# IN-SITU CATALYTIC PYROLYSIS REACTION OF SUGARCANE BAGASSE OVER NICKEL-CERIUM/HZSM-5 FOR ENHANCED HYDROCARBONS IN PYROLYSIS OIL

### VEKES A/L BALASUNDRAM

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy

School of Chemical and Energy Engineering Faculty of Engineering Universiti Teknologi Malaysia

SEPTEMBER 2018

I would like to dedicate my thesis to my beloved mother and father

### ACKNOWLEDGEMENT

First and foremost, I would like to take this opportunity to thank my respectful supervisor Dr. Norazana Ibrahim for her tremendous support, encouragement, guidance, critics and friendly in the successful completion of this research. I am also very thankful to my co-supervisor, Dr. Ruzinah Isha from Universiti Malaysia Pahang for her guidance, constructive ideas, and motivation all the way from Pahang to ensure outstanding output from this research. I would also like to show my greatest appreciation to my second co-supervisor, Assoc. Prof. Dr. Mohd Kamaruddin Abd. Hamid for his extended support and guidance throughout this research journey. I could not have done this without their support. This research also would not have been possible without the help of technical staffs Mr Mohd Zaid, Mr Ahmad, and Mr Muhammad Khairul from UTM Institute for Oil and Gas (IFOG) who have provided assistance at various occasions.

I would also like to take this opportunity to express my deepest gratitude to all staffs from postgraduate office of School of Chemical and Energy Engineering and a special thanks to Mrs Lijah Rosdi for her continuous encouragement and friendly atmosphere throughout this research. I am indebted to Universiti Teknologi Malaysia (UTM) for providing research grants for smooth research progress. I also would like to express my gratitude to Ministry of Higher Education (MOHE) for providing MyBrain15. Finally, heartfelt thanks to my lovely mother Mrs. Sandra Murugas and my lovely father Mr. T.P. Balasundram for their encouragement throughout this research journey. I am also would like to thank my two sisters Mrs. Jayasri and Ms. Venolia for giving motivation and love in my life and also my brother-in-law Mr. Ghopalen.

### ABSTRACT

The catalytic of oxygenated pyrolysis vapour over HZSM-5 catalyst is of the preferred method to enhance the quality of pyrolysis oil. However, the content of C<sub>6</sub>  $-C_8$  hydrocarbons in pyrolysis oil produced by this method is still low. Thus, the main aim of this study is to investigate the in-situ catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 - C_8$  hydrocarbons in pyrolysis oil over nickel-cerium/HZSM-5 catalyst. The first aim was to synthesize catalysts via incipient wetness impregnation and characterize via X-ray diffraction, field emission scanning electron microscopy-energy dispersive X-ray, Brunauer Emmett Teller, Fourier transform infrared, and temperature programmed desorption of ammonia. The HZSM-5 was fixed at 94 wt.%, while the balance 6 wt.% was impregnated at nickel to cerium mass ratios as follows: 1:5 (NC1), 2:4 (NC2), 3:3 (NC3), 4:2 (NC4), and 5:1 (NC5). The second aim was to investigate the performance of catalyst in the catalytic of oxygenated pyrolysis vapours into enhanced  $C_6 - C_8$  hydrocarbons via in-situ fixed bed reactor at pyrolysis reaction temperature ranging from 400 - 600°C. The catalyst to biomass mass ratios was as follows: 0.5:1.0 (CB1), 1.0:1.0 (CB2), 1.5:1.0 (CB3), 2.0:1.0 (CB4), 2.5:1.0 (CB5), and 3.0:1.0 (CB6). The results show that the in-situ catalytic of oxygenated pyrolysis vapours were significantly influenced by pyrolysis reaction temperatures, catalyst to biomass mass ratios, and nickel to cerium mass ratios. The highest total contents of  $C_6 - C_8$  hydrocarbons in pyrolysis oil (8.82%) is attained at pyrolysis reaction temperature of 500 °C, catalyst to biomass mass ratio of 1:1, and nickel to cerium mass ratio of 3:3. The third aim was to optimize the process parameters via response surface methodology, in which the optimized  $C_6 - C_8$  hydrocarbons in pyrolysis oil (8.90%) can be achieved at pyrolysis reaction temperature of 505 °C, catalyst to biomass mass ratio of 1.1:1.0, nickel to cerium mass ratio of 3.14:2.86. The final aim was to perform the kinetic analysis of catalytic pyrolysis process. For the kinetic analysis, the catalytic pyrolysis has achieved higher activation energy (34.02 – 122.23 kJ/mol) than the non-catalytic pyrolysis (17.17 – 66.90 kJ/mol) using the Flynn-Wall-Ozawa method. The reaction mechanisms of non-catalytic and catalytic pyrolysis obtained via the Coats-Redfern method follows power law (n = 1) and chemical reaction (n = 2) respectively. Finally, the catalytic of oxygenated pyrolysis vapours over nickel-cerium/HZSM-5 catalyst can produce high contents of hydrocarbon fuel directly from sugarcane bagasse.

### ABSTRAK

Pemangkin wap pirolisis oksigen dengan menggunakan mangkin HZSM-5 adalah kaedah pilihan untuk meningkatkan kualiti minyak pirolisis. Bagaimanapun, kandungan hidrokarbon  $C_6 - C_8$  dalam minyak pirolisis yang terhasil dengan kaedah ini adalah masih rendah. Oleh itu, matlamat utama kajian ini adalah untuk mengkaji in-situ pemangkin wap pirolisis oksigen daripada hampas tebu ke hidrokarbon C<sub>6</sub> – C<sub>8</sub> dalam minyak pirolisis menggunakan mangkin nikel-serium/HZSM-5. Matlamat pertama adalah untuk menghasilkan mangkin melalui impregnasi basah dan dicirikan melalui belauan sinar-X, mikroskop penyebaran emisi medan elektron-sinar-X penyebaran tenaga, Brunauer Emmett Teller, spektroskopi infra-merah jelmaan Fourier, dan penyahjerapan ammonia berprogram suhu. HZSM-5 telah ditetapkan pada 94 % berat, manakala 6 % berat adalah berdasarkan pada nisbah jisim nikel kepada serium: 1:5 (NC1), 2:4 (NC2), 3:3 (NC3), 4:2 (NC4), dan 5:1 (NC5). Matlamat kedua adalah untuk mengkaji prestasi mangkin dalam proses peningkatan wap pirolisis oksigen ke hidrokarbon  $C_6 - C_8$  dalam reaktor padatan tetap in-situ pada suhu tindak balas pirolisis iaitu 400 - 600 °C. Nisbah jisim mangkin kepada biojisim ialah 0.5:1.0 (CB1), 1.0:1.0 (CB2), 1.5:1.0 (CB3), 2.0:1.0 (CB4), 2.5:1.0 (CB5), dan 3.0:1.0 (CB6). Hasil keputusan menunjukkan bahawa in-situ pemangkin wap pirolisis oksigen amat dipengaruhi oleh suhu tindak balas pirolisis, nisbah jisim mangkin kepada biojisim, dan nisbah jisim nikel kepada serium. Kandungan hidrokarbon C<sub>6</sub> – C<sub>8</sub> yang tertinggi dalam minyak pirolisis (8.82%) telah dicapai pada suhu tindak balas pirolisis 500 °C, nisbah jisim mangkin kepada biojisim iaitu 1:1, dan nisbah jisim nikel kepada serium iaitu 3:3. Matlamat ketiga ialah untuk mengoptimumkan parameter proses melalui kaedah gerak balas permukaan yang telah mengoptimumkan hidrokarbon  $C_6 - C_8$  dalam minyak pirolisis (8.90%) boleh dicapai pada suhu tindak balas pirolisis 505 °C, nisbah jisim mangkin kepada biojisim iaitu 1.1:1.0, nisbah jisim nikel kepada serium iaitu 3.14:2.86. Matlamat akhir adalah untuk melaksanakan analisis kinetik proses pirolisis mangkin. Pirolisis bermangkin telah mencapai tenaga pengaktifan yang tinggi (34.02 – 122.23 kJ/mol) berbanding pirolisis biojisim (17.17 – 66.90 kJ/mol) menggunakan kaedah Flynn-Wall-Ozawa. Mekanisme tindak balas pirolisis tanpa bermangkin dan bermangkin diperoleh melalui kaedah Coats-Redfern masing-masing adalah mematuhi hukum kuasa (n = 1) dan tindak balas kimia (n = 2). Akhirnya, peningkatan wap pirolisis oksigen menggunakan mangkin nikel-serium/HZSM-5 boleh menghasilkan bahan api hidrokarbon yang tinggi daripada hampas tebu.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xi
	LIST OF FIGURES	xiii
	LIST OF ABBREVIATIONS	xvii
	LIST OF SYMBOLS	xix
	LIST OF APPENDICES	XX
1	INTRODUCTION	1
	1.1 Research Background	1
	1.2 Problem Statement	5
	1.3 Research Objectives	7
	1.4 Scope of Research	8
	1.5 Research Significance	9
	1.6 Thesis Outline	10
2	LITERATURE REVIEW	11
	2.1 Introduction	11
	2.2 Biomass Feedstock	12
	2.3 Pyrolysis of Biomass	14
	2.3.1 Pyrolysis Mechanism	15

	2.3.2	Properties of Pyrolysis Oil	18
2.4	Enhai	ncement of Biomass Pyrolysis Vapour	21
2.5	Catal	ytic Pyrolysis over Zeolite Catalyst	23
	2.5.1	Zeolites	25
	2.5.2	Influence of Zeolite Catalyst on Catalytic Pyrolysis	30
2.6	Metal	Modified HZSM-5 for $C_6 - C_8$ Hydrocarbons	
	Produ	iction	42
	2.6.1	Properties of HZSM-5 Catalyst	42
	2.6.2	Metal Modified HZSM-5 Catalyst	43
	2.6.3	Alkali and Alkaline Earth Metal Modified on HZSM-5	45
	2.6.4	Transition Metal Modified on HZSM-5	48
	2.6.5	Rare Earth Metal Modified on HZSM-5	54
	2.6.6	Multifunctional Metal Modified on HZSM-5	58
	2.6.7	Concluding Remarks on Metal Modified HZSM-5	66
2.7	Optin	nization via Response Surface Methodology	68
	2.7.1	Central Composite Design	70
	2.7.2	Box-Behnken Design	71
	2.7.3	Concluding Remark on RSM	73
2.8	Kinet	ic Analysis of Catalytic Pyrolysis of Biomass	73
	2.8.1	Thermogravimetric Analysis	75
	2.8.2	Concluding Remark on Kinetic Analysis	81
2.9	Sumn	nary of Chapter	81
ME	THO	DOLOGY	82
3.1	Introc	luction	82
3.2	Biom	ass Preparation and Characterization	83
3.3	Catal	yst Preparation and Characterization	85
	3.3.1	Phase Analysis	87
	3.3.2	Surface Morphology and Elemental Loading Analysis	87
	3.3.3	Surface Area and Pore Size Analysis	87
	3.3.4	Framework Vibration Analysis	88

viii

3

3.3.5 Acidic Analysis	88
3.3.6 Coke Analysis	89
3.4 In-situ Catalytic of Oxygenated Pyrolysis Vapours	89
3.4.1 Characterization of Pyrolysis Oil	93
3.5 Optimization via Response Surface Methodology	94
3.6 Kinetic Analysis	96
3.7 Summary of Chapter	102
<b>RESULTS AND DISCUSSION</b>	103
4.1 Introduction	103
4.2 Biomass Characterization	104
4.3 Catalyst Characterization	106
4.3.1 Phase Analysis	107
4.3.2 Surface Morphology and Elemental Loading	109
4.3.3 Surface Area and Pore Size Analysis	113
4.3.4 Framework Vibration Analysis	117
4.3.5 Acidic Analysis	120
4.3.6 Summary of Catalyst Characterization	123
4.4 In-situ Catalytic of Oxygenated Pyrolysis Vapours	124
4.4.1 Effect of Catalytic Pyrolysis Reaction Temperature on Pyrolysis Product Yields	124
4.4.2 Effect of Catalyst to Biomass Mass Ratio on Pyrolysis Product Yields	150
4.4.3 Effect of Nickel to Cerium Mass Ratio on Pyrolysis Product Yields	175
4.5 Response Surface Methodology	202
4.5.1 Statistical Analysis	205
4.5.2 Optimization Analysis	211
4.5.3 Summary of Response Surface Methodology	212
4.6 Kinetic Analysis of Catalytic and Non-Catalytic Pyrolysis	213
4.6.1 Thermogravimetric Analysis	214
4.6.2 Flynn-Wall-Ozawa Method	221
4.6.3 Coats-Redfern Method	224
4.6.4 Summary of Kinetic Analysis	227

