

Fractional Catalytic Pyrolysis Technology for the Production of Upgraded Bio-oil using FCC Catalyst

Nii Ofei D. Mante

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in
partial fulfillment of the requirements for the degree of

Doctor of Philosophy
In
Biological Systems Engineering

Chenming (Mike) Zhang, Chair
Foster A. Agblevor, Co-Chair
S. Ted Oyama
Charles E. Frazier
Ronald G. McClung

December 19, 2011
Blacksburg, Virginia

Keywords: Fractional catalytic pyrolysis, FCC catalyst, bio-oil, biomass, response surface
methodology, recycling of non-condensable gases, Y-zeolite, ZSM-5

© Copyright 2011, Nii Ofei Mante
All Rights Reserved

Fractional Catalytic Pyrolysis Technology for the Production of Upgraded Bio-oil using FCC Catalyst

Nii Ofei D. Mante

ABSTRACT

Catalytic pyrolysis technology is one of the thermochemical platforms used to produce high quality bio-oil and chemicals from biomass feedstocks. In the catalytic pyrolysis process, the biomass is rapidly heated under inert atmosphere in the presence of an acid catalyst or zeolite to promote deoxygenation and cracking of the primary vapors into hydrocarbons and small oxygenates. This dissertation examines the utilization of conventional fluid catalytic cracking (FCC) catalyst in the fractional catalytic pyrolysis of hybrid poplar wood. The influence of Y-zeolite content, steam treatment, addition of ZSM-5 additive, process conditions (temperature, weight hourly space velocity (WHSV) and vapor residence time) and recycling of the non-condensable gases (NCG) on the product distribution and the quality of the bio-oil were investigated.

The first part of the study demonstrates the influence of catalytic property of FCC catalyst on the product distribution and quality of the bio-oil. It was found that FCC catalyst with higher Y-zeolite content produces higher coke yield and lower organic liquid fraction (OLF). Conversely, FCC catalyst with lower Y-zeolite content results in lower coke yield and higher OLF. The results showed that higher Y-zeolite content extensively cracks dehydrated products from cellulose decomposition and demethoxylates phenolic compounds from lignin degradation. The Y-zeolite promoted both deoxygenation and coke forming reactions due to its high catalytic activity and large pore size. Higher Y-zeolite content increased the quality of the bio-oil with respect to higher heating value (HHV), pH, density, and viscosity. The steam treatment at 732 °C and 788 °C decreased the total BET surface area of the FCC catalyst. The findings suggest that steam treatment reduces the coking tendency of the FCC

catalyst and enhances the yield of the OLF. Analysis of the bio-oils showed that the steamed FCC catalyst produces bio-oil with lower viscosity and density. Gas chromatography and ^{13}C -NMR spectrometry suggest that steam treatment affect the catalyst selectivity in the formation of CO , CO_2 , H_2 , CH_4 , $\text{C}_2\text{-C}_5$ hydrocarbons and aromatic hydrocarbons. The addition of ZSM-5 additive to the FCC catalyst was found to alter the characteristic/functionality of the catalytic medium. The product slate showed decrease in coke yield and increase in OLF with increase in ZSM-5 additive. The FCC/ZSM-5 additive hybrid catalysts produced bio-oils with relatively lower viscosity and higher pH value. The formation of CO_2 , CH_4 , and H_2 decreased whilst C_5 and aromatic hydrocarbons increased with increase in ZSM-5 additive level.

The second part of the work assesses the effect of operating conditions on the catalytic pyrolysis process. The response surface methodology study showed reaction temperature to be the most influential statistically significant independent variable on char/coke yield, concentration of non-condensable gases, carbon content, oxygen content, pH and viscosity of the bio-oils. The WHSV was the most important statistically significant independent variable that affects the yield of organic liquid and water. Adequate and statistically significant models were generated for the prediction of the responses with the exception of viscosity. Recycling of the NCG in the process was found to potentially increase the liquid yield and decrease char/coke yield. The experiments with the model fluidizing gases showed that CO/N_2 , CO_2/N_2 , $\text{CO}/\text{CO}_2/\text{N}_2$ and H_2/N_2 increase the liquid yield and CO_2/N_2 decrease char/coke yield. The results showed that recycling of NCG increases the higher heating value and the pH of the bio-oil as well as decreases the viscosity and density. The concept of recycling the NCG in the catalytic cracking of biomass vapors with FCC catalyst improved the overall process. The evaluation of the reactivity of conventional FCC catalyst towards bio-based molecules provide essential direction for FCC catalyst formulation and design for the production of high quality bio-oils from catalytic pyrolysis of biomass.

ACKNOWLEDGMENTS

I would like to sincerely acknowledge the support and opportunity given me by my advisor Dr. Foster F. Agblevor throughout my time as a graduate student. It has been a privilege to work under his guidance and counsel. Dr. Agblevor is an excellent mentor and I appreciate his dedication to my progress and the diligence with which he addressed my research problems. I am also grateful to Ronald G. McClung for his encouragement, assistance and expertise over the course of my work. Ron ensured I had all the catalytic materials needed for the study and I am very thankful to him. I would like also to extend my deepest appreciation and gratitude to Dr. S. Ted Oyama , Dr. Chenming (Mike) Zhang and Dr. Charles E. Frazier for their advice, suggestions and guidance that helped shape the focus of my research. They have been supportive and I am grateful for the time they have invested. I wish to thank the staff of Biological Systems Engineering Department especially Barbara Wills, Linda Altizer, Denton Yoder, Allen Yoder, Susan Rosebrough, Amy Egan and Teresa Cox for their invaluable assistance and friendship. These wonderful staff members did everything in their power to help me with any problem or need. I wish to make special mention of Dr. Saied Mostaghimi (Director of VAES and CALS Associate Dean for Research and Graduate Studies) as well as Dr. Mary Leigh Wolfe (Department Head) for their warm personality and advice. I thank Robert Andrews of BASF Catalysts LLC (Iselin, NJ, USA) for inspecting and characterizing the catalyst samples.

I want to give special thanks to my family, for their unconditional support, encouragement and love. I appreciate the commitment of my father Honorable Adu Mante and my mother Erica Mante in every step of my education. Dad, your fatherly care and love have always been my bedrock. Words cannot express how I appreciate your help. Mum, your unceasing and steadfast prayers have helped me each step through this journey and I thank you for your devotion.

I dedicate this research work to my lovely and dearest wife Pearl. You have been by my side through it all and have equally shared this load. I thank you for your love, patience, dedication, help, encouragement and inspiration.

Lastly, I would like to acknowledge funding support from U.S. Department of Energy (DOE) for the catalytic studies on biomass, contract# DE-FG36-08GO18214-1.

Above all, I thank my Lord and Savior Jesus Christ for his guidance, wisdom and unfailing love.

TABLE OF CONTENTS

ABSTRACT	II
ACKNOWLEDGMENTS	IV
TABLE OF CONTENTS.....	VI
LIST OF FIGURES.....	IX
LIST OF TABLES	XII
CHAPTER 1	1
INTRODUCTION AND OBJECTIVES	1
1.1 INTRODUCTION	1
1.2 OBJECTIVES	5
REFERENCES	7
CHAPTER 2	14
FLUID CATALYTIC CRACKING OF BIOMASS PYROLYSIS VAPORS	14
2.0. ABSTRACT	14
2.1. INTRODUCTION	15
2.2 EXPERIMENTAL	17
2.2.1. <i>Materials</i>	17
2.2.2. <i>Surface area measurement</i>	18
2.2.3. <i>Catalytic cracking of pyrolysis vapors</i>	19
2.2.4. <i>Gas Analysis</i>	20
2.2.5. <i>Spent catalyst Analysis</i>	21
2.2.6. <i>Liquid Product Analysis</i>	22
2.2.7 <i>Aging and stability test</i>	23
2.3. RESULTS AND DISCUSSION.....	23
2.3.1. <i>Product Yields</i>	23
2.3.2. <i>Gas Analysis</i>	27
2.3.3. <i>Characterization of spent catalyst</i>	31
2.3.4. <i>Physico-chemical Properties of bio-oils</i>	33
2.3.5. <i>Aging and stability studies</i>	40
2.4. CONCLUSION	42
2.5. REFERENCES	43
CHAPTER 3	47
EFFECT OF HYDROTHERMAL TREATMENT OF FCC CATALYST AND ZSM-5 ADDITIVE ON FRACTIONAL CATALYTIC PYROLYSIS OF BIOMASS.....	47
3.0. ABSTRACT	47
3.1. INTRODUCTION	48
3. 2. MATERIALS AND METHODS	50

3.2.1. Biomass Feedstock	50
3.2.2. Steam treatment of FCC Catalyst	50
3.2.3. Fractional catalytic pyrolysis	50
3.2.4 Bio-oil Analysis	51
3.3. RESULTS AND DISCUSSION	52
3.3.1. Hydrothermal treatment of FCC catalyst	52
3.3.2. Effect of hydrothermal treatment of FCC catalyst on the product yields	54
3.3.3. Gas Analysis	58
3.3.4. Physical properties of bio-oils	61
3.3.5. ¹³ C-NMR spectrometry of bio-oils	63
3.4. CONCLUSION	67
3.5 REFERENCES	68
CHAPTER 4	73
FRACTIONAL CATALYTIC PYROLYSIS OF BIOMASS: THE USE OF ZSM-5 BASED ADDITIVE AS CO-CATALYST TO FCC CATALYST	73
4.0 ABSTRACT	73
4.1. INTRODUCTION.	74
4. 2. MATERIALS AND METHODS	76
4.2.1. Biomass Feedstock	76
4.2.2. FCC Catalyst and ZSM-5 additive	76
4.2.3. Fractional catalytic pyrolysis	77
4.2.4. Bio-oil Analysis	79
4.3. RESULTS AND DISCUSSION	80
4.3.1. Reactor configuration	80
4.3.2. Product Yield Analysis	83
4.3.3. Gas Yield Analysis.....	87
4.3.4 Physico-chemical Analysis of Bio-oils	91
4.4. CONCLUSION	98
4.5 REFERENCES	99
CHAPTER 5	106
A RESPONSE SURFACE METHODOLOGY STUDY ON FRACTIONAL CATALYTIC PYROLYSIS OF BIOMASS WITH FCC CATALYST	106
5.0. ABSTRACT	106
5.1. INTRODUCTION	107
5. 2. MATERIAL AND METHODS.....	110
5.2.1. Biomass Feedstock	110
5.2.2. FCC Catalyst	110
5.2.3. Design of Experiments (DOE)	111
5.2.4. Statistical Analysis.....	112
5.2.3. Fractional catalytic pyrolysis	113
5.2.4. Bio-oil Analysis	114
5.3. RESULTS AND DISCUSSION	115

5.3.1. Summary	115
5.3.3. Char/Coke Production	120
5.3.4. Non-condensable gas (NCG) production.	125
5.3.5. Water production	130
5.3.6. Carbon and Oxygen content of the bio-oil	132
5.3.6. pH and viscosity of the bio-oil	136
5.4.0. CONCLUSION	140
5.5 REFERENCES	141
CHAPTER 6	148
THE INFLUENCE OF RECYCLING NON-CONDENSABLE GAS IN THE FRACTIONAL CATALYTIC PYROLYSIS OF BIOMASS.	148
6.0 ABSTRACT	148
6.1. INTRODUCTION	149
6.2. MATERIALS AND METHODS	151
6.2.1. MATERIALS	151
6.2.3. Fractional catalytic pyrolysis of hybrid poplar	151
6.2.4. Bio-oil Analysis	152
6.3. RESULTS AND DISCUSSION	154
6.3.1 Product yields	154
6.3.2 Gas Analysis	157
6.3.2.1. Effect of Recycling	158
6.3.2.2 Model gas studies	161
6.3.3. Spectrometric Analysis of bio-oils	166
6.3.4. Physical properties of bio-oils	171
6.4. CONCLUSIONS	175
6.5 REFERENCES	176
CHAPTER 7	181
7.0 CONCLUSION	181

List of Figures

Figure 2.1. Schematic diagram of the fluidized bed reactor unit	21
Figure 2.2a. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the pyrolysis of hybrid poplar wood using sand as pyromedia at 465 °C and a WHSV of 1.5 h ⁻¹	29
Figure 2.2b. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the pyrolysis of hybrid poplar wood using kaolin as pyromedia at 465 °C and a WHSV of 1.5 h ⁻¹	29
Figure 2.2c. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the catalytic cracking of hybrid poplar vapors using steamed FCC-L as pyromedia at 465 °C and a WHSV of 1.5 h ⁻¹	30
Figure 2.2d. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the catalytic cracking of hybrid poplar vapors using steamed FCC-H as pyromedia at 465 °C and a WHSV of 1.5 h ⁻¹	30
Figure 2.3. TGA curves of the various spent catalyst. (Kaolin, FCC-L and FCC-H).....	33
Figure 2.4a. FTIR spectra of bio oils from sand, kaolin, FCC-L and FCC-H showing the cracking of C-C-O and C-O stretching vibrations (1150 – 1030 cm ⁻¹) in levoglucosan and other aliphatic/alicyclic ring alcohols	36
Figure 2.4b. FTIR spectra of bio oils from sand, kaolin, FCC-L and FCC-H showing cracking of C=O (1710-1700 cm ⁻¹) and formation of rig modes at 1600 cm ⁻¹	37
Figure 2.4c. FTIR spectra of bio oils from sand, kaolin, FCC-L and FCC-H showing out-of-plane C-H bending bands in substituted aromatic hydrocarbons (770-710 cm ⁻¹)	37
Figure 2.5. ¹³ C-NMR spectra of non catalytic oil and catalytic oils: (A) non catalytic oil; (B) bio oil from steamed FCC-L; (C) bio oil from steamed FCC-H	39
Figure 2.6. Relative distribution of Carbon atoms from the integration of ¹³ C-NMR spectra of bio-oils from Silica sand, FCC-L catalyst and FCC-H catalyst (percentage carbon total).....	40
Figure 2.7. One year stability studies on the catalytic oils produced from FCC-H and FCC-L catalyst	41
Figure 3.1 ¹³ C-NMR spectra of bio-oil produced with FCC catalyst at vapor residence of 6.5 s.....	64
Figure 3.2. ¹³ C-NMR spectra of bio-oil produced with PZSM-5 additive at vapor residence of 6.5 s	65

