

การเปลี่ยนพอลิเอทิลีนไปเป็นก๊าซโซลีนบนตัวเร่งปฏิกิริยา HZSM-5



นายสมสุข ไตรศุภกิตติ

สถาบันวิทยบริการ

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CONVERSION OF POLYETHYLENE INTO GASOLINE ON HZSM-5 CATALYST



Mr.Somsuk Trisupakitti

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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By Mr.Somsuk Trisupakitti

Department Petrochemistry and Polymer Science

Thesis Advisor Assistant Professor Tharapong Vitidsant, Ph.D.

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

..... Dean of Faculty of Science
(Associate Professor Wanchai Phothiphichitr, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

..... Thesis Advisor
(Assistant Professor Tharapong Vitidsant , Ph.D.)

..... Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

..... Member
(Suchaya Nitivattananon, Ph.D.)

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จุดมุ่งหมายหลักของงานวิจัยนี้ มุ่งที่จะศึกษาการเปลี่ยนพอลิเอทิลีนไปเป็นก๊าซโซลีนบนตัวเร่งปฏิกิริยา HZSM-5 ในเครื่องปฏิกรณ์ขนาดเล็ก ซึ่งมีเส้นผ่าศูนย์กลางภายใน 30 มิลลิเมตร โดยการเปลี่ยนแปลงค่าตัวแปรดังนี้ ความดันของก๊าซไฮโดรเจนระหว่าง 10-30 กก./ตร.ซม., อุณหภูมิของปฏิกิริยาระหว่าง 400-480 องศาเซลเซียสและเวลาที่ใช้ทำปฏิกิริยาระหว่าง 30-60 นาที จากผลทดลองพบว่าอุณหภูมิที่ให้ปริมาณน้ำมันได้สูงสุดที่ 450 องศาเซลเซียส อุณหภูมินี้นำมาใช้เพื่อทดสอบผลของความดันของก๊าซไฮโดรเจน, เวลาที่ใช้ทำปฏิกิริยา และอัตราส่วนโมลซิลิกอนต่ออลูมินาของตัวเร่งปฏิกิริยา HZSM-5

ผลิตภัณฑ์น้ำมันที่วิเคราะห์โดยใช้เทคนิคก๊าซโครมาโทกราฟี (GC Simulated Distillation) พบว่า HZSM-5 เป็นตัวเร่งปฏิกิริยาที่เหมาะสม โดยที่อุณหภูมิ 450 องศาเซลเซียส ความดันของก๊าซไฮโดรเจน 30 กก./ตร.ซม. และเวลาในการทำปฏิกิริยา 60 นาที ผลิตภัณฑ์น้ำมันที่ได้มีปริมาณเนฟทา 20-45%, เคโรซีน 8-16%, น้ำมันก๊าด 9-16% และโมเลกุลสายโซ่ยาว 3-14%

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ภาควิชา ลายมือชื่อนิสิต

สาขาวิชา..... ลายมือชื่ออาจารย์ที่ปรึกษา.....

ปีการศึกษา..... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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SOMSUK TRISUPAKITTI : CONVERSION OF POLYETHYLENE INTO GASOLINE ON HZSM-5 CATALYST. THESIS ADVISOR : ASSISTANT PROFESSOR THARAPONG VITIDSANT, Ph.D. 89 pp. ISBN 974-346-410-7

The main objective of this research was aimed to study the conversion of polyethylene into gasoline using HZSM-5 catalyst in a microreactor width of 30 mm inside diameter by varying operating conditions as pressure of hydrogen gas range of 10 to 30 kg/cm², reaction temperature range of 400 to 480 °C and reaction time range of 30 to 60 min for each catalyst. From the results, it was found that reaction temperature of 450 °C was the temperature that yielded the highest quantity of oil product. This temperature was also used in studying the effect of pressure for hydrogen gas, reaction time and mole ratio Si/Al of HZSM-5 catalyst.

The analyzed oil product from Gas Chromatography (GC Simulated Distillation) was found that HZSM-5 was suitable and used as catalyst at 450 °C, hydrogen pressure at 30 kg/cm² and reaction time 60 min. The product yield was in the range 20-45 % Naphtha, 8-16 % Kerosene, 9-16 % Gas Oil and 3-14 % Long Residues.

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

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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	PAGE
ABSTRACT (IN THAI)	vi
ABSTRACT (IN ENGLISH)	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF FIGURES.....	viii
LIST OF TABLES.....	ix
CHAPTER	
I. INTRODUCTION.....	1
II. LITERATURE REVIEWS.....	3
Polyethylene.....	3
2.1 Physical and chemical properties.....	4
2.2 Production.....	5
2.3 Low-density polyethylene.....	5
2.4 High-density polyethylene.....	7
2.5 Application.....	9
III. THEORY.....	13
3.1 History of Zeolites.....	13
3.1.1 Previous history.....	13
3.1.2 Industrial history.....	14
3.1.2.1 Synthetic zeolites.....	14
3.1.2.2 Natural zeolites.....	15
3.2 Structure of zeolite	16
3.2.1 Small pore zeolites.....	20
3.2.2 Medium pore zeolites.....	21
3.2.3 Large pore zeolites.....	21

3.3 X and Y Zeolite Structures.....	23
3.4 Zeolites as Catalysts.....	26
3.4.1 Potential versatility of zeolites as catalysts.....	26
3.4.1.1 Crystal voidage and channels.....	26
3.4.1.2 Variable pore sizes.....	27
3.4.1.3 Ion exchange.....	28
3.4.1.4 Salt occlusion.....	28
3.4.1.5 Framework modification.....	29
3.5 Zeolite Active Sites.....	29
3.5.1 Acid Sites.....	29
3.5.2 Generation of acid centers	30
3.5.3 Basic Sites.....	35
3.6 Shape-Selectivity Catalysis.....	35
3.7 Mechanism of Cracking Processes.....	41
3.7.1 Thermal cracking.....	41
3.7.2 Catalytic cracking.....	43
IV. EXPERIMENT.....	48
4.1 Raw material.....	48
4.2 Types of catalyst	48
4.3 Analyzing structure of crystallites by X-ray diffraction.....	48
4.4 Apparatus and Reaction Method.....	48
4.5 Functional Group Compositional Analysis.....	50
4.6 The reaction products were analyzed by Gas Chromatographs.....	50
V. RESULTS AND DISCUSSION.....	52
5.1 X-Ray Diffraction Patterns.....	52
5.2 Functional Group Compositional Analysis.....	52
5.3 Effect of raw material on conversion of oil product.....	58
5.4 Effect of catalysts on composition of oil product.....	58
5.5 Effect of reaction temperature on composition of oil product.....	59

5.6	Effect of mass of catalyst to 20 g of polyethylene on composition of oil product.....	63
5.7	Effect of reaction time on composition of oil product.....	63
5.8	Effect of pressure of hydrogen on composition of oil product	67
5.9	Effect of type of plastics on composition of oil product	70
5.10	Comparison of this work with other work	72
VI.	CONCLUSIONS AND RECOMMENDATIONS.....	73
	REFERENCES.....	75
	APPENDICES	78
	APPENDIX A. Data for study of conversion of polyethylene into gasoline using HZSM-5 type catalyst.....	79
	APPENDIX B. Peaks of product from Fourier transform infrared Spectrophotometry.....	82
	APPENDIX C. Peaks of product from gas chromatograph.....	84
	VITA.....	89

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

FIGURE	PAGE
3.1 SiO ₄ or AlO ₄ tetrahedra.....	17
3.2 Secondary building units (SBU's) found in the zeolite structures.....	18
3.3 Typical zeolite pore geometries.....	18
3.4 Small pore zeolite.....	22
3.5 ZSM-5 and ZSM-11 chanel system.....	22
3.6 Large pore zeolite.....	23
3.7 Sodalite cage structure.....	24
3.8 Perspective views of the Fuajosite structure.....	25
3.9 Diagram of the surface of a zeolite framework.....	32
3.10 Water molecules coordinate to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity.....	33
3.11 Lewis acid site developed by dehydroxylation of Bronsted acid site.....	34
3.12 Steam dealumination process in zeolite.....	34
3.13 The enhancement of acid strength of OH group by their interaction with dislodge aluminum species.....	35
3.14 Diagram depicting the three type of selectivity.....	36
3.15 Correlation between pore size(s) of various zeolite and kinetic diameter of some molecules.....	39
4.1 The Reaction Experimental Unit for conversion of polyethylene into gasoline using HZSM-5 type catalyst.....	49
5.1 X-ray diffraction patterns for HZSM-5 mole ratio Si/Al is 18.....	54
5.2 X-ray diffraction patterns for HZSM-5 mole ratio Si/Al is 44.....	55
5.3 Fourier transform infrared spectrum of oil derived from HDPE	56
5.4 Fourier transform infrared spectrum of oil derived from LDPE.....	56
5.5 Fourier transform infrared spectrum of oil derived from PS.....	57
5.6 Fourier transform infrared spectrum of oil derived from LDPE/PS.....	57

5.7 Polyethylene conversion on HZSM-5 (Si/Al=44) catalyst with various types of polyethylene.....	60
5.8 Polyethylene conversion on HZSM-5 and Silica-Alumina catalyst with various type of catalysts.....	61
5.9 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various reaction Temperature.....	62
5.10 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various weight of catalyst.....	64
5.11 Polyethylene conversion on Silica-Alumina catalyst with various reaction time.....	65
5.12 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various reaction time.....	66
5.13 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various initial hydrogen pressure.....	68
5.14 Polyethylene conversion on HZSM-5 (Si/Al=44) catalyst with various initial hydrogen pressure.....	69
5.15 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various type of plastics.....	71

LIST OF TABLES

TABLE	PAGE
2.1 Typical Properties of Polyethylene.....	4
3.1 Zeolites and their secondary building units.....	19
3.2 Correlation between zeolite properties and catalytic functionality.....	27
3.3 Kinetic diameters of various molecules based on the Lennard-Jones relationship..	38
3.4 Shape of the pore mouth opening of known zeolite structures.....	40
A-1 Product distribution of all conditions.....	79
B-1 Peaks of product from Fourier transform infrared Spectrophotometry.....	81
C-1 Peaks of product from Gas Chromatograph.....	84



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

INTRODUCTION

Polyethylene is the major member of a group of chemical compounds known as polyolefins. It is one of the most widely used polymer among the thermoplastic materials. Polyethylene is produced in various forms in terms of density : low, intermediate, and high density polyethylene. It may be obtained in granules, powders, films, rods, tubes and sheets and molded products through such processes as injection molding, fluidized bed coating, blow molding, extrusion, vacuum forming, casting and calendering.

Polyethylene is used for many purposes, such as for the manufacture of containers, electrical insulation, housewares, chemical tubing, toys, freezer bags, flexible ice cube trays, Snap-On lids and battery parts. High-density polyethylene is used extensively for bottles and containers because of its ease of processing, toughness and economy.

The problem of waste disposal is increasing with the use of increasing amounts of plastic materials. Organized recovery presently exists only in the case of production wastes inside polymer factories. In domestic garbage there is an ever increasing portion of plastic wastes, the destruction of which requires expensive equipment. Protection of the environment requires improved packaging materials which are self-destructing which will be degraded very rapidly when exposed to the effects of sunlight, humidity, rain fall and soil bacterias. It was expected that polymers degrading under the influence of the atmospheric agents would solve the problem of waste disposal.

Therefore, this work aims to investigate the performances of the tested HZSM-5 zeolite catalyst on polyethylene (PE) conversion to gasoline reaction.

The objective of this study

- (1) To investigate the performance of the prepared HZSM-5 zeolite catalyst on polyethylene (PE) conversion to gasoline.
- (2) To investigate the effect of reaction conditions (temperature, pressure of hydrogen gas, time, type of zeolites) of the above reaction.

The scope of this study

- (1) Analyzing structure of HZSM-5 by X-ray diffraction, XRD.
- (2) Analyzing functional group of oil product by Fourier transform infrared spectroscopy.
- (3) Investigate the performance of the prepared catalyst on the polyethylene (PE) conversion to gasoline under the following condition ;
 - Pressure of hydrogen gas range of 10-30 kg/cm²
 - Reaction temperature range of 400-480 °C
 - Reaction time range of 30-60 min.
 - Mole Ratio Si/Al of HZSM-5 Catalyst ; Si/Al = 18, 40
 - Mass of catalyst per polyethylene, 0.1 and 0.5 g per 20 g of LDPE

The reaction products were analyzed by Gas Chromatographs.

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CHAPTER II

LITERATURE REVIEW

Polyethylene

Polyethylene, $n(\text{CH}_2-\text{CH}_2)_n$ is the most extensively used thermoplastic. The ever-increasing demand for polyethylene is partly due to the availability of the monomer, ethylene, from abundant raw materials: associated gas, and naphtha. The ease of processing of the polymer, its relative low cost, its resistance to chemicals, and its flexibility are also strong influences. All these and other factors lead to generally strong market demand for polyethylene.

High-pressure polymerization of ethylene was introduced in the 1930's. The discovery of new titanium catalysts by Karl Ziegler in 1953 opened a new era for the polymerization of ethylene at lower pressures.

The two most widely used grades of polyethylene are low-density polyethylene, LDPE, which has branched chains, and high-density polyethylene, HDPE, which is predominantly linear. Low-density polyethylene is produced by free radical initiated polymerization at high pressure while high-density polyethylene is produced by low-pressure process with a metallic oxide catalyst of the Ziegler type.

The main difference between the two grades of polyethylene is that LDPE is more flexible because of its lower crystallinity. This lower crystallinity is caused by the presence of branches of two or four carbons along the back-bone of the polymer. HDPE is more closely packed because of the absence of branches and thus the molecules are closer to the another and less permeable to gases.

Several processes can produce polymers with a wide range of densities that cover both the low and high-density ranges as well as medium density polymers.

2.1 Physical and chemical properties

Probably the most important property of polyethylene is its molecular weight and its distribution within a sample. Methods used to determine molecular weights are numerous. A widely used one is viscosity and the melt flow index, MFI, measure the extent of polymerization. A polymer with a high melt flow index has a low melt tensile strength.

Polyethylene is to some extent permeable to most gases. The higher density polymers are less permeable than the lower density ones. Polyethylene, in general, has a low degree of water absorption and is not attacked by dilute acids and alkalis. However, concentrated acids attack it. Its overall chemical resistance is excellent. Hydrocarbons and chlorinated hydrocarbons and swell slowly in these solvents affect polyethylene. Tensile strength of polyethylene is relatively low, but impact resistance is high. The use of polyethylene in insulation is due to its excellent electrical resistance properties. Table 2.1 [20] gives some of the properties of low and high density polyethylene.

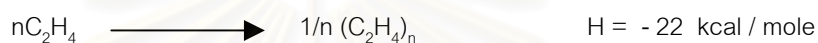
Table 2.1 Typical Properties of Polyethylene

Polymer	Melting point range °C	Density g/cm ³	Degree of crystallinity %	Stiffness modules psi x 10 ³
Branched, Low density	107~121	0.92	60~65	25~30
Medium density	0.935	75	60~65
Linear, High density				
Ziegler type	125~132	0.95	85	90~110
Phillips type	0.96	91	130~150

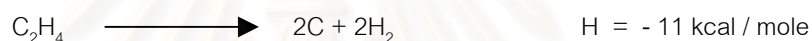
2.2 Production

The polymerization of ethylene is an exothermic reaction from which 850 calories are released for each gram of ethylene. For this reason, an adequate method of removing the heat of reaction is needed. Polyethylene decomposes at high temperatures, even in the absence of air. Explosions might take place if the temperature is not controlled. The decomposition products are methane, carbon, and hydrogen. Reactions that take place in the reactor are:

Polymerization

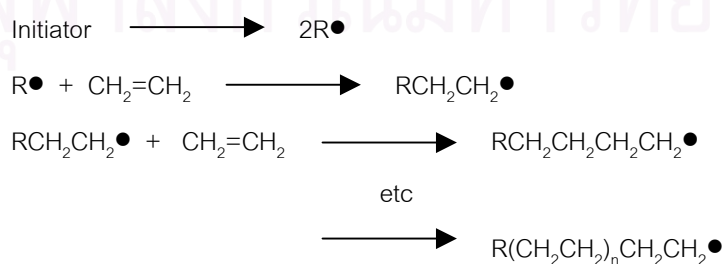


Decomposition

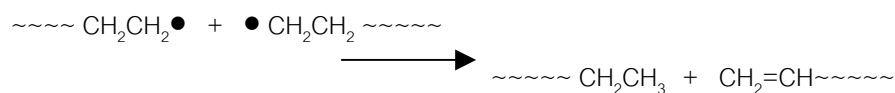
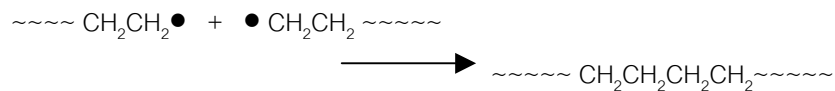


2.3 Low-density polyethylene

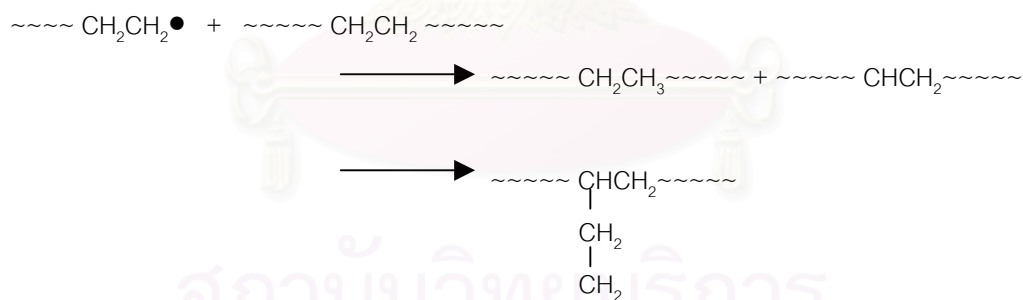
Low-density polyethylene is made by free radical polymerization. The reaction is carried out at temperatures from 80 to 300 °C and pressures in the range 1000 to 3000 atm. Either oxygen or organic peroxide is used as the initiator. Initiation and propagation occur as follows:



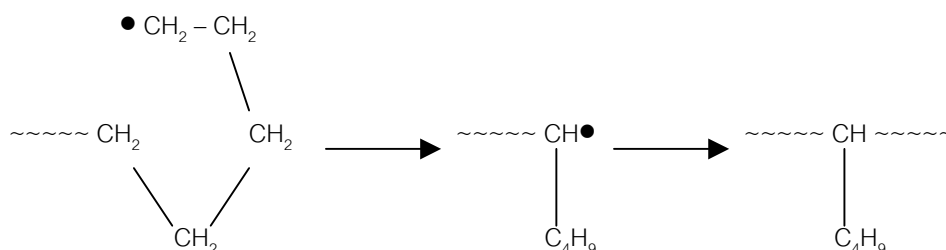
Termination occurs by coupling and disproportionation of free radicals :



If the above reactions were the only one to occur during the polymerization, the product would be linear polyethylene, with the structure $[-\text{CH}_2\text{CH}_2-]_n$. In fact, low-density polyethylene does not have this structure. Its molecules, far from being linear, are quite highly branched. Typically they have one or two long branches and a much larger number of short branches of up to five carbon atoms. These branches result from chain transfer reactions, in which hydrogen atom abstraction results in the active center being transferred from one position to another. In intermolecular chain transfer, the free radical site is transferred from the growing radical to a finished polymer molecule. This leads to the formation of a Long Branch:



In intermolecular chain transfer, the radical site is moved from one position on the radical to another a few carbon atoms away, resulting in the formation of a short branch:



As we will see shortly, the branching has a profound effect on the properties of the polymer.

The pressures used in the manufacture of low-density polyethylene are exceptionally high for a chemical process. Since the use of such pressures is expensive both in terms of capital costs and of operating cost, the question arises as to why they are used. The reason is that it is only at very high pressures, i.e. at high ethylene concentrations, that the propagation reactions are fast enough for high molecular weight polymer to be formed.

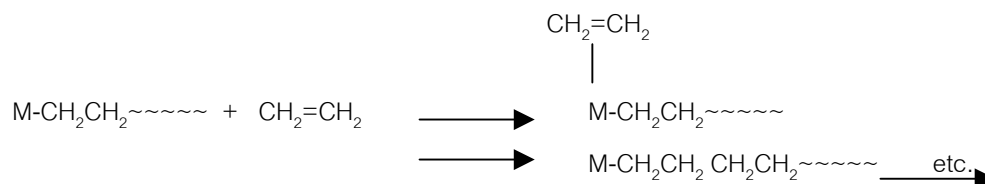
2.4 High-density polyethylene

High-density polyethylene is made by an entirely different type of process, called *co-ordination* or *Ziegler polymerization*. This was discovered by Karl Ziegler in 1953, and the first commercial production of HDPE was about two years after that.

The catalyst systems developed by Ziegler consist of complexes formed from aluminium alkyls and transition metal halides, typically triethylaluminium and titanium tetrachloride. In the presence of such catalysts, polymerization of ethylene occurs at about 100°C and at moderate pressures. Originally the reaction was carried out in an inert solvent such as hexane, but now it is also carried out in the gas phase. Quite separately from Ziegler, other workers developed system for carrying out this type of polymerization over transition metal oxide catalysts.

