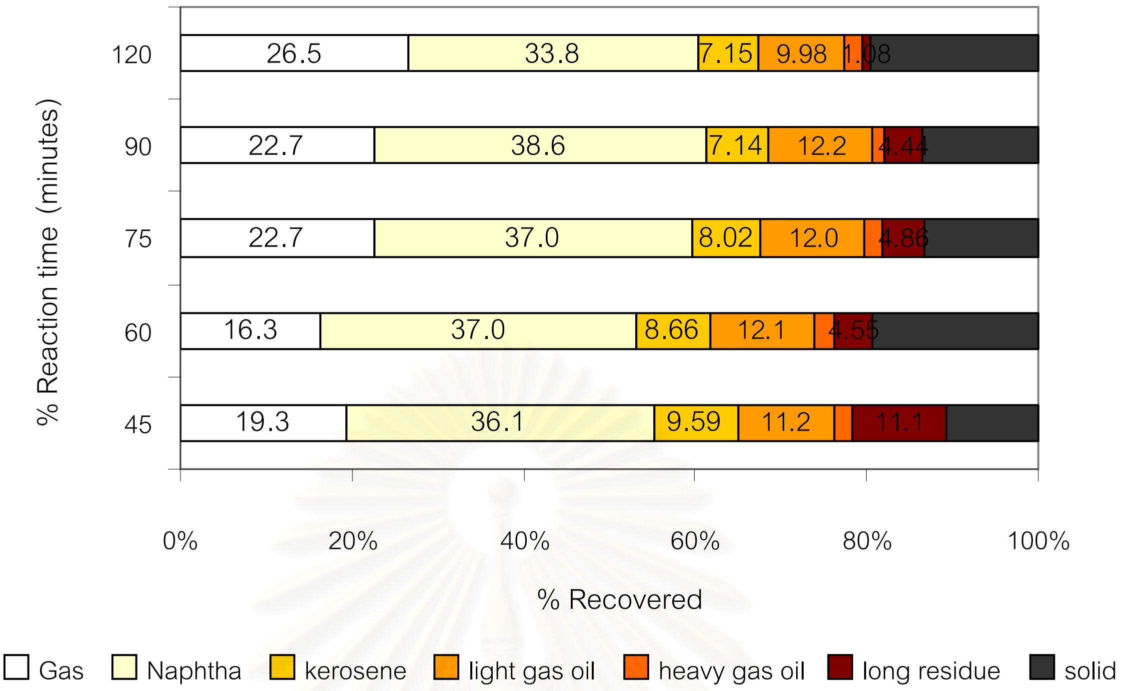


Figure 4.4 Effect of reaction time range of 45-120 minutes on product composition at 450°C of reaction temperature 2.5 % by wt Fe/activated carbon catalyst, 100 psi of initial hydrogen pressure and 6 : 4 of used lubricating oil and ABS.

From Table 4.8 and figure 4.4 show that when the reaction time was increased from 45 to 120 minutes, the % yield of oil product decreased from 70.1 % to 54.0 % because long chains hydrocarbon were cracked to short chain to become gaseous product (C_1-C_5) which is related to the increasing % yield of gas product as carrying more reaction time. When reaction time were increased from 45 to 90 minutes, % naphtha increased directly from 36.1 % to 38.6 % while the reaction time between 90 to 120 minutes, % naphtha decreased from 38.6 % to 33.8 %, whereas other components were the same composition. All of the experiments, the solid product were slightly increased. The maximum % yield of naphtha, low % solid and gas, it showed that this condition cause thermal cracking (changing long chain hydrocarbon to short chain) corresponding to catalytic the moderate chain hydrocarbon. When the reaction time was longer than 90 minutes the catalytic reaction was nearly faster than thermal cracking and long time also caused coking at the surface of catalyst; as result % naphtha and % yield of light oil product were decreased.

In the same way also observed that when the longer reaction time, the overall percentage of short chain hydrocarbon such as naphtha, kerosene, gas oil and long residue decreased, while solid increased. This means that this time caused the decreased activity of catalytic cracking, but thermal cracking still working.

In conclusion, the optimum of reaction time was 90 minutes, because this time gave the highest %naphtha composition as 38.6 % and %kerosene, 7.14% and low residue.

4.3.5 Effect of mass of catalyst on liquid product distribution

The study of mass of catalyst on the catalytic cracking process of used lubricating oil and ABS with Fe/activated carbon catalyst was performed by operating in various mass of catalyst : 0, 0.5, 1.5, 2.5, 3.5 and 5.0 % by wt Fe/activated carbon catalyst were treated under 100 psi of initial hydrogen pressure at reaction time 90 minutes, reaction temperature 450°C and 6 : 4 of used lubricating oil and ABS. The product distribution was shown in **Table 4.9** and **figure 4.5.**

Table 4.9 Effect of mass of Fe/activated carbon catalyst on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS..

