

**CATALYTIC PYROLYSIS OF WASTE TIRE OVER Y-BASED
CATALYSTS: SYNERGISTIC EFFECT BETWEEN Pd-Pt**



Thirapat Latthikawiboon

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma, and
Case Western Reserve University

2010


530051


Thesis Title: Catalytic Pyrolysis of Waste Tire over Y-based Catalysts:
Synergistic effect between Pd-Pt
By: Mr. Thirapat Latthikawiboon
Program: Petrochemical Technology
Thesis Advisors: Assoc. Prof. Sirirat Jitkarnka

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.


..... Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:


.....
(Assoc. Prof. Sirirat Jitkarnka)


.....
(Asst. Prof. Apanee Luengnaruemitchai)


.....
(Dr. Natthakorn Kraikul)

บทคัดย่อ

ฉัตรภัทร์ ลัทธจิภาวิบูลย์: การไพโรไลซิสยางรถยนต์หมดสภาพโดยใช้ตัวเร่งปฏิกิริยาเวลายซีโอไลต์โดยการทำงานร่วมกันของพาลาเดียมและแพลตตินัม (Catalytic Pyrolysis of Waste Tire over Y-based Catalysts: Synergistic Effect between Pd-Pt) อ. ที่ปรึกษา
รศ. ดร. ศิริรัตน์ จิตการคำ 114 หน้า

กระบวนการไพโรไลซิสยางรถยนต์หมดสภาพให้เป็นเชื้อเพลิงเป็นวิธีหนึ่งในการแก้ปัญหาเชื้อเพลิงขาดแคลนและลดการสะสมของขยะยางรถยนต์ในสิ่งแวดล้อม และการใช้เวลายซีโอไลต์ที่มีการเติมโลหะสองชนิด (แพลตตินัมและพาลาเดียม) เป็นตัวเร่งปฏิกิริยาในกระบวนการไพโรไลซิสสามารถปรับปรุงคุณภาพและปริมาณของผลิตภัณฑ์ได้ ซึ่งเกิดจากการทำงานร่วมกันของโลหะสองชนิดและความต้านทานต่อการเสื่อมสภาพสูงนั่นเอง งานวิจัยนี้เป็นการศึกษาการเตรียมตัวเร่งปฏิกิริยาและอัตราส่วนระหว่างโลหะสองชนิดที่ส่งผลต่อคุณภาพและปริมาณของผลิตภัณฑ์ไพโรไลซิส รวมถึงองค์ประกอบในตัวเร่งปฏิกิริยาที่ให้ผลิตภัณฑ์ที่มีคุณภาพเหมาะสมที่สุด โดยผลิตภัณฑ์ดังกล่าวประกอบด้วยแก๊สและน้ำมัน น้ำมันจากการไพโรไลซิสจะถูวิเคราะห์คุณภาพจากการหาปริมาณสารไฮโดรคาร์บอนอิ่มตัวและปริมาณสารประกอบอะโรมาติกส์ในผลิตภัณฑ์ รวมถึงมีการวิเคราะห์สัดส่วนของปิโตรเลียมในผลิตภัณฑ์น้ำมัน ได้แก่ แนฟทา, น้ำมันก๊าด, น้ำมันดีเซลเบา, น้ำมันดีเซลหนัก เป็นต้น จากผลการทดลองพบว่าการใช้ตัวเร่งปฏิกิริยาที่เติมโลหะสองชนิดนั้น ทำให้ผลิตภัณฑ์น้ำมันที่มีปริมาณไฮโดรคาร์บอนอิ่มตัวและปริมาณแนฟทามากกว่าการใช้ตัวเร่งปฏิกิริยาที่มีโลหะชนิดเดียวซึ่งเกิดจากการทำงานร่วมกันของโลหะสองชนิด และพบว่าการใช้ตัวเร่งปฏิกิริยาที่เตรียมโดยการเติมโลหะแบบทีละตัวโดยเติมโลหะแพลตตินัมก่อนที่อัตราส่วนปริมาณของพาลาเดียมต่อปริมาณของโลหะทั้งหมดในตัวเร่งปฏิกิริยา เท่ากับ 0.2 และ 0.8 สามารถที่จะนำมาใช้เพื่อการผลิตน้ำมันที่มีความเสถียรสูงได้ เพราะผลิตภัณฑ์ที่ได้จากตัวเร่งปฏิกิริยานี้มีปริมาณของไฮโดรคาร์บอนอิ่มตัวสูง และปริมาณซัลเฟอร์ในน้ำมันต่ำ