The mechanism of co-ordination polymerization is complicated. We will simply consider it in outline.

The polymer chain grows at active metal sites on the catalyst, molecules of ethylene being first co-ordinate to the site, and then inserted between it and the growing chain:



Chain transfer to polymer does not occur, and the polymer obtained is linear. It is this fact that accounts for the difference between its properties and those of low-density polyethylene.

One of the reasons why polymers have useful mechanical properties is that there are large attractive forces between the very big polymer molecules. In non-polar polymers like polyethylene the attractions are due to Van Der Waal's forces. In other polymers, dipole-dipole interactions or hydrogen bonding may be involved. It can be appreciated that the more closely and regularly the polymer molecules can pack together, the stronger will be the forces between them. In high-density polyethylene, with its regular linear structure, the molecules can pack together very closely in orderly arrays, called *crystalline regions*, for most of their lengths. In low-density polyethylene the branches tend to get in the way, and a much smaller proportion of the total length of the molecules is in close packed ordered regions. This results in the polymer being softer, less strong and having a lower melting point than the linear polymer, and also, as is indicated by the name, in its having a lower density.

The two products have different ranges of application, reflecting their different properties and also the fact that low-density polyethylene has traditionally been cheaper than high-density polyethylene. This price relationship may seem strange in view of the costs associated with the operating pressures in the low-density polyethylene process. It arose from the fact that, originally at least the cost of making and handling the catalyst in the HDPE process, and the cost of removal of catalyst residues from the polymer, more than outweighed the cost of high pressure operation. With modern high activity catalysts this is probably no longer the case, and the price differential probably reflects the fact that for many applications high density polyethylene is the superior product.

The situation became more complicated in the late 1970s when the misleadingly named **linear low-density polyethylene** (LLDPE) was introduced. This is made by copolymerizing ethylene with small amounts of 1-alkenes, such as 1-butene or 1-hexene, in the presence of Ziegler catalysts. It has short branches. By varying the nature and proportion of the comonomer, a substantial degree of 'tailoring' of polymer properties is possible. It is expected that linear low-density polyethylene will to a considerable extent displace the conventional low-density polymer from the market.

2.5 Application

Products made from polyethylene are numerous and range from building materials and sheets. It is an inexpensive plastic that can be molded into almost any shapes, extruded into fiber or filament, and blown or precipitated into film or foil. Because it is more flexible and more transparent, the low-density polymer is used in sheets, films, and injection molding. High-density polyethylene are extensively used in blow-molded containers. About 85 percent of the blow-molded bottles are produced from HDPE. Irrigation pipes made from polyvinyl chloride and high-density polyethylene, HDPE, are widely used. Pipes made from HDPE are flexible, tough, and corrosion resistant. These pipes are used for carrying corrosive and/or abrasive materials, such as gypsum, slurry, and various chemicals. Corrosion resistant pipes are also used in well drilling and crude oil transfer. Spun-bounded polyethylenes are extremely fine fibers interconnected in a continuous network. Their use includes notebook and reference book covers, wall covering tags labels, etc. The point-bonded, spun-banded polyethylene are used, for example, as laboratory coats, aprons, garments and sleeping bag liners.

Uemichi et al., [1] studied conversion of polyethylene into gasoline-range fuel by two-stage catalytic degradation using silica-alumina and HZSM-5 zeolite. A two-stage catalytic degradation of polyethylene using amorphous silica-alumina and HZSM-5 zeolite catalysts in series has been developed for converting the polymer into high-

quality gasoline-range fuels. Compared with the one-stage degradation over each catalyst, the two-stage method provides some advantages. They were an improved gasoline yield and a high octane number despite low aromatics content. Significant results were obtained when silica-alumina and HZSM-5 were used in a weight ratio of 9:1 as upper and lower catalysts, respectively, in a flow reactor. The reverse sequence of catalysts showed no advantage. It was suggested that large pores and moderate acidity of the silica-alumina loaded in the upper layer operated favorably to catalyze the degradation of polyethylene into liquid hydrocarbons. The resulting oils showed low quality, and they were transformed into high-quality gasoline on the strongly acidic sites of the HZSM-5 loaded in the lower layer at the expense of oil yield. Increase in concentration of isoparaffins and aromatics contributed to the upgrading.

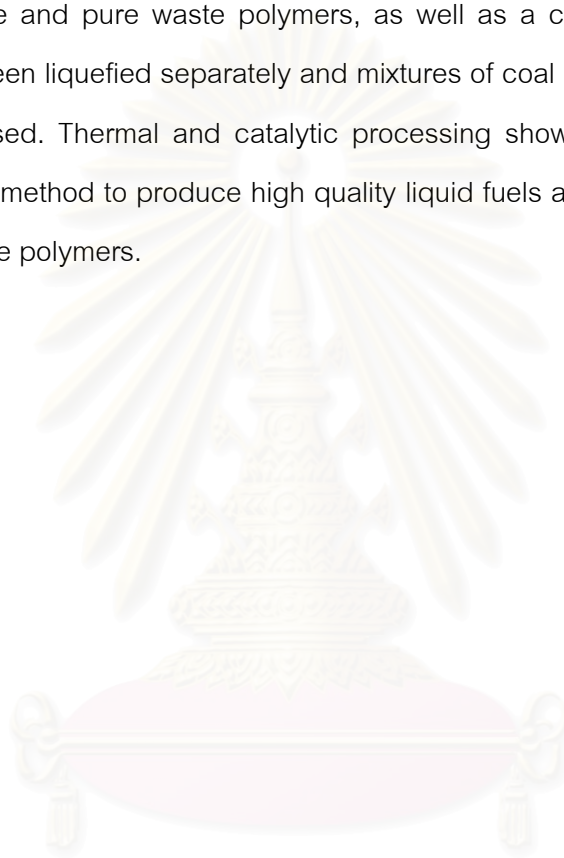
Paul T. Williams and Elizabeth A. Williams, [22] studied interaction of plastics in mixed-plastics pyrolysis. The pyrolysis of mixed-plastic waste has been proposed as a means of recycling to produce petrochemical feedstock. The interaction of the main plastic types in plastic mixtures is significant in predicting the likely yield 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 °C/min to a final temperature of 700 °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 was determined. The main gases produced from the individual plastics were hydrogen, methane, ethane, ethene, 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 a 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 less than expected from the individual molecular weights. Compositional analysis of the oil/wax showed that changes in the concentration of aromatic hydrocarbons and polycyclic aromatic hydrocarbons were produced with the mixture compared to that expected from the individual plastics.

Sharratt et al.,[4] studied investigation of the catalytic pyrolysis of high-density polyethylene over a HZSM-5 catalyst in a laboratory fluidized-bed reactor. High-density polyethylene (HDPE) was pyrolyzed over HZSM-5 catalyst using a specially developed laboratory fluidized-bed reactor operating isothermally at ambient pressure. The influence of reaction conditions including temperature, ratios of HDPE to catalyst feed, and flow rates of fluidizing gas was examined. The sodium form of siliceous ZSM-5, silicalite, containing very few or no catalytically active sites, gave very low conversions of polymer to volatile hydrocarbons compared with HZSM-5 (Si/Al = 17.5) under the same reaction conditions. Experiments carried out with HZSM-5 gave good yields of volatile hydrocarbons with differing selectivities in the final products dependent on reaction conditions. Catalytic pyrolysis of HDPE performed in the fluidized-bed reactor was shown to produce valuable hydrocarbons in the range of C_3 ~ C_5 carbon number with a high olefinic content. The production of olefins with potential value as a chemical feedstock is potentially attractive and may offer greater profitability than production of saturated hydrocarbons and aromatics.

Arandes et al., [6] studied transformation of several plastic wastes into fuels by catalytic cracking. The thermal and catalytic cracking of several plastic wastes (polypropylene, polystyrene, polystyrene-polybutadiene) dissolved in refinery LCO has been studied in a riser simulator, under operating conditions (catalyst, temperature, contact time, C/O ratio) that are similar to commercial FCC units. The results of the product distribution show the interest of this strategy, which may be integrated into refinery operation for large-scale tertiary exploitation of plastic wastes.

Anderson et al., [23] 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 materials 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.



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CHAPTER III

THEORY

Zeolites are finding applications in many areas of catalysis and molecular sieve, generating interest in these materials in industrial and academic laboratories. As catalyst, zeolites exhibit appreciable acid activity with sharp-selectivity features not available in the compositional equivalent amorphous catalysts. In addition, these material can act as supports for numerous catalytically active metals. The porous framework of the zeolites enables them to act as molecular sieves i.e., they are used to separate molecular mixtures on the basis of size and shape molecule compounds or for the selective adsorption of gases. These unique properties are utilized in diverse industrial processes such as the purification of water as well as other liquids and gases, chemical separation catalysis, and decontamination of radioactive wasters.

3.1 History of Zeolites

3.1.1 Previous history [8]

The history of zeolites began in 1756 when the Swedish mineralogist Cronstedt discovered zeolite material, stilbite. He recognized zeolites as a new class of materials consisting of hydrated aluminosilicates of alkali and alkaline earths. Because the crystals exhibit swelling and boiling when heated in a blowpipe fame, Cronstedt called the mineral a “zeolite” derived from two Greek words, “zeo” and “lithos” meaning “to boil” and “a stone”. In 1777 Fontana described the phenomenon of adsorption on charcoal. In 1840 Damour observed that crystals of zeolites could be reversibly dehydrated with no apparent change in their transparency or morphology. Schafhautle reported the hydrothermal synthesis of quartz in 1845 by heating a “gel” silica with water in an autoclave. Way and Thompson (1850) clarified the nature of ion exchange in soils. Eichhorn in 1858 showed the reversibility of ion exchange on zeolite materials. St. Clarife

Deville reported the first hydrothermal synthesis of a zeolite, Irbyniyr, in 1862. In 1866 Friedel developed the idea that structure of dehydrated zeolites consists of open spongy frameworks after observing that various liquids such as alcohol, benzene, and chloroform were occluded by dehydrated zeolites. Grandjean in 1909 observed that dehydrated chabazite adsorbs ammonia, air, hydrogen and other molecules, and in 1925 Weigel and Steinhoff reported the first molecular sieve effect. They noted that dehydrated chabazite crystals rapidly adsorbed water, methyl alcohol, ethyl alcohol and formic acid but essentially excluded acetone, ether or benzene. In 1927 Leonard described the first use of x-ray diffraction for identification in mineral synthesis. The first structures of zeolites were determined in 1930 by Taylor and Pauling. In 1932 McBain established the term “molecular sieve” to define porous solid materials that act as sieves on a molecular scale.

Thus, by the mid-1930's the literature described the ion exchange, adsorption, molecular sieve and structural properties of zeolite minerals as well as a number of reported syntheses of zeolites. The latter early synthetic work remains unsubstantiated because of incomplete characterization and the difficulty of experimental reproducibility.

Barrer began his pioneering work in zeolite adsorption and synthesis in the mid-1930's to 1940's. He presented the first classification of the then known zeolites based on molecular size consideration in 1945 and in 1948 reported the first defined synthesis of zeolite including the synthetic analogue of the zeolite mineral merdenite.

3.1.2 Industrial history [8]

3.1.2.1 Synthetic zeolites

Barrer's in the mid-late 1940's inspired the Linde Division of Union Carbide Corporation to initiate studies in zeolite synthesis in search of new approaches for separation and purification of air. Between 1949 and 1954 R.M. Milton and coworker

D.W. Breck discovered a number of commercially significant zeolites, type A, X and Y. In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial material for separation and purification. The earliest applications were the drying of refrigerant gas and nature gas. In 1955 T.B. Reed and D.W. Breck reported the structure of synthesis zeolite A. In 1959 Union Carbide marketed the "ISOSIV" process for normal-isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. Also in 1959 a zeolite Y-based catalyst was marketed by Carbide as an isomerization catalyst.

In 1962 Mobil Oil introduced the use of synthetic of zeolite X as a cracking catalyst. In 1969 Grace described the first modification chemistry based on steaming zeolite Y to form an "ultrastable" Y. In 1967-1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. In 1974 Henkel introduced zeolite A in detergents as a replacement for the enviromentally suspect phosphates. By 1977 industry-wide 22,000 tons of zeolite Y were in use in catalytic cracking. In 1977 Union Carbide introduced zeolite for ion-exchange separations.

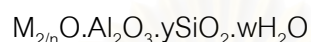
3.1.2.2 Natural zeolites [8]

For 200 years following their discovery by Cronsted, zeolite mineral (or natural zeolite) were considered to occur typically as minor constituent in cavities in basaltic and volcanic rock. Such occurrences precluded their being obtained in mineable quantities for commercial use. From 1950 to 1962 major geologic discoveries revealed the widespread occurrence of a number of natural zeolite in sedimentary deposits throughout the Western United States. The discoveries resulted from the use of x-ray diffraction to examine very fine-grained (1-5 μm) sedimentary rock. Some zeolites occur in large near monomineralic deposits suitable for mining. Those that have been commercialized for adsorbent applications include chabazite, erionite, modernite and clinoptilolite.

3.2 Structure of Zeolite

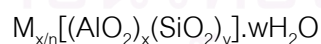
Zeolite are crystalline aluminosilicates of group IA and IIA elements such as sodium, potassium, magnesium, and calcium.

Chemically, they are represented by the empirical formula : [8]



Where y is 2 to 10, n is the cation valence, and w represents the water contained in the voids of the zeolite. Structurally, zeolite are complex, crystalline inorganic polymer based on an infinitely extending three-dimensional, four-connected framework of AlO_4 and SiO_4 tetrahedra (Figure 3.1) linked to each other by the sharing of oxygen ions. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation. The framework structures contain channels or interconnected voids that are occupied by the cations and water molecule. The cations are mobile and ordinary undergoes ion exchange. The water may be removed reversibly, generally by the application of heated, which leaves intact a crystalline host structure permeated by the micropores and voids which may amount to 50% of the crystals by volume.

The structure formula of zeolite is based on the crystallographic unit cell, the smallest unit of structure, represented by : [8]



Where n is the valence of cation M, w is the number of water molecules per unit cell, x and y are total number of tetrahedra per unit cell, and y/x is 10 to 100.

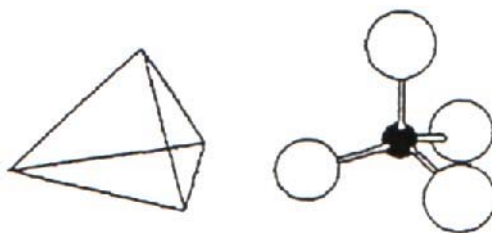


Figure 3.1 SiO_4 or AlO_4 tetrahedra [9].

In most zeolite structures the primary structural units, the AlO_4 or SiO_4 tetrahedra, are assembled into secondary building units (SBU). The final structure framework consists of assemblages of secondary units.

A secondary building unit consists of selected geometric groupings of those tetrahedra, which can be used to describe all of known zeolite structures. These secondary building unit consist of 4(S4R), 6(S6R) and 8(S8R)-member single ring, 4-4 (D4R), 6-6(D6R), 8-8(D8R)-member double ring, and 4-1, 5-1, 4-4-1 branch ring [10]. The topologies of these units are shown in figure 3.2. Also listed are the symbols used to describe them. Most zeolite framework can be generated from several different SBU's. Description of known zeolite structures based on their SBU's are listed in Table 3.1[10]. Both zeolite ZSM-5 and ferrierite are described by their 5-1 building units. Offertile, zeolite L, cancrinite, and erionite are generated using only single 6-member rings. Some zeolite structures can be described by several units.

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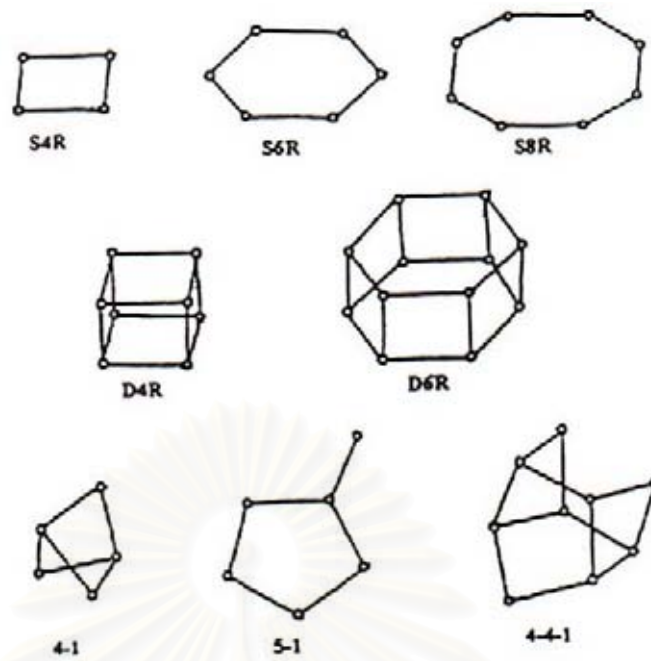


Figure 3.2 Secondary building units (SBU's) found in the zeolite structures [10].

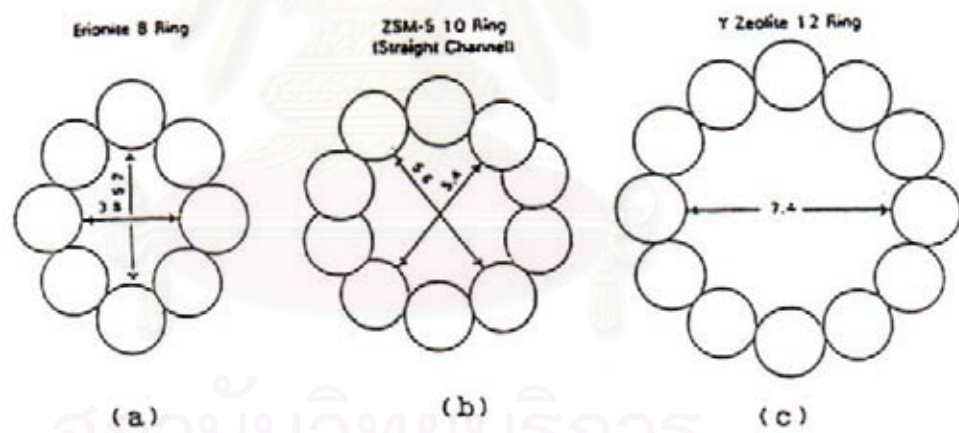


Figure 3.3 Typical zeolite pore geometries [12].

Table 3.1 Zeolites and their secondary building units. The nomenclature used is consistent with that presented in Figure 3.2 [11].

Zeolite	Secondary Building Units								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Bikitaite								X	
Li-A (BW)	X	X	X						
Analcime	X	X							
Yugawaralite	X		X						
Episitbite								X	
ZSM-5								X	
ZSM-11								X	
Ferrierite								X	
Dachiardite								X	
Brewsterite	X								
Laumonite		X							
Mordenite								X	
Sodalite	X	X							
Henulandite									X
Stibite									X
Natrolite							X		
Thomsonite							X		
Edingtonite							X		
Cancrinite		X							
Zeolite L		X							
Mazzite	X								
Merlinoite	X		X			X			
Phillipsite	X		X						
Losod		X							

Table 3.1 (Continued)

Zeolite	Secondary Building Units								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Erionite	X	X							
Paulingite	X								
Offretite		X							
TMA-E (AB)	X	X							
Gismondine	X		X						
Levyne		X							
ZK-5	X	X	X		X				
Chabazite	X	X			X				
Gmelinite	X	X	X		X				
Rho	X	X	X				X		
Type A	X	X	X	X					
Faujasite	X	X			X				

The catalytically most significant are those having pore opening characterized by 8-, 10-, 12-rings of oxygen atoms. Some typical pore geometries are shown in Figure 3.3 [12].

3.2.1 Small pore zeolites

Structures of some small pore zeolite are illustrated in Figure 3.4. The erionite structure, Figure 3.4 (a), is hexagonal containing “supercage” supported by column of cancrinite units linked through double 6 rings. Access to, and between, the supercages is gained through 8 rings.

In the chabazite framework, Figure 3.4 (b), the double rings layer sequence is ABCABC, and the 6 rings units are linked together through titled 4 ring units. The framework contains large ellipsoidal cavities, Figure 3.4 (c), each entered through six 8 rings units, These cavities are joined via their 8 ring units, forming a 3 dimensional channel system.

3.2.2 Medium pore zeolites

The channel system of zeolite ZSM-5, represented in Figure 3.5, shows a unique pore structure that consists of two intersecting channel systems: one straight ($5.5 \times 5.6 \text{ \AA}$) and other sinusoidal ($5.1 \times 5.4 \text{ \AA}$) and perpendicular to the former. Both channel systems have ten-membered ring elliptical openings.

3.2.3 Large pore zeolites

Mordenite, Figure 3.6 (a), is characterized by a one dimensional system of parallel elliptical channels, defined by 12 oxygen ring.

The faujasite structure, Figure 3.6 (b), is built up of truncated octahedra interconnected via double 6 ring units. Faujasite contains extremely large supercages ($\sim 13 \text{ \AA}$ diameter) entered through 12 oxygen ring.