% of catalyst	Gas product (%yield)	Oil product (%yield)	Solid (%yield)	Oil products (% recovered)				
				naphtha	kerosene	light gas oil	heavy gas oil	long residue
0	20.1	58.8	21.1	30.1	5.94	15.9	4.78	2.08
0.5	23.9	61.8	14.2	34.6	7.71	12.9	1.92	4.71
1.5	21.1	64.1	14.9	36.1	6.99	12.6	1.99	6.40
2.5	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
3.5	22.2	64.0	13.7	36.3	7.14	13.0	1.98	5.60
5.0	25.5	58.9	15.6	33.8	7.68	10.8	1.83	4.87

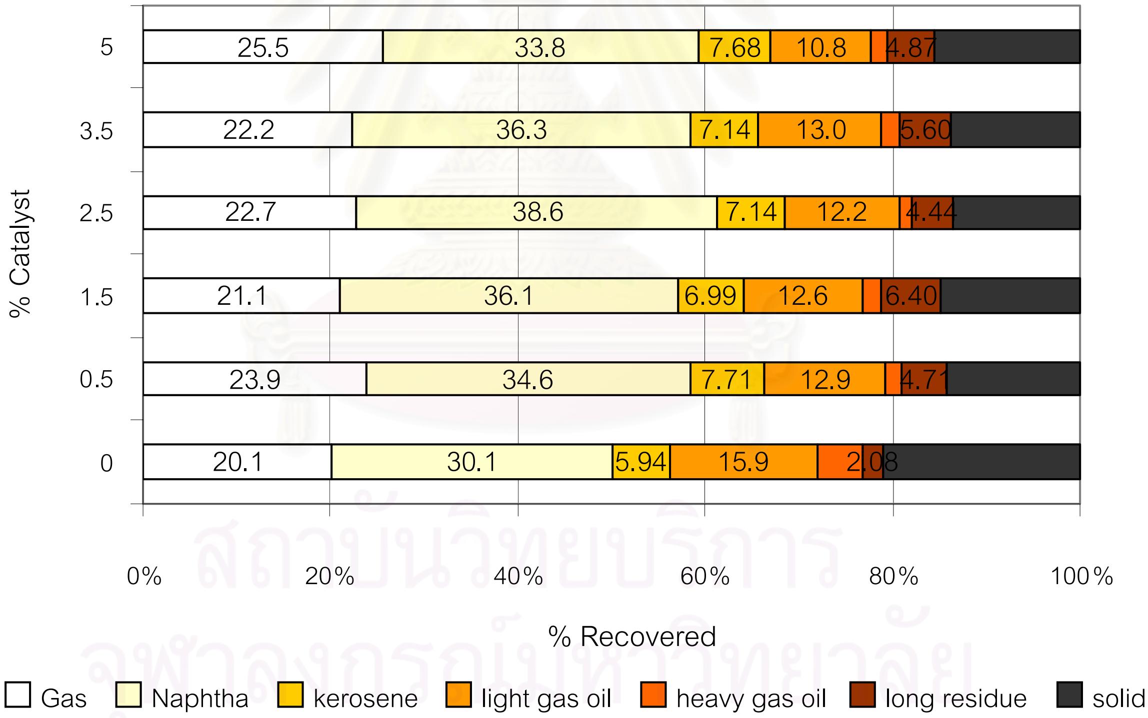


Figure 4.5 Effect of mass of Fe/activated carbon catalyst range of 0.0-5.0 % by wt on product composition at 450°C of reaction temperature, 100 psi of initial hydrogen pressure, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS.

Table 4.9 and Figure 4.5 show the insignificant effect of catalyst mass when the %mass of catalyst was increased from 0.5 % to 5.0 %, the yield of oil and gas product were constant at 61-64 % and 21-25 %, respectively. It was observed the difference between using and without using catalyst. The oil yield was 61-64 % and 58 %, naphtha, 34-38 % and 30 %, kerosene, 7 %, and gas oil 13 % and 21 %, respectively. It was confirmed to the result of 2^k factorial experiment.

From the results, It obviously noticed that yield of naphtha increasing from 34.6% to 38.6% when increasing mass catalyst from 0.5 % by wt to 2.5 % by wt But when the mass of catalyst increasing from 2.5 % by wt to 5.0 % by wt, yield of naphtha decreasing from 38.60% to 33.8%. When catalyst was used less than 2.5 % by wt consequence to the reactant can be reacted with catalyst in low frequency. Long chain hydrocarbon can be converted to short chain hydrocarbon (naphtha) in low yield composition. Although, the mass of catalyst more than 2.5 % by wt, it caused to increase frequency of reactant can be reacted to catalyst. Long chain hydrocarbon can be converted to gaseous product which caused to % yield of naphtha was lower quantity than used 2.5 % by wt of catalyst. The optimum mass of catalyst was 2.5 % by wt.

In this study, 2.5 % by wt of Fe/activated carbon gave the highest light oil composition as 63.8 % and 38.6 % naphtha, 7.14% kerosene, 13.7 % gas oil and low residue.

4.3.6 Effect of initial hydrogen pressure on product distribution

The study of initial hydrogen pressure on the catalytic cracking process of used lubricating oil and ABS with Fe/activated carbon catalyst was performed by operating in various initial hydrogen pressure; blank (under nitrogen atmosphere), 100, 150, and 200 psi, with 2.5 % by wt of catalyst, reaction time 90 minutes, reaction temperature 450°C and 6 : 4 of used lubricating oil and ABS. The product distribution was shown in **Table 4.10** and **figure 4.6.**

Table 4.10 Effect of initial hydrogen pressure on product composition at 450°C of reaction temperature, 2.5 % by wt of catalyst, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS.