4

	4.7 Summary of Chapter	228
5	CONCLUSION	230
	5.1 Conclusions	230
	5.2 Recommendations	233
REFE	RENCES	235
Appen	dices A – B	253 - 257

## LIST OF TABLES

TABLE NO.	TITLE		
2.1	Chemical composition (wt.%) of wood pyrolysis oil (Rezaei <i>et al.</i> , 2014)	18	
2.2	Properties of wood pyrolysis oil and heavy fuel oil (Zhang <i>et al.</i> , 2013a)	19	
2.3	Characteristics of zeolite porous materials (Xu et al., 2016)	28	
2.4	Summary of literature on catalytic of oxygenated pyrolysis vapour over zeolite catalyst	38	
2.5	Summary of literature on catalytic of oxygenated pyrolysis vapour over metal modified HZSM-5 catalyst	60	
2.6	Summary of kinetic parameters	79	
3.1	Synthesized catalyst samples	85	
3.2	The operating conditions for pyrolysis experiments	91	
3.3	The dimension of fixed bed reactor system	92	
3.4	Design matric using Box-Behnken design and experimental results	95	
3.5	Reaction model functions and its mechanism	101	
4.1	Physicochemical properties of sugarcane bagasse (SB)	104	
4.2	Chemical compositions of synthesized catalysts	112	
4.3	Textural properties of synthesized catalysts	114	
4.4	FTIR peak assignments	119	
4.5	TPD-NH <sub>3</sub> of synthesized catalysts	122	
4.6	The effect of catalytic pyrolysis reaction temperature on pyrolysis products yield (wt.%)	125	

4.7	The effect of catalytic pyrolysis reaction temperature (400–600°C) on relative contents (%) of organic compounds in pyrolysis oil. The bold values represent the total contents of the relative type of compounds. (Fixed parameter: Catalyst to biomass mass ratio of 1:1 and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	139
4.8	The effect of catalyst to biomass mass ratio on the pyrolysis product distribution (wt.%)	150
4.9	The effect of catalyst to biomass mass ratios on relative contents (%) of organic compounds in pyrolysis oil. The numerical bold values represent the total contents of the relative type of compounds. (Fixed parameter: Pyrolysis reaction temperature at 500 °C and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	163
4.10	The effect of nickel to cerium mass ratio on the pyrolysis products yield (wt.%) at NC0 (HZSM-5), NC1 (1 wt.% Ni : 5 wt.% Ce), NC2 (2 wt.% Ni : 4 wt.% Ce), NC3 (3 wt.% Ni : 3 wt.% Ce), NC4 (4 wt.% Ni : 2 wt.% Ce), and NC5 (5 wt.% Ni : 1 wt.% Ce)	176
4.11	The effect of nickel to cerium mass ratio on relative contents (%) of organic compounds in pyrolysis oil at NCO, NC1, NC2, NC3, NC4, and NC5 catalysts. The numerical bold values represent the total contents of the relative type of compounds at each catalyst. (Fixed parameter: Pyrolysis reaction temperature at 500 °C and catalyst to biomass mass ratio of 1:1)	191
4.12	The effect of operating factors on $C_6 - C_8$ hydrocarbons in pyrolysis oil	203
4.13	Factors and levels in the Box-Behnken design	204
4.14	Design matric using Box-Behnken design and experimental results	204
4.15	Analysis of variances for the model	205
4.16	Confirmation runs at optimized factors	211
4.17	Kinetics parameters for non-catalytic and catalytic pyrolysis at multiple heating rates using Coats-Redfern method	226
4.18	Mean squared error (MSE) between actual and predicted TG-DTG for non-catalytic and catalytic samples	227

## LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Comparison of world energy consumption by source for primary energy between the year 2013 and 2040 (International Energy Outlook, 2016)	2
1.2	Annual energy production rate in Malaysia (Chen, 2012)	2
1.3	Upgrading mechanism of biomass derived oxygenated pyrolysis vapours into hydrocarbons via catalytic pyrolysis (Veses <i>et al.</i> , 2015)	4
2.1	Type of biomass available in Malaysia (Mekhilef et al., 2011)	12
2.2	Total projected annual biomass availability in Malaysia (Million Metric Tonnes) (Mekhilef <i>et al.</i> , 2011)	13
2.3	Pathways involved in the primary mechanisms of the conversion of biomass constituents (M: Monomer; MW: Molecular Weight) (Collard and Blin, 2014)	17
2.4	Biomass conversion processes (Shun et al., 2013)	21
2.5	Reaction pathways of deoxygenation process of pyrolysis vapours (Mortensen <i>et al.</i> , 2011)	23
2.6	Overall reaction pathway proposed for conversion of pyrolysis oil over zeolite catalysts (TE: thermal effect; TCE: thermo-catalytic effect) (Rezaei <i>et al.</i> , 2014)	24
2.7	Aluminosilicate of zeolite (The Essential Chemical Industry, 2013)	26
2.8	Mechanism for the formation of Brønsted and Lewis acid sites within the zeolite framework (Hara <i>et al.</i> , 2015)	27

2.9	Reaction mechanisms in the catalyst (A = Volatile reactant molecules, B = Volatile product molecules) (Fogler 2006)			
	(1 <sup>o</sup> glei, 2000)	29		
2.10	The ZSM-5 (MFI) structure: (a) the pentasil unit; (b) chains of pentasil units; (c) layers of these chains; and (d) layers linked (Čejka <i>et al.</i> , 2010)			
2.11	The channel system of MFI topology system (Fujiyama <i>et al.</i> , 2014)			
2.12	Flowchart of RSM study (Omar and Amin, 2011)	68		
2.13	Central composite designs for the optimization of (a) two variables and (b) three variables (Ates and Erginel, 2016)	70		
2.14	Box-Behnken design for the optimization of three variables (Ferreira <i>et al.</i> , 2007)	72		
3.1	Summary of overall research methodology	83		
3.2	Methodology of Sugarcane Bagasse Preparation and Characterization			
3.3	Methodology of Catalysts Preparation and Characterization	86		
3.4	Schematic diagram of fixed bed pyrolyzer system	90		
3.5	Flowchart of kinetic analysis	97		
4.1	Images of synthesized catalysts: (a) NC0 (HZSM-5), (b) NC1 (1 wt.% Ni : 5 wt.% Ce), (c) NC2 (2 wt.% Ni : 4 wt.% Ce), (d) NC3 (3 wt.% Ni : 3 wt.% Ce), (e) NC4 (4 wt.% Ni : 2 wt.% Ce), and (f) NC5 (5 wt.% Ni : 1 wt.% Ce)	106		
4.2	XRD patterns of synthesized catalysts: (a) NC0 (HZSM-5), (b) NC1 (1 wt.% Ni : 5 wt.% Ce), (c) NC2 (2 wt.% Ni : 4 wt.% Ce), (d) NC3 (3 wt.% Ni : 3 wt.% Ce), (e) NC4 (4 wt.% Ni : 2 wt.% Ce), and (f) NC5 (5 wt.% Ni : 1 wt.% Ce)	108		
4.3	FESEM micrographs of synthesized catalysts: (a) NC0 (HZSM-5), (b) NC1 (1 wt.% Ni : 5 wt.% Ce), (c) NC2 (2 wt.% Ni : 4 wt.% Ce), (d) NC3 (3 wt.% Ni : 3 wt.% Ce), (e) NC4 (4 wt.% Ni : 2 wt.% Ce), and (f) NC5 (5			
	wt.% Ni : 1 wt.% Ce)	110		

xiv

4.4	X-ray mapping of elemental constituents [blue dots for nickel (Ni) constituents and green dots for cerium (Ce) constituents] within the microstructure micrographs of synthesized catalysts: (a-1 & a-2) NC0 (HZSM-5), (b- 1 & b-2) NC1 (1 wt.% Ni : 5 wt.% Ce), (c-1 & c-2) NC2 (2 wt.% Ni : 4 wt.%), (d-1 & d-2) NC3 (3 wt.% Ni : 3 wt.% Ce), (e-1 & e-2) NC4 (4 wt.% Ni : 2 wt.% Ce), and (f-1 & f-2) NC5 (5 wt.% Ni : 1 wt.% Ce)	112
4.5	N2 isothermal adsorption plot of synthesized catalysts	116
4.6	FTIR analysis of synthesized catalysts: (a) NC0 (HZSM-5), (b) NC1 (1 wt.% Ni : 5 wt.% Ce), (c) NC2 (2 wt.% Ni : 4 wt.% Ce), (d) NC3 (3 wt.% Ni : 3 wt.% Ce), (e) NC4 (4 wt.% Ni : 2 wt.% Ce), and (f) NC5 (5 wt.% Ni : 1 wt.% Ce)	118
4.7	TPD-NH <sub>3</sub> profiles of synthesized catalysts: (a) NC0 (HZSM-5), (b) NC1 (1 wt.% Ni : 5 wt.% Ce), (c) NC2 (2 wt.% Ni : 4 wt.% Ce), (d) NC3 (3 wt.% Ni : 3 wt.% Ce), (e) NC4 (4 wt.% Ni : 2 wt.% Ce), and (f) NC5 (5 wt.% Ni : 1 wt.% Ce)	121
4.8	The effect of catalytic pyrolysis reaction temperatures on pyrolysis product yield (wt.%) (Fixed parameter: Catalyst to biomass mass ratio of 1:1 and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	125
4.9	Relative contents (%) of organic compounds in pyrolysis oil at 400–600 °C temperature range (Fixed parameter: Catalyst to biomass mass ratio of 1:1 and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	128
4.10	The effect of pyrolysis reaction temperature on hydrocarbons content (%) in pyrolysis oil at 400 – 600 °C temperature range (Fixed parameter: Catalyst to biomass mass ratio of 1:1 and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	135
4.11	The effect of catalyst to biomass mass ratio (Fixed parameter: Pyrolysis reaction temperature at 500 °C and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	151
4.12	Relative contents (%) of organic compounds in pyrolysis oil at CB1–CB6 mass ratios (Fixed parameter: Pyrolysis reaction temperature at 500 °C and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	153
4.13	The effect of catalyst to biomass mass ratio on hydrocarbons content (%) in pyrolysis oil (Fixed parameter: Reaction temperature at 500 °C and Nickel to Cerium mass ratio of 3:3 on HZSM-5)	160

