

196

ไฮโดรไอโซเมอไรเซชันของไบโพลีเอทิลีนชนิดความหนาแน่นสูง

นางสาวสุนันท์ อินทรปรีชา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สหสาขาวิชาปิโตรเคมี-โพลีเมอร์

สาขาวิชาวิทยาศาสตร์โพลีเมอร์

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2539

ISBN 974-636-165-1

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

I 20608475

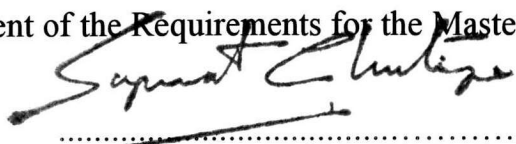
**HYDROISOMERIZATION OF HIGH DENSITY
POLYETHYLENE WAX**

Miss Sunan Intarapreecha

**A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
Multidisciplinary of Petrochemistry and Polymer
Program of Polymer Science
Graduate School
Chulalongkorn University
Academic Year 1996
ISBN 974-636-165-1**

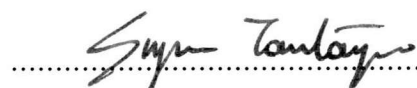
Thesis Title HYDROISOMERIZATION OF HIGH DENSITY
 POLYETHYLENE WAX
By Miss Sunan Intarapreecha
Department Polymer Science
Thesis Advisor Assistant Professor Amorn Petsom, Ph.D.

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

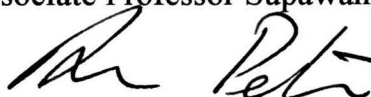


..... Dean of Graduate School
(Professor Supawat Chutivongse, M.D.)

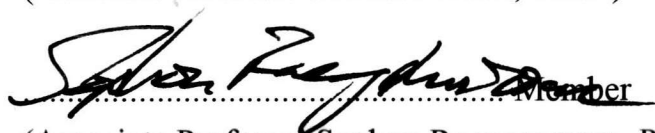
Thesis Committee



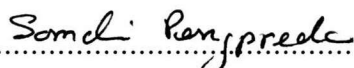
..... Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)



..... Thesis Advisor
(Assistant Professor Amorn Petsom, Ph.D.)



..... Member
(Associate Professor Sophon Roengsumran, Ph.D.)



..... Member
(Assistant Professor Somchai Pengprecha, Ph.D.)



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

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสี่เหลี่ยมนี้เพียงแผ่นเดียว

สุนันท์ อินทรปรีชา : ไฮโดรไอโซเมอไรเซชันของไฮโพลีเอทิลีนชนิดความหนาแน่นสูง
(HYDROISOMERIZATION OF HIGH DENSITY POLYETHYLENE WAX)

อ. ที่ปรึกษา : ผศ.ดร. อมร เพชรสม , 95 หน้า. ISBN 974-636-165-1

งานวิจัยนี้ได้ศึกษาการทำปฏิกิริยาไฮโดรไอโซเมอไรเซชันของไฮโพลีเอทิลีนชนิดความหนาแน่นสูง โดยใช้ตัวเร่งปฏิกิริยาประเภท 2 หน้าที คือ แพลตินัม-ฟลูออไรด์บนอะลูมินา ซึ่งประกอบด้วย แพลตินัม 0.3 เปอร์เซ็นต์ และ ฟลูออไรด์ 0.5 เปอร์เซ็นต์ การศึกษากระทำโดยการแปรค่าปริมาณตัวเร่งปฏิกิริยาในช่วง 5-9 เปอร์เซ็นต์โดยน้ำหนัก อุณหภูมิในช่วง 300-400 องศาเซลเซียส ภายใต้ความดันของก๊าซไฮโดรเจนในช่วง 300-500 ปอนด์ต่อลูกบาศก์นิ้ว และศึกษาถึงผลของเวลาในช่วง 10-240 นาที สำหรับสภาวะที่เหมาะสมในการทำปฏิกิริยาไฮโดรไอโซเมอไรเซชันของไฮโพลีเอทิลีนชนิดความหนาแน่นสูง คือ ที่ปริมาณตัวเร่งปฏิกิริยา 5 เปอร์เซ็นต์โดยน้ำหนัก อุณหภูมิ 300 องศาเซลเซียส ความดัน 300 ปอนด์ต่อลูกบาศก์นิ้ว และเวลา 10 นาที ผลที่ได้คือผลิตภัณฑ์ที่มีคุณสมบัติเป็นน้ำมันดีเซล

ภาควิชา สาขาวิชาปิโตรเคมี-โพลีเมอร์
สาขาวิชา วิทยาศาสตร์โพลีเมอร์
ปีการศึกษา 2539.....

