การเปลี่ยนพอลิเมอร์อะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนเป็นเชื้อเพลิงสังเคราะห์บนตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์

นางสาวกุลวดี เผือกนาโพธิ์

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CONVERSION OF ACRYLONITRILE-BUTADIENE-STYRENE POLYMER TO SYNTHETIC FUELS ON Fe/ACTIVATED CARBON CATALYST

Miss Kulwadee Pueaknapo

A Thesis Submitted in Partial Fulfillment of the Requirements
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By	Miss Kulwadee Pueaknapo
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กุลวดี เผือกนาโพธิ์ : การเปลี่ยนพอลิเมอร์อะคริโลไนไทรล์-บิวทาไดอีน-สไตรีนเป็นเชื้อเพลิงสังเคราะห์บนตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์.(CONVERSION OF ACRYLONITRILE-BUTADIENE-STYRENE POLYMER TO SYNTHETIC FUELS ON Fe/ACTIVATED CARBON CATALYST) อ. ที่ปรึกษา : รศ.ดร.ธราพงษ์ วิทิตศานต์, จำนวนหน้า 114 หน้า ISBN 974-03-0968-2.

จุดมุ่งหมายหลักของงานวิจัยนี้ มุ่งศึกษาการเปลี่ยนพอลิเมอร์อะคริโลไนไทรล์-บิวทาไดอีน-ไสตรีนไปเป็นน้ำมันบนตัวเร่งปฏิกิริยาเหล็กบนถ่านกัมมันต์ในเครื่องปฏิกรณ์ขนาดเล็ก ซึ่งมีเส้นผ่านศูนย์กลางภายใน 30 มิลลิเมตร และปริมาตร 70 มิลลิลิตร โดยการเปลี่ยนแปลงค่าตัวแปรดังนี้ อุณหภูมิของปฏิกิริยาระหว่าง 390-450 องศาเซลเซียส ความดันของก๊าซไฮโดรเจนระหว่าง 20-40 กก./ตร.ซม. เวลาที่ใช้ทำปฏิกิริยาระหว่าง 30-90 นาที ปริมาณตัวเร่งปฏิกิริยาระหว่าง 0-0.75 กรัม และปริมาณเหล็กบนถ่านกัมมันต์ (1, 5 และ 10 เปอร์เซ็นต์)

ผลิตภัณฑ์น้ำมันที่วิเคราะห์โดยใช้เครื่องก๊าซโครมาโตกราฟีชนิดจำลองการกลั่น พบว่าเหล็กบนถ่านกัมมันต์เป็นตัวเร่งปฏิกิริยาที่เหมาะสมในการแตกพอลิเมอร์อะคริโลไนไทรล์-บิวทาไดอีน-สไตรีน โดยสภาวะที่เหมาะสมในการทำปฏิกิริยามีดังต่อไปนี้คือ อุณหภูมิ 430 องศาเซลเซียส ความดันของก๊าซไฮโดรเจน 40 กก./ตร.ซม. เวลาในการทำปฏิกิริยา 60 นาที ปริมาณตัวเร่งปฏิกิริยา 0.6 กรัม และปริมาณเหล็กบนถ่านกัมมันต์ไม่มีผลต่อผลิตภัณฑ์น้ำมัน ผลิตภัณฑ์น้ำมันที่ได้มีปริมาณแนฟทา 45%, เคโรซีน 4.8%, ก๊าซออยล์ 8.1% และโมเลกุลสายโซ่ยาว 9.1% นอกจากนั้น จากผลเสปคตรัมของเครื่องอินฟราเรดสเปคโตรสโคปี พบหมู่ฟังก์ชันของสารอะโรมาติก จึงแสดงว่าผลิตภัณฑ์น้ำมันที่ได้มีค่าออกเทนสูงและยังพบสารประกอบไนโตรเจนในน้ำมันปริมาณน้อยด้วย

ภาควิชา.. ลายมือชื่อนิสิต...
สาขาวิชา..ลายมือชื่ออาจารย์ที่ปรึกษา.......................................
ปีการศึกษา 2544 ลายมือชื่ออาจารย์ทีปรึกษาร่วม................................

4373402023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
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KULWADEE PUEAKNAPO : THESIS TITLE. (CONVERSION OF ACRYLONITRILE-BUTADIENE-STYRENE POLYMER TO SYNTHETICS FUELS ON Fe/ACTIVATED CARBON CATALYST) THESIS ADVISOR : ASSOCIATE PROFESSOR THARAPONG VITIDSANT,Ph.D., 114 pp. ISBN 974-03-0968-2.

The main objective of this research was aimed to study the conversion of acrylonitrile-butadiene-styrene (ABS) into oil product using iron on activated carbon catalyst. Experiment was done in a microreactor width of 30 mm inside diameter and volume of 70 ml by varying operating conditions. Temperature and pressure of hydrogen gas were first varied between 390 and 450 ^{o}C, 20 to 40 kg/cm^{2}, respectively. While reaction time, amount of catalyst and percentage loading of iron were varied between 30 and 90 min, 0 and 0.75 g and 1, 5, 10% on activated carbon catalyst, respectively.

The analyzed oil product from Gas Chromatography (GC Simulated Distillation) was found that iron on activated carbon catalyst was suitable to crack ABS. The optimum condition was 430 ^{o}C, hydrogen pressure at 40 kg/cm^{2}, reaction time 60 min, amounts of catalyst 0.6 g and independent of percent loading of iron. The product yield at this condition was in the range of 45% naphtha, 4.8% kerosene, 8.1% gas oil and 9.1% long residues. Moreover, the product showed aromatic functional group, by means of Fourier-Transform Infrared Spectrometer, which indicated the presence of high octane number and also showed low intensity of N-containing.

Department..Student’s signature..
Field of study..Advisor’s signature..
Academic year 2001 Co-advisor’s signature......................................

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Finally, deepest gratitude goes to parents : Khun Narin and Khun Nongkran for their sincere love and concern, and for hardship encountered in these past twenty-two years raising her and teaching her how to take care of herself.

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CHAPTER I
INTRODUCTION

Plastics are being produced and utilized worldwide at an increasing rate in each subsequent year. Plastics are manufactured for various uses including, but not limited to, consumer packing, wires, pipes, containers, bottles, appliances, electrical/electronic parts, and automotive parts. Plastics are produced from petroleum and composed primarily of hydrocarbons but also contain antioxidants and colorants. Plastics once used are not effectively recycled and are difficult to collect from the consumer and then to separate into specific types[1]. Most of the post-consumed plastic is landfill or incenerated but they have not gain social acceptance as the methods for disposing of the waste, and they are becoming legally restricted because of strong pollution concerns [2]. Around 7% of waste plastics is recycled to produce low-grade plastic products such as plastic sacks, pipes, plastic fencing, garden furniture [3].

Due to the limited of world's reserve of coal and crude oil, great effects are being made to find other carbon sources as feedstock materials for the production of fuels. The degradation of waste plastic into fuel represents a sustainable way, for the recovery of the organic content of the polymeric waste, for saving valuable petroleum resources in addition to protecting the environment.

All waste materials are post-consumed since each has been used to some degree and has some level of contamination. Waste plastics may be contaminated with a variety of materials such as foodstuff, or detergent or motor oil, In addition, many different types of plastics are produced. Therefore, to recycle plastic waste to produce fuels, the plastic materials must be carefully separated and cleaned so that only one type of plastic is present. Many plastics also contain inorganics that have been added to improve mechanical strength and thermal resistance or as flame retardants. Consequently, only a small amount of waste plastics is currently being recycled into fuels that can be used directly as recycled materials [4]. Municipal waste plastic is a mixture of polymers which contains about 3-5 wt % acrylonitrile-butadiene-styrene polymer (ABS). The production capacity of acrylonitrile-butadiene-styrene polymer (ABS) in Thailand are around 136,000 tons per year.

Thermal degradation studies on acrylonitrile-butadiene-styrene polymer (ABS) have mainly been performed by thermogravimetry or thermomanometry. The result showed that the kinetics and mechanism of degradation depend on the chemical structure of the polymer and the experimental conditions. Various studies have exmined the changes that occur in the thermal properties of materials when acrylonitrile-butadiene-styrene polymer (ABS) is grafted or blended with other polymers. In addition there have been studies concerning the thermal behavior of polyacrylonitrile or styrene-acrylonitrile binary copolymers. Day and co-workers (1999) presented some results from acrylonitrile-butadiene-styrene polymer (ABS) thermal degradation in a pyrolysis/ gas chromatography/ mass spectrometry system, alone and together with poly(vinyl chloride) (PVC) **[5]**. However, no study was made with special interest in using catalyst to produce acrylonitrile-butadiene-styrene polymer (ABS) degradation products as fuel oil.

The process to serve these intended purposes have been done through catalytic cracking reaction by iron on activated carbon under hydrogen atmosphere in microreactor. It is found that the advantage of using catalyst is that activated carbon has high carbon, low inorganic and high acidity which is suitable for cracking reaction of high molecular weight hydrocarbon. Therefore, the purpose of this present study was to investigate conversion of acrylonitrile-butadiene-styrene polymer (ABS) to synthetic fuel on Fe/activated carbon catalyst.

The objectives of this research are :

To study the hydrocracking of acrylonitrile-butadiene-styrene polymer (ABS) by using iron on activated carbon catalyst in microreactor.

To search for the optimum conditions of catalytic cracking reaction to yield suitable percentage of products and composition.

To investigate and analyze oil products, conversion and products distribution produced from cracking reaction.

The scopes of this research are :

To investigate the performance of the prepared catalyst on the acrylonitrile-butadiene-styrene polymer (ABS) conversion to oil under the following conditions;

- Reaction temperature range of 390-450 ^{O}C
- Ratio of acrylonitrile-butadiene-styrene polymer (ABS) per catalyst : 15 g per 0.3-0.75 g
- Pressure of hydrogen gas range of 20-40 kg/cm^2
- Reaction time range of 30-90 min
- % Fe on activated carbon of catalyst per acrylonitrile-butadiene-styrene polymer (ABS) 1, 5, 10% per 15 g

CHAPTER II

LITERATURE REVIEW

Acrylonitrile-Butadiene-Styrene Polymer (ABS)

The name ABS polymer is derived from the initial letters of the three main monomers - acrylonitrile, butadiene and styrene, used in its preparation. ABS is not a random terpolymer of acrylonitrile, butadiene and styrene. Although such a random terpolymer can be prepared by simultaneous polymerization of the three monomers, experiments have been confined to a laboratory scale and the properties of this terpolymer are technically unattractive. At a butadiene content of up to 20%, the terpolymer has unsuitable impact strength and low heat deformation resistance. At higher butadiene contents in the random terpolymer, rubber - like behavior is exhibited. These products have not been produced commercially. Industrially important ABS polymers are two - phase polymer systems. A modifying rubber (usually polybutadiene or the butadiene copolymer with styrene or acrylonitrile) is dispersed as small discrete particles throughout the continuous phase (matrix) of a styrene copolymer with acrylonitrile (SAN), where part of the SAN copolymer is grafted onto the rubber particles. Thus, the ABS polymer is rubber - modified SAN copolymer.

It follows from these considerations and also from information on the microphase structure of ABS polymers, that it is quite incorrect to describe this type of polymer as "ABS terpolymer " or "ABS copolymer" as sometimes happens. The incorrectness of this terminology has been pointed out in the literature. The actual copolymer-the SAN copolymer-constitutes only part of the two-phase system, and the random terpolymer is not present at all. Thus, the correct term is "ABS polymer".

The fraction of rubber component in ABS polymers is usually varies from 10 to 25% for blending with polyvinyl chloride can even contain over 45% rubber. The higher rubber content and the different type of polymer forming the continuous phase result in the ABS polymers having a number of properties better than common grades of high - impact polystyrenes. Thus, ABS polymers occupy an intermediate position between inexpensive, mass - produced commodity plastics (standard polystyrene, polypropylene, etc.) and the much more expensive engineering plastics (polycarbonates, polyacetals, etc.), that are used for engineering and other high - performance applications [6].

The capacity of ABS polymer from world class producer is shown in **Table 2.1**

Table 2.1 The capacity of ABS polymer from world class producer [5].

PRODUCER	CAPACITY (Millions pounds/year)
Bayer, Addyston, Ohio	450
Diamond Polymers, Akron, Ohio	50
Dow, Allyn's Point, Conn.	55
Dow, Hanging Rock, Ohio	140
Dow, Midland, Mich.	195
GE Plastics, Bay St. Louis, Miss.	280
GE plastics, Ottawa, Ill.	475
GE plastics, Washington, W.Va.	160
Total	1,805

2.1 Principles and Technology in the Production of ABS Polymers [6]

ABS polymers can be prepared by mechanical blending of the individual components or by grafted polymerization of a mixture of styrene with acrylonitrile in the presence of a suitable rubber component. Emulsion technology has been employed for blended types of ABS polymers and is used in various forms for grafted types, for example, emulsion - suspension procedures or the emulsion - bulk process, in which the polybutadiene latex forms a substrate for grafting in suspension or bulk polymerization in the next step

2.1.1 Blended types

2.1.1.1 Melt blending

The oldest approach to the modification of the toughness of SAN copolymer is mechanical blending with rubber. The copolymer of butadiene with acrylonitrile was usually used as the rubber component to obtain adequate compatibility.

However, after through blending of the rubber in the homogeneous blends, it acts as a plasticizer of the SAN copolymer with only a small increase in the impact strength. Optimal dispersion of the rubber particles can be achieve only with sufficiently cross - linked rubber containing 30 to 50 % gel. The blend is processed on the mill roll at a temperature of 150 to 250 ^{O}C or in a Banbury mixer at a temperature of up to 235 ^{O}C.

2.1.1.2 Blending in latex form

Both the component copolymers can readily be prepared by emulsion polymerization, and it is sometimes advantageous to blend them to the latex stage. SAN copolymer latex and butadiene - acrylonitrile latex are fed in a suitable ratio from the storage tanks into the blending tank; an antioxidant emulsion is also added simultaneously. After complete mixing, the latex mixture is coagulated using an electrolyte solution and the crumbs obtained are washed and dried. Once again, optimal properties can be obtained only with mechanical processing of the blend. Simultaneously, additives are also incorporated into the polymer in this stage, such as lubricants, colourants, additional antioxidants, etc.

The greatest drawback of ABS polymers prepared by mechanical blending is their decreased impact strength at low temperature. In addition, processing is difficult and injection molded products, have poor surface properties. These disadvantages are eliminated for grafted types, which have almost completely replaced blended types. However, the blending principle is sometimes also used at certain stages in the preparation of ABS polymers.

2.1.2 Grafted types

2.1.2.1 Emulsion technology

Grafting in emulsion remains the most widely used methods for the production of ABS polymers, even though emulsion technology is more complicated than other procedures. Its advantages lie in its ability to yield a wide variety of products and the rapid conversion of one grade to another. Most grades of ABS polymers for injection molding applications are produced by emulsion technology.

This process is practiced industrially in a great many forms. The oldest procedures carry out grafting of the polybutadiene separately from the preparation of the SAN copolymer. In the usual procedure, polybutadiene latex containing 30 to 60% polybutadiene is first prepared by emulsion polymerization. After addition of a short - stopping agent, removal of residual unpolymerizes monomer and filtration of the latex, a mixture of styrene and acrylonitrile monomers, a further emulsifier and a molecular weight modifier are added. The mixture is stirred at 50 ^{O}C to permit adsorption of the monomer by the latex particles. Polymerization is initiated by addition of water - soluble initiator and proceeds at a temperature of about 80 ^{O}C; it is controlled so that most of the monomers are grafted onto the polybutadiene particles. The latex of the grafted polymer, with a relatively high polybutadiene content, is then blended in the required ratio with the separately prepared SAN copolymer latex. At this stage, the procedure is completely analogous to that employed in the preparation of ABS polymers by mechanical blending of the latex. However, the grafted polymer can also be isolated by coagulation in the form of crumbs and dried and blended with SAN copolymer in a plastic state. It is then also possible to employ SAN copolymer prepared by suspension, bulk or solution polymerization. The described alternative is thus a combination of grafting and blending. Separate preparation of the components permits better control of their composition and structure and thus also of the final ABS polymer properties.

It is also possible to prepare the final product directly in a single step by grafting in emulsion. A mixture of styrene and acrylonitrile monomers is then added to the polybutadiene latex, either all at once at the beginning of the polymerization or gradually in several batches. The final latex of the ABS polymer contains both the grafted and free SAN copolymer.

In both variations, after devolatilization of the unreacted monomer, the ABS polymer is isolated from the latex by coagulation with an electrolyte solution at an elevated temperature, 100 ^{O}C. The powder obtained is washed in a centrifuge, and dried in a drier; after mixing with additives, such as pigments, dyes, lubricants, it is extruded and cut into pellets and packed for transport.

Recently, some disadvantages of emulsion technologies have become important; they include high-energy consumption, high consumption of additives and ecological problems connected with disposal of wastewater. There is thus a tendency to use combined technology, which employs the advantages of relatively simple emulsion preparation of rubber particles with defined dimensions, morphology and grafting in the first stage. The next step consists either of the already described method of melt blending with SAN copolymer, prepared by a method other than emulsion polymerization or the process is completed by suspension or bulk methods as described below.

2.1.2.2 The emulsion-suspension procedure

This method eliminates the problems connected with coagulation of ABS latex and drying of the fine ABS polymer powder. The final product consists of beads, similar to those obtained in purely suspension polymerization. The first step of grafting in emulsion consists of polymerization of a mixture of styrene and acrylonitrile in the presence of polybutadiene latex. After 20% conversion is attained, the emulsion is broken, additional styrene and acrylonitrile are added with a suspension stabilizer and the polymerization is completed in suspension. Addition of a coagulation agent ($MgSO_4$) during suspension formation contributes to the formation of large rubber particles.

2.1.2.3 The technology of bulk polymerization

In its classical form, bulk polymerization is suitable only for the preparation of ABS polymers with low polybutadiene contents, as polybutadiene has rather low solubility in a mixture of styrene with acrylonitrile. This factor limits the maximum attainable impact strength of the polymer. Further problems are connected with the high viscosity of the polymerizing mixture at higher conversion. These problems can be eliminated to a certain degree if the bulk polymerization is carried out in the presence of a small amount of solvent.

Ethyl benzene or toluene is usually employed in amounts up 20%. As a relatively small amount of solvent is used, the production technology is practically identical with the bulk process and this type of process is mostly included in the category of bulk polymerization rather than polymerization in solution. Modern reactor design permits successful bulk polymerization even at high viscosities of the reaction mixture provided that a suitable temperature program is employed.

The bulk grafting technology has so far been used only by a few companies but is considered very promising, especially in new variation combining emulsion and bulk technologies.

2.1.2.4 The emulsion-bulk procedure

Here, the raw material is not butadiene rubber as in the pure bulk technology, but rather polybutadiene latex. Instead of dissolving the rubber in a monomer mixture, a dispersion of the rubber particles is made by adding latex directly to the monomer mixture, permitting an increasing in the rubber content in the ABS polymer compared to that for the classical process. ABS polymer with bimodal distribution of the rubber particles can be readily prepared by partial agglomeration of the rubber particles in the latex or by using the lattices with different particle sizes.

The polybutadiene latex employed should have a gel content of at least 75% to avoid changes in the size of the rubber particles in later production stages. First, part of the styrene and acrylonitrile are grafted onto the polybutadiene in emulsion. The latex particles are then extracted into a newly added monomer mixture in the presence of a coagulant (e.g. $MgSO_4$). After separation of the aqueous phase, the partially grafted polybutadiene forms a stable dispersion in the styrene-acrylonitrile mixture. Further polymerization is a continuous bulk process; the first step (up to conversion of 40 to 70%) is carried out in a stirred autoclave and the next stage in a tower plug-flow reactor. The heat of reaction is removed by a cooling jacket and by recycling of the evaporated monomer, as well as through evaporation of retained water. The polymerizing system is maintained at the boiling point, so that the polymerization temperature can be controlled by adjusting the pressure in the reactor. Polymerization is carried out to high degrees of conversion and the unreacted monomers are removed in the evacuated zone of the extruder.

If has been stated that the production costs of emulsion-bulk technology correspond to only 73% of that for the purely emulsion technology.

2.1.2.5 The bulk-suspension process

In this process, only prepolymerization is carried out by the bulk process and polymerization is completed in suspension after phase inversion. The rubber particles in ABS polymer prepared by this technology are much larger (< 0.5 μm), with a negative effect on the gloss of the final polymer. As the suspended particles in this systems have an increased tendency to coalesce together, good suspension stabilization is necessary. The disposal of waste waters in an important problem. Acrylonitrile, which would create a toxic hazard, must be removed.

The bulk-suspension process for polymerization has been used industrially since 1964, but is now employed by only a few companies. Polymers prepared by the bulk-suspension process contain only very low concentration of nonpolymeric additives. This technology is especially suitable for grades designed for extrusion of sheets and films.

2.2 Polymerization [7, 8]

Grafting is an important method for obtaining a strong bond between rubber particles and the surrounding resin. For this reason it is an essential feature in the manufacture of ABS polymer.

Grafting of the styrene-acrylonitrile copolymers onto an elastomer is achieved by copolymerization in the presence of the elastomer. Possible mechanisms for this process include radical abstraction from the polybutadiene :

$$\overset{\bullet}{I} + \text{-}(CH_2CH{=}CHCH_2)\text{-} \longrightarrow IH + \text{-}(\overset{\bullet}{C}HCH{=}CHCH_2)\text{-} \qquad (1)$$

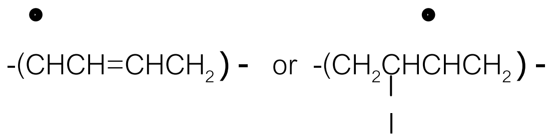
or radical addition to polybutadiene:

$$\overset{\bullet}{I} + \text{-}(CH_2CH{=}CHCH_2)\text{-} \longrightarrow \text{-}(CH_2\underset{\displaystyle I}{\underset{|}{C}}H\overset{\bullet}{C}HCH_2)\text{-} \qquad (2)$$

$\overset{\bullet}{I}$ is an initiator radical or a radical from growing copolymer chain. Radical attack on the substrate polybutadiene competes with formation of styrene-acrylonitrile copolymer.

$$\overset{\bullet}{I} + nM \longrightarrow IM_n^{\bullet} \qquad (3)$$

M is styrene or acrylonitrile monomer and $M_n^{\bullet}$ is a growing linear styrene-acrylonitrile polymer radical. The polydiene radical $P^{\bullet}$ formed in equations 1 and 2, where $P^{\bullet}$ =



$-(\dot{C}HCH{=}CHCH_2)-$ or $-(CH_2\underset{I}{C}H\dot{C}HCH_2)-$ can now alternatively initiate polymerization, combine with a growing linear copolymer radical, induce cross-linking, or undergo chain transfer.

$$P^{\bullet} + n\,M \longrightarrow PM_n^{\bullet} \qquad \text{(grafting by addition)} \qquad (4)$$

$$P^{\bullet} + {}^{\bullet}M_n \longrightarrow PM_n \qquad \text{(grafting by termination)} \qquad (5)$$

$$P^{\bullet} + P \longrightarrow P\text{—}P^{\bullet} \qquad \text{(cross-linking)} \qquad (6)$$

$$P^{\bullet} + RSH \longrightarrow PH + RS^{\bullet} \qquad \text{(chain transfer)} \qquad (7)$$

where RSH is a chain-transfer agent.

It has been reported that the ratio of grafted copolymer to free copolymer depend on the nature of the initiator; this specific catalyst effect suggests that the grafting process includes interaction of elastomer with the initiator, i.e., $I^{\bullet}$ is an initiator fragment in equation 1 or 2. Systematic studies of the effects of polymerization variables on the characteristics of the graft copolymer have been described. The degree of grafting is a function of the 1,2-vinyl content of the polybutadiene, monomer concentration, type and initiator concentration, extent of conversion, temperature, and mercaptan concentration.

2.3 Properties [6]

Common types of ABS polymers have an average composition of 21 to 27% acrylonitrile, 12 to 25% butadiene and 54 to 63% styrene. Styrene contributes good processibility and stiffness to the final ABS, butadiene increases the impact strength, and acrylonitrile improves the chemical and heat deformation resistance.

The properties of ABS polymers are strongly affected by the molecular characteristic of both the elastomer phase and the SAN copolymer forming the matrix. An increase in the molecular weight of the SAN copolymer leads to a decrease in the fluidity, an increase in the impact strength, suppression of creep, increased resistance to surface-active substances and an increase in the tensile strength. Narrowing of the molecular weight distribution leads to an increase in the tensile strength, decrease in shrinkage, improved dimensional stability and increased creep resistance. On the other hand, a broad molecular weight distribution improves the flow properties and mould filling but increases the heat and pressure sensitivity of the melt. An increase in the content of elastomers improves the impact strength but also results in an increased melt viscosity and decreased heat deformation resistance, aging resistance and stiffness. The properties of this multi-phase system are also affected by conditions at the interface between the rubber and the thermoplastic matrix.

ABS polymer has low density (1020 to 1060 kg m^{-3}) and the bulk density of the pellets is also low, usually 500 to 600 kg m^{-3}. The material is opaque as a result of the different refractive indices of the two phases. The presence of the polar nitrile group results in a certain affinity of the ABS polymer for water or water vapor. An increase in the humidity content can lead to complications in processing and to deterioration in some properties. Manufactures recommend that the material should be pre dried, usually at a temperature of 80 to 90 ^{O}C for a period of two to four hours, with a pellet layer of not thicker than 3 to 4 cm. The less favorable properties of ABS polymer include low resistance to weathering, decreased resistance to surface-active substances and its flammability.

The most important mechanical properties include the notched impact strength and flexural modulus of elasticity. Depending on its impact strength, material is classified as high-,medium- or low-impact polymer. Typical properties of ABS polymer is shown in **Table 2.2**.

Table 2.2 Typical properties of ABS polymer **[8]**

Properties	grade classifications			
	high impact	medium impact	low impact	heat resistant
<u>Mechanical @ 23 ^{O}C</u>				
Impact strength, J/m	375-640	215-375	105-215	105-320
Tensile strength, mPa	33-41	41-48	41-52	41-52
Elongation, %	15-70	10-50	5-30	5-20
Tensile modulus, GPa	1.7-2.1	2.1-2.5	2.1-2.6	2.1-2.6
Hardness (HRC)	88-90	95-105	105-110	105-110
Specific gravity	1.02-1.04	1.04-1.05	1.05-1.07	1.04-1.06
<u>Thermal</u>				
Deflection temp., annealed ^{O}C, 1820 kPa	93-99	96-102	96-104	102-112
Linear coefficient of thermal expansion, $^{O}C^{-1}$E-5	9.5-11.0	7.8-8.8	7.0-8.2	6.5-9.3

The thermal properties of ABS polymer are characterized mainly by the glass transition temperature, Tg. An increase in temperature of the material leads to a decrease in the tensile strength and an increase in the ductility and toughness. However, the modulus of elasticity in tension decreases. Heat resistant grades exhibit a flatter dependence of the modulus of elasticity on the temperature.

The electrical properties of ABS polymer can be classified among polymers with very good electrical insulation properties.

