# IMPROVEMENT OF FUEL PROPERTIES VIA HYDROGENATION AND RING OPENING: STUDIES ON TETRALIN/1,3-DIMETHYLCYCLOHEXANE



Siraprapha Dokjampa

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

2007

# 502045

Thesis Title:	Improvement of Fuel Properties via Hydrogenation and Ring
	Opening: Studies on Tetralin/1,3-Dimethylcyclohexane
By:	Siraprapha Dokjampa
Program:	Petrochemical Technology
Thesis Advisors:	Assoc. Prof. Thirasak Rirksomboon
	Prof. Daniel E. Resasco
	Prof. Somchai Osuwan
	Dr. Siriporn Jongpatiwut

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

Nantayo Janumet College Director

(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:** 

Sumaeth land dy

(Assoc, Prof. Sumaeth Chavadej)

Mun Stand

(Prof. Daniel E. Resasco)

J. hnj

(Dr. Siriporn Jongpatiwut)

(Assoc. Prof. Thirasak Rirksomboon)

(Prof. Somchai Osqyan)

issanu Meeyoo) c. Prof. V

(Asst. Prof. Sirirat Jitkarnka)

#### ABSTRACT

4581003063: Petrochemical Technology

Siraprapha Dokjampa: Improvement of Fuel Properties via Hydrogenation and Ring Opening: Studies on Tetralin/1,3-Dimethylcyclohexane. Thesis Advisors: Assoc. Prof. Thirasak Rirksomboon, Prof. Daniel E. Resasco, Prof. Somchai Osuwan, and Dr. Siriporn Jongpatiwut 102 pp.

Keywords: Hydrogenation/ Ring Opening/ Tetralin/ 1,3-Dimethylcyclohexane

Due to environmental concerns, the reduction of aromatics in gasoline and diesel fuel is focused on many countries around the world. However, the decrease in aromatic contents via the hydrogenation process ended up with low octane number gasoline. Although, in the case of diesel fuel, the reduction of aromatics is closely related to an increase in cetane number, the saturation of aromatics using the conventional two-stage process might not be able to approach fuel requirements for the near future. Recently, the opening of the naphthenic ring was introduced as one of the promising reactions for both cetane and octane number improvement which depends on the positions of the cleavage of the C-C bond. In this work, the hydrogenation of tetralin on Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts in a gas phase reaction was investigated. It was found that the product selectivities depend on the intrinsic properties of the metal and the cis- to trans-decalin isomerization. A selective catalyst toward the cis-decalin product with low isomerization activity is more preferred to maximize cis-decalin, which facilitates ring opening products in subsequent processes. In addition, the ring opening of 1,3-dimethylcyclohexane (1,3-DMCH) was also carried out on Ir catalysts and promoted Ir catalysts with K or Ni. It is postulated that only the cleavage of the C-C bond at the unsubstituted position of 1,3-DMCH is desired in order to yield high branched chain hydrocarbon products which are required for octane number improvement. It was found that the addition of K or Ni altered the metal dispersion and metal-support interaction. Consequently, the product distribution can be modified using appropriate ratios of Ir to K or Ir to Ni.

# บทคัดย่อ

ศิรประภา ดอกจำปา : การปรับปรุงคุณภาพของเชื้อเพลิงโดยการเติมไฮโดรเจนของเต-ตระลินและการเปิดวงของ 1,3-ไดเมทธิลไซโคลเฮกเซน (Improvement of Fuel Properties via Hydrogenation and Ring Opening: Studies on Tetralin/1,3-Dimethylcyclohexane) อ. ที่ปรึกษา : รศ.ดร. ธีรศักดิ์ ฤกษ์สมบูรณ์ ศ.ดร. แดเนียล อี รีซัสโก ศ.ดร. สมชาย โอสุวรรณ และ ดร. ศิริพร จงผาติวุฒิ 102 หน้า