4.14	The effect of nickel to cerium mass ratio on the pyrolysis product yields at NC0 (HZSM-5), NC1 (1 wt.% Ni : 5 wt.% Ce), NC2 (2 wt.% Ni : 4 wt.% Ce), NC3 (3 wt.% Ni : 3 wt.% Ce), NC4 (4 wt.% Ni : 2 wt.% Ce), and NC5 (5 wt.% Ni : 1 wt.% Ce) catalysts (Fixed parameter: Pyrolysis reaction temperature at 500 °C and catalyst to biomass mass ratio of 1:1)	176
4.15	Relative contents (%) of organic compounds in pyrolysis oil at NC0 (HZSM-5), NC1 (1 wt.% Ni : 5 wt.% Ce), NC2 (2 wt.% Ni : 4 wt.% Ce), NC3 (3 wt.% Ni : 3 wt.% Ce), NC4 (4 wt.% Ni : 2 wt.% Ce), and NC5 (5 wt.% Ni : 1 wt.% Ce) catalysts (Fixed parameter: Reaction temperature at 500 °C and catalyst to biomass mass ratio of 1:1)	180
4.16	The hydrocarbons content (%) in pyrolysis oil at NC0 (HZSM-5), NC1 (1 wt.% Ni : 5 wt.% Ce), NC2 (2 wt.% Ni : 4 wt.% Ce), NC3 (3 wt.% Ni : 3 wt.% Ce), NC4 (4 wt.% Ni : 2 wt.% Ce), and NC5 (5 wt.% Ni : 1 wt.% Ce) catalysts (Fixed parameter: Reaction temperature at 500 °C and catalyst to biomass mass ratio of 1:1)	187
4.17	Relationship between predicted and actual responses of $C_6 - C_8$ hydrocarbon contents in pyrolysis oil	207
4.18	Three-dimensional (3D) response surface plot to show the effects of all factors on the contents of $C_6 - C_8$ hydrocarbon in pyrolysis oil: (a) effects of reaction temperature and catalyst to biomass mass ratio (X <sub>1</sub> X <sub>2</sub> ); (b) effects of reaction temperature and nickel to cerium mass ratio (X <sub>1</sub> X <sub>3</sub> ); (c) effects of catalyst to biomass mass ratio and nickel to cerium mass ratio (X <sub>1</sub> X <sub>2</sub> )	210
4.19	TG-DTG curves of non-catalytic samples at 5, 10, 20, and 30 $^{\circ}$ C/min; (a) TG curve of mass loss and (b) DTG curve	215
4.20	TG-DTG curves of catalytic samples at 5, 10, 20, and 30 $^{\circ}C/min$ ; (a) TG curve of mass loss and (b) DTG curve	216
4.21	TG mass loss at 5, 10, 20, and 30 °C/min for non-catalytic and catalytic samples	217
4.22	Regression lines of $log \beta$ and $l000/T(K^{-1})$ for different conversion: (a) non-catalytic and (b) catalytic pyrolysis	222
4.23	Activation energy (kJ/mol) of non-catalytic and catalytic pyrolysis over conversion (%)	223

### LIST OF ABBREVIATIONS

A	-	Pre-exponential Factor
BBD	-	Box-Behnken design
BET	-	Brunauer Emmett Teller
Ce	-	Cerium
CR	-	Coats-Redfern
DTG	-	Differential Thermogravimetric
E	-	Activation Energy
FESEM-EDX	-	Field Emission Scanning Electron Microscopy- Energy Dispersive X-ray
FTIR	-	Fourier Transform Infrared Spectroscopy
FWO	-	Flynn-Wall-Ozawa
GC/MS	-	Gas Chromatography/Mass Spectrometry
HZSM-5	-	Hydrogen exchanged Zeolite Socony Mobile Five
MSE	-	Mean Squared Error
NC0	-	HZSM-5 Catalyst
NC1	-	1 wt.% Ni : 5 wt.% Ce : 94 wt.% HZSM-5
NC2	-	2 wt.% Ni : 4 wt.% Ce : 94 wt.% HZSM-5
NC3	-	3 wt.% Ni : 3 wt.% Ce : 94 wt.% HZSM-5
NC4	-	4 wt.% Ni : 2 wt.% Ce : 94 wt.% HZSM-5
NC5	-	5 wt.% Ni : 1 wt.% Ce : 94 wt.% HZSM-5
Ni	-	Nickel
RSM	-	Response Surface Methodology
SB	-	Sugarcane Bagasse
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	-	Silica to Alumina Mole Ratio

TGA	-	Thermogravimetric Analysis
TG	-	Thermogravimetric
TPD-NH <sub>3</sub>	-	Temperature Programmed Desorption Ammonia
ТРО	-	Temperature-Programmed Oxidation
XRD	-	X-ray Diffraction

### LIST OF SYMBOLS

°C	-	Degree Celsius	
Κ	-	Kelvin Degree	
$R^2$	-	The Determination of Coefficient	
wt.%	-	Weight Percent in Dry Basis	
nm	-	Nanometre	
mm	-	Millimetre	
min	-	Minute	
mL	-	Milliliter	
g	-	Gram	
μL	-	Microliter	
μm	-	Micrometre	
m/z	-	Mass/Charge Number of Ions	
$\beta_1, \beta_2, \beta_3$	-	The Linear Terms	
$\beta_{11}, \beta_{22}, \beta_{33}$	-	The Squared Terms	
$\beta_{12}, \beta_{13}, \beta_{23}$	-	The Interaction Terms	
$\beta_0$	-	The Offset Term	
$X_1$	-	The Coded Forms of Input Variable for Pyrolysis Reaction Temperature	
X <sub>2</sub>	-	The Coded Forms of Input Variable for Catalyst to Biomass Mass Ratio	
X <sub>3</sub>	-	The Coded Forms of Input Variable for Nickel to Cerium Mass Ratio	
Y	-	The Predicted Total Contents of $C_6 - C_8$ Hydrocarbons in Pyrolysis Oil	
°C/min	-	Heating Rate/Ramping Rate	

## LIST OF APPENDICES

APPENDIX		TITLE	PAGE
А	Catalyst Preparation		253
В	List of Publication		256

### **CHAPTER 1**

#### INTRODUCTION

### 1.1 Research Background

The  $C_6 - C_8$  hydrocarbons have potential market value as gasoline enhancers in the petrochemical industry specifically for the transportation sector (Escola *et al.*, 2012). It is because the  $C_6 - C_8$  hydrocarbons have a characteristic of high volatility that could easily vaporise and diffuse into the combustion chamber. Moreover, the  $C_6 - C_8$  hydrocarbons can be used as high value-added chemical feedstock to manufacture various products such as synthetic fibres, plastics, and detergents (Zheng *et al.*, 2014a). Hence, the market demands for  $C_6 - C_8$  hydrocarbons are increasing worldwide due to their wide applications (Zhou *et al.*, 2014). Currently, these hydrocarbons are produced from petroleum feedstock and petroleum reserves around the world are depleting at a rapid rate (Li *et al.*, 2014). According to the prediction done by U.S. Energy Information Administration (2016), a 60% decrease in global energy consumption is foreseen by 2040 as shown in Figure 1.1. This situation has enhanced the exploration of renewable feedstock for the production of renewable hydrocarbons (Zhou *et al.*, 2014).

Apart of the world energy, Malaysia's main energy resources are petroleum (37 %), natural gas (25 %), coal (21 %), and hydroelectric (9 %) as shown in Figure

1.2 (Chen, 2012). Malaysia is also potential for renewable energy resources including biomass (50 %), hydroelectric (35 %), wind (9 %), geothermal (5 %), and solar (1 %) as shown in Figure 1.2. Interestingly, biomass is the only renewable source of organic carbon and hydrogen, in which can be converted into hydrocarbon fuels (Kantarelis *et al.*, 2013). Hence, among Malaysia's renewable resources, biomass is in abundance in which could be defined as attractive sustainable feedstock for the production of alternative energy. Biomass energy is the most potential renewable energy resource as an alternative to fossil fuel in producing hydrocarbons.



**Figure 1.1** Comparison of world energy consumption by source for primary energy between the year 2013 and 2040 (International Energy Outlook, 2016)



**Figure 1.2** Annual energy production rates in Malaysia (Chen, 2012)

Biomass resources in Malaysia can be categorized into three major sources such as agricultural waste, forest residues, and municipal solid waste (Mekhilef *et al.*, 2011). However, the main sources of biomass are from agricultural waste such as oil palm fronds, oil palm trunks, coconut husk, and sugarcane bagasse (Shafie *et al.*, 2012). The conversion of biomass into renewable fuel energy can be performed via various thermochemical technologies such as combustion, gasification, and pyrolysis (Kantarelis *et al.*, 2014). Among the conversion routes, pyrolysis process is considered as the most promising method to generate higher liquid oil yields in the range of 50 - 75 wt.% which depending on the type of biomass and pyrolysis operating conditions (Momayez *et al.*, 2015). Notably, pyrolysis process is defined as the thermochemical decomposition of biomass in the absence of oxygen at moderate temperatures ( $400 - 600 \, ^{\circ}$ C) (Jahirul *et al.*, 2012). In detail, the decomposition of biomass releases products in the form of volatile compounds and solid char. The volatile compounds are then condensed into pyrolysis oil, while non-condensable gaseous are collected as permanent gases (CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>).

Consequently, pyrolysis oil from pyrolysis of biomass consists of highly oxygenated compounds such as ketones, phenols, and aldehydes including a low fraction of hydrocarbons. This is mainly due to the nature of biomass structure that has high oxygen elements. Moreover, during pyrolysis, the heat propagates into biomass structure and starts to degrade the lignocellulosic components (hemicellulose, cellulose, and lignin) in biomass. Other than that, the thermal degradation of each component in biomass is at a different temperature range that depends on the complex structure of components. Therefore, pyrolysis process is only beneficial on breaking the complex structure (lignocellulosic) into a simpler form of chemical compounds such as furans. Meanwhile, the possibility of converting oxygen-rich compounds into hydrocarbons in pyrolysis oil is still very low. Most scholars report that the catalytic pyrolysis is the solution to enhance the oxygenated compounds into hydrocarbons in pyrolysis oil (Galadima and Muraza, 2015; Rezaei *et al.*, 2014; Zhang *et al.*, 2013a).