2.4 Processing and Applications [6, 9]

ABS polymer is the highest-volume thermoplastic resin used in engineered applications. Its staple markets (transportation, appliances, piping and electronics) are all strong. As automobile manufactures strive to reduce the weight of cars and trucks, ABS polymer will grow in transportation applications that emphasize strength and heat resistance. Though ABS polymer is mature, producers continue to identify new applications and develop value-added grades.

The entire common moulding technologies can carry out-processing. The material must be pre dried for all types of processing technology. A substantials proportion of the manufactured material is processed by injection moulding techniques. The temperature of the individual section in the injection moulding machine varies from 170 to 240 ^{O}C, the melt temperature is from 220 to 260 ^{O}C and the mould temperature varies between 40 and 80 ^{O}C.

Extrusion is the second most widely used processing technology employed for ABS polymers. Extrusion temperatures usually vary between 160 and 250 ^{O}C , with a polishing roll temperature of 90 to 110 ^{O}C.

Extrusion of ABS polymer is increasingly carried out using a twin screw extruder. These machines have a short retention time for the material and yield a very homogeneous melt. Devolatilizing of the material is also more effective than when using a single-screw extruder.

ABS polymer can also be processes by blow moulding compression moulding and rotational moulding.

The main applications of ABS polymer depend on their good properties over a wide range of temperature, periods and environments. Such flexibility allows ABS polymer to be used in transportation, 26 percent; appliances, 25 percent; piping, 13 percent; electronics, 11 percent; and miscellaneous applications, including medical devices, toys and luggage, 25 percent. The demand of ABS polymer in 1998 is 1.29 billion pounds, 1999 is 1.30 billion pounds and expected in 2003 is 1.39 billion pounds. The current price is 67cent to 70 cent per pound.

2.5 Literature Reviews

Williams et al., [3] studied interaction of plastics in mixed-plastics pyrolysis. The pyrolysis of mixed-plastic waste has been proposed as a means of recycling to produce petrochemical feedstock. The interaction of the main plastic types in plastic mixtures is significant in predicting the likely yields and composition of products from different plastic mixtures. The six main plastics in municipal solid waste are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride)(PVC), and poly(ethylene terephthalate)(PET). Each of the plastics was pyrolyzed individually in a fixed-bed reactor heated at 25 ^{O}C/min to a final temperature of 700 ^{O}C. Polystyrene was then mixed with each of the other five plastics in a ratio of 1:1 and pyrolyzed in the fixed-bed reactor under the same pyrolysis conditions. The yield and composition of the derived oil/wax and gases were determined. The main gases produced from the individual plastics were hydrogen, methane, ethane, propane, propene, butane, and butene and for the PET plastic carbon dioxide and carbon monoxide. Hydrogen chloride was also produced with PVC. Analysis of the oil/wax showed that the polyalkene plastics, HDPE, LDPE and PP, gave a mainly aliphatic composition consisting of a series of alkanes, alkenes, and alkadienes. PVC gave a mainly aromatic oil, and PS and PET, which have aromatic groups in their structures, also showed more aromatic composition. There was a higher gas yield from the mixtures of the plastics with PS than would be expected from the pyrolysis of the individual plastics, coupled with a reduction in the oil/wax phase. The average molecular weight of the oil/wax from the mixed plastics was lower than expected from the individual molecular weight. Compositional analysis of the oil/wax showed that changes in the concentration of aromatic hydrocarbons and polycyclic aromatic hydrocarbon were produced with the mixture compared to that expected from the individual plastics.

Brebu et al., **[5]** studied the thermal degradation of the acrylonitrile-butadiene-styrene polymer (ABS) that was carried out at different temperatures from 360 to 440 ^{O}C in static and dynamic atmospheres of nitrogen, using semibatch operation. Nitrogen-containing compounds were found in all three degradation fractions : gases (as NH_3 and HCN), oil, and residue. The percentage of the oil fraction increases with the increase of the degradation temperature. At 440 ^{O}C 63 wt% of the initial ABS feed was recovered in the oil fraction. The nitrogen concentration of the oil fraction was in the range of 29-40 mg/ml. 4-Phenylbutyronitrile is the main N-containing degradation product (16-19 wt % in oil). N-compounds were also found as aliphatic and aromatic nitriles, amino derivatives, and heterocyclic compounds containing one or two N atoms such as pyridine, pyrimidine, and quinoline. Dynamic atmospheres of nitrogen and the residence time of the products in the reactor affect the oil recovery rate and the distribution of nitrogen in the degradation products.

Anderson et al., **[10]** studied coliquefaction of coal and waste polymers. Coal can be converted into distillable liquid fuels with the addition of hydrogen. Waste polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) contain hydrogen at levels of approximately fourteen percent. Since such a small fraction of the plastic and other polymer material are currently recycled these materials could, in principle, provide the hydrogen to aid in the liquefaction of coal. Coal alone and pure waste polymers, as well as a commingled waste polymer mixture, have been liquefied separately and mixtures of coal and various polymers have been coprocessed. Thermal and catalytic processing shows that such coprocessing can be a viable method to produce high quality liquid fuels and to mitigate the disposal problem of waste polymers.

Liu et al., **[11]** investigated pyrolysis of polystyrene waste in a specially designed laboratory fluidized-bed reactor apparatus in the range 450-700 ^{o}C with nitrogen as the carrier gas and 20-40 mesh quartz sand as the fluidization medium, operating isothermally at atmospheric pressure. The main products of PS fluidized pyrolysis were mainly styrene monomer, dimer and trimer also. The product spectrum can be described as a function of pyrolysis temperature. The yield of liquid products at various temperatures was more than 90 wt.% and the formation of gas and coke was relatively insignificant. The secondary reaction decreased the yield of styrene monomer but favored the formation of monoaromatics with boiling point lower than 200 ^{o}C. The optimal pyrolysis temperature to maximize styrene monomer yield (78.7%) was 600 ^{o}C. Some monoaromatics with boiling point lower than 200 ^{o}C could also be obtained as high-octane gasoline fraction. By vacuum rectification, styrene monomer with 99.6 wt.% purity could be obtained. The approach to increasing the yields of styrene monomer and other monoaromatics by re-pyrolyzing the heavier liquid fraction is also suggested.

Kaoru et al., **[12]** studied an iron supported coal-derived active carbon catalyst which showed excellent activity for liquefaction of polypropylene (PP) at low temperature (380 ^{O}C) to give colorless distillates selectivity (92 wt %). Free radical on active carbon should initiate cracking reaction by hydrogen abstraction from polypropylene to form hydrocarbon radical. However, the consecutive cracking of the hydrocarbon radical is suppressed by hydrogenation on the iron particle to give colorless distillates selectivity.

Phungtum [13] studied the conversion of polypropylene into oil product using iron on activated carbon catalyst in a microreactor, 30 mm inside diameter and inner volume of 75 ml, by varying operation conditions as pressure of hydrogen gas range of 28 to 50 kg/cm^2, reaction temperature between 395 and 455 °C and reaction time 30 to 90 min for each catalyst. From the results, it was found that reaction temperature of 435 °C was the temperature that yielded the highest quantity of oil product. After that, the study of the effect of hydrogen gas pressure, reaction time and ratio of polypropylene to iron on activated carbon catalyst were carried out. The analyzed oil product from Gas Chromatography (GC Simulated Distillation) was found that iron on activated carbon was suitable and used as catalyst at 435 °C, hydrogen pressure at 30 kg/cm^2 and reaction time 60 min. The product yield was in the range 40-65% naphtha, 12-14% kerosene, 10-13% gas oil and 4-5% long residues.

Zmierczak et al., [14] investigated the depolymerization-liquefaction reactions of representative polystyrene and styrene-butadiene copolymer (non-vulcanized SBR) samples as a function of processing variables, i.e. temperature (350-450 °C), time (15-120 min), H_2 pressure (500-2500 psig), and the presence of catalysts. Two solid superacids, i.e. Fe_2O_3/SO_4^{2-} and ZrO_2/SO_4^{2-}, which differ in acidity were used in the study. The detailed composition of products was determined by GC/MS. Typical products from a polystyrene sample (average MW 280000) contained benzene, toluene, (C_2-C_5) alkyl- and alkenylbenzenes, 1,3-diphenylalkanes and triphenyalkanes, accompanied by some indanes, tetralins, naphthalenes and polyphenyls, whereas products from non-vulcanized SBR (MW 140000) contained, in addition to the above, C_5-C_9 paraffins and cycloparaffins, (C_5-C_8) alkyl- and alkenylbenzenes, cyclopentylbenzenes, and cyclohexylbenzenes. The changes in product composition as a function of the above processing variables were determined and conditions for preferential (> 85 wt.%) production of gasoline-range liquid fuels established. The observed change in composition as a function of reaction time and temperature allowed for elucidation of mechanistic aspects of high-temperature depolymerization-liquefaction processes, including the role of catalytic effects.

CHAPTER III
THEORY

3.1 Metal Catalyst [15,16]

Metal catalyst are of particular interest for reactions involving hydrogen, such as hydrogenation, hydrogenolysis, and catalytic reforming. The use of iron for ammonia synthesis and for the Fischer-Tropsch reaction, and nickel for steam reforming and methanation. In many of applications, the metal is highly dispersed on a support, in aggregates so small that many or most of the atom present are on the surface. Metal also may be useful for oxidation reactions, such as supported silver for oxidation of ethylene to ethylene oxide, platinum-rhodium wire gauze for the partial oxidation of ammonia to nitric oxide.

For metals and metal allows in particular, relationships have been sought between collective properties and catalytic behavior. The metallic state was generally described by the simple band model or the Pauling valence structure theory. The electron transfer between substrate and catalyst **(Fig 3.1)** are acceptor reaction and donor reaction. Acceptor reactions, electrons flow from catalyst to substrate; the adsorbate acts as an acceptor (examples: starting materials with high electron affinity; reactions in which oxygen is mobilized). Donor reactions, electron flow from substrate to catalyst (examples: substrates that readily release electrons, i.e. reducing agents with low ionization energies; reaction in which H_2 or CO is mobilized.

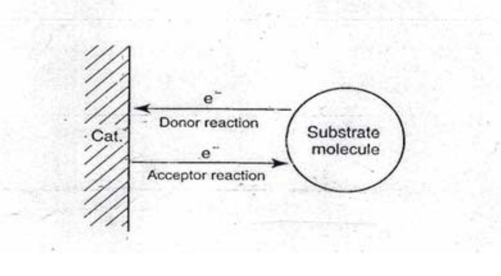


Figure 3.1 Electron transfer between catalyst and substrate [15]

In metal the valence shell is formed by s or d band. The main-group elements with their s bands are typical electron donors and form strong bonds with electron acceptors such as sulfur or oxygen; stable sulfides and oxides are formed. These metals are therefore not suitable as catalysts. In contrast the transition metals with their d bands are excellent catalysts. It is noteworthy that both hydrogenations and oxidations can be carried out with d-block elements.

The electronic structure of the transition metals is described by the band model. According to this model the metal is a collective source of electrons and electron holes (Fig 3.2). In a row of the periodic table, the metals on the left have fewer d electrons to fill the bands. There are two regions of energetic states, namely, the valence band and the conduction band with mobile electrons or position holes. The potential energy of the electrons is characterized by the Fermi level, which corresponds to the electrochemical potential of the electrons and electron holes. The position of the Fermi level also indicates the number density of electrons in the band model.

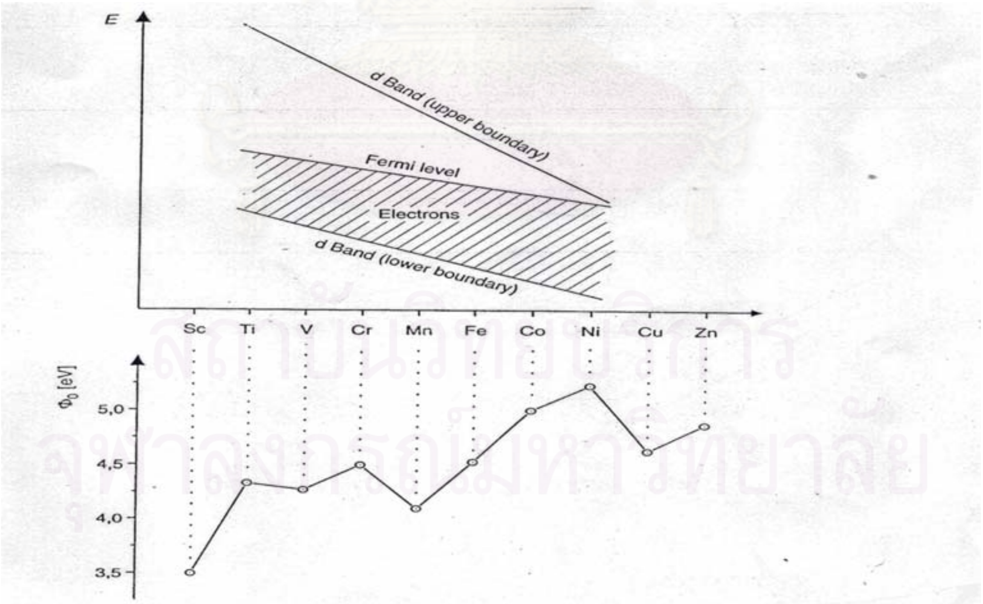


Figure 3.2 Electron density of the 3d band and work function ϕ_o of the transition metals of the fourth period [15]

Metals normally have a narrow d band. The catalytic properties are strongly influencedby the occupational density of the electrons in this band. In many cases a direct relationship has been found between the catalytic activity of transition metals and the electronic properties of the unfilled d bands. This is shown by the general trend of the rate of adsorption along the transition metal rows. For molecular species strong binding is observed on the left-hand side of a row. For molecular species it was found that the rate of dissociative adsorption on the nobel metals increases from right to left as a function of the d-band occupation. Besides the electron occupation of the d bands, another description can be used for obtaining correlation, namely, the valence bond theory of metals. The bonding in transition metal is partially due to unpaired electrons in bonding d orbital.

Maximum catalytic activity is associated with rapid but not too strong chemisorption of reactants. The heat of adsorption of gases such as oxygen, nitrogen, hydrogen and ammonia, ethylene, and acetylene on metals decreases in a continuous manner as one proceeds across groups VB, VIB, VIIB, and $VIII_1$, $VIII_2$, and $VIII_3$ of the metals in either the first, second or third transition series. Group IB metals do not readily adsorb some gases, e.g., hydrogen, since the dissociation of hydrogen is the rate-limiting process and this has a activation energy. Hydrogen atoms can be chemisorbed under conditions where molecular hydrogen is not chemisorbed.

Hydrogenation reactions are carried out with a wide variety of reactants. The most active metallic catalysts are those in group VIII. This is readily rationalized in terms of adsorption effects; the strength of adsorption on, for example, group VB and VIB metals is too strong, that on IB metals is too weak or nonexistent. Within group VIII relative activity differences vary with the nature of the reaction and require a more detailed examination of the mechanism.

Hydrogenolysis of a hydrocarbon is a cleavage of a C-C bond accompanied by hydrogenation to form two molecules from one. Hydrogenolysis of paraffins is of great importance in petroleum processing in which it is sometimes a desired reaction, as in commercial hydrocracking, and sometimes not desired, as in catalytic reforming. The mechanism probably involves as the first step adsorption of the paraffin on a group of sites with dissociation of a hydrogen atom. A commonly studied model of the reaction is that of ethane and hydrogen to form methane. The relative activity of metals changes more with position in the periodic table for ethane hydrogenolysis than it does for hydrogenation. Group VIII metals are again the most active. In the first transition series maximum activity is shown for the third subgroup element, nickel, but in the second and third transition series it is shown for the first subgroup element, ruthenium or osmium.

3.2 Catalyst Preparation and Manufacture [16]

Most catalyst are either a finely divided metal supported on a carrier such as alumina or silica, or a compound, more or less complex, either on a carrier or unsupported. Metal-sulfide catalysts are prepared first as the oxide and then treated with hydrogen sulfide or another sulfur compound in the presence of hydrogen to convert it to the sulfide. Either of two types of processes, generally termed the precipitation method and the impregnation method, is commonly used for making catalysts. The first involves in its initial stages the mixing of two or more solutions or suspensions of material, causing precipitation; this is followed by filtration, washing, drying, forming, and heating. Simple wet mixing without precipitation is occasionally used, but it may not provide the degree of intimate contact between species that is usually desired. High temperatures can subsequently be applied to provide homogeneity and compound formation by thermal diffusion and solid-state reaction, but this usually causes an undesired degree of sintering and consequent loss of surface area. Sometimes the desired degree of mixing can be achieved by kneading.

If a carrier is to be incorporated in the final catalyst, the original precipitation is usually carried out in the presence of a suspension of the finely divided support, or a compound or suspension that will eventually be converted to the support may be initially present in solution. The final size and shape of the catalyst particles are determined by the forming process, which may also affect pore size and pore -size distribution. Larger pores can be introduced into a catalyst by incorporating into the mixture 5 to 15 percent of wood flour, cellulose, starch or other material that can subsequently be burned out. Final catalyst material rejected for chemical or physical reasons may in some cases by recycled without harm to product specifications by powdering it and incorporating it into the catalyst mixture. Such incorporation, however, may change the pore size distribution of the final catalyst. With a gelatinous precipitate, mechanical manipulation may have a significant effect on the ultimate pore size distribution. After it is dried and formed, the precursor catalyst is activated; that is, it is converted into its active form through physical and chemical changes. This typically involves heating to cause calcination or decomposition, followed by reduction if a metallic catalyst is desired. In some cases a supported metal catalyst is pyrophoric, and reduction is carried out in the plant reactor rather than by the catalyst manufacturer to avoid hazards upon shipping and reactor loading. Some advantages of the precipitation method are that it generally provides more uniform mixing on a molecular scale of the various catalyst ingredients, the distribution of active species through the final catalyst particle is uniform, and the ultimate sizes and shapes are not limited to the forms in which desired carriers are available.

Also more control may be available over pore size and pore size distribution. If two or more metal compounds are present, in a batch-type operation they may precipitate at different rates or in sequence rather than simultaneously, thus affecting the final structure of the solid. Both the ultimate physical and chemical structure of the catalyst are frequently very sensitive to the pH of the precipitation, in which case precipitation is carried out continuously in a well-mixes vessel with careful control of pH. Impregnation is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution, usually aqueous, of one or more suitable metallic compounds. The carrier is then dried, and the catalyst is activated as in the case of precipitated catalysts. The size and shape of the catalyst particles are that of the carrier. The impregnation technique requires less equipment since the filtering and forming steps are eliminated and washing may not be needed. It is the preferred process in preparing supported noble metal catalysts, for which it is usually economically desirable to spread out the metal in as finely divided a form as possible. The noble metal is usually present in the order of 1 %wt or less of the total. This makes maximum use of a very expensive ingredient; in a precipitated catalyst some of the active ingredient may be enclosed by other material present and thus unavailable for reaction.

3.2.1 Precipitation method of catalysts

3.2.1.1 Precipitation

In a common procedure an aqueous metal salt solution is contacted with an aqueous alkali, ammonium hydroxide or ammonium carbonate, to case the precipitation of an insoluble metal hydroxide or carbonate. These can be readily converted to oxides by heating. The starting compounds are generally chosen because of their availability and high water solubility, and in some cases to avoid introducing elements that may be deleterious in the final catalyst or that may cause difficulties in subsequent processing. Control of air and water pollution is also and important factor. NO_x from nitrates must be removes, e.g., by scrubbing with aqueous alkali; many heavy metals are more or less toxic and cannot be simply discharged. If the final catalyst is to be a supported metal, sulfate may be undesirable, since it can be reduced to a sulfide, which is a common poison for metal catalysts, the metal nitrate salt is often preferred because it usually is highly water soluble, generally available, and cheap, but NO_x control is required. An organic compound such as a formate or oxalate may be used, although these are more expensive and organic fragments from their decomposition on heating may adsorb on the catalyst to cause partial inactivation. Also, the average ultimate metal particle size may be considerably different if it is formed by decomposition of a compound rather than by reduction of an oxide. Sulfates and chlorides are generally water-soluble, but the anions must usually be removed by washing, and disposal of waste water may be problem. A preferred base is usually ammonium hydroxide since it leaves no cation residue, but it may complex with some metals and keep them in solution.

If a relatively crystalline precipitate is formed, the size of crystals may affect the ultimate particle size of a supported metal catalyst. Thus, fine crystals may be desired to produce high surface area of a supported metal catalyst, but crystals that are too fine may be difficult to filter. The size of such crystals may be controlled by a variety of techniques. In a multi component catalyst, crystals may be smaller if the metals are truly coprecipitated rather than precipitated in sequence. Crystal size may also be affected by temperature and by stirring, since this affects nucleation and the degree of supersaturation. Ripening, in which a precipitated is allowed to stand for a period, can allow for re-crystallization in which small and/or amorphous particles dissolve and crystalline particles grow. This may convert a gelatinous precipitate to a more crystalline and filterable solid.

Silicic acid and a number of metal hydroxides, e.g., those of aluminum, iron, and titanium, form gelatinous colloids, this can make them extreamly difficult to filter or to purify by washing. Such gels may be coagulated by electrolytes, but the process of washing to remove electrolyte impurities may cause them to re-disperse into colloidal solution, termed peptization. Hence, a silicic acid gel may be washed with dilute hydrochloric acid, or an aluminum hydroxide gel with aqueous ammonium nitrate, to maintian an ionic enviroment and hence the coagulated form. The additives can be subsequently removed by heating, gels readily occlude ionic impurities, which may be difficult to remove by washing. The possobility of reaction between carrier and reagents should also be considered in this step. Thus, acidic solutions of reagents may react with basic carriers, and vice versa.

3.2.1.2 Forming operations

The nature of the forming operations is determined by a balance among several factors, including rheological properties of the mixture, and the necessity to achieve satisfactory strength, an open-pore structure, and high activity in the ultimate catalyst, in addition to economics. Relatively hard materials, which typically have high melting points, cannot be made into pellets without suitable additives. Operations causing an increase in crushing strength usually also decrease pore volume and average pore size, and hence may cause diffusion limitations. Typically, commercial catalysts have a void fraction of about 0.5 cm^3 of voids per cubic centimeter of porous pellet.

3.2.1.3 Calcination

This may have several purposes. One is to eliminate extraneous material such as binders and die lubricants, as well as volatile and unstable anions and cations that have been previously introduced, but are not desired in the final catalyst. Second, a substantially elevated temperature is usually needed to increase the strength of the final pellet or extrudate by causing incipient sintering. Excessive sintering will reduce the catalyst activity by reducing surface area, and it may also cause diffusion limitations by reduction of pore size, so an optimum is desired. If a metallic catalyst is the ultimate goal, conversion to the oxide form is frequently sought prior to reduction. If a complex catalyst is the goal, a substantially elevated firing temperature may be required to cause mixing by diffusion of individual species to form a desired compound or crystal phase. In any event, the catalyst should be heated under controlled conditions to a temperature at least as high as will be encountered in the plant reactor to remove bound water, carbon dioxide, etc. If these decompositions occur to a significant extent in the plant, they may cause structural weakness in pellets, leading to breakup, dusting, and so on, that may cause excessive pressure drop and premature reactor shutdown.

For small production runs, conventional batch-type multi tray driers and calciners are common, but labor costs are high. For larger production runs, a continuous rotary, kiln may be used. More precise temperature control is achievable with a continuous tunnel kiln. This may be heated electrically with numerous zones so that temperature rise can be programmed. Trays may be fastened onto a stainless steel mesh belt and automatically loaded and dumped, or trays may be placed and removed manually.

Upon heating pellets in a tray calciner, an exothermic reaction may develop that can lead to excessively high temperature locally, affecting the catalyst adversely. The effect can stem form an exothermic decomposition reaction, as in the thermal decomposition of an ammonium copper chromate to form a "copper chromite" catalyst or by reactions among pellet ingredients, such as that between a metal nitrate and organic admixtures such as cellulose, graphite, or stearates. Combustion in air of these organic substance or of remaining organic solvents may also occur. The effect is most pronounced with thick layers of pellets from which heat generated internally cannot easily escape. It may be controlled by using a slower rate of heat up or using thinner layers of pellets, although it may necessary to use layers as thin as inch or so.

3.2.1.4 Reduction to the metal

Most commonly, a metal is formed by reduction of the oxide at an elevated temperature by contract with flowing hydrogen or hydrogen diluted with nitrogen, the latter for safety reasons. A considerable excess of hydrogen may be required to sweep away the product water. If present in too high concentration, water vapor may accelerate the sintering of an oxide, and it can also retard the rate of the reduction reaction by forming a hydroxylated surface.

Some metal compounds can be reduced by chemical reagents, such as formaldehyde, formic acid, or hydrazine, but these methods are usually more expensive.

Alternately, the metal may be formed by decomposition of an organic compound, as by decomposition of nickel formate to yield deposited nickel. In this case, however, organic fragments may become adsorbed onto the metallic catalyst, possibly giving rise to considerably different properties than that of a catalyst reduced in hydrogen. Moreover, the ultimate metal particle size is determined by the sintering characteristics of the metal produced, whereas in oxide reduction, particle size may be determined in part, in a rather complicated way, by the formation of metal nuclei and their growth from the oxide particles.

3.2.2 Impregnation

Two methods of contacting may be distinguished. The support is sometimes dipped into an excess quantity of solution, whereupon the uptake is the sum of solution occluded in the pore plus material adsorbed on the pore surfaces. If two or more compounds are present, they are frequency adsorbed on the support surface in a ratio different from that in the solution, and solution concentrations also change with continued contacting. Additions to the solution must take these effects into account. Moreover, material may be dissolved from the support into the treating solution. More precise control is achieved by a technique termed dry impregnation, or impregnation to incipient wetness, which is commonly used industrially. A batch of the 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 few case, the active ingredient may be fixed inside the catalyst by immersing the impregnated catalyst in a reagent to cause precipitation to occur. Oxide supports such as alumina and silica are readily wet by aqueous solutions, as are most activated 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 pores closed at on end are nearly filled, and the solution of gas in the liquid assists 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 than incipient impregnation.

3.2.2.1 Distribution through pellet

Most metal reagents are adsorbed to varying degrees on most supports, but the characteristics of the process are complicated since various types of adsorption are possible. Silica and zeolites are acidic and adsorb cations. Alumina is amphoteric. Titania is also amphoteric, but more acidic than alumina. For these adsorbents the relative adsorption of cations and anions can be controlled by adjusting pH. Metal ions may be cation-exchanged with a surface containing hydroxyl groups or containing alkali or alkaline earth-metal ion, or they may be held by coordination. The surface structure of the carrier may also be altered by the impregnation procedure, thus changing its adsorption characteristics. The ultimate degree of dispersion of metal through the catalyst pellet is also determined by the interplay of a large number of factors whose relative importance varies with circumstances. These include the method of impregnation, the strength of adsorption, the extent to which the metal compound is present as occluded solute (that in the bulk liquid in the pores) in contrast to adsorbed species on pore walls, and the chemical reactions that occur upon heating and drying.