ลายมือชื่อนิสิต สุนันท์ อินทรปรีชา
ลายมือชื่ออาจารย์ที่ปรึกษา อมร เพชรสม
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสี่เหลี่ยมนี้เพียงแผ่นเดียว

C785293 : MAJOR POLYMER SCIENCE

KEY WORD: HYDROISOMERIZATION / WAX / CRACKING

SUNAN INTARAPREECHA : HYDROISOMERIZATION OF HIGH DENSITY
POLYETHYLENE WAX. THESIS ADVISOR : ASSIST. PROF. AMORN PETSOM, Ph.D.
95 pp. ISBN 974-636-165-1

The hydroisomerization reactions of High Density Polyethylene wax in the presence of catalysts were systematically investigated as a function of processing variables i.e. catalyst concentration (5-9 % by wt), temperature (300-400 °C), hydrogen pressure (300-500 psig) and reaction time (10-240 min). Platinum fluorided alumina catalyst, which contains 0.3% Pt and 0.5% F, was used in the study. The detailed composition of products were determined by GC/MS. Products from the reaction contained C₁₁ - C₂₅ and C₁₁-C₁₆ as the main component. The changes in product composition as a function of the above processing variables were determined and conditions for preferential production of diesel fuel were established.

The reaction that operated at 300 °C, 300 psig hydrogen pressure, 10 min. and 5% by wt of catalyst is optimal. Products from these conditions were accepted to be low speed diesel.

ภาควิชา..... สหสาขาวิชาปิโตรเคมี-โพลีเมอร์

สาขาวิชา..... วิทยาศาสตร์โพลีเมอร์

ปีการศึกษา..... 2539

ลายมือชื่อนิสิต..... สันนท์ อินทรปรีชา

ลายมือชื่ออาจารย์ที่ปรึกษา..... 

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..... -

ACKNOWLEDGEMENTS

The author wishes to express her deepest gratitude to her advisor, Assistant Professor Dr. Amorn Petsom for his advice, valuable criticism and generous encouragement throughout the course of this research. She is sincerely grateful to Associate Professor Dr. Sophon Roengsumran for his useful guidance and understanding.

She would like to thank Mrs. Ratanavalee In-ochanon for her advice and help. She also wishes to thank the thesis committee for their valuable suggestions and comments.

The special thanks are due to the Petroleum Authority of Thailand for their help in determining all of the diesel properties in this research. And thanks are also due to everyone who has contributed suggestion and support during this research.

Finally, the author would like to express her greatest appreciation to her parents for their support throughout her entire education.

CONTENTS

	Page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
ABBREVIATIONS.....	xv
CHAPTER	
1. INTRODUCTION.....	1
2. THEORETICAL CONSIDERATION.....	6
2.1 Wax.....	6
2.1.1 Petroleum Waxes.....	7
2.1.2 Animal Waxes.....	7
2.1.3 Vegetable Waxes.....	8
2.1.4 Mineral Waxes.....	8
2.1.5 Synthetic Waxes.....	8
2.2 Hydroisomerization Reaction and Bifunctional Catalyst.....	9
2.2.1 Preparation and Structure of Bifunctional Catalyst.....	12
2.2.2 Metallic Component.....	13
2.2.3 Acidic Component.....	14

CONTENTS(continued)

	Page
2.3 Diesel Fuels.....	15
2.3.1 General Characteristics of Diesel Fuel.....	16
2.4 Literature reviews.....	20
3. EXPERIMENTAL.....	26
3.1 Apparatus and Instruments.....	26
3.2 Materials.....	29
3.3 Preparation of Catalysts.....	29
3.3.1 Measuring Pore Volume of Alumina Support.....	29
3.3.2 Impregnation of Platinum and Fluoride on Alumina Support.....	30
3.3.3 Activation of platinum fluoride on alumina catalyst.....	30
3.4 Characterization of platinum fluoride on alumina catalyst.....	31
3.5 Hydroisomerization Process.....	31
3.5.1 Reaction Procedure.....	31
3.5.2 The Effect of Catalyst Concentration on Hydroisomerization.....	31
3.5.3 The Effect of Temperature on Hydroisomerization.....	32
3.5.4 The Effect of Hydrogen Pressure on Hydroisomerization.....	32

CONTENTS(continued)

	Page
3.5.5 The Effect of Reaction Time on Hydroisomerization.....	32
3.6 Determination of Diesel Oil Properties.....	32
3.6.1 Spectroscopic properties.....	33
3.6.2 Physical properties.....	33
4. RESULTS AND DISCUSSION.....	34
4.1 Characterization of Platinum Fluoride on Alumina Catalyst.....	34
4.2 Hydroisomerization Process.....	35
4.2.1 Effect of Catalyst Concentration.....	35
4.2.2 Effect of Temperature.....	39
4.2.3 Effect of Hydrogen Pressure.....	42
4.2.4 Effect of Reaction Time.....	46
4.3 Determination of Diesel Oil Properties.....	49
4.3.1 Spectroscopic properties.....	49
4.3.2 Physical properties.....	49
5. CONCLUSION.....	51
SUGGESTIONS FOR FUTURE WORK.....	52
REFERENCES.....	53
APPENDICES.....	58
VITA.....	95