Recently the catalytic pyrolysis has received much attention as most promising catalytic upgrading method of oxygenated pyrolysis vapours from biomass pyrolysis into hydrocarbons. This is due to advantages of catalytic pyrolysis such as operating at atmospheric pressure (1 atm) and considered as a cost-effective system (Kan et al., 2016). Generally, catalyst and biomass are feed together into a single reactor labelled as in-situ catalytic pyrolysis system (Montoya et al., 2015). Then, the generated oxygenated vapours are enhanced into hydrocarbons before entering condensation system. Meanwhile, another system is known as ex-situ catalytic pyrolysis, in which the catalyst is placed separately in secondary reactor, whereas biomass is in the first reactor (Resende, 2016). Compared to the ex-situ method, the in-situ likely reduces the capital and operating costs (Dickerson and Soria, 2013). The in-situ method has high efficiency on conversion of oxygenates into hydrocarbons in pyrolysis oil due to an immediate contact of volatile compounds at active acid sites of catalyst (Jahirul et al., 2012). Besides, the heterogeneous catalyst could be easily separated from the reaction process. Moreover, oxygen element in oxygenated compounds are removed trough series of reactions such as dehydration  $(H_2O)$ , decarboxylation  $(CO_2)$ , and decarbonylation (CO) as shown in Figure 1.3 (Veses et al., 2015). Finally, fewer oxygenates are left with a tremendously higher selectivity of hydrocarbons in pyrolysis oil.



**Figure 1.3** Upgrading mechanism of biomass derived oxygenated pyrolysis vapours into hydrocarbons via catalytic pyrolysis (Veses *et al.*, 2015)

Currently, the incorporation of metals into Hydrogen exchanged Zeolite Socony Mobil Five (HZSM-5) catalyst has been successfully synthesized for catalytic of oxygenated pyrolysis vapours. The incorporated metals could be either from a group of alkali earth metals, alkaline earth metals, transition metals, and rare earth metals. In general, HZSM-5 catalyst alone contains some special properties such as balanced acid sites and good textural properties. Meanwhile, metals are added into the HZSM-5 framework to prevent rapid deactivation of catalyst (coking) and simultaneously extend its lifetime during pyrolysis of biomass. For this reason, the catalytic of oxygenated pyrolysis vapours could be enhanced by incorporating metal on the HZSM-5 framework. In conclusion, biomass is a renewable energy resource which has tremendous advantages over economic, political, and social compared to conventional petroleum fuels and other renewable energy resources. Meanwhile, the utilisation of sustainable biomass via catalytic pyrolysis is the most promising technique used to enhance the biomass-derived oxygenated pyrolysis vapour. It is because catalytic pyrolysis of biomass could directly increase the C<sub>6</sub>- $C_8$  hydrocarbon contents in pyrolysis oil that has wide applications. On the other hand, the dependence of  $C_6 - C_8$  hydrocarbons from petroleum fractions could be reduced with biomass as alternative feedstock. Finally, the catalytic pyrolysis requires the development and application of novel catalysts that are capable of both catalytic cracking and coke reduction.

### **1.2 Problem Statement**

Global warming and limitations of fossil fuels reserved have forced the exploration biomass as new sources of renewable energy. For example, combustion of fossil fuel releases greenhouse gases (CO,  $CO_2$ ,  $H_2$ , and  $CH_4$ ) that contribute to rising in global warming. The emissions of greenhouse gases are expected to increase from 43 million tons in 2005 to 110 million tons by 2020 (Shafie *et al.*, 2012). Meanwhile, Malaysia is gifted with abundant supplies of biomass resources that mainly come from agricultural wastes such as oil palm fronds, sugarcane

bagasse, coconut husk, and rice husk that increases annually. However, it was reported that only 10 % of the total biomass is utilised as boiler fuels to generate steam and electricity for the internal energy of agricultural mill, while 90 % of biomass is discarded as wastes and finally proceed for landfilling (Awalludin *et al.*, 2015).

Alternatively, renewable fuel energy ( $C_6 - C_8$  hydrocarbons) could be produced from the conversion of biomass through pyrolysis process (Zhang *et al.*, 2013a). However, the biomass-derived pyrolysis oil contains low yields of hydrocarbons ( $\leq 1$  %) due to the presence of oxygen-rich compounds ( $\leq 97$  wt.%) such as acids, alcohols, furans, ester, ether, ketones, phenols, sugars, and aldehydes in pyrolysis oil (Rezaei *et al.*, 2014). Besides that, the raw pyrolysis oil has some promising properties, such as less toxicity, good lubricity, and greater biodegradation than the conventional petroleum fuels (Zhang *et al.*, 2013a). Hence, biomass-derived oxygenated pyrolysis vapours should be enhanced into  $C_6 - C_8$  hydrocarbons via catalytic pyrolysis process. The HZSM-5 is widely preferred to be used as solid acid catalysts in the catalytic pyrolysis to enhance the biomass-derived oxygenated pyrolysis vapours into hydrocarbons (Rahimi and Karimzadeh, 2011).

However, the catalytic pyrolysis of oxygenated pyrolysis vapours over HZSM-5 catalyst has several shortcomings, such as low organic liquid yield, low selectivity, short lifetime, and higher coke formation that deactivate the catalyst (Zhang *et al.*, 2013a). The formation of coke is the results of the production of heavy compounds that changes the catalytic activity of the catalyst in pyrolysis process (Botas *et al.*, 2012). Therefore, the goal of this research is to extensively study the in-situ catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 - C_8$  hydrocarbons in pyrolysis oil over the newly developed metal modified HZSM-5 catalyst, with the main aim to increase the  $C_6 - C_8$  hydrocarbons in pyrolysis oil.

### **1.3** Research Objectives

The main objective of this research is to investigate the in-situ catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 - C_8$  hydrocarbons in pyrolysis oil using fixed-bed reactor. The specific objectives of this research are:

- i. to synthesize and characterize the Nickel-Cerium/HZSM-5 catalysts for the in-situ catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 C_8$  hydrocarbons in pyrolysis oil. In addition, the sugarcane bagasse as pyrolysis feedstock is also characterized.
- ii. to investigate the performance of Nickel-Cerium/HZSM-5 catalysts in catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 C_8$  hydrocarbons in pyrolysis oil.
- iii. to optimize process parameters of catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 - C_8$  hydrocarbons in pyrolysis oil via response surface methodology (RSM).
- iv. to perform kinetic analysis of catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 C_8$  hydrocarbons over selected Nickel-Cerium/HZSM-5 catalyst.

### **1.4** Scope of Research

In order to achieve the objectives of this research, the following scopes have been identified:

- i. Synthesis of Nickel-Cerium/HZSM-5 catalysts at various nickel to cerium mass loading ratio (1:5, 2:4, 3:3, 4:2, and 5:1) on HZSM-5 via incipient wetness impregnation (IWI) method. Characterization of Nickel-Cerium/HZSM-5 catalysts via x-ray diffraction (XRD), field emission scanning electron microscopy-energy dispersive x-ray (FESEM-EDX), Brunauer Emmett Teller (BET), Fourier transform infrared (FTIR), temperature programmed desorption of ammonia  $(TPD-NH_3),$ and temperature-programmed oxidation (TPO). Then, the characterization of sugarcane bagasse such as proximate analysis, elemental analysis, and calorific value via thermogravimetric analyser (TGA), elemental analyser, and bomb calorimeter respectively.
- ii. Screening and testing the catalytic performance of Nickel-Cerium/HZSM-5 catalysts on catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 C_8$  hydrocarbons in pyrolysis oil at pyrolysis reaction temperatures (400, 450, 500, 550, and 600 °C), catalyst to biomass mass ratio (0.5:1.0, 1.0:1.0, 1.5:1.0, 2.0:1.0, 2.5:1.0, and 3.0:1.0), and nickel to cerium mass loading ratio (1:5, 2:4, 3:3, 4:2, and 5:1) on HZSM-5 via insitu fixed bed reactor.
- iii. Determination of optimum value of process parameters for catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 C_8$  hydrocarbons in pyrolysis oil over selected Nickel-Cerium/HZSM-5 catalyst via Box-Behnken design (BBD) in response surface methodology (RSM). Three process parameters were investigated in the optimization such as pyrolysis reaction temperatures, catalyst to biomass mass ratio, and nickel to cerium mass loading ratio on HZSM-5.

v. Determination of kinetic parameters such as activation energy and preexponential factor for catalytic of oxygenated pyrolysis vapours from sugarcane bagasse into enhanced  $C_6 - C_8$  hydrocarbons in pyrolysis oil over selected Nickel-Cerium/HZSM-5 catalyst using Coats-Redfern (CR) and Flynn-Wall-Ozawa (FWO) methods.

### 1.5 Research Significance

This research utilised Nickel-Cerium/HZSM-5 catalyst as benign catalyst for enhanced hydrocarbons ( $C_6 - C_8$ ) production in pyrolysis oil via in-situ catalytic pyrolysis reaction. The addition of nickel (transition metal) and cerium (rare earth metal) into HZSM-5 framework can enhance the oxygenated pyrolysis vapours into  $C_6 - C_8$  hydrocarbons as renewable chemicals in pyrolysis oil and remarkably reduce the undesired formation of coke materials that could prolong the lifetime of the catalyst. The process variables at optimum conditions can be used to conduct the process more efficiently and to enable excellent utilisation of biomass, specifically for larger scale processes. Furthermore, the kinetic parameters obtained should be able to describe the reaction mechanisms of in-situ catalytic pyrolysis of biomass under the influence of pyrolysis reaction temperature, catalyst to biomass mass ratio, and nickel to cerium mass ratio. In addition, the  $C_6 - C_8$  hydrocarbons in pyrolysis oil can be used as combustion fuel for power generation, as feedstock for high valueadded chemical production, transportation fuel, and gasoline enhancers in the petrochemical industry. The results disclosed the potential of this study to be implemented in biomass conversion to  $C_6 - C_8$  hydrocarbons under mild process conditions. Hence, the  $C_6 - C_8$  hydrocarbons from the in-situ catalytic pyrolysis reaction of biomass over Nickel-Cerium/HZSM-5 catalyst can gradually replace the conventional petroleum feedstock and improve the waste management of biomass.

### REFERENCES

- Abnisa, F., Daud, W. M. A. W. (2014). A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. Energy Conversion and Management, 87, 71-85. doi.org/10.1016/j.enconman.2014.07.007
- Aboyade, A. O., Carrier, M., Meyer, E. L., Knoetze, H., Görgens, J. F. (2013). Slow and pressurized co-pyrolysis of coal and agricultural residues. Energy Conversion and Management, 65, 198-207. doi.org/10.1016/j.enconman.2012.08.006
- Alvarez, J., Lopez, G., Amutio, M., Bilbao, J., Olazar, M. (2014). Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor. Fuel, 128, 167-169. doi.org/10.1016/j.fuel.2014.02.074
- Angulakshmi, V. S., Sivakumar, N., Karthikeyan, S. (2012). Response Surface Methodology for optimizing Process Parameters for Synthesis of Carbon Nanotubes. Journal Environmental Nanotechnology, 1(1), 40-45. doi.org/10.13074/jent.2012.10.121019
- Asadieraghi, M., Daud, W. M. A. W. (2015). In-depth investigation on thermochemical characteristics of palm oil biomasses as potential biofuel sources. Journal of Analytical and Applied Pyrolysis, 115, 379-391. doi.org/10.1016/j.jaap.2015.08.017
- Ates, F., Erginel, N. (2016). Optimization of bio-oil production using response surface methodology and formation of polycyclic aromatic hydrocarbons (PAHs) at elevated pressures. Fuel Processing Technology, 142, 279-286. doi.org/10.1016/j.fuproc.2015.10.026
- Awalludin, A. F., Sulaiman, O., Hashim, R., Nadhari, W. N. A. W. (2015). An overview of the oil palm industry in Malaysia and its waste utilization through thermochemical conversion, specifically via liquefaction. Renewable and Sustainable Energy Reviews, 50, 1469-1484.