The situation may be further complicated by attack on the support. Silica gel is attacked at high pH, and alumina, which is amphoteric, is attacked at a pH that is either too high or too low. Indeed, during the impregnation of an alumina support with an acidic liquid, some solution of alumina may first occur, followed by precipitation as the pH increases. It may be desirable to control this effect by using a buffer. It is also possible to control the deposition by competitive adsorption, e.g., by adding a citrate to the impregnation solution. This procedure has been used to embed a catalytically active layer slightly inside a catalyst particle. Such a structure may be desired for prolongation of catalyst life in an application in which poisons are deposited on the outside surface of a porous catalyst support. An example is supported platinum catalysts for oxidation of pollutants in automobile engine exhaust. In general, use of the dipping method with a great excess of solution should lead to an essentially uniform deposit of adsorbed material if sufficient time is allowed for diffusion of reagent species to the interior and if side reactions are unimportant. If adsorption is initially nonuniform and not too strong, redistribution continues even after the pellet is removed from solution, leading to a more uniform distribution. The dry process can also effect the distribution of an active ingradient. The crystallite size of a resulting supported metal catalyst may also be alerted if a considerable portion of the soluble metal is occluded rather than adsorbed. Again, the effects are complex, and little can be said of general guidance. Initially, evaporation occurs at the outer surface of the particle, but liquid evaporated from small pores will be replaced by liquid drawn from large pore by capillarity. The places where crystallization begins and the ultimate distribution of metal depend on such factors as the initial degree of saturation of the liquid, the rate of nucleation, the rate of heating, connectivity (the degree of connection of liquid paths between pores) at the time of crystallization, and the possibility of surface migration. Commercially available impregnated catalysts are usually found to have a higher concentration of metal at the outside than at the center, even when a more or less uniformly deposited catalyst is desired.

3.3 Catalyst Support

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 an inherently weak catalyst. However, the carrier may actually contribute catalytic activity, depending on the reaction and reaction conditions, and it may react to some extent with other catalyst ingredients 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 powder incorporated into a mixture to be precipitated, or the carrier may itself be precipitated from solution in the manufacturing process. some substances such as colloidal alumina or colloidal silica may play a double role, acting as a binding agent in catalyst manufacture and as a carrier in the ultimate product. Alumina in the γ 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. Large area carriers are sometimes loosely referred to as active carriers in contrast to small area inert carriers, 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 important:

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 implies fine pores, but relatively small pores, such as < 2 nm, may become plugged in catalyst preparation, especially if high loadings are sought).
6. Low cost.

3.3.1 Activated carbon [17]

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 of an activated carbon particle, it looks like a beehive. It consists, principally of carbon

(87 to 97%) but also contains such element as hydrogen, oxygen, sulfur and nitrogen, as well as various compounds either originating from the raw material used in its production or generated during its manufacture. Activated carbon has the ability to absorb various substances both from the gas and liquid phases. It is widely used for adsorption of pollutants from gaseous and liquid steams, for recovery of solvent and as a catalyst or catalyst support. In the nuclear industry, activated carbon is used for adsorption of iodine and nobles gases from gaseous effluents. One of the most important fields in terms of consumption is in water and wastewater treatment. To obtain these activated carbons from cheap and readily available precursors. Raw materials for the production of activated carbon such as wood, peat, coconut, shell, coal.

3.3.1.1 Production of activated carbon

Activated carbon is usually produced by the carbonization and activation of carbonaceous materials.

- Carbonization (or pyrolysis)

The carbonaceous material that constitutes the basis for the production of activated carbon by the steam-gas method must meet certain requirements among which the most important are: (i) low content of volatile matter, (ii) high content of elemental carbon, (iii) definite porosity and (iv) sufficient strength of attrition. Of course, raw materials do not meet all these requirments simultaneously and therefore they require carbonization.

This is one of the most important steps in the production process of activated carbons since it is in the course of carbonization that the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular, so that free interstices remain between them and apparently as the result of deposition and decomposition of tarry substances, these becomes filled or at least blocked by disorganized ("amorphous") carbon. These are three clear stages in the carbonization process: (a) loss of water in the 27-197 ^{o}C range: (b) primary pyrolysis in the 197-497 ^{o}C range with evolution of most gases and tars with formation of the basic structure of the char: (c) consolidation of char structure at 497-847 ^{o}C with a very small weight loss.

The resulting carbonized product has only a very small adsorption capacity. Presumably, at least for carbonization at lower temperature (400-600 ^{o}C), part of the tar remains in the pores between the crystallites and on their surface. A carbon with a large adsorption capacity, however, can be produced only by activating the carbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon.

- Activation

Generally, there are two main types of production of activated carbon:

a) By carbonizing material with the addition of activating agents ($ZnCl_2$, $CaCl_2$, H_3PO_4). This method is generally known as "chemical activation".

b) By allowing the inactive carbonized product (prepared by the usual methods of carbonization) to react with oxidizing gases (steam, carbon dioxide, oxygen). This method is generally known as "physical activation"

a) Chemical activation

For chemical activation, the common chemicals used are dehydrating agent such as $ZnCl_2$, $CaCl_2$, $MgCl_2$ and some acids such as H_3PO_4 and H_2SO_4. The activated agent influences the pyrolytic processes so that the formation of tar is restricted to minimum and the amount of the aqueous phase in the distillate is also less than that in the normal carbonization. The activation agent also changes the chemicals nature of the cellulose substrate by dehydration, which decomposes the organic substances by the action of the action of heat and prevents the formation of tar.

Chemical activated is usually carried out at temperatures from 400-600 °C. These temperature are lower than those needed for activation with gaseous agent (physical activation). An important factor in chemical activation is the degree (coefficent) of impregnation; this is the weight ratio of the anhydrous activation salt to the dry starting material. The effect of the degree of impregnation on the resulting product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores which are freed by its extraction. For small degree of impregnation the increase in the total pore volume of the product which increase in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of large-diameter pores increases and the volume of the smallest decreases.

b) Physical activation

The basic method of activating coal-based granules consists of their treatment with oxidizing gases (steam, carbon dioxide, oxygen) at elevated temperatures. In the activation process, carbon reacts with the oxidizing agent and the resulting carbon oxides diffuse from the carbon surface. Owning to the partial gasification of the granules or grains, a porous structure builds up inside them. The structure of the carbonization product consists of a system of crystallites similar to those of graphite bonded by aliphatic type bonds to yield a spatial polymer. The spaces between the neighboring crystallites constitute the primary porous structure of the carbon. The pores of the carbonized granules are often filled with tar decomposition products and are blocked with amorphous carbon. This amorphous carbon reacts in the initial oxidation step, and as a result the closed pores open and new ones are formed.

In the process of further oxidation, the carbon of the elementary crystallites enters into reaction due to which the existing pores widen. Deep oxidation leads to a reduction in the total volume of micropores due to the burning off of the walls between the neighbouring pores, and in consequence the adsorptive properties and mechanical strength of material decrease. In the first stage of activation, when burn-off is of not higher than 10% (which occurs at low reaction times), this disorganized carbon is burnt out preferentially and the closed and clogged pores between the sheets are freed. In the course of further activation at the second stage, carbon of the aromatic sheet is burnt. When the burn-off is less than 50%, a microporous activated carbon is obtained, when it is large than 75% (which occurs at high reaction times) a macroporous product is obtained; and when the burn-off is between 50 and 75%, the product is of mixed structure and contains both micro- and macropores. Development of macropores due to coalescence or widening of micropores under fast reaction conditions. Carbon oxidation is a complex heterogeneous process encompassing the transport of reagents to the surface of the particles, their diffusion into the pores, chemisorption on the pore surface, reaction with carbon, desorption of the reaction products, and diffusion of these products to the particle surface. The concentration profile of the oxidizing agent of the granule volume, and hence the formation of the carbon porous structure, depends of the rate of the particular steps of the process.

At low temperatures the rate of the chemical reaction of carbon with the oxidizing agent is small, so it is this reaction that limits the overall rate of the process. This results in a dynamic equilibrium becoming established between the concentration of the oxidizing agent in the pores and that in the interparticle spaces. In such a case the activation process yields a homogeneous product with a uniform distribution of the pores throughout the whole volume of the granule, with increase of the oxidation temperature.

The rate of the chemical reaction increases much faster than that of diffusion, and then the overall rate of the process becomes limited by the rate of transport of the oxidizing agent into the granule. At very high temperatures the oxidation reaction rate becomes so high that the whole oxidizing agent reacts with carbon on the external surface of the granule. In such a case significant losses of the material occur due to superficial burn-off, and the porous structure is not formed. The rate of the oxidation process is limited by the reactivity of the initial carbonaceous material towards the oxidizing agent. The greater is the reactivity of the substrates, the lower the optimal temperature of the process at which uniform formation of pores in the granule.

- Pyrolysis and steam activation

Usually the production of activated carbons involves two stages: the carbonization of the raw materials followed by a high temperature activation, at 800 - 1,000 °C, of the resulting chars. The method used in this study combines the two stages into a single one, while the treatment temperature is considerably lower, 600-800 °C. This method is preferable to the two-stage treatment from an economic point of view. During the pyrolysis and steam activation of carbon-containing materials the following main processes take place:

1. Oxidation-thermolytic conversion of the carbon material leading to the accumulation of oxygen-containing groups.
2. A thermal destruction process including the decomposition of the oxygen-containing groups accompanied by the formation of carbon oxides and water.
3. Condensation processes.
4. Deeper penetration of the water molecules and opening up of the initially closed pores into the structure of the carbon materials.

3.3.1.2 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 purge 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 begins early during the carbonization process of the starting material. Thus sets a 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.

Macropores are those having effective radii ≥ 100-200 nm and their volume is not entirely filled with adsorbate via the mechanism of capillary condansation (it may occur only for a relative pressure of adsorbate of nearly one). The volumes of macropores are usually in the range 0.2-0.8 cm^3/g and the maximum of volume distribution curves according to the radii are usually in the range 500-2000 nm. The values of their specific surface area not exceeding 0.5 m^2/g are negligibly small when compared with the surface of the remaining type of pore. Consequently macropores are most of great important in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains as accessible to the particles of adsorbate.

Mesopores, also known as transitional pores, have effective radii falling in the range of 1.5-1.6 nm to 100-200 nm. The process of filling their volume with adsorbate take place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.1-0.5 cm^3/g and their specific surface area in the range of 20-100 m^2/g. The maximum of the distribution curve of their volume versus their redii is mostly in the range of 4-20 nm. Mesopores, beside their significant contribution to adsorption, also perform as the main transport arteries for the adsorbate.

Micropores have sizes comparable with those of adsorbed molecules. Their effective radii are usually smaller than 1.5-1.6 nm and for average activated carbons their volumes usually lie between 0.2-0.6 cm^3/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the non porous surface, which cause a particular large increase of adsorption capacity for small equilibrium pressure of adsorbate. In micropores, adsorption proceeds via the mechanism of volume filling. For some activated carbon, the microporous structure may have a complex nature, e.g. two overlapping microporous structure: firstly one for effective pore radii smaller than 0.6-0.7 nm and termed specific micropores, and the secondly one exhibiting pore radii from 0.6-0.7 to 1.5-1.6 nm termed supermicropores.

3.3.1.3 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 heteroatoms are grouped at the surface of activated. Apart from their different locations, the heterotoms 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 ganerally 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.

3.3.1.4 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' Federation (CEFIC). The tests require highly processional laboratories and advanced equipment. Most of the testing methods have been developed and approved by such organizations as the American Society for Testing Material (ASTM), the American Water Works Association (AWWA), the Deutsches Institute for Normung e.V. (DIN), or the International Organization for Standardization (ISO).

- 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.

- 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 shapes, sizes and densities of the individual particles is indispensable for determining the size of unit packages.

- Adsorption test

The 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 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 for 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 from of 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 determined, for example, by the BET method. The specific 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 molecule is significant.

- *Methylene blue adsorption.* The methylene blue value gives an indication of the adsorption capacity of and activated carbon for molecules having similar dimensions to methylene blue, it also gives an indication of the specific surface area of the carbon which results from the existence of mesopores of dimensions greater than 1.5 nm.

- 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 granule (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 consist mainly of oxides and in smaller amounts, of sulfates, carbonates, and other compoumds of iron, aluminum 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 activated carbon and dimensions of its particles, to constant mass. The weight of the ashed carbon is expressed as a percentage of the weight of the original carbon sample.

3.3.1.5 Uses of activated carbon

The advantage of using activated carbon is that in certain circumstances a single stage of adsorption may replace several and physical separations or it may permit separation of compounds of the same boiling point. As state earlier, activated carbon are used mainly in the purification and decolorization of liquids and as such are used mostly in powder form and derived from cellulose raw materials (about 85% of total use). Some advantages of using activated carbon are listed below:

Dry cleaning solvent. With the increase in dry cleaning in recent years, particularly in coin-operated machines, the need has arisen for convenient on the spot method of purifying the solvent which with the passage of time because contaminated with oils and grease. These become rancid as well as dark colored and impact obnoxious odors to the cleaning liquid. The odors are reduced but not eliminates by distillation of the solvents. Activated carbon has proved to be effective in decolorizing and deodorizing.

Sugar. The main action of the carbon is in decolorization but it also removes nitrogenous substance and lyophilic colloids. By doing so it improves filtration, reduces foaming during evaporation and increasing the speed of crystallization. When saturated the carbon is removed and regenerated by heating in steam and air at a red heat.

Water. Water is usually treated with chlorine to destroy bacteria but this can at times impart an unpleasant taste, which is especially marked when the chlorine has reacted with micro-organisms and with phenol. The bad taste becomes very noticeable when the supplying river is at a low level but it can be removed by treating the water with activated carbon. This should be an increasing market, particularly if the cost of activated carbon can be reduced.

Tyres. It has been found that white wall tyres retain their whiteness better if activated carbon is incorporated in the reinforcing carbon black.

Pharmaceuticals. Activated carbon has the property of concentrating the active component from a broth. The desires component can be recovered from the carbon by solvents. Penicillin was the first to be treated on a large scale by this method. With the increasing emphasis being placed on pollution by effluents it would seem that activated carbon may play an important part in reducing this problem.

Foodstuffs. Here activated carbons are used to remove soaps and peroxides from edible fats to prevent poisoning of hydrogenation catalysts. They also improve color and flavour, e.g. in soup stocks and vinegar, and improve the storage properties of freshly distilled whisky.

Gas phase carbons. These should have the following properties : (i) high absorptive capacity; (ii) high retention; (iii) high selectivity in the presence of water vapor; (iv) low flow resistance; (v) high resistance to breakage; (vi) complete release of vapor at increased temperature and decreased pressure.

3.4 Mechanism of Cracking Processes

Cracking processes were assigned to three fundamental classes;

3.4.1 Thermal cracking [18,19]

Thermal cracking, where free radicals (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 called the "RK-theory" as follows to explain 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 much closely approach each other. Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of tertiary > secondary > primary free radical.

Cracking of either the original or isomerized radical then takes place at a carbon-carbon bond located in the β position to the carbon atom lacking one hydrogen atom. Cracking at the β position gives directly an alpha olefin and a 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 many 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 radicals are derived from cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive recracking, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with feedstock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction

An example schematic representation of polyolefin cracking is as follows:

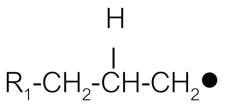
1. Initiation Step

$$R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \xrightarrow{\text{heat, } h\nu} R_1\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\bullet + R_2\bullet$$

2. Propagation Step

2.1 β-fission

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



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

2.2 Chain Transfer

$$R_1\text{-}CH_2\text{- }(CH_2)_4\text{-}CH_3 + H^{\bullet} \longrightarrow R_1\text{-}\overset{\bullet}{C}H\text{- }(CH_2)_4\text{-}CH_3 + H_2$$

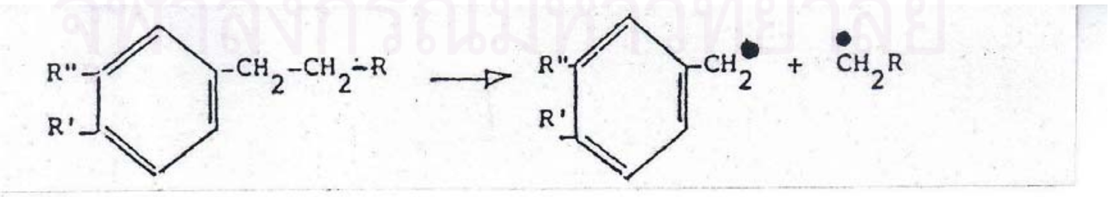
3. Termination

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

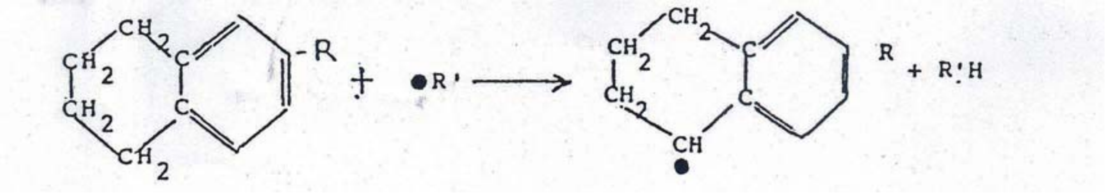
$$R_3\text{-}CH_2\text{-}CH_2^{\bullet} + {}^{\bullet}CH_2\text{-}CH_2\text{-}R_4 \longrightarrow R_3\text{-}CH_2\text{-}CH_3 + CH_2{=}CH\text{-}R_4$$

An example schematic representation of aromatic cracking is as follows:

1. Initiation Step

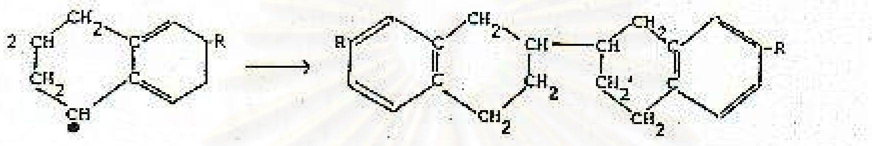


2. Chain Transfer

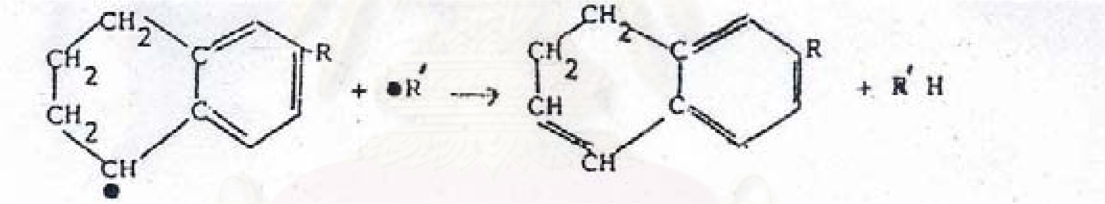


3. Termination

Coupling



Disproportionation



3.4.2 Catalytic cracking [14, 20, 21, 22]

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

A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer-lived and accordingly more selective than free radicals.

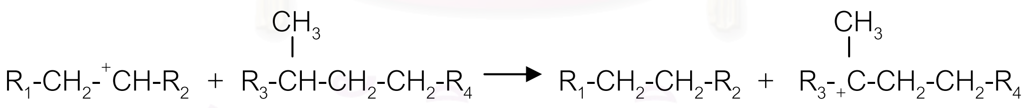
There are two possibilities for the initial step in the catalytic cracking of polyloefin. The most involves the simultaneous loss of a hydride ion from the polyolefin molecule and of a proton from the acidic catalyst surface. This produces a carbonium ion in combination with acid anion and molecular hydrogen:

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

Alternatively a small amount of olefin, created by thermal cracking could initiate the reaction:

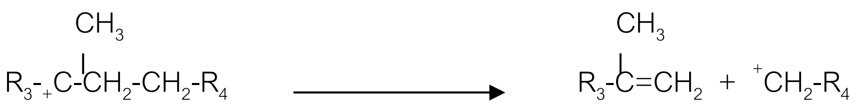
$$R_1\text{-}CH\text{=}CH\text{-}R_2 \;+\; H^+A^- \longrightarrow R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \;+\; A^-$$

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



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

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:



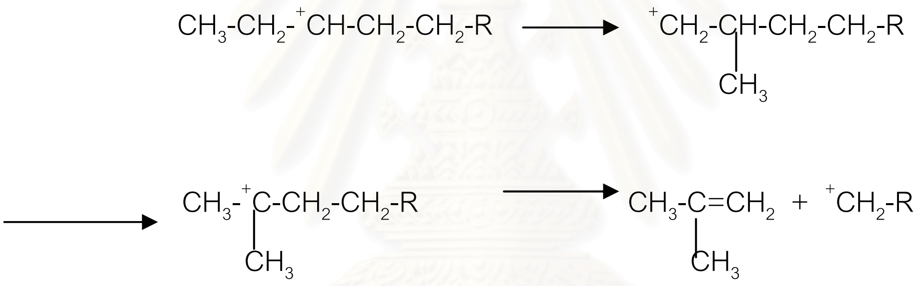
$$R_3\text{-}{}_+\overset{\overset{CH_3}{|}}{C}\text{-}CH_2\text{-}CH_2\text{-}R_4 \longrightarrow R_3\text{-}\overset{\overset{CH_3}{|}}{C}\text{=}CH_2 \;+\; {}^+CH_2\text{-}R_4$$

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

$$^{+}CH_2\text{-}R_4 \longrightarrow CH_3\text{-}{}^{+}CH\text{-}R_5$$

Subsequent step involve further β-scission and hydride transfer and proceed until the chain becomes so short that cracking at the β position 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:



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

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

In case of polystyrene cracking, Vitidsant [21] proposed mechanistic pathways by Fe/AC catalyst. It occurred by beta fission as shown below by thermal cracking or abstracting of hydrogen atom at surface of activated carbon. Therefore it resulted monomer, dimer and trimer as the major products.

An example schematic representation of polystyrene cracking is shown in **Fig. 3.3**.

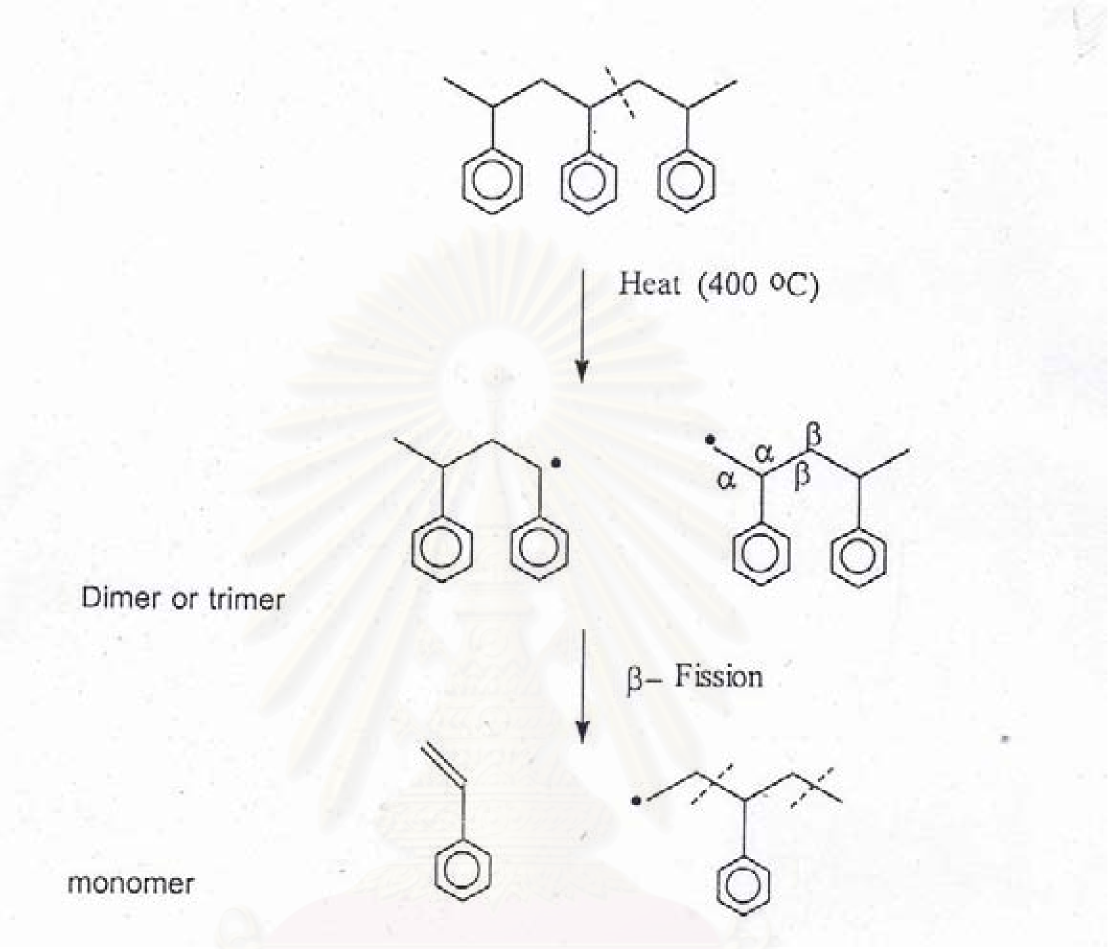


Figure 3.3 Proposed mechanistic pathways for the catalytic cracking of polystyrene by Fe/AC catalyst.

Moreover, Zmierczak et al. **[14]** proposed mechanistic pathways for the depolymerization-liquefaction of polystyrenes by superacid catalyst (Fe_2O_3/SO_4^{2-}, ZrO_2/SO_4^{2-}). The scheme is shown in **Fig. 3.4**.

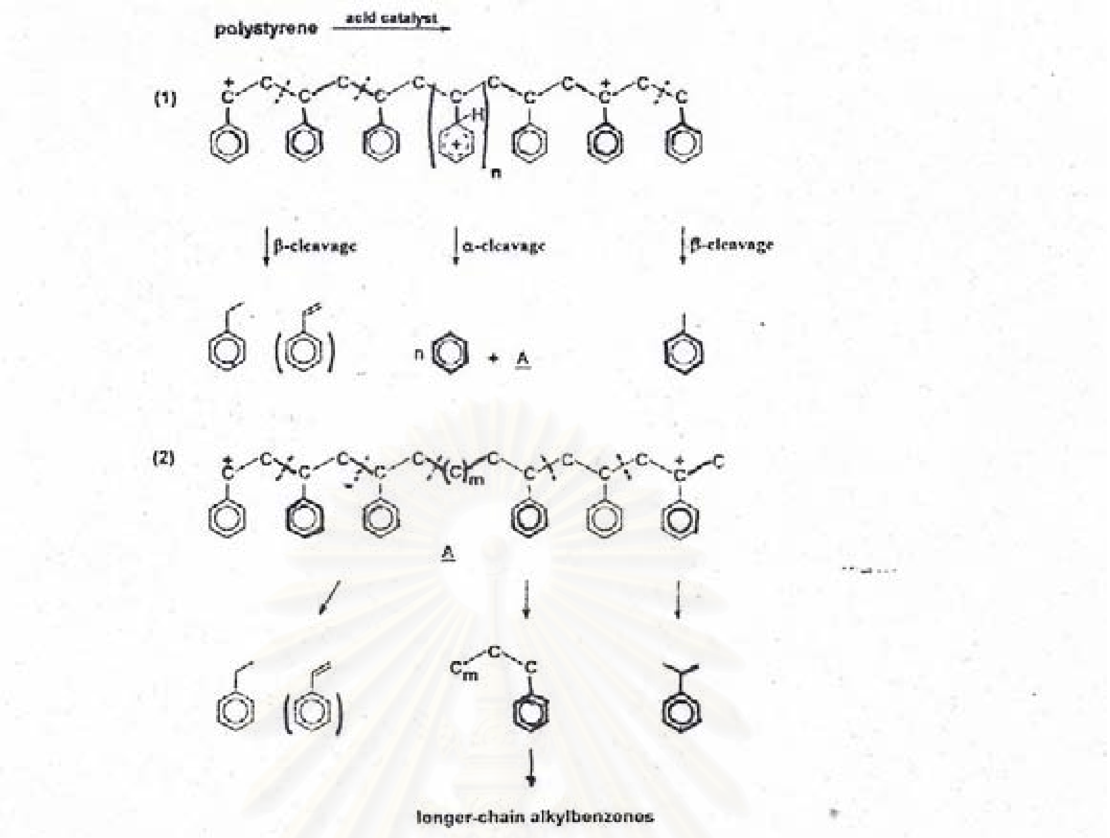


Figure 3.4 Proposed mechanistic pathways for the depolymerization-liquefaction of polystyrenes by superacid catalyst.