ABSTRACT

5171026063: Petrochemical Technology

Thirapat Latthikawiboon: Catalytic Pyrolysis of Waste Tire over Y-based Catalysts: Synergistic effect between Pd-Pt

Thesis Advisors: Assoc. Prof. Sirirat Jitkamka, 114 pp.

Keywords: Pd / Pt / Bimetallic catalyst / pyrolysis / hydrogenation

The waste tire pyrolysis is the promising way to solve the problems of insufficient fuel resources. Its products consist of gas and oil with insufficient qualities for direct uses in engines. Using the bimetallic, Pd and Pt, on Y-zeolite was expected to increase the quality and quantity of pyrolytic products due to the synergistic effect between the two metals. In this work, two different methods: co-impregnation (Pd-Pt/Y) and successive impregnation techniques (Pd*-Pt/Y and Pd-Pt*/Y; the asterisk indicates the metal impregnated first) were used for preparing the bimetallic catalysts. The amounts of Pd per total metals (α_{Pd}) were relatively varied as 0, 0.2, 0.4, 0.6, 0.8, and 1 %wt for both sets of catalysts prepared. The objectives were to examine the quantity and quality of the pyrolytic products and to verify the effective composition of catalyst for the production of high quality products. Among the significant results, using the bimetallic catalysts produced high quality oil with a high saturated hydrocarbon and low sulfur content due to the synergistic effect between the Pd and the Pt. The Pd-Pt*/Y at $\alpha_{Pd} = 0.2$ and 0.8 with high metal dispersion, wide size distribution, and high sulfur tolerance, can expectedly produce a highly-stable fuel with the reason that these ratios gave a large amount of saturated hydrocarbons and low number of aromatics and sulfur contents.

ACKNOWLEDGEMENTS

Firstly, I would like to thank my advisor, Assoc. Prof. Sirirat Jitkarnka, who had always cared and paid attention to my work since the beginning, giving valuable suggestions and recommendations which all are important to reach to this success of work though.

Further, a grateful mention to one PPC alumni, Dr. Nguyen Anh Dung who also shared his experience and recommendations, and guided the preliminary experiments and procedures. Also, I thank my friends for the great willing. They were helpful, and always collaborated me until passing through the obstacles.

This thesis work was mutually funded by the Petroleum and Petrochemical College, Chulalongkorn University, Thailand Research Fund, and the Commission on Higher Education, and the National Center of Excellent for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

I also would like to thank all staff of the Petroleum and Petrochemical, College for helpfulness in mending the instruments, and for every recommendations in instrumental analysis.

Inevitably, very kind supports from my family made me have a chance to study here, and I thank for their important encouragement until the achievement of my thesis work.

TABLE OF CONTENTS

	PAGE
Title page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	xiii
 CHAPTER	
I. INTRODUCTION	1
II LITERATURE REVIEW	4
III EXPERIMENTAL	16
3.1 Materials	16
3.2 Equipment	16
3.3 Chemicals and Solvents	16
3.4 Methodology	17
3.4.1 Bimetallic Catalyst Preparation	17
3.4.2 Pyrolysis process	18
3.4.3 Catalyst characterization	20
3.4.4 Oil analysis	22
3.4.5 Gas analysis	23