Figure 3.3. ^{13}C -NMR spectra of bio-oil produced with ZSM-5 additive at vapor residence of 6.5 s.....	65
Figure 4.1a. 1-Stage fluid bed reactor	
Figure 4.1b. 2-Stage fluid bed reactor.....	79
Figure 4.2a. Typical temperature and gas flow profiles for the 1-stage reactor.....	82
Figure 4.2b. Typical temperature and gas flow profiles for the 2-stage reactor	82
Figure 4.3. Effect of blending ZSM-5 additive with FCC catalyst on organic, water, char/coke and gas yields.....	86
Figure 4.4. ^{13}C -NMR spectra of various whole bio-oil from two- stage reactor using steamed catalyst blends	96
Figure 5.1. Plot of actual yield versus predicted yield of organic liquid.....	118
Figure 5.2a. Contour Plot of temperature versus WHSV in coded units showing interaction effect on the organic liquid yield.	119
Figure 5.2b. Contour Plot of WHSV versus vapor residence time in coded units showing interaction effect on the organic liquid yield.	120
Figure 5.3. Plot of actual yield versus predicted yield for char/coke	122
Figure 5.4 . Contour Plot of temperature versus WHSV in coded units showing interaction effect on the char/coke yield.	123
Figure 5.5. Plot of actual yield versus predicted yield for concentrations of H_2 , CH_4 , CO and CO_2	126
Figure 5.6. Contour Plot showing interaction effect of AB on CO_2 , H^2 , CO , and AC on CH_4 concentrations	130
Figure 5.7. Plot of actual yield versus predicted for carbon and oxygen content of the bio-oil.....	134
Figure 5.8a. Plot of actual yield versus predicted for carbon and oxygen content of the bio-oil.....	135
Figure 5.8b. Plot of actual yield versus predicted for carbon and oxygen content of the bio-oil.....	135
Figure 5.9. Contour Plot of WHSV versus vapor residence time in coded units showing interaction effect on the pH of the bio-oil.	137
Figure 6.1. Schematic diagram of the fluidized bed pyrolysis reactor unit	153
Figure 6.2a. Gas evolution plot showing the actual mole concentration of the gases during the recycling of the non-condensable gases in catalytic cracking of hybrid polar wood vapors using FCC catalyst at a vapor residence time of 6.5 s.....	159

Figure 6.2b. Gas evolution plot showing the actual mole concentration of the gases during the recycling of the non-condensable gases in catalytic cracking of hybrid polar wood vapors using FCC/FeCrCu/CoMo catalyst blend at a vapor residence time of 6.5 s	159
Figure 6.3. Gas evolution plot showing the effect of the various model gas mixtures on the concentration of H ₂ , CO ₂ , CO and CH ₄ in catalytic cracking of hybrid polar wood vapors using FCC catalyst at a vapor residence time of 3 s	162
Figure 6.4. A plot showing the effect of the model gas mixtures on the variation in the in the mole ratio of CO ₂ /CO and H ₂ /CO in catalytic cracking of hybrid polar wood vapors using FCC catalyst at a vapor residence time of 6.5 s	165
Figure 6.5. ¹³ C-NMR spectra of bio-oils shoing the effect of fluidizing gas (A) FCC; (B) FCC-recycle (C) FCC/FeCrCu/CoMo; (D) FCC/FeCrCu/CoMo-Recycle	167
Figure 6.6. ¹³ C-NMR spectra of bio-oils shoing the effect of fluidizing gas (A) 100% N ₂ ; (B) CO ₂ /N ₂ ; (C) CO/N ₂ and (D) H ₂ /N ₂	169

List of Tables

Table 2.1 Elemental composition and calorific value of hybrid poplar wood (Moisture free basis).....	18
Table 2.2. Characteristics of FCC catalysts.....	19
Table 2.3. Catalytic cracking Product Distribution	24
Table 2.4. Characteristics of the spent catalyst.....	31
Table 2.5. Physico-chemical Properties of the collected bio-oils	35
Table 3.1. Catalytic properties of Catalyst.....	51
Table 3.2. Effect of steam treatment on catalyst surface area	53
Table 3.3. Production distribution of fractional Catalytic pyrolysis of hybrid poplar	57
Table 3.4. Nitrogen free compositional analysis by weight of the gaseous product from the catalytic pyrolysis of hybrid poplar at a vapor residence of 6.5 s	61
Table 3.5. Physical Properties of the bio-oil fractions produced at a vapor residence of 6.5 s	62
Table 4.1. FCC Catalyst description	77
Table 4.2. Effect of catalyst configuration on catalyst losses.....	83
Table 4.3. Individual gas yields, wt% of biomass.....	89
Table 4.4. Physical properties of bio-oil produced from single stage reactor using fresh catalyst blends	92
Table 4.5. Physical properties of bio-oil produced from 1- stage reactor using steamed catalyst blends	93
Table 4.6. Physical properties of bio-oil produced from the 2- stage reactor using steamed catalyst blends	94
Table 4.7. ¹³ C-NMR Integration of whole bio-oil from 2- stage reactor using steamed catalyst blends....	97
Table 5.1 . Catalytic properties of FCC Catalyst.....	110
Table 5.2. Box-Behnken Experimental design	116
Table 5.3. Analysis of Variance Table for Organic liquid yield at 95% confidence level.....	117
Table 5.4. Analysis of Variance Table for Char/Coke yield with 95% of confidence level	121
Table 5.5. Analysis of Variance Table for the concentrations of H ₂ , CH ₄ , CO and CO ₂ with 95% of confidence level.....	127

Table 5.6. Analysis of Variance Table for water yield with 95% of confidence level	131
Table 5.7. Analysis of Variance Table for carbon and oxygen content with 95% of confidence level	134
Table 5.8. Analysis of Variance Table for the pH and viscosity of the bio-oil at 95% of confidence level.....	137
Table 6.1. Production distribution of fractional Catalytic cracking of hybrid poplar	156
Table 6.2. Average molar composition of the non-condensable pyrolysis gas sample at a time interval of 3.5 mins during the catalytic cracking of hybrid polar wood vapors	164
Table 6.3. ^{13}C NMR of biocrude oils produced from complete recycle of non-condensable gas.....	168
(Percentage carbon total)	168
Table 6.4. ^{13}C NMR of biocrude oils produced under N_2 , CO/N_2 , CO_2/N_2 and H_2/N_2 gas mixtures. (Percentage carbon total)	170
Table 6.5. Physical properties of bio-oils produced from complete recycle of non-condensable gas.....	172
Table 6.6. Physical properties of bio-oils produced at vapor residence of 3 s under N_2 , CO/N_2 , CO_2/N_2 and $\text{CO}/\text{CO}_2/\text{N}_2$ gas mixtures.....	174
Table 6.7. Physical properties of bio-oils produced at vapor residence of 6.5 s under N_2 , CO/N_2 , CO_2/N_2 and H_2/N_2 gas mixtures.....	174

CHAPTER 1

Introduction and Objectives

1.1 Introduction

The development of renewable energy to supplement petroleum is of importance in ensuring energy security, economic growth and a safe environment. Among the renewable energy sources, biomass is currently the largest [1]. In the United States, it supplied about 4 quadrillion Btu (quad) of energy which accounted for 4.4 % of the 2010 total energy consumption (97.89 quad)[2]. In an effort to increase the use of biomass derived feedstocks, advanced technologies for the conversion of biomass into other forms of energy are actively being pursued. Pyrolysis technology is one of the efficient thermochemical processes that transforms biomass into liquid, solid and gaseous products [3]. The liquid product which is known as bio-oil is a complex mixture of over 300 organic compounds, mainly consisting of acids, alcohols, sugars, aldehydes, esters, ketones, phenols, guaiacols, syringols, furans and aromatics.[3]. The bio-oil is considered to be one of the promising fuels[4] that can be used as a partial substitute for fossil fuels and chemicals [5-7]. However, the use of bio-oil either directly or mixed with conventional fuel is problematic due to some drawbacks in the bio-oil properties. It is highly oxygenated, viscous, corrosive, unstable, very complex and low in energy [8].

In recent years, considerable attention has been given to the upgrading of bio-oil into fuels with improved quality. The upgrading processes seek to remove or selectively transform undesirable oxygenated compounds (eg. aldehydes, ketones, carboxylic acids, levoglucosan, etc.) which are mainly responsible for the poor quality of the bio-oil. Hydroprocessing and catalytic cracking are the main routes used in upgrading bio-oils. A comprehensive review by Elliott[9] described various studies that

have been undertaken over the past 25 years in the field of hydroprocessing of bio-oils. Most of the studies were based on hydrodeoxygenation, a process performed in hydrogen donating solvents under high pressures (50-160 bars) with conventional commercial Co-Mo and Ni-Mo sulfides supported on Al_2O_3 . Hydroprocessing is an effective method in transforming bio-oil to hydrocarbon rich fuel. However, the use of high pressure, hydrogen donor solvents, and catalyst coking makes it less favorable [10-13].

In contrast, catalytic cracking of bio-oil or pyrolysis vapors offers advantages such as atmospheric processing, the use of a wide variety of catalysts and no hydrogen requirement [11-41]. There are two approaches in catalytic cracking of bio-oils and pyrolysis vapors. The off-line catalytic cracking (post pyrolysis catalysis) where the bio-oil is used as feed [18, 23, 31, 33, 35, 37, 39, 42, 43] and online catalytic cracking or fractional catalytic pyrolysis (in situ), which integrates fast pyrolysis with catalytic upgrading. Most recent studies[11, 12, 14, 16, 17, 19-21, 24, 26, 27, 32, 37, 39, 41, 44, 45] have focused on in situ catalytic upgrading as it eliminates the vaporization of the bio-oil before catalytic cracking and also results in relatively higher hydrocarbon yields and lower char/coke yields compared to the former method.

Research on catalytic cracking of bio-oil/catalytic pyrolysis have broadly been performed with various types of catalyst including ZSM-5, silicalite, Y-zeolite, silica-alumina, beta zeolite, X-zeolite, clinoptilolite, AL-MCM-41, SBA-15, mordenite, mesoporous Al_2O_3 and sulphated zirconia[10, 11, 16-19, 22, 32, 34, 38, 43, 46-49]. However, zeolites (ZSM-5, mordenite and faujasite) have been shown to be effective at converting biomass derived molecules into hydrocarbons through cracking and shape selective reactions [10-12, 22, 41, 42, 46, 50-53]. After the discovery of ZSM-5 by Mobil Research and Development Laboratories in the 1960s and 1970s, ZSM-5 has remained as the most commonly used zeolite for the upgrading of bio-oil into hydrocarbons. ZSM-5 has been proven to be effective for the conversion of methanol and biomass derived compounds into gasoline [54-56]. It is well known to be

shape selective for the production of aromatics and olefins [11, 18, 22, 36, 38, 43, 50]. Earlier work by Chang and Silvestri [54] as well as Weisz et al.[55] showed that biomass pyrolysis vapor and related oxygenated compounds can be converted over ZSM-5 to hydrocarbons. Diebold and Scahill [57] upgraded softwood pyrolysis vapors to aromatic gasoline using ZSM-5. Chen et al.[23] also used ZSM-5 catalyst to convert bio-oil and related model compounds to gasoline. Adjaye and Bakhshi [18, 43] studied the upgrading of fast pyrolysis oil with different catalyst and found HZSM-5 to be more effective in converting bio-oil to aromatic hydrocarbons. Agblevor et al.[14, 58] also showed that HZSM-5 catalyst selectively converts wood pyrolysis vapors into phenolics such as phenols, cresols and catechols. Vitolo et al. [36] upgraded pyrolytic oil over different zeolites and observed that HZSM-5 produced highly deoxygenated oils. The influence of several zeolite structures including beta, Y, ZSM-5 and Mordenite were investigated by Aho et al. [19] and ZSM-5 was reported to have the highest liquid. Another study by William et al. [38] showed highest hydrocarbon yield for ZSM-5 when compared with other zeolites. The study by Putun et al. [11] also showed that ZSM-5 produces more aromatics and has a lesser tendency for coke formation. Recently, French et al.[10] evaluated 40 different catalysts for hydrocarbon production from biomass feedstocks and reported that, the highest yield of hydrocarbons was achievable with nickel, cobalt, iron and gallium substituted ZSM-5. The ZSM-5 zeolite as has been demonstrated is effective at transforming bio-oils/vapors into hydrocarbon fuels. Nevertheless, the exploration of other potential catalysts is still crucial in the development of an advanced catalytic technology for the conversion of biomass into bio-oils with improved quality.

The fluid catalytic cracking (FCC) catalyst is the main cracking catalyst used in the petroleum refinery for upgrading heavy hydrocarbon molecules to more valuable petroleum products [59, 60]. The FCC catalyst contains Y-zeolite as its primary active component due to its acidity, hydrothermal stability, and pore size [61-64]. The application of FCC catalyst in cracking hydrocarbons has been extended to

biomass conversion. Earlier studies include the use of FCC catalyst for tar cracking and improving the heating value of the gas from steam gasification of biomass in a fluidized bed reactor[65, 66]. However, the FCC catalyst was found to be less effective and deactivates quickly when used in biomass gasification for tar cracking [67]. In recent studies, the FCC catalyst has been shown to be promising in converting biomass into hydrocarbon rich bio-oil. Lappas et al.[52] reported on the catalytic pyrolysis of biomass over FCC catalyst. Zhang et al.[12] investigated catalytic fast pyrolysis of biomass in a fluidized bed reactor using both fresh and spent FCC catalyst. Samolada et al.[68] also evaluated the performance of FCC catalyst in the production of bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking. Adam et al.[16] found that the equilibrium FCC catalyst used in comparison studies produced more promising products. Corma et al.[47] also investigated the catalytic cracking of glycerol and sorbitol with fresh and equilibrium FCC catalyst. They reported that FCC catalyst was effective at removing oxygen from biomass derived molecules.

The extension of the application of FCC catalyst for catalytic conversion of biomass would potentially pave the way for the integration of catalytic cracking of biomass intermediates into the FCC process in existing refineries with minor modifications. The implementation of these concepts will greatly reduce the total capital investment required for producing transportation fuels from biomass derived feedstocks. However, the use of Y-zeolite or commercial FCC catalyst containing Y-zeolite produces high yields of coke and water with poor liquid yields relative to ZSM-5 catalyst [10-12, 16, 18, 19, 22, 38, 47, 68]. A study by Lappas et al.[52] suggested that the use of FCC catalyst for biomass catalytic cracking is not suitable since it mainly produces water and coke.

Nevertheless, due to the flexibility of the FCC process to respond to changing feedstock (Resid cracking), product requirement (High octane number) and environmental regulations (NO_x and SO_x control), the FCC catalyst could be tailored for catalytic conversion of biomass into fuels and chemicals. Studies have shown that the cracking of gasoil with FCC catalyst are influenced by a number of catalyst

properties including Y-zeolite content [62, 69], matrix content [64, 70-72], unit cell size [61, 63] and rare earth content [60, 73]. Generally, the performances of the FCC catalyst depend on the crystalline Y-zeolite and the matrix [59, 64, 74, 75].