In this scheme carbonium ions along the polymeric chain can be formed either by hydride abstraction at benzylic positions or by protonation of aromatic rings. β-cleavage (of benzylic carbonium ions) at the end position or adjacent to the end positions can produce either ethylbenzene (plus styrene) or toluene. Likewise, cumene can be produced by β-cleavage of a corresponding end group, having two carbon atoms attached to the benzylic carbon. Benzylic carbonium ions at internal C positions will undergo consecutive β-cleavage reactions into smaller polymeric fragments which will ultimately depolymerize by the above indicated β-cleavage of end (or adjacent to the end) benzylic carbonium ions.

In a competitive pathway, carbonium ions produced by protonation of aromatic rings in the polymeric chain could undergo α-cleavage leading to benzene plus a product in which some sites have a longer aliphatic chain between two aromatic rings (A). Further cleavage of such intermediates will yield longer chain alkyl- and alkenylbenzene, which undergo to a limited extent intramolecular cyclization reactions leading to cycloalkylbenzenes, indanes and some tetrahydronaphthalenes.The above-indicated protonation of benzene rings as a source for formation of benzene. In addition, some benzene can be formed by dealkylation of intermediate alkylbenzenes.

3.4.3 Hydrocracking [22]

Hydrocracking is essentially catalytic cracking in the presence of hydrogen. It is one of the most versatile petroleum refining schemes adapted to process low value stocks. Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene. The process can also use feeds with high aromatic content.

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

$$RCH_2CH_2R' \xrightarrow{\text{catalyst}} RCH_2\overset{+}{C}HR' + H^-$$

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

$$RCH_2^{+}CHR' \xrightarrow{-H^{+}} RCH{=}CHR'$$

$$RCH_2^{+}CHR' \xrightarrow{\beta \text{ scission}} R'CH{=}CH_2 + R^{+}$$

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

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

Other reactions that occur during hydrocracking are the fragmentation followed by hydrogenation (hydrogenolysis) of the complex asphaltenes and heterocyclic compounds normally present in the feeds.

Hydrocracking reaction conditions vary widely, depending on the feed and the required products. Temperature and pressure range from 400 to 480 ^{o}C and 35 to 170 atmospheres, respectively. Space velocities in the range of 0.5 to 2.0 hr^{-1} are applied.

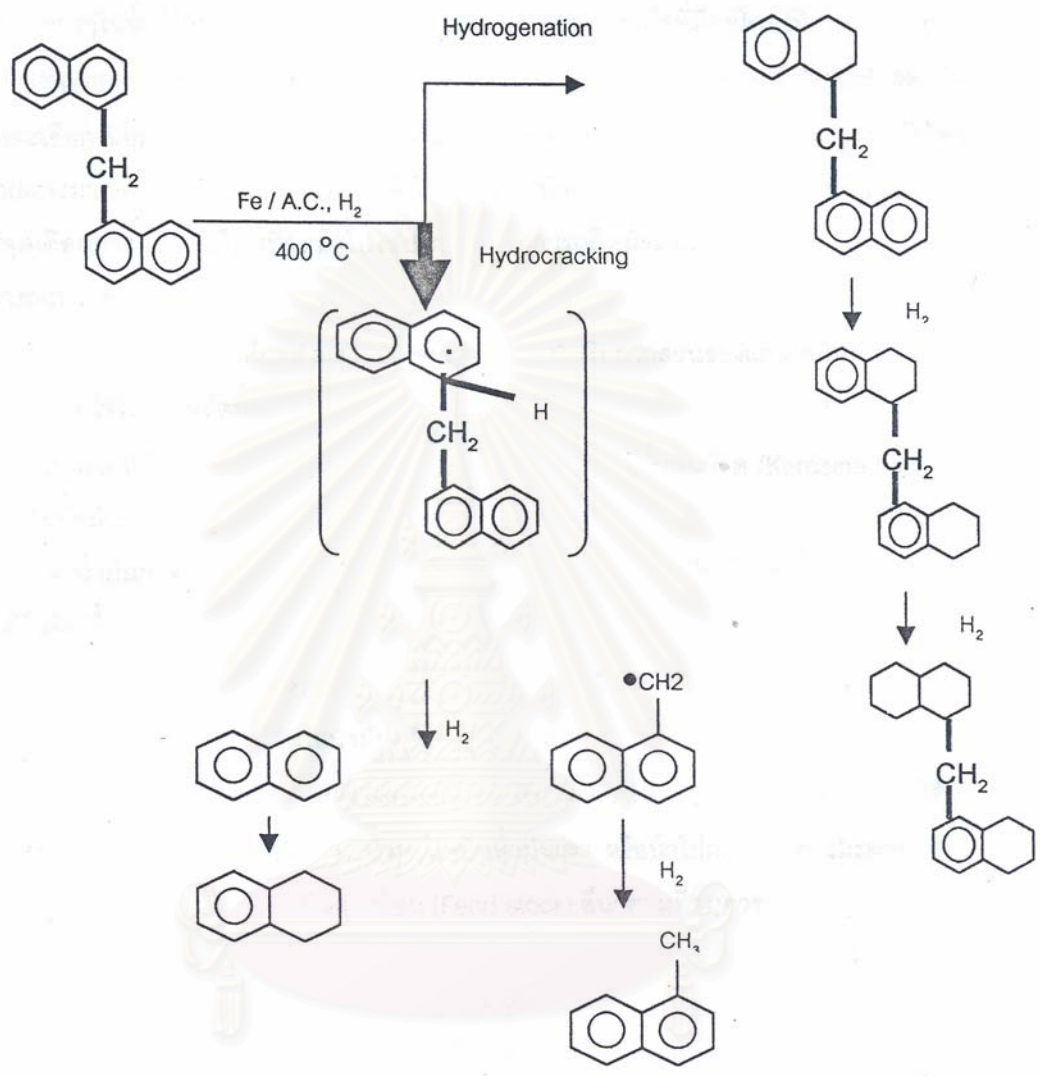


Fig. 3.5 Proposed mechanistic pathways for the hydrogenation/hydrocracking of aromatic compound in DNM (di(1-naphthyl)methane) by Fe/activated carbon at 400 °C.

CHAPTER IV

EXPERIMENTAL SETUP

4.1 Raw Material and Chemical

The model plastic of acrylonitrile-butadiene-styrene polymer (ABS) used in experiments as commercial grade (code : GA850) was supplied from Thai Petrochemical Industry Public Company Limited. It was virgin plastics of 3x3x2 mm size granules. The ratio of acrylonitrile-butadiene-styrene was 20-25, 16-20 and 55-64%, respectively. The catalyst used in this study was an iron supported on activated carbon. It was ground to around 0.3 mm., the BET area was around 692-719 m^2/g. Hydrogen gas (purity 99.5% minimum) and toluene (commercial grade; purity 80% minimum) were used as chemical reagents.

4.2 Apparatus and Instrument

4.2.1 The reaction of acrylonitrile-butadiene-styrene polymer (ABS) with Fe/activated carbon was carried out by using a microreactor (shown in **Fig.4.1**). The microreactor is a stainless steel tube SS.316 with an inner volume of 70 cm^3 , 30 mm inside diameter, (shown in **Fig. 4.2**). It was heated by an electricity 450 watt, and the temperature was measured by thermocouple type R size of 1.6 mm diameter. The temperature was controlled to an accuracy of $\pm 5\ ^{O}C$ by means of a programmable temperature controller. The shaking of microreactor was controlled by a control speed motor.

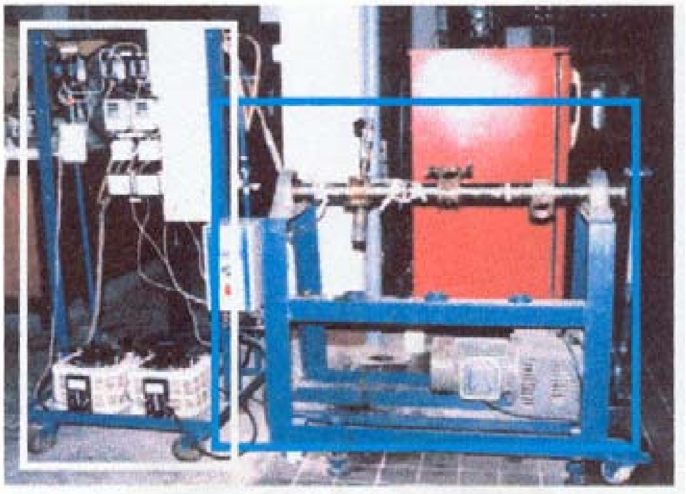


Figure 4.1 The reaction experimental unit for conversion of ABS into oil products using Fe/AC catalyst.

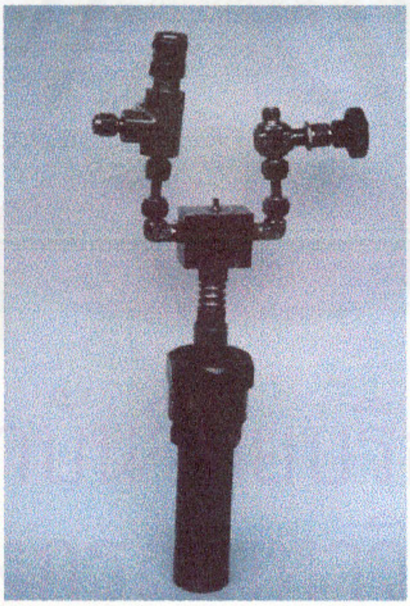


Figure 4.2 The microreactor

4.2.2 Vacuum pump

The separation of liquid oil from catalyst and residue by using the vacuum filter ,pressure 1 kg/cm^2, (shown in **Fig 4.3**).

Figure 4.3 The vacuum filter

4.2.3 Gas Chromatography (GC Simulated Distillation)

The boiling range distribution determination by distillation is simulated by the use of gas chromatograph (GC Simulated Distillation), Perkin Elmer, followed ASTM D2887-93 at PTT Research and Technology Institute. A nonpolar packed or open tubular (capillary) gas chromatographic column is used to separate the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at a reproducible linear rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a known mixture of hydrocarbons covering the boiling range expected in the sample. The boiling range distribution can be obtained.

4.2.4 Fourier-Transform Infrared Spectrometer (FTIR)

The functional groups of oil product was analyzed by FTIR, Perkin Elmer, model 1760X, at Thai Petrochemical Industry Public Company Limited (TPI).

4.2.5 Scanning Electron Microscope (SEM)

The surface of solid products was analyzed by SEM, Jeol, model JSM-6400, at Scientific and Technology Research Equipment Center, Chulalongkorn University.

4.3 Experimental Procedure

4.3.1 The catalyst preparation process is described as follows :

- A preparation of iron on activated carbon has been done through impregnation method with different iron percentage at 1, 5 and 10%
- About 200 g of each type of catalyst are prepared with the following steps :

Distillate water was poured to an equal height of activated carbon in a container before putting into vacuum equipment for 3 hours and finally air bubble will be found on its surface. The catalyst was then impregnated with an aqueous solution of ferric nitrate $(Fe(NO_3))_3$ with required percentage of iron on deaerated activated carbon at room temperature for 2 hours. The slurry was then dried with a vacuum rotary evaporator at 80 ^{o}C for 3 hours, and further dried to powder activated carbon by putting it in an oven overnight at 120 ^{O}C. Then, $(Fe(NO_3))_3$ which is in pore of activated carbon was calcined at 450 ^{O}C for 3 hours. The catalyst was reduced with hydrogen at 400 ^{O}C for 1 hour and then presulfated with hydrogen sulfide at 450 ^{O}C for 1 hour before cooling down at room temperature.

4.3.2 Procedure of the experiment

15 g of ABS and required amount of catalyst were put in a 70 ml-microreactor under hydrogen atmosphere. Heating coil, insulator, and thermocouple were parted around the reactor. The reactor was fixed with a shaker at 120 rpm while its reaction corresponds to a required time. After that, the reactor was cooled down by removing the insulator and the heater coil, then blowing it with fan and keeping it cooler until it goes down to a room temperature. The oil yield was filtered and kept some of it for analysis by distillation gas chromatograph to find out oil composition and filtering all of yield products by using toluene as a solvent of products remaining in the reactor. Remainders in the filter are the catalyst and coke or solid. As a result, the data obtained from this process are usable for calculating conversion percentage.

4.3.3 The composition analysis of products by Gas Chromatograph

The boiling ranges of oil yield were determined by Gas Chromatograph (GC Simulated Distillation) at PTT Research and Technology Institute for naphtha (IBN-200 ^{O}C), kerosene (200-250 ^{O}C), gas oil (250-300 ^{O}C), and long residue (up to 350 ^{O}C) [23].

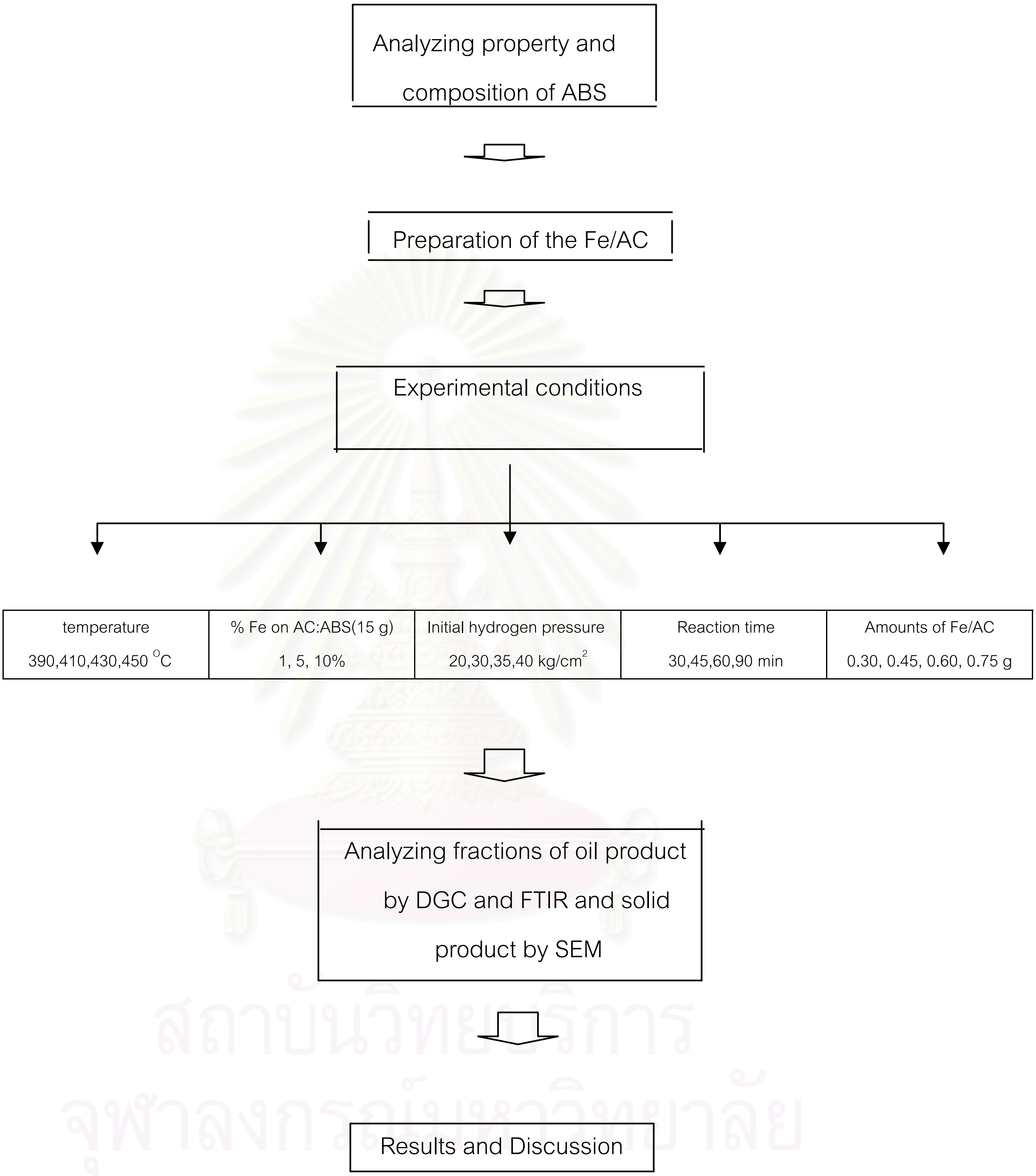


Figure 4.4 Experiment scheme of the hydrocracking of acrylonitrile-butadiene-styrene polymer (ABS) by Fe/AC catalyst

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Experimental Results

The experimental results of hydrocracking of acrylonitrile-butadiene-styrene polymer (ABS) by Fe/activated carbon catalyst, by investigating its influences on percentage conversion of the products and yielded oil composition, were obtained. The examined variables were percentage of iron loading on activated carbon, temperature, a ratio of acrylonitrile-butadiene-styrene polymer (ABS) and catalyst, initial pressure of hydrogen gas and reaction time. Results from different conditions and those of oil composition analysis are illustrated in **Table A-1 and Table A-2**. The influences of each variables mentioned above are shown in **Figs. 5.1 - 5.12**, respectively.

5.1.1 Influences of percentages of iron on activated carbon on composition of oil product

The influence of amount of iron on activated carbon was performed by varied the percentage of iron 1, 5 and 10%. The cracking reaction was carried out at 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen pressure, 60 min of reaction time and 0.6g of catalyst.

Fig 5.1 shows that the percentages of gas, oil and solid yield were not significantly different because the percentages of gases were varied in the range of 2.3-2.7%, solid 30.4-31.9% and oil yield 65.4-67%. After investigating the influence on percentage loading of iron on activated carbon, we have not determined the oil composition by GC Simulated Distillation because we were sure that the oil having same pattern and gave similar oil composition. Poonsuk Phungtum **[13]** studied the conversion of polypropylene into oil product using iron on activated carbon catalyst. The analyzed oil product from GC Simulated Distillation was found that the percentage of oil yield and composition were not significantly different as well.

Table 5.1 shows the surface specific area before using in reaction. It was found that when iron was impregnated on the surface of pure activated carbon, the surface decreased slightly about 5.3%, it means that there were attached iron metal crystals in the pores of activated carbon, and it seemed no influence of percentages loading of iron on surface area. The surface area of each type of percentages loading iron was not significant different. It implied that each percentages loading of iron caused the same covering of plastics on metal crystal situating throughout all the pores of activated carbon, therefore it was observed no effect of surface area on the oil yield and composition of the former experiments.

Table 5.1 Surface specific area (BET) of pure activated carbon and any loading of iron on activated carbon **[13]**.

Iron loading (% by weight)	BET area (m^2/g)
Pure activated carbon	746
1% Fe/activated carbon	719
5% Fe/activated carbon	692
10% Fe/activated carbon	706

In conclusion, the percentages of iron on activated carbon did not significantly influence on the oil yield and composition.

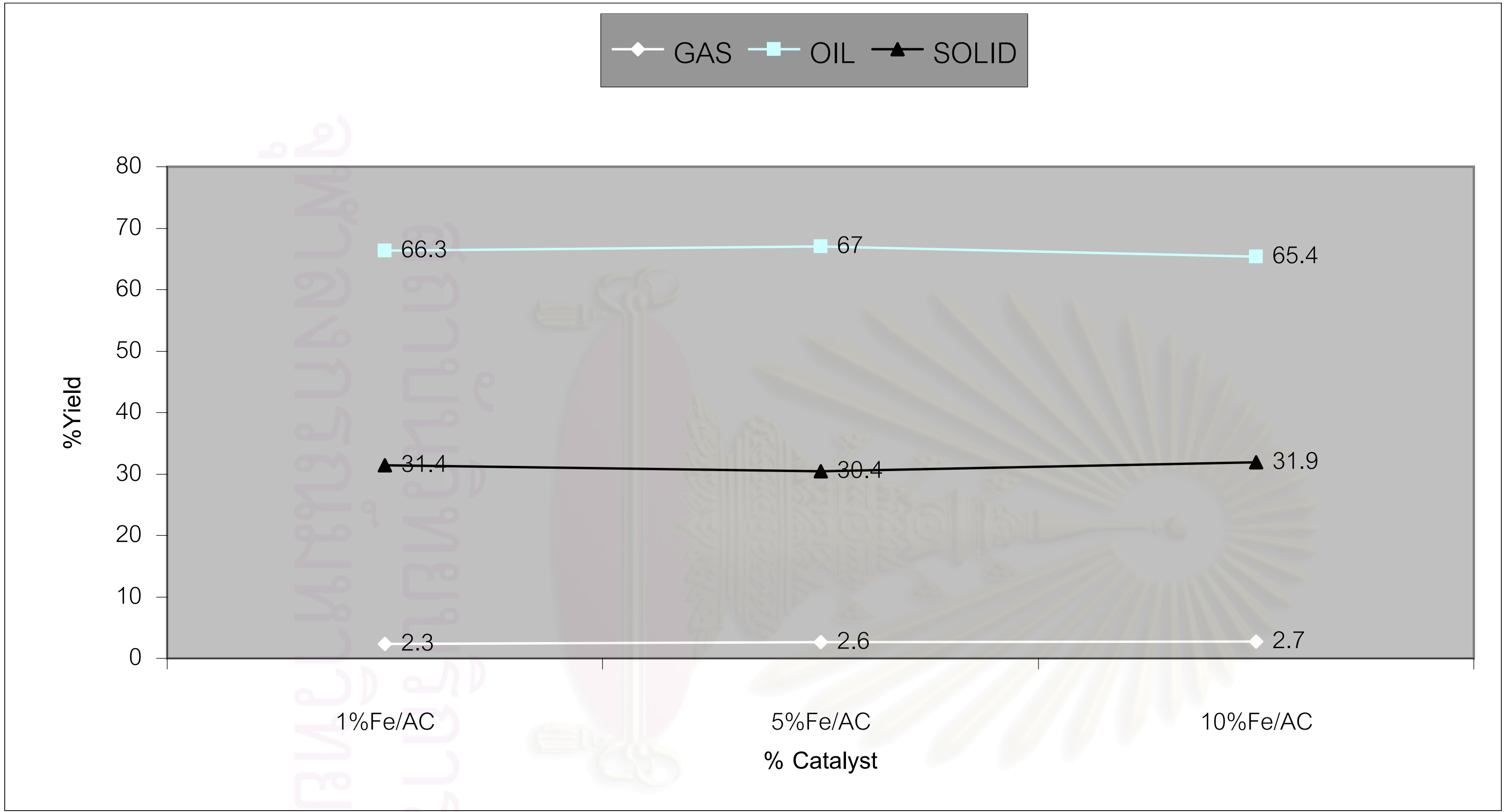


Figure 5.1 Product yield of ABS with various percentage of iron on activated carbon (0.3 mm) catalyst.

Reaction conditions : 15 g of ABS, 40 kg/cm2, 60 min and 430 C.

5.1.2 Influences of reaction temperature on composition of oil product

The influences of reaction temperature on the cracking of used acrylonitrile-butadiene-styrene polymer (ABS) was performed by operating at various reaction temperatures: 390, 410, 430 and 450 °C by using 0.45 g of 5% Fe/AC catalyst under hydrogen pressure 30 kg/cm^2 and fixing reaction time at 60 min.

The characteristic of obtained product at reaction temperature lower than 390 °C was mainly the mixture of oil and wax. Therefore, the experiment was carried out at reaction temperature over 390 °C. The percentage of oil fraction from cracking as a function of temperature was shown in **Fig 5.2**. It shows that the percentage of naphtha increases from 49.6 to 65% with an increasing of the temperature from 390 to 430 °C and reached to 67.8% at 450 °C. While other compositions decrease with an increasing of reaction temperature. It can be pointed out that low reaction temperature was not suitable to crack ABS polymer because of existing mixture of oil and wax product. It also showed that thermal cracking at low temperature was not enough to break down ABS polymer to lower hydrocarbon comparing to high temperature of 430 and 450 °C, because of the lowest naphtha (49.6-57.6%) and the highest heavy oil product, long residues (23.1-20.1%). Moreover, **Fig 5.3** shows that gas yield from low reaction temperature was very low, 1.2-1.5%, whereas, increased to 2.5% at 430 °C and largely increased to 20% at 450 °C. Therefore, this confirmed that low reaction temperature hardly cracks a complicated structure of ABS polymer.

Fig 5.4 shows the comparison of product distributions at high temperature, 430 and 450 °C, and the characteristic of obtained oil product was true oil. It was found that naphtha and other oil component at 430 °C were slightly higher than 450 °C, while gases yield was much lower and solid yield was higher than at 450 °C. This is because an increase in temperature induced a large amount of thermal cracking of ABS polymer to be lower hydrocarbon, whereas high temperature yields lighter hydrocarbon gas, even decreasing solid yield. So 430 °C is more suitable to crack ABS polymer than 450 °C.

However, it should be remarked that high temperature yields large amount of solid component. Brebu et al **[5]** studied the thermal degradation of ABS that was carried out at different temperatures from 360 to 440 °C in static and dynamic atmospheres of nitrogen. They found that at static atmosphere of nitrogen, the percentage solid yield decreased from 72.9 to 28.7% with the increase of the temperature from 360 to 440 °C. Their result corresponded with this result that solid yield decreased from 36.2 to 26.7% with the increase of the temperature from 430 to 450 °C. But it is still high solid yield when compared with simple structure polymer such as polypropylene. Poonsuk Phungtum **[13]** studied the conversion of polypropylene into oil product using iron on activated carbon catalyst in a microreactor. The operation conditions were pressure of hydrogen gas range of 28 to 50 kg/cm^2, reaction temperature between 395 and 455 °C and reaction time 30 to 90 min for each catalyst. The analyzed oil product from GC Simulated Distillation was shown that iron on activated carbon was suitable to be used as catalyst at 435 °C, hydrogen pressure at 30 kg/cm^2 and reaction time 60 min. The product yield was 2.34% of gas, 96.33% of oil and 1.33 % of solid. Kaoru et al. **[12]** studied an iron supported coal-derived active carbon catalyst for liquefaction of polypropylene. It was found that reaction temperature of 400 °C and reaction time of 60 min was suitable to crack polypropylene and obtained 2.5% of gas, 92% of oil and 5.5% of solid. In case of ABS polymer, because it contains complicated molecule such as crosslinked rubber, graft polymer, aromatic ring. Normally, thermal cracking takes place before and followed by catalytic cracking **[13]**. So, in the first step, it is hard to crack ABS to be lower molecule by thermal cracking. Then in the second step, catalyst does not effectively react with that molecule. So, it tends to be incomplete cracking reaction and effected to high solid yield.