CHAPTER	PAGE
VI RESULTS AND DISCUSSION	24
4.1 Effect of preparation and metal ration pyrolysis products	25
4.1.1 Product yield	25
4.1.2 Chemical compositions in oils	27
4.1.3 Petroleum fractions in maltene	33
4.1.4 Light olefins and liquid petroleum gas	35
4.2 Characterization of Pd and Pt bimetallic catalysts	38
4.2.1 Bimetallic interaction	38
4.2.2 Metal dispersion, metal particle size, and size distribution	42
4.2.3 Sulfur tolerance and coke deposition	46
V CONCLUSIONS AND RECOMMENDATIONS	50
5.1 Conclusions	50
5.2 Recommendations	51
REFERENCES	52
APPENDICES	58
Appendix A Temperature Profile	58
Appendix B Pyrolysis Product Yields	74
Appendix C Chemical Composition in Maltenes	76
Appendix D True Boiling Point Profiles	78
Appendix E Liquid Petroleum Fractions in Maltenes	94
Appendix F Pyrolysis Gas Composition Yields	100
Appendix G The Amount of Metal Loading on The Catalysts	106
Appendix H The Amount of Sulfur Deposition on The Catalysts	107

	PAGE
Appendix I TEM IMAGES, Metal Particle Sizes, and Size Distribution	108
CURRICURUM VITAE	114

LIST OF TABLES

TABLE	PAGE
3.1 Optimized composition and volumes of mobile phased for preparative separation of petroleum maltenes on used chromatographic column.	23
4.1 Physical and chemical properties of Y-zeolite	24
4.2 Catalyst samples in this work	25
4.3 Amount of polar-aromatic compounds in the maltenes determined by liquid chromatography	31
4.4 Metal particle size and the metal dispersion of catalyst samples	43
A1 Temperature profiles of pyrolysis without a catalyst	58
A2 Temperature profiles of pyrolysis with Y-zeolite	59
A3 Temperature profiles of pyrolysis with Pd/Y catalyst	60
A4 Temperature profiles of pyrolysis with Pt/Y catalyst	61
A5 Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.8$)	62
A6 Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.6$)	63
A7 Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.4$)	64
A8 Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.2$)	65
A9 Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.8$)	66
A10 Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.6$)	67
A11 Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.4$)	68
A12 Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.2$)	69

TABLE	PAGE	
A13	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.8$)	70
A14	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.6$)	71
A15	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.4$)	72
A16	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.2$)	73
B1	Effect of Y-zeolite, Pt/Y, and Pd/Y catalysts on product yields	74
B2	Effect of preparation and metal ratio of bimetallic catalysts on product yields	74
C1	Effect of Y-zeolite, Pt/Y, and Pd/Y catalysts on the chemical composition of oil	76
C2	Effect of Pd-Pt/Y catalysts on the chemical composition of oil	76
C3	Effect of Pd*-Pt/Y catalysts on the chemical composition of oil	76
C4	Effect of Pd-Pt*/Y catalysts on the chemical composition of oil	76
D1	True boiling point curves of pyrolysis without a catalyst	78
D2	True boiling point curves of pyrolysis with Y-zeolite catalyst	79
D3	True boiling point curves of pyrolysis with Pd/Y catalyst	80
D4	True boiling point curves of pyrolysis with Pd/Y catalyst	81
D5	True boiling point curves of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.8$)	82
D6	True boiling point curves of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.6$)	83
D7	True boiling point curves of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.4$)	84

TABLE	PAGE
D8 True boiling point curves of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.2$)	85
D9 True boiling point curves of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.8$)	86
D10 True boiling point curves of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.6$)	87
D11 True boiling point curves of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.4$)	88
D12 True boiling point curves of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.2$)	89
D13 True boiling point curves of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.8$)	90
D14 True boiling point curves of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.6$)	91
D15 True boiling point curves of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.4$)	92
D16 True boiling point curves of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.2$)	93
E1 Influence of Y, Pd/Y, and Pt/Y catalysts on petroleum fractions	94
E2 Influence of bimetallic catalysts prepared by co-impregnation (Pd-Pt/Y) on petroleum fractions	94
E3 Influence of bimetallic catalysts prepared by successive-impregnation with loading Pd first (Pd*-Pt/Y) on petroleum fractions	95
E4 Influence of bimetallic catalysts are prepared by successive-impregnation with loading Pt first (Pd-Pt*/Y) on petroleum fractions	95
F1 Influence of Y-zeolite, Pd/Y, and Pt/Y catalysts on the yield of gas compositions	100