LIST OF TABLES

TABLE	Page
2.1 Three Generations of Paraffin Isomerization Catalysts.....	12
2.2 Rate of Dehydrogenation of Cyclohexane over different catalysts (temperature 427 °C, pressure 7 atm).....	14
4.1 HDPE wax conversion from hydroisomerization as a function of catalyst concentration.....	36
4.2 HDPE wax conversion from hydroisomerization as a function of reaction time.....	39
4.3 HDPE wax conversion from hydroisomerization as a function of hydrogen pressure.....	43
4.4 HDPE wax conversion from hydrpoisomerization as a function of reaction time.....	46
4.5 Properties of the optimum condition product.....	49
B1 Composition of products from hydroisomerization as a function of catalyst concentration	68
B2 The molecular weight distribution of products from hydroisomerization as a function of catalyst concentration.....	69
B3 Composition of products from hydroisomerization as a function of temperature.....	70
B4 The molecular weight distribution of products from hydroisomerization as a function of temperature.....	71
B5 Composition of products from hydroisomerization as a function of hydrogen pressure.....	72
B6 The molecular weight distribution of products from hydroisomerization as a function of hydrogen pressure.....	73
B7 Composition of products from hydroisomerization as a	

LIST OF TABLES(continued)

	Page
B8 The molecular weight distribution of products from hydroisomerization as a function of reaction time.....	75
B9 Composition of products from hydroisomerization as a function of catalyst concentration (second time).....	76
B10 The molecular weight distribution of products from hydroisomerization as a function of catalyst concentration (second time).....	77
B11 Composition of products from hydroisomerization as a function of temperature (second time).....	78
B12 The molecular weight distribution of products from hydroisomerization as a function of temperature (second time).....	79
B13 Composition of products from hydroisomerization as a function of hydrogen pressure(second time).....	80
B14 The molecular weight distribution of products from hydroisomerization as a function of hydrogen pressure (second time).....	81
B15 Composition of products from hydroisomerization as a function of reaction time (second time).....	82
B16 The molecular weight distribution of products from hydroisomerization as a function of reaction time (second time).....	83

LIST OF FIGURES

FIGURE	Page
1.1 Plastic consumption trend of Thailand and other countries.....	3
1.2 PE, PP and PVC demand in Thailand.....	4
3.1 Floor Stand Reactor.....	27
3.2 Reactor Fitting.....	28
4.1 Composition trend of products from hydroisomerization as a function of catalyst concentration.....	37
4.2 Composition trend of products from hydroisomerization as a function of catalyst concentration (second time).....	38
4.3 Composition trend of products from hydroisomerization as a function of temperature.....	40
4.4 Composition trend of products from hydroisomerization as a function of temperature (second time).....	41
4.5 Composition trend of products from hydroisomerization as a function of hydrogen pressure.....	44
4.6 Composition trend of products from hydroisomerization as a function of hydrogen pressure (second time).....	45
4.7 Composition trend of products from hydroisomerization as a function of reaction time	47
4.8 Composition trend of products from hydroisomerization as a function of reaction time (second time).....	48
A1 A plot of x-ray diffraction data of alumina.....	60
A2 A plot of x-ray diffraction data of platinum fluoride on alumina.....	61
A3 A plot of x-ray diffraction data of catalyst from US. Pat. No. 4,923,841.....	62

LIST OF FIGURES(continued)

	Page
A4 A plot of x-ray diffraction data of commercial catalyst.....	63
A5 A plot of SEM / EDX data of alumina.....	64
A6 A plot of SEM / EDX data of platinum fluoride on alumina catalyst.....	65
A7 ^{13}C NMR(CDCl_3) spectrum of product from hydroisomerization at optimum condition.....	66
B1 GC/MS chromatogram of products from hydroisomerization as a function of catalyst concentration.....	84
B2 GC/MS chromatogram of products from hydroisomerization as a function of temperature.....	85
B3 GC/MS and GC Chromatogram of products from hydroisomerization as a function of hydrogen pressure.....	86
B4 GC chromatogram of products from hydroisomerization as a function of reaction time.....	87
B5 GC chromatogram of products from hydroisomerization as a function of reaction time(continued).....	88
B6 GC chromatogram of products from hydroisomerization as a function of catalyst concentration (second time).....	89
B7 GC chromatogram of products from hydroisomerization as a function of catalyst concentration (second time)(continued).....	90
B8 GC chromatogram of products from hydroisomerization as a function of temperature (second time).....	91
B9 GC Chromatogram of products from hydroisomerization as a function of hydrogen pressure (second time).....	92
B10 GC chromatogram of products from hydroisomerization as a function of reaction time (second time).....	93

LIST OF FIGURES(continued)

	Page
B11 GC chromatogram of products from hydroisomerization as a function of reaction time (second time).....	94

ABBREVIATIONS

HDPE	=	High Density Polyethylene
PE	=	Polyethylene
PP	=	Polypropylene
PVC	=	Polyvinylchloride
psi	=	pound per square inches
min	=	minute
hrs	=	hours
MWD	=	Molecular Weight Distribution
GC/MS	=	Gas Chromatography / Mass Spectrometer