In conclusion, in case of temperature, the suitable temperature of 430 °C yields percentage value of gas, naphtha, kerosene, light gas oil, heavy gas oil, long residues and solid at 2.5, 38.9, 3.6, 4.5, 3.6, 9.2 and 37.7%, respectively.

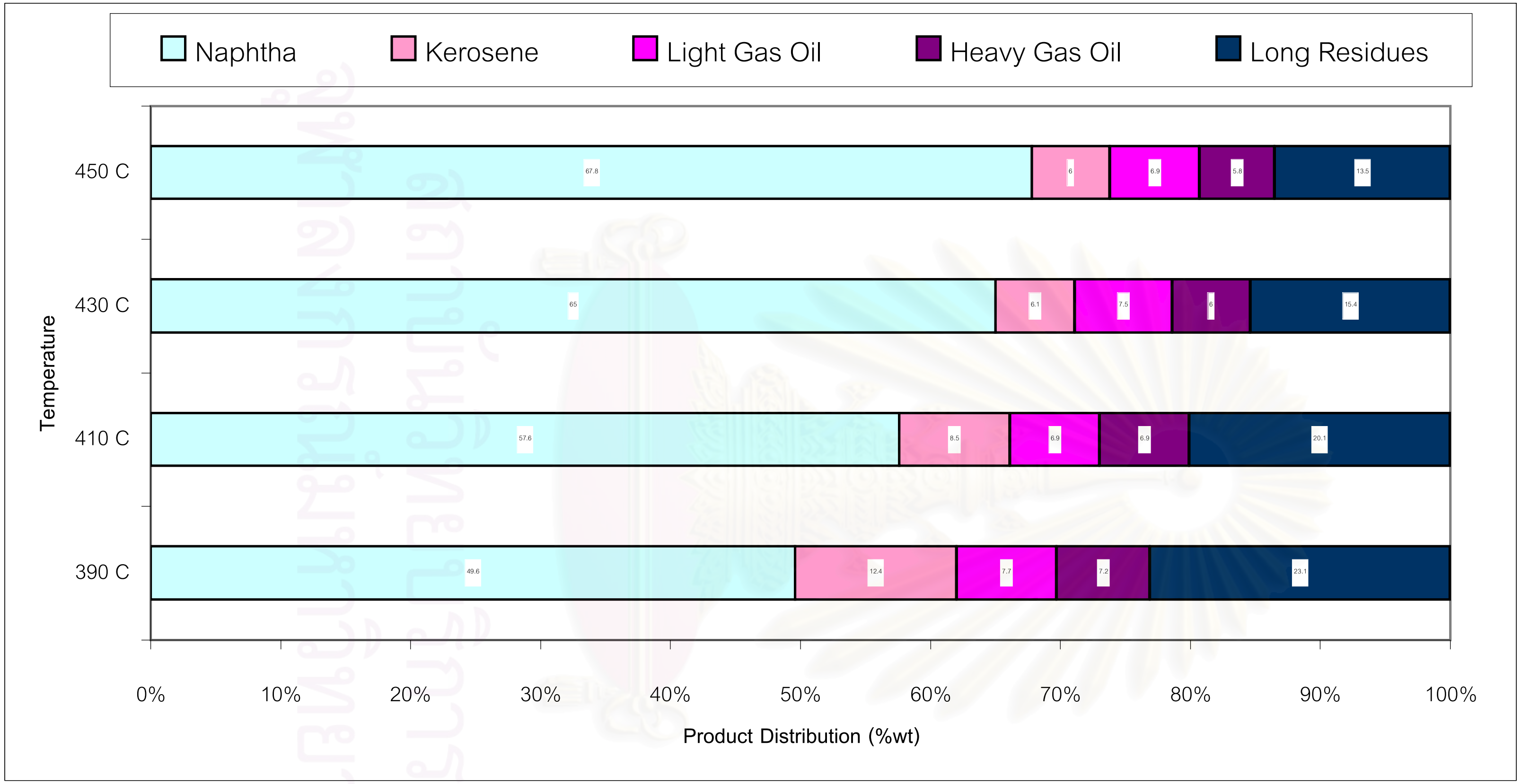


Figure 5.2 Oil distribution of ABS on 5% Fe/AC (0.3 mm) catalyst with various reaction temperatures.

Reaction conditions : 15 g of ABS, 30 kg/cm2, 60 min and 0.45 g of catalyst.

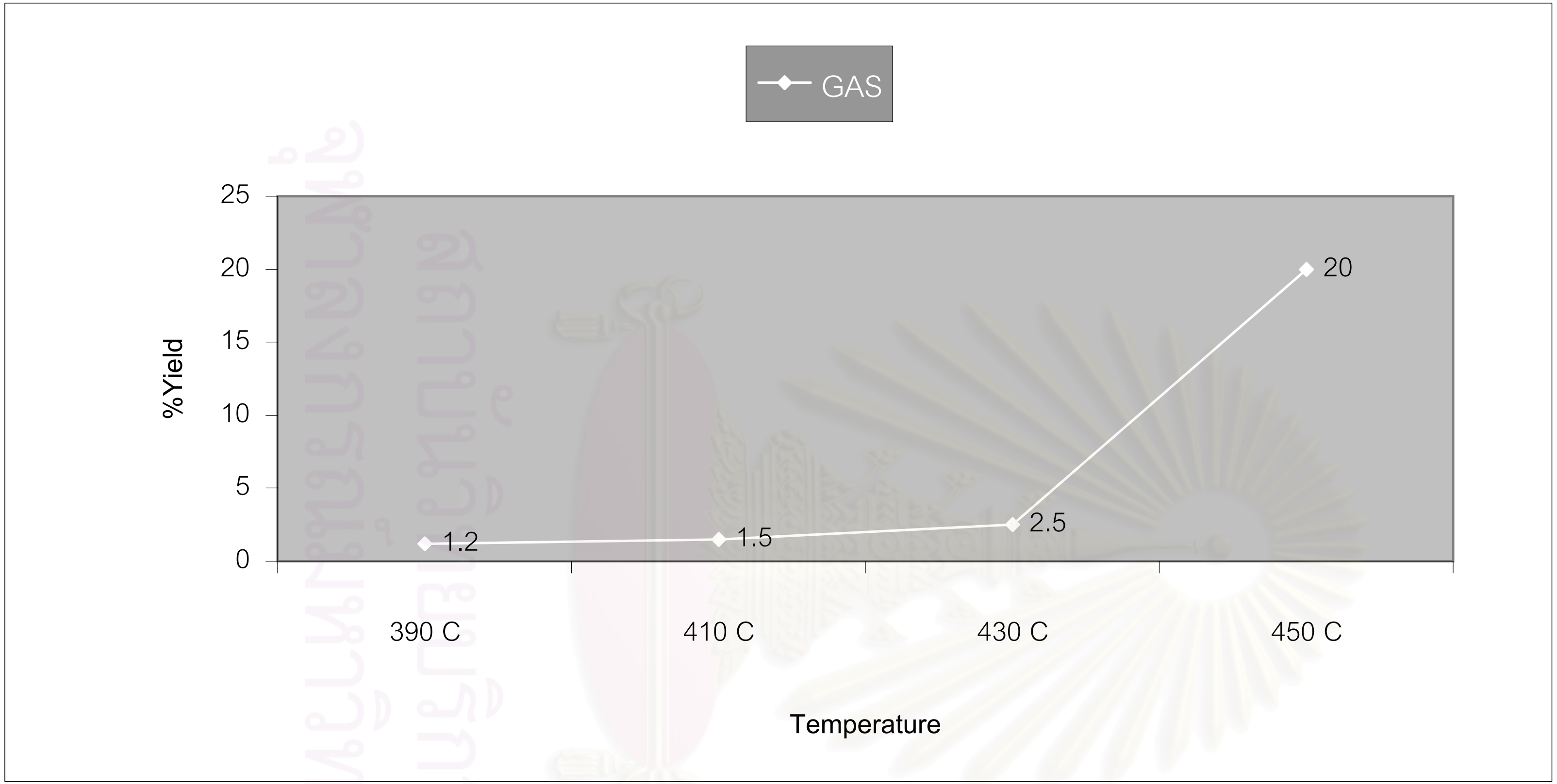


Figure 5.3 Gas yield of ABS on 5% Fe/AC (0.3 mm) catalyst with various reaction temperatures.

Reaction conditions : 15 g of ABS, 30 kg/cm2, 60 min and 0.45 g of catalyst.

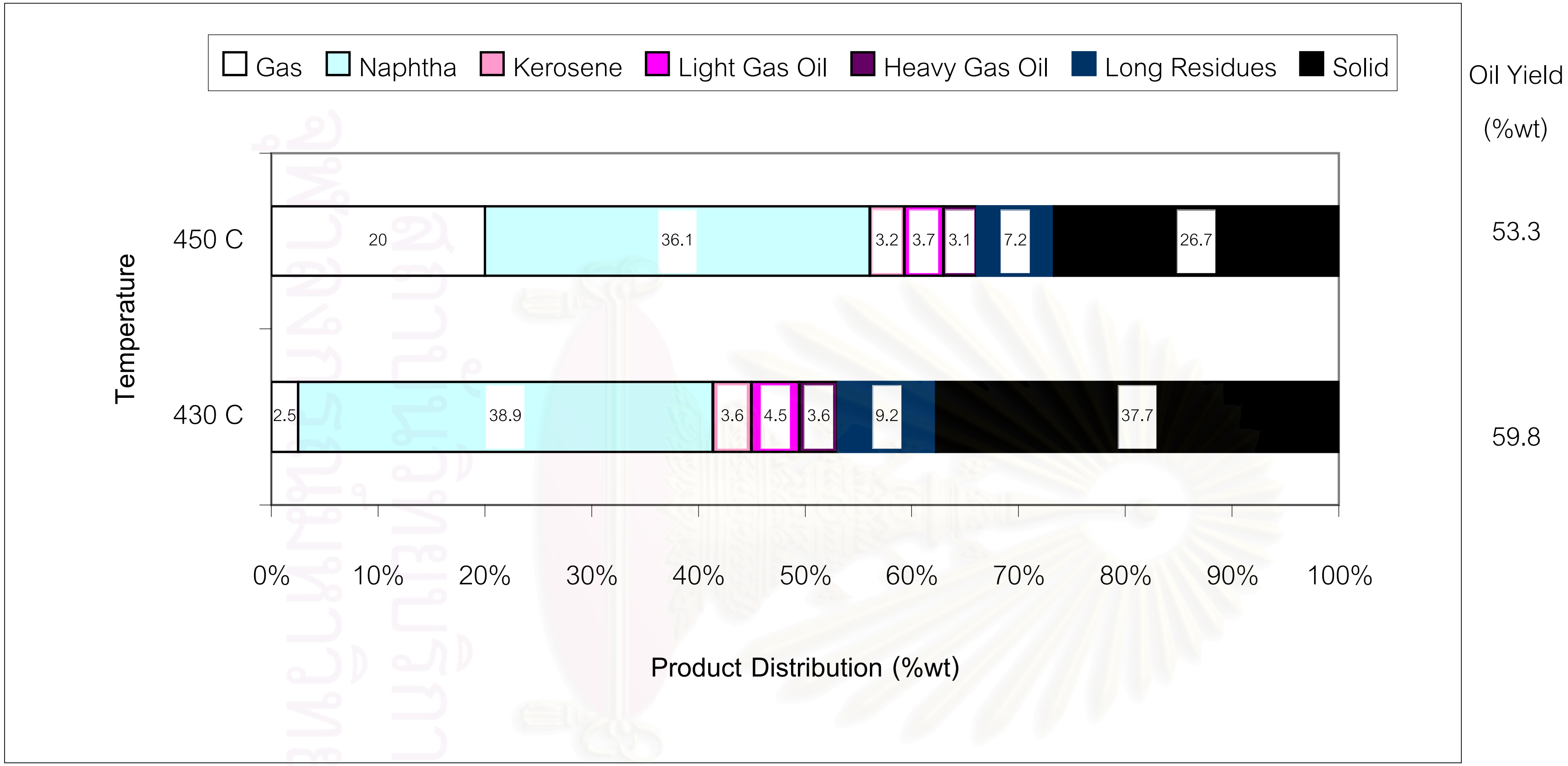


Figure 5.4 ABS conversion on 5% Fe/AC (0.3 mm) catalyst with various reaction temperatures.

Reaction conditions : 15 g of ABS, 30 kg/cm2, 60 min and 0.45 g of catalyst.

5.1.3 Influences of initial pressure of hydrogen gas on composition of oil product

The influence of hydrogen pressure was performed at various pressures at 20, 30, 35 and 40 kg/cm^2. ABS was carried out by fixing the condition at 430 ^oC of reaction temperature, 60 min of reaction time and 0.45 g of 5%Fe/AC catalyst. The compositions of products and oil yield from hydrocracking oil were shown in **Fig 5.5**.

Fig 5.5 shows that the product compositions change with change in hydrogen pressure. The increasing of hydrogen pressure from 20-40 kg/cm^2 increased % yield of oil product from 56.3 to 64.3%. It can be explained that during an experiment at stable temperature, thermal and catalytic crackings should be proceeded in the same manner. However, an increase in amount of hydrogen helps to stimulate cracking reaction and causes higher catalytic cracking reaction. This confirmed by the theory of spill over of hydrogen on catalyst, that is during the reaction, some hydrogen at the surface of catalyst is consumed, so the higher pressure of hydrogen, the more mass transfer from gas phase to solid surface of catalyst. Therefore it causes high conversion and more quantity of recovery product. So it shows a higher trend of naphtha from 36.1 to 41.3% with the increase of the pressure from 20 to 35 kg/cm^2 and approaching to 42.8% at 40 kg/cm^2. Other oil composition and gas yield are not changed while solid dramatically reduces from 41.1 to 34.9% with the increase of the pressure from 20 to 35 kg/cm^2 and slightly decreases to 33.7% at 40 kg/cm^2.

This result corresponded with one of Poonsuk Phungtum's results **[13]**. It showed that a higher pressure of hydrogen gas causes an increase in the amount of oil product and the percentage of naphtha from 50.22% at 28 kg/cm^2 to 57.11% at 50 kg/cm^2 and causes much decrease of solid from 5.13 to 1.01% with a fixed condition at 10% Fe/AC catalyst, 15 g of polypropylene, 60 min of reaction time and temperature of 415 ^oC. Moreover, the result of experiment at temperature of 435 ^oC had the same trend as the result of temperature of 415 ^oC.

From the discussion, it could be said conclusively that the optimum hydrogen pressure was either 35 or 40 kg/cm^2. For 40 kg/cm^2 of the pressure, it showed the highest oil product yield (64.3%), the highest naphtha (42.8%) and kerosene (4.3%), while, solid was the lowest.

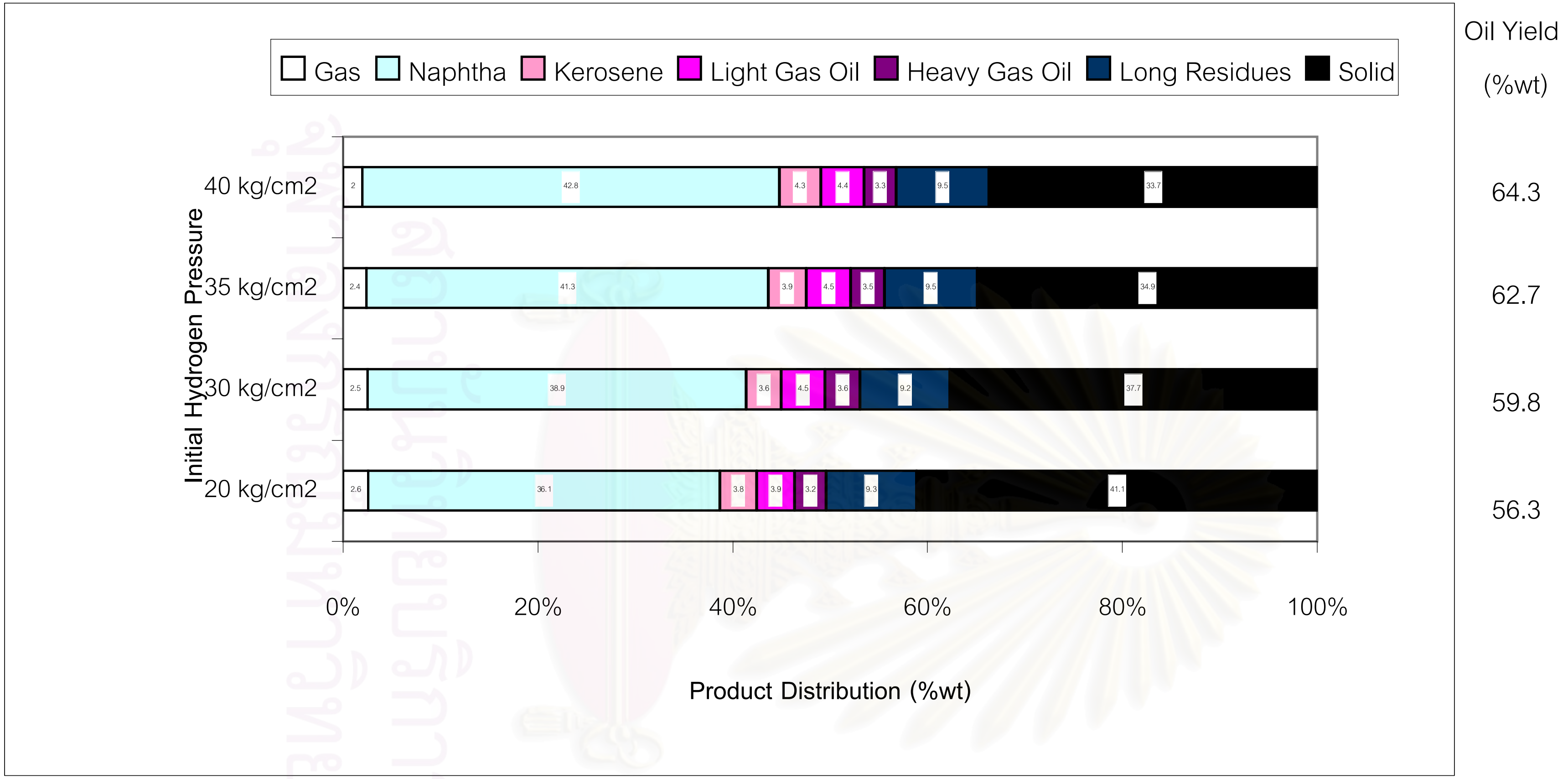


Figure 5.5 ABS concersion on 5% Fe/AC (0.3 mm) catalyst with various initial hydrogen pressures.

Reaction conditions : 15 g of ABS, 60 min, 430 C and 0.45 g of catalyst.

5.1.4 Influences of reaction time on composition of oil product

The influences of reaction time was performed by various time at 30, 45, 60 and 90 min. ABS was carried out by fixing the condition at 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen and 0.45 g of 5% Fe/AC catalyst. The compositions of products and oil yield from cracking reaction were shown in **Fig. 5.6**.

Fig. 5.6 shows that when the reaction time increased from 30 to 60 min, the % yields of oil and % naphtha increased whereas other components except solid being the same quantities. Solid yield decreased, and especially decreased largely from 45 to 60 min. After reaction time over 60 min, it was observed that the decreasing of % yield of oil and % naphtha, in contrast we noticed the more increasing of gas. The experiments were fixed the temperature and pressure of hydrogen, so the thermal and catalytic crackings were occurred the same phenomena. When the reaction time increased to 60 min., it was obtained the maximum % yield, % naphtha and lowest % solid, it means that this reaction time was appropriate. In the same way we also observed that when the longer time of reaction (60 to 90 min), the yield of gas largely increased considerably from 1.9 to 8 % and yield of solid increased slightly from 33.7 to 34.8%. It means that the longer time leads to more thermal and catalytic cracking. Longer cracking can change hydrocarbon into low hydrocarbons, as a result there is a clear increment in value of gas. Longer reaction time also caused coking at the surface of catalyst, therefore it was observed decreasing of naphtha and yields.

In conclusion, the optimum reaction time was 60 min, because this time gave the highest yield of oil 64.3% and naphtha 42.8% at condition of 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen and 0.45 g of 5% Fe/AC catalyst.

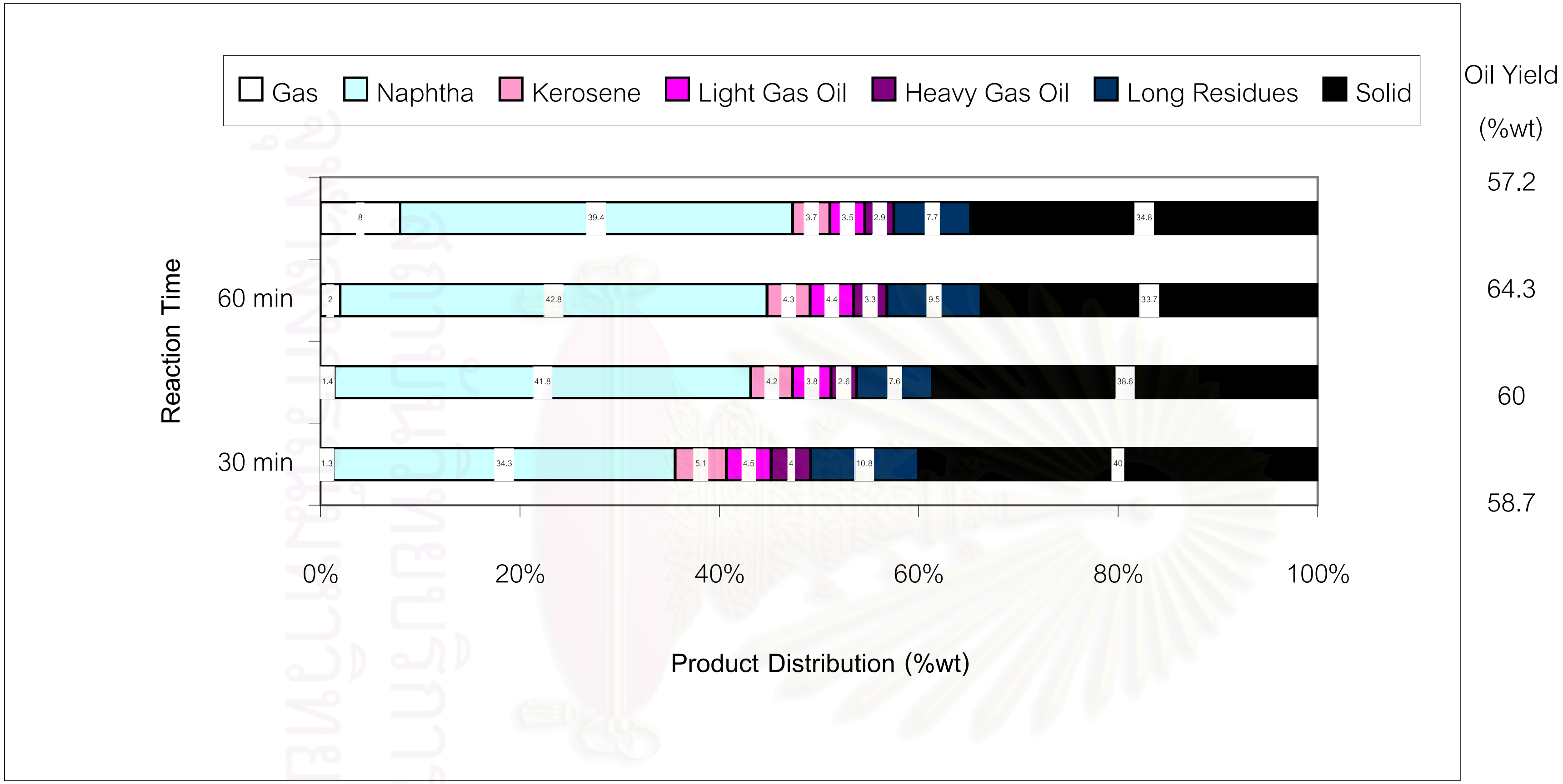


Figure 5.6 ABS conversion on 5% Fe/AC (0.3 mm) catalyst with various reaction times.

Reaction conditions : 15 g of ABS, 430 C, 40 kg/cm2 and 0.45 g of catalyst.

5.1.5 Influences of amounts of iron on activated carbon catalyst on composition of oil product

The influence of ratio of ABS to catalyst was performed by varying amounts of 5% Fe/AC catalyst; 0, 0.3, 0.45, 0.6 and 0.75 g per 15 g of ABS. The reaction was carried out at the condition; 430 ^{o}C of reaction temperature, 40 kg/cm^{2} of hydrogen pressure and 60 min of reaction time. The product yield and compositions of products obtained from cracking were shown as in **Fig 5.7** and **Fig 5.8**, respectively.

Fig 5.7 shows that the oil yield increases from 56.3 to 67% with the increase of the amount of catalyst from 0 to 0.6 g and solid yield correspondingly decreases from 40.8 to 30.4%. The gas yield is insignificant and almost consistent. It means that the catalytic cracking was more important at higher mass of catalyst (0.6 g), it is due to more possibility to contact the catalyst. When the amount of catalyst increases to 0.75 g, the oil yield largely decreases to 53.2%. It means that when a higher mass of catalyst contact with ABS, it caused higher rate of cracking as same as coking, therefore, it was noticed clearly that the percentages of solid yield increased from 30.4 to 43.8% .

Fig 5.8 shows the comparison of product distribution between thermal cracking reaction (without catalyst) and catalytic cracking (0.6 g). It was observed in case of reactions with and without catalyst that there was significant difference between them, namely the naphtha increased 5% and solid decreased 10.4%.

In conclusion, the ratio of ABS to catalyst parameter is very important for the product selectivity. The suitable ratio of 15 g per 0.6 g yields percentage value of gas, naphtha, kerosene, light gas oil, heavy gas oil, long residues and solid at 2.6, 45, 4.8, 4.5, 3.6, 9.1 and 30.4%, respectively.

The proposed reaction model of hydrogen cracking on activated carbon is shown in **Fig 5.9**. In this scheme free radical on activated carbon should initiate a cracking reaction by hydrogen abstraction to form a hydrocarbon radical. Cracking of ABS takes places at a carbon-carbon bond located in the β position to the free radical. The primary radical derived from this step many recrack many times at the β bone to give distillate.