TABLE		PAGE
F2	Influence of metal ratio of bimetallic catalysts (Pd-Pt/Y) on the yield of gas compositions	100
F3	Influence of metal ratio of bimetallic catalysts (Pd*-Pt/Y) on the yield of gas compositions	101
F4	Influence of metal ratio of bimetallic catalysts (Pd-Pt*/Y) on the yield of gas compositions	101
G1	Amounts of Pd and Pt metal loading on the catalyst samples	106
H1	Amount of sulfur content in oil product and on the catalysts	107

LIST OF FIGURES

FIGURE	PAGE
2.1 Proposed reaction scheme for the hydroconversion of tetralin on bifunctional catalysts.	11
2.2 Phase diagram for Pd-Pt alloy.	13
2.3 Schematic diagram of the zeolite-Y.	14
3.1 An autoclave reactor in the experiment.	19
3.2 Diagram of the pyrolysis process.	20
4.1 Effect of metal ratio and catalyst preparation on (a) liquid product yield and (b) gas product yield.	26
4.2 Effect of metal ratio and catalyst preparation on saturated hydrocarbon yield in the oil products.	28
4.3 Effect of metal ratio and catalyst preparation on saturated hydrocarbons/total aromatics ratios.	29
4.4 Effect of the bimetallic catalysts on the sulfur content in oil products.	32
4.5 Effect of metal ratio and catalyst preparation on: (a) naphtha yield, (b) kerosene yield, and (c) gas oil yield in maltenes.	34
4.6 Effect of metal ratio and catalyst preparation on: (a) Light olefins, and (b) LPG yields.	36
4.7 TPR profiles of bimetallic catalysts: (a) Pd-Pt/Y, (b) Pd*-Pt/Y, and (c) Pd-Pt*/Y catalysts.	39
4.8 TEM images and the size distribution of the bimetallic catalysts: (a) Pd-Pt/Y at $\alpha_{Pd} = 0.6$, (b) Pd-Pt*/Y at $\alpha_{Pd} = 0.2$, and (c) Pd-Pt*/Y at $\alpha_{Pd} = 0.8$.	45
4.9 Sulfur deposition on the bimetallic catalysts.	47
4.10 Coke formation on the bimetallic catalysts.	48
A1 Temperature profiles of pyrolysis without a catalyst.	58
A2 Temperature profiles of pyrolysis with Y-zeolite.	59
A3 Temperature profiles of pyrolysis with Pd/Y zeolite.	60

FIGURE	PAGE
A4	Temperature profiles of pyrolysis with Pt/Y zeolite. 61
A5	Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.8$). 62
A6	Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.6$). 63
A7	Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.4$). 64
A8	Temperature profiles of pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.2$). 64
A9	Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.8$). 66
A10	Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.6$). 67
A11	Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.4$). 68
A12	Temperature profiles of pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.2$). 69
A13	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.8$). 70
A14	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.6$). 71
A15	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.4$). 72
A16	Temperature profiles of pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.2$). 73
B1	Influence of Pd-Pt/Y catalysts on product yields. 75
B2	Influence of Pd*-Pt/Y catalysts on product yields. 75
B3	Influence of Pd-Pt*/Y catalysts on product yields. 75
C1	Effect of the α_{Pd} of co-impregnation catalysts (Pd-Pt/Y) on the chemical composition of oil. 77