Currently, there is no information on how the active ingredient (Y-zeolite) and the matrix of the FCC catalyst affect biomass catalytic pyrolysis in terms of product yield and bio-oil quality. Importantly, there is a need to improve upon the catalytic conversion of biomass using FCC catalyst by increasing bio-oil yield and quality as well as minimizing coke formation to prolong catalyst life. The line of research conducted in this dissertation embodies the catalytic pyrolysis technology for the production of upgraded bio-oil using FCC catalyst.

1.2 Objectives

The core of the research is to examine the influence of the aforementioned characteristics of the FCC catalyst and process conditions on the catalytic pyrolysis of hybrid poplar wood. The suggested approach would provide a practical method for using commercial FCC catalyst for the production of high quality bio-oil that is less corrosive, less viscous, high in energy and stable. The specific objectives are as follows.

- 1. Study the Influence of Y-zeolite content in FCC catalyst on the catalytic pyrolysis of biomass.** A comparative study using catalyst matrix (no Y-zeolite), low Y-zeolite catalyst (FCC-L) and high Y-zeolite catalyst (FCC-H) to understand the effect of Y-zeolite content in FCC catalyst on the product distribution and quality of the bio-oil will be undertaken.
- 2. Investigate the effect of deactivation due to catalyst regeneration by steaming.** The FCC catalyst and ZSM-5 additives will be steamed (hydrothermal treatment) to realistically simulate catalyst deactivation as observed in a commercial unit. The effect of the catalyst deactivation by steaming will be then ascertained on the fractional catalytic pyrolysis of hybrid poplar.

- 3. Perform Response Surface Methodology (RSM) Study.** A response surface methodology will be developed to find suitable catalytic conditions (temperature, catalytic residence time and weight hourly space velocity (WHSV)) for the catalytic cracking of biomass using the FCC catalyst.
- 4. Study the use of ZSM-5 additive as a co-catalyst to FCC catalyst.** Study the use of a commercial ZSM-5 based additive as a co-catalyst to FCC catalyst in enhancing the catalytic pyrolysis process.
- 5. Investigate the influence of recycling non-condensable gases.** A mixture of CO, CO₂, H₂ and other hydrocarbon gases from the fractional catalytic pyrolysis system using FCC catalyst will be recycled with time to act as both fluidizing gas and reactive gas. The effect on product distribution and bio-oil quality will be assessed.

REFERENCES

1. Perlack, R.D., *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, 2005. p. Medium: ED.
2. Energy Information Administration, *Renewable Energy Consumption and Electricity Preliminary Statistics 2010*, 2011, U.S. Department of Energy, : Washington, DC 20585.
3. Mohan, D., C.U. Pittman, and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review*. Energy & Fuels, 2006. **20**(3): p. 848-889.
4. Czernik, S., D.K. Johnson, and S. Black, *Stability of wood fast pyrolysis oil*. Biomass and Bioenergy, 1994. **7**(1-6): p. 187-192.
5. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil*. Energy & Fuels, 2004. **18**(2): p. 590-598.
6. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils-State of the Art for the End Users*. Energy & Fuels, 1999. **13**(4): p. 914-921.
7. Diebold, J.P. and S. Czernik, *Additives To Lower and Stabilize the Viscosity of Pyrolysis Oils during Storage*. Energy & Fuels, 1997. **11**(5): p. 1081-1091.
8. Bridgwater, A.V. and S.A. Bridge, *Biomass Pyrolysis Liquids, Upgrading and Utilisation*, ed. A.V. Bridgwater and G. Grassi 1991, London: Elsevier.
9. Elliott, D.C., *Historical Developments in Hydroprocessing Bio-oils*. Energy & Fuels, 2007. **21**(3): p. 1792-1815.
10. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
11. Pütün, E., B.B. Uzun, and A.E. Pütün, *Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor*. Energy & Fuels, 2009. **23**(4): p. 2248-2258.
12. Zhang, H., R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.
13. Zhang, Q., J. Chang, Wang, and Y. Xu, *Upgrading Bio-oil over Different Solid Catalysts*. Energy & Fuels, 2006. **20**(6): p. 2717-2720.

14. Agblevor, F.A., S. Beis, O. Mante, and N. Abdoulmoumine, *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood*. Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.
15. Agblevor, F.A., O. Mante, N. Abdoulmoumine, and R. McClung, *Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis*. Energy & Fuels, 2010. **24**(7): p. 4087-4089.
16. Adam, J., E. Antonakou, A. Lappas, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, and G. Øye, *In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials*. Microporous and Mesoporous Materials, 2006. **96**(1-3): p. 93-101.
17. Adam, J., M. Blazsó, E. Mészáros, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, and G. Øye, *Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts*. Fuel, 2005. **84**(12-13): p. 1494-1502.
18. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways*. Fuel Processing Technology, 1995. **45**(3): p. 185-202.
19. Aho, A., N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D.Y. Murzin, *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.
20. Ates, F., A.E. Pütün, and E. Pütün, *Fixed bed pyrolysis of Euphorbia rigida with different catalysts*. Energy Conversion and Management, 2005. **46**(3): p. 421-432.
21. Ates, F., A.E. Pütün, and E. Pütün, *Catalytic pyrolysis of perennial shrub, Euphorbia rigida in the water vapour atmosphere*. Journal of Analytical and Applied Pyrolysis, 2005. **73**(2): p. 299-304.
22. Carlson, T., G. Tompsett, W. Conner, and G. Huber, *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
23. Chen, N.Y., D.E. Walsh, and L.R. Koenig, *Fluidized-Bed Upgrading of Wood Pyrolysis Liquids and Related Compounds*, in *Pyrolysis Oils from Biomass* 1988, American Chemical Society: Washington, DC. p. 277-289.
24. Iliopoulou, E.F., E.V. Antonakou, S.A. Karakoulia, I.A. Vasalos, A.A. Lappas, and K.S. Triantafyllidis, *Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts*. Chemical Engineering Journal, 2007. **134**(1-3): p. 51-57.

25. Lappas, A.A., D.K. Iatridis, and I.A. Vasalos, *Production of Liquid Biofuels in a Fluid Catalytic Cracking Pilot-Plant Unit Using Waxes Produced from a Biomass-to-Liquid (BTL) Process*. Industrial & Engineering Chemistry Research, 2010.
26. Lappas, A.A., M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, and I.A. Vasalos, *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
27. Li, H.-y., Y.-j. Yan, and Z.-w. Ren, *Online upgrading of organic vapors from the fast pyrolysis of biomass*. Journal of Fuel Chemistry and Technology, 2008. **36**(6): p. 666-671.
28. Peng, J., P. Chen, H. Lou, and X. Zheng, *Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol*. Bioresource Technology, 2009. **100**(13): p. 3415-3418.
29. R. K. Sharma, N.N.B., *Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals*. The Canadian Journal of Chemical Engineering, 1991. **69**(5): p. 1071-1081.
30. Radlein, D.S.A.G., S.L. Mason, J. Piskorz, and D.S. Scott, *Hydrocarbons from the catalytic pyrolysis of biomass*. Energy & Fuels, 1991. **5**(5): p. 760-763.
31. Ramesh K. Sharma, N.N.B., *Catalytic upgrading of fast pyrolysis oil over hzsm-5*. The Canadian Journal of Chemical Engineering, 1993. **71**(3): p. 383-391.
32. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
33. Sharma, R.K. and N.N. Bakhshi, *Conversion of non-phenolic fraction of biomass-derived pyrolysis oil to hydrocarbon fuels over HZSM-5 using a dual reactor system*. Bioresource Technology, 1993. **45**(3): p. 195-203.
34. Srimat T. Srinivas, A.K.D.N.N.B., *Thermal and catalytic upgrading of a biomass-derived oil in a dual reaction system*. The Canadian Journal of Chemical Engineering, 2000. **78**(2): p. 343-354.
35. Vitolo, S., B. Bresci, M. Seggiani, and M.G. Gallo, *Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading-regenerating cycles*. Fuel, 2001. **80**(1): p. 17-26.
36. Vitolo, S., M. Seggiani, P. Frediani, G. Ambrosini, and L. Politi, *Catalytic upgrading of pyrolytic oils to fuel over different zeolites*. Fuel, 1999. **78**(10): p. 1147-1159.
37. Williams, P.T. and H.M. Chishti, *Two stage pyrolysis of oil shale using a zeolite catalyst*. Journal of Analytical and Applied Pyrolysis, 2000. **55**(2): p. 217-234.

38. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. Biomass and Bioenergy, 1994. **7**(1-6): p. 223-236.
39. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(1): p. 39-61.
40. Williams, P.T. and N. Nugranad, *Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks*. Energy, 2000. **25**(6): p. 493-513.
41. Zhang, H., R. Xiao, H. Huang, and G. Xiao, *Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor*. Bioresource Technology, 2009. **100**(3): p. 1428-1434.
42. Gayubo, A.G., B. Valle, A.s.T. Aguayo, M.n. Olazar, and J. Bilbao, *Attenuation of Catalyst Deactivation by Cofeeding Methanol for Enhancing the Valorisation of Crude Bio-oil*. Energy & Fuels, 2009. **23**(8): p. 4129-4136.
43. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts*. Fuel Processing Technology, 1995. **45**(3): p. 161-183.
44. Aho, A., N. Kumar, A.V. Lashkul, K. Eränen, M. Ziolek, P. Decyk, T. Salmi, B. Holmbom, M. Hupa, and D.Y. Murzin, *Catalytic upgrading of woody biomass derived pyrolysis vapours over iron modified zeolites in a dual-fluidized bed reactor*. Fuel, 2010. **In Press, Corrected Proof**.
45. Lappas, A., M. Papapetrou, and I. Vasalos, *Fluid Catalytic Cracking VII, Materials, Methods and Process Innovations* 2007. 166.
46. Chew, T.L. and S. Bhatia, *Effect of catalyst additives on the production of biofuels from palm oil cracking in a transport riser reactor*. Bioresource Technology, 2009. **100**(9): p. 2540-2545.
47. Corma, A., G.W. Huber, L. Sauvanaud, and P. O'Connor, *Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst*. Journal of Catalysis, 2007. **247**(2): p. 307-327.
48. Lu, C.B., J.Z. Yao, W.G. Lin, and W.L. Song, *Study on biomass catalytic pyrolysis for production of bio-gasoline by on-line FTIR*. Chinese Chemical Letters, 2007. **18**(4): p. 445-448.
49. Natalie G. Wilson, P.T.W., *Investigation into the potential of a novel superacid catalyst for the catalytic upgrading of pyrolytic bio-oil*. International Journal of Energy Research, 2003. **27**(2): p. 131-143.

50. Gayubo, A.G., B. Valle, A.s.T. Aguayo, M. Olazar, and J. Bilbao, *Olefin Production by Catalytic Transformation of Crude Bio-Oil in a Two-Step Process*. Industrial & Engineering Chemistry Research, 2009. **49**(1): p. 123-131.
51. Guo, X., Y. Zheng, B. Zhang, and J. Chen, *Analysis of coke precursor on catalyst and study on regeneration of catalyst in upgrading of bio-oil*. Biomass and Bioenergy, 2009. **33**(10): p. 1469-1473.
52. Lappas, A.A., S. Bezerghianni, and I.A. Vasalos, *Production of biofuels via co-processing in conventional refining processes*. Catalysis Today, 2009. **145**(1-2): p. 55-62.
53. Yakovlev, V.A., S.A. Khromova, O.V. Sherstyuk, V.O. Dundich, D.Y. Ermakov, V.M. Novopashina, M.Y. Lebedev, O. Bulavchenko, and V.N. Parmon, *Development of new catalytic systems for upgraded bio-fuels production from bio-crude-oil and biodiesel*. Catalysis Today, 2009. **144**(3-4): p. 362-366.
54. Chang, C.D. and A.J. Silvestri, *The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts*. Journal of Catalysis, 1977. **47**(2): p. 249-259.
55. Weisz, P.B., W.O. Haag, and P.G. Rodewald, *Catalytic Production of High-Grade Fuel (Gasoline) from Biomass Compounds by Shape-Selective Catalysis*. Science, 1979. **206**(4414): p. 57-58.
56. Weisz, P.B. and J.F. Marshall, *High-Grade Fuels from Biomass Farming: Potentials and Constraints*. Science, 1979. **206**(4414): p. 24-29.
57. Diebold, J. and J. Scahill, *Biomass to Gasoline*, in *Pyrolysis Oils from Biomass* 1988, American Chemical Society. p. 264-276.
58. Agblevor, F.A. and S. Besler-Guran, *Fractional pyrolysis of biomass for high value products*. ACS Fuel Chemistry Division Preprints 2002. **47**(1): p. 374-375.
59. Huber, George W. and A. Corma, *Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass*. Angewandte Chemie International Edition, 2007. **46**(38): p. 7184-7201.
60. de la Puente, G. and U. Sedran, *Conversion of methylcyclopentane on rare earth exchanged Y zeolite FCC catalysts*. Applied Catalysis A: General, 1996. **144**(1-2): p. 147-158.
61. Al-Khattaf, S., *The influence of Y-zeolite unit cell size on the performance of FCC catalysts during gas oil catalytic cracking*. Applied Catalysis A: General, 2002. **231**(1-2): p. 293-306.
62. Dight, L.B., Leskiewicz, Mark A., Bogert, David C., *High zeolite content FCC catalysts and method for making them.*, 1990, ENGELHARD CORP (US).