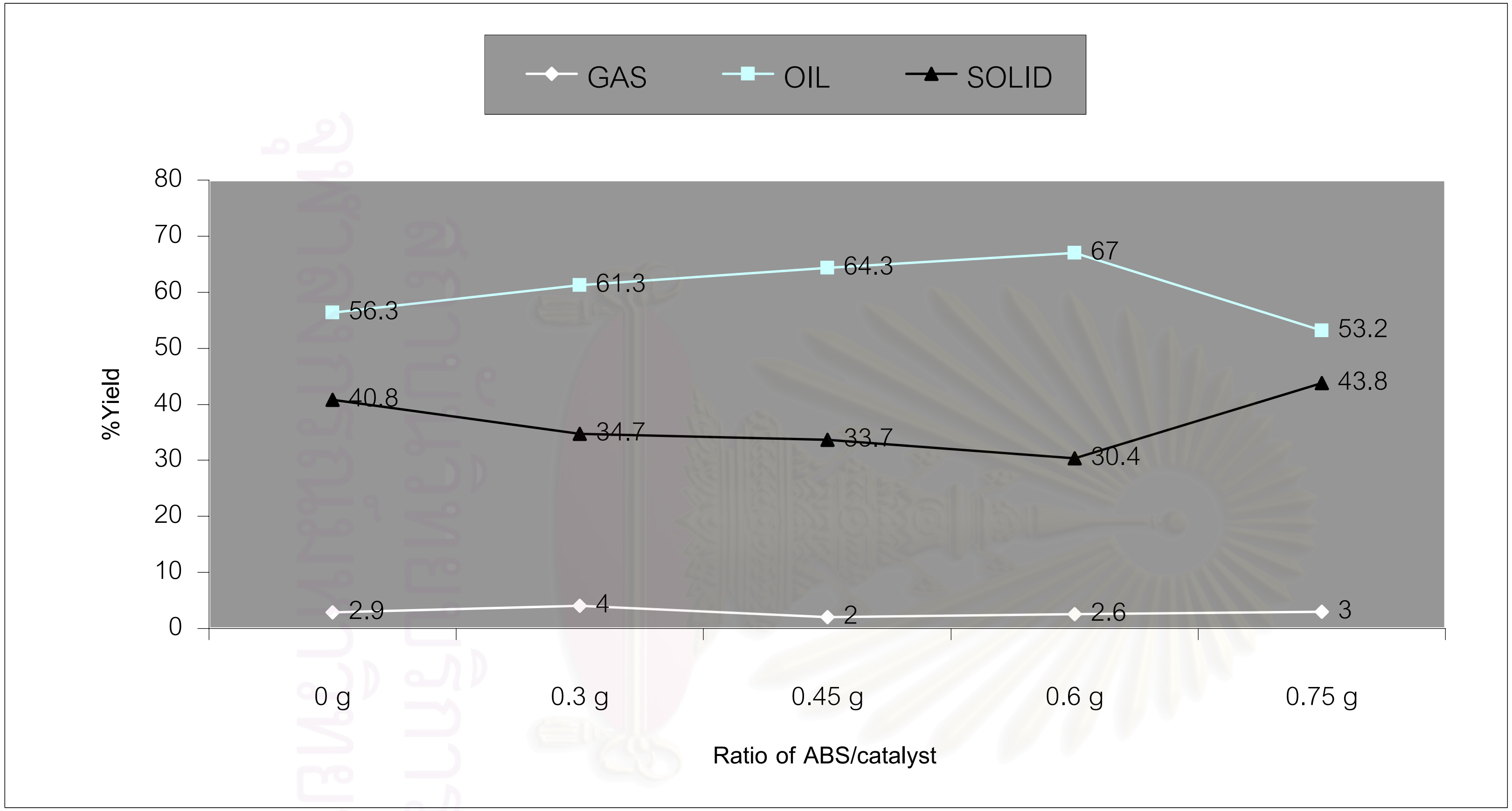


Figure 5.7 Product yield of ABS with various amounts of 5% Fe/AC (0.3 mm) catalyst.

Reaction conditions : 15 g of ABS, 40 kg/cm2, 60 min and 0.45 g of catalyst.

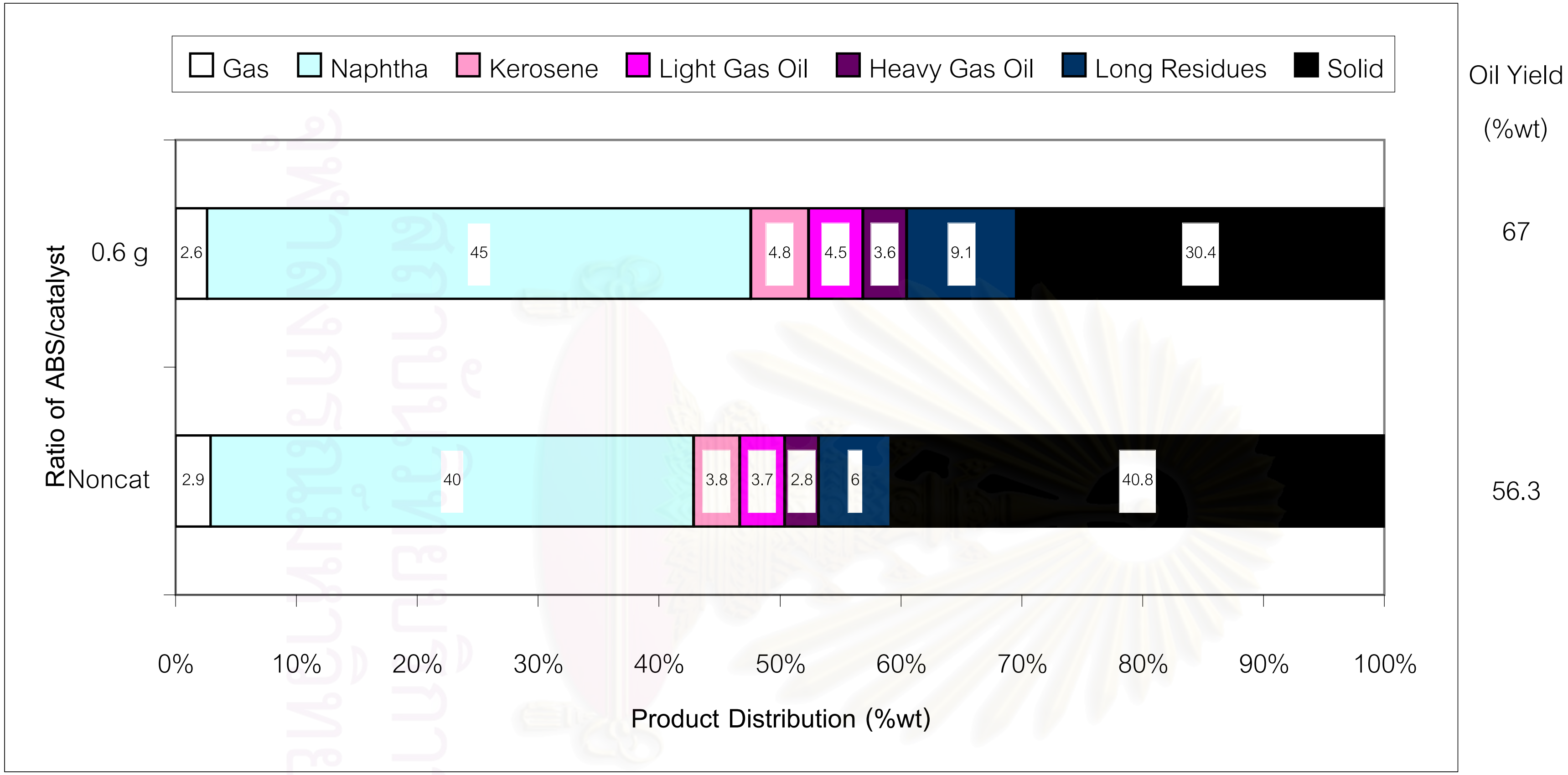


Figure 5.8 ABS conversion with various amounts of 5% Fe/AC (0.3 mm) catalyst.

Reaction conditions : 15 g of ABS, 40 kg/cm2, 60 min and 430 C.

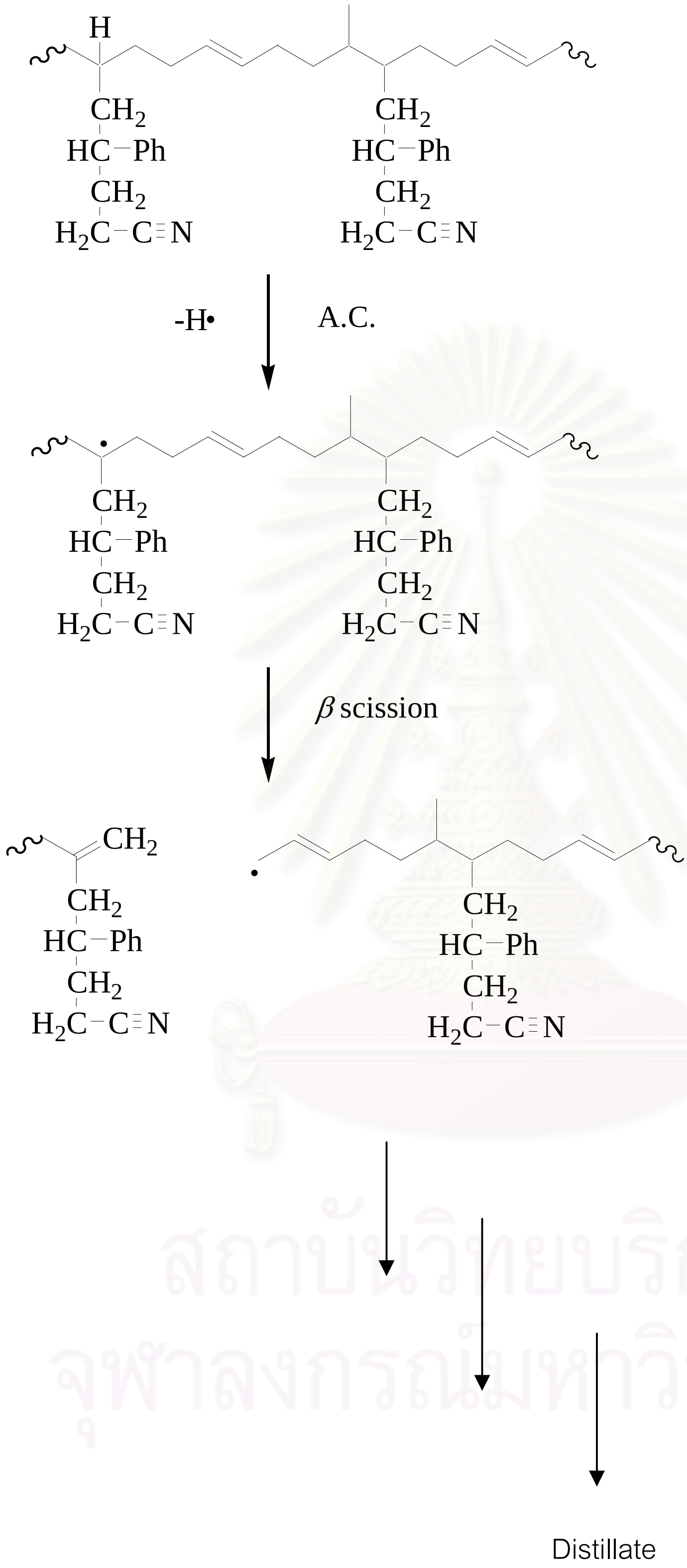


Figure 5.9 Proposed reaction model of hydrogen cracking on activated carbon

5.1.6 Characterization of functional groups of oil product by FTIR

Fig 5.10 shows the functional group compositional analysis of the oil derived from the catalytic cracking reaction of 15 g of ABS, 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen pressure, 60 min of reaction time and 0.6 g of 5%Fe/AC catalyst by Fourier transform infrared (FTIR) spectrometry. The oil product showed a strong presence of both aromatic and aliphatic functional groups. The strong peak at 1601 cm^{-1} is an indication of the presence of C=C stretching of aromatic skeletal and the additional strong peaks at 1495 and 1455 also show C=C stretching of aromatic skeletal. However the peak at 1455 cm^{-1} may overlap with C-H bending of -CH$_2$ and -CH$_3$ functional groups. In addition, there are very strong peaks present at 700 and 760 cm^{-1} and two peaks between 3000 and 3100 cm^{-1} showing the presence of aromatic compounds in the oil. The presence of peaks at 3060 and 3028 cm^{-1} indicate the presence of C-H stretching of aromatic and the presence of peak at 700 and 760 cm^{-1} indicates the presence of substituted aromatic groups, monosubstituted and/or disubstituted (1,2- or 1,3-) and/or trisubstituted (1,2,3-). Williams [3] studied the interaction of plastics in mixed-plastics pyrolysis. The six main plastics in municipal solid waste are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PCV) and poly(ethylene terephthalate) (PET). PS was then mixed with each of the other five plastics in a ratio of 1:1 and pyrolyzed in the fixed-bed reactor under the same pyrolysis conditions. Analysis of oil/wax showed that the polyalkene plastics, HDPE, LDPE and PP, gave mainly aliphatic composition consisting of a series of alkanes, alkenes and alkadienes. PVC gave mainly aromatic oil, and PS and PET, which have aromatic groups in their structures, also showed a more aromatic composition. The oil/wax derived from the pyrolysis of PS produced strong peaks present in the aliphatic functional groups. There are strong peaks present in the region from 675 to 900 cm^{-1} and three strong peaks between 3000 and 3050 cm^{-1} showing a very significant presence of aromatic compounds in the oil/wax.

The peaks between 3000 and 2800 cm^{-1} indicate the presence of -CH_3, -CH_2, and C-H functional groups, which are indicative of aliphatic species. ABS produces a mainly aromatic oil, consequently the aliphatic functional groups indicated by the FTIR spectrum probably indicates that these aliphatic groups are present as alkyl groups attached to aromatic rings.

Unlike other common polymers such as polyethylene, polypropylene, and polystyrene, ABS contains nitrogen (N) in the acrylonitrile units. When ABS is cracked, this N can lead to the formation of ammonia or very toxic hydrogen cyanide in the gas fraction and N-containing compounds in the oil fraction. It is well known that N can lead to the corrosion of engine parts and the formation of very harmful compounds when the oils are used as fuel. Thermal and catalytic hydrodenitrogenation is the common method used by the petrochemical industry to reduce, as much as possible, the amount of the N-containing compounds in the oil. However side reactions can occur during hydrodenitrogenation, resulting in the formation of additional N-containing compounds that are more difficult to eliminate than the original ones. [5] The low intensity peak at 2223 cm^{-1} from FTIR spectrum is an indication of the presence of -C≡N stretching conjugated with aromatic ring. We suppose that this functional group reduced in the case of synthetic oil obtained from polymer waste because the degradation is conducted under suitable conditions. N-containing compounds in ABS structure may be cracked to high quantity of gas such as HCN or NH_3 and effect to low quantity of N-containing compounds in oil. Brebu et al. [5] studied the degradation of the ABS by a semibatch operation at temperatures between 400 and 440 °C. The result shows oil with 29-40 mg/mL concentration of N. The temperature of degradation significantly affects the rate of the evolution and the amount and the quality of the degradation oil. Moreover 50 wt% of the degradation oils consists of hydrocarbon and as such it represents a possible hydrocarbon source of fuel provided the concentration of N-containing compounds can be decreased to an acceptable level.

Overall it may be concluded that on the basis of the broad analysis of functional group composition by FTIR that the derived oils from ABS gave spectrum which indicate the aromatic functional group present show high octane number. Moreover it also shows low intensity of N-containing in oil.

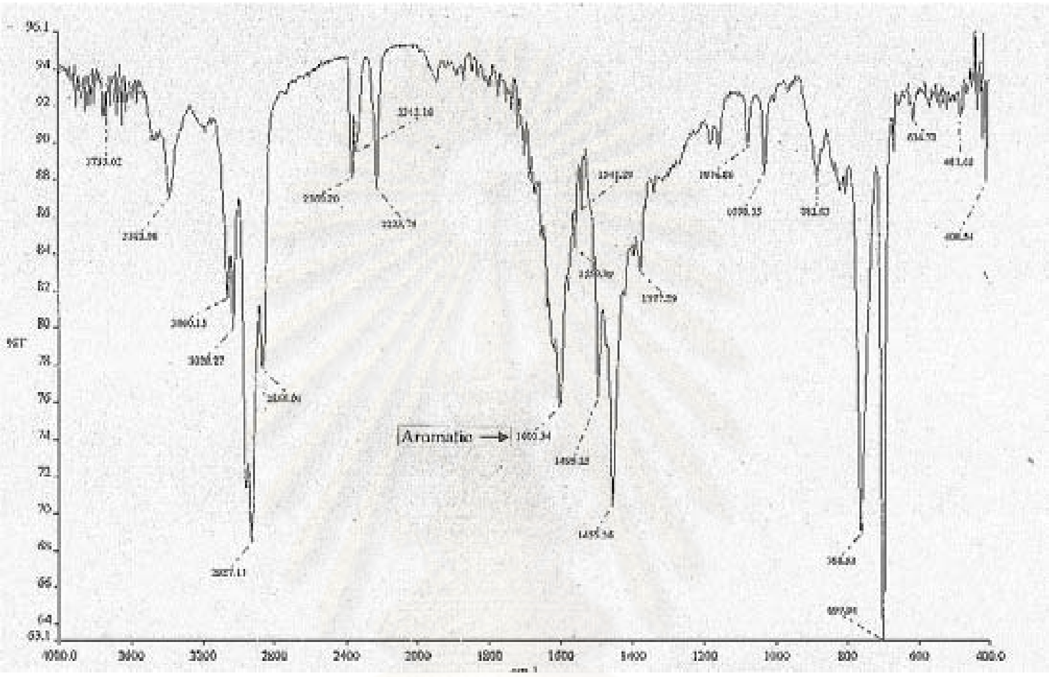
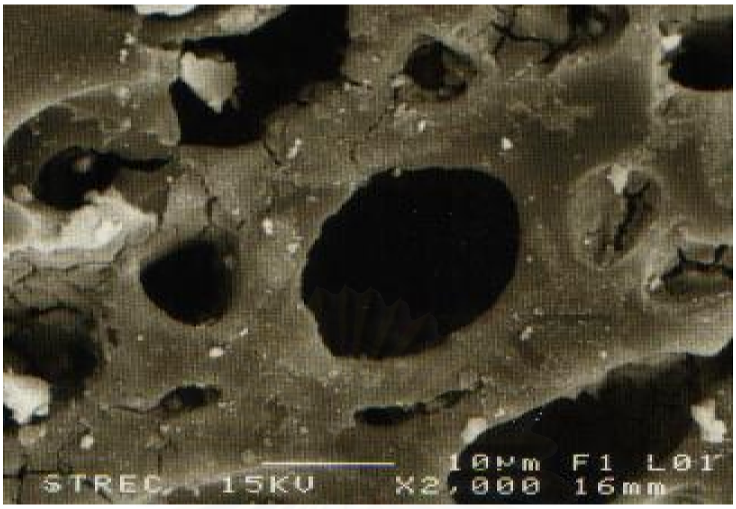


Figure 5.10 FTIR spectrum of oil product derived from catalytic cracking reaction of 15 g of ABS, 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen pressure, 60 min of reaction time and 0.6 g of 5%Fe/AC catalyst

5.1.7 Characterization of surface area of activated carbon before and after using in reaction by SEM

Comparison of catalyst before and after used in reaction showed that the structure was changed as shown in **Figs 5.11** and **5.12**. In **Fig 5.12**, the unchanged plastic as a form of coke covered throughout the surface of catalyst, as a result there was more solids (30.4%) at optimum condition in the product.



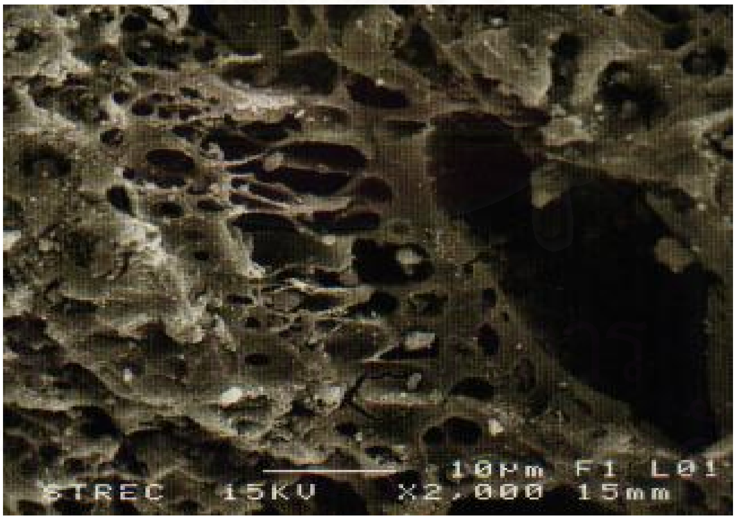
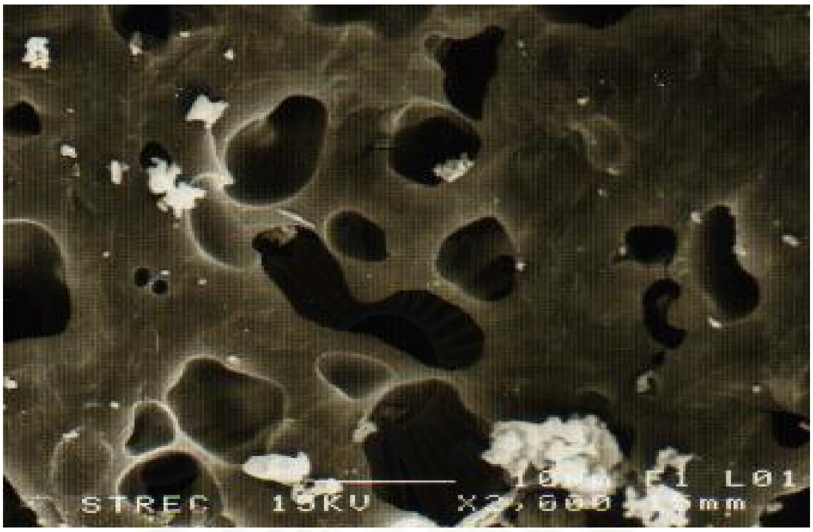


Figure 5.11 Surface area of iron on activated carbon before using in reaction



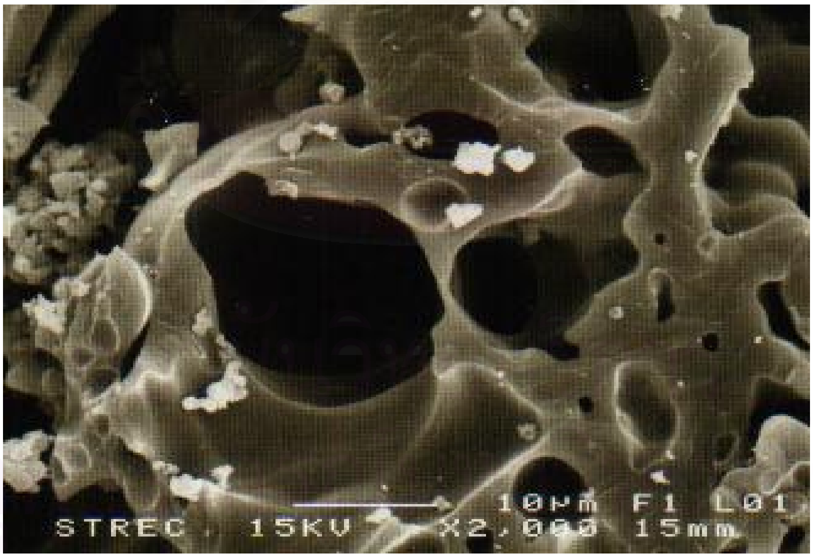


Figure 5.12 Surface area of catalyst after using in reaction

5.2 Comparison of This Work with Other Works.

The comparison of this work with Brebu's. **[5]** was presented with fractions of gases, oils and solids shown in **Table 5.2**.

Table 5.2 Comparison of this work with Brebu's.

Description	This work	Brebu
Plastic	ABS granule	ABS powder
Acrylonitrile/Butadiene/ Styrene ratio	20-25%, 16-20%, 55-64%	19-22%, 37-39%, 30-32%
Catalyst	Fe/AC (0.6 g)	-
<u>Conditions</u>		
Amount of plastic	15 g	10 g
Temperature	430 °C	440 °C
Reaction time	60 min (total 90 min)	107 min (total 540 min)
Atmosphere	H_2	N_2
Initial Pressure	40 kg/cm^2	1 kg/cm^2
<u>Results</u>		
Gases (% wt)	2.6	7.8
Oils (% wt)	67.0	63.5
Naphtha (% wt)	45.0	n.a
Kerosene (% wt)	4.8	n.a
Light gas oil (% wt)	4.5	n.a
Heavy gas oil (% wt)	3.6	n.a
Long residues (% wt)	9.1	n.a
Solids (% wt)	30.4	28.7

* n.a = non available data

Brebu et al. studied thermal cracking of acrylonitrile-butadiene-styrene (ABS). ABS polymer was put in a batch apparatus using glass reactor, internal diameter of 30 mm. and a total length of 350 mm., under N_2 atmosphere. The reactor was operated at different temperature programs and atmospheres. Prior to degradation, the reactor was flushed with N_2 at a flow rate of 20 cm^3/min while the temperature of the furnace was maintained at 120 ^{o}C for 1 hour in order to eliminate adsorbed water. The zero time for the experiment was taken when the furnace was heated at 3 ^{o}C/min from 120 ^{o}C to the final degradation temperatures, which were fixed at 360-440 ^{o}C. The total reaction time was 540 min in all cases.

From **Table 5.2**, at 440 ^{o}C of static N_2 atmosphere, Brebu et al. obtained 63.5% of oil yield, 7.8% of gas yield and 28.7% of solid yield whereas this work obtained 67.0% of oil yield, naphtha 45 %, kerosene 4.8 %, light gas oil 4.5 %, heavy gas oil 3.6 % and long residues 9.1 %, 2.6% of gas yield and 30.4% of solid yield. This result can be explained that at nearly same reaction temperature, 430 and 440 ^{o}C, showed nearly oil yield and solid yield because thermal cracking having the same rate of reaction. However, this result showed higher oil yield than that of Brebu which catalytic cracking was promoted by Fe/AC catalyst and from increasing hydrogen pressure. It helps to increase cracking reaction to obtain oil yield. But quality of oil yield was not compared due to no data available of oil distribution from Brebu's work. However, it should be showed higher quality of oil yield due to the effect of catalytic cracking reaction. And this work was carried out shorter time than that of Brebu's work. Refer to Brebu's work, the reaction was taken longer time and yields more gas quantity.

CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

The following conclusions from this study have been drawn :

1. The influences of hydrocracking of acrylonitrile-butadiene-styrene polymer (ABS) by using iron on activated carbon catalyst was studied in a microreactor. The temperature was varied from 390-450 ^{O}C, 20-40 kg/cm^2 of initial hydrogen pressure, 30-90 min of reaction time, 0-0.75 g of amounts of catalyst and 1, 5, 10 percent loading of iron on catalyst. Analysis of the products was performed by using GC Simulated Distillation, Fourier-Transform Infrared Spectrometer and Scanning Electron Microscope.

2. From the experimental results obtained from this study, it may be concluded as follows :

    2.1 Percentage of iron on activated carbon does not affect on oil composition because the percentages of gas, oil and solid yield were not significantly different.
    2.2 Suitable reaction temperature is 430 ^{o}C because the characteristic of obtained product is true oil and contain the highest quantity of naphtha and other oil component.
    2.3 Suitable hydrogen pressure is 40 kg/cm^2 because an increasing of hydrogen gas pressure causes an increasing in the amount of oil product and the percentage of naphtha.
    2.4 Suitable reaction time is 60 min because it is obtained the maximum percentages of yield and naphtha and the lowest percentages of solid. The longer reaction time (90 min) caused coking at the surface of catalyst, therefore it shows the decreasing of naphtha and yields.