- Balasundram, V., Ibrahim, N., Kasmani, R.M., Hamid, M.K.A., Isha, R., Hasrinah, H., Ali, R.R. (2017). Thermogravimetric catalytic pyrolysis and kinetic studies of coconut copra and rice husk for possible maximum production of pyrolysis oil. Journal of Cleaner Production, 167, 218-228. doi.org/10.1016/j.jclepro.2017.08.173
- Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S., Escaleira, L.A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta, 76, 965-977. doi.org/10.1016/j.talanta.2008.05.019
- Bi, J., Liu, M., Song, C., Wang, X., Guo, X. (2011). C<sub>2</sub>-C<sub>4</sub> light olefins from bioethanol catalyzed by Ce-modified nanocrystalline HZSM-5 zeolite catalysts. Applied Catalysts B: Environmental, 107(1-2), 68-76. doi.org10.1016/j.apcatb.2011.06.038
- Bi, P., Wang, J., Zhang, Y., Jiang, P., Wu, X., Liu, J., Xue, H., Wang, T., Li, Q. (2015). From lignin to cycloparaffins and aromatics: Directional synthesis of jet and diesel fuel range biofuels using biomass. Bioresource Technology, 183, 10-17. doi.org/10.1016/j.biortech.2015.02.023
- Biddy, M., Abhijit, D., Susanne, J., Aye, M. (2013). In-situ catalytic fast pyrolysis technology pathway: National Renewable Energy Laboratory.
- Botas, J. A., Serrano, D. P., Carcía, A., Vicente, J. de., Ramos, R. (2012). Catalytic conversion of rapeseed oil into raw chemicals and fuels over Ni- and Momodified nanocrystalline ZSM-5 zeolite. Catalysis Today, 195(1), 59-70. doi.org/10.1016/j.cattod.2012.04.061
- Botas, J. A., Serrano, D. P., García, A., Ramos, R. (2014). Catalytic conversion of rapeseed oil for the production of raw chemicals, fuels and carbon nanotubes over Ni-modified nanocrystalline and hierarchical ZSM-5. Applied Catalysis B: Environmental, 145, 205-215. doi.org/10.1016/j.apcatb.2012.12.023
- Cai, Y., Fan, Y., Li, X., Chen, L., Wang, J. (2016). Preparation refined bio-oil by catalytic transformation of vapors derived from vacuum pyrolysis of rape straw over modified HZSM-5. Energy, 102, 95-105. doi.org/10.1016/j.energy.2016.02.051
- Carlson, T. R., Jae, J., Lin, Y., Tompsett, G. A., Huber, G. W. (2010). Catalytic fast pyrolysis of glucose with HZSM-5: The combined homogeneous and heterogeneous reactions. Journal of Catalysis, 270, 110-124. doi.org/10.1016/j.jcat.2009.12.013

- Čejka, J., Corma, A., Zones, S. (2010). Zeolites and Catalysis. Federal Republic of Germany: WILEY-VCH Verlag GmbH & Co. KGaA.
- Chen, W. (2012, December 4). Renewable Energy Status in Malaysia. Retrieved From the Global Green Synergy website: http://www.ggs.my
- Chen, B., Chai, Z., He, H., Huang, C., Liu, Y., Yi, W., Wei, X., An, J. (2016). Towards a full understanding of the nature of Ni(II) species and hydroxyl groups over highly siliceous HZSM-5 zeolite supported nickel catalysts prepared by a deposition-precipitation method. Dalton Trans, 45, 2720-2739. doi.org/10.1039/c4dt00399c
- Cheng, Y and Huber, G.W. (2011). Chemistry of Furan Conversion into Aromatics and Olefins over HZSM-5: A Model Biomass Conversion Reaction. ACS Catal, 1, 611-628. doi.org/10.1021/cs200103j
- Cheng, Y., Jae, J., Shi, J., Fan, W., Huber, G. W. (2012). Production of renewable aromatic compounds by catalytic fast pyrolysis of lignocellulosic biomass with bifunctional Ga/ZSM-5 catalysts. Angew. Chem. Int. Ed., 51, 1387-1390. doi.org/10.1002/ange.201107390
- Chew, J., Doshi, V., Yong, S., Bhattacharya, S. (2016). Kinetic study of torrefaction of oil palm shell, mesocarp and empty fruit bunch. Journal of Thermal Analysis and Calorimetry, 126(2), 709-715. doi.org/10.1007/s10973-016-5518-3
- Chu, S., Subrahmanyam, A.V., Hubert, G.W. (2013). The pyrolysis chemistry of a β-O-4 type oligomeric lignin model compound. Green Chemistry, 15, 125-136. doi.org/10.1039/c2gc36332a
- Collard, F., Blin, J., Bensakhria, A., Valette, J. (2012). Influence of impregnated metal on the pyrolysis conversion of biomass constituents. Journal of Analytical and Applied Pyrolysis, 95, 213-226. doi.org/10.1016/j.jaap.2012.02.009
- Collard, F., Blin, J. (2014). A review on pyrolysis of biomass constituents: Mechanism and composition of the products obtained from the conversion of cellulose, hemicellulose and lignin. Renewable and Sustainable Energy Reviews, 38, 294-608. doi.org/10.1016/j.rser.2014.06.013
- Demirbaş A. (2003). Relationships between lignin contents and fixed carbon contents of biomass samples. Energy Conversion and Management, 44, 1481-1486.

- Dickerson, T., Soria, J. (2013). Catalytic Fast Pyrolysis: A Review. Energies, 6, 514-538. doi.org/10.3390/en6010514
- Doronin, V. P., Sorokina, T. P., Lipin, P. V., Potapenko, O. V., Korotkova, N. V., Gordenko, V. I. (2015). Development and introduction of zeolite containing catalysts for cracking with controlled contents of rare earth elements. Catalysis in Industry, 7(1), 12-16. doi.org/10.1134/S2070050415010043
- Doumer, M. E., Arízaga, G. G. C., da Silva, D. A., Yamamoto, C. I., Novotny, E. H., Santos, J. M., dos Santos, L. O., Jr, A. W., de Andrade, J. B., Mangrich, A. S. (2015). Slow pyrolysis of different Brazilian waste biomasses as sources of soil conditioners and energy, and for environmental protection. Journal of Analytical and Applied Pyrolysis, 113, 434-443. doi.org/10.1016/j.jaap.2015.03.006
- El-Sayed, S.A., Mostafa, M.E. (2015). Kinetic Parameters Determination of Biomass Pyrolysis Fuels Using TGA and DTA Techniques. Waste Biomass Valor, 6, 401-415. doi.org/10.1007/s12649-015-9354-7
- Epelde, E., Ibañez, M., Aguayo, A. T., Gayubo, A. G., Bilbao, J., Castaño, P. (2014).
  Differences among the deactivation pathway of HZSM-5 zeolite and SAPO-34 in the transformation of ethylene or 1-butene to propylene. Microporous and Mesoporous Materials, 195, 284-293.
  doi.org/10.1016/j.micromeso.2014.04.040
- Escola, J. M., Aguado, J., Serrano, D. P., Briones, L., Díaz de Tuesta, J. L., Calvo, R., Fernandez, E. (2012). Conversion of polyethylene into Transportation Fuels by the Combination of Thermal Cracking and Catalytic Hydroreforming over Ni-Supported Hierarchical Beta Zeolite. Energy and Fuels, 26, 3187-3195. doi.org/10.1021/ef300938r
- Fan, Y., Cai, Y., Li, X., Yu, N., Yin, H. (2014). Catalytic upgrading of pyrolytic vapors from the vacuum pyrolysis of rape straw over nanocrystalline HZSM-5 zeolite in a two-stage fixed-bed reactor. Journal of Analytical and Applied Pyrolysis, 108, 185-195. doi.org/10.1016/j.jaap.2014.05.001
- Fan, L., Chen, P., Zhou, N., Liu, S., Zhang, Y., Liu, Y., Wang, Y., Omar, M.M., Peng, P., Addy, M., Cheng, Y., Ruan, R. (2018). In-situ and ex-situ catalytic upgrading of vapors from microwave-assisted pyrolysis of lignin. Bioresource Technology, 247, 851-858. doi.org/10.1016/j.biortech.2017.09.200

- Fanchiang, W., Lin, Y. (2012). Catalytic fast pyrolysis of furfural over H-ZSM-5 and Zn/H-ZSM-5 catalysts. Applied Catalysis A: General, 419-420, 102-110. doi.org/10.1016/j.apcata.2012.01.017
- Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G.P., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N.L. (2007). Analytica Chimica Acta, 597, 179-186. doi.org/10.1016/j.aca.2007.07.011
- Fogler, H. S. (2006). Elements of Chemical Reaction Engineering 3<sup>rd</sup> Ed. Prentice-Hall, Michigan.
- Foster, A. J., Jae, J., Cheng, Y. T., Huber, G. W., Lobo, R. F. (2012). Optimizing the aromatic yield and distribution from catalytic fast pyrolysis of biomass over ZSM-5. Applied Catalysis A: General, 423-424, 154-161. doi.org/10.1016/j.apcata.2012.02.030
- Fujiyama, S., Seino, S., Kamiya, N., Nishi, K., Yoza, K., Yokomori, Y. (2014). Adsorption structures of non-aromatic hydrocarbons on silicalite-1 using the single-crystal X-ray diffraction method. Physical Chemistry Chemical Physics, 16(30), 15839-15845. doi.org/10.1039/c4cp01860e
- Galadima, A., Muraza, O. (2015). In situ fast pyrolysis of biomass with zeolite catalysts for bioaromatics/gasoline production: A review. Energy Conversion and Management, 105, 338-354. doi.org/10.1016/j.enconman.2015.07.078
- Goenka, R., Parthasarathy, P., Gupta, N.K., Biyahut, N.K., Narayanan, S. (2015). Kinetic analysis of biomass and comparison of its chemical compositions by thermogravimetric, wet and experimental furnace methods. Waste Biomass Valor, 6, 989-1002. doi.org/10.1007/s12649-015-9402-3
- Gollakota, A. R. K., Reddy, M., Subramanyam, M. D., Kishore, N. (2016). A review on the upgradation techniques of pyrolysis. Renewable and Sustainable Energy Review, 58, 1543-1568. doi.org/10.1016/j.rser.2015.12.180
- Guo, F., Dong, Y., Lv, Z., Fan, P., Yang, S., Dong, L., 2015. Pyrolysis kinetics of biomass (herb residue) under isothermal condition in a micro fluidized bed. Energy Conversion and Management, 93, 367-376. doi.org/10.1016/j.enconman.2015.01.042
- Han, W., Tang, Z., Zhang, P., Lu, G. (2013). Study of One Step Synthesis of Rare Earth Zeolite (Ln-ZSM-5) and Application for Low Temperature CO Catalytic Oxidation. Catalysis Surveys from Asia, 17(3), 147-155.