ในปัจจุบันนี้หลายประเทศทั่วโลกต่างเล็งเห็นถึงความสำคัญของพลังงานสะอาคเพิ่มมาก ขึ้น ซึ่งการลดความเข้มข้นของสารอะ โรเมติกส์ในเชื้อเพลิง โดยการเปลี่ยนให้เป็นวงแหวนอิ่มตัว ้ด้วยการเติมไฮโครเจนก็เป็นอีกทางเลือกหนึ่งที่นิยมใช้ แต่เป็นที่ทราบดีว่าก่าออกเทนของวงแหวน ้อิ่มด้วมีก่าต่ำกว่าสารอะ โรเมติกส์มาก ด้วยเหตุนี้การลดกวามเข้มข้นของสารอะ โรเมติกส์ด้วยวิธี ดังกล่าวส่งผลให้ก่าออกเทนในน้ำมันเบนซินลคลง แม้ในกรณีของน้ำมันคีเซลวงแหวนอิ่มดัวจะ ส่งผลดีต่อค่าซีเทน แต่การใช้เทคโนโลยีแบบดั้งเดิม (กระบวนการแบบ 2 ขั้นตอน) เพียงอย่าง เดียวก็ไม่สามารถรองรับความต้องการของมาตรฐานน้ำมันในอนาคตได้ ดังนั้นการเปิดวงของวง แหวนอิ่มตัวจึงเป็นอีกแนวทางหนึ่งที่ส่งผลดีต่อทั้งก่าซีเทนและก่าออกเทน ซึ่งขึ้นอยู่กับตำแหน่ง ของการแตกวง งานวิจัยชิ้นนี้ได้แบ่งเป็นสองส่วน ส่วนแรกได้ศึกษาการทำให้อิ่มตัวของสารเตตระ ลิน ด้วยการเติมไฮโดรเจนบนตัวเร่งปฏิกิริยาได้แก่ แพลททินัม พัลลาเดียม และนิเกิลบนอะลูมินา จากการศึกษาพบว่าการเลือกเกิดผลิตภัณฑ์ซีส-เดกกาลินหรือทราน-เดกกาลินขึ้นกับธรรมชาติของ ้ตัวเร่งปฏิกิริยาและปฏิกิริยาไอโซเมอร์ไรเซชั่น การเลือกตัวเร่งปฏิกิริยาที่เอื้อต่อการเลือกเกิด ผลิตภัณฑ์ซีส-เคคคาลิน และในขณะเคียวกันตัวเร่งปฏิกิริยาตั้งกล่าวต้องมีความสามารถในการ เกิดปฏิกิริยาไอโซเมอร์ไรเซชันต่ำจะสามารถเพิ่มผลิตภัณฑ์ซีส-เคกกาลินซึ่งมีความสามารถในการ แตกวงได้ดี กว่าในกระบวนการต่อไปได้ ส่วนที่สองได้ศึกษาการแตกวงของสาร1,3-ไดเมทธิลไซ โคลเฮก เซนบนตัวเร่งปฏิกิริยาอิริเดียมและอิริเดียมที่มีการเติมโพแทสเซียมหรือนิเกิล สำหรับการ แตกวงระหว่างการ์บอนสองตัวของสาร1,3-ไคเมทธิลไซโกลเฮกเซนในดำแหน่งที่การ์บอนนั้นๆมี พันธะกับการ์-บอนอื่นเพียงสองตัวเท่านั้นที่ให้ผลิตภัณฑ์ที่ให้ก่าออกเทนสูง จากการศึกษาพบว่า การผสมอิริเคียมด้วยโพแทสเซียม หรือนิเกิลทำให้เกิดการเปลี่ยนแปลงของการกระจายตัวของ ้โลหะอิริเคียมและพันธะระหว่างโลหะอิริเคียมและตัวรองรับ ซึ่งส่งผลโคยตรงต่อการเปลี่ยนแปลง กล่าวคือการเติมโพแทสเซียมหรือนิเกิลในปริมาณที่เหมาะสมบน การเลือกเกิดของผลิตภัณฑ์

ตัวเร่งปฏิกิริยาอิริเคียมสามารถเลือกการแตกวงของวงแหวนอิ่มตัวในตำแหน่งที่ด้องการได้

#### ACKNOWLEDGEMENTS

I would like to acknowledge the organization and the generous guidance and assistance of the following individuals in completing this research project:

First of all, I would like to gratefully acknowledge the generosity of the Ph.D. Program from the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0147/2547), the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials Thailand, and the Oklahoma Center for the Advancement of Science and Technology (OCAST), which have made grants to finance my research.