2.5 Suitable catalytic weight is 0.6 g because the higher mass of catalyst, the higher possibility to contact the polymer. But too high mass of catalyst (0.75 g) caused higher rate of cracking as same as coking.

At temperature 430 ^{O}C, hydrogen pressure 40 kg/cm^2 , reaction time 60 min with 5%Fe/AC , the oil yield, gas, naphtha, kerosene, gas oil, long residues and solid were 67.0,2.6,45.0,4.8,4.5,3.6,9.1,30.4 %, respectively.

3. The derived oils show aromatic functional group by means of Fourier-Transform Infrared Spectrometer which indicated the presence of high octane number and also show low intensity of N-containing in oil.

Recommendations :

Arising from this research is suggested that the type of catalyst that used in this research should be changed to Pt on Silica/Aluminum which had been reported that it was the most suitable catalyst for PE, PP, PS, and PET cracking **[10]** and ZnO_2/SO_4^{2-} (super acid catalyst) which had been reported that it was the most suitable catalyst for SBR cracking **[14]**. The comparison of obtained oil product from various catalyst should be carried out.

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APPENDICES

APPENDIX A

DATA FOR CONVERSION OF ACRYLONITRILE-BUTADIENE-STYRENE POLYMER TO SYNTHETIC FUELS ON Fe/ACTIVATED CARBON CATALYST

Table A-1 : The condition reactions of all parameter for conversion of ABS polymer to synthetic fuels on Fe/AC catalyst.

BATCH NO.	CONDITION					ABS(g)	CAT.(g)	GAS		SOLID		OIL YIELD(%)
	TEMP(^{o}C)	P(kg/cm^2)	t(min)	CAT.(g)	%Fe (0.3 mm)			AMOUNT (g)	YIELD (%)	AMOUNT (g)	YIELD (%)	
1	390	30	60	0.45	5	15.0050	0.4507	0.18	1.2			OIL+SOLID
2	410	30	60	0.45	5	15.0058	0.4506	0.23	1.5			OIL+SOLID
3	430	30	60	0.45	5	15.0075	0.4667	0.38	2.5	6.1245	37.7	59.8
4	450	30	60	0.45	5	15.0072	0.4499	3.0	20	4.4543	26.7	53.3
5	390	30	60	0.45	5	15.0141	0.4507	0.18	1.2			OIL+SOLID
6	390	20	60	0.45	5	15.0075	0.4509	0.17	1.1			OIL+SOLID
7	390	0	60	0.45	5	15.0086	0.4504	0.13	0.9			OIL+SOLID
8	390	30	90	0.45	5	15.0031	0.4503	0.2	1.3			OIL+SOLID
9	390	30	60	0.45	5	15.0042	0.4497	0.14	1.0			OIL+SOLID
10	390	30	30	0.45	5	15.0078	0.4500	0.17	1.1			OIL+SOLID
11	430	35	60	0.45	5	15.0018	0.4510	0.36	2.4	5.6866	34.9	62.7
12	430	40	60	0.45	5	15.0032	0.4504	0.30	2.0	5.5065	33.7	64.3
13	430	20	60	0.45	5	15.0062	0.4507	0.39	2.6	6.6182	41.1	56.3

BATCH NO.	CONDITION					ABS(g)	CAT.(g)	GAS		SOLID		OIL YIELD(%)
	TEMP(^{o}C)	P(kg/cm^2)	t(min)	CAT.(g)	%Fe (0.3 mm)			AMOUNT (g)	YIELD (%)	AMOUNT (g)	YIELD (%)	
14	390	20	60	0.45	5	15.0081	0.4504	0.18	1.2			OIL+SOLID
15	390	40	60	0.45	5	15.0031	0.4500	0.18	1.2			OIL+SOLID
16	390	35	60	0.45	5	15.0013	0.4506	0.18	1.2			OIL+SOLID
17	390	30	60	0.45	5	15.0103	0.4502	0.16	1.1			OIL+SOLID
18	390	20	60	0.45	5	15.0014	0.4503	0.17	1.1			OIL+SOLID
19	390	0	60	0.45	5	15.0109	0.4503	0.16	1.1			OIL+SOLID
20	430	40	45	0.45	5	15.0119	0.4509	0.21	1.4	6.2455	38.6	60
21	430	40	30	0.45	5	15.0104	0.4511	0.20	1.3	6.4553	40	58.7
22	430	40	15	0.45	5	15.0180	0.4502	0.14	0.9			OIL+SOLID
23	430	40	90	0.45	5	15.0005	0.4506	1.20	8.0	5.6708	34.8	57.2
24	430	40	60	0.3	5	15.0046	0.3004	0.60	4.0	5.5119	34.7	61.3
25	430	30	60	0	-	15.0074	0	0.43	2.9	6.1274	40.8	56.3
26	430	40	60	0.75	5	15.0108	0.7507	0.45	3.0	7.3209	43.8	53.2

BATCH NO.	CONDITION					ABS(g)	CAT.(g)	GAS		SOLID		OIL YIELD(%)
	TEMP(°C)	P(kg/cm^2)	t(min)	CAT.(g)	%Fe (0.3 mm)			AMOUNT (g)	YIELD (%)	AMOUNT (g)	YIELD (%)	
27	430	40	60	0.6	5	15.0197	0.6001	0.39	2.6	5.1729	30.4	67
28	430	0	60	0.45	5	15.0099	0.4505	0.50	3.3	7.2766	45.5	51.2
29	430	40	60	0	-	15.0097	0	0.50	3.3	5.9154	39.4	57.3
30	430	40	60	0.6	10	15.0182	0.6008	0.40	2.7	5.3919	31.9	65.4
31	430	40	60	0.6	1	15.0036	0.6001	0.35	2.3	5.3262	31.5	66.2
32	430	40	60	0.45	10	15.0139	0.4501	0.47	3.1	6.5546	40.7	56.2
33	430	40	60	0.6	1	15.0092	0.6010	0.34	2.3	5.3211	31.4	66.3
34	430	40	60	0.45	1	15.0037	0.4502	0.44	2.9	6.5500	40.7	56.4
35	410	40	60	0.45	5	15.0046	0.4503	0.24	1.6			OIL+SOLID

Table A-2: The percentage of oil composition by GC Simulated Distillation.

BATCH NO.	Naphtha 65-200 °C	Kerosene 200-250 °C	Light Gas Oil 300-350 °C	Heavy Gas Oil 300-350 °C	Long Residues > 350 °C
1	49.6	12.4	7.7	7.2	23.1
2	57.6	8.5	6.9	6.9	20.1
3	65	6.1	7.5	6.0	15.4
4	67.8	6.0	6.9	5.8	13.5
11	65.9	6.2	7.1	5.6	15.2
12	66.5	6.7	6.8	5.1	14.9
13	64.2	6.8	7.0	5.7	16.3
20	69.7	7.0	6.4	4.3	12.6
21	58.4	8.7	7.7	6.8	18.4
23	68.8	6.5	6.2	5.0	13.5
25	71.1	6.7	6.6	5.0	10.6
27	67.2	7.2	6.7	5.3	13.6

APPENDIX B

GRAPH OF PRODUCT FROM GAS CHROMATOGRAPH (GC SIMULATED DISTILLATION)

Figure B.1 Oil composition at condition 390 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.2 Oil composition at condition 410 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.3 Oil composition at condition 430 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.4 Oil composition at condition 450 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.5 Oil composition at condition 430 °C of reaction temperature, 35 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.6 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.7 Oil composition at condition 430 °C of reaction temperature, 20 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.8 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 45 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

Figure B.9	Oil composition at condition 430 ^{o}C of reaction temperature, 40 kg/cm^{2} of hydrogen, 30 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.
Figure B.10	Oil composition at condition 430 ^{o}C of reaction temperature, 40 kg/cm^{2} of hydrogen, 90 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.
Figure B.11	Oil composition at condition 430 ^{o}C of reaction temperature, 40 kg/cm^{2} of hydrogen, 60 min of reaction time and no catalyst by GC Simulated Distillation.
Figure B.12	Oil composition at condition 430 ^{o}C of reaction temperature, 40 kg/cm^{2} of hydrogen, 60 min of reaction time and 0.6 g of 5% Fe/AC catalyst by GC Simulated Distillation.

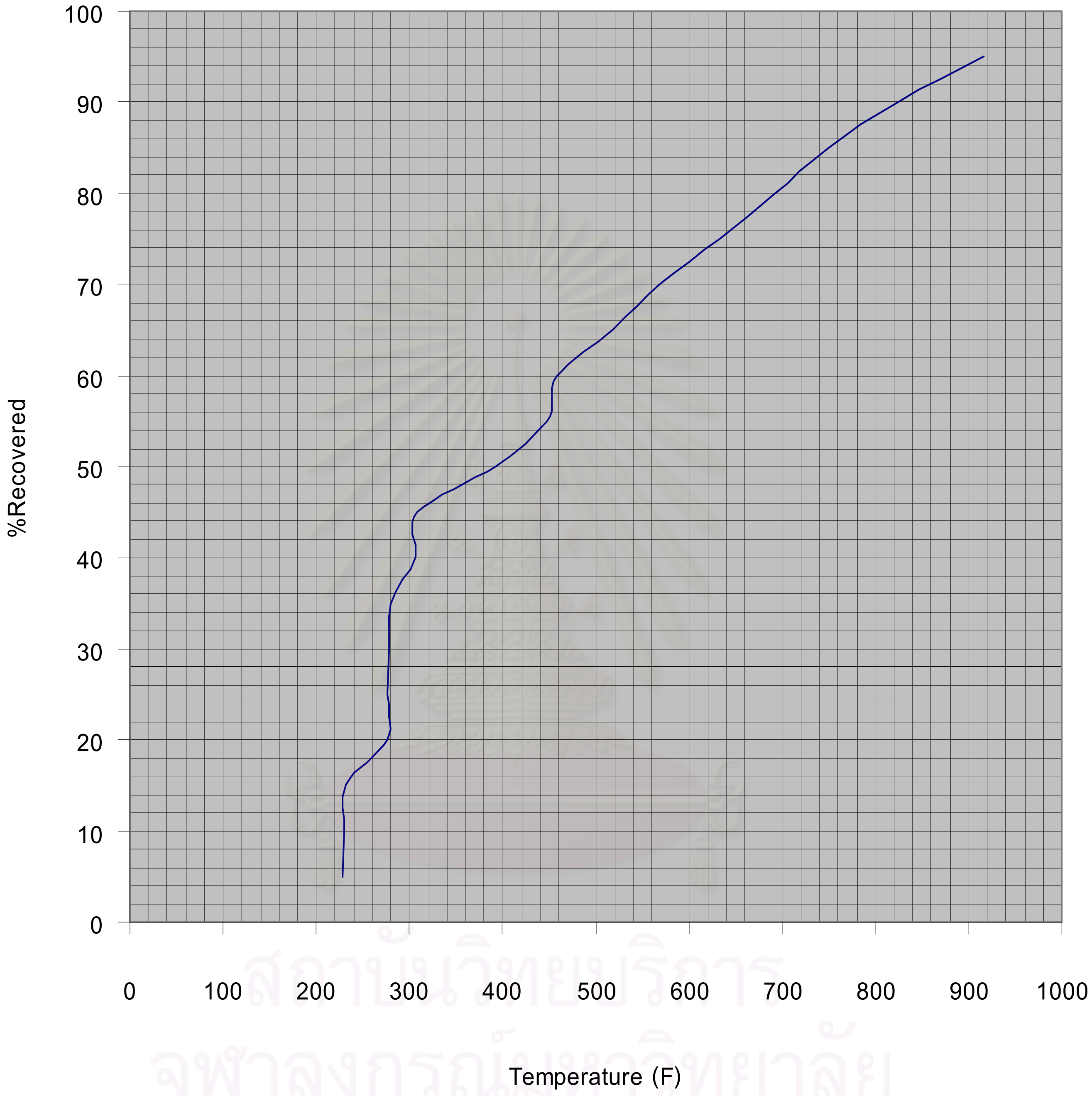

Figure B.1 Oil composition at condition 390 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

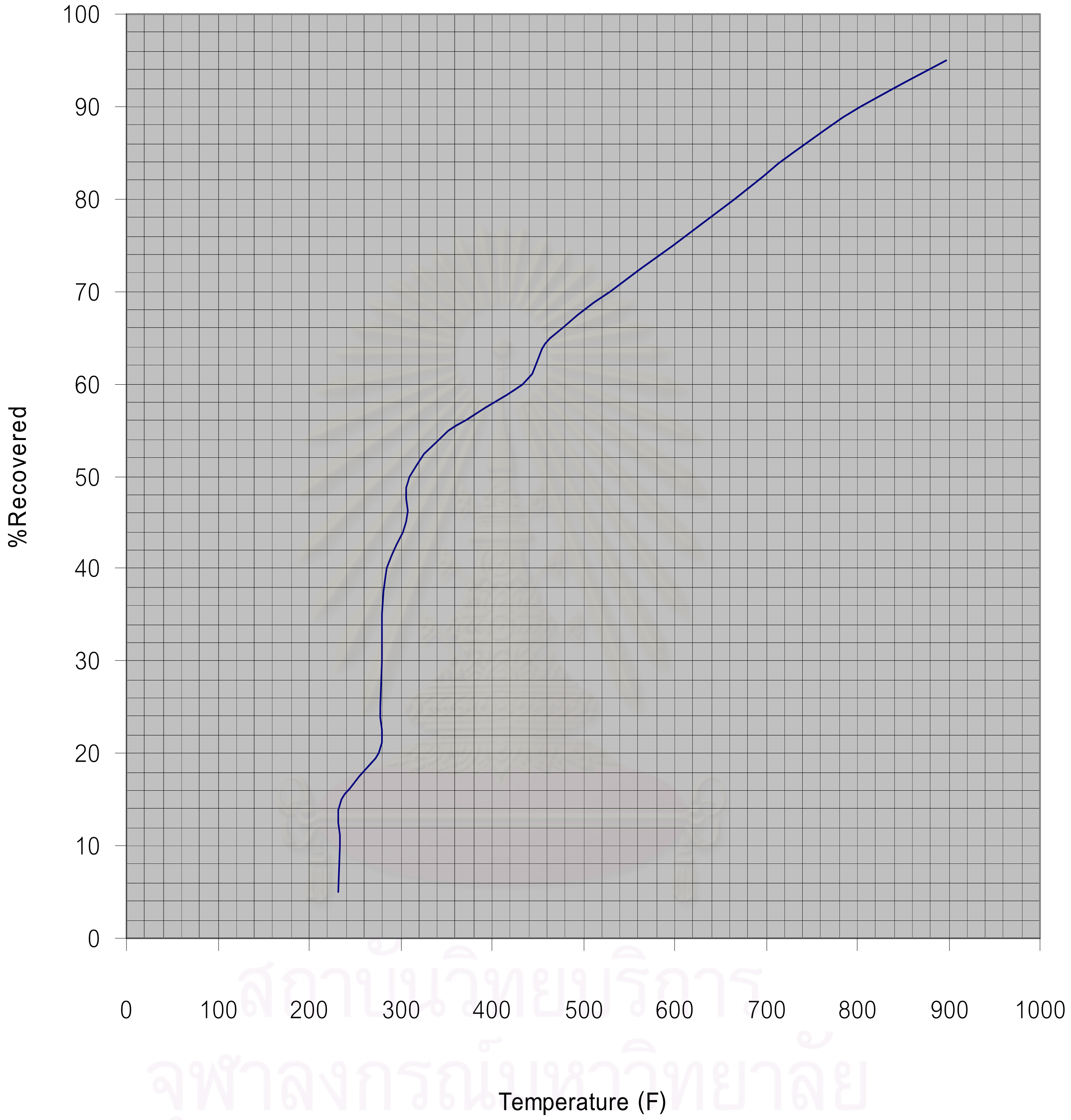

Figure B.2 Oil composition at condition 410 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

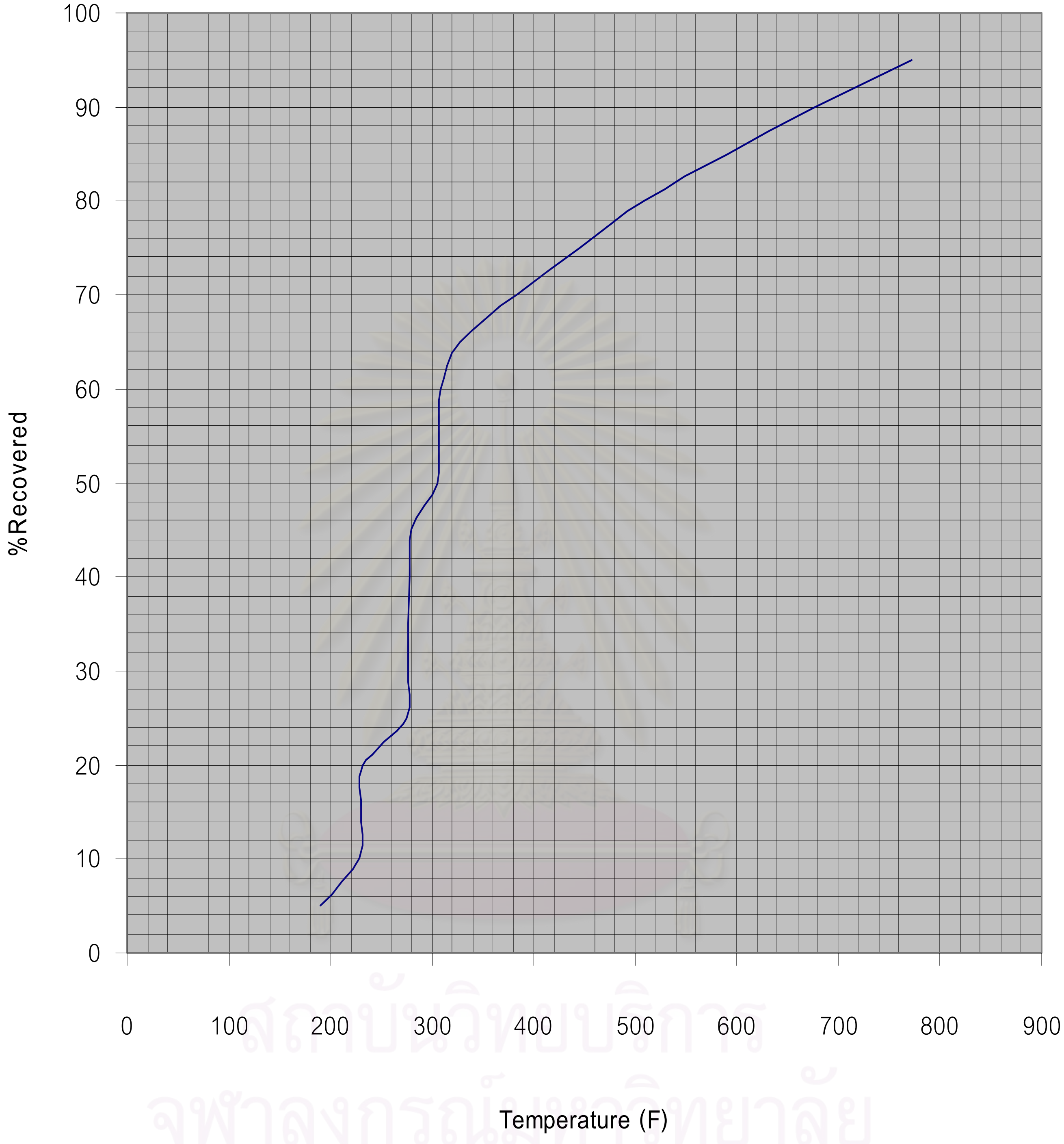

Figure B.3 Oil composition at condition 430 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

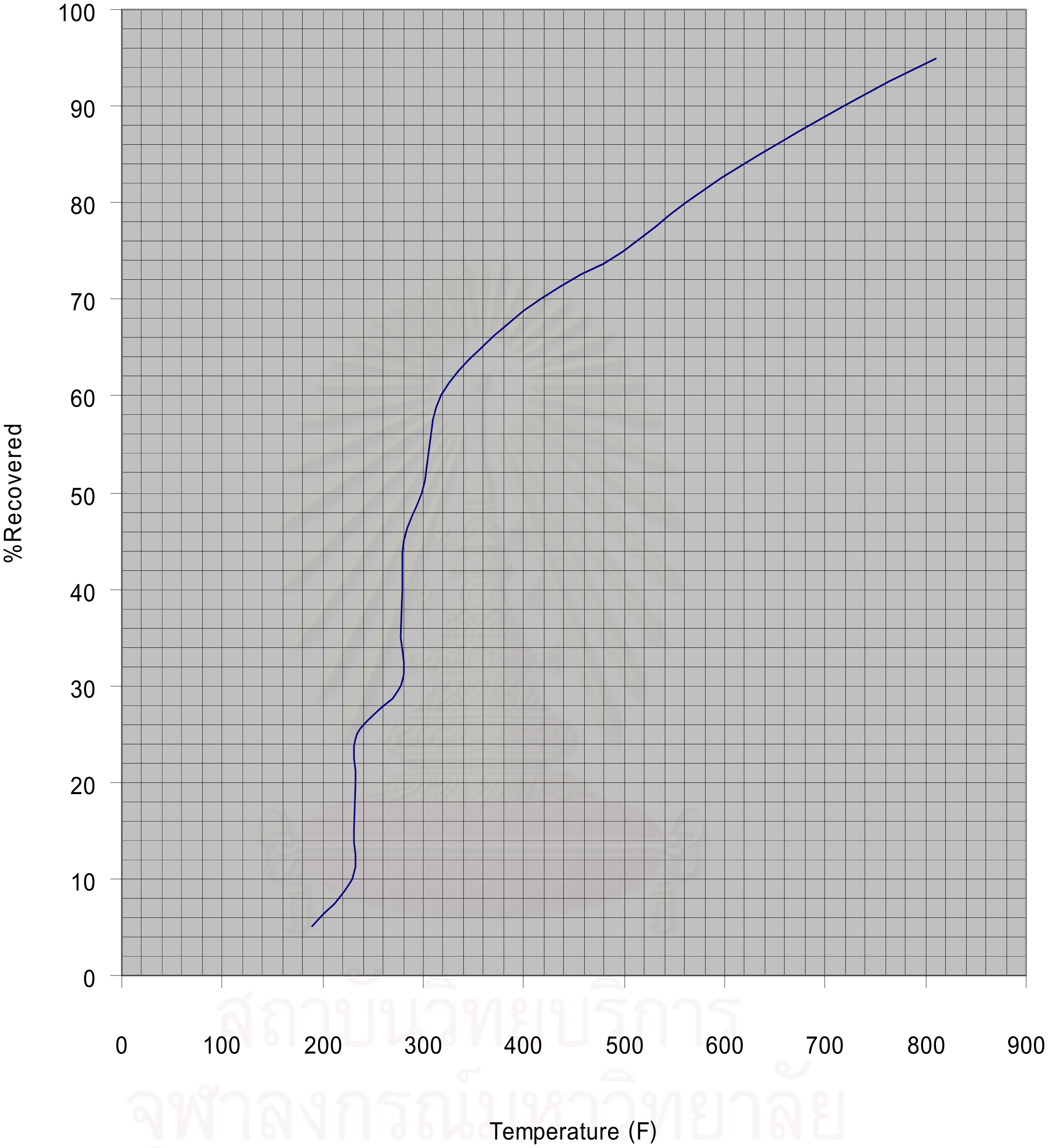

Figure B.4 Oil composition at condition 450 °C of reaction temperature, 30 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

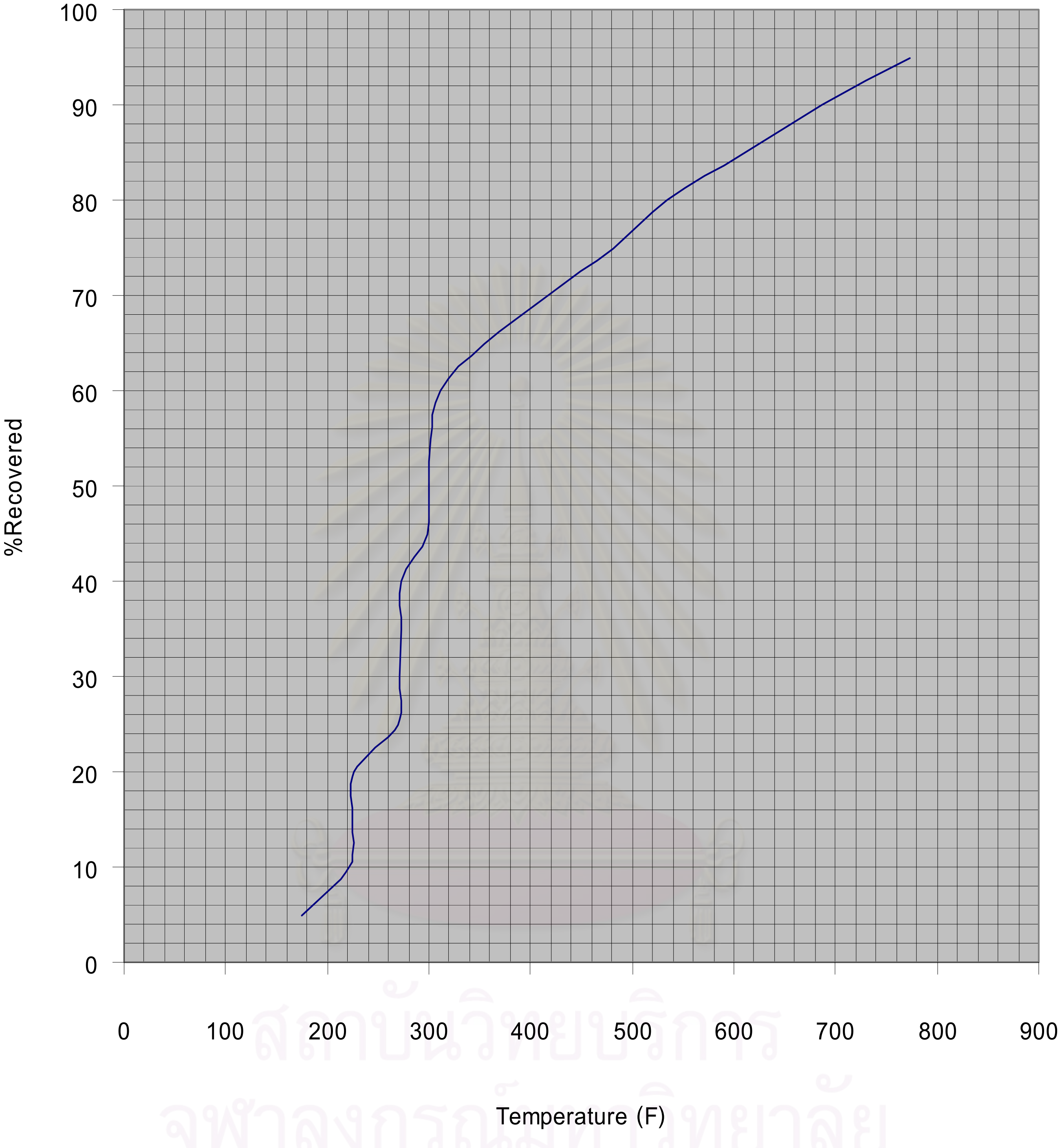

Figure B.5 Oil composition at condition 430 °C of reaction temperature, 35 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