FIGURE	PAGE
C2 Effect of the α_{Pd} of successive-impregnation catalysts (Pd*-Pt/Y) on the chemical composition of oil.	77
C3 Effect of the α_{Pd} of successive-impregnation catalysts (Pd-Pt*/Y) on the chemical composition of oil.	77
D1 True boiling point curves of oils and chemical compositions obtained from pyrolysis without a catalyst.	78
D2 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Y-zeolite catalyst.	79
D3 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd/Y catalyst.	80
D4 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pt/Y catalyst.	81
D5 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.8$).	82
D6 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.6$).	83
D7 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.4$).	84
D8 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt/Y catalyst ($\alpha_{Pd} = 0.2$).	85
D9 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.8$)	86
D10 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.6$)	87

FIGURE	PAGE
D11 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.4$)	88
D12 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd*-Pt/Y catalyst ($\alpha_{Pd} = 0.2$)	89
D13 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.8$)	90
D14 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.6$)	91
D15 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.4$)	92
D16 True boiling point curves of oils and chemical compositions obtained from pyrolysis with Pd-Pt*/Y catalyst ($\alpha_{Pd} = 0.2$)	93
E1 Effect of bimetallic catalysts (Pd-Pt/Y) on petroleum fractions.	96
E2 Effect of bimetallic catalysts (Pd*-Pt/Y) on petroleum fractions.	96
E3 Effect of bimetallic catalysts (Pd-Pt*/Y) on petroleum fractions.	96
E4 Effect of catalyst preparation method on naphtha yield.	97
E5 Effect of catalyst preparation method on kerosene yield.	97
E6 Effect of catalyst preparation method on LGO yield.	98
E7 Effect of catalyst preparation method on HGO yield.	98
E8 Effect of catalyst preparation method on long residue yield.	99
F1 Influence of bimetallic catalysts (Pd-Pt/Y) on gas yields.	102

FIGURE		PAGE
F2	Influence of bimetallic catalysts (Pd*-Pt/Y) on gas yields.	102
F3	Influence of bimetallic catalysts (Pd-Pt*/Y) on gas yields.	103
F4	Influence of bimetallic catalysts (Pd-Pt/Y) on light olefins.	103
F5	Influence of bimetallic catalysts (Pd*-Pt/Y) on light olefins.	103
F6	Influence of bimetallic catalysts (Pd-Pt*/Y) on light olefins.	104
F7	Influence of bimetallic catalysts (Pd-Pt/Y) on LPG yield.	104
F8	Influence of bimetallic catalysts (Pd*-Pt/Y) on LPG yield.	104
F9	Influence of bimetallic catalysts (Pd-Pt*/Y) on LPG yield.	105
I1	TEM image and size distribution of the Pd/Y catalyst.	108
I2	TEM image and size distribution of the Pd/Y catalyst.	108
I3	TEM image, size distribution, and metal composition of the Pd-Pt/Y catalyst at $\alpha_{Pd} = 0.2$.	109
I4	TEM image, size distribution, and metal composition of the Pd-Pt/Y catalyst at $\alpha_{Pd} = 0.4$.	109
I5	TEM image, size distribution, and metal composition of the Pd-Pt/Y catalyst at $\alpha_{Pd} = 0.6$.	110
I6	TEM image, size distribution, and metal composition of the Pd-Pt/Y catalyst at $\alpha_{Pd} = 0.8$.	110
I7	TEM image, size distribution, and metal composition of the Pd*-Pt/Y catalyst at $\alpha_{Pd} = 0.2$.	111
I8	TEM image, size distribution, and metal composition of the Pd*-Pt/Y catalyst at $\alpha_{Pd} = 0.4$.	111
I9	TEM image, size distribution, and metal composition of the Pd*-Pt/Y catalyst at $\alpha_{Pd} = 0.6$.	112

FIGURE		PAGE
I10	TEM image, size distribution, and metal composition of the Pd*-Pt/Y catalyst at $\alpha_{Pd} = 0.8$.	112
I11	TEM image, size distribution, and metal composition of the Pd-Pt*/Y catalyst at $\alpha_{Pd} = 0.4$.	113
I12	TEM image, size distribution, and metal composition of the Pd-Pt*/Y catalyst at $\alpha_{Pd} = 0.6$.	113