My PhD life might not be possible without the kind supervisions from Assoc. Prof. Thirasak Rirksomboon and Prof. Somchai Osuwan. They always sincerely proffered many suggestions. I am also appreciative of the helpfulness, tireless guidance and patient demeanour of Dr. Siriporn Jongpatiwut. A special gratitude is expressed to my US advisor, Prof. Daniel E. Resasco. I still remember my first day at OU and his warm welcome. He contributed his unconditioned kindness and, more importantly, his innovative ideas to the thesis. My work might not be possible without the supervision from all of my advisors.

I especially extend my appreciation to Assoc. Prof. Sumaeth Chavadej, Asst. Prof. Sirirat Jitkarnka, and Assoc. Prof. Vissanu Meeyoo for their recommendations serving as committee members.

The first step of the experimental part might not have been initiated without the helpfulness of C. P. O. Poon Arjpru. I would like to express my sincere gratitude for his assistance. He usually encourages me to solve many problems. I also would like to express my thanks to other PPC, OU and ConocoPhillips staff.

I especially extend many thanks to two of my colleagues during my research overseas. Firstly, Phoung T. Do, who is more than a colleague. She also stayed by my side when I faced problems. The other one, González-Cortés Sergio was always ready to lend a hand. I appreciate their kindness. And I also would like to thank all of my lovely friends at OU and PPC.

Finally, I would like to express my gratitude for the inspiration from my family.

# **TABLE OF CONTENTS**

Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	xi
List of Figures	xiii
List of Schemes	xviii

# CHAPTER

Ι	INTRODUCTION	1
II	LITERATURE REVIEW	4
	2.1 Types of Aromatic Compounds in the Petroleum	
	Fractions	4
	2.2 Revolution of the Refining Process	 4
	2.3 Future Aspects	5
	2.4 Hydrogenation of Aromatics	7
	2.5 Ring Opening Reactions	10
	2.5.1 Ring Opening of Naphthenic Molecules	10
	2.5.2 Cetane Number of the Ring Opening Products	14
	2.5.3 Prediction of Octane Number from Ring	
	Opening Products	21
III	EXPERIMENTAL	24
	3.1 Materials	24
	3.1.1 Hydrogenation of Tetralin	24
	3.1.1.1 Catalyst Preparation	24

IV

3.1.1.2 Reactants for Catalytic Activity	
Testing	24
3.1.2 Ring Opening of 1,3-Dimethylcyclohexane	24
3.1.2.1 Catalyst Preparation	24
3.1.2.2 Reactants for Catalytic Activity	
Testing	24
3.2 Catalyst Preparation	25
3.2.1 Catalysts for Hydrogenation Reaction	25
3.2.2 Catalysts for Ring Opening Reaction	25
3.3 Catalytic Activity Testing	26
3.3.1 Hydrogenation Reaction	26
3.3.2 Ring Opening Reaction	26
COMPARATIVE STUDY OF HYDROGENATION	
OF TETRALIN ON SUPPORTED Ni, Pt, AND Pd	
CATALYSTS	29
4.1 Abstract	29
4.2 Introduction	30
4.3 Experimental	33
4.3.1 Catalyst Preparation and Characterization	33
4.3.2 Catalytic Activity Tests	34
4.4 Results and Discussion	35
4.4.1 Kinetics Study	35
4.4.2 Trans/Cis Decalin Ratio	39
4.4.3 Isomerization of Cis-to-Trans Decalin in the	
Presence of Tetralin on Pt and Ni Catalysts	42
4.5 Conclusions	44
4.6 Acknowledgements	45
4.7 References	45