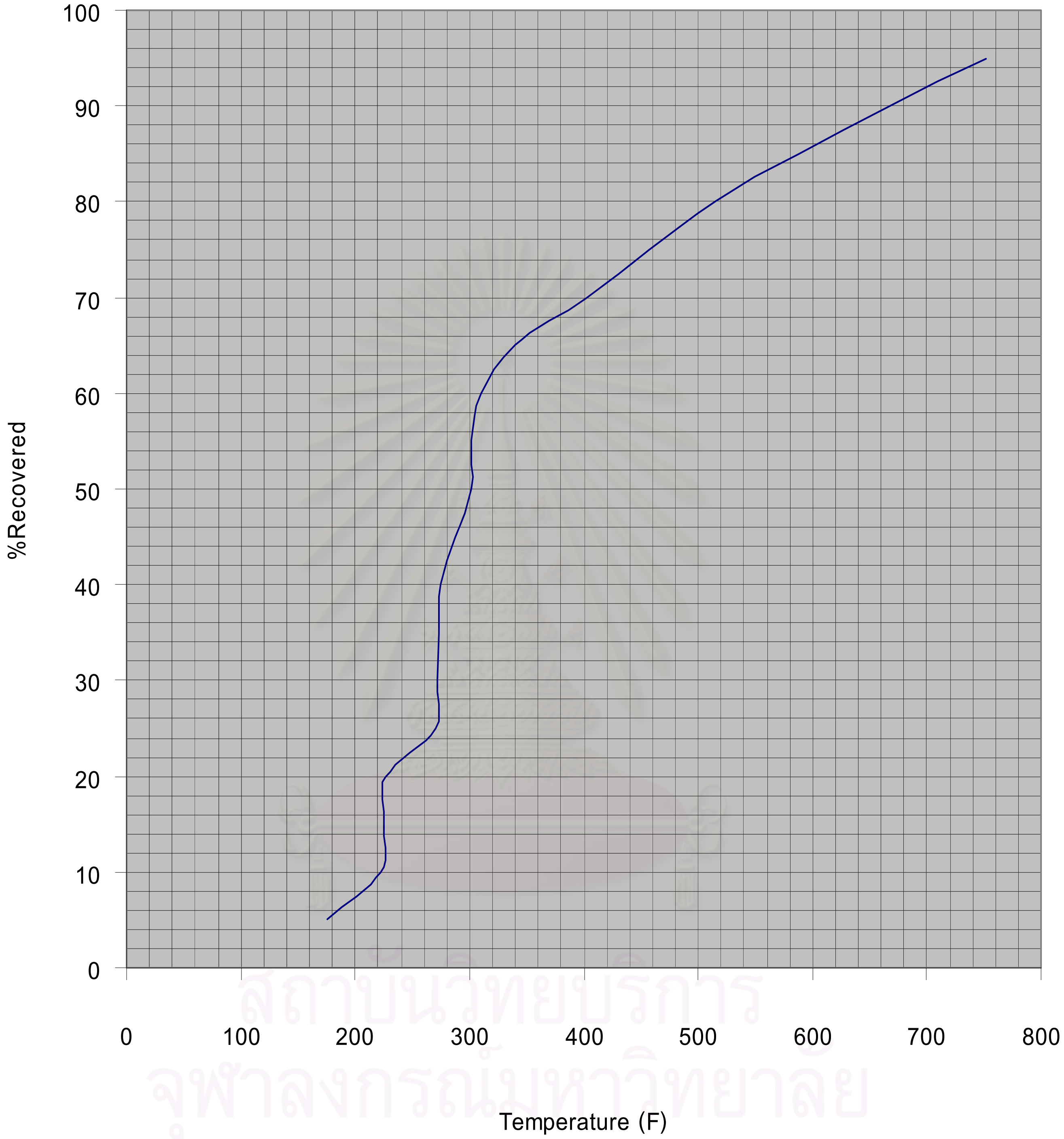

Figure B.6 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

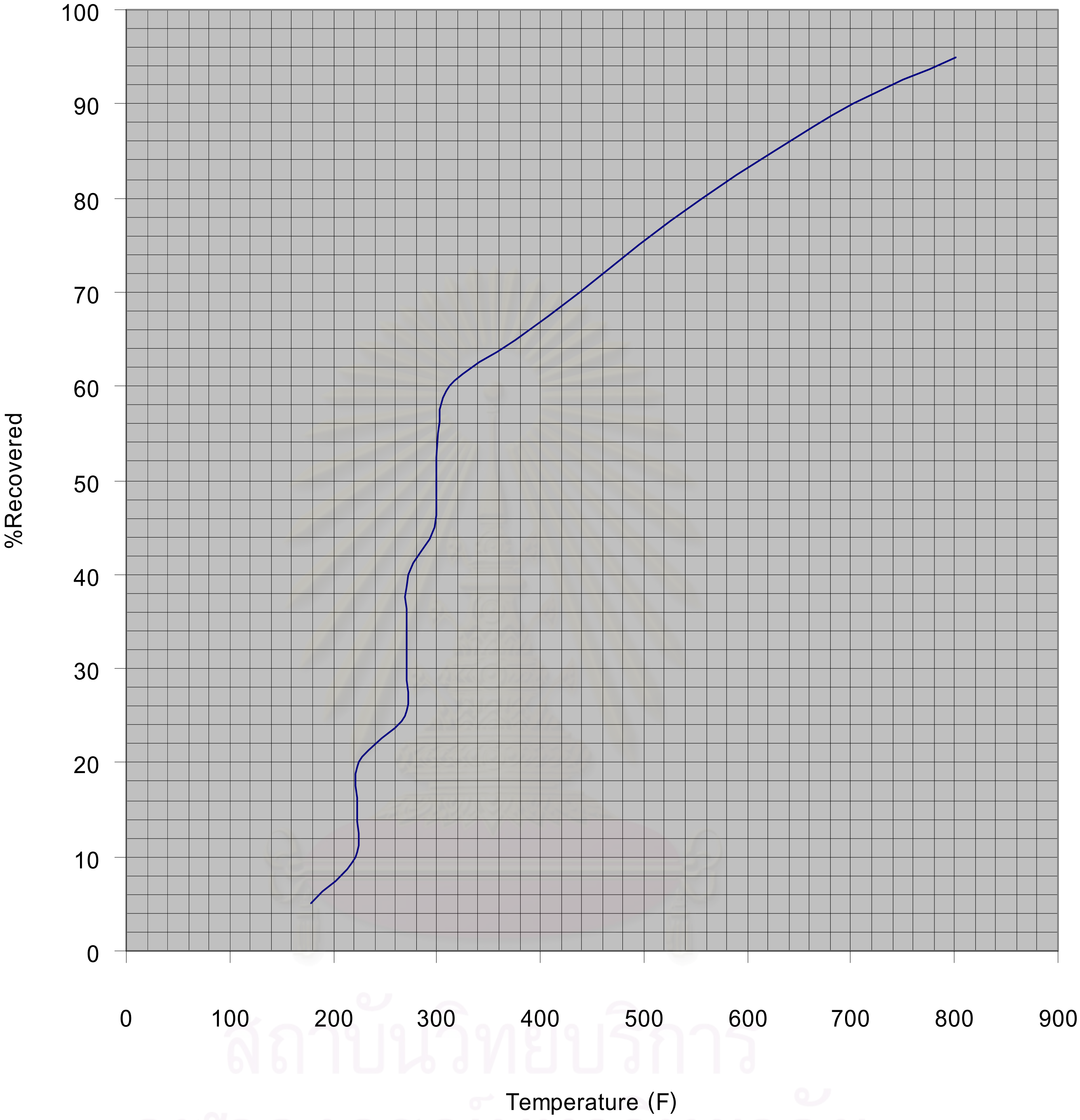

Figure B.7 Oil composition at condition 430 °C of reaction temperature, 20 kg/cm^2 of hydrogen, 60 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

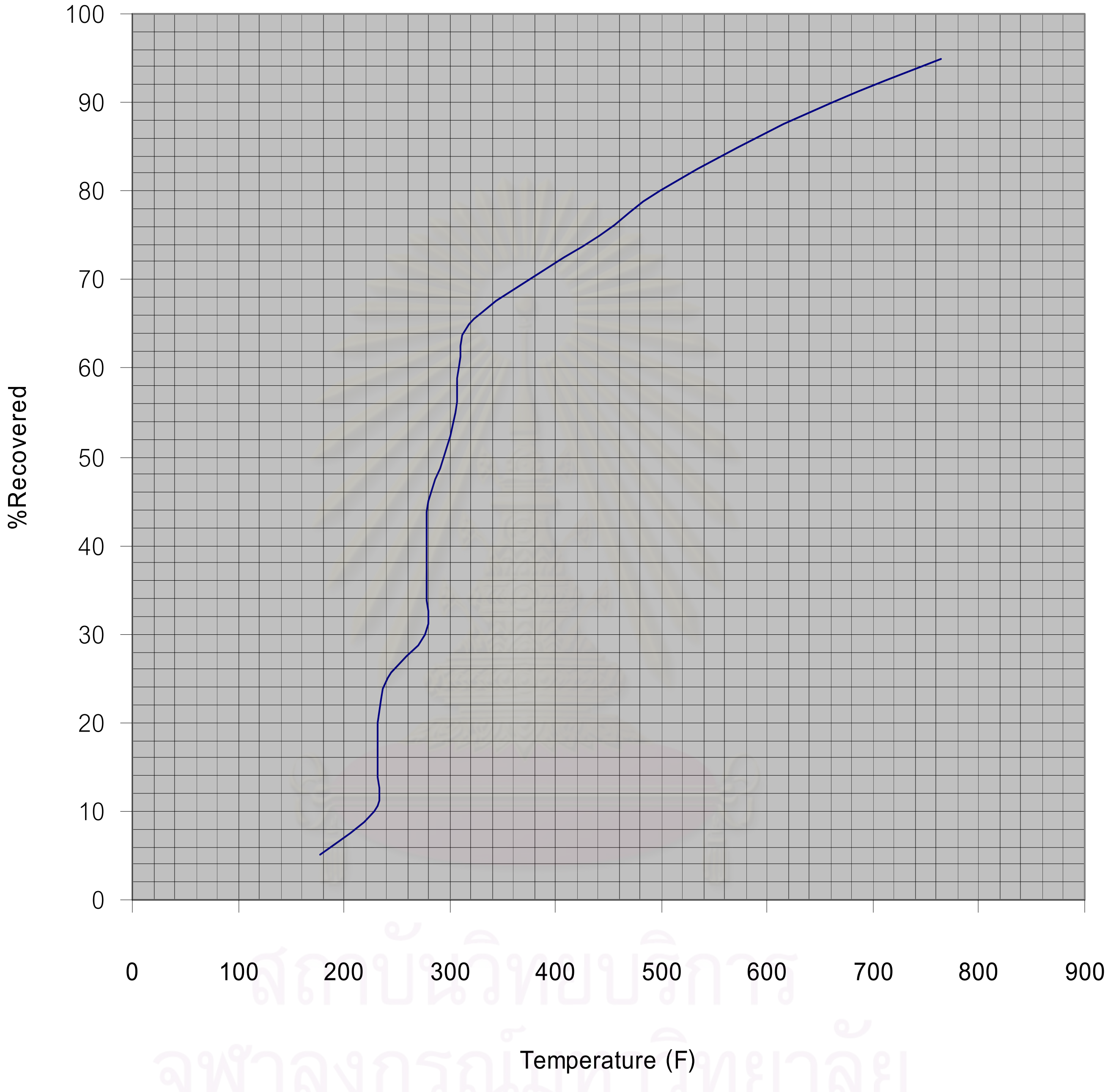

Figure B.8 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 45 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

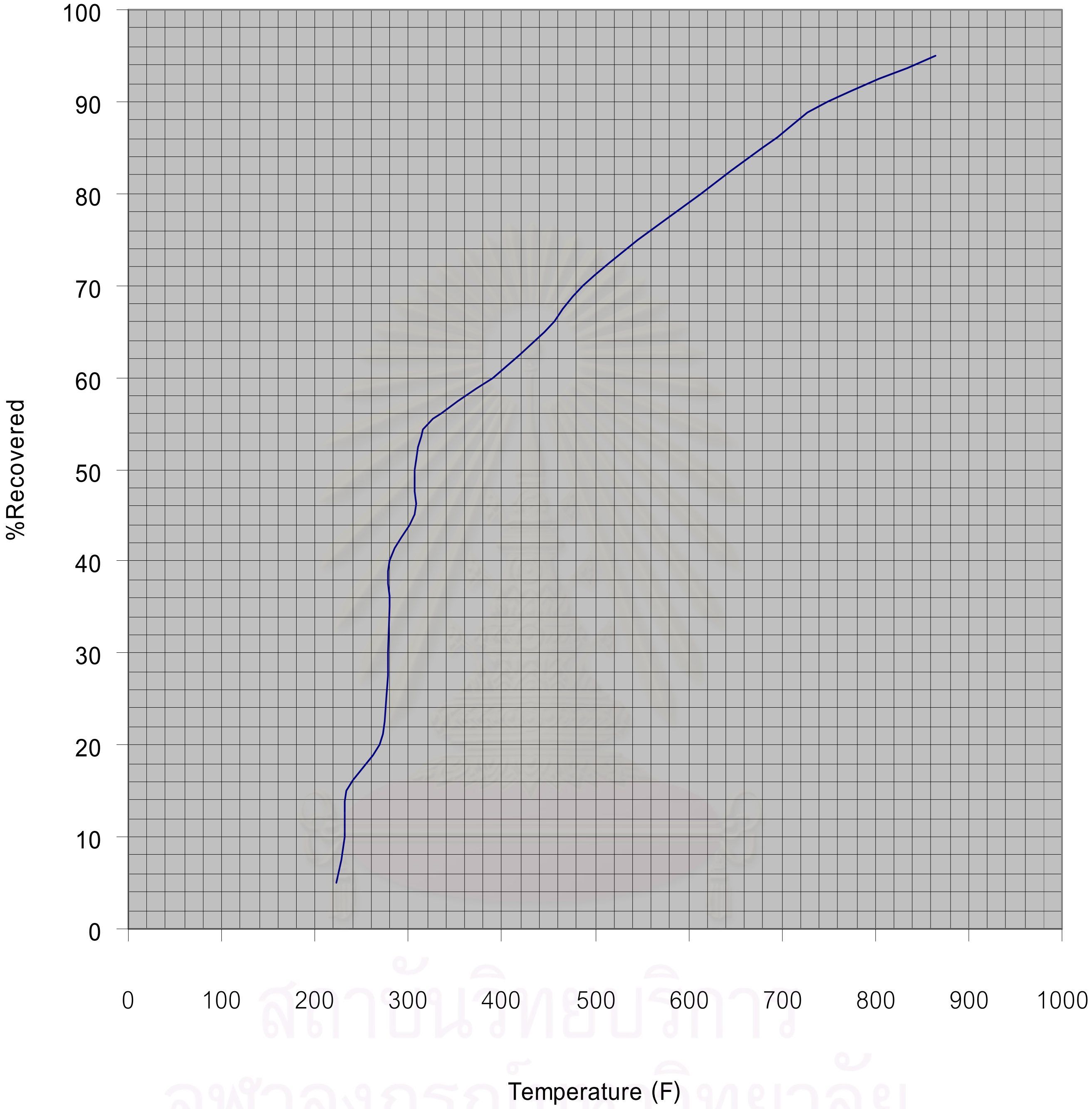

Figure B.9 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 30 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

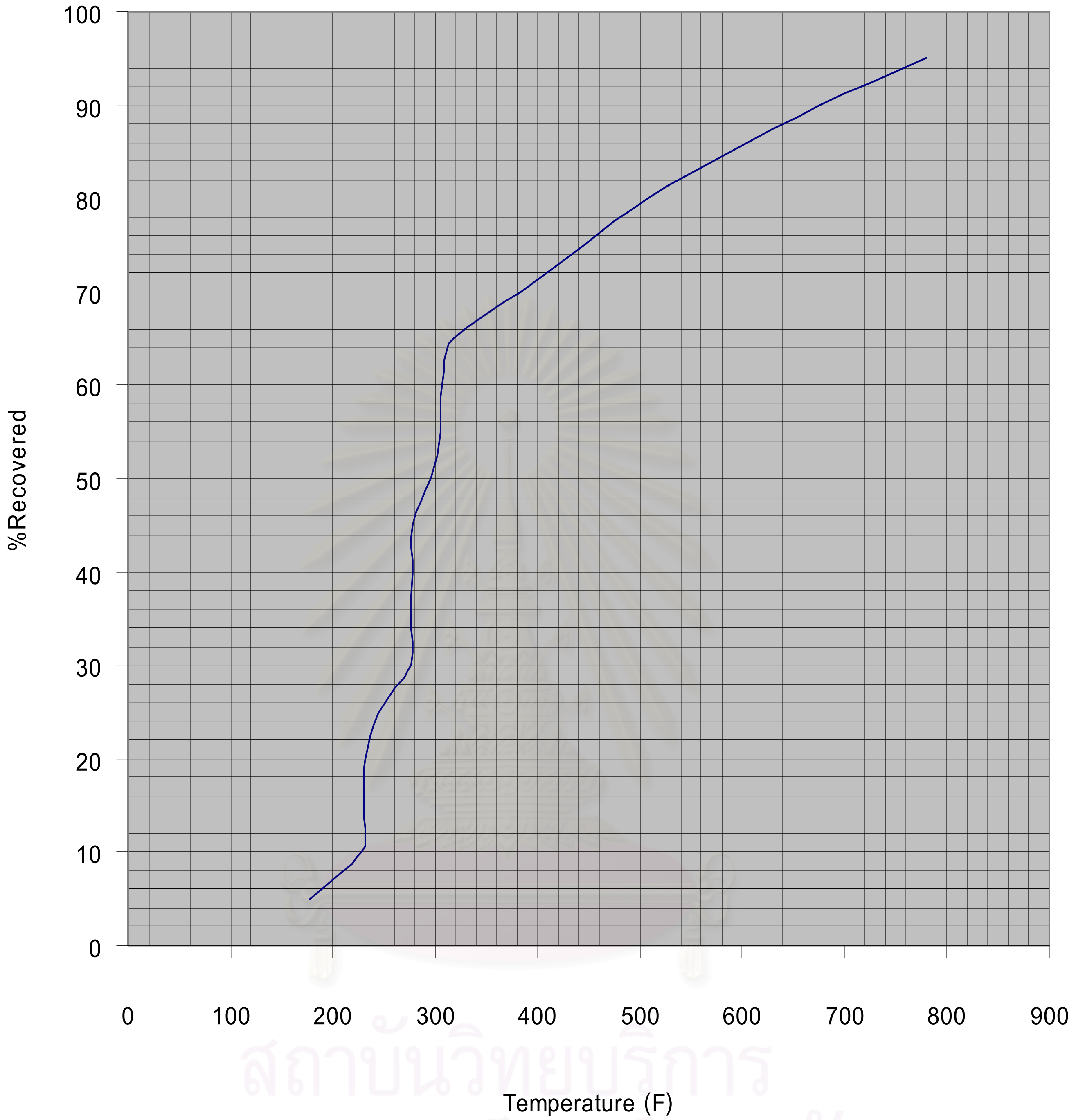

Figure B.10 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 90 min of reaction time and 0.45 g of 5% Fe/AC catalyst by GC Simulated Distillation.

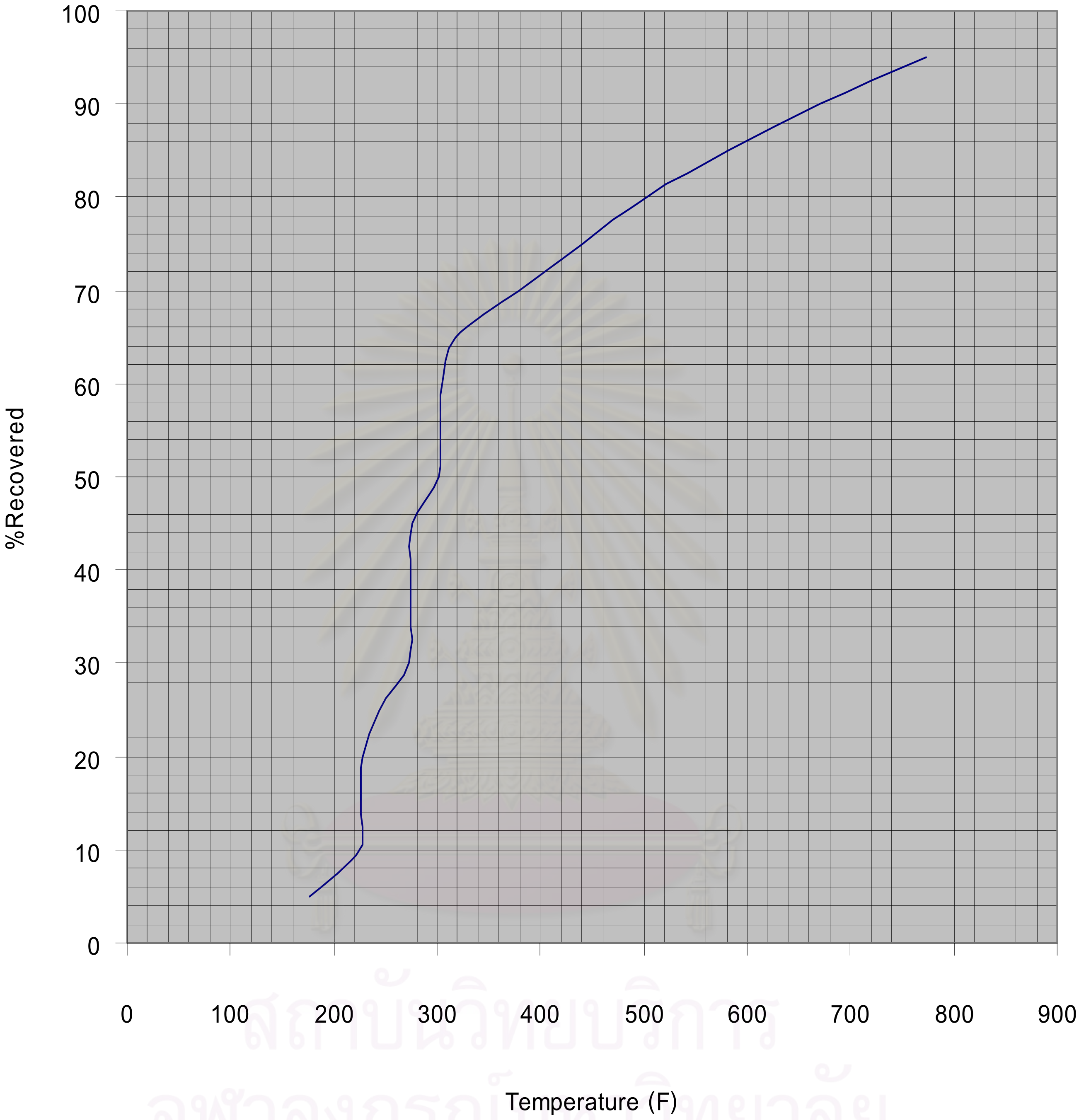

Figure B.11 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 60 min of reaction time and no catalyst by GC Simulated Distillation.

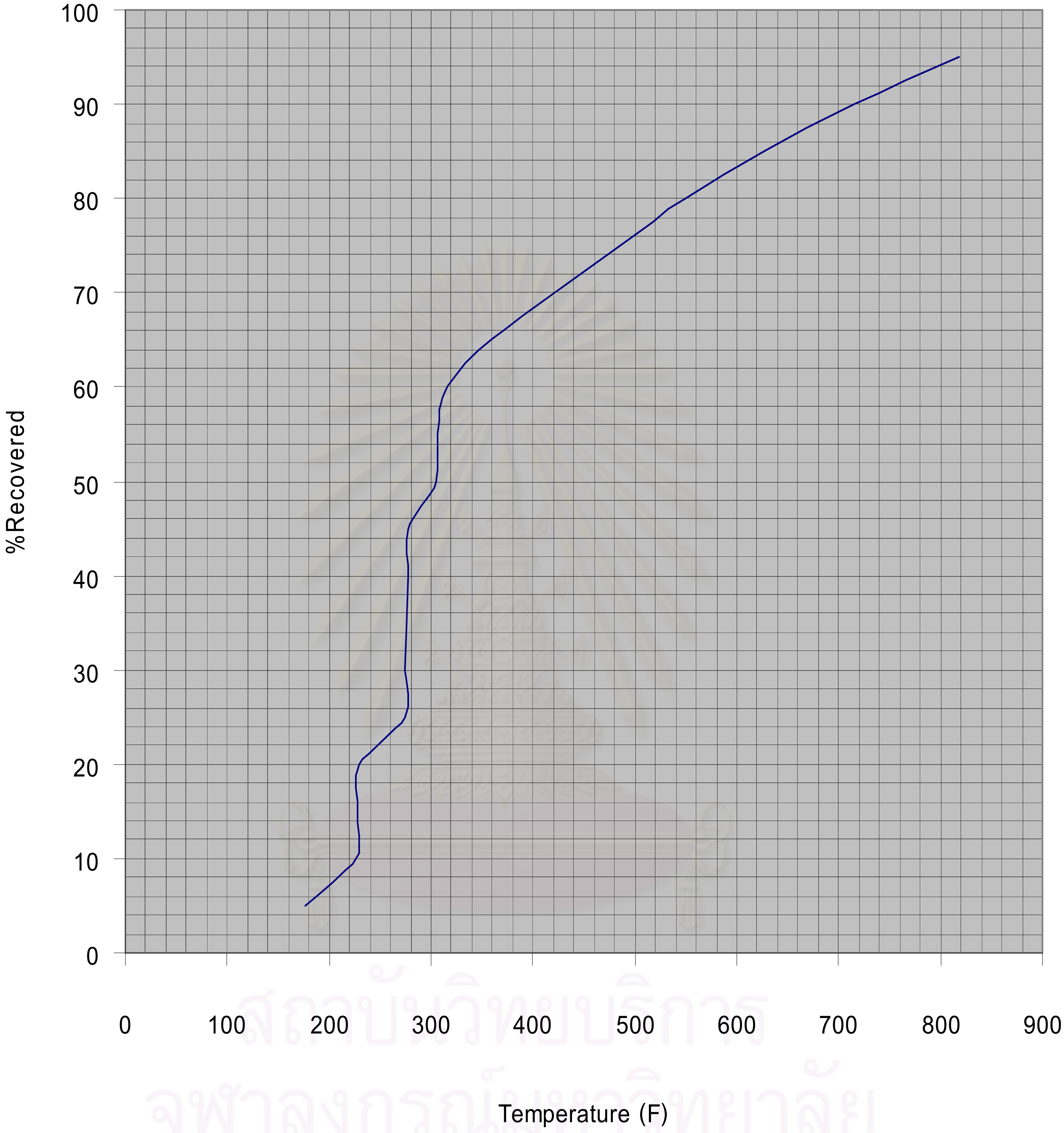

Figure B.12 Oil composition at condition 430 °C of reaction temperature, 40 kg/cm^2 of hydrogen, 60 min of reaction time and 0.6 g of 5% Fe/AC catalyst by GC Simulated Distillation.

VITA

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