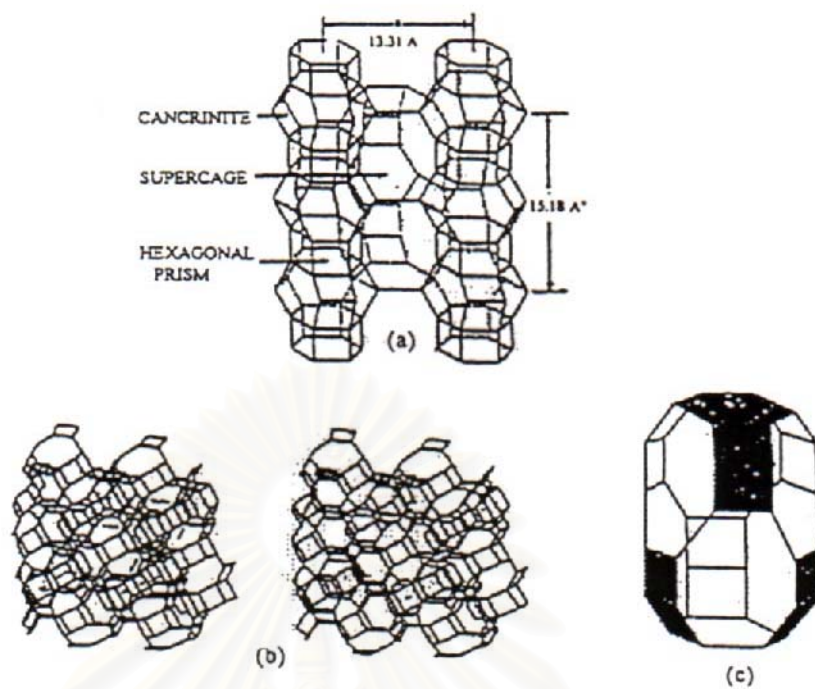


Figure 3.4 Small pore zeolite (a) Erionite framework
(b) Chabazite framework (c) Chabazite cavity [12]

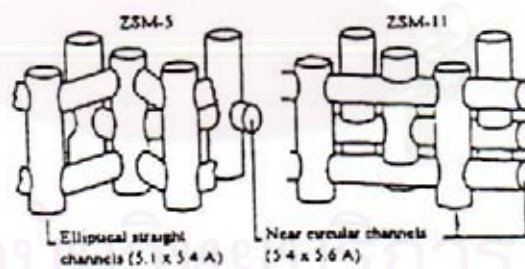


Figure 3.5 ZSM-5 and ZSM-11 channel systems [12].

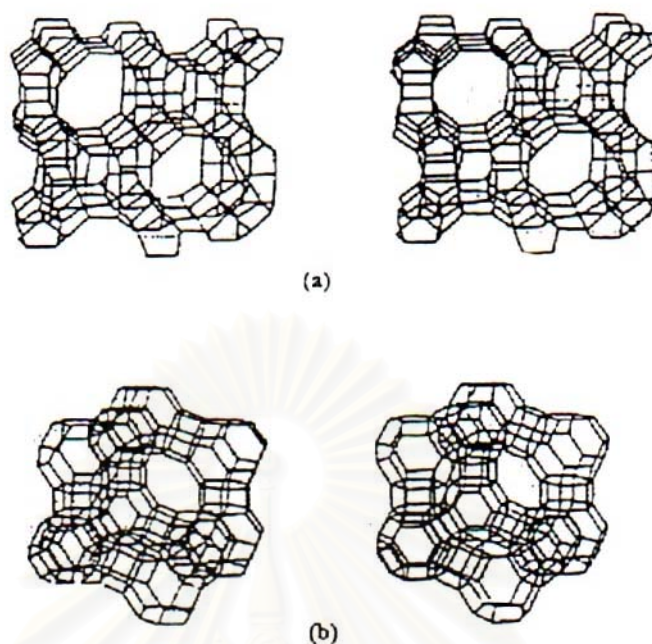


Figure 3.6 Large pore zeolites
 (a) Mordenite framework
 (b) Faujasite framework [12].

3.3 X and Y Zeolite Structures [13]

X zeolite, Y zeolite and faujasite have topologically similar structures. They differ in their characteristic silica-to-alumina ratios and consequently differ in their crystal-lattice parameter, with a variation of about 2 percent over the range of permissible Si/Al ratios. They also differ in properties as cation composition, cation location, cation exchangeability, thermal stability, adsorptive and catalytic character.

In the X and Y zeolites and faujasite, the silica and alumina tetrahedra are joined together to form a cuboctahedron, as shown in Figure 3.7. This unit referred to as a sodalite unit or truncated octahedron, contains 24 silica and alumina tetrahedra. The sodalite unit is the secondary building block of a number of zeolites, including sodalite,

zeolite A, zeolite X, zeolite Y and faujasite. Molecules can penetrate into this unit through the six-membered oxygen rings, which have a free diameter 2.6 \AA , the unit contains spherical void volume with 6.6 \AA free diameter. Since the pore diameter is so small, only very small molecules, e.g., water, helium, hydrogen, or ions can enter the sodalite cage.

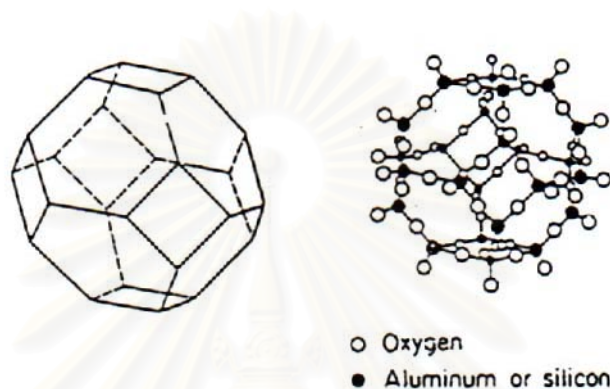


Figure 3.7 Sodalite cage structure. A formal representation of a truncated octahedron is shown on the left, and individual atoms are indicated on the right ; the lines in the structure on the left represent oxygen anions, and the points of intersection represent silicon or aluminium ions [13].

The unit cell of the faujasite-type zeolite is cubic with a unit-cell dimension of 25 \AA , and it contains 192 silica and alumina tetrahedra. The unit cell dimension varies with Si/Al ratio. Each sodalite unit in the structure is connected to four other sodalite units by six bridge oxygen ions connecting the hexagonal faces of two units, as shown in Figure 3.8. The truncated octahedra are stacked like carbon atom in a diamond. The oxygen bridging unit is referred to as a hexagonal prism, and it may be considered another secondary unit. This structure results in a supercage (sorption cavity) surrounded by 10 sodalite unit which is sufficient large for an inscribed sphere with a diameter of 12 \AA . The opening into this large cavity is bounded by 6 sodalite units, resulting in a 12 member oxygen ring with a 7.4 \AA free diameter. Each cavity is connected to four other

cavities, which in turn are themselves connected to three additional cavities to form a highly porous framework structure.

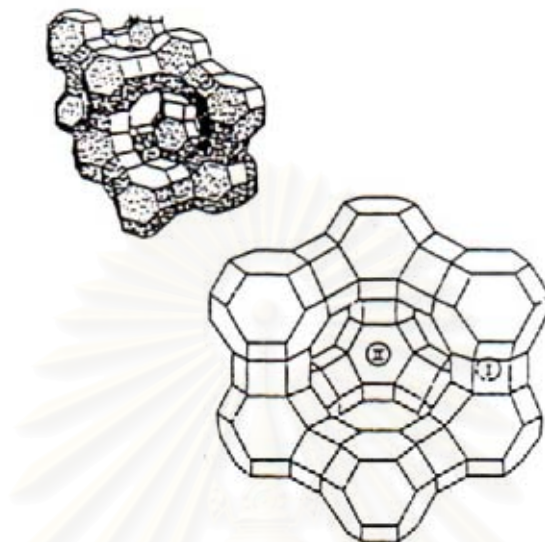


Figure 3.8 Perspective views of the faujasite structure. The silicon or aluminium ions are located at the corner and the oxygen ions near the edges. Type I and II sites are indicated ; the supercage is in the center [13].

This framework structure is the most open of any zeolite and is about 51 percent void volume, including the sodalite cage; the supercage volume represents 45 percent of the unit cell volume. The main pore structure is three-dimensional and large enough to admit large molecules, e.g., naphthalene and fluorinated hydrocarbon. It is within the pore structure that the locus of catalytic activity resides for many reactions. A secondary pore structure involving the sodalite unit exists but its apertures are too small to admit most molecules of interest in catalysis.

3.4 Zeolites as Catalysts [9]

The first use of zeolite as catalysts occurred in 1959 when zeolite Y was used as an isomerization catalyst by Union Carbide. More important was the first use of zeolite X as a cracking catalyst in 1962, based upon earlier work by Plank and Rosinski. They noted that relatively small amounts of zeolites could be incorporated into the then-standard silica/alumina or silica/clay catalysts. The use of zeolite in this way as promoters for petroleum cracking greatly improved their performance.

3.4.1 Potential versatility of zeolites as catalysts

Vaughan has graphically described zeolites as “molecules boxes” which have variable dimensions suited to the encouragement of molecular rearrangements inside their confined geometry. The conditions inside the ‘box”, and of box itself, can be controlled in a variety of ways based upon the unique properties of zeolite frameworks as summarized in Table 3.2.

3.4.1.1 Crystal voidage and channels

Although some heterogenous reactions will take place at the external crystal surface, most practical zeolite catalysis takes place inside the framework. Here zeolites have the advantage of a very large internal surface, about 20 times larger than their external surface for the more open framework (e.g. zeolite X and Y). This internal capacity provides the appropriate surfaces at which catalytic transformation can take place. In the faujasite zeolite is typically in the series of large cavities easily available via three-dimensional open-pore networks.

Further flexibility which is useful for planned catalytic uses arises in the more recently produced zeolites with subtle different cavity and channel systems. ZSM-5, for instance, has a three-dimensional system linked via intersections rather than cavities and mordenite catalysis seems to take place only in the largest channels.

Table 3.2 Correlation between zeolite properties and catalytic functionality [9].

Property	Catalytic Functionality
Crystal voidage and channels	Extensive internal surface to encourage catalytic processes.
Variable pore size	Creates both reactant and product selectivity via molecules sieving.
Ion exchange	Cations (i) control pore size, (ii) create high potential energy field within voidage (active site) and (iii) enable distribution of catalytically active metals on the zeolite substrate.
Salt occlusion	Controls pore size, provide another method of metal incorporation and can improve thermal stability and poisoning resistance.
Framework modification	Varies lattice change (by synthesis or modification) to enhance active site production and thermal stability.

3.4.1.2 Variable pore sizes

Given that catalytic reaction takes place largely within zeolite framework, access to this environment is patently controlled by oxygen windows. This is diffusion limited process, as is the effect of product molecules after transformations have taken place. This means that zeolites have very special practical advantages over the more traditional catalysts, in that admit only certain reactant molecules and this can be potentially tailored to produced selected product. This selectivity is known as “shaped-selective catalysis” and controlled by “configurational diffusion” – this phrase was coined by Weiss to express a diffusion regiment in which useful catalytic reactions and promoted by virtue of a matching of size, shapes and orientation of the reactant product molecules to the geometry of zeolitic framework.

3.4.1.3 Ion exchange

Perhaps more relevant is the way in which ion exchange can be employed to place cations into very specific framework sites so as to create small volumes of high electrostatic field. These fields are “active sites” to which an organic reactant molecule can be attracted thus promoting the bond distortion and rupture essential to molecular rearrangements.

Another feature of ion exchange is that it provides a route for the introduction of metal cations with a view to their subsequent reduction to metal particles. These exist in the so-called “bifunctional” zeolite catalysts used to effect both hydrogenation and dehydrogenation reactions.

3.4.1.4 Salt occlusion

The introduction of a salt molecule into a zeolite can be the first stage in the incorporation of a metal for subsequent reduction as mentioned above. It can also be used to enhance thermal stability. Yet another purpose is to “pacify” zeolite cracking catalysts. The problem here is that crude oil contains metal cations (Ni, Cu, V, Fe) originating from the metal porphyrins thought to play an inherent part in the geological formation of oil. These metals create unwanted reactivity causing carbon (coke) formation and subsequent loss of catalytic properties. The occlusive introduction of stannates, bismuth, or antimonates pacifies these metals to extend useful catalyst bed life. It enables the refinery to cope with a variety of crude oil from different oil fields and illustrates the flexible technology which can be achieved in zeolite catalysis.

Other salt treatments, via phosphates or fluorides, have been used to improve performance.

3.4.1.5 Framework modification

The electrostatic field of zeolite can be manipulated by isomorphous substitution into framework Si and Al sites, This can be done by synthetic or modification routes. When the Si:Al ratio is close to 1 the field strength is at its highest as is the cation content- i.e. the conditions of maximum negative charge on the framework. An increase of the Si:Al causes a greater separation of negative charge and hence higher field gradients (obviously also condition by cation position and cation types). In this way, the catalytic activity can be controlled, and parameters altered. A well known example of these effects is the way in which the thermal and chemical stabilities of synthetic faujasite can be critically altered by aluminum removal.

Framework substitution also can be created by the introduction atoms other than Si and Al into tetrahedral sites via synthesis or modification. The ZSM-5 can accept B and Ga into tetrahedral sites by simple salt treatment as mentioned earlier, although a similar reaction in other frameworks is by no means as facile.

3.5 Zeolite Active sites

3.5.1 Acid sites

Classical Bronsted and Lewis acid models of acidity are used to classify the active sites on zeolites. Bronsted acidity is proton donor activity; a tridiagonally coordinated alumina atom is an electron deficient and can accept an electron pair, therefore as a Lewis acid [14,15].

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite [16]. Since the number of acidic OH groups depend on the number of aluminum zeolite's framework, decrease in Al content is expected to reduce catalytic activity of zeolite. If the effect of increase in the acidic centers, increase Al content, shall result in enhancement of catalytic activity.

Based on electrostatic consideration, the charge density at a cation site increases with increasing Si/Al. It was conceived that these phenomena are relate to reduction of electrostatic interaction between framework sites, and possibly to difference in the order of aluminum in zeolite crystal-the location of Al in crystal structure [15].

Recently it has been reported the mean charge on proton was shifted regularly towards higher values as the Al content decreased [14]. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms, were decreased. This evidence emphasized that the entire acid strength distribution (weak, medium, strong) was shifted towards stronger values. That is the weaker acid sites become stronger with the decrease in Al content.

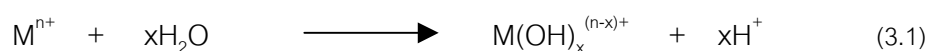
An important in thermal and hydrothermal stability has been described to the lower density of hydroxyls groups which is parallel to the Al content [14].

A longer distance between hydroxyl groups decreases the probability of dehydrogenation that generates defects on structure of zeolites.

3.5.2 Generation of acid centers

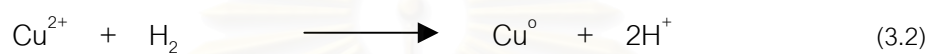
Protonic acid centers of zeolite are generated in various ways. Figure 3.9 depicts the thermal decomposition of ammonium exchange zeolites yielding the hydrogen form [10].

The Bronsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 3.10 [17].



The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very acidic centers by hydrolysis phenomena.

The Bronsted acid sites are also generated by the reduction of transition metal cations. The concentration of OH groups of zeolite containing transition metals was noted to increase by reduction with hydrogen at 250-450 °C to increase with the rise of the reduction temperature [17].



The formation of Lewis acidity from Bronsted sites is depicted in Figure 3.12 [17]. The dehydration reaction decreases the number of protons and increases that of Lewis sites.

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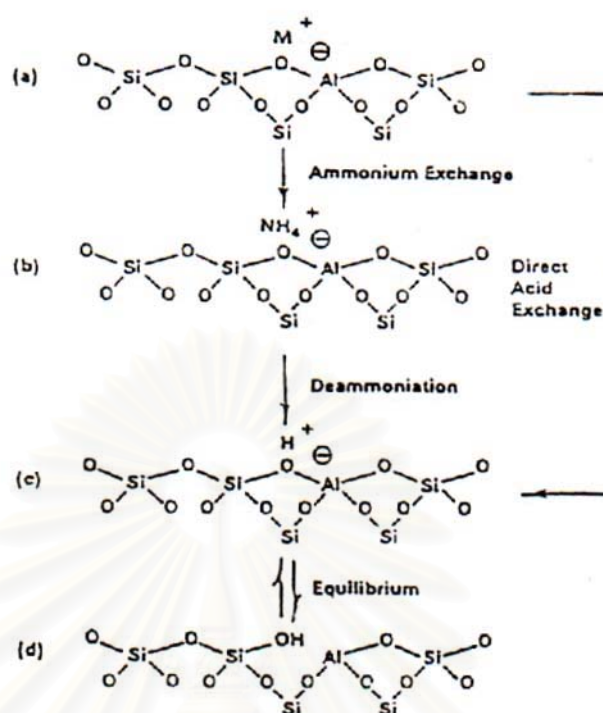


Figure 3.9 Diagram of the surface of a zeolite framework

- (a) In the as-synthesized form M^+ is either an organic cation or an alkali metal cation.
- (b) Ammonium in exchange produces the NH_4^+ exchanged form.
- (c) Thermal treatment is used to remove ammonia, producing the H^+ , the acid form.
- (d) The acid form in (c) is in equilibrium with the form shown in (d), where there is a silanol group adjacent to a tricoordinate aluminum

[10].

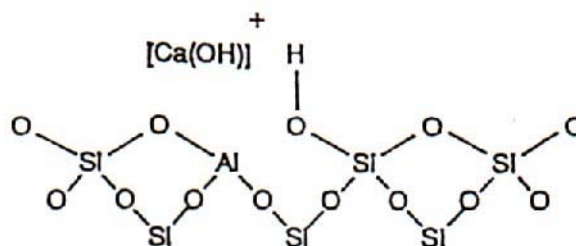


Figure 3.10 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity [17].

Bronsted (OH) and Lewis (-Al-) sites can be presented simultaneously in the structure of zeolite at high temperature. Dehydroxylation is thought to occur in ZSM-5 zeolite above 500 °C and calcination at 800-900 °C produces irreversible dehydroxylation which causes deflection in crystal structure of zeolite.

Dealumination is believed to occur during dehydroxylation which may result from the steam generation within the sample. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in Figure 3.12 [17]. The extent of dealumination monotonously increases with the partial pressure of steam.

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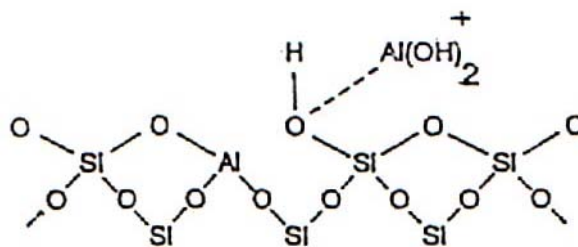


Figure 3.13 The enhancement of acid strength of OH group by their interaction with dislodge aluminum species [17].

The enhancement of the acid strength of OH groups recently proposed to be pertinent to their interaction with those aluminum species sites tentatively expressed in Figure 3.13 [17]. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.

3.5.3 Basic sites

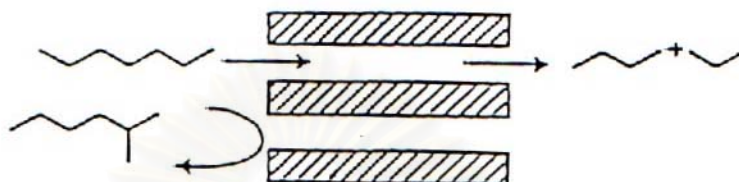
In certain instances reactions have been shown to be catalyzed at basic (cation) sites in zeolites without any influence from acid sites. The best characterized example of this is that of K-Y which splits n-hexane isomers at 500 °C. The potassium cations have been shown to control the unimolecular cracking (β -scission). Free radical mechanisms also contribute to surface catalytic reactions in these studies.

3.6 Shape – Selectivity Catalysis

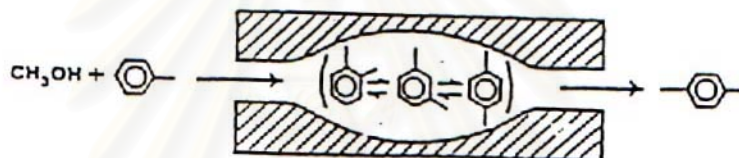
Many reactions involving carbonium ions intermediates are catalyzed by acidic zeolites. With respect to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any other acidic oxides. What zeolite add is shape selectivity effect. The shape selectivity characteristic of zeolites influence their catalytic phenomena by three modes; reactant shape selectivity, product shape

selectivity and transition state shape selectivity [10, 18, 19]. These type of selectivity are depicted in Figure 3.14 [10].

a) Reactant selectivity



b) Product selectivity



c) Transient state selectivity

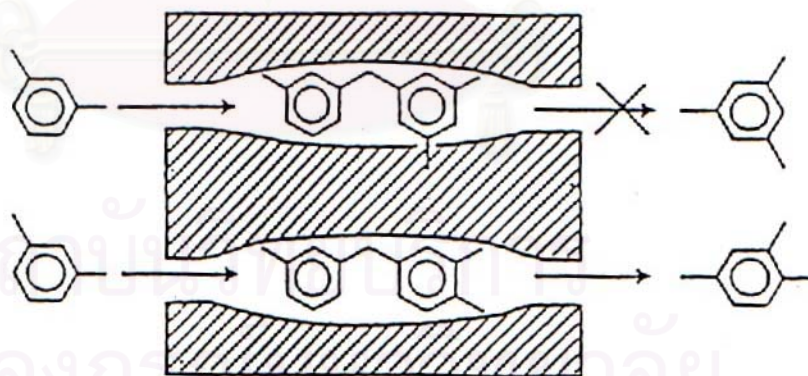


Figure 3.14 Diagram depicting the three types of selectivity [10].