63. Tonetto, G., J. Atias, and H. de Lasa, *FCC catalysts with different zeolite crystallite sizes: acidity, structural properties and reactivity*. Applied Catalysis A: General, 2004. **270**(1-2): p. 9-25.
64. Hosseinpour, N., Y. Mortazavi, A. Bazyari, and A.A. Khodadadi, *Synergetic effects of Y-zeolite and amorphous silica-alumina as main FCC catalyst components on triisopropylbenzene cracking and coke formation*. Fuel Processing Technology, 2009. **90**(2): p. 171-179.
65. Corella, J., J. Herguido, J. González-Saiz, F.J. Alday, and J.L. Rodriguez-Trujillo, *Fluidized bed steam gasification of biomass with dolomite and with a commercial FCC catalyst in Research in Thermochemical Biomass Conversion*, A.V. Bridgwater and J.L. Kuester, Editors. 1988, Elsevier Appl. Sci: London. p. 754-765.
66. Mudge, L.K., E.G. Baker, M.D. Brown, and W.A. Wilcox, *Catalytic destruction of tars in biomass-derived gases*, in *Research in Thermochemical Biomass Conversion*, A.V. Bridgwater and J.L. Kuester, Editors. 1988, Elsevier Applied Science: London and New York. p. 1141-1155.
67. Bridgwater, A.V., *Catalysis in thermal biomass conversion*. Applied Catalysis A: General, 1994. **116**(1-2): p. 5-47.
68. Samolada, M.C., W. Baldauf, and I.A. Vasalos, *Production of a bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking*. Fuel, 1998. **77**(14): p. 1667-1675.
69. Klaptsov, V.F., B.K. Nefedov, A.A. Maslova, and M.A. Khlebnikova, *Influence of zeolite content and nature of matrix on properties of cracking catalysts*. Chemistry and Technology of Fuels and Oils, 1985. **21**(12): p. 607-609.
70. Von Ballmoos, R. and C.-M.T. Hayward, *Matrix vs Zeolite Contributions to the Acidity of Fluid Cracking Catalysts*, in *Studies in Surface Science and Catalysis* 1991, Elsevier. p. 171-183.
71. Silverman, L., S. Winkler, J. Tiethof, and A. Witoshkin. *Matrix Effects in Catalytic Cracking*. in *1986 NPRA ANNUAL MEETING*. 1986. Los Angeles, California.
72. Al-Khattaf, S., *The Influence of Alumina on the Performance of FCC Catalysts during Hydrotreated VGO Catalytic Cracking*. Energy & Fuels, 2002. **17**(1): p. 62-68.
73. de la Puente, G. and U. Sedran, *Evaluation of hydrogen transfer in FCC catalysts. A new approach for cyclohexene as a test reactant*. Chemical Engineering Science, 2000. **55**(4): p. 759-765.
74. Fogassy, G., N. Thegarid, G. Toussaint, A.C. van Veen, Y. Schuurman, and C. Mirodatos, *Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units*. Applied Catalysis B: Environmental, 2010. **96**(3-4): p. 476-485.

75. Tonetto, G.M., M.L. Ferreira, J.A. Atias, and H.I. de Lasa, *Effect of steaming treatment in the structure and reactivity of FCC catalysts*. AIChE Journal, 2006. **52**(2): p. 754-768.

CHAPTER 2

Fluid Catalytic Cracking of Biomass Pyrolysis Vapors

2.0. Abstract

Catalytic cracking of pyrolysis oils/vapors offers the opportunity of producing bio-oils which can be co-processed with petroleum feedstocks in today's oil refinery. Zeolite cracking of pyrolysis oils potentially produce hydrocarbon products which can further be converted into gasoline. Catalyst properties and process conditions are critical in producing and maximizing desired product. In our studies, catalyst matrix (kaolin) and two commercial fluid catalytic cracking (FCC) catalysts, FCC-H and FCC-L with different Y-zeolite contents were investigated. The catalytic cracking of hybrid poplar wood was conducted in a 50 mm bench scale bubbling fluidized bed pyrolysis reactor at 465 °C with a weight hourly space velocity of 1.5 h⁻¹. The results showed that the yields and quality of the bio-oils were functions of the Y-zeolite content of the FCC catalyst. The char/coke yield was highest for the higher Y-zeolite catalyst. The organic liquid yields decreased inversely with increase in zeolite content of the catalyst whereas the water and gas yields increased. Analysis of the oils by both FT-IR and ¹³C-NMR indicated that the catalyst with higher zeolite content (FCC-H) was efficient in the removal of compounds like levoglucosan, carboxylic acids and the conversion of methoxylated phenols to substituted phenols and benzenediols. The cracking of pyrolysis products by kaolin suggests that the activity of the FCC catalyst on biomass pyrolysis vapors can be attributed to both Y-zeolite and matrix. The FCC-H catalyst produced more improved oil. The oil was low in oxygen (22.67 wt. %), high in energy (29.79 MJ/kg) and relatively stable over 12 months storage period.

2.1. Introduction

Securing energy for the future requires strategic development of alternative fuels and chemicals from renewable sources. Renewable energy offers cleaner environment, green jobs and stable prices for consumers. Bio-oils obtained from pyrolysis of biomass are considered to be one of the promising fuels [1] that can be used as a partial substitute for fossil fuels [2-4]. Pyrolysis is an efficient thermochemical process that transforms any biomass into liquid fuels and chemicals [5]. However, the use of pyrolysis oils either directly or mixed with conventional fuel is problematic.

In recent years, considerable attention has been given to the upgrading of bio-oils/pyrolysis vapors into biofuels that are stable, low in oxygen, less viscous, less corrosive and high in energy. The lack of these desirable properties in the raw pyrolysis oils are attributed to the high levels of undesirable oxygenated compounds in the oil [6, 7]. Hence, the removal or selective transformation of the oxygenated functionalities is vital in upgrading bio oils. Hydroprocessing and catalytic pyrolysis are the main routes used in upgrading bio-oils to date. In the quest for an economical and efficient bio-oil upgrading technology, the use of a conventional petroleum refinery process in existing infrastructure would facilitate production of transportation fuel from biomass derived feedstocks.

Fluid catalytic cracking (FCC) is the heart of the petroleum refinery process for upgrading heavy hydrocarbon molecules to more valuable petroleum products [8, 9]. During FCC process, hot catalyst is contacted with heavy gas oil to produce cracked products and coke. It is envisioned that FCC process could be applied to oxygenated bio-oil components to produce hydrocarbon fuels. Similarly, catalytic pyrolysis could be integrated into FCC processes for biomass conversion. The implementation of these concepts in existing refineries with minor modifications will greatly reduce the total capital investment required for producing transportation fuels from oxygenated feedstocks.

Since the discovery of crude oil cracking over an acid leached clay catalyst by Eugene Houdry in the 1920s [10], FCC catalyst has become the main cracking catalyst used in the petroleum refinery today. FCC catalysts are fine powders with bulk density ranging from 0.80 to 0.96 g/cm³ and particle size distribution between 10 and 150 µm. FCC catalysts have four major components: crystalline Y-zeolite, matrix, binder, and filler [8, 11-13]. The Y-zeolite is the primary active component due to its acidity, hydrothermal stability, and pore size [11, 14-16]. It can range from about 15-40 weight percent of the catalyst [17, 18]. The matrix comprises 60-85 wt.% of the commercial FCC catalyst and contains alumina, silica-alumina or natural clay depending on the catalyst synthesis technology [19]. The performance of the catalyst could be influenced by the matrix composition but to a lesser extent than the zeolite. The matrix and zeolite can affect product selectivity, quality and resistance to poisons [19]. Thus, the general activity and selectivity of the FCC catalyst is dependent on the catalyst formulations.

There is considerable interest in exploring the use of FCC catalyst for upgrading pyrolysis bio-oils/vapors [20-31]. Lappas et al. [25] reported on the catalytic pyrolysis of biomass over FCC catalyst. Zhang et al. [20] investigated catalytic fast pyrolysis of biomass in a fluidized bed reactor using both fresh and spent FCC catalyst. Samolada et al. [31] also evaluated the performance of FCC catalyst in the production of bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking. Adam et al. [21] used equilibrium FCC catalyst in a comparative studies of seven mesoporous catalyst. Corma et al. [26] investigated the catalytic cracking of glycerol and sorbitol, as representative of biomass derived oxygenates with six different catalysts, including fresh and equilibrium FCC catalyst. In catalytic cracking of bio-oils or pyrolysis vapors, oxygen is rejected in the form of CO, CO₂ and H₂O. One of the major problems reported in many of the biomass catalytic pyrolysis studies especially when using Y-zeolite or commercial FCC catalyst containing Y-zeolite is the formation of high coke and water with poor liquid yields. Y-zeolite catalyst is also known to be less efficient in the

conversion of pyrolysis oils/ vapors into hydrocarbons [21, 22, 32-36] because of its larger pore size (7.4 μm) and higher BET surface area compared to medium pore size zeolite (ZSM-5) [24, 25, 33, 35-37].

The difference in the catalytic effect of FCC catalyst on biomass based feedstock is expected since FCC catalyst is mainly used to crack petroleum crude oils which are pure hydrocarbons. Bio-oils contain more than 300 different oxygenated compounds and upgrading them all together using acid catalyst could be challenging. Nevertheless, due to the flexibility in FCC process to respond to changing feedstock (Resid cracking), product requirement (High octane number) and environmental regulations (NO_x and SO_x control), FCC catalyst could be tailored for cracking bio-oil in existing FCC units.

In this paper, we attempted to investigate the role of the active ingredient (Y-zeolite) in the FCC catalyst used in the catalytic pyrolysis of biomass. We conducted a comparative study using catalyst matrix (no Y-zeolite), low Y-zeolite catalyst (FCC-L) and high Y-zeolite catalyst (FCC-H) to understand the effect of Y-zeolite content in FCC catalyst on the product distribution and quality of the bio-oil.

2.2 Experimental

2.2.1. Materials

Samples of air dried hybrid poplar wood were ground to pass a 1-mm screen in a Wiley mill prior to all experiments. The moisture content was determined using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). The elemental composition and calorific value of the hybrid poplar wood shown in Table 2.1 was performed by Galbraith Analytical Laboratory (Knoxville, TN, USA). The catalyst matrix (kaolin) and the commercial fluid cracking catalysts (FCC-L and FCC-H) were supplied and characterized by BASF Catalysts LLC (Iselin, NJ, USA). The catalysts were steamed at 732.2 $^{\circ}\text{C}$ with 100% steam for 4 h in a fluidized state to reduce the activity of the fresh catalyst so that its performance was a representative of an equilibrium catalyst.

Table 2.1 Elemental composition and calorific value of hybrid poplar wood (Moisture free basis)

Elemental Composition (wt.%)	Hybrid poplar wood
C	49.09
H	5.29
N	<0.5
O	44.76
S	<0.05
Cl	<97ppm
Ash	0.862
HHV(MJ/kg)	18.4

2.2.2. Surface area measurement

The multi point Brunanuer, Emmett and Teller (BET) method was used to determine the total surface areas of the various catalysts. The measurements were based on isothermal adsorption of nitrogen in accordance to the procedure described in ASTM D3663 using a Micrometrics TriStar instrument. The samples prior to measurements were degassed at 300 °C for 4 h. Relative pressures (P/P_0) of 0.08, 0.11, 0.14 and 0.17 were used. The data from the multipoint determination was used to calculate the matrix surface area using the t-plot method of Lippens and deBoers. The difference between the BET surface area and the matrix surface was considered to be the zeolite surface area. The characteristics of the kaolin and the FCC catalyst used are shown in Table 2.2.

Table 2.2. Characteristics of FCC catalysts

Sample	Kaolin	Fresh FCC-H	Steamed FCC-H	Fresh FCC-L	Steamed FCC-L
Surface Area (m ² /g)	13	480	391	147	73
Zeolite Area (m ² /g)	5	362	287	87	36
Matrix Area (m ² /g)	8	118	104	60	37
Zeolite/Matrix ratio	0.63	3.07	2.76	1.46	0.97
Zeolite content (%)	0.71	51.7	41.0	12.4	5.1

2.2.3. Catalytic cracking of pyrolysis vapors

Catalytic cracking of hybrid poplar was carried out using a bench scale bubbling fluidized bed unit (Figure 2.1) at the Biological Systems Engineering Bioresource Lab, Virginia Tech, VA, USA. [38-40]. The unit consisted of a K-Tron volumetric feeder (K-Tron Process Group, Pitman, NJ), a 50 mm bubbling fluidized bed reactor equipped with a 100 μ m porous metal gas distributor, hot gas filter, two chilled water condensers and an electrostatic precipitator. The reactor was externally heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC) and the temperatures were measured and controlled by three K-thermocouples inserted into a thermal well in the reactor. 150 g of biomass was charged into the feed hopper and was continuously fed for an hour into a hot bed of FCC catalyst/kaolin maintained between 450-475 °C. The catalytic media was fluidized with 6 L/min of nitrogen gas to ensure intimate and uniform contact between the feed and the catalyst throughout the reactor as well as to minimize the losses of fine catalyst into the hot gas filter. The contact time was approximately 5 s and the weight hourly space velocity (WHSV) was 1.5 h⁻¹. Silica sand was used for blank runs.

The mixture of char, entrained catalyst, gases and vapors that exited the reactor was separated by a hot gas filter maintained at 380 °C. The separated gases and vapors were then passed through two condensers connected in series. The condensers were maintained at average temperature of –8 °C with a 50/50 cooling mixture of ethylene glycol and water from an 18-L refrigerated circulating bath (Haake, Karlsruhe, Germany). Any condensable gases and aerosols that escaped from the condenser were captured by an electrostatic precipitator (ESP) kept at 16–20 kV. The temperatures across the reactor, hot gas filter and the condensers were controlled and monitored using an Omega multiscan (1200) acquisition system with TempView 2.1 program. The mass of char/coke was determined gravimetrically by weighing the hot gas filter and the reactor before and after each pyrolysis experiment. The total mass of bio-oil was also determined gravimetrically by weighing the condensers and electrostatic precipitator before and after each experiment. The total mass of the non-condensable gas was calculated by difference. Each experiment was replicated 3 times and the average yields were expressed in percentage on a moisture free basis.

2.2.4. Gas Analysis

The non-condensable gases were sampled at intervals and were analyzed by a SRI Multiple Gas Analyzer#2 (Model 8610C, SRI Instruments, Torrance, CA) with two packed columns. The molecular Sieve 13× column separated CH₄ and CO, and all compounds in the C₁–C₄ range were separated by the Hayesep-D column. Flame ionization detector (FID) equipped with a methanizer was used for detection. The GC oven temperature was programmed to maintain 50 °C for 8 min, followed by a 20 °C/min ramp to 200 °C and holding at 200 °C for 25 min. The gas chromatogram was analyzed using PeakSimple 3.67 program. The GC was calibrated with a standard gas mixture consisting of H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, and C₂H₆ in nitrogen balance (Supelco, Bellefonte, PA).