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	24.5	61.6	13.8	30.2	7.64	10.7	1.91	11.1
100	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
150	23.5	62.1	14.4	38.3	7.21	11.3	1.43	3.93
200	23.4	62.1	14.4	38.2	6.99	10.0	1.92	4.95

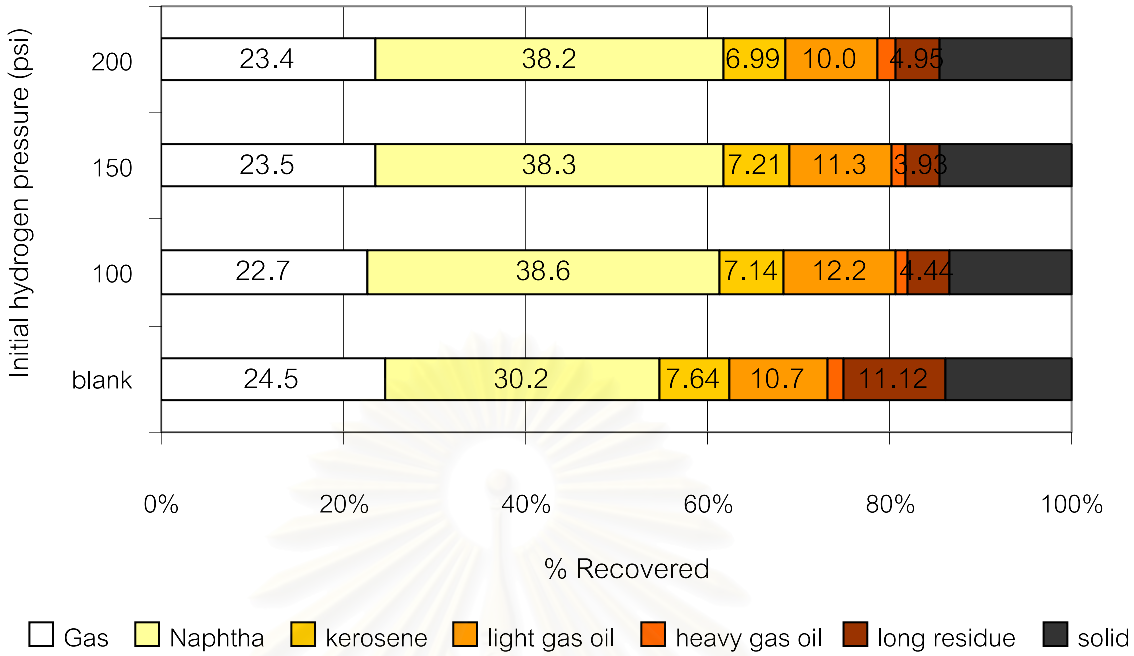


Figure 4.6 Effect of initial hydrogen pressure range of blank-200 psi on product distribution at 450°C of reaction temperature, 2.5 % by wt of catalyst, 90 minutes of reaction time and 6: 4 of used lubricating oil and ABS.

Table 4.10 and figure 4.6 show the insignificant effect of initial hydrogen pressure when the initial hydrogen pressure was increased from 100 psi to 200 psi. The % yield of oil and gases product were constant at 62-63% and 22-23%, respectively. It was observed the difference between using and without using initial hydrogen pressure. The oil yield was 62-63 % and 61 %, naphtha, 38 % and 30 %, kerosene, 7 %, and 7.5%, respectively. It was confirmed to the result of 2^k factorial experiment. When hydrogen concentration increased, it would promote the catalytic reaction by increasing more hydrogen radical. Thus, catalytic cracking could be occurred at 100 psi of initial hydrogen pressure as a result.

In conclusion, initial hydrogen pressure at 100 psi gave the highest light oil yield as 63.8 % and 38.6 % naphtha, 7.14 % kerosene, 16.7 % gas oil and low residue.

4.3.7 Comparison of type of catalyst on product distribution

The comparison of the efficiency of 3 types of catalyst of Fe/activated carbon, Ni-Mo/Al_2O_3, HZSM-5 and thermal cracking reaction. The condition was fixed at 2.5 % by wt of each catalyst, reaction time 90 minutes, reaction temperature 450°C and 6 : 4 of used lubricating oil and ABS. The product distribution were shown in **Table 4.11** and **figure 4.7**.

Table 4.11 Effect of type of catalyst on product composition at 450°C of reaction temperature, 2.5 % by wt of each catalyst, 100 psi of initial hydrogen pressure, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS.

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	20.5	58.8	20.7	28.3	5.94	9.52	1.65	13.3
Fe / AC	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
Ni - Mo /Al_2O_3	25.9	60.6	13.5	34.5	6.06	10.3	1.82	7.88
HZSM - 5	30.0	59.0	11.0	34.5	7.26	12.7	1.21	3.40

*Fe/AC = Fe/activated carbon

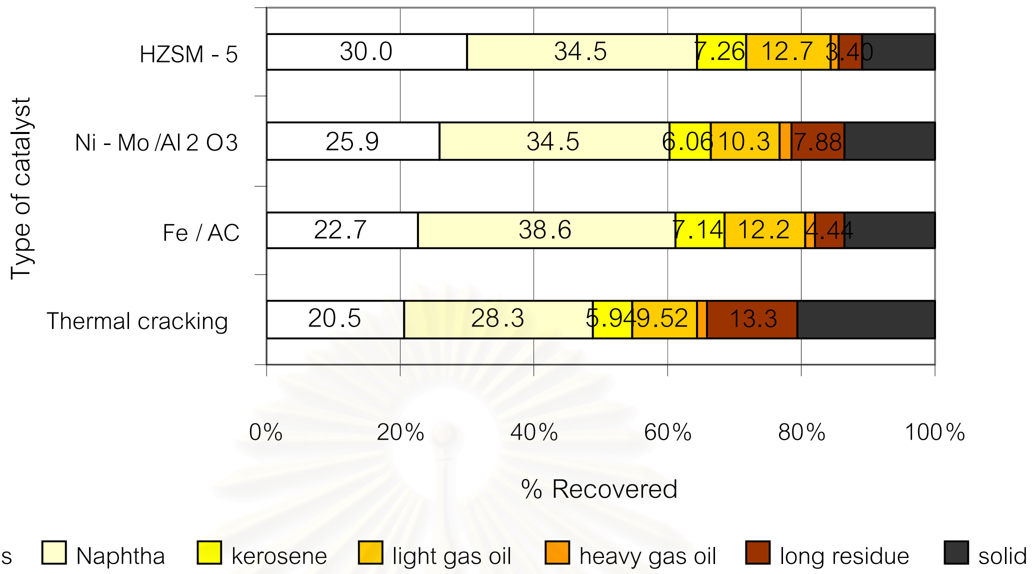


Figure 4.7 Effect of type of catalyst on product composition at 450°C of reaction temperature, 2.5 % by wt of each catalyst, 100 psi of initial hydrogen pressure, 90 minutes of reaction time and 6 : 4 of used lubricating oil and ABS.