Reactant or change selectivity results from the limited diffusibility of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites.

Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reactions. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect arising from local environment around the active site, the rate constant for a reaction mechanism is reduced if the space required for formation of necessary transition state is restricted.



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Table 3.3 Kinetic diameters of various molecules based on the Lennard-Jones relationship [18].

	Kinetic Diameter (Angstroms)
He	2.60
H ₂	2.89
O ₂	3.46
N ₂	3.64
NO	3.17
CO	3.76
CO ₂	3.30
H ₂ O	2.65
NH ₃	2.60
CH ₄	3.80
C ₂ H ₂	3.30
C ₂ H ₄	3.90
C ₃ H ₈	4.30
n-C ₄ H ₁₀	4.30
Cyclopropane	4.23
i-C ₄ H ₁₀	5.00
n-C ₅ H ₁₂	4.90
SF ₆	5.50
Neopentane	6.20
(C ₄ F ₉) ₃ N	10.20
Benzene	5.85
Cyclohexane	6.00
m-xylene	7.10
p-xylene	6.75
1,3,5 trimethylbenzene	8.50
1,3,5 triethylbenzene	9.20
1,3 diethylenebenzene	7.40
1-methylnapthalene	7.90
(C ₄ H ₉) ₃ N	8.10

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and can pass through openings which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of molecules must be taken into account.

Table 3.3 [18] presents values of selected critical molecular diameters and Table 3.4 [10] presents values of the effective pore size of various zeolites. Correlation between pore size(s) and kinetic diameter of some molecules are depicted in Figure 3.15 [18].

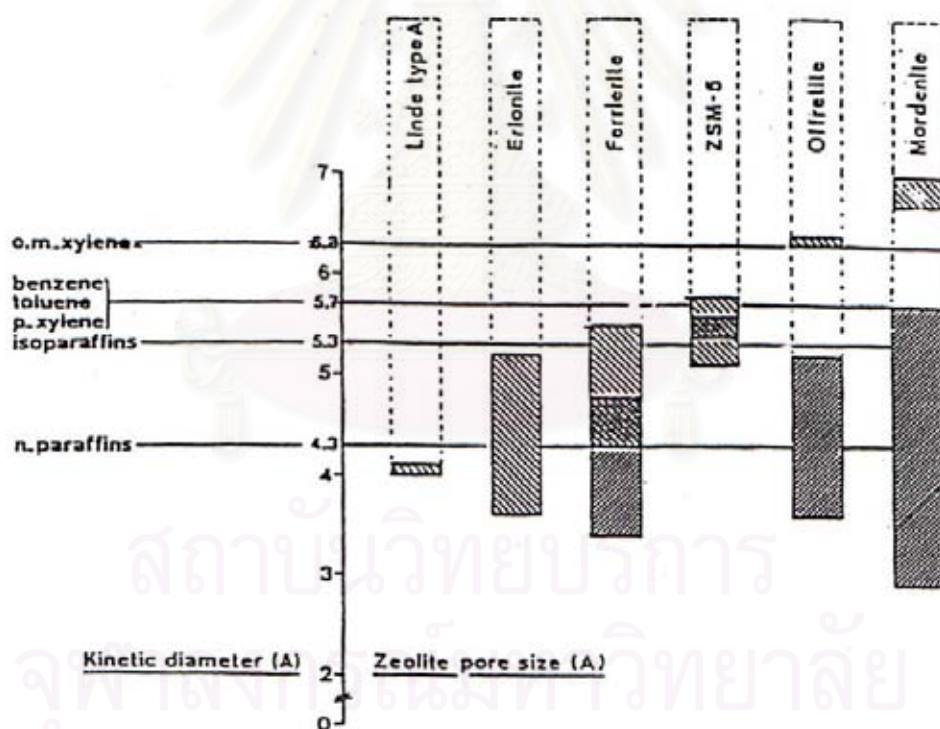


Figure 3.15 Correlation between pore size(s) of various zeolites and kinetic diameters of some molecules [18].

Table 3.4 Shape of the pore mouth opening of known zeolite structures. The dimensions are based on two parameters, The T atom forming the channel opening (8, 10, 12 ring) and the crystallographic free diameters of the channels. The channels are parallel to the crystallographic axis shown in brackets (e.g.<100>) [10].

STRUCTURE	4-MEMBER RING	10-MEMBER RING	12-MEMBER RING
Bikitaite	3.2x4.9[001]		
Brewstente	2.3x5.0[100] 2.7x4.1[001]		
Cancrinite			6.2[001]
Chabazite	3.6x3.7[001]		
Dachiardite	3.6x4.8[001]	3.7x6.7[010]	
TMA-E	3.7x4.8[001]		
Edingtonite	3.5x3.9[110]		
Epistibite	3.7x4.4[001]	3.2x5.3[100]	
Erionite	3.6x5.2[001]		
Faujasite			7.4<111>
Ferrierite	3.4x4.8[010]	4.3x5.5[001]	
Gismondine	3.1x4.4[100] 2.8x4.9[010]		
Gmelinite	3.6x3.9[001]		7.0[001]
Heulandite	4.0x5.5[100] 4.1x4.7[001]	4.4x7.2[001]	
ZK-5	3.9<100>		
Laumontite		4.0x5.6[100]	
Levyne	3.3x5.3[001]		
Type A	4.1<100>		
Type L			7.1[001]
Mazzite			7.4[001]
ZSM-11		5.1x5.5[100]	
Merlinoite	3.1x3.5[100] 3.5x3.5[010] 3.4x5.1[001] 3.3x3.3[001]		
ZSM-5		5.4x5.6[010] 5.1x5.5[100]	
Mordenite	2.9x5.7[010]		6.7x7.0[001]
Natrolite	2.6x3.9<101>		
Offretité	3.6x5.2[001]		6.4[001]
Paulingite	3.9<100>		
Phillipsite	4.2x4.4[100] 2.8x4.8[010] 3.3[001]		
Rho	3.9x5.1<100>		
Stibite	2.7x5.7[101]	4.1x6.2[100]	
Thomsonite	2.6x3.9[101] 2.6x3.9[010]		
Yugawaralite	3.1x3.5[100] 3.2x3.3[001]		

3.7 Mechanism of Cracking Processes

Cracking processes were assigned to two fundamental classes ;

3.7.1 Thermal cracking [21]

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.

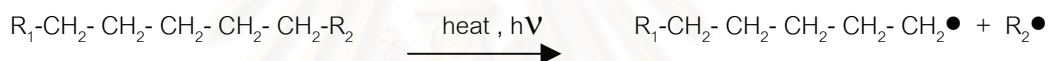
Cracking of either the original or isomerized radical then takes place at a carbon-carbon bond located in the β position to the carbon atom lacking one hydrogen atom. Cracking at the β position gives directly an alpha olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in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

The primary radical derived from this step may immediately recombine at the β bond 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 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 cracking, 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.

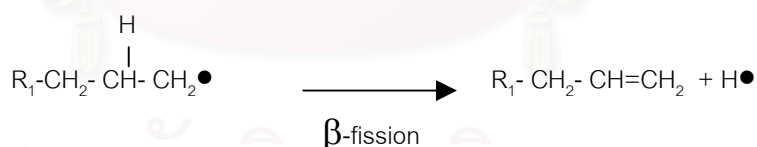
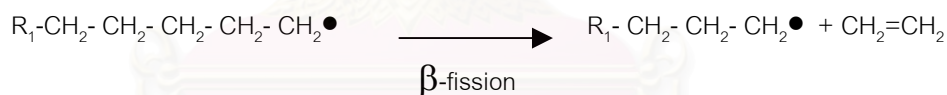
A schematic representation of polyethylene cracking is as follows;

1. Initiation Step

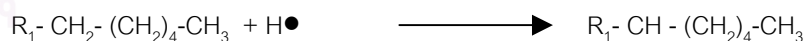


2. Propagation Step

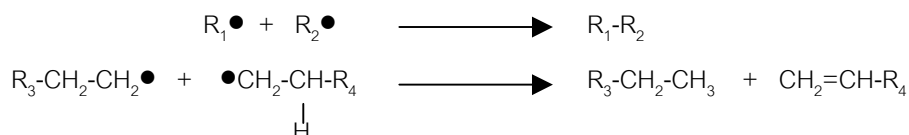
2.1 β -fission



2.2 Chain transfer



3. Termination Step



3.7.2 Catalytic cracking [26]

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

Commercial cracking catalysts can be divided into three classes: [24]

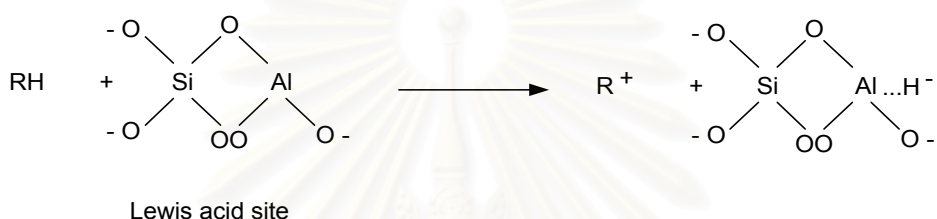
- 1 Acid-treated natural aluminosilicates
- 2 Amorphous synthetic silica-alumina
- 3 Crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves.

Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are:

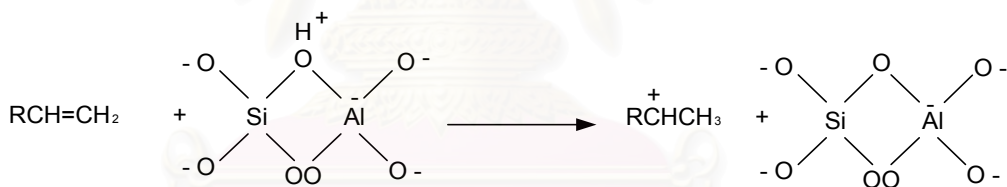
1. Higher activity
2. Higher gasoline yields at a given conversion
3. Product of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons
4. Lower coke yield
5. Increased isobutane production

A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer lived and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbonium ions. The following illustrates the different ways by which carbonium ions may be generated in the reactor :

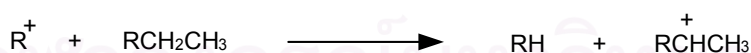
1. Abstraction of a hydride ion by a Lewis acid site from a hydrocarbon



2. Reaction between a Bronsted acid site (H^+) and an olefin

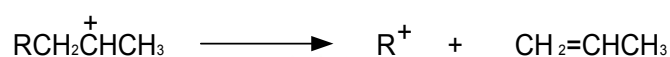


3. Reaction of a carbonium ion formed from step 1 or 2 with another hydrocarbon by abstraction of a hydride ion



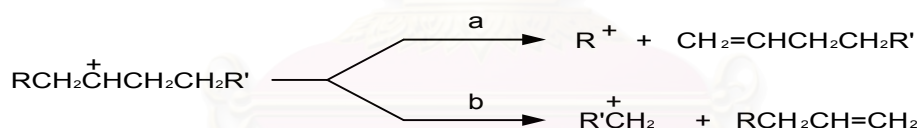
Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position. The formed carbonium ion can rearrange through a methide-hydride shift similar to what has been explained in catalytic reforming. This isomerization reaction is responsible for a high ratio of branched isomers in the products.

The most important cracking reaction, however, is the carbon-carbon β bond scission. A bond at a position beta to the positively-charged carbon breaks heterolytically, yielding an olefin and another carbonium ion. This can be represented by the following example :



The new carbonium ion may experience another β scission, rearrange to a more stable carbonium ion, or react with a hydrocarbon molecule in the mixture and produce a paraffin.

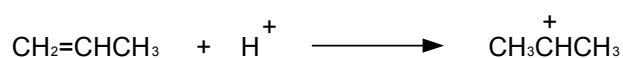
The carbon-carbon β scission may occur on either side of the carbonium ion, with the smallest fragment usually containing at least three carbon atoms. For example, cracking a secondary carbonium ion formed from a long chain paraffin could be represented as follows :



If $\text{R} = \text{H}$ in the above example, then according to the β scission rule (an empirical rule) only route b becomes possible, and propylene would be a product :

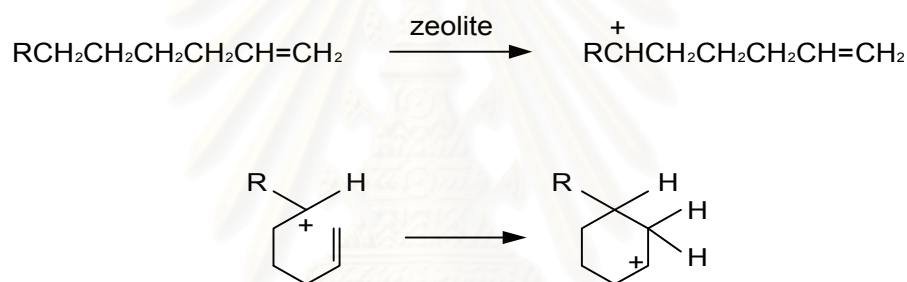


The propene may be protonated to an isopropyl carbonium ion :



An isopropyl carbonium ion cannot experience a β fission (no C-C bond β to the carbon with the positive charge). It may either abstract a hydride ion from another hydrocarbon, yielding propane, or revert back to propene by eliminating a proton. This could explain the relatively higher yield of propene from catalytic cracking units than from thermal cracking units.

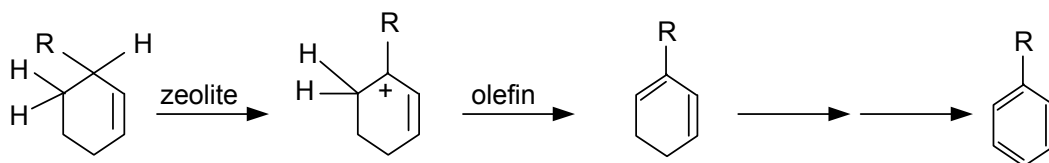
Aromatization of paraffins can occur through a dehydrocyclization reaction. Olefinic compounds formed by the β scission can form a carbonium ion intermediate with the configuration conducive to cyclization. For example, if a carbonium ion such as that shown below is formed (by any of the methods mentioned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



Once cyclization has occurred, the formed carbonium ion can lose a proton, and a cyclohexene derivative is obtained. This reaction is aided by the presence of an olefin in the vicinity ($\text{R}-\text{CH}=\text{CH}_2$).



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



During the cracking process, fragmentation of complex polynuclear cyclic compounds may occur, leading to formation of simple cycloparaffins. These compounds can be a source of C₆, C₇ and C₈ aromatics through isomerization and hydrogen transfer reactions.

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



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CHAPTER IV

EXPERIMENT

4.1 Raw material

All types of plastic used in experiments were supplied from Thai Petrochemical Industry Public Company Limited. They were virgin plastics of 3-4 mm. diameter pellets.

4.2 Types of catalyst

The catalysts were obtained from Professor Fujimoto's catalytic research laboratory, the University of Tokyo which had the ratio of Si/Al 18 and 44.

4.3 Analyzing structure of crystallites by X-ray diffraction

X-ray diffraction patterns (XRD ; Perkin Elmer 1760X) of the catalysts were performed by Scientific And Technological Research Equipment Center Chulalongkorn University (STREC).

4.4 Apparatus and Reaction Method

The reaction was carried out by using apparatus shown in **Figure 4.1**. A mass of 20 g of low-density polyethylene were put in a stainless steel reactor of 30 mm inner diameter and 0.5 g of catalyst. Hydrogen gas was supplied from a cylinder to fill into the inside of the reactor with a pressure of 30 kg/cm². The reactor was heated from room temperature to 450 °C and maintain at this temperature for any reaction times. The reaction temperature was controlled by a programmable temperature controller. The oil products were analyzed by Gas Chromatograph (GC Simulated Distillation).

Polyethylene conversion reaction was carried out under the following conditions :

- Pressure of hydrogen gas range of 10-30 kg/cm²
- Reaction temperature range of 400-480 °C
- Reaction time range of 30-60 min.
- Mole Ratio Si/Al of HZSM-5 Catalyst, 18 and 44
- Mass of catalyst per polyethylene, 0.1 and 0.5 per 20 g of polyethylene



Figure 4.1 The Reaction Experimental Unit for conversion of polyethylene into gasoline using HZSM-5 type catalyst.

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4.5 Functional-Group Compositional Analysis

Functional group of oil product was analyzed by Fourier Transform Infrared Spectrometry at Scientific and Technological Research Equipment Center Chulalongkorn University (STREC).

4.6 The reaction products were analyzed by Gas Chromatographs

The boiling ranges of oil yield were determined by Gas Chromatograph (GC Simulated Distillation) at PTT Research and Technology Institute for naphtha (IBP-200 °C) , kerosene (200-250 °C) , gas oil (250-350 °C) and long residue (up to 350 °C)⁽³⁴⁾.



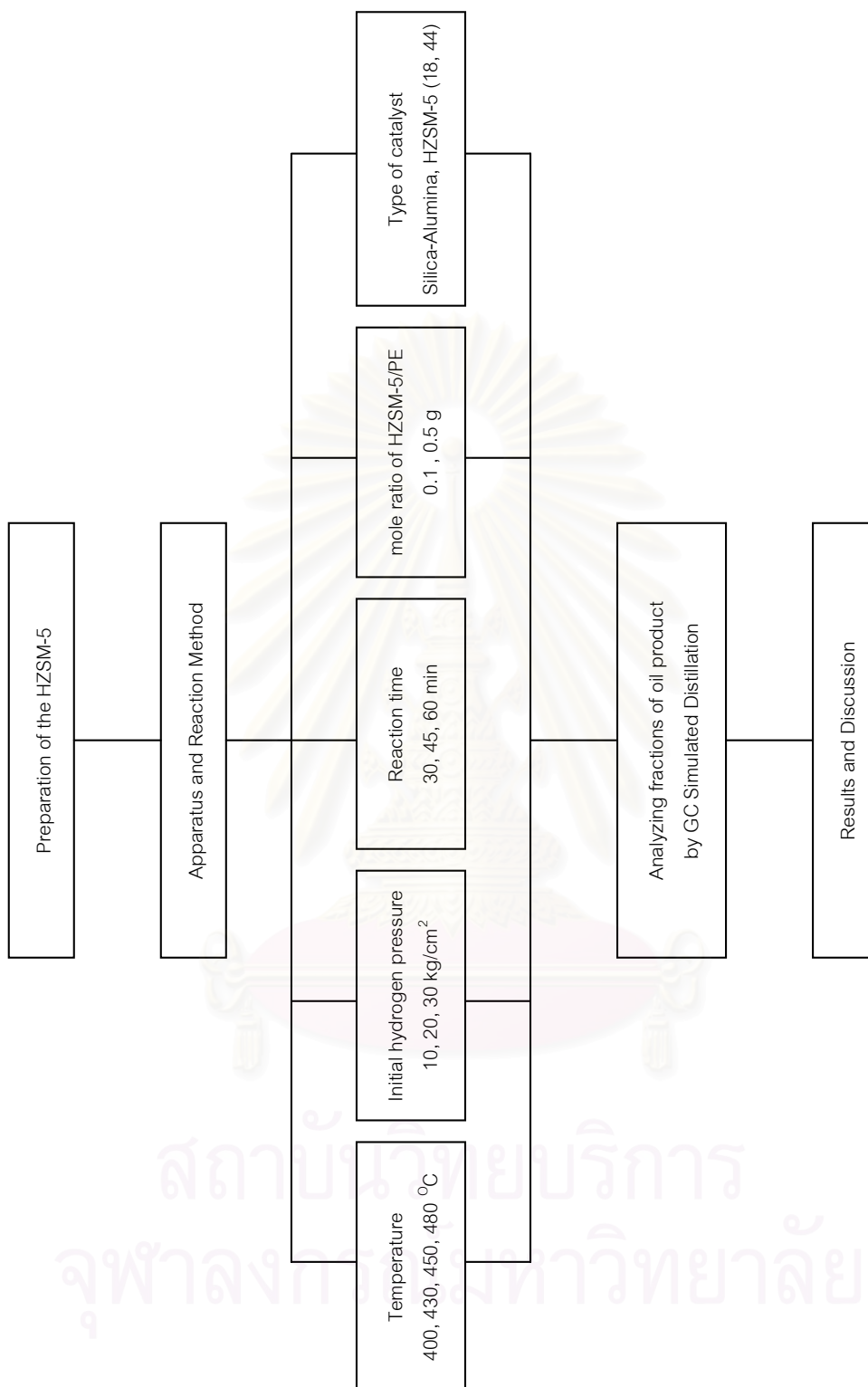


Figure 4.2 Experiment scheme of the conversion of polyethylene into gasoline on HZSM-5 catalyst.