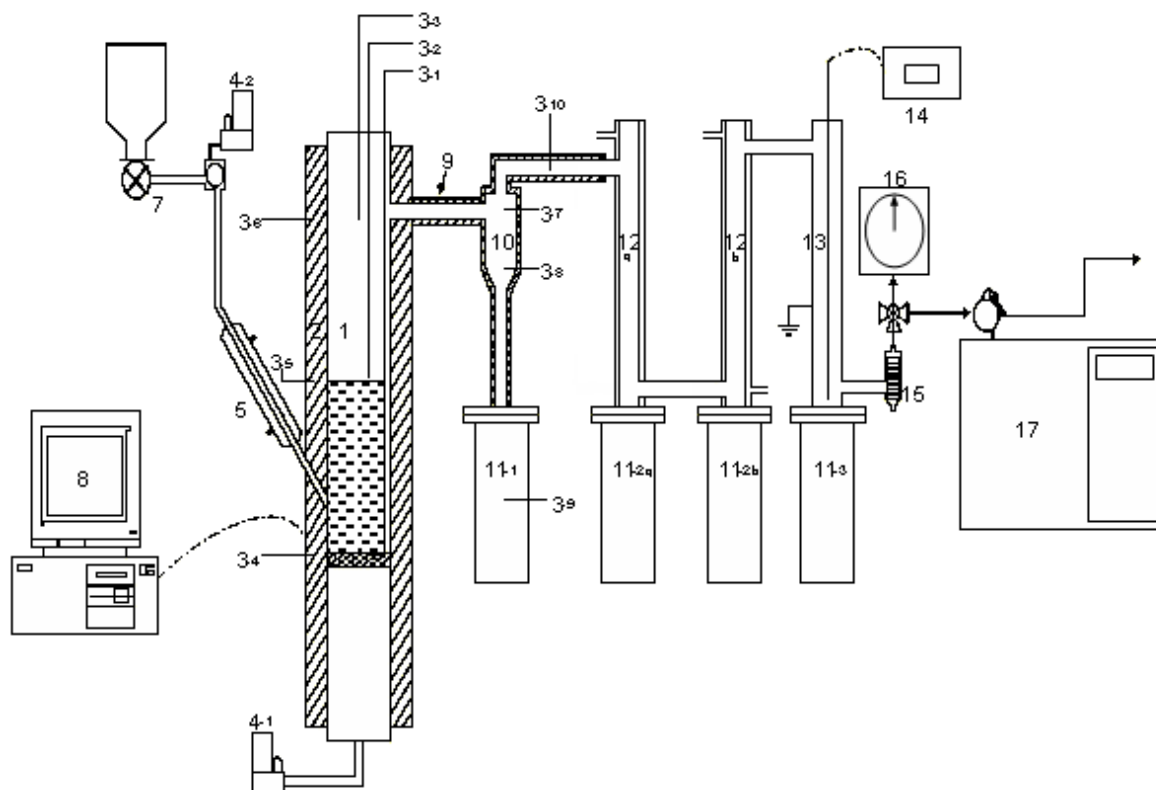


Figure 2.1. Schematic diagram of the fluidized bed reactor unit

(1-Fluidized bed, 2- Furnace, 3- Thermocouple, 4-Mass flow controller, 5- jacketed air-cooled feeder tube, 6-Hopper, 7-Screw feeder, 8-Computer, 9-Heating tape, 10-Hot gas filter, 11-Reservoir, 12- Condenser, 13-ESP, 14-AC power supply, 15-Filter, 16-Wet gas meter, 17-Gas Chromatograph)

2.2.5. Spent catalyst Analysis

Retsch analytical sieve shaker (Model AS 200) and ASTM E11 test sieves (63, 75, 124 and 180 μm) were used to obtain clean spent catalyst from the mixture with char. Samples of the clean spent catalyst were analyzed for coke using TA Instruments Q600 SDT. Approximately 30 mg of sample was subjected to thermogravimetric analysis with 100 mL/min of air as purge gas. The heating rate was at 20 $^{\circ}\text{C}/\text{min}$ from 25 to 900 $^{\circ}\text{C}$. Elemental composition (CHN) and surface areas of the spent catalyst were also determined.

2.2.6. Liquid Product Analysis

The liquid products were collected in the two condensers and the ESP. The liquids from each reservoir were kept and analyzed separately. The elemental composition (C, H, N, O, S, and Cl), ash and HHV of the oils collected from the ESP were determined by Galbraith Analytical Laboratory (Knoxville, TN, USA). The pH was measured using an Accumet pH Meter with F-55500-10 Accumet pH probe (Cole-Parmer Instrument Company, Vernon Hills, IL, USA). The pH data were obtained after 5-10 min stabilization of the mechanically stirred oil. The kinematic viscosity of the freshly produced oils were measured at 40 °C with a Cannon-Fenske viscometer according to ASTM D 445 method in a water bath equipped with Fisher Scientific model 730 lab liquid heater. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used and 50 mL of methanol was placed in the titration vessel and conditioned. About 60-100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass was recorded. The densities of the oils were determined at 23 °C using a Mettler Toledo DA-110M density meter (Greifensee, Switzerland) according to ASTM D4052. Calibrations were done prior to measurements with distilled water free of bubbles. The values were reported to 3 decimal places in g/cm³. 50 mg of each sample was subjected to a Fourier-transform infrared (FTIR) analysis. The spectra were obtained over a range of 4000-650 cm⁻¹ using an IR spectrometer (Nicolet Avatar, 370 DTGS) equipped with a DTGS-KBR. 128 scans at a 4 cm⁻¹ resolution and a gain of 4.0 were used. The ¹³C- NMR spectra of the oils were recorded on a Varian Unity 400 MHz NMR spectrometer. The observing frequency for the ¹³C nucleus was 100.58 MHz. 1.0 g of ESP oil was dissolved in 0.7 mL of deuterated dimethyl sulfoxide (δ-DMSO) and 20 µL of tetramethylsilane (TMS) in a 5 mm sample tube. The pulse width was 9.6 µs, the acquisition time was

1.36 s, and the recycle delay was 1 s. The spectra were obtained with 3000 scans and a sweep width of 25.0 MHz. All the analyses of the bio-oils were done in 3 replicates.

2.2.7 Aging and stability test

The stability and aging test of the catalytic pyrolysis oils were conducted with about 30 g of sample in 50 mL glass vials tightly sealed with a plastic cap. They were stored in a cabinet under laboratory ambient conditions for 12 months. The viscosity measurements of all the samples were taken at a six months interval. In anticipation of increase in viscosity of the oils, a Brookfield DV-II+ Pro viscometer (Brookfield Engineering laboratories, Inc. MA, USA.) equipped with a programmable thermosel temperature controller for easy analysis was used instead of Cannon Fenske viscometer. The dynamic viscosity measurement was conducted at 50 °C with Spindle SC4-18 and speed ranging from 1-60 rpm. A 7 mL sample was used and the reading of the instrument stabilized within 5-15 min.

2.3. Results and Discussion

2.3.1. Product Yields

To investigate the role of Y-zeolite content in a commercial FCC catalyst on the catalytic cracking of biomass pyrolysis vapors, experiments with and without catalyst were carried out. The inspection of the various catalyst used are shown in Table 2.2. The fresh FCC-H and the fresh FCC-L catalyst samples contained about 51% and 12% of Y-zeolite respectively. To mimic FCC operation, the fresh catalysts (FCC-H and FCC-L) were mildly steamed at 732.2 °C for 4 h to produce catalysts that have physical, chemical and catalytic properties that simulate what will be found in an operating petrochemical commercial unit. The surface area measurements showed that the catalyst surface areas, especially of the zeolite decreased after steaming. There was a loss of about 20% of the zeolite surface area for FCC-H catalyst and over 50% loss of zeolite surface area in the FCC-L catalyst. During steaming, the zeolite in

the fresh catalyst experienced high temperature and steam partial pressure resulting in the decomposition of the zeolite as shown by the micropore surface areas. The steam treatment also caused the microspheres to collapse, especially in the FCC-L catalyst.

Table 2.3. Catalytic cracking Product Distribution

Pyromedia	Product Yield Distribution (wt.%)				
	Total Liquid	Organic	Water	Char & Coke	Gas
Silica sand	66.0	51.0	15.0	15.1	18.9
Kaolin	60.1	41.51±1.2	18.6±1.0	18.88±0.4	21.01±1.3
Fresh FCC-L	43.5	23.9±0.6	19.6±1.8	19.7±1.3	36.3±0.9
Steamed FCC-L	43.95	25.35±1.1	18.6±1.2	18.9±1.4	37.1±0.8
Fresh FCC-H	40.7	14.0±1.9	26.7±2.4	25.2±0.7	32.8±1.6
Steamed FCC-H	41.2	16.5±1.0	24.7±0.5	22.9±0.7	35.9±0.7

Table 2.3 shows the product yields in terms of organic, water, char/coke and gas for all the pyromedia samples. From the results, it was clear that pyrolysis of hybrid poplar wood with kaolin, FCC-L, and FCC-H influenced the product distribution. The organic liquid fraction decreased from 51.0 wt.% to 14.0 wt.%, water yield increased from 15.0 wt.% to 26.7 wt.% and char/coke yield increased from 15.1 wt.% to 25.2 wt.% relative to the non-catalytic pyrolysis on the silica sand. The catalytic cracking of wood pyrolysis vapors with kaolin and the FCC catalysts produced lower yields of organics and higher yields of water, char/coke and gas compared to the blank run on silica sand. As seen in the product yield distribution (Table 2.3), the steamed catalyst produced different yields compared to their fresh forms. The steamed catalyst gave slightly lower char/coke yields and higher organic and gas yields when compared with the fresh catalyst. The differences in the catalytic behavior of the fresh and steamed

FCC catalysts can be explained based on the fact that the activity of the fresh catalyst was overwhelmingly high and the reduction in activity caused by the steam treatment resulted in relatively higher organic and lower char/coke yield.

A number of previous studies using FCC catalyst and H-Y zeolite have reported higher coke and lower organic yields compared to some of the catalyst used in our study. Zhang et al. [20] studied catalytic cracking of corn cobs in a fluidized bed with 30% each of fresh and spent FCC catalyst, they reported oil fraction yield of 11.8 wt.% and 18.1 wt.% respectively. The char/coke yield was between 26-34 wt.%. Similarly, William et al. [37] used Y-zeolite for catalytic cracking of biomass in a fluidized bed reactor and reported char/coke yield of 36.6 wt.% and total liquid yield of 25.03 wt.%. Adam et al. [21] also reported as high as 42 wt.% for coke and 19.52 wt.% for organic liquid yield when equilibrium FCC catalyst was used in a fixed bed for in situ catalytic upgrading of biomass derived fast pyrolysis vapors. Aho et al. [35] used the proton form of Y-zeolite in the catalytic cracking of biomass and observed lower oil yield (9.0 wt.%), higher char/coke (23.2 wt. %) and higher gas yield (51.1 wt.%). The variation in the yields reported in literature can be attributed to differences in initial feedstock characteristics, process conditions, reactor configuration and importantly catalyst formulation.

The current results show that the Y-zeolite content of the FCC catalyst strongly influences the degree of cracking of the primary pyrolysis vapors. The use of FCC catalyst containing high amount of Y-zeolite extensively cracks the organic vapor fraction which consequently leads to higher coke and water formation. The fresh FCC-H which contained about 51% Y-zeolite and a zeolite/matrix ratio of 3.07 produced the least organic yield (14 wt. %) and the highest char/coke yield (25.2 wt. %). The fresh FCC-L catalyst with 12.4 % zeolite and zeolite/matrix ratio of 1.46 produced relatively higher organic yield (23.9 wt.%) and lower char/coke (19.6 wt.%) compared to the FCC-H catalyst. The higher the zeolite content or the zeolite/matrix ratio, the higher the catalytic activity since the Y-zeolite provides the bulk

of the catalytic activity. Generally, the acid site strength, concentration and distribution in both the zeolite and matrix influence catalytic cracking activity and selectivity [41]. Bronsted acid sites are predominantly within the Y-zeolite pore structure and are known to be the main sites for catalytic cracking reactions [42] due to the hydroxyl groups attached to the framework [43, 44]. In our study, we observed that dehydration reaction that leads to high yields of water and coke was imminent in the use of FCC-H catalyst (see Table 2.3). Thus, it can be inferred that Bronsted acid sites promoted dehydration reactions.

The results also showed that the catalyst matrix (kaolin) influenced the product distribution. The use of kaolin reduced the organic yield (41.51 wt. %) and increased the yields of char/coke (18.8 wt.%), water (18.6 wt.%) and gas (21.01 wt.%). The kaolin had a total surface area of $13 \text{ m}^2\text{g}^{-1}$ and it was expected to show no significant effect on the pyrolysis vapors. However, from the results it appeared that the matrix was active enough to crack the biomass pyrolysis vapors. The effect seen in the use of the catalyst matrix suggests that the matrix has the ability to crack oxygenated molecules leading to an increase in the formation of gas, water and coke. It can be inferred from this effect that pre-cracking of the biomass macromolecules occurs first in the catalyst matrix before catalytic cracking in the pore of the Y-zeolite of the FCC catalyst. This observation is important because it suggest that catalyst matrix design can equally be used to improve upon the overall catalytic cracking of biomass pyrolysis vapors.

In the cracking of petroleum feedstocks, the use of FCC catalyst with high zeolite content and low matrix content is highly desirable as it improves both cracking activity and gasoline selectivity. On the other hand, the use of high zeolite FCC catalyst for cracking primary pyrolysis vapors as shown in the current work may not be desirable as it produces more coke and water. Thus, the use of a highly active FCC catalyst in cracking biomass pyrolysis vapors doesn't necessary result in higher bio-oil yields as is the case for petroleum cracking. One of the main challenges in catalytic pyrolysis is how to maximize organic

liquid yield and at the same time produce bio-oil with improved qualities. Since the amount of Y-zeolite in the FCC catalyst is crucial for biomass catalytic cracking, an FCC catalyst that is less active but selective enough to promote deoxygenation reactions in the cracking of biomass vapors would be preferred for such application.

2.3.2. Gas Analysis

The use of kaolin and the FCC catalysts increased the gas fraction due to cracking of the primary organic vapors into carbon oxides and light hydrocarbons. The permanent gases that exited the condensation train were identified and monitored by an SRI GC throughout the duration of the run. Figures 2.2a-d show a nitrogen free compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min for silica sand, kaolin, steamed FCC-L and steamed FCC-H respectively. The gaseous product from the non-catalytic run on silica sand consisted of about 87 % (w/w) of carbon oxides and 12.5 % (w/w) of light hydrocarbons (C_1 - C_5) and some trace of hydrogen. CO_2 was the highest carbon oxide and butane was the highest hydrocarbon gas produced. In contrast, CO was the predominant gas produced when kaolin and FCC catalyst were used. The average concentration of CO in the producer gases from kaolin, steamed FCC-L and steamed FCC-H were 46.9 % (w/w), 50.1% (w/w) and 51.5% (w/w) respectively. The goal of catalytic cracking of biomass pyrolysis vapors is to reduce the oxygen content of the bio-oil to improve its quality. During catalytic cracking, the oxygen is removed as CO, CO_2 and H_2O . It is clear from the graph in figure 2.2d that the steamed FCC-H catalyst with higher zeolite content produced higher concentrations of CO especially within the first 30 min of run. The rejection of oxygen through the formation of CO_2 is a preferable route but from our work it appeared that the FCC catalyst promoted decarbonylation reactions over decarboxylation reaction. The average CO/ CO_2 ratio was 1.2 for kaolin and 1.5 for both FCC-L and FCC-H. The catalyst matrix (kaolin) in comparison to the FCC catalyst tested produced lower concentration of CO. Other

individual gases that were enhanced during the catalytic cracking of the vapors were CH_4 , C_3H_8 , C_4H_{10} and H_2 . The FCC-H catalyst produced higher concentration of CH_4 and FCC-L produced higher concentration of C_4H_{10} . Higher concentration of H_2 was observed from cracking using the catalyst matrix (kaolin).