From Table 4.11 and figure 4.7 showed that all of catalyst gives nearly % yield of oil product. The Fe/activated carbon gave highest light oil *i.e.*, % naphtha, kerosene and light gas oil. The thermal cracking gave the highest heavy hydrocarbon product, solid while and low naphtha composition. It was obviously noticed that, the role of catalyst to convert of used lubricating oil and ABS was very important. When HZSM-5 gave high gaseous product more than other catalysts because of its acidic catalyst. 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 were non-acidic catalyst, the mechanism of cracking were produced hydrogen radical.

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/activated carbon 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 4.8.**

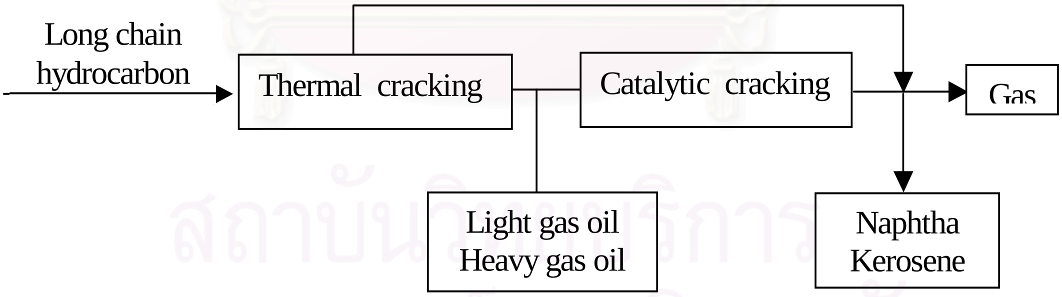


Figure 4.8 The model of the thermal and catalytic reaction

The mechanism of Fe/Activated carbon catalyst was developed by free radical as shown **in figure 4.9**.

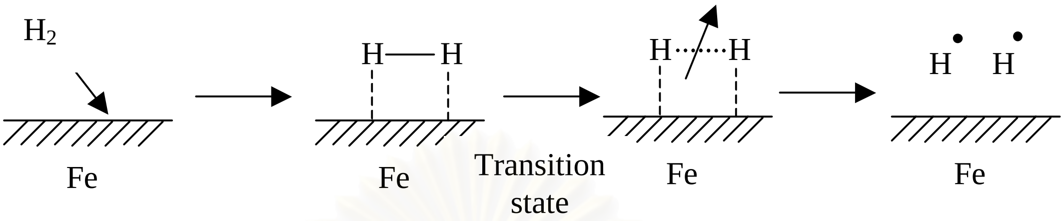
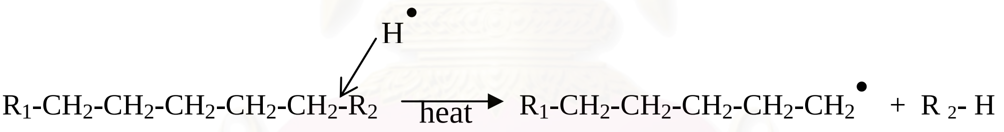


Figure 4.9 The mechanism on surface of Fe/activated carbon catalyst

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

1. Initial step



$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \xrightarrow[\text{heat}]{H^\bullet} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^\bullet + R_2\text{-}H \quad (4.1)$$

2. Propagation Step

2.1 **β-fission**

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^\bullet \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2^\bullet + CH_2=CH_2 \quad (4.2)$$

$$R_1\text{-}CH_2\text{-}\overset{\overset{\textstyle H}{|}}{C}H\text{-}CH_2^\bullet \xrightarrow{\beta\text{-fission}} R_1\text{-}CH_2\text{-}CH=CH_2 + H^\bullet \quad (4.3)$$

3. Termination Step

$$R_1^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}R_2 \qquad (4.4)$$

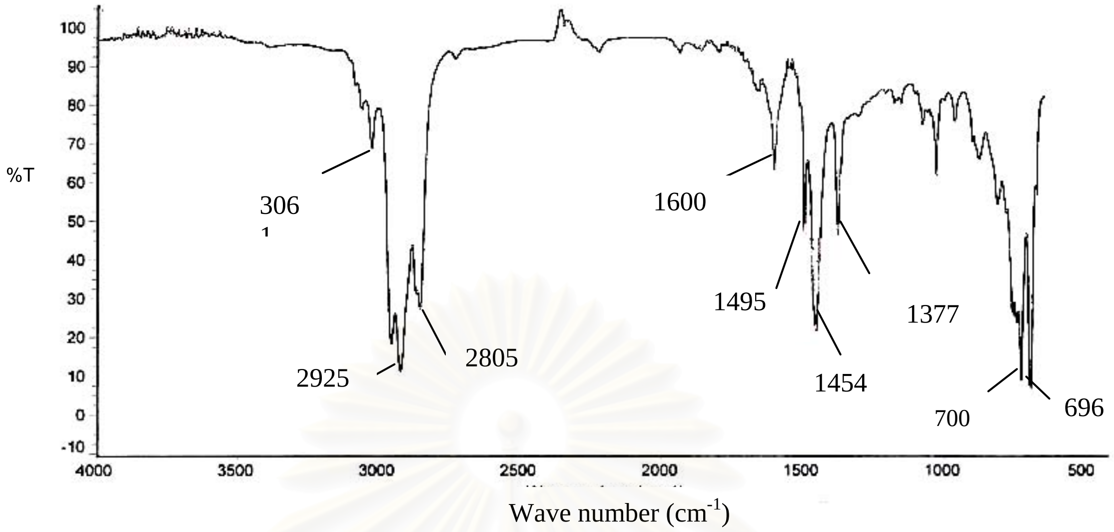
$$R_1\text{-}CH_2\text{-}CH_2^{\bullet} + {}^{\bullet}CH_2\text{-}\overset{\displaystyle H}{\overset{|}{C}}H\text{-}R_4 \longrightarrow R_3\text{-}CH_2\text{-}CH_3 + CH_2{=}CH\text{-}R_4 \qquad (4.5)$$