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 X-Ray Diffraction Patterns

The x-ray diffraction patterns for the crystals were shown in **Figures 5.1-5.2**. The patterns of HZSM-5 confirmed the same type as that of The International Zeolite Association⁽²⁹⁾. Framework of HZSM-5 zeolite with a Si/Al ratio of 18 as **Figure 5.1**, similar to H-mordenite zeolite. The structure is built up from pentagonal interconnected via 12 oxygen ring units and contains extremely large supercages, 0.74 nm diameter. **Figure 5.2** indicated that the HZSM-5 zeolite with a Si/Al ratio of 44 also has the pentasil pore opening structure typical for the general HZSM-5 catalyst. The structure of this zeolite is channel which has 0.55 nm pore diameter and entered through 10 oxygen ring.⁽¹²⁾

5.2 Functional-Group Compositional Analysis

Figures 5.3-5.5 showed the functional-group compositional analysis of the liquid yield from the conversion of HDPE, LDPE, and PS. Also **Figure 5.6** showed the functional-group compositional analysis of LDPE/PS analyzed by Fourier transform infrared (FT-IR) spectroscopy.

The polyalkene plastics, HDPE and LDPE showed the same traces FT-IR spectra since their polymer structures are very similar. Their thermal degradations are likely to produce similar compounds in the liquid yield.

Figure 5.5 showed the functional-group compositional analysis of the liquid yield from PS produced a strong presence of both aromatic and aliphatic functional groups. It has been shown that liquid yield from PS produces mainly aromatic oil, consequently the

aliphatic functional groups indicated by the FT-IR spectra probably indicated that these aliphatic groups were present as alkyl groups attached to aromatic rings.

The FT-IR spectra from the liquid yield from the conversion of LDPE/PS, was shown in Figure 5.6 . The polyalkene plastics of LDPE, when mixed with PS gave very similar FT-IR spectra, which consisted essentially of the mixed spectra from each component. Each of the spectra contained the majority of alkane and alkene peaks which derived from the polyalkene plastics and the mainly aromatic peaks derived from the PS.



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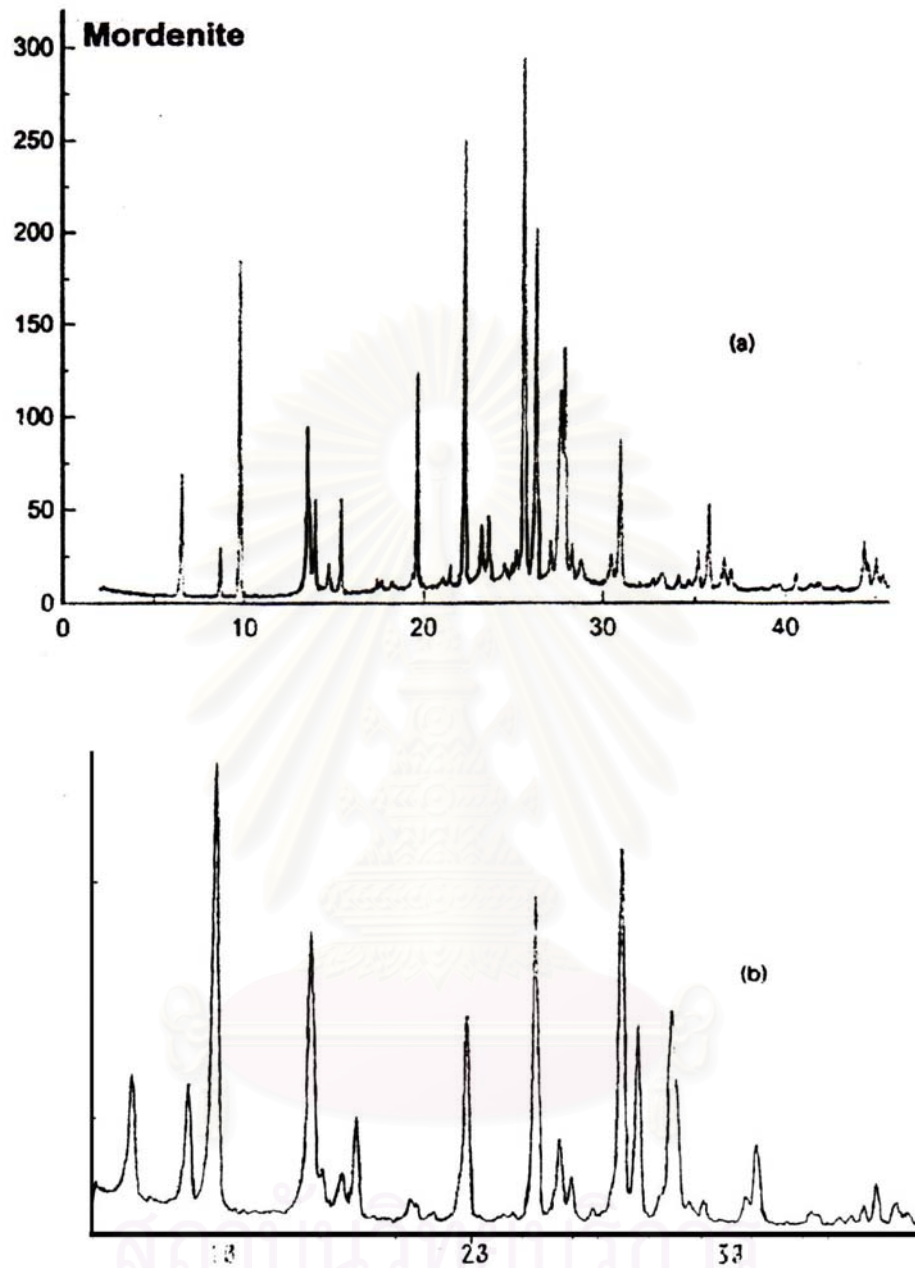


Figure 5.1 Comparisons of X-ray diffraction patterns for (a) HZSM-5 of The International Zeolite Association [29], (b) HZSM-5 mole ratio Si/Al is 18.

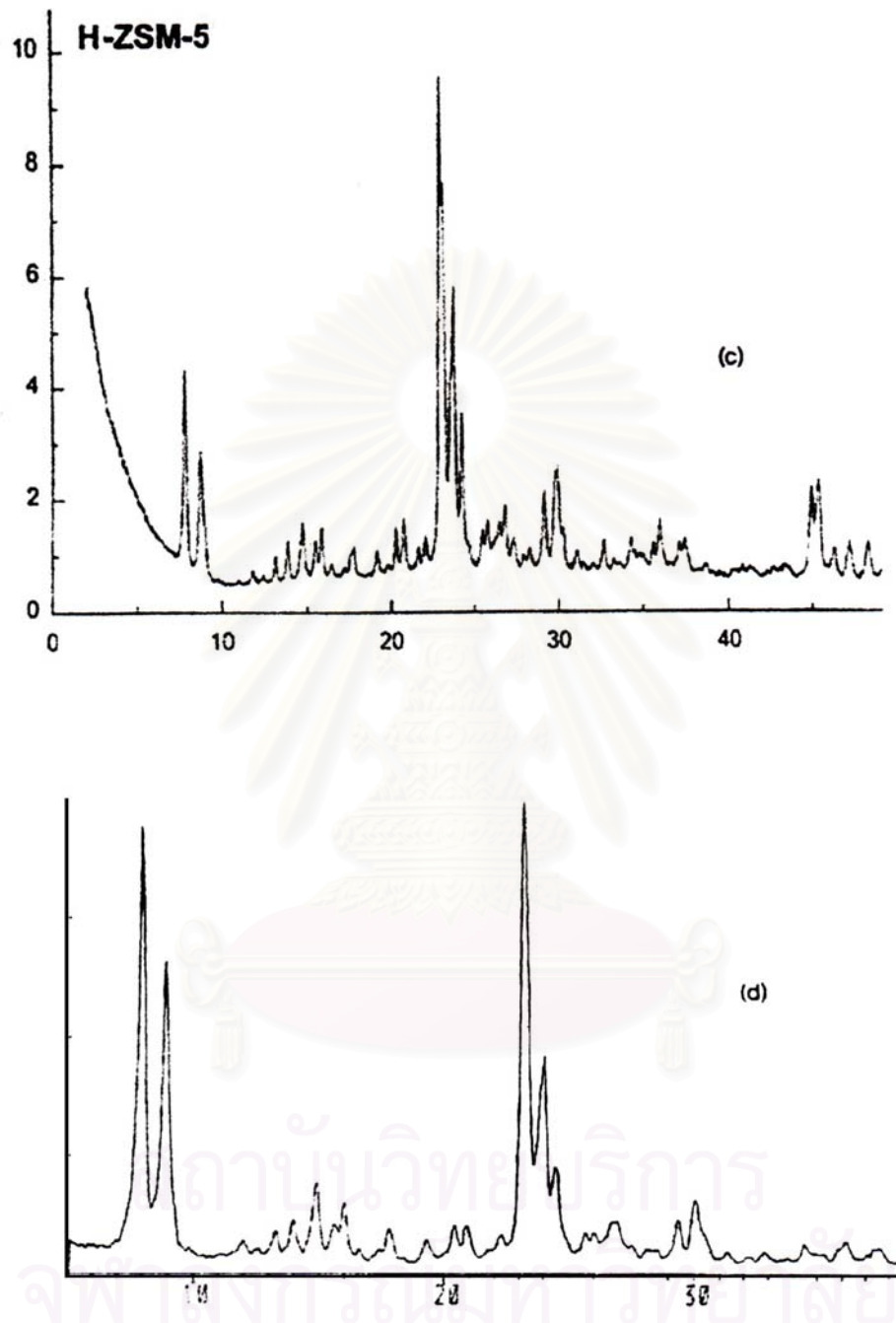


Figure 5.2 Comparisons of X-ray diffraction patterns for (c) HZSM-5 of The International Zeolite Association [29] , (d) HZSM-5 mole ratio Si/Al is 44.

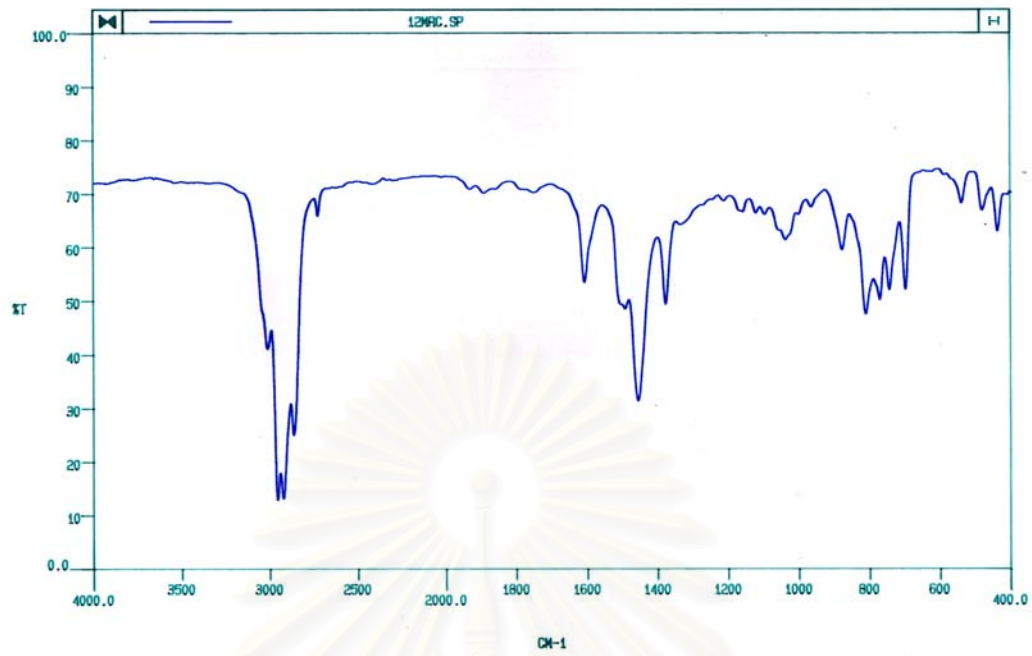


Figure 5.3 Fourier transform infrared spectrum of oil derived from HDPE.

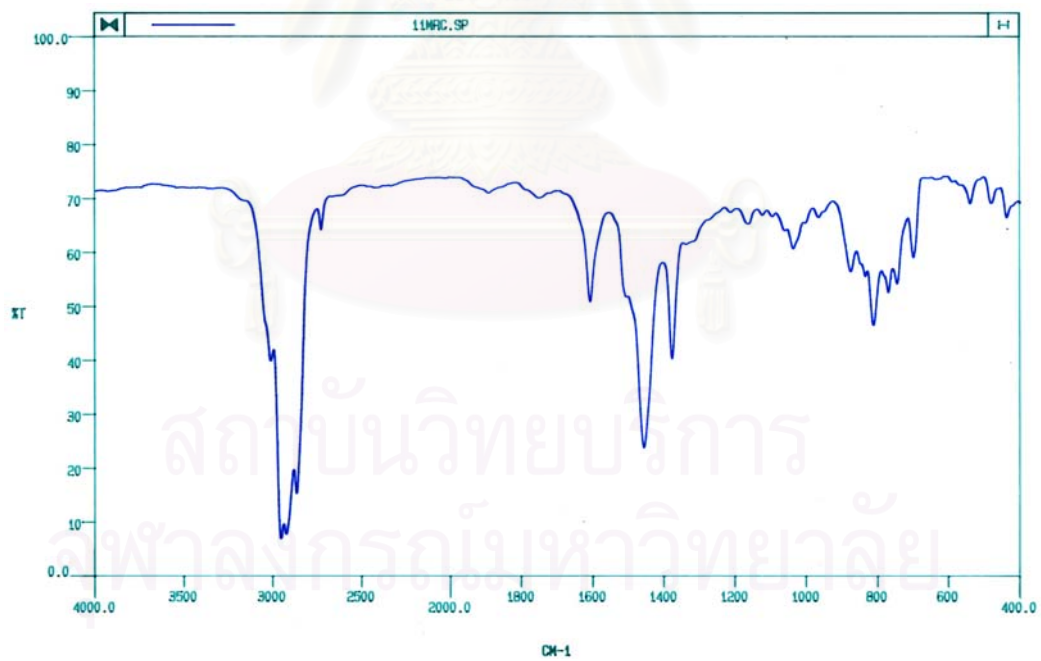


Figure 5.4 Fourier transform infrared spectrum of oil derived from LDPE.

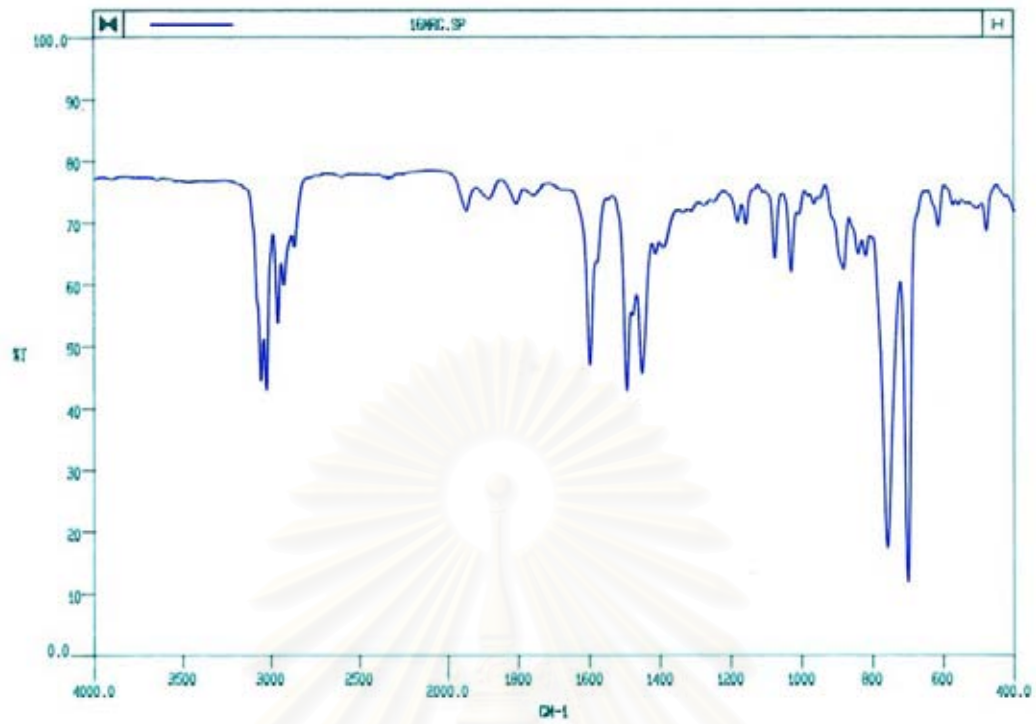


Figure 5.5 Fourier transform infrared spectra of oil derived from PS.

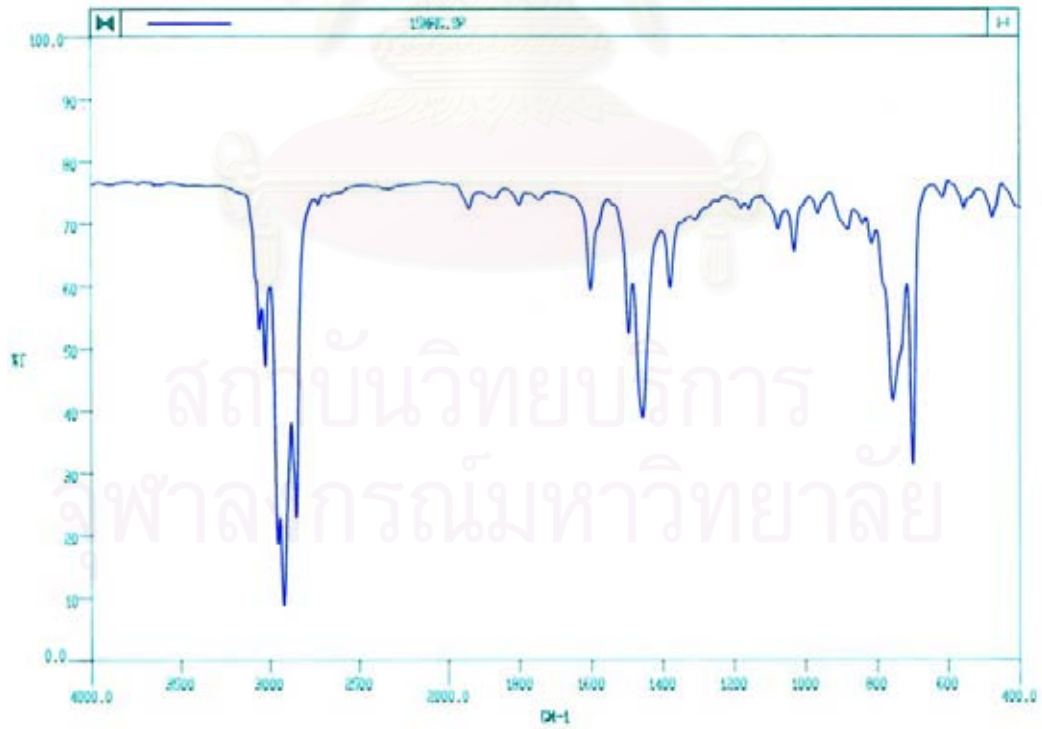


Figure 5.6 Fourier transform infrared spectra of oil derived from LDPE/PS.

5.3 Effect of raw material on conversion of oil product

Figure 5.7 showed the effect of using low- and high density polyethylene (LDPE and HDPE) , respectively as different raw material on composition of oil product. Experiments were carried out at 30 kg/cm² of hydrogen gas, temperature 450 °C, 20 g of polyethylene, 60 min of reaction time and 0.5 g of HZSM-5 zeolite with a Si/Al ratio of 44. The results revealed that the compositions of gas, naphtha, light gas oil and heavy gas oil were not significantly different while kerosene, long residue and solid were slightly different. These could be explained that the catalytic cracking of LDPE proceeded easier than the degradation of HDPE, because of high-density polyethylene was typically formed by linear macromolecules, where as low-density polyethylene was characterized by more degree of branching than HDPE, as a result the more cracking of LDPE than HDPE which we could notice that the total % of heavy hydrocarbon from kerosene and solid of HDPE was slightly more than LDPE, and it confirmed also the % of yield from LDPE was more than about 2%. For this reason, the next experiment LDPE was used as a reactant for studying the effect of parameters.

5.4 Effect of catalysts on composition of oil product

Figure 5.8 showed the effect of the catalytic cracking of low-density polyethylene on different types of catalyst such as SiO₂-Al₂O₃ , HZSM-5 (Si/Al=18) and HZSM-5 (Si/Al=44). The pore size average of SiO₂-Al₂O₃ and HZSM-5 are in the range of 2-8 nm and 0.4-0.8 nm⁽¹³⁾, these showed that SiO₂-Al₂O₃ was mesopore while HZSM-5 was micropore. When the reaction took place, firstly high temperature caused thermal cracking to break down the heavy molecules to moderate molecules such as kerosene or gas oil after that these molecules could enter the pore size of catalyst and the catalytic reaction was occurred. Normally zeolite HZSM-5 was activity more than SiO₂-Al₂O₃ , because of high acidity at the surface of zeolite. When using zeolite for cracking , the carbon-carbon bond scission easily crack to liquid yield such as naphtha preferentially, and consequently the long residues were low (6.35%) comparing the

using of $\text{SiO}_2\text{-Al}_2\text{O}_3$ 9.75%. We noticed in **Figure 5.8** that HZSM-5 (Si/Al=44) gave high percentage of naphtha (44.48%), low long chain hydrocarbon comparing to HZSM-5 (Si/Al=18) and $\text{SiO}_2\text{-Al}_2\text{O}_3$ which gave naphtha 36.12% and 20.99% respectively. From the result of the effect of types of catalyst which implied the acidity of the catalyst. The more acidity, the more naphtha was obtained and the less long chain hydrocarbon such as kerosene, gas oil, long residues and solid. For this reason, the HZSM-5 of which Si/Al is 44 was appropriate to be used as catalyst.