From the graphs (Figures 2.2a-d), it can be seen that the concentration of the gases produced from the catalytic runs varied over the course of the experiment. Evidently, the variation in the concentration of the gases was more prominent with the use of FCC-H catalyst. The concentration of CO decreased from 59.6 % (w/w) to 47.2% (w/w) after 30 min of run (see Figure 2.2d). As discussed above, FCC-H catalyst with higher content of Y-zeolite was associated with enhanced production of CO from decarbonylation reactions. The reduction in the concentration of CO and the variation in the concentration of other permanent gases were attributed to catalyst deactivation due to the formation of coke. On the contrary, the FCC-L catalyst which contained lower Y-zeolite content did not experience such catalyst deactivation despite the slight variation in the concentration of the gases. The catalyst matrix (kaolin) also did not show much variations and its behavior could be compared to that of the silica sand used for the non-catalytic run. Hence, Y-zeolite content of the FCC catalyst affects the degree to catalyst deactivation during catalytic cracking of biomass vapors.

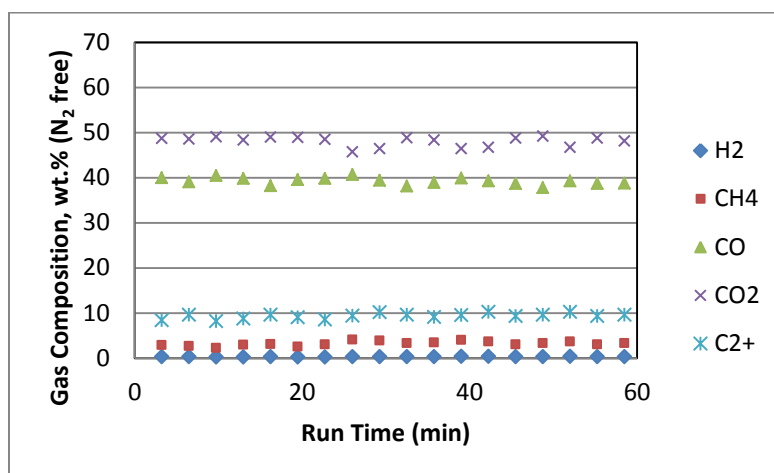


Figure 2.2a. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the pyrolysis of hybrid poplar wood using sand as pyromedia at 465 °C and a WHSV of 1.5 h⁻¹

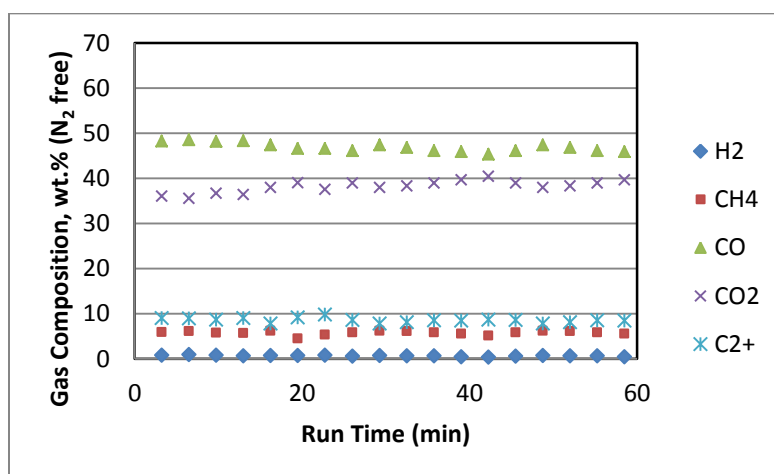


Figure 2.2b. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the pyrolysis of hybrid poplar wood using kaolin as pyromedia at 465 °C and a WHSV of 1.5 h⁻¹

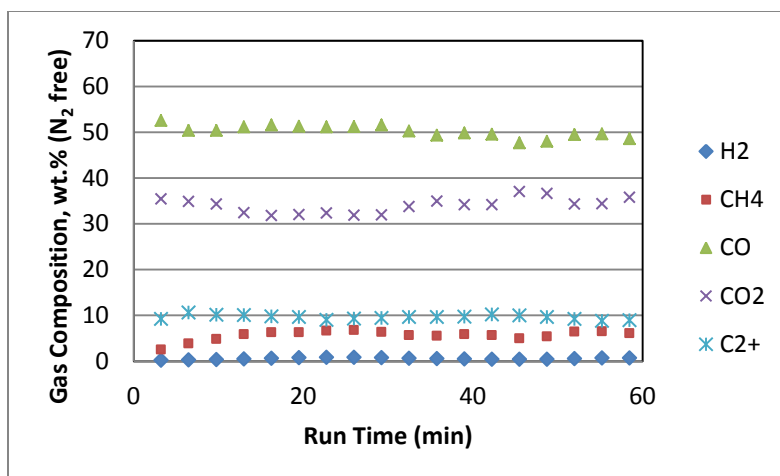


Figure 2.2c. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the catalytic cracking of hybrid poplar vapors using steamed FCC-L as pyromedia at 465 °C and a WHSV of 1.5 h⁻¹

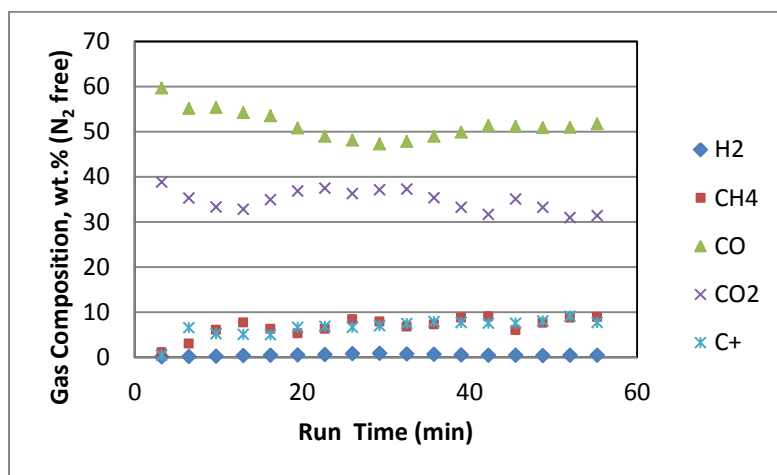


Figure 2.2d. Compositional analysis by weight of the gaseous product at a sampling time interval of 3.25 min during the catalytic cracking of hybrid poplar vapors using steamed FCC-H as pyromedia at 465 °C and a WHSV of 1.5 h⁻¹

2.3.3. Characterization of spent catalyst

In catalytic cracking of biomass vapors, carbonaceous residues (coke) deposit rapidly on the catalyst and consequently deactivate the catalyst with the time on stream. Coke formation blocks active sites and pores and hence reduces its activity. The formation of coke is still one of the biggest issues in catalytic upgrading of pyrolytic oil/vapor. To examine the role of zeolite in coke formation during biomass catalytic pyrolysis, spent catalyst were obtained from the char and catalyst mixture using a Retsch analytical sieve shaker and ASTM E11 test sieves (63, 75, 124 and 180 μm). The quantitative amount of coke deposition on the spent catalyst (FCC-L and FCC-H) was determined using TA Instruments Q600 SDT under 100 mL/min of air. The TGA curves are shown in Figure 2.3 and the following equation was used for calculating the relative amount of coke deposited on the catalyst.

$$Y_{\text{coke}} = \text{wt.}\%_{100^{\circ}\text{C}} - \text{wt.}\%_{750^{\circ}\text{C}} \quad (1)$$

Table 2.4. Characteristics of the spent catalyst

Pyromedia	Amount of coke on catalyst (%)	C (%)	H (%)	C/H molar ratio	SA (m^2/g)	MSA (m^2/g)	~zeolite
Silica sand	0.68	0.62	-	-	-	-	-
Kaolin	4.82	4.67	0.18	2.16	-	-	-
Fresh FCC-L	9.19	8.47	0.35	2.02	-	-	-
Steamed FCC-L	4.86	4.72	0.19	2.07	65	30	5
Fresh FCC-H	21.14	19.87	1.35	1.22	-	-	-
Steamed FCC-H	14.15	13.88	0.90	1.28	185	81	14.86

Table 2.4 shows the characteristics of the various spent catalyst. As can be seen clearly from the results, the FCC-H catalyst formed large amount of coke relative to FCC-L catalyst. The BET surface area measurements of the steamed FCC-L and steamed FCC-H catalyst notably reveal the loss of zeolite and matrix surface area due to the deposition of coke. It was found that the surface area of the FCC-L catalyst reduced from 73 to 65 m²/g with a loss of 10% in total catalyst surface area. The FCC-H catalyst relatively suffered severe catalyst deactivation and the total catalyst surface area reduced from 391 to 185 m²/g. The formation of coke on the FCC-H catalyst caused a loss of about 64% of the zeolite surface area. This explains the reduction in the CO concentration and the variations in the concentration of the other gases identified during the cracking of pyrolysis vapors.

The coke which has a pseudo- graphitic structure is known to be formed through extensive dehydration and dehydrogenation of polycyclic aromatics compounds [36]. This also explains why the formation of large amount of char/coke reported for FCC-H catalyst was accompanied with higher water yields (see Table 2.2). The Y-zeolite which is made of three dimensional faujasite structure, 1.2 -1.3 nm supercage and 12-ring channel system can admit coke precursor molecules in the pore structure of the catalyst [33, 36, 37]. The coke precursor molecule form polycyclic aromatic hydrocarbons (PHA) at the acidic sites and block the pores. In contrast, small pore size ZSM-5 zeolite has been shown to have lower coking tendency because the formation of polyaromatic compounds is hindered by the narrow pore channels [24, 25, 33, 35-37]. The C to H molar ratio suggests the nature of the coke deposited on the catalyst. The C to H molar ratio for kaolin and FCC-L catalyst were about 2 and that of FCC-H catalyst was about 1. This means that, the coke deposited on the FCC-H is possibly very aromatic and hard to ignite coke since it contains very low hydrogen content. Nonetheless, the TGA analysis showed that regeneration conditions at about 700 °C is sufficient enough for full combustion of the catalyst coke. The kaolin and FCC-L on the other hand showed close to twice the amount of the hydrogen content of the

coke formed on the FCC-H catalyst. This therefore suggests that low zeolite content FCC catalyst forms lesser coke which can be readily combusted due to the nature of the coke. Our data suggest that the amount of coke formed on FCC catalyst during cracking of biomass pyrolysis vapors can be controlled by varying the zeolite content.

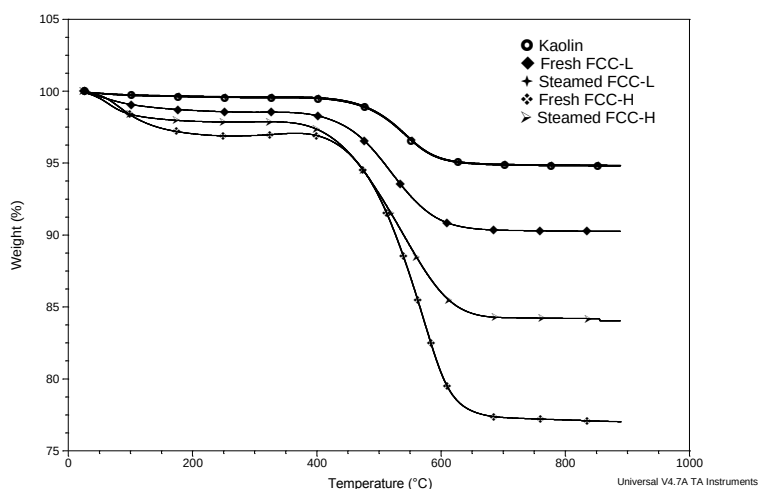


Figure 2.3. TGA curves of the various spent catalyst. (Kaolin, FCC-L and FCC-H)

2.3.4. Physico-chemical Properties of bio-oils

The liquid products were collected from the ESP and the two condensers connected in series. Homogenous aqueous phase containing 65 -75 wt% of water was collected from the condensers. The bio-oil fraction was collected from the ESP and contained about 2-5 wt% of water. The aqueous fraction and the oil fraction were kept and analyzed separately. In this work, we reported on the properties and the chemical composition of the various bio-oil fractions. In catalytic pyrolysis of biomass, the purpose is to produce oil that is stable, low in oxygen, less viscous, high in energy and less corrosive. The properties of the bio-oils in Table 2.5 showed that the use of high zeolite FCC catalyst produces more

improved oil. The oil from steamed FCC-H had high carbon content (70.43 wt.%), low oxygen content (22.67 wt.%), high HHV (29.79MJ/kg), low viscosity (55 cSt) and relatively high pH (3.30) compared to the non-catalytic bio-oil. The effect of the catalyst on the bio-oil was seen as an increase in pH and energy value and a decrease in viscosity and density. The elemental analysis also showed the FCC catalyst decreased the oxygen content and increased the carbon content of the bio-oils. Nevertheless, it is worth noting that the properties of the oils from both FCC-L and FCC-H were generally similar. One would have expected that the FCC-H catalyst with about 51 % Y-zeolite to produce oil with distinct properties. The similarity in the oil properties can be explained by the fact the catalyst with the high zeolite content was very active that it coked quickly and deactivated and hence the composite oil collected was not a true representative of that produced by the active catalyst. The result from using the steamed FCC-H partly supports this explanation. Because the steamed catalyst had a reduced activity compared to the fresh form, it did not coke quickly and consequently its performance over the period of the experiment was higher. In summary, the FCC catalyst improved the quality of the bio-oil in the order of FCC-H > FCC-L > kaolin.

The bio-oils produced from non-catalytic pyrolysis of biomass are chemically complex and contain over 300 compounds that belong to carboxylic acids, hydroxyacetaldehydes, hydroxyketones, alcohols, sugars, phenols, guaiacols, syringols, furans and aromatics[5]. The use of catalyst produces bio-oil with a defined slate of chemicals due to catalytic cracking of some of the above mentioned oxygenated functionalities. In our study, Fourier-transform infrared (FT-IR) and ¹³C-Nuclear magnetic resonance (¹³C-NMR) spectrometry were specifically used to identify changes in both carbon and oxygen functionalities in the bio-oil. Levoglucosan which is a major product from cellulose[45, 46] and methoxyphenols [47] which are primary products of lignin decomposition as well as ketones, aldehydes, acids and hydrocarbons were identified.