In conclusion, the Fe/activated carbon catalyst shows the best efficiency to convert used lubricating oil and ABS over other catalysts and thermal cracking.

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

Figure 4.10 shows the functional group compositional analysis of the oil derived from catalytic reaction of 20 g of used lubricating oil and ABS of 6 : 4, 450°C of reaction temperature, 100 psi of hydrogen pressure, 90 minutes of reaction time and 2.5 % by wt of Fe/activated carbon 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} was indication of the presence of C=C stretching of aromatic skeleton and the additional strong peaks at 1495 cm^{-1} and 1454 cm^{-1} also showed C=C stretching of aromatic skeleton. In addition, there are very strong peaks present at 700 and 730 cm^{-1} indicated the substituted aromatic groups and the low intensity peak between 3000 and 3100 cm^{-1} shows the presence of C-H stretching of aromatic.

Figure 4.11 shows the functional group of benzene oil octane number 95 by Fourier transform infrared (FT-IR) spectrometry. It showed a strong spectrum of both aromatic and aliphatic functional group same function 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 high octane number.



.**Figure 4.10** FT-IR spectrum of oil product derived from catalytic reaction of 20 g of used lubricating oil and ABS of 6 : 4, 450°C of reaction temperature, 100 psi of hydrogen pressure, 90 minutes of reaction time and 2.5 % by wt of catalyst.

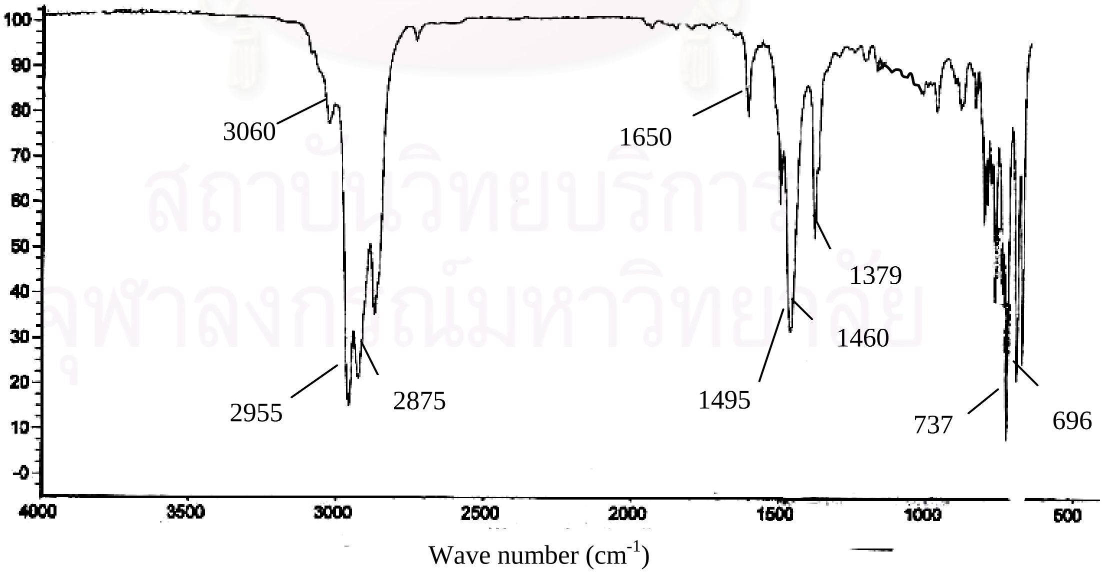


Figure 4.11 FT-IR spectrum of gasoline octane number 95

In conclusion that on the basis of the analysis of functional group composition by FT-IR' derived from used lubricating oil and ABS gave spectrum which indicate the aromatic functional group from styrene unit in ABS which show high octane number.

4.5 Comparison of this work with other works

The comparison of this work with Peaknapo, K. (2001) and 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 Ni-Mo/Al_2O_3 catalyst and Peaknapo, K. studied the conversion of ABS polymer to synthetic fuels on Fe/activated carbon.

From Table 4.12, at 450^{o}C, 90 min, 5 % by wt of Ni-Mo/Al_2O_3 catalyst Kaewsaiyoy, A. obtained 77.4 % of oil yield, naphtha 35.7 %, kerosene 8.25 %, gas oil 12.9 %, and long residue 14.4 %. At 430^{o}C, 60 min, 5 % by wt of Fe/activated carbon catalyst Peaknapo, K. obtained 58.1 % of oil yield, naphtha 45.0 %, kerosene 4.80 %, gas oil 8.10%, and long residue 9.10%. Whereas this work obtained 63.8 % of oil yield, naphtha 38.1 %, kerosene 7.14 %, gas oil 12.2 %, and long residue 13.5 %. This result showed higher yield of naphtha that of Kaewsaiyoy's because this 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 hydrocarbon. On the other hand, this result showed lower yield of naphtha that Peaknapo's because this work was used mixture of ABS and used lubricating oil which were cracked difficultly into short chain hydrocarbon than ABS only. But this work still show high yield of oil and high yield of light oil composition.