 $\mathbf{V}$ 

TUNING TH	E SELECTIVE OF RING OPENING	
OF 1,3-DIME	THYLCYCLOHEXANE WITH THE	
ADDITION O	<b>DF POTASSIUM OVER Ir/SiO<sub>2</sub></b>	
CATALYSTS	5	48
5.1 Abstract		48
5.2 Introducti	on	49
5.3 Experiment	ntal	51
5.3.1 Cat	alyst Preparation	51
5.3.2 Cat	alyst Characterization	51
5.3.	2.1 Elemental Analysis	51
5.3.	2.2 Chemisorption of CO	52
5.3.	2.3 Temperature Programmed Reduction	
	(TPR)	52
5.3.	2.4 X-ray Photoelectron Spectroscopy	
	(XPS)	52
5.3.	2.5 Extended X-ray Absorption Fine	
	Structure (EXAFS) and Near Edge X-	
	ray Absorption Fine Structure	
	(NEXAFS)	53
5.3.3 Cat	alytic Activity Measurement and Data	
Ana	alysis	54
5.4 Results ar	nd Discussion	54
5.4.1 Cha	aracterization	54
5.4.	1.1 Metal Dispersion and Particle Size of	
	Ir Catalysts	54
5.4.	1.2 Temperature Programmed Techniques	55
5.4	1.3 X-ray Photoelectron Spectroscopy	56

VI

5.4.1.4 Extended X-ray Absorption Fine	
Structure and Near Edge X-ray	
Absorption Fine Structure	57
5.4.2 Catalytic Activity	61
5.5 Conclusions	65
5.6 Acknowledgements	66
5.7 References	66
RING OPENING OF 1,3-DIMETHYLCYCLO-	
HEXANE ON Ir CATALYSTS. MODIFICATION OF	
<b>DISTRIBUTION BY ADDITION OF Ni AND K TO</b>	
IMPROVE FUEL PROPERTIES	69
6.1 Abstract	69
6.2 Introduction	70
6.3 Experimental	73
6.3.1 Materials Investigated	73
6.3.2 Catalyst Characterization	73
6.3.3 Catalytic Activity Measurements	74
6.4 Results and Discussion	74
6.4.1 Characteristics of the Catalysts Investigated	74
6.4.2 Ring Opening of 1,3-DMCH on Monometallic	
Ir Catalysts	76
6.4.3 Reactions on Bimetallic Ni-Ir Catalysts	84
6.4.4 Reactions on K-Promoted Ir Catalysts	86
6.4.5 Impact of the Ring Opening and	
Hydrogenolysis Reactions on Octane Number	
and Ried Vapor Pressure of the Product	
Mixture	88
6.5 Conclusions	91

6.5 Conclusions

CHAPTER		PAGE
	6.6 Acknowledgements	91
	6.7 References	92
VII	CONCLUSIONS AND RECOMMENDATIONS	94
	REFERENCES	97
	CURRICULUM VITAE	100

# LIST OF TABLES

# TABLE

# **CHAPTER II**

Predicted cetane numbers of ring contraction products of the	
reaction pathway of acid-catalyzed ring opening of decalin	
(Santana et al., 2006)	16
Predicted cetane numbers of ring opening products of the	
reaction pathway of acid-catalyzed ring opening of decalin	
(Santana <i>et al.</i> , 2006)	17
Predicted cetane numbers of alkane products of the reaction	
pathway of acid-catalyzed ring opening of decalin (Santana	
<i>et al.</i> , 2006)	18
Parameters values for octane number calculation (Ghosh et	
al., 2006)	23
	Predicted cetane numbers of ring contraction products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana <i>et al.</i> , 2006) Predicted cetane numbers of ring opening products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana <i>et al.</i> , 2006) Predicted cetane numbers of alkane products of the reaction pathway of acid-catalyzed ring opening of decalin (Santana <i>et al.</i> , 2006) Parameters values for octane number calculation (Ghosh <i>et</i> <i>al.</i> , 2006)