- Han, X., He, Y., Zhao, H., Wang, D. (2014). Optimizing of preparation conditions of activated carbon from the residue of desilicated rice husk using response surface methodology. Korean Journal Chemical Engineering, 31(10), 1810-1817. doi.org/10.1007/s11814-014-0103-6
- Hara, M., Nakajima, K., Kamata, K. (2015). Recent progress in the development of solid catalysts for biomass conversion into high value-added chemicals.
  Science and Technology of Advanced Materials, 16(3), 1-22.
  doi.org/10.1088/1468-6996/16/3/034903
- Hartmann, M., Machoke, A. G., Schwieger, W. (2016). Catalytic test reactions for the evaluation of hierarchical zeolites. Chem. Soc. Rev., 45, 3313-3330. doi\_org/10.1039/c5cs00935a
- Hoff, T. C., Gardner, D. W., Thilakaratne, R., Proano-Aviles, J., Brown, R. C., Tessonnier, J. (2017). Elucidating the effect of desilication on aluminum-rich ZSM-5 zeolite and its consequences on biomass catalytic fast pyrolysis. Applied Catalysis A: General, 529, 68-78. doi.org/10.1016/j.apcata.2016.10.009
- Huang, Y., Wei, L., Crandall, Z., Julson, J., Gu, Z. (2015). Combining Mo-Cu/HZSM-5 with a two stage catalytic pyrolysis system for pine sawdust thermal conversion. Fuel, 150, 656-663. doi.org/10.1016/j.fuel.2015.02.071
- Huber, G. W., Chheda, J. N., Barrett, C. J., Dumesic, J. A. (2005). Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates. Sciene, 308, 1446-1450. doi.org/10.1126/science.1111166
- Iliopoulou, E. F., Stefanidis, S. D., Kalogiannis, K. G., Delimitis, A., Lappas, A. A., Triantafyllidis, K. S. (2012). Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. Applied Catalysis B: Environmental, 127, 281-290. doi.org/10.1016/j.apcatb.2012.08.030
- International Zeolite Association (IZA). (2014). Retrieved From the International Zeolite Association website: http://www.iza-structure.org/database
- Isa, K. M., Daud, S., Hamidin, N., Ismail, K., Saad, S. A., Kasim, F. H. (2011). Thermogravimetric analysis and the optimization of bio-oil yield from fixedbed pyrolysis of rice husk using response surface methodology (RSM). Industrial Crops and Products, 33, 481-487. doi.org/10.1016/j.indcrop.2010.10.024

- Isha, R., Williams, P. T. (2012). Experimental design methodology for optimizing catalytic performance of Ni/Ce/α-Al<sub>2</sub>O<sub>3</sub> catalyst for methane steam reforming. Journal of the Energy Institute, 85, 22-28. doi.org/10.1179/174396711X13116932752155
- Jahirul, M. L., Rasul, M. G., Chowdhury, A. A., Ashwath, N. (2012). Biofuels Production through Biomass Pyrolysis-A Technological Review. Energies, 5, 4952-5001. doi.org/10.3390/en5124952
- Jamaluddin, M. A., Ismail, K., Ishak, M. A. M., Ghani, Z. Ab., Abdullah, M. F., Safian, M. T., Idris, S. S., Tahiruddin, S., Yunus, M. F. M., Hakimi, N. I. N. M. (2013). Microwave-assisted pyrolysis of palm kernel shell: Optimizing using response surface methodology (RSM). Renewable Energy, 55, 357-365. doi.org/10.1016/j.renene.2012.12.042
- Jayaraman, K., Gökalp, I. (2015). Pyrolysis, combustion and gasification characteristics of miscanthus and sewage sludge. Energy Conversion and Management, 89, 83-91. doi.org/10.1016/j.enconman.2014.09.05
- Jin, S. H., Lee, H. W., Ryu, C., Jeon, J., Park, Y. (2015). Catalytic fast pyrolysis of Geodae-Uksae 1 over zeolites. Energy, 81, 41-46. doi.org/10.1016/j.energy.2014.10.059
- Jung, J. S., Park, J. W., Seo, G. (2005). Catalytic cracking of n-octane over alkalitreated MFI zeolites. Applied Catalysis A: General, 288, 149-157. doi.org/10.1016/j.apcata.2005.04.047
- Jung, K. A., Nam, C. W., Woo, S. H., Park, J. M. (2016) Response surface method for optimization of phenolic compounds production by lignin pyrolysis. Journal of Analytical and Applied Pyrolysis, 120, 409-415. doi.org/10.1016/j.jaap.2016.06.011
- Kabir, G., Hameed, B. H. (2017). Recent progress on catalytic pyrolysis of lignocellulosic biomass to high-grade bio-oil and bio-chemicals. Renewable and Sustainable Energy Reviews, 70, 954-967. doi.org/10.1016/j.rser.2016.12.001
- Kan, T., Strezov, V., Evans, T. J. (2016). Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable and Sustainable Energy Reviews, 57, 1126-1140. doi.org/10.1016/j.rser.2015.12.185

- Kantarelis, E., Yang, W., Blasiak, W. (2013). Effects of Silica-Supported Nickel and Vanadium on Liquid Products of Catalytic Steam Pyrolysis of Biomass. Energy Fuels, 28, 591-599. doi.org/10.1021/ef401939g
- Kantarelis, E., Yang, W., Blasiak, W. (2014). Effect of zeolite to binder ratio on product yields and composition during catalytic steam pyrolysis of biomass over transition metal modified HZSM-5. Fuel, 122, 119-125. doi.org/10.1016/j.fuel.2013.12.054
- Keyvanloo, K., Towfighi, J. (2010). Comparing the catalytic performances of mixed molybdenum with cerium and lanthanide oxides supported on HZSM-5 by multiobjective optimization of catalyst compositions using nondominated sorting genetic algorithm. Journal of Analytical and Applied Pyrolysis, 88, 140-148. doi.org10.1016/j.jaap.2010.03.007
- Kim, B., Kim, Y., Jae, J., Watanabe, C., Kim, S., Jung, S., Kim, S. C., Park, Y. (2015a). Pyrolysis and catalytic upgrading of Citrus unshiu peel. Bioresource Technology, 194, 312-319. doi.org/10.1016/j.biortech.2015.07.035
- Kim, J., Lee, J. H., Park, J., Kim, J. K., An, D., Song, I. K., Choi, J. W. (2015b). Catalytic pyrolysis of lignin over HZSM-5 catalysts: Effect of various parameters on the production of aromatic hydrocarbon. Journal of Analytical and Applied Pyrolysis, 114, 273-280. doi.org/10.1016/j.jaap.2015.06.007
- Khor, K. H., Lim, K. O., Alimuddin, Z. A. Z. (2010). Laboratory-scale Pyrolysis of Oil Palm Trunks. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 32(6), 518-531. doi.org/10.1080/15567030802612374
- Konno, H., Tago, T., Nakasaka, Y., Ohnaka, R., Nishimura, J., Masuda, T. (2013). Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha. Microporous and Mesoporous Materials, 175, 25-33. doi.org/10.1016/j.micromeso.2013.03.016
- Li, X., Shen, B., Xu, C. (2010). Interaction of titanium and iron oxide with ZSM-5 to tune the catalytic cracking of hydrocarbons. Applied Catalysis A: General, 375, 222-229. doi.org/10.1016/j.apcata.2009.12.033
- Li, G., Yan, L., Zhao, R., Li, F. (2014). Improving aromatic hydrocarbons yield from coal pyrolysis volatile products over HZSM-5 and Mo-modified HZSM-5. Fuel, 130, 154-159. doi.org/10.1016/j.fuel.2014.04.027

- Li, P., Li, D., Yang, H., Wang, X., Chen, H. (2016). Effects of Fe-, Zr-, and Co-Modified Zeolites and Pretreatments on Catalytic Upgrading of Biomass Fast Pyrolysis Vapors. Energy Fuels, 30, 3004-3013. doi.org/10.1021/acs.energyfuels.5b02894
- Liu, C., Wang, H., Karim, A. M., Sun, J., Wang, Y. (2014). Catalytic fast pyrolysis of lignocellulosic biomass. Chem Soc Rev, 43(22), 7594-7623. doi.org/10.1039/c3cs60414d
- Loiola, A. R., Andrade, J. C. R. A., Sasaki, J. M., da Silva, L. R. D. (2012). Structural analysis of zeolite NaA synthesized by a cost-effective hydrothermal method using kaolin and its use as water softener. Journal of Colloid and Interface Science, 367, 34-39. doi.org/10.1016/j.jcis.2010.11.026
- Lorenzetti, C., Conti, R., Fabbri, D., Yanik, J. (2016). A comparative study on the catalytic effect of H-ZSM5 on upgrading of pyrolysis vapors derived from lignocellulosic and proteinaceous biomass. Fuel, 166, 446-452. doi.org/10.1016/j.fuel.2015.10.051
- Lu, C., Song, W., Lin, W. (2009). Kinetics of biomass catalytic pyrolysis. Biotechnology Advances, 27, 583-587. doi.org/10.1016/j.biotechadv.2009.04.014
- Luo, G., Resende, F. L. P. (2016). In-situ and ex-situ upgrading of pyrolysis vapors from beetle-killed trees. Fuel, 166, 367-375. doi.org/10.1016/j.fuel.2015.10.126
- Ma, Z., Troussard, E., van Bokhoven, J. A. (2012). Controlling the selectivity to chemicals from lignin via catalytic fast pyrolysis. Applied Catalysis A: General, 423-224, 130-136. doi.org/10.1016/j.apcata.2012.02.027
- Makowski, W., Mlekodaj, K., Majda, D. (2013). Characterization of acidic zeolite catalysts by thermodesorption and cracking of n-nonane. Microporous and Mesoporous Materials, 166, 137-143. doi.org/10.1016/j.micromeso.2012.04.034

Manya, J.J., Velo, E., Puigjaner, L. (2003). Kinetics of Biomass Pyrolysis: a Reformulated Three-Parallel-Reactions Model. Ind. Eng. Chem. Res, 42,

434-441. doi.org/10.1021/ie020218p

Mekhilef, S., Saidur, R., Safari, A., Mustaffa, W. E. S. B. (2011). Biomass energy in Malaysia: Current state and prospects. Renewable and Sustainable Energy Review, 15, 3360-3370. doi.org.10.1016/j.rser.2011.04.016