Table 4.12 Comparison of this work with other works

Description	Kaewsaiyoy, A.	Peuaknapo, K.	This work
Feed	Used lubricating oil	ABS	Used lubricating oil + ABS
Catalyst	Ni-Mo/Al_2O_3	Fe/AC	Fe/AC
Temperature (^oC)	450	430	430-450
Time (minutes)	90	60	90
% Catalyst	5.0	5.0	2.5
Results (% yield)			
% Oil	77.4	58.1	63.8
Naphtha	35.7	45.0	38.1
Kerosene	8.25	4.80	7.14
Gas oil	12.9	8.10	12.2
Long residue	14.4	9.10	13.5

CHAPTER V

CONCLUSIONS

5.1 Conclusion

In this research, the mixture of used lubricating oil and acrylonitrile-butadiene-styrene (ABS) was used to convert to light oil product by catalytic cracking with Fe/activated carbon catalyst. To achieve this objective, the reaction conditions were varied in terms of ratio of used lubricating oil and acrylonitrile-butadiene-styrene (ABS), reaction temperature, reaction time, initial hydrogen pressure and percentage of catalyst. The following conclusion from this study have been drawn:

The Fe/activated carbon catalyst was prepared. The analysis of percentage of Fe was determined using XRF. The Fe impregnated was 4.67 wt% It was error from the calculation 6.6%. The BET surface area of catalyst was performed using BET analyzer. It has 774 m^2/g.

This study aims to study the catalytic cracking of used lubricating oil and acrylonitrile-butadiene-styrene (ABS) with Fe/activated carbon in 70 ml micro-reactor, was used 6 : 4 of used lubricating oil and ABS, the temperature was varied from 400-450°C, 0-200 psi of initial hydrogen pressure, 45-90 minutes of reaction time and 0-5 % by wt of Fe/activated carbon catalyst. Analysis of oil product was performed using DGC. It may be concluded that the optimum condition: the ratio of used lubricating oil and ABS 6: 4, reaction temperature 430-450°C, initial hydrogen pressure 100 psi, 90 minutes of reaction time and 2.5 % by wt of Fe/activated carbon catalyst.

The products from the optimum condition were range of 22.7-23.4 % of gas range of 62.6-63.8 % of oil and range of 13.5-13.9 % of solid. The oil products distribution were ranged of 37.9-38.6 % of naphtha, range of 7.14-7.64 % of kerosene, range of 12.2-13.2 % of light gas oil, range of 1.40-1.48 % of heavy gas oil, range of 2.38-4.44 % of long residue.

To compare efficiency of Ni-Mo/Al_2O_3 , HZSM-5 and thermal cracking were compared with Fe/activated carbon catalyst. It was found that Fe/activated carbon catalyst shows better efficiency than other catalysts because it was used same reaction time and percentage of catalyst, while it gave highest light oil especially naphtha composition.

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, train lube oil and can be change the type of plastic such as PP, PS and so forth.

2. The type of metal used for impregnation can be changed to another type such as Ni, Mo or bimetal.

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

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APPENDICES

APPENDIX A

DATA OF 2^k FACTORIAL EXPERIMENTAL DESIGN FROM CATALYTIC CRACKING OF ABS AND USED LUBRICATING OIL ON Fe/ACTIVATED CARBON

Table A Product distribution from 2^k factorial experimental design conditions on catalytic cracking of ABS and used lubricating oil with Fe/Activated carbon catalyst.

Batch No .	(A) % catalyst	(B) Pressure (psi)	(C) Time (min)	(D) Temperature (^{0}C)	Yield of gas %	Yield of liquid %	Yield of solid %	Naphtha %	Kerosene %	Light gas oil %	Heavy gas oil %	Long residue %
1	0.5	100	45	400	4.56	79.7	15.7	24.3	7.97	14.0	3.78	29.7
2	5.0	100	45	400	2.38	80.2	17.4	20.8	7.53	13.9	4.32	33.6
3	0.5	200	45	400	5.42	77.1	17.4	19.6	6.43	12.0	3.98	35.1
4	5.0	200	45	400	13.9	71.9	14.2	22.2	7.80	12.5	4.02	25.3
5	0.5	100	90	400	14.3	71.5	14.2	22.6	7.90	14.0	3.97	23.0
6	5.0	100	90	400	18.0	67.6	14.3	26.3	6.89	11.4	3.89	19.2
7	0.5	200	90	400	9.56	77.7	12.7	20.7	8.12	12.6	3.96	32.4
8	5.0	200	90	400	16.3	69.3	14.4	25.0	6.99	14.9	3.99	18.5
9	0.5	100	45	450	27.4	57.1	15.5	31.7	8.75	7.96	2.34	6.36
10	5.0	100	45	450	26.7	56.1	17.1	31.8	9.07	7.86	2.45	4.99
11	0.5	200	45	450	26.2	61.9	11.9	31.4	9.90	7.44	2.51	10.6
12	5.0	200	45	450	21.4	64.2	14.3	37.1	8.98	7.35	1.98	8.83
13	0.5	100	90	450	28.8	57.7	13.6	31.4	8.95	7.65	1.86	7.77
14	5.0	100	90	450	25.2	60.7	14.2	41.0	8.34	6.98	1.94	2.45
15	0.5	200	90	450	24.9	61.9	13.3	41.1	8.20	6.98	1.67	3.88
16	5	200	90	450	27.2	59.7	13.0	40.6	8.24	6.89	1.99	1.98

APPENDIX B

DATA OF OPTIMUM CONDITIONS ON PRODUCT FROM CATALYTIC CRACKING OF ABS AND USED LUBRICATING OIL ON Fe/ACTIVATED CARBON

Table B The products distribution from optimum conditions of all parameters on catalytic cracking of ABS and used lubricating oil with Fe/Activated.