# **CHAPTER IV**

4.1	Characterization of the catalysts investigated	34
4.2	Tetralin hydrogenation activity on different catalysts	
	Reaction conditions: 3540 kPa, 548K, H <sub>2</sub> /HC=25, TOS=6 h	35
4.3	Kinetics parameters for the hydrogenation of tetralin $(r_1, as$	
	shown below) and cis-to-trans decalin isomerization $(r_2, as$	
	shown below) at 3540 kPa and 548 K, $H_2/HC=25$ ,	
	TOS = 6 h	39

### CHAPTER V

5.1	Compositions, metal dispersion of Ir/SiO <sub>2</sub> and Ir-K/SiO <sub>2</sub>	
	catalysts	55
5.2	Electron binding energies of the core levels for Ir 4f, K 2p	
	and Si 2p in the K ion-promoted Ir/SiO <sub>2</sub> catalysts	57

5.3	Structural parameters of iridium obtained from fitting of	
	EXAFS data using theoretical references developed with	
	FEFF	60

# **CHAPTER VI**

6.1	Composition and metal dispersions of the 0.9 wt.% Ir-	
	containing catalysts	75
6.2a	Liquid product distribution from 1,3-DMCH at 603 K, 3540	
	kPa, H <sub>2</sub> /HC ratio of 30, and time on stream of 2 hours over	
	the different catalysts investigated (low conversion)	77
6.2b	Liquid product distribution from 1,3-DMCH at 603 K, 3540	
	kPa, H <sub>2</sub> /HC ratio of 30, and time on stream of 2 hours over	
	the different catalysts investigated (high conversion)	78

# **LIST OF FIGURES**

# FIGURE

# PAGE

# **CHAPTER II**

2.1	Two-stage process for diesel aromatics removal.	5
2.2	Ring opening mechanisms on metal catalyst (Do et al.,	
	2006).	13
2.3	Ratio of substituted C-C cleavage to unsubstituted C-C	
	cleavage of 1,3-DMCH over Ir on different supports.	
	Without considering secondary hydrogenolysis, the ratio of	
	(2-MC7 + 4-MC7)/2,4-DMC6 would represent the ratio of	
	(a+b)/c cleavage (the statistical value of (a+b)/c is 2). $\blacktriangle$ =	
	$Ir/Al_2O_3$ ; $\diamond = Ir/SiO_2$ ; $\Box = Ir/TiO_2$ (Do <i>et al.</i> , 2006).	14
2.4	Predicted cetane numbers of intermediates and products of	
	the reaction pathway of acid-catalyzed ring opening of	
	decalin (Santana et al., 2006).	15
2.5	Predicted cetane numbers of intermediates and products of	
	the reaction pathway of metal-catalyzed ring opening of	
	decalin via dicarbene mechanism (Santana et al., 2006).	19
2.6	Predicted cetane numbers of intermediates and products of	
	the reaction pathway of metal-catalyzed ring opening of	
	decalin via substituted C-C bond cleavage mechanism	
	(Santana et al., 2006).	19
2.7	Predicted cetane numbers of intermediates and products of the	
	reaction pathway of the opening of one ring of	20
	perhydrophenanthrene.	
2.8	Predicted cetane numbers and specific volume of typical	
	products of selective ring opening (Santana et al., 2006).	21

# FIGURE

# **CHAPTER III**

3.1	Schematic of the experimental set up for hydrogenation and	
	ring opening reaction.	27
3.2	A photograph of the experimental apparatus.	28