The FT-IR spectra of the various bio-oils (Figure 2.4a-c) distinctively showed the effect of matrix and Y-zeolite content in FCC catalyst on the decomposition products of both polysaccharides and lignin in wood. The absorption bands between 1030 and 1150 cm^{-1} due to C-O stretching vibrations in levoglucosan and other aliphatic/alicyclic ring alcohols were cracked to some extent in the order FCC-H > FCC-L > kaolin (Figure 2.4a) and as a result the intensities of those bands were reduced.

Table 2.5. Physico-chemical Properties of the collected bio-oils

Property	Bio-oils					
	Sand	Kaolin	Fresh FCC-L	Steamed FCC-L	Fresh FCC-H	Steamed FCC-H
Moisture content (wt %)	2.95	3.20	2.25	2.26	3.10	2.90
pH	2.60	2.95	2.90	3.16	3.39	3.30
Density @ 23°C, g/cm^3	1.21	1.19	1.18	1.19	1.17	1.16
Kinematic viscosity, at 40°C (cSt)	285	150	111	145	84	55
Elemental Composition (Moisture Free Basis)						
C (%)	60.67	62.1	67.66	66.45	68.21	70.43
H (%)	6.67	6.39	6.39	6.94	6.43	6.90
N (%)	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
O* (%)	32.94	31.01	25.94	26.61	25.35	22.67
Ash Content, (wt %)	<0.08	<0.08	<0.08	<0.09	<0.05	<0.05
Higher Heating Value (MJ/kg)	24.48	-	28.44	28.37	28.58	29.79

* by difference

Additionally, intensity of the C=O band at 1705 cm^{-1} due to carboxylic acids, ketones and aldehydes extensively decreased in the FCC-H catalyst oils. Therefore, it suggests that the cracking of these compounds probably require catalyst with higher catalytic activity. Notable bands indicating substituted aromatic hydrocarbons (3033 , 1600 , and 745 cm^{-1}), aliphatic hydrocarbons (2963 , 2936 , 1459 , and 1362 cm^{-1}) and phenols (1200 and 753 cm^{-1}) increased in intensity for bio oils produced with FCC-L and FCC-H catalysts.

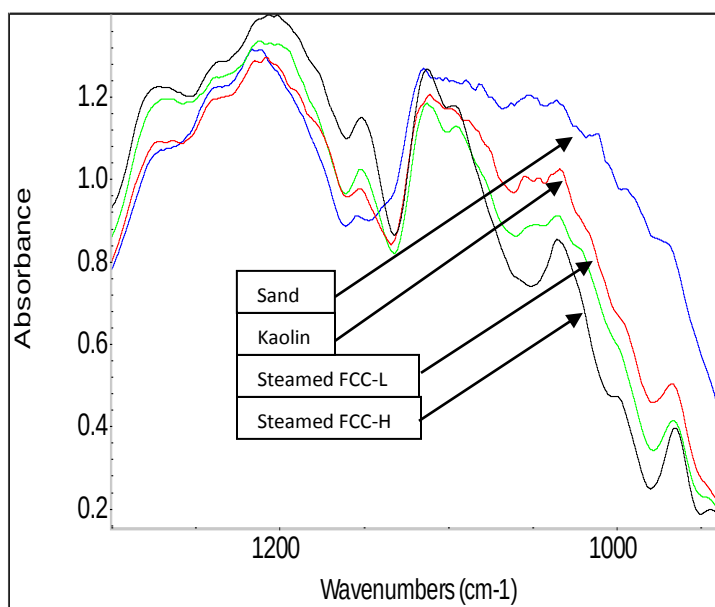


Figure 2.4a. FTIR spectra of bio oils from sand, kaolin, FCC-L and FCC-H showing the cracking of C-C-O and C-O stretching vibrations ($1150 - 1030\text{ cm}^{-1}$) in levoglucosan and other aliphatic/alicyclic ring alcohols

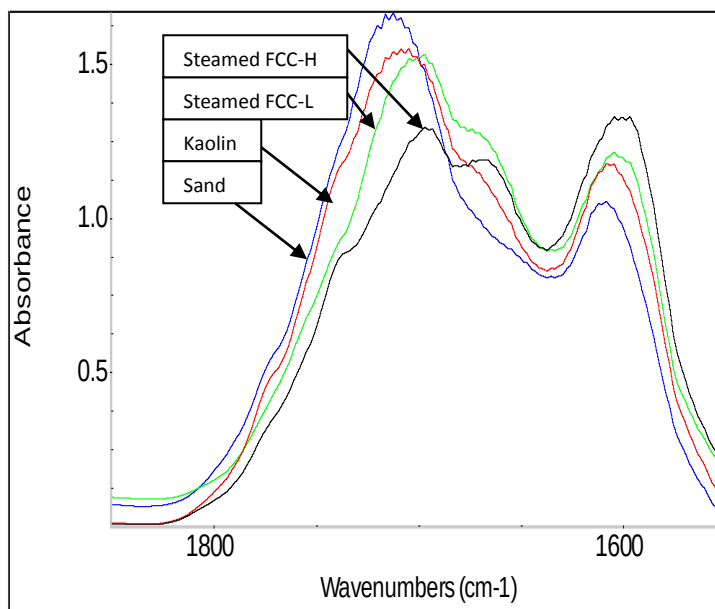


Figure 2.4b. FTIR spectra of bio oils from sand, kaolin, FCC-L and FCC-H showing cracking of C=O (1710-1700 cm⁻¹) and formation of ring modes at 1600 cm⁻¹

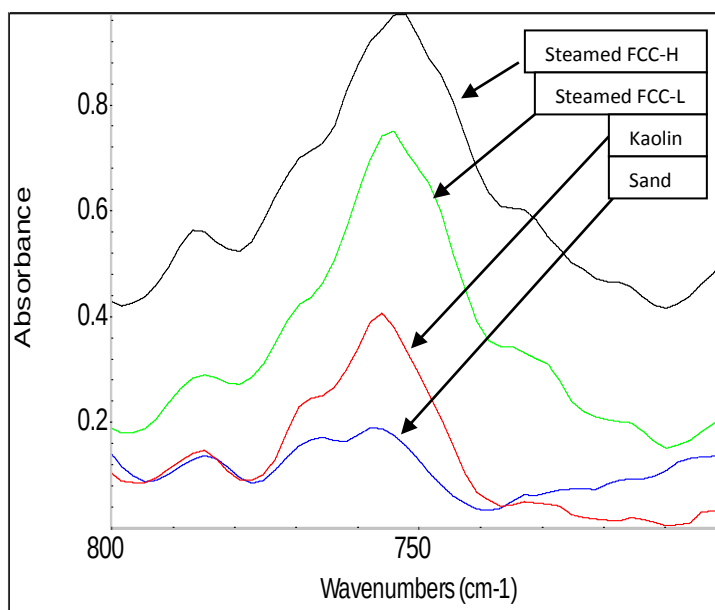


Figure 2.4c. FTIR spectra of bio oils from sand, kaolin, FCC-L and FCC-H showing out-of-plane C-H bending bands in substituted aromatic hydrocarbons (770-710 cm⁻¹)

The ^{13}C -NMR spectra of bio-oils from sand, FCC-L and FCC-H catalyst are shown in Figure 2.5. The difference between the bio-oils can be seen in the change in intensities of the various chemical shifts between 0 and 210 ppm. The region between 0 and 35 ppm were attributed to aliphatic side chains, the signal at 56.2 ppm was assigned to methoxyl carbon in guaiacyl and syringyl motifs. The carbons showing between 60 and 103 ppm were due to alcohols and carbohydrate decomposition products, signals from 105-160 ppm were attributed to aromatics and olefins. The chemical shift between 160-180 were assigned to carboxylic acids and their derivatives and finally signals that appeared within 180 and 210 ppm were attributed to ketones and aldehydes. The intense signals at 173 and 21 ppm which were assigned to acetic acid were most intense in the non-catalytic oil, but decreased in intensity after catalytic cracking of the vapors. Levoglucosan signals at 65.3, 72, 73.9, 74.1, 76.9 and 102.6 ppm also decreased in intensity as well as the methoxyl carbon (56.2 ppm) with the use of FCC catalyst. The spectra indicated that deoxygenation of the pyrolytic vapor were through decarboxylation, demethoxylation/demethylation and cracking of carbohydrate and alcohols. Thus, catalytic cracking of pyrolysis vapors produced an oil that was rich in aromatic hydrocarbons, phenols and substituted phenols which showed signals at 20.5, 115, 120, 129 and 157 ppm. It is interesting to note that the aldehydes and ketones were not noticeably affected. The results from the ^{13}C -NMR spectra were in agreement with the FTIR spectra and evidently show that FCC catalyst cracks polysaccharides readily and also depolymerizes lignin decomposition products via demethoxylation/demethylation to produce mainly lower molecular weight phenols and aromatic hydrocarbons. The relative distribution of carbon atoms chart (Figure 2.6) confirms that the FCC-H catalyst by far was able to produce bio-oil that was rich in aliphatic hydrocarbons, aromatics, olefins and phenolics. The FCC-H catalyst extensively cracked the levoglucosan, anhydrosugars, alcohols, ethers, carboxylic acids, ester carbonyls, ketones and aldehydes fractions in the pyrolysis vapors.

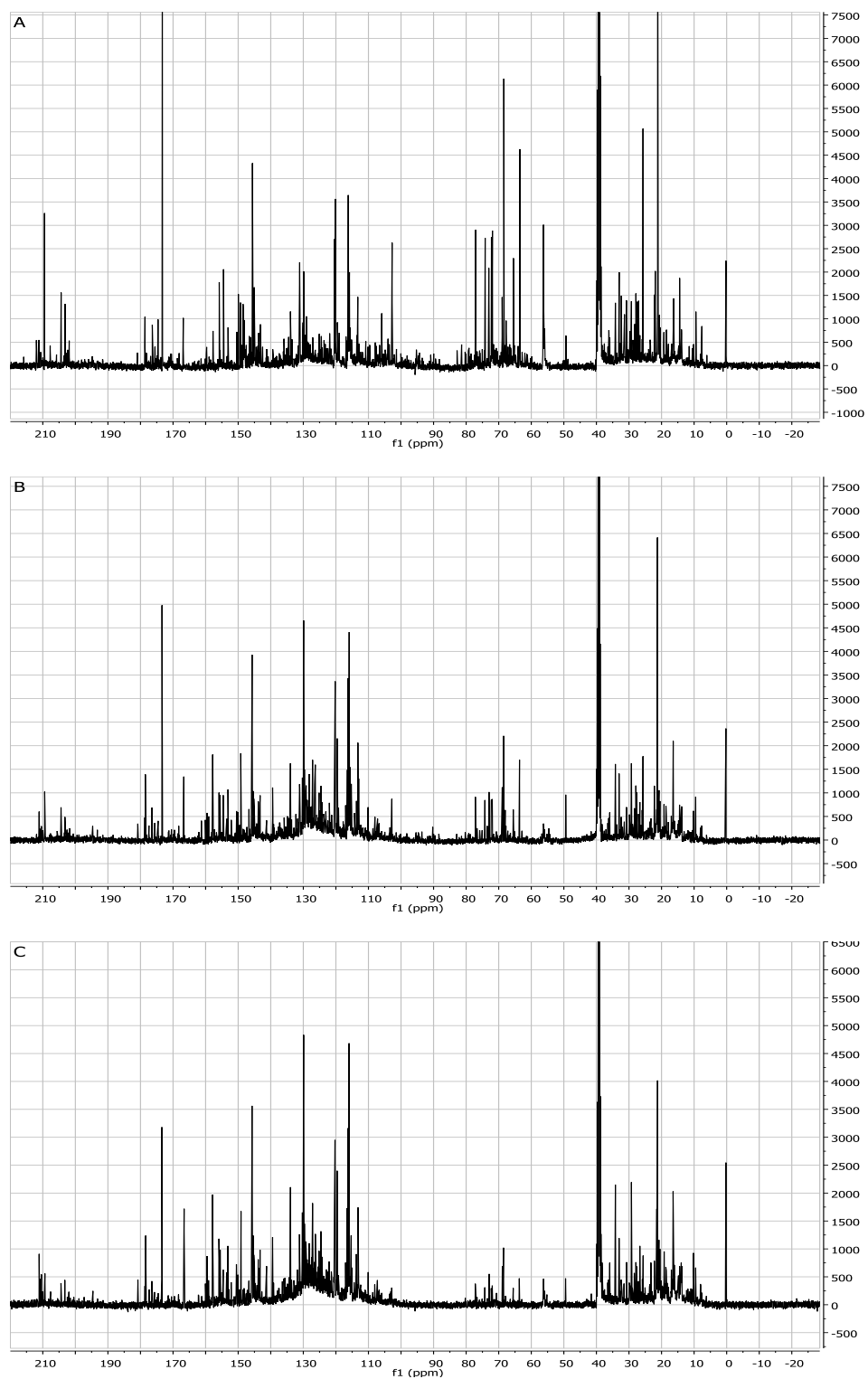


Figure 2.5. ^{13}C -NMR spectra of non catalytic oil and catalytic oils: (A) non catalytic oil; (B) bio oil from steamed FCC-L; (C) bio oil from steamed FCC-H