5.5 Effect of reaction temperatures on composition of oil product

The reaction temperature was set up more than $400\text{ }^\circ\text{C}$, because it totally turned to oil liquid product. For this reason we varied only three values of temperature 430, 450 and $480\text{ }^\circ\text{C}$. If we used more than $480\text{ }^\circ\text{C}$, the product could be largely cracked and became gases and solid at the surface of catalyst. When the temperature increased from $430\text{ }^\circ\text{C}$ to $450\text{ }^\circ\text{C}$, in **Figure 5.9** we found that the percent oil yield product increased by 10%, because the higher temperature ($450\text{ }^\circ\text{C}$) accelerating the thermal cracking which changed LDPE to kerosene and gas oil. After that kerosene and gas oil was catalytically cracked at the surface of HZSM-5 to convert to naphtha and gases (normally $\text{C}_1\text{-C}_4$). We noticed that at $450\text{ }^\circ\text{C}$ kerosene and gas oil were more than those of $430\text{ }^\circ\text{C}$ about 5% and 6% respectively. In the contrary we found total solid increased by 2% at the surface of catalyst which meant that coking occurred also at the same time. When the temperature reached to $480\text{ }^\circ\text{C}$, we noticed the decreasing largely of naphtha and kerosene about 9% and 8% respectively. It seemed that when higher temperature was used, light hydrocarbon could be cracked more, as a result we found the % of gases increasing about 20%, because thermal cracking was faster than catalytic cracking. The result of this effect showed that temperature of $450\text{ }^\circ\text{C}$ gave the appropriate % oil yield, naphtha, kerosene and gas oil.

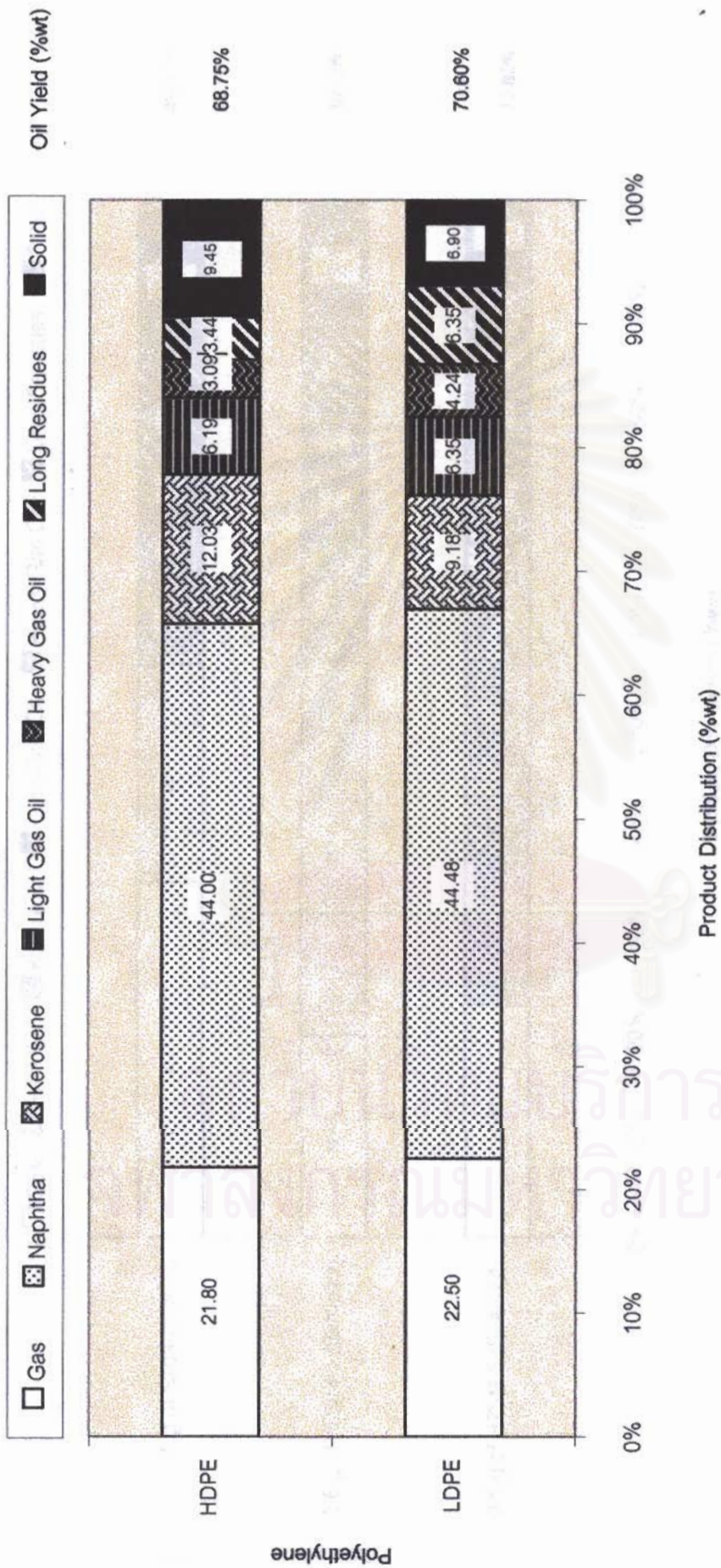


Figure 5.7 Polyethylene conversion on HZSM-5 (Si/Al=44) catalyst with various type of polyethylene.

Reaction conditions : 20 g of polyethylene, 30 kg/cm², 60 min, 450 °C and 0.5 g of catalyst.

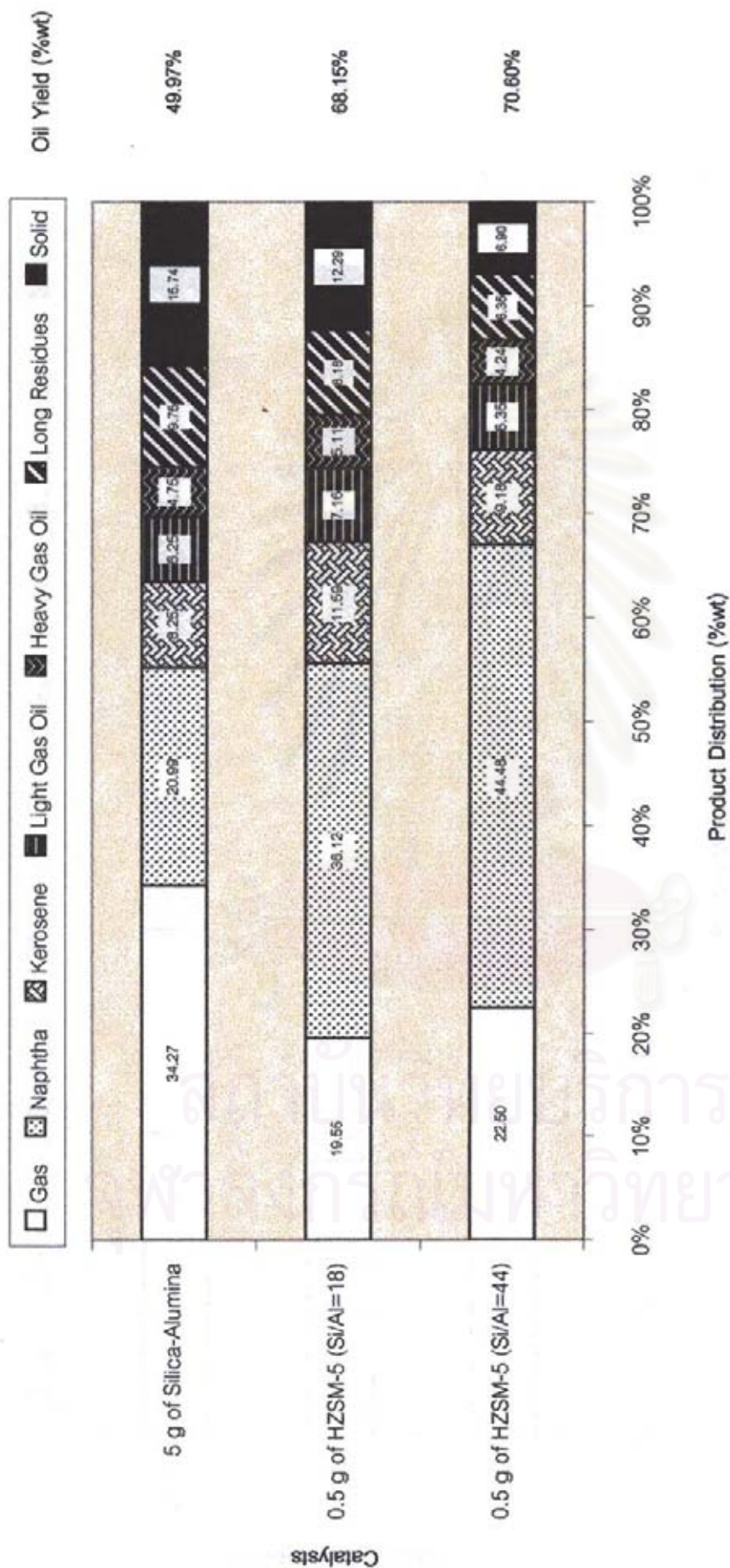


Figure 5.8 Polyethylene conversion on HZSM-5 and Silica-Alumina catalyst with various type of catalysis.

Reaction conditions : 20 g of LDPE, 30 kg/cm², 60 min and 450 °C for reaction temperature.

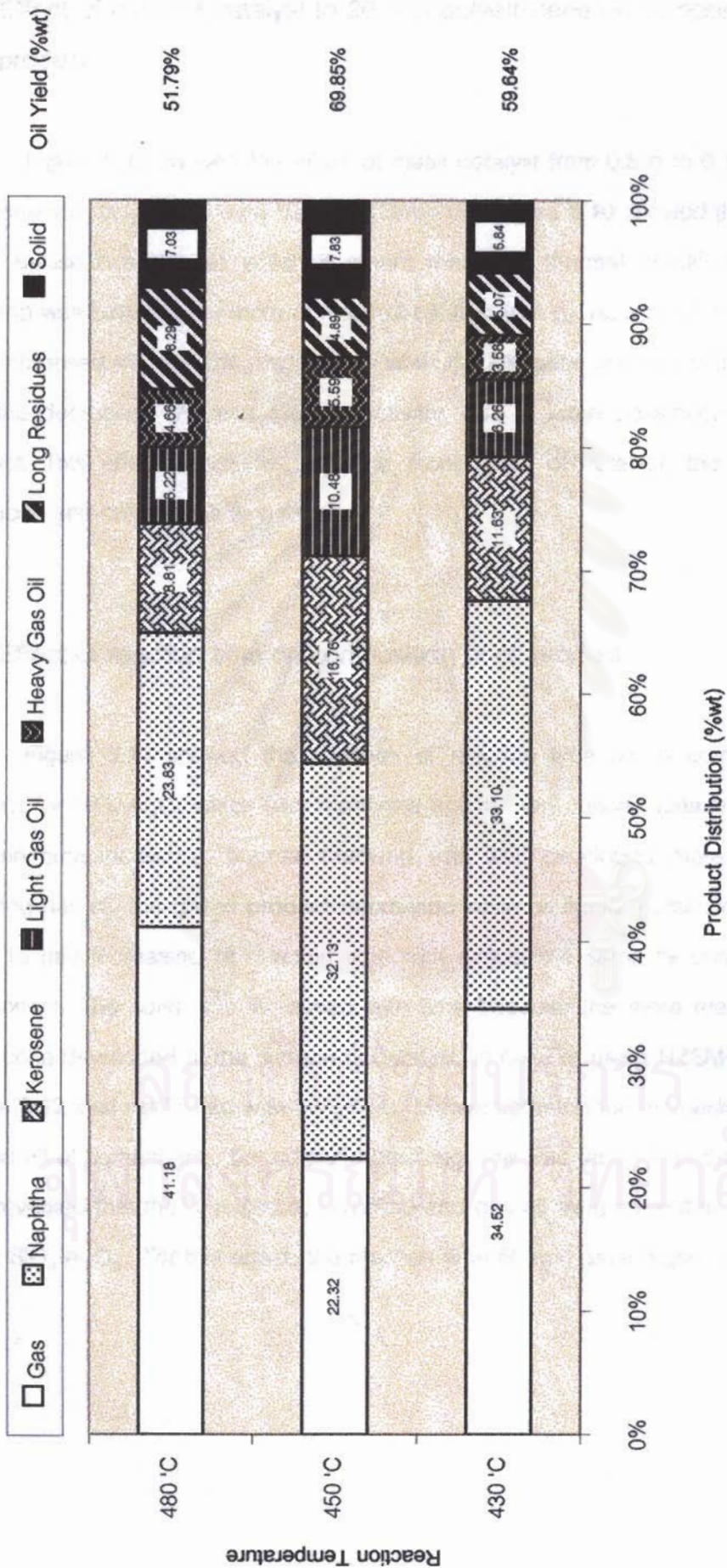


Figure 5.9 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various reaction temperatures.

Reaction conditions : 20 g of LDPE, 30 kg/cm², 60 min and 0.1 g of catalyst.

5.6 Effect of mass of catalyst to 20 g of polyethylene on composition of oil product

Figure 5.10 showed the effect of mass catalyst from 0.5 g to 0.1 g per 20 g of low-density of polyethylene on HZSM-5 (Si/Al=18). Figure 5.10 showed the difference of % of kerosene and solid which it meant that after thermal cracking, the catalytic cracking was better at the more of mass of catalyst (0.5 g). As a result the naphtha and solid increased 4% and 5% respectively while the kerosene and gas oil being source of naphtha decreased 5% and 4% respectively, due to more possibility to contact the catalyst. This effect concluded that the more mass of catalyst, the more naphtha produced and coking was also more.

5.7 Effect of reaction time on composition of oil product

Figure 5.11 showed the variation of reaction time on % composition of oil product for $\text{SiO}_2\text{-Al}_2\text{O}_3$ which was moderate acidity. We noticed clearly that when the reaction time increased, thermal cracking was well developed more than catalytic cracking namely the gases product decreased while oil liquid increased about 2% for each 15 min increasing of reaction time with almost the same % composition of oil component. The solid was increased with time because the more reaction time, the more coke developed at the surface of catalyst. In case of using HZSM-5 (Si/Al=18) in Figure 5.12 was confirmed with $\text{SiO}_2\text{-Al}_2\text{O}_3$ but we obtained the increasing of %yield of oil and all of component, but catalytic cracking now was faster than thermal cracking, so it revealed that the % naphtha, kerosene and gas oil were more than that in case of using $\text{SiO}_2\text{-Al}_2\text{O}_3$. For this effect, the reaction time 60 min gave higher naphtha and oil yield.

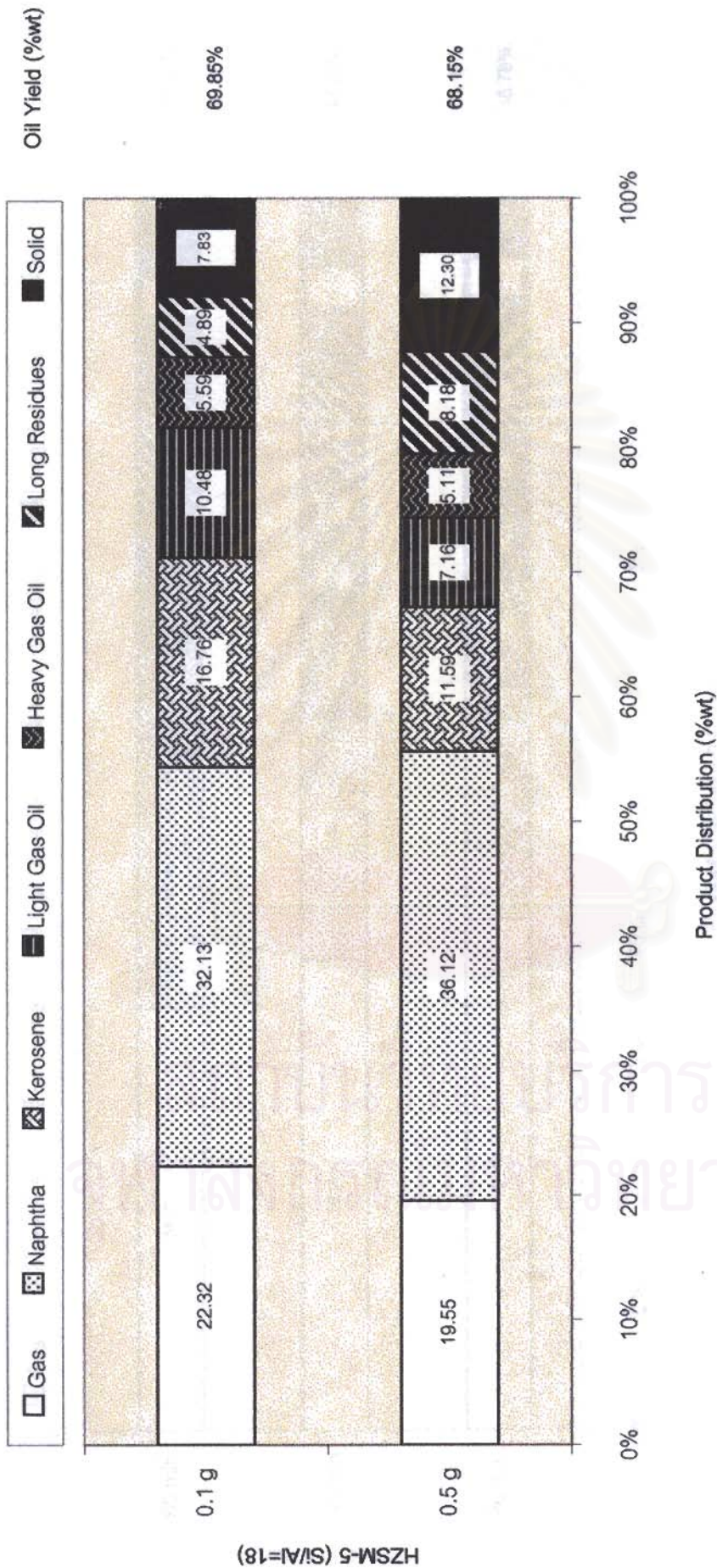


Figure 5.10 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various weight of catalyst.

Reaction conditions : initial hydrogen pressure 30 kg/cm², 60 min, 450 °C and 20 g of LDPE.

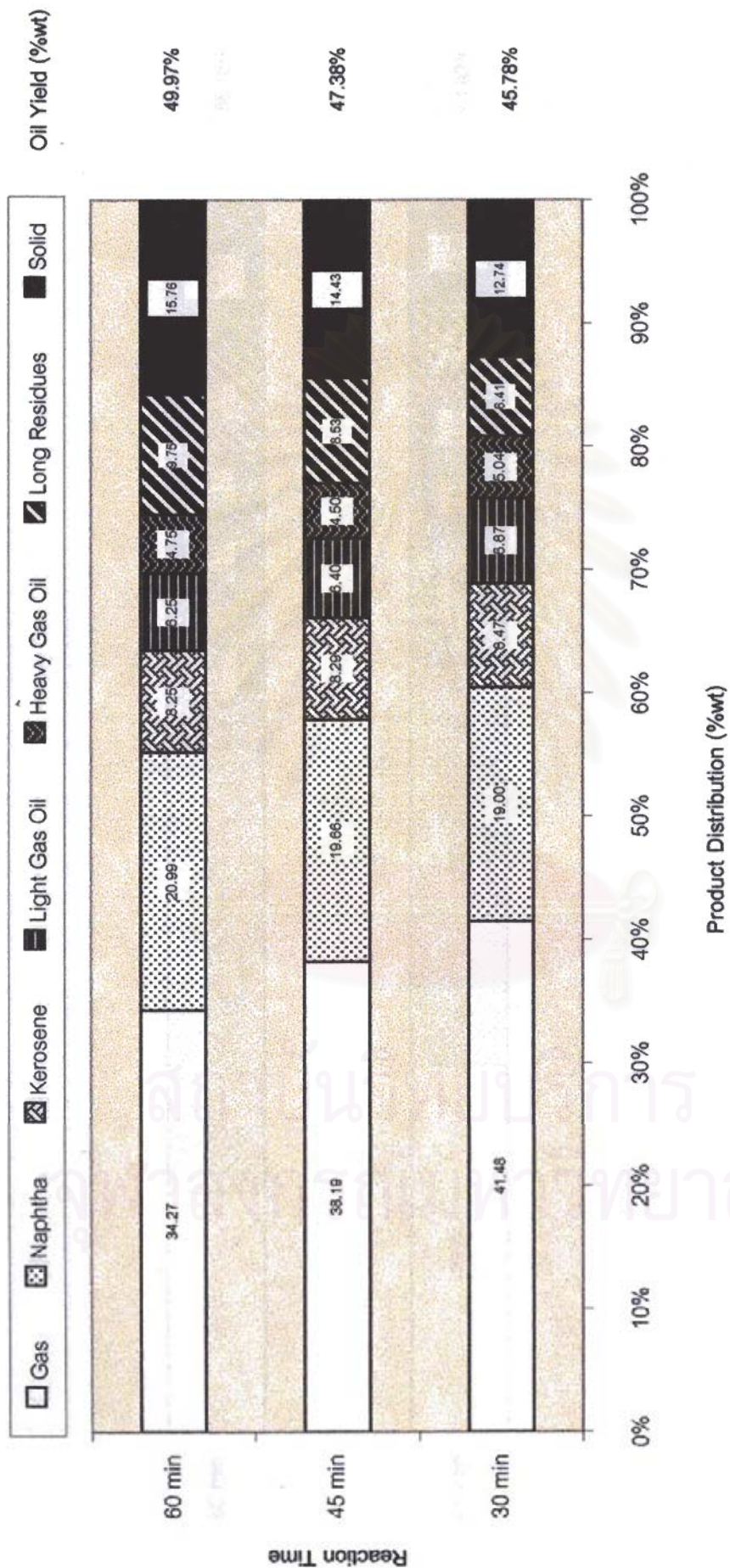


Figure 5.11 Polyethylene conversion on Silica-Alumina catalyst with various reaction time.