# **CHAPTER IV**

4.1	Tetralin conversion to decalin as a function of space time	
	during hydrogenation in a flow reactor at 3540 kPa and 548	
	K H <sub>2</sub> /HC=25, TOS = 6 h. ■, Pt/Al <sub>2</sub> O <sub>3</sub> ; $\bigcirc$ , Ni/Al <sub>2</sub> O <sub>3</sub> ; $\triangle$ ,	
	Pd/Al <sub>2</sub> O <sub>3</sub> . Solid lines are the results of the kinetic model.	37
4.2	Cis-to-Trans decalin isomerization in pure decalin feed	
	(trans:cis feed ratio is 60:40). Reaction conditions: 3540 kPa	
	and 548 K, $H_2/HC=25$ , $TOS = 3$ h. $\blacksquare$ , $Pt/Al_2O_3$ ; $\bigcirc$ ,	
	Ni/Al <sub>2</sub> O <sub>3</sub> ; $\triangle$ , Pd/Al <sub>2</sub> O <sub>3</sub> . Solid lines are the results of the	
	kinetic model.	38
4.3	Trans/cis-decalin ratio of tetralin hydrogenation as a	
	function of tetralin conversion. Reaction conditions: 3540	
	kPa and 548 K, H <sub>2</sub> /HC=25, TOS = 3 h. $\blacksquare$ , Pt/Al <sub>2</sub> O <sub>3</sub> ; $\bigcirc$ ,	
	Ni/Al <sub>2</sub> O <sub>3</sub> ; $\triangle$ , Pd/Al <sub>2</sub> O <sub>3</sub> .	40
4.4a	Rate of cis-to-trans isomerization in a combined feed $(\blacksquare)$	
	(tetralin:cis-decalin:transdecalin, 20:32:48) compared to the	
	isomerization rate obtained in a pure decalin feed ( $\Box$ )	
	(cis:trans, 40:60) on Pt/Al <sub>2</sub> O <sub>3</sub> as a function of W/F. Solid	
	lines are the results of the kinetic model.	43
4.4b	Rate of cis-trans isomeriation in mixed feed $(\bullet)$	
	(tetralin:cis-decalin: trans-decalin, 20:32:48) compared to	
	rate of cis-trans isomerization in pure feed ( $\bigcirc$ ) (cis:trans,	
	40:60) onNi/Al <sub>2</sub> O <sub>3</sub> as a function of W/F. Solid lines are the	
	results of the kinetic model.	44

### **CHAPTER V**

5.1	Temperature-programmed reduction profiles of the catalytic	
	precursors of potassium (K) promoted Ir/SiO <sub>2</sub> catalysts.	56
5.2	Amplitudes of the Fourier transforms of EXAFS data of	
	samples measured in H <sub>2</sub> at room temperature after reduction	
	at 723 K. Solid lines show the corresponding Fourier	
	transforms of the fitted functions.	59
5.3	Surface representation of the potassium influence over	
	silica-supported Ir particles.	60
5.4	Effect of the potassium loadings on 1,3-DMCH conversion	
	and the (2-MC7+4-MC7/2,4-DMC6) ratios. Reactions were	
	carried out at 593 K, 3540 kPa and $H_2/HC$ ratio of 30.	62
5.5	Yield of 2,4-DMC6 product on $Ir/SiO_2$ ( $\Box$ ) and $Ir-2K/SiO_2$	
	( $\blacksquare$ ), and yield of (2-MC7+4-MC7) on Ir/SiO <sub>2</sub> ( $\bigcirc$ ) and Ir-	
	$2K/SiO_2(\bullet)$ from 1,3-DMCH conversion. Reactions were	
	conducted at 593 K, total pressure of 3540 kPa and $H_2/HC$	
	ratio of 30.	64

# **CHAPTER VI**

6.1	Temperature-programmed reduction of Ir, Ni and IrNi	
	catalysts.	75
6.2	Octane number and vapor pressure of typical products of	
	1,3-DMCH ring opening.	79
6.3	Yield of high octane number products (2,4-DMC6, 2,4-	
	DMC5, 2MC5, 3MC5) on $Ir/Al_2O_3$ ( $\blacksquare$ ) and $Ir/SiO_2$	
	(●)catalysts.	80