Batch No.	Temperature (^{o}C)	Time (minutes)	Pressure (psi)	Catalyst (%)	Gas Product (%Yield)	Oil Product (%Yield)	Solid (%Yield)	Oil products (% recovered)				
								Naphtha	Kerosene	Light gas oil	gas oil	Long residue
1	400	90	100	2.5	23.0	71.5	5.49	28.1	7.97	15.1	2.17	18.2
2	415	90	100	2.5	23.0	70.0	7.01	34.2	8.41	13.7	1.50	12.2
3	430	90	100	2.5	23.5	62.6	13.9	37.9	9.14	13.2	1.48	0.88
4	450	90	100	2.5	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
5	470	90	100	2.5	24.8	58.3	16.9	34.7	5.62	10.5	1.11	6.33
6	450	45	100	2.5	19.3	70.1	10.7	36.1	9.59	11.2	2.10	11.11
7	450	60	100	2.5	16.3	64.4	19.3	37.0	8.66	12.1	2.20	4.55
8	450	75	100	2.5	22.7	64.0	13.3	37.0	8.02	12.0	2.10	4.86
9	450	90	100	2.5	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
10	450	120	100	2.5	26.5	54.0	19.5	33.8	7.15	10.0	2.00	1.08
11	450	90	blank	2.5	24.5	61.6	13.8	30.2	7.64	10.7	1.91	11.1
12	450	90	100	2.5	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
13	450	90	150	2.5	23.5	62.1	14.4	38.3	7.21	11.3	1.43	3.93
14	450	90	200	2.5	23.4	62.1	14.4	38.2	6.99	10.0	1.92	4.95
15	450	90	100	0	20.1	58.8	21.1	30.1	5.94	15.9	4.78	2.08
16	450	90	100	0.5	23.9	61.8	14.2	34.6	7.71	12.9	1.92	4.71
17	450	90	100	1.5	21.1	64.1	17.4	36.1	6.99	12.6	1.99	2.08
18	450	90	100	2.5	22.7	63.8	13.5	38.6	7.14	12.2	1.40	4.44
19	450	90	100	3.5	22.2	64.0	17.4	36.3	7.14	13.0	1.98	2.08
20	450	90	100	5.0	25.5	58.9	15.6	33.8	7.68	10.8	1.83	4.87

APPENDIX C

ANALYZING OF LIQUID PRODUCTS

1. The chromatogram of product distribution of liquid products

The liquid products were dissolved in 1:100 by volume of carbon disulfide. The liquid products were analyzed using Simulated Distillation Gas Chromatograph. (DGC) in standard ASTM D 2887. The example chromatogram was shown in

figure C1.

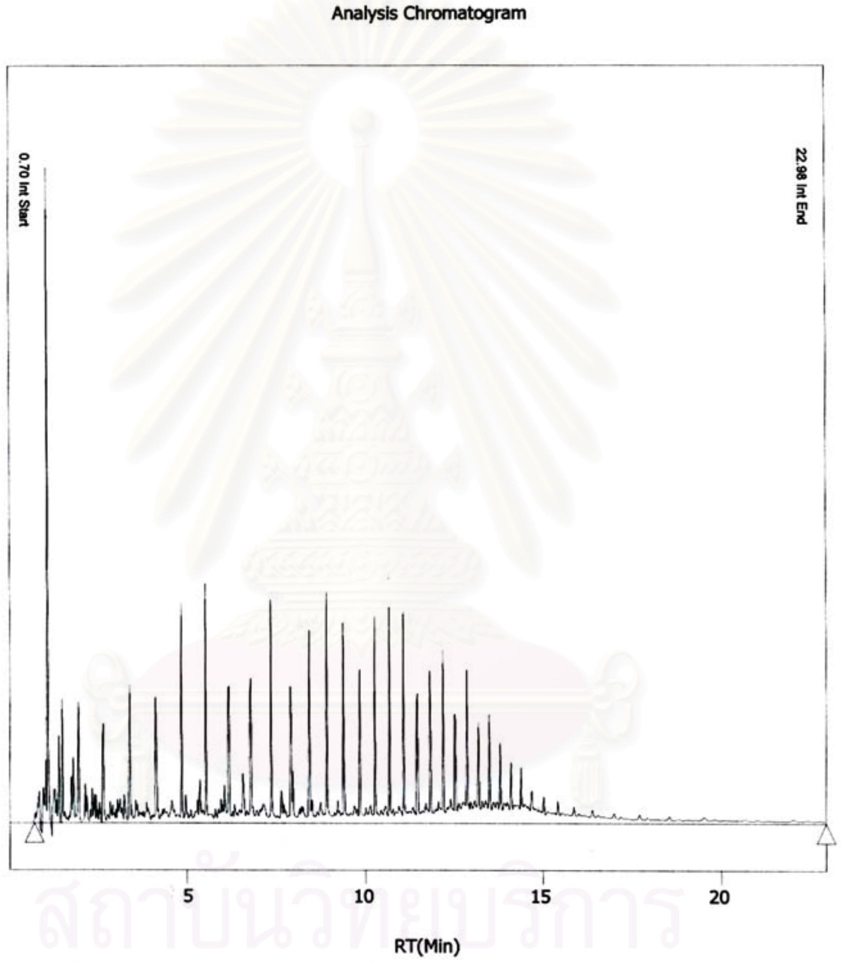

Figure C1 The chromatogram of liquid product from optimum conditions; 450°C of reaction temperature, 90 minutes of reaction time, 100 psi of initial hydrogen pressure, 2.5% by wt of catalyst.