Reaction conditions : 20 g of LDPE, 30 kg/cm², 450 °C and 5 g of catalyst.

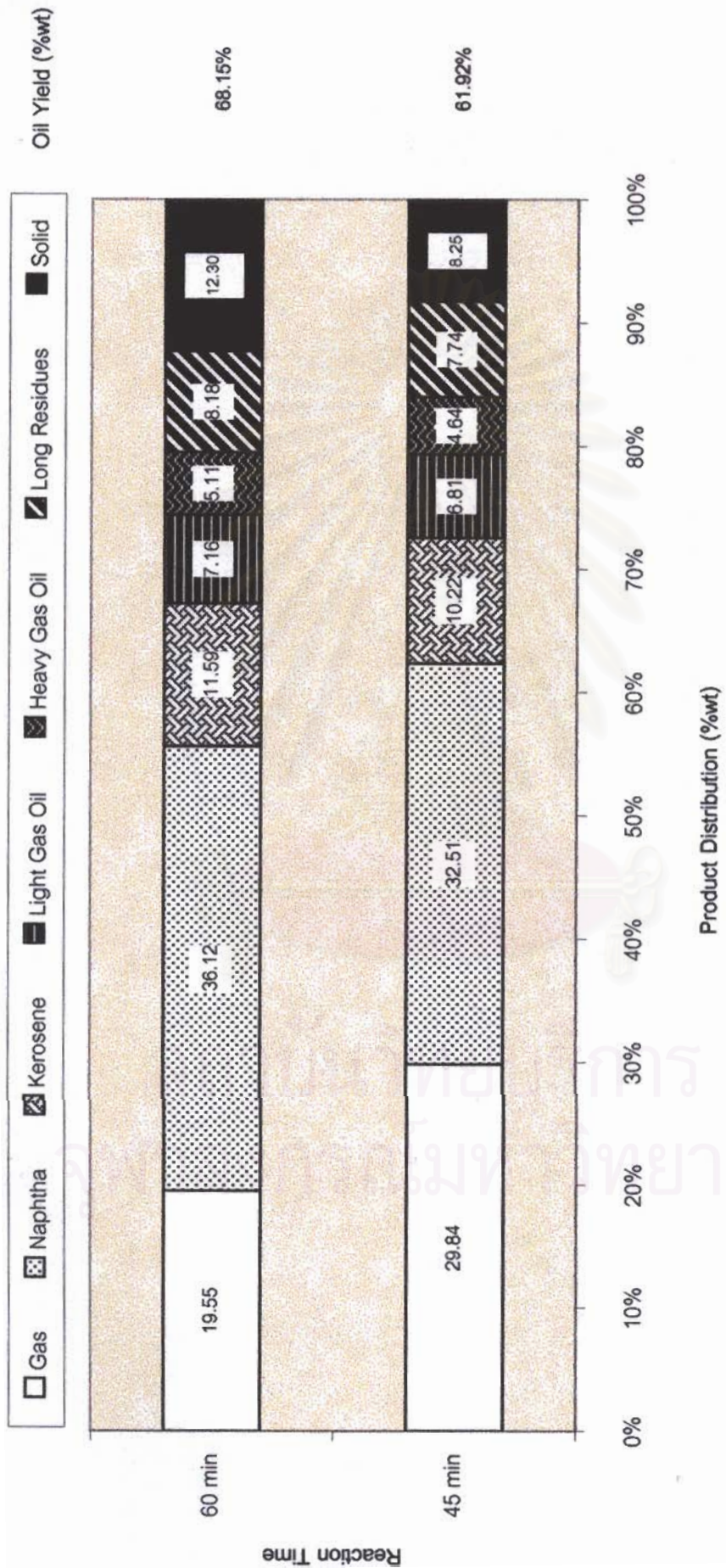


Figure 5.12 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various reaction time.
 Reaction conditions : 20 g of polyethylene, 30 kg/cm², 450 °C and 0.5 g of catalyst.

5.8 Effect of pressure of hydrogen on composition of oil product

Figure 5.13 showed the effect of variation of hydrogen pressure range from 10-30 kg/cm² on % composition of oil product. The initial hydrogen pressure was responsible to the catalytic cracking step. It was noticed that when the pressure increased the %yield of oil, naphtha, kerosene, light gas oil and solid increased, while gases, long residues decreased. These expressed that catalytic cracking takes place very well in higher pressure of hydrogen. Normally HZSM-5 gave protons from the structural surface of zeolite to the long chain hydrocarbon for cracking and these hydrogen compensated at the surface by hydrogen feed. This phenomena was called spill over so the pressure increased it clearly observed naphtha increasing from 25.88% to 32.13% , kerosene from 9.38% to 16.78% and %yield from 64.69% to 69.85% when the pressure increased from 10 to 30 kg/cm² . It seemed pressure 30 kg/cm² was better condition because of the higher naphtha and kerosene which were the principle oil product. Figure 5.14 showed the % composition of oil product by using HZSM-5 (Si/Al=44). It was observed the same trends as the case of HZSM-5 (Si/Al=18) but HZSM-5 (Si/Al=44) gave high naphtha at 30 kg/cm² about 43.60% which was more than 8% and 9% of hydrogen pressure at 20 and 10 kg/cm² respectively.

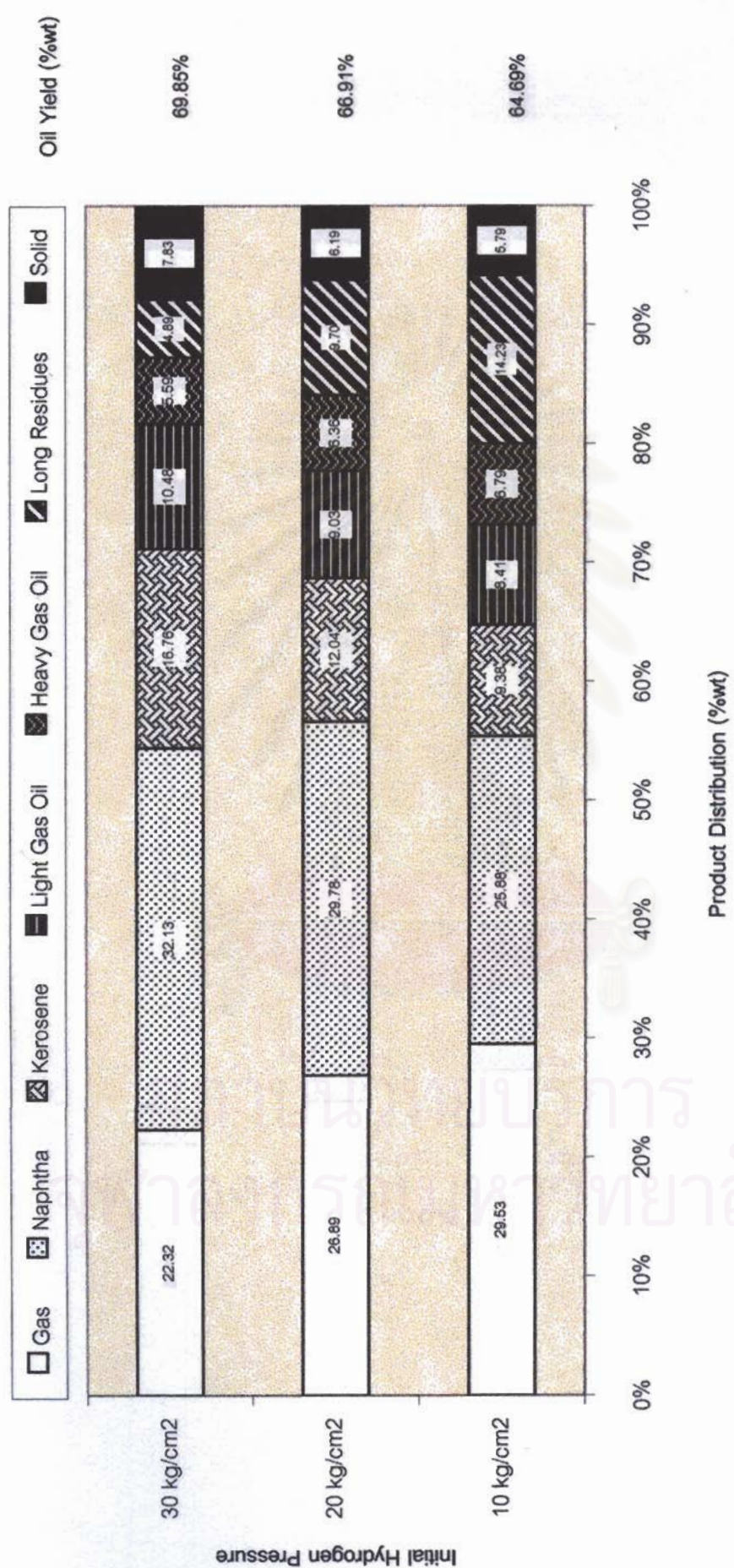


Figure 5.13 Polyethylene conversion on HZSM-5 (Si/Al=18) catalyst with various initial hydrogen pressures.

Reaction conditions : 20 g of LDPE, 450 °C, 60 min and 0.1 g of catalyst.

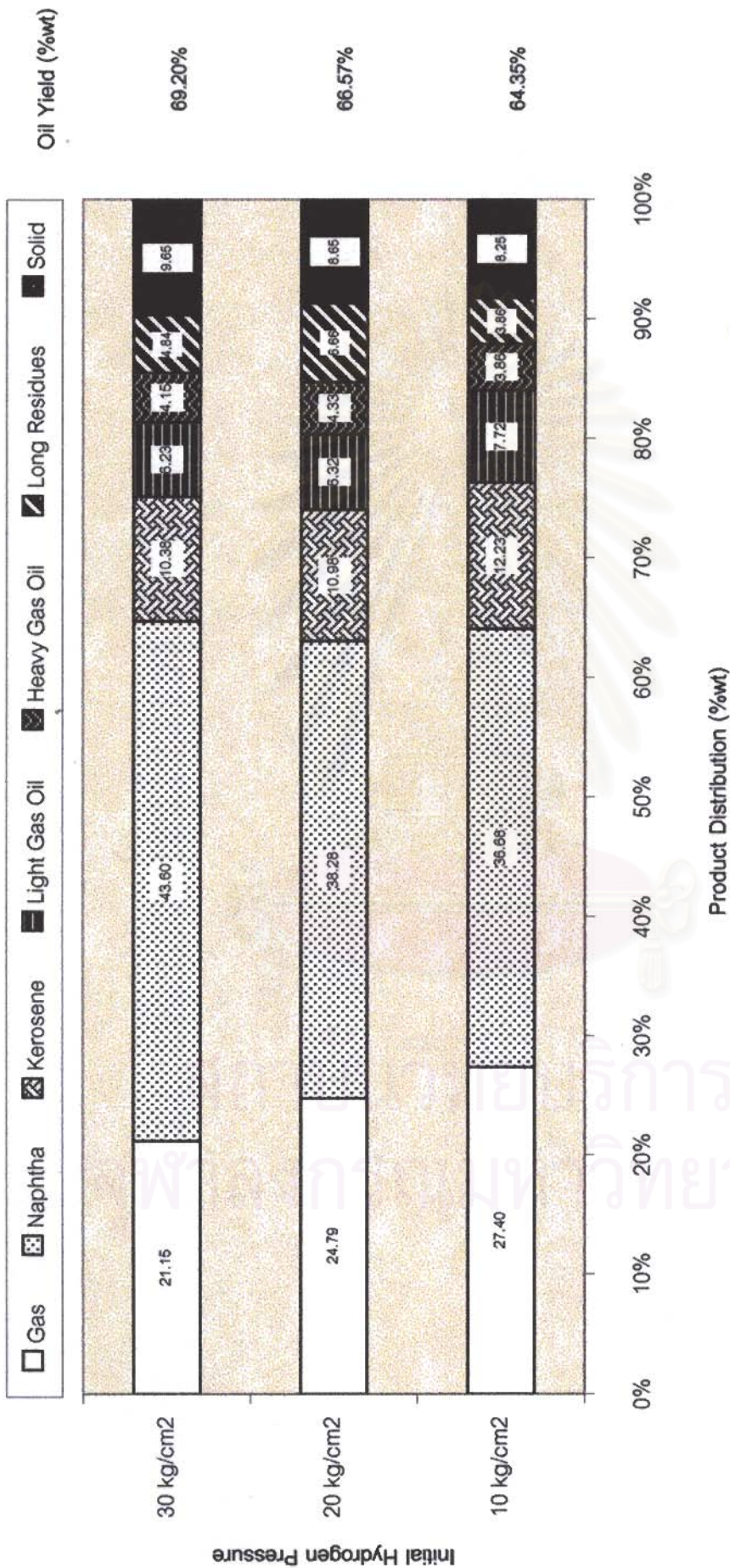


Figure 5.14 Polyethylene conversion on HZSM-5 (Si/Al=44) catalyst with various initial hydrogen pressures.
 Reaction conditions : 20 g of LDPE, 450 °C, 60 min and 0.1 g of catalyst.

5.9 Effect of type of plastics on composition of oil product

Figure 5.15 showed that PS gave maximum % naphtha and % yield of oil product, because PS was normally linear and easily cracked by HZSM-5 and the product especially naphtha was composed of aromatics. LDPE and PS gave the moderate naphtha while LDPE gave the minimum. The same trend as naphtha was found in the long residues while kerosene was found. In the contrary, kerosene and naphtha that we found in the former experiment had the ratio about 1:2. It meant that in LDPE, it was very hard to convert kerosene (C_{12} - C_{18}) to naphtha because of strong linear bonding while when we mixed LDPE with PS, the situation was went to the condition in case of existing PS namely naphtha increased 7% while kerosene decrease 8%, nevertheless if we saw the overall heavy oil (free naphtha) the %component were the same, the difference was only naphtha.

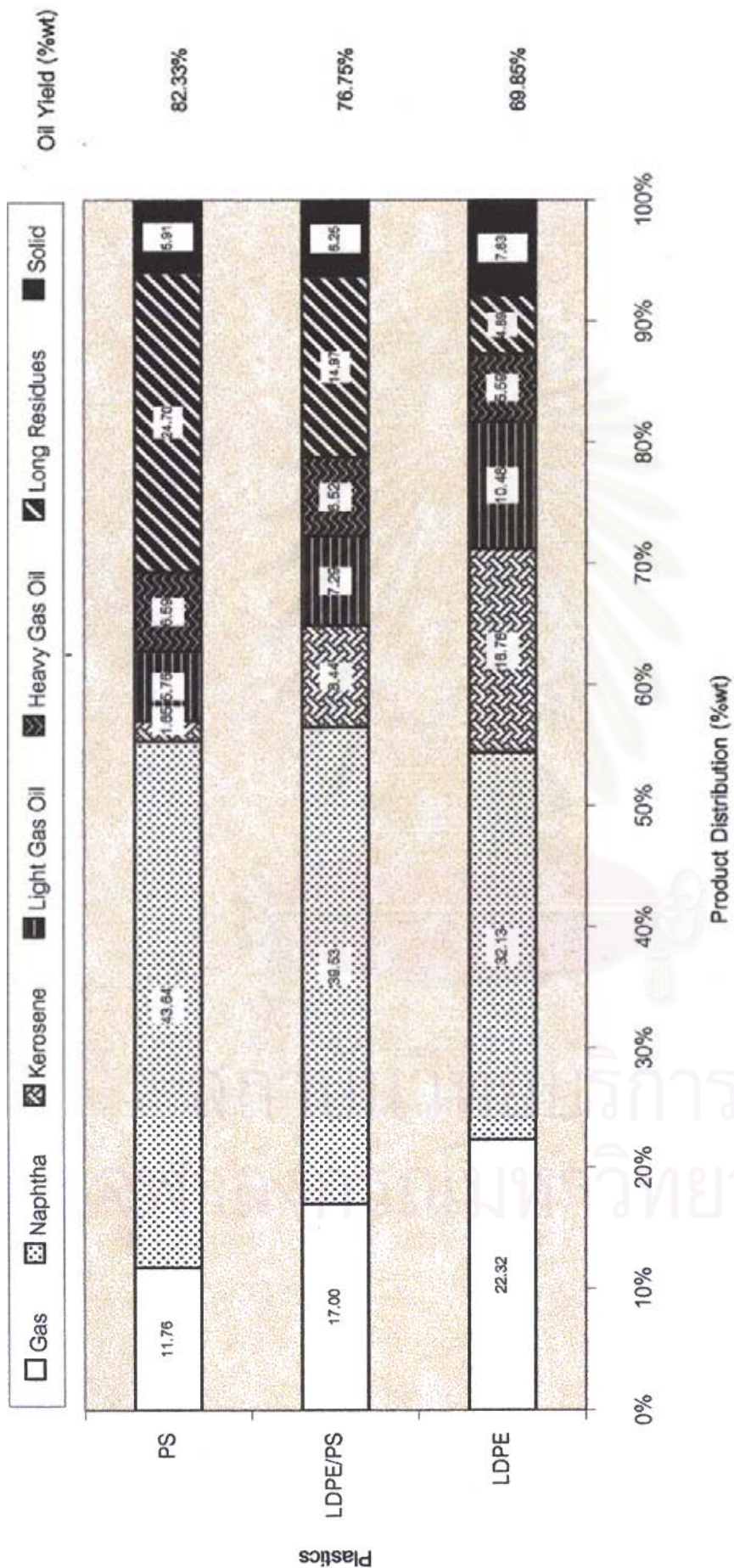


Figure 5.15 Polyethylene conversion on HZSM-5 (Si/AI=18) catalyst with various type of plastics.

Reaction conditions : initial hydrogen pressure 30 kg/cm², 450 °C, 60 min and 20 g of plastic.

5.10 Comparison of this work with other work

The comparison of this work with Ohkita, H. et al.⁽³⁾ (1993) was presented with fractions of gases, oils and solids and expressed in term of wt% in **Table 5.1** .

Table 5.1 Comparison of this work with Ohkita, H. et al.(1993)

Description	This work (2000)		Ohkita, H. et al. (1993)
	Plastic	LDPE	LDPE
Catalyst	HZSM-5	HZSM-5	HZSM-5
Si/Al ratio	18	44	14
<u>Conditions</u>			
Temperature	450 °C	450 °C	400 °C
Reaction time	60 min	60 min	3 hr
<u>Results</u>			
Oils (wt%)	68.15	70.60	45.00
Gases (wt%)	19.55	22.50	50.00
Solids (wt%)	12.30	6.90	1.00

Ohkita, H. et al. studied catalytic degradation of low-density polyethylene. The catalytic degradation was carried out using 15 g of LDPE packed at the bottom of a stainless steel reactor (45 mm in diameter) heated at 400 °C. In the middle part of the reactor 1.5 g of HZSM-5 catalyst with Si/Al ratio of 14. Nitrogen gas was supplied at the bottom of the reactor with a flow rate of 50 ml/min in order to purge oxygen from the reactor. From **Table 5.1** , Ohkita, et al. gave 45% of oil yield whereas this work gave 70.60% of oil yield. This result can be explained that hydrogen pressure will transfer hydrogen ion to carbonium ion more than nitrogen pressure while solid of this work was more than Ohkita's work, because HZSM-5 used this work was acidity more than Ohkita's .

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions from this study have been drawn :

1. Catalysts used for conversion of polyethylene into gasoline are Silica-Alumina and HZSM-5 zeolite catalyst
2. This work aims to investigate the performances of the tested HZSM-5 zeolite catalyst on polyethylene to gasoline reaction, the temperature was varied from 400-480 °C , 10-30 kg/cm² of initial hydrogen pressure and 30-60 min of reaction time. Analysis of the products were performed using GC Simulated Distillation. Turbid dark brown liquid yield was obtained.
3. From the experimental results obtained from this study , it may be concluded that the effects of reaction temperature, reaction time, pressure of hydrogen gas and mole ratio Si/Al of HZSM-5 catalyst on the reaction process were as follows ;

3.1 The characterization of X-ray diffraction of HZSM-5 of study showed the same structure as HZSM-5 of the International Zeolite Association.