6.4	Selectivities of hydrogenolysis of 2,4-DMC6 at different C-	
	C bond position was conducted at 603 K and 3540 kPa.	
	$H_2/HC$ ratio of 30, whsv of 0.008 h on $Ir/Al_2O_3$ and 0.025 h	
	on Ir/SiO <sub>2</sub> . Products 2,4-DMC5 (from C1-C2); 3-MC6 and	
	2MC6 (from C1-C3); 2-MC5, iso-C4 and iso-C5 (from C2-	
	C3).	81
6.5	Selectivities of hydrogenolysis of 2-DMC7 at different C-C	
	bond position was conducted at 603 K and 3540 kPa. $H_2/HC$	
	ratio of 30, whsv of 0.008 h on $Ir/Al_2O_3$ and 0.025 h on	
	Ir/SiO2. Products 2,4-DMC5 (from C1-C2); 3-MC6 and	
	2MC6 (from C1-C3); 2-MC5, iso-C4 and iso-C5 (from C2-	
	C3).	82
6.6a	Yield of high octane number products from ring opening of	
	1,3-DMCH over Ir/Al <sub>2</sub> O <sub>3</sub> catalyst. Reaction was conducted	
	at 603 K and 3540 kPa, H₂/HC ratio of 30. □, 2,4-DMC6;	
	■ , 2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.	83
6.6b	Yield of high octane number products from ring opening of	
	1,3-DMCH over $Ir/SiO_2$ catalyst. Reaction was conducted at	
	603 K and 3540 kPa, H <sub>2</sub> /HC ratio of 30. $\Box$ , 2,4-DMC6;	
	2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.	84
6.6c	Yield of high octane number products from ring opening of	
	1,3-DMCH over IrNi <sub>0.3</sub> Al catalyst. Reaction was conducted	
	at 603 K and 3540 kPa, H₂/HC ratio of 30. □, 2,4-DMC6;	
	■ , 2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.	85
6.6d	Yield of high octane number products from ring opening of	
	1,3-DMCH over IrKAl catalyst. Reaction was conducted at	
	603 K and 3540 kPa, H <sub>2</sub> /HC ratio of 30. $\Box$ , 2,4-DMC6; $\blacksquare$ ,	
	2,4-DMC5; ▲, 2-MC5; ●, 3-MC5.	86

PAGE

# FIGURE

. .

6.7	Ratio of di-branched to mono-branched C8 products from	
	1,3-DMCH ring opening as a function of total conversion.	
	Reaction conducted at 603 K and 3540 kPa, H <sub>2</sub> /HC ratio of	
	30. Catalysts: ■, IrAl; ●, IrSi; △ IrNi0.3Al; □, IrK2.5Al.	87
6.8	Octane number of product mixture from ring opening of 1,3-	
	DMCH, calculated by method of Ref. [38]. $\blacksquare$ , IrAl; $\bullet$ , IrSi;	
	$\triangle$ IrNi0.3Al; $\Box$ , IrK2.5Al.	89
6.9	Reid vapor pressure (RVP) of product mixture from ring	
	opening of 1,3-DMCH. ■, IrAl; ●, IrSi; △ IrNi0.3Al; □,	
	IrK2.5Al.	90

PAGE

# **LIST OF SCHEMES**

### SCHEME

# PAGE

# **CHAPTER II**

2.1	Reaction pathway of tetralin hydrogenation (Weitkamp et	
	<i>al.</i> , 1968).	9
2.2	Reaction pathway for isomerization of cis- to trans-decalin	
	(Huang and Kang, 1995).	10
2.3	Aromatics saturation (ASAT) of multi-ring aromatic	
	followed by selective ring opening (SRO) provides density	
	and cetane number benefits (McVicker et al., 2002).	11

# **CHAPTER V**

5.1	Cetane numbers and reaction pathways for the primary	
	products from ring opening reaction of 1,3-DMCH.	61

# **CHAPTER V**

6.1	Some of the ring opening (primary) and hydrogenolysis	
	(secondary) products obtained from 1,3-DMCH on Ir	
	catalysts.	71