2. The boiling point distillation graph

The chromatogram obtained from DGC were converted to the boiling point distillation graph using program Simulated Distillation that calibrated with standard petroleum oil from ASTM D2887 chromatogram and Blank chromatogram. The boiling point distillation graph was shown in **figure C2** and the last step the distribution of liquid product was determined as it boiling point as respected in chapter III.

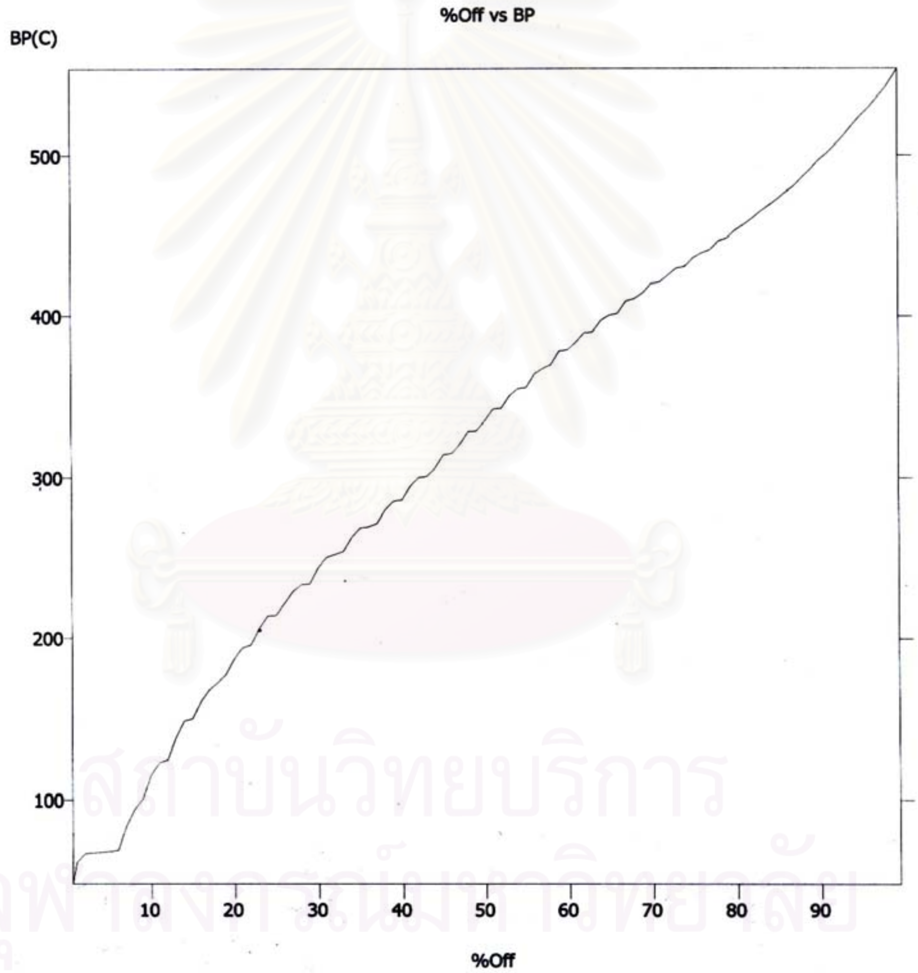

Figure C2 The boiling point distillation graph of liquid product from optimum conditions; 450°C of reaction temperature, 90 minutes of reaction time, 100 psi of initial hydrogen pressure, 2.5% by wt of catalyst.

APPENDIX D

CALCULATION OF IMPREGNATED Fe ON ACTIVATED CARBON

AND

CALCULATION OF PRODUCT YIELD AND PRODUCT COMPOSITION

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 50.0 g of 5 wt %. Fe/activated carbon

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

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

$$= 15.31 \text{ g}$$

In conclusion, we must used $Fe(NO_3)_2 . 9H_2O$ 15.31 g dissolved in excess water before impregnated on activated carbon 50 g by wet impregnation process.

2. Calculation of product yield and % yield of products composition

$$\text{\%yield of gas} = \frac{\text{weight of gas x 100}}{\text{total weight of reactant}}$$

$$\text{\%yield of oil} = \frac{\text{weight of oil x 100}}{\text{total weight of reactant}}$$

$$\text{\%yield of solid} = \frac{\text{weight of solid x 100}}{\text{total weight of reactant}}$$

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

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

$$\%\ \text{light gas oil} = \frac{\%\ \text{off light gas oil from DGC} \times 100}{\%\ \text{oil yield}}$$

$$\%\ \text{heavy gas oil} = \frac{\%\ \text{off heavy gas oil from DGC} \times 100}{\%\ \text{oil yield}}$$

$$\%\ \text{long residue} = \frac{\%\ \text{off long residue from DGC} \times 100}{\%\ \text{oil yield}}$$

VITAE

Miss Siwathida Insuk was born on January, 30, 1980 in Sukhothai. She received the B.Sc. Degree in Industrial Chemistry at King's Momkutt Institute of Technology North Bangkok in 2001. 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.