- Mekhilef, S., Barimani, M., Safari, A., Salam, Z. (2014). Malaysia's renewable energy policies and programs with green aspects. Renewable and Sustainable Energy Reviews, 40, 497-504. doi.org/10.1016/j.rser.2014.07.095
- Mendes, F. L., Ximenes, V. L., de Almeida, M. B. B., Azevedo, D. A., Tessarolo, N. S., Pinho, A. R. (2016). Catalytic pyrolysis of sugarcane bagasse and pinewood in a pilot scale unit. Journal of Analytical and Applied Pyrolysis, 122, 395-404. doi.org/10.1016/j.jaap.2016.08.001
- Mihalcik, D. J., Mullen, C. A., Boateng, A. A. (2011). Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components. Journal of Analytical and Applied Pyrolysis, 92, 224-232. doi.org.10.1016/j.jaap.2011.06.001
- Mochizuki, T., Chen, S., Toba, M., Yoshimura, Y. (2013). Pyrolyzer-GC/MS system-based analysis of the effects of zeolite catalysts on the fast pyrolysis of Jatropha husk. Applied Catalysis A: General, 456, 174-181. doi.org/10.1016/j.apcata.2013.02.022
- Momayez, F., Darian, J. T., Sendesi, S. M. T. (2015). Synthesis of zirconium and cerium over HZSM-5 catalysts for light olefins production from naphtha. Journal of Analytical and Applied Pyrolysis, 112, 135-140. doi.org/10.1016/j.jaap.2015.02.006
- Montoya, J. I., Valdés, C., Chejne, F., Gómez, C. A., Blanco, A., Marrugo, G., Osorio, J., Castillo, E., Aristóbulo, J., Acero, J. (2015). Bio-oil production from Colombian bagasse by fast pyrolysis in a fluidized bed: An experimental study. Journal of Analytical and Applied Pyrolysis, 112, 379-387. doi.org/10.1016/j.jaap.2014.11.007
- Mortensen, P. M., Grunwaldt, J. –D., Jensen, P. A., Knudsen, K. G., Jensen, A. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. Applied Catalysis A: General, 407, 1-19. doi.org/10.1016/j.apcata.2011.08.046
- Mukarakate, C., Zhang, X., Stanton, A. R., Robichaud, D. J., Ciesielski, P. N., Malhotra, K. Donohoe, B. S., Gjersing, E., Evans, R. J., Heroux, D. S., Richards, R., Lisa, K., Nimlos, M. R. (2014). Real-time monitoring of the deactivation of HZSM-5 during upgrading of pine pyrolysis vapors. Green Chemistry, 16(3), 1444-1461. doi.org/10.1039/c3gc42065e
- Mullen, C. A., Boateng, A. A. (2015). Production of Aromatic Hydrocarbons via Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites. ACS Sustainable Chemistry and Engineering, 3, 1623-1631.

- Munir, S., Daood, S. S., Nimmo, W., Cunliffe, A. M., Gibbs, B. M. (2009). Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. Bioresource Technology, 100, 1413-1418. doi.org/10.1016/j.biortech.2008.07.065
- Näfe, G., López-Martinez, M. –A., Dyballa, M., Hunger, M., Traa, Y., Hirth, Th., Klemm, E. (2015). Deactivation behavior of alkali-metal zeolites in the dehydration of lactic acid to acrylic acid. Journal of Catalysis, 329, 413-424. doi.org/10.1016/j.jcat.2015.05.017
- Nam, H., Capareda, S. (2015). Experimental investigation of torrefaction of two agricultural wastes of different composition using RSM (response surface methodology. Energy, 91, 507-516. doi.org/10.1016/j.energy.2015.08.064
- Naqvi, S. R., Uemura, Y., Yusup, S. (2014). Catalytic pyrolysis of paddy husk in a drop type pyrolyzer for bio-oil production: The role of temperature and catalyst. Journal of Analytical and Applied Pyrolysis, 106, 57-62. doi.org/10.1016/j.jaap.2013.12.009
- Naqvi, S.R., Uemura, Y. (2015). Kinetic study of the catalytic pyrolysis of paddy husk by use of thermogravimetric data and the Coats-Redfern model. Res. Chem. Intermed, 41, 9743-9755. doi.org/10.1007/s11164-015-1962-0
- Niu, X., Gao, J., Miao, Q., Dong, M., Wang, G., Fan, W., Qin, Z., Wang, J. (2014). Influence of preparation method on the performance of Zn-containing HZSM-5 catalysts in methanol-to-aromatics. Microporous and Mesoporous Materials, 197, 252-261. doi.org/10.1016/j.micromeso.2014.06.027
- Niu, X., Gao, J., Wang, K., Miao, Q., Dong, M., Wang, G., Fan, W., Qin, Z., Wang, J. (2017). Influence of crystal size on the catalytic performance of H-ZSM-5 and Zn/H-ZSM-5 in the conversion of methanol to aromatics. Fuel Processing Technology, 157, 99-107. doi.org/10.1016/j.fuproc.2016.12.006
- Oasmaa, A., Fonts, I., Pelaez-Samaniego, M. R., Garcia-Perez, M. E., Garcia-Perez, M. (2016). Pyrolysis Oil Multiphase Behavior and Phase Stability: A Review. Energy Fuels, 30, 6179-6200. doi.org/10.1021/acs.energyfuels.6b01287
- Olsbye, U., Svelle, S., Bjørgen, M., Beato, P., Janssens, T. V. W., Joensen, F., Bordiga, S., Lillerud, K. P. (2012). Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity. Angew. Chem. Int. Ed., 51, 5810-5831. doi.org/10.1002/anie.201103657

- Omar, W.N.N.W., Amin, N.A.S. (2011). Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass and Bioenergy, 35, 1329-1338. doi.org/10.1016/j.biombioe.2010.12.049
- Osman, N. B., Othman, H. T., Karim, R. A., Mazlan, M. A. F. (2014). Biomass in Malaysia: Forestry-based residues. International Journal of Biomass and Renewables, 3(1), 7-14.
- Park, Y., Yoo, M. L., Jin, S. H., Park, S. H. (2015). Catalytic fast pyrolysis of waste pepper stems over HZSM-5. Renewable Energy, 79, 20-27. doi.org/10.1016/j.renene.2014.10.005
- Pham, T. N., Sooknoi, T., Crossley, S. P., Resasco, D. F. (2013). Ketonization of Carboxylic Acids: Mechanisms, Catalysts, and Implications for Biomass Conversion. American Chemical Society Catal, 3, 2456-2473. doi.org/10.1021/cs400501h
- Pham, T. N., Shi, D., Resasco, D. F. (2014). Evaluating strategies for catalytic upgrading of pyrolysis oil in liquid phase. Applied Catalysis B: Environmental, 145, 10-23. doi.org/10.1016/j.apcatb.2013.01.002
- Phan, B. M. Q., Duong, L. T., Nguyen, V. D., Tran, T. B., Nguyen, M. H. H., Nguyen, L. H., Nguyen, D. A., Luu, L. C. (2014). Evaluation of the production potential of bio-oil from Vietnamese biomass resources by fast pyrolysis. Biomass and Bioenergy, 62, 74-81. doi.org/10.1016/j.apcatb.2013.01.002
- Rahimi, N., Karimzadeh, R. (2011). Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. Applied Catalysis A: General, 398, 1-17. doi.org/10.1016/j.apcata.2011.03.009
- Rahimi, N., Moradi, D., Sheibak, M., Moosavi, E., Karimzadeh, R. (2016). The influence of modification methods on the catalytic cracking of LPG over lanthanum and phosphorus modified HZSM-5 catalysts. Microporous and Mesoporous Materials, 234, 215-223. doi.org/10.1016/j.micromeso.2016.07.010

Ranganath, M. S., Vipin, Harshit. (2014). Optimization of Process Parameters in Turning Operation Using Response Surface Methodology: A Review. International Journal of Emerging Technology and Advanced Engineering, 4(10), 351-360.

- Resende, F. L. P. (2016). Recent advances on fast hydropyrolysis of biomass. Catalysis Today, 269, 148-155. doi.org/10.1016/j.cattod.2016.01.004
- Rezaei, P. S., Shafaghat, H., Daud, W. M. A. W. (2014). Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review. Applied Catalysis A: General, 469, 490-511. doi.org/10.1016/j.apcata.2013.09.036
- Romero, M. D., Calles, J. A., Rodriguez, A. (1997). Influence of the Preparation Method and Metal Precursor Compound on the Bifunctional Ni/HZSM-5 Catalysts. Ind. Eng Chem. Res., 36, 3533-3540.
- Santos, K. G., Lira, T. S., Gianesella, M., Lobato, F. S., Murata, V. V., Barrozo, M. A. S. (2011). BAGASSE PYROLYSIS: A COMPARATIVE STUDY OF KINETIC MODELS. Chemical Engineering Communications, 199(1), 109-121. doi.org/10.1080/00986445.2011.575906
- Serapiglia, M. J., Mullen, C. A., Lawrence, B. S., Boateng, A. A. (2015). Variability in pyrolysis product yield from novel shrub willow genotypes. Biomass and Bioenergy, 72, 74-84. doi.org/10.1016/j.biombioe.2014.11.015
- Shackleford, A., Masak, T., Fu, Q., Smith, G. M., Yilmaz, B., BASF Corporation, Culp, R. D., Gawecki, P., Shell Global Solutions. (2015). An alternative to rare earth elements in FCC catalysts – the use of Phinesse at Shell Sarnia. Hydrogen Engineering, 20(9), 50-56.
- Shafie, S. M., Mahlia, T. M. I., Masjuki, H. H., Ahmad-Yazid, A. (2012). A review on electricity generation based on biomass residue in Malaysia. Renewable and Sustainable Energy Reviews, 16(8), 5879-5889. doi.org/10.1016/j.rser.2012.06.031
- Sharma, A., Pareek, V., Zhang, D. (2015). Biomass pyrolysis-A review of modelling, process paramaters and catalytic studies. Renewable and Sustainable Energy Reviews, 50, 1081-1096. doi.org/10.1016/j.rser.2015.04.193
- Shen, D., Jin, W., Hu, J., Xiao, R., Luo, K. (2015a). An overview on fast pyrolysis of the main constituents in lignocellulosic biomass to valued-added chemicals: Structures, pathways and interactions. Renewable and Sustainable Energy Review, 51, 761-774. doi.org/10.1016/j.rser.2015.06.054
- Shen, D., Zhao, J., Xiao, R., Gu, S. (2015b). Production of aromatic monomers from catalytic pyrolysis of black-liquor lignin. Journal of Analytical and Applied Pyrolysis, 111, 47-54. doi.org/10.1016/j.jaap.2014.12.013