3.2 Two kinds of HZSM-5 zeolites and Silica-Alumina have been examined as catalysts for conversion of polyethylene into gasoline. HZSM-5 zeolites showed excellent activity for the reaction to give high naphtha with research distillation values higher than 36% approximately. Strong acid sites of the catalyst were essential to the selective formation of the valuable products.

3.3 The appropriate reaction temperature range was 400-480 °C. At temperature of 450 °C, the oil yield, gas, naphtha, kerosene, gas oil, long residues, and solid were 69.85 , 22.32 , 32.12 , 16.76 , 16.07 , 4.89 , and 7.83%, respectively.

3.4 HZSM-5 catalyzed degradation resulted in much greater amount of oil yield compared with degradation over Silica-Alumina. In the using of the HZSM-5 catalyst at 450 °C , the % conversion of oil yield and naphtha were 61.92% and 32.51% respectively at 45 min reaction time, higher than in case of using Silica-Alumina (49.97% of oil yield and 20.99% of naphtha at 60 min reaction time).

3.5 The initial hydrogen pressure of 30 kg/cm² was the appropriate condition because HZSM-5 (Si/Al=44) gave the highest oil yield 69.20% and naphtha 43.60% .

Recommendations :

1. Investigate the change of local structure of Al in ZSM-5 framework during the modification of cation form such as Ga, Ti, Fe and Zn respectively.
2. Study in detail the type of acidity , i.e. Bronsted and Lewis type of the catalyst including their role on conversion of polyethylene into gasoline.

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APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX A

DATA FOR STUDY OF CONVERSION OF POLYETHYLENE INTO
GASOLINE USING HZSM-5 TYPE CATALYST

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table A-1 Product distribution of all conditions.

No.	Raw Material	Catalyst	H ₂ (kg/cm ²)	Temp. (°C)	Time (min)	Solid (g)	% Solid	Oil Yield (g)	% Yield	Gas (g)	% Gas	% Naphtna 65-200 °C	% Kerosene 200-250 °C	% Light Gas Oil 250-300 °C	% Heavy Gas Oil 300-350 °C	% Long Residues > 350 °C
1-MRN	LDPE = 20.04 g.	Blank test	30	450	60	1.24	6.19%	8.06	40.22%	10.74	53.59%	15.69%	6.64%	5.63%	4.42%	7.84%
2-MRC	LDPE = 20.05 g.	HZSM-5 (Si/Al = 18) = 0.11 g.	10	450	60	1.16	5.79%	12.97	64.69%	5.92	29.53%	25.89%	9.38%	8.41%	6.79%	14.23%
3-MRC	LDPE = 20.19 g.	HZSM-5 (Si/Al = 18) = 0.11 g.	20	450	60	1.25	6.19%	13.51	66.91%	5.43	26.89%	29.78%	12.04%	9.03%	6.36%	9.70%
4-MRC	LDPE = 20.06 g.	HZSM-5 (Si/Al = 18) = 0.10 g.	30	400	60											
WAX																
5-MRC	LDPE = 20.02 g.	HZSM-5 (Si/Al = 18) = 0.11 g.	30	430	60	1.17	5.84%	11.94	59.64%	6.91	34.52%	33.10%	11.63%	6.26%	3.58%	5.07%
6-MRC	LDPE = 20.43 g.	HZSM-5 (Si/Al = 18) = 0.1 g.	30	450	60	1.60	7.83%	14.27	69.85%	4.56	22.32%	32.13%	16.76%	10.48%	5.59%	4.89%
7-MRC	LDPE = 20.06 g.	HZSM-5 (Si/Al = 18) = 0.1 g.	30	480	60	1.41	7.03%	10.39	51.79%	8.26	41.18%	23.83%	8.81%	6.22%	4.66%	8.29%
8-MRC	LDPE = 20.00 g.	HZSM-5 (Si/Al = 44) = 0.1 g.	10	450	60	1.65	8.25%	12.87	64.35%	5.48	27.40%	36.68%	12.23%	7.72%	3.86%	3.86%
9-MRC	LDPE = 20.01 g.	HZSM-5 (Si/Al = 44) = 0.12 g.	20	450	60	1.73	8.65%	13.32	66.57%	4.96	24.79%	38.28%	10.98%	6.32%	4.33%	6.66%
10-MRC	LDPE = 20.00 g.	HZSM-5 (Si/Al = 44) = 0.1 g.	30	450	60	1.93	9.65%	13.84	69.20%	4.23	21.15%	43.60%	10.38%	6.23%	4.15%	4.84%
11-MRC	LDPE = 20.00 g.	HZSM-5 (Si/Al = 44) = 0.51 g.	30	450	60	1.38	6.90%	14.12	70.60%	4.50	22.50%	44.48%	9.18%	6.35%	4.24%	6.35%
12-MRC	HDPE = 20.00 g.	HZSM-5 (Si/Al = 44) = 0.53 g.	30	450	60	1.89	9.45%	13.75	68.75%	4.36	21.80%	44.00%	12.03%	6.19%	3.09%	3.44%
13-MRC	LDPE = 20.01 g.	HZSM-5 (Si/Al = 18) = 0.5 g.	30	450	45	1.65	8.25%	12.39	61.92%	5.97	29.84%	32.51%	10.22%	6.81%	4.64%	7.74%

Table A-1 (Continues).

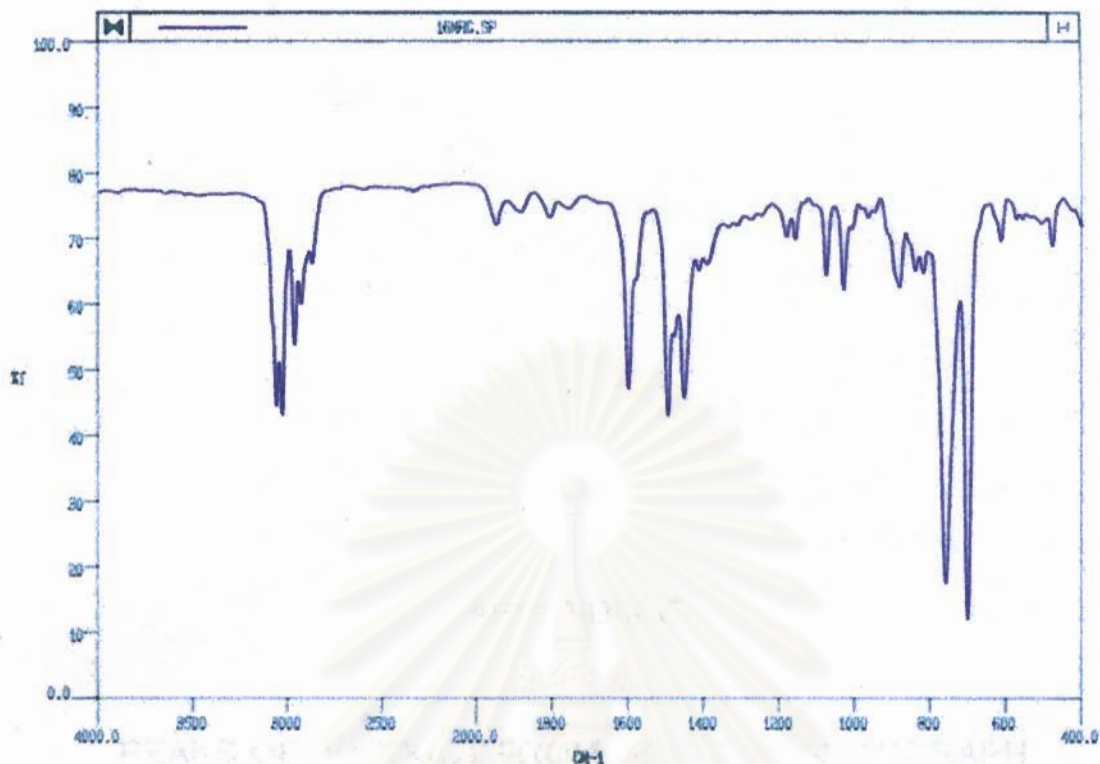
No.	Raw Material	Catalyst	H ₂ (kg/cm ²)	Temp. (°C)	Time (min)	Solid (g)	% Solid	Oil Yield (g)	% Yield	Gas (g)	% Gas	% Naphtna 65-200 °C	% Kerosene 200-250 °C	% Light Gas Oil 250-300 °C	% Heavy Gas Oil 300-350 °C	% Long Residues > 350 °C
14-MRC	LDPE = 20.00 g.	HZSM-5 (Si/Al = 18) = 0.5 g.	30	450	60	2.46	12.30%	13.63	68.16%	3.91	19.55%	36.12%	11.59%	7.16%	5.11%	8.18%
6-MRC	LDPE = 20.43 g.	HZSM-5 (Si/Al = 18) = 0.1 g.	30	450	90	1.60	7.83%	14.27	69.85%	4.56	22.32%	32.13%	16.76%	10.48%	5.59%	4.89%
15-MRC	LDPE/PS = 20.00 g.	HZSM-5 (Si/Al = 18) = 0.1 g.	30	450	90	1.25	6.25%	15.35	76.75%	3.40	17.00%	39.53%	8.44%	7.29%	6.52%	14.97%
18-MRC	PS = 19.98 g.	HZSM-5 (Si/Al = 18) = 0.1 g.	30	450	60	1.18	5.91%	16.45	82.33%	2.35	11.76%	43.64%	1.65%	6.76%	6.59%	24.70%
17-MRC	LDPE = 20.01 g.	Silica-Alumina = 5.02 g.	30	450	30	2.55	12.74%	9.16	45.78%	8.30	41.48%	19.00%	8.47%	6.87%	5.04%	6.41%
18-MRC	LDPE = 20.03 g.	Silica-Alumina = 5.06 g.	30	450	45	2.89	14.43%	9.49	47.38%	7.65	38.19%	19.66%	8.29%	6.40%	4.50%	8.53%
19-MRC	LDPE = 19.99 g.	Silica-Alumina = 5.01 g.	30	450	60	3.15	15.76%	9.99	49.97%	6.65	34.27%	20.99%	8.25%	6.25%	4.75%	6.75%



APPENDIX B

PEAKS OF PRODUCT FROM FOURIER TRANSFORM INFRARED
SPECTROPHOTOMETER

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



16 MRC.SP

- 201 ALKYL GROUP - GENERAL
- 258 AROMATIC COMPOUND - GENERAL
- 263 AROMATIC COMPOUND - MONO OR POSSIBLY DISUBSTITUTED
- 2101 SIMPLE AROMATIC HYDROCARBON
- 2102 AROMATIC HYDROCARBON - GENERAL
- 2104 AROMATIC HYDROCARBON - MONO OR DISUBSTITUTED
- 2105 AROMATIC HYDROCARBON - POSSIBLY PHENYL SUBSTITUTED

PSUs above may be subject to interference. Consult Manual.



APPENDIX C

PEAKS OF PRODUCT FROM GAS CHROMATOGRAPH
(GC Simulated Distillation)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



PTT RESEARCH AND TECHNOLOGY INSTITUTE
PETROLEUM AUTHORITY OF THAILAND

Analytical and Petrochemical Research Department

71 Moo 2 Phahonyothin Rd., Wangnoi, Ayutthaya, 13170 Thailand. Tel. 537-3000 ExL 2402-3 Fax. 537-3000 Ext. 2401

CERTIFICATE OF ANALYSIS

CERT NO. : 26/5/2543 [Page :1/2] REF NO. : 79/43
 SAMPLE NAME : 17-MRC SAMPLING DATE : _____
 SAMPLE ID. : FU 036/43 SAMPLE CONDITION : Good
 SAMPLE FROM : Chulalongkorn University RECEIVED DATE : 11/04/43
 SAMPLING LOCATION : - ANALYSIS DATE : 19/04/43

Test Item	Method	Unit	Result
Boiling Range Distribution	ASTM D2887-93 (Modified Method)	°F	
% Recovered			
IBP			180
5			208
10			236
15			267
20			288
25			308
30			336
35			357
40			385
45			410
50			434
55			460
60			490

THIS CERTIFICATE OF ANALYSIS IS REFERED TO ONLY SUBMITTED SAMPLE(S). IT IS YOUR RESPONSIBLE TO USE HERE IN RESULTS IN ANY PURPOSES. EXCEPT IN FULL, THIS CERTIFICATE SHALL NOT BE REPRODUCED WITHOUT THE WRITTEN APPROVAL OF THE DIVISION MANAGER OR DEPARTMENT DIRECTOR.



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CERTIFICATE OF ANALYSIS

CERT NO. : 26/5/2543 [Page :2/2]

Test Item	Method	Unit	Result
% Recovered (Cont.)			
65			524
70			562
75			600
80			646
85			696
90			759
95			848
FBP			999

REMARK : IBP (Initial Boiling Point) - the temperature at which a cumulative corrected area count equal to 0.5% of the total sample area

FBP (Final Boiling Point) - the temperature at which a cumulative corrected area count equal to 99.5% of the total sample area

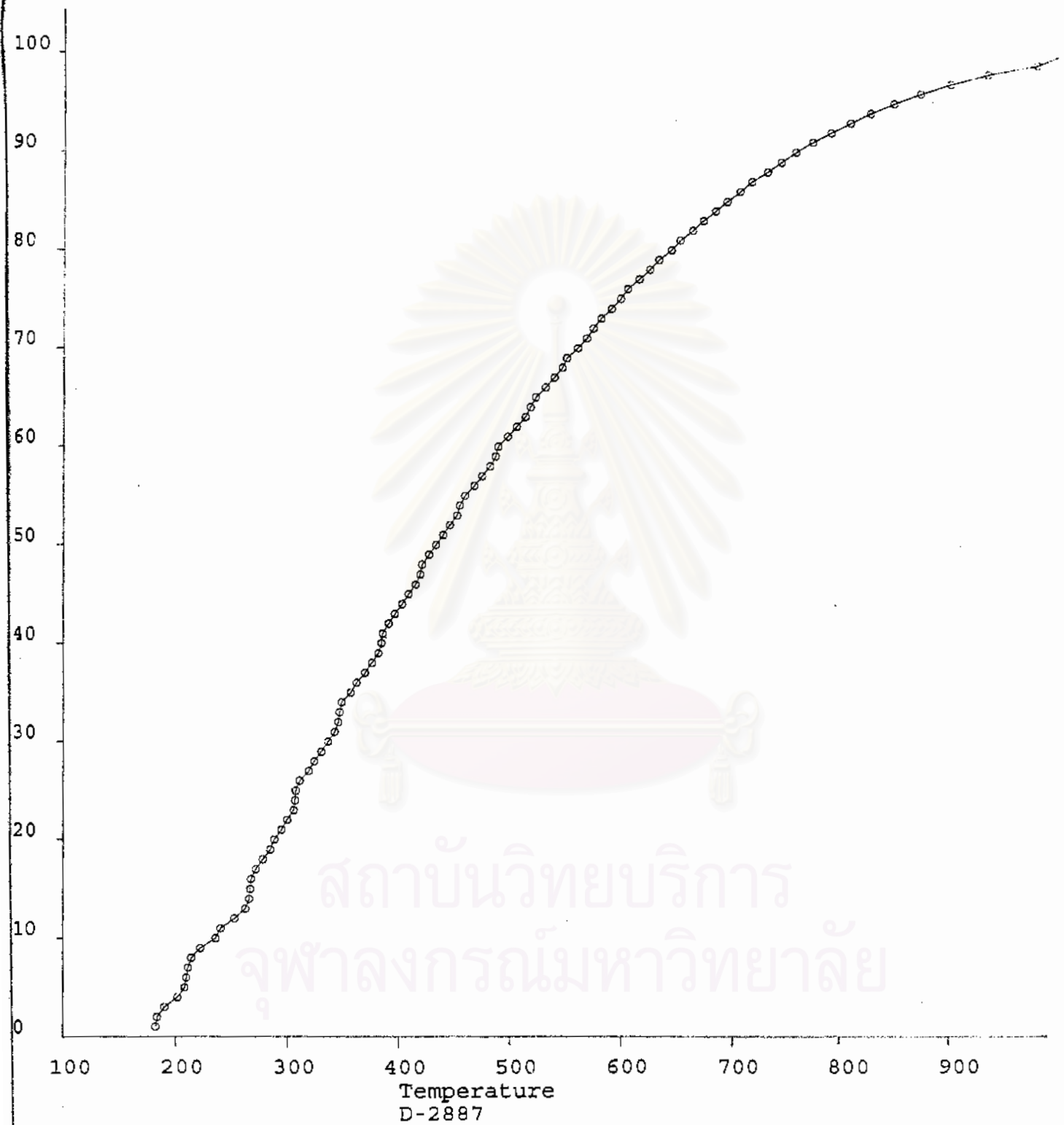
APPROVED BY : *C. Tonkunakorn*

(Mr. Chatree Tonkunakorn)

POSITION : Division Manager

DATE OF ISSUE : 08/05/2000

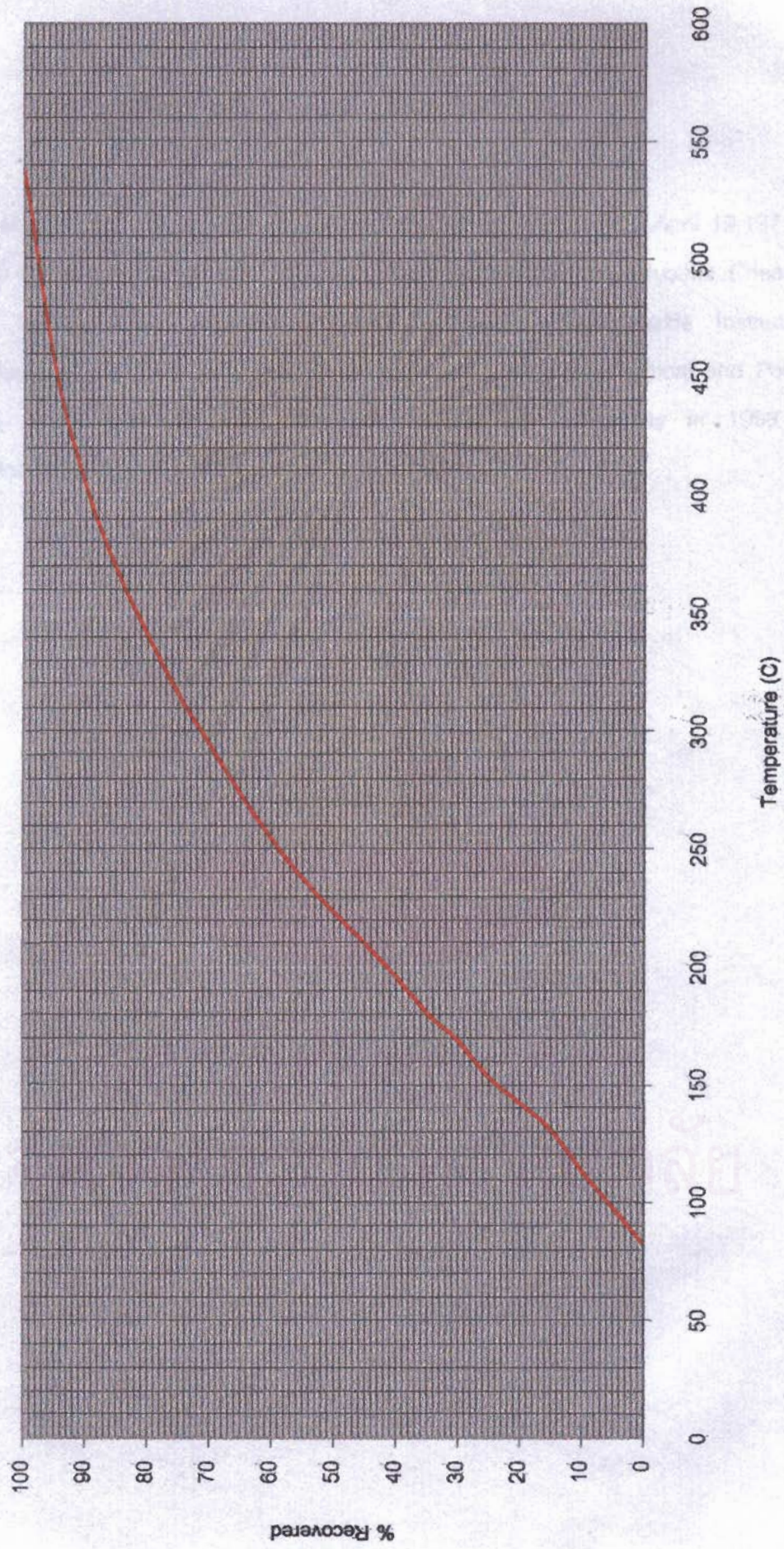
ff



File Name : "FU036/43"
 File : C:\TC4\D2887\OIL_064.arn
 Operator : "supot"
 Collected : 4/26/00 @ 2:42:34 AM
 Dis Calculated : 5/8/00 @ 2:16:08 PM

Dis Method : c:\sd\2887\ptt_3.287
 stored on 4/25/00 @ 3:28:52 PM by supot

Sample Name : 17-MRC



VITA

Mr. Somsuk Trisupakitti was born in Bangkok, Thailand on April 19,1971. He received his Bachelor Degree of Science from Department of Industrial Chemistry, Faculty of Agricultural Engineering and Technology, Rajamangala Institute of Technology in 1994. He continued his Master's study at Petrochemical and Polymer Science Department, Graduate School, Chulalongkorn University in 1998 and completed the program in 2000.



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