- Shen, D., Zhao, J., Xiao, R. (2016). Catalytic transformation of lignin to aromatic hydrocarbons over solid-acid catalyst: Effect of lignin sources and catalyst species. Energy Conversion and Management, 124, 61-72. doi.org/10.1016/j.enconman.2016.06.067
- Shi, N., Liu, Q., Jiang, T., Wang, T., Ma, L., Zhang, Q., Zhang, X. (2012). Hydrodeoxygenation of vegetable oils to liquid alkane fuels over Ni/HZSM-5 catalysts: Methyl hexadecanoate as the model compound. Catalysis Communications, 20, 80-84. doi.org/10.1016/j.catcom.2012.01.007
- Shun, T., Zhijun, Z., Jainping, S., Qingwen, W. (2013). Recent progress of catalytic pyrolysis of biomass by HZSM-5. Chinese Journal of Catalysis, 34, 641-650. doi.org/10.1016/S1872-2067(12)60531-2
- Stefanidis, S. D., Kalogiannis, K. G., Iliopoulou, E. F., Michailof, C. M., Pilavachi, P. A., Lappas, A. A. (2014). A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. Journal of Analytical and Applied Pyrolysis, 105, 143-150. doi.org/10.1016/j.jaap.2013.10.013
- Sun, L., Guo, X., Xiong, G., Wang, X. (2012). Ethylation of coking benzene with ethanol over nano-sized ZSM-5 zeolites: Effects of rare earth oxides on catalyst stability. Catalysts Communications, 25, 18-21. doi.org/10.1016/j.catcom.2012.03.036
- Talmadge, M.S., Baldwin, R.M., Biddy, M.J., McCormick, R.L., Beckham, G.T., Ferguson, G.A., Czernik, S., Magrini-Bair, K.A., Foust, T.D., Metelski, P.D., Hetrick, C., Nimlos, M.R. (2014). A perspective on oxygenated species in the refinery integration of pyrolysis oil. Green Chemistry, 16, 407-453.
- Thangalazhy-Gopakumar, S., Adhikari, S., Gupta, R.B. (2012). Catalytic Pyrolysis of Biomass over H<sup>+</sup>ZSM-5 under Hydrogen Pressure. Energy Fuels, 26, 5300-5306. doi.org/10.1021/ef3008213
- The Essential Chemical Industry. (2013). Catalysis. Retrieved From the Essential Chemical Industry website: http://www.essentialchemicalindustry.org/ catalysis
- U.S Energy Information Administration. (2016, May 12). International Energy Outlook 2016. Retrieved From the U.S Energy Information Administration website: https://www.repsol.com/es\_en/corporacion/conocer-repsol/contextoenergetico/matriz-energetica-mundial

- Valle, B., Castaño, P., Olazar, M., Bilbao, J., Gayubo, A. G. (2012). Deactivating species in the transformation of crude bio-oil with methanol into hydrocarbons on a HZSM-5 catalyst. Journal of Catalysis, 285(1), 304-314. doi.org/10.1016/j.jcat.2011.10.004
- Velden, M. V. de., Baeyens, J., Brems, A., Janssens, B., Dewil, R. (2010). Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. Renewable Energy, 35, 232-242. doi.org/10.1016/j.renene.2009.04.019
- Veses, A., Aznar, M., Martínez, J. D., López, J. M., Navarro, M. V., Callén, M. S., Murillo, R., Garcia, T. (2014). Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts. Bioresource Technology, 162, 250-258. doi.org/10.1016/j.biortech.2014.03.146
- Veses, A., Puértolas, B., Callén, M. S., García, T. (2015). Catalytic upgrading of biomass derived pyrolysis vapors over metal-loaded ZSM-5 zeolites: Effect of different metal cations on the bio-oil final properties. Microporous and Mesoporous Materials, 209, 189-196. doi.org/10.1016/j.micromeso.2015.01.012
- Veses, A., Puértolas, B., López, J. M., Callén, M. S., Solsona, B., Garcia, T. (2016).
   Promoting Deoxygenation of Bio-Oil by Metal-Loaded Hierarchical ZSM-5
   Zeolites. ACS Sustainable Chemistry and Engineering, 4, 1653-1660.
   doi.org/10.1021/acssuschemeng.5b01606
- Vichaphund, S., Aht-ong, D., Sricharoenchaikul, V., Atong, D. (2014). Catalytic upgrading pyrolysis vapors Jatropha waste using metal promoted ZSM-5 catalysts: An analytical PY-GC/MS. Renewable Energy, 65, 70-77. doi.org/10.1016/j.renene.2013.07.016
- Vichaphund, S., Aht-ong, D., Sricharoenchaikul, V., Atong, D. (2015). Production of aromatic compounds from catalytic fast pyrolysis of Jatropha residues using metal/HZSM-5 prepared by ion-exchange and impregnation methods. Renewable Energy, 79, 28-37. doi.org/10.1016/j.renene.2014.10.013
- Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., Sbirrazzuoli, N. (2011). ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochimica Acta, 520, 1-19. doi.org/10.1016/j.tca.2011.03.034

- Wang, Y., He, T., Liu, K., Wu, J., Fang, Y. (2012). From biomass to advanced biofuel by catalytic pyrolysis/hydro-processing: Hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis. Bioresource Technology, 108, 280-284. doi.org/10.1016/j.biortech.2011.12.132
- Wang, S., Zhou, Y., Liang, T., Guo, X. (2013). Catalytic pyrolysis of mannose as a model compounds of hemicellulose over zeolites. Biomass and Bioenergy, 57, 106-112. doi.org/10.1016/j.biombioe.2013.08.003
- Wang, K., Kim, K. H., Brown, R. C. (2014a). Catalytic pyrolysis of individual components of lignocellulosic biomass. Green Chemistry, 16, 727-735. doi.org/10.1039/c3gc41288a
- Wang, C., Liu, Q., Song, J., Li, W., Li, P., Xu, R., Ma, H., Tian, Z. (2014b). High quality diesel-range alkanes production via a single-step hydrotreatment of vegetable oil over Ni/zeolite catalyst. Catalysis Today, 234, 153-160. doi.org/10.1016/j.cattod.2014.02.011
- Wang, Y., Wang, J. (2016). Multifaceted effects of HZSM-5 (Proton-exchanged Zeolite Socony Mobil-5) on catalytic cracking of pinewood pyrolysis vapor in a two-stage fixed bed reactor. Bioresource Technology, 214, 700-710. doi.org/10.1016/j.biortech.2016.05.027
- White, J. E., Catallo, W. J., Legendre, B. L. (2011). Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. Journal of Analytical and Applied Pyrolysis, 91, 1-33. doi.org/10.1016/j.jaap.2011.01.004
- Xioning, W., Zhen, Z., Chumming, X., Aijun, D., Li, Z., Guiyuan, J. (2007). Effects of Light Rare Earth on Acidity and Catalytic Performance of HZSM-5 Zeolite for Catalytic Cracking of Butane to Light Olefins. Journal of Rare Earths, 25, 321-328. doi.org/10.1016/S1002-0721(07)60430-X
- Xu, R., Liu, J., Liang, C., Jia, W., Li, F., Guo, H. (2011). Effect of alkali metal ion modification on the catalytic performance of nano-HZSM-5 zeolite in butane cracking. Journal of Fuel Chemistry and Technology, 39(6), 449-454. doi.org/10.1016/S1872-5813(11)60029-7
- Xu, M., Mukarakate, C., Robichaud, D. J., Nimlos, M. R., Richards, R. M., Trewyn,
   B. G. (2016). Elucidating Zeolite Deactivation Mechanisms During Biomass
   Catalytic Fast Pyrolysis from Model Reactions and Zeolite Syntheses. Top
   Catal, 59, 73-85. doi.org/10.1007/s11244-015-0507-5

- Yang, Z., Kumar, A., Apblett, A. (2016). Integration of biomass catalytic pyrolysis and methane aromatization over Mo/HZSM-5 catalysts. Journal of Analytical and Applied Pyrolysis, 120, 484-492. doi.org/10.1016/j.jaap.2016.06.021
- Yao, F., Wu, Q., Lei, Y., Guo, W., Xu, Y. (2008). Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis. Polymer Degradation and Stability, 93, 90-98. doi.org/10.1016/j.polymdegradstab.2007.10.012
- Yildiz, G., Pronk, M., Djokic, M., Van, G. K. M., Ronsse, F., Van, D. R., Prins, W. (2013). Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. Journal of Analytical and Applied Pyrolysis, 103, 343-351. doi.org/10.1016/j.jaap.2013.02.001
- Yildiz, G., Ronsse, F., Duren, R. V., Prins, W. (2016). Challenges in the design and operation of processes for catalytic fast pyrolysis of woody biomass. Renewable and Sustainable Energy Reviews, 57, 1596-1610. doi.org/10.1016/j.rser.2015.12.202
- Yuan, C., Liu, H., Zhang, Z., Lu, H., Zhu, Q., Chen, Y. (2015). Alkali-metalmodified ZSM-5 zeolites for improvement of catalytic dehydration of lactic acid to acrylic acid. Chinese Journal of Catalysts, 36, 1861-1866. doi.org/10.1016/S1872-2067(15)60970-6
- Zakaria, Z. Y., Linnekoski, J., Amin, N. A. S. (2012). Catalyst screening for conversion of glycerol to light olefins. Chemical Engineering Journal, 207-208, 803-813. doi.org/10.1016/j.cej.2012.07.072
- Zhang, L., Liu, R., Yin, R., Mei, Y. (2013a). Upgrading of bio-oil from biomass fast pyrolysis in China: A review. Renewable and Sustainable Energy Reviews, 24, 66-72. doi.org/10.1016/j.rser.2013.03.027
- Zhang, H., Zheng, J., Xiao, R. (2013b). Catalytic Pyrolysis of Willow Wood with Me/HZSM-5 (Me = Mg, K, Fe, Ga, Ni) to Produce Aromatics and Olefins. BioResources, 8(4), 5612-5621.
- Zhang, M., Resense, F. L. P., Moutsoglou, A. (2014). Catalytic fast pyrolysis of aspen lignin via Py-GC/MS. Fuel, 116, 358-369. doi.org/10.1016/j.fuel.2013.07.128
- Zhang, Y., Chen, P., Lou, H. (2016a). In situ catalytic conversion of biomass fast pyrolysis vapors on HZSM-5. Journal of Energy Chemistry, 25, 427-433. doi.org/10.1016/j.jechem.2016.03.014

- Zhang, B., Zhang, Z., Xie, Q., Liu, S., Ruan, R. (2016b). Two-step fast microwaveassisted pyrolysis of biomass for bio-oil production using microwave absorbent and HZSM-5 catalyst. Journal of Environmental Sciences, 45, 240-247. doi.org/10.1016/j.jes.2015.12.019
- Zhao, Y., Pan, T., Zuo, Y., Guo, Q., Fu, Y. (2013). Production of aromatic hydrocarbons through catalytic pyrolysis of 5-Hydroxymethylfurfural from biomass. Bioresource Technology, 147, 37-42. doi.org/10.1016/j.biortech.2013.07.068
- Zheng, A., Zhao, Z., Chang, S., Huang, Z., Wu, H., Wang, X., He, F., Li, H. (2014a). Effect of crystal size of ZSM-5 on the aromatic yield and selectivity from catalytic fast pyrolysis of biomass. Journal of Molecular Catalysis A: Chemical, 383-384, 23-30. doi.org/10.1016/j.molcata.2013.11.005
- Zheng, Y., Zhao, J., Xu, F., Li, Y. (2014b). Pretreatment of lignocellulosic biomass for enhanced biogas production. Progress in Energy and Combustion Science, 42, 35-53. doi.org/10.1016/j.pecs.2014.01.001
- Zheng, Y., Wang, F., Yang, X., Huang, Y., Liu, C., Zheng, Z., Gu, J. (2017). Study on aromatics production via the catalytic pyrolysis vapor upgrading of biomass using metal-loaded modified H-ZSM-5. Journal of Analytical and Applied Pyrolysis, 126, 169-179. doi.org/10.1016/j.jaap.2017.06.011
- Zhou, G., Li, J., Yu, Y., Li, X., Wang, Y., Wang, W., Komarneni, S. (2014). Optimizing the distribution of aromatic products from catalytic fast pyrolysis of cellulose by ZSM-5 modification with boron and co-feeding of lowdensity polyethylene. Applied Catalysis A: General, 487, 45-53. doi.org/10.1016/j.apcata.2014.09.009