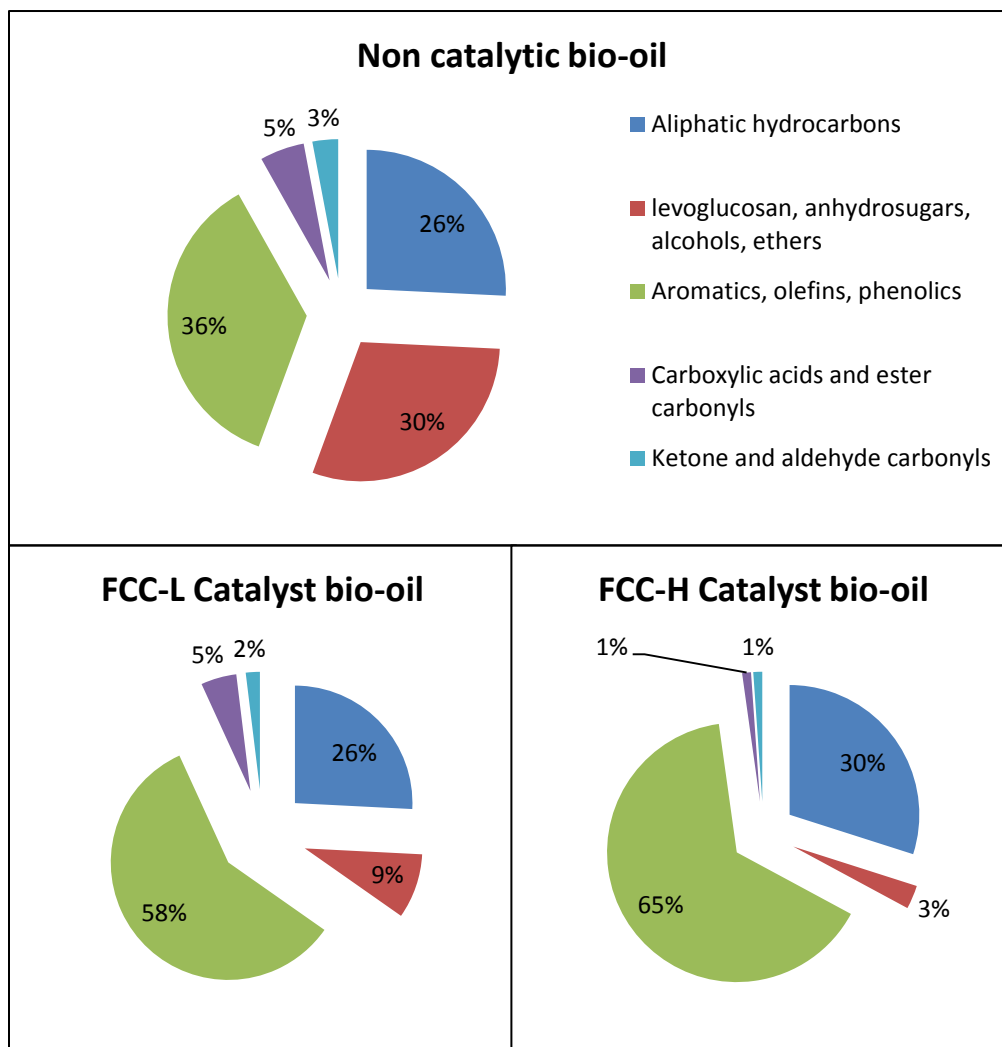


Figure 2.6. Relative distribution of Carbon atoms from the integration of ^{13}C -NMR spectra of bio-oils from Silica sand, FCC-L catalyst and FCC-H catalyst (percentage carbon total)

2.3.5. Aging and stability studies

The catalytic oils were tested for their stability at room temperature for 12 months and their viscosity measurements were monitored at six months intervals. Figure 2.7 shows a plot of change in the viscosity of the bio-oils over 12 months period. The stability studies showed that the bio-oil from FCC-H

was about 4 times more stable than the bio-oil produced from the FCC-L catalyst. This can be explained by the fact that the catalyst with higher zeolite content was effective at cracking compounds like levoglucosan, acids, aldehydes and multifunctional phenols which are believed to be bio-oil polymerization precursors [48]. The presence of levoglucosan in the bio-oil can also increase the viscosity, levoglucosan solidifies with time at room temperature and hence its removal is crucial in producing bio-oil with lower viscosity. Organic acids in the oil are not only responsible for the corrosion but they also play important role in reactions leading to bio-oil aging. Aldehydes are also known to promote many of proposed reactions that lead to bio oil instability [48]. The relative stability of the bio-oil produced with FCC-H suggests that the oil contains less of these undesirable oxygenates as shown by FT-IR and ^{13}C -NMR.

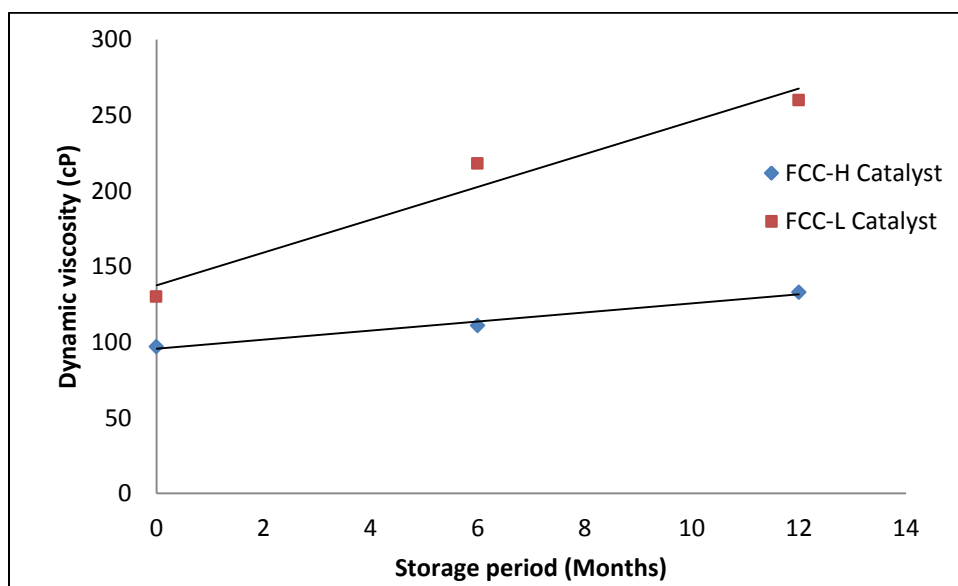


Figure 2.7. One year stability studies on the catalytic oils produced from FCC-H and FCC-L catalyst

2.4. Conclusion

The Y-zeolite content and matrix (kaolin) of commercial FCC catalyst have been shown in our work to influence the catalytic cracking of pyrolytic vapors from wood. The lowest organic fraction and highest water and char/coke formation were reported for the catalyst with higher zeolite content (FCC-H). The differences in the effect seen using FCC-L and FCC-H was attributed mainly to their zeolite content of the catalyst. However, it is worth mentioning that the catalyst matrix (kaolin) was able to crack some of the pyrolysis vapors but to a lesser extent. Hence the overall effect seen in the FCC catalyst were both due to matrix and to a larger extent zeolite cracking reactions. The study showed that coke formation in biomass catalytic pyrolysis using FCC catalyst can be controlled by reducing the zeolite content. FTIR and ^{13}C NMR spectrometry showed that the cracking of levoglucosan, carboxylic acids, methoxyphenols and other anhydrosugars is a function of zeolite content. The removal of undesirable oxygenates like organic acids, levoglucosan, aldehydes and methoxyphenols retarded reactions that lead to instability of the oil when stored.

2.5. References

1. Czernik, S., D.K. Johnson, and S. Black, *Stability of wood fast pyrolysis oil*. Biomass and Bioenergy, 1994. **7**(1-6): p. 187-192.
2. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil*. Energy & Fuels, 2004. **18**(2): p. 590-598.
3. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils-State of the Art for the End Users*. Energy & Fuels, 1999. **13**(4): p. 914-921.
4. Diebold, J.P. and S. Czernik, *Additives To Lower and Stabilize the Viscosity of Pyrolysis Oils during Storage*. Energy & Fuels, 1997. **11**(5): p. 1081-1091.
5. Mohan, D., C.U. Pittman, and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review*. Energy & Fuels, 2006. **20**(3): p. 848-889.
6. Bridgwater, A.V., *Biomass Fast Pyrolysis*. Thermal Science, 2004. **8**(2): p. 49.
7. Bridgwater, A.V., D. Meier, and D. Radlein, *An overview of fast pyrolysis of biomass*. Organic Geochemistry, 1999. **30**(12): p. 1479-1493.
8. Huber, George W. and A. Corma, *Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass*. Angewandte Chemie International Edition, 2007. **46**(38): p. 7184-7201.
9. de la Puente, G. and U. Sedran, *Conversion of methylcyclopentane on rare earth exchanged Y zeolite FCC catalysts*. Applied Catalysis A: General, 1996. **144**(1-2): p. 147-158.
10. Avidan, A.A., *Origin, Development and Scope of FCC Catalysis*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 1-39.
11. Hosseinpour, N., Y. Mortazavi, A. Bazyari, and A.A. Khodadadi, *Synergetic effects of Y-zeolite and amorphous silica-alumina as main FCC catalyst components on triisopropylbenzene cracking and coke formation*. Fuel Processing Technology, 2009. **90**(2): p. 171-179.
12. Fogassy, G., N. Thegarid, G. Toussaint, A.C. van Veen, Y. Schuurman, and C. Mirodatos, *Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units*. Applied Catalysis B: Environmental, 2010. **96**(3-4): p. 476-485.
13. Tonetto, G.M., M.L. Ferreira, J.A. Atias, and H.I. de Lasa, *Effect of steaming treatment in the structure and reactivity of FCC catalysts*. AIChE Journal, 2006. **52**(2): p. 754-768.
14. Al-Khattaf, S., *The influence of Y-zeolite unit cell size on the performance of FCC catalysts during gas oil catalytic cracking*. Applied Catalysis A: General, 2002. **231**(1-2): p. 293-306.

15. Dight, L.B., Leskowicz, Mark A., Bogert, David C., *High zeolite content FCC catalysts and method for making them.*, 1990, ENGELHARD CORP (US).
16. Tonetto, G., J. Atias, and H. de Lasa, *FCC catalysts with different zeolite crystallite sizes: acidity, structural properties and reactivity*. Applied Catalysis A: General, 2004. **270**(1-2): p. 9-25.
17. Al-Khattaf, S., *The Influence of Alumina on the Performance of FCC Catalysts during Hydrotreated VGO Catalytic Cracking*. Energy & Fuels, 2002. **17**(1): p. 62-68.
18. Klaptsov, V.F., B.K. Nefedov, A.A. Maslova, and M.A. Khlebnikova, *Influence of zeolite content and nature of matrix on properties of cracking catalysts*. Chemistry and Technology of Fuels and Oils, 1985. **21**(12): p. 607-609.
19. Woltermann, G.M., J.S. Magee, and S.D. Griffith, *Commercial Preparation and Characterization of FCC Catalysts*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 105-144.
20. Zhang, H., R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.
21. Adam, J., E. Antonakou, A. Lappas, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, and G. Øye, *In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials*. Microporous and Mesoporous Materials, 2006. **96**(1-3): p. 93-101.
22. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
23. Lappas, A.A., M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, and I.A. Vasalos, *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
24. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
25. Lappas, A.A., S. Bezergianni, and I.A. Vasalos, *Production of biofuels via co-processing in conventional refining processes*. Catalysis Today, 2009. **145**(1-2): p. 55-62.
26. Corma, A., G.W. Huber, L. Sauvanaud, and P. O'Connor, *Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst*. Journal of Catalysis, 2007. **247**(2): p. 307-327.

27. Graça, I., F.R. Ribeiro, H.S. Cerqueira, Y.L. Lam, and M.B.B. de Almeida, *Catalytic cracking of mixtures of model bio-oil compounds and gasoil*. Applied Catalysis B: Environmental, 2009. **90**(3-4): p. 556-563.
28. Lee, K.-H., S.-G. Jeon, K.-H. Kim, N.-S. Noh, D.-H. Shin, J. Park, Y. Seo, J.-J. Yee, and G.-T. Kim, *Thermal and catalytic degradation of waste high-density polyethylene (HDPE) using spent FCC catalyst*. Korean Journal of Chemical Engineering, 2003. **20**(4): p. 693-697.
29. Lee, K.-H. and D.-H. Shin, *A comparative study of liquid product on non-catalytic and catalytic degradation of waste plastics using spent FCC catalyst*. Korean Journal of Chemical Engineering, 2006. **23**(2): p. 209-215.
30. Li, H., B. Shen, J.C. Kabalu, and M. Nchare, *Enhancing the production of biofuels from cottonseed oil by fixed-fluidized bed catalytic cracking*. Renewable Energy, 2009. **34**(4): p. 1033-1039.
31. Samolada, M.C., W. Baldauf, and I.A. Vasalos, *Production of a bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking*. Fuel, 1998. **77**(14): p. 1667-1675.
32. Pütün, E., B.B. Uzun, and A.E. Pütün, *Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor*. Energy & Fuels, 2009. **23**(4): p. 2248-2258.
33. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways*. Fuel Processing Technology, 1995. **45**(3): p. 185-202.
34. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. Biomass and Bioenergy, 1994. **7**(1-6): p. 223-236.
35. Aho, A., N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D.Y. Murzin, *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.
36. Carlson, T., G. Tompsett, W. Conner, and G. Huber, *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
37. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(1): p. 39-61.
38. Agblevor, F.A., S. Beis, S.S. Kim, R. Tarrant, and N.O. Mante, *Biocrude oils from the fast pyrolysis of poultry litter and hardwood*. Waste Management, 2010. **30**(2): p. 298-307.

39. Agblevor, F.A., S. Beis, O. Mante, and N. Abdoulmoumine, *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood*. Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.
40. Mante, O.D. and F.A. Agblevor, *Influence of pine wood shavings on the pyrolysis of poultry litter*. Waste Management, 2010. **30**(12): p. 2537-2547.
41. Scherzer, J., *Correlation Between Catalyst Formulation and Catalytic Properties*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 145-182.
42. Ward, J.W., *The nature of active sites on zeolites : III. The alkali and alkaline earth ion-exchanged forms*. Journal of Catalysis, 1968. **10**(1): p. 34-46.
43. Jacobs, P.A., H.E. Leeman, and J.B. Uytterhoeven, *Active sites in zeolites : I. Cumene cracking activity of NH₄Y zeolites after different reactor pretreatments*. Journal of Catalysis, 1974. **33**(1): p. 17-30.
44. Scherzer, J. and J.L. Bass, *Infrared spectra of ultrastable zeolites derived from type Y zeolites*. Journal of Catalysis, 1973. **28**(1): p. 101-115.
45. Adam, J., M. Blazsó, E. Mészáros, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, and G. Øye, *Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts*. Fuel, 2005. **84**(12-13): p. 1494-1502.
46. Carlson, T.R., J. Jae, Y.-C. Lin, G.A. Tompsett, and G.W. Huber, *Catalytic fast pyrolysis of glucose with HZSM-5: The combined homogeneous and heterogeneous reactions*. Journal of Catalysis, 2010. **270**(1): p. 110-124.
47. Faix, O., I. Fortmann, J. Bremer, and D. Meier, *Thermal degradation products of wood*. European Journal of Wood and Wood Products, 1991. **49**(5): p. 213-219.
48. Diebold, J.P., *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils*, in *Other Information: PBD: 27 Jan 1999* 1999.

CHAPTER 3

Effect of Hydrothermal Treatment of FCC Catalyst and ZSM-5 Additive on Fractional Catalytic Pyrolysis of Biomass

3.0. Abstract

Fresh FCC catalyst and ZSM-5 additives were hydrothermally treated with 100% steam at 732 °C (1350 °F) and 788 °C (1450 °F) for 4 h in a fluidized bed reactor. The catalytic pyrolysis of hybrid poplar wood with fresh and steam treated catalysts were conducted in a 50 mm bench scale bubbling fluidized bed reactor at 475 °C and a weight hourly space velocity (WHSV) of 2 h⁻¹. BET surface area measurements showed a reduction of 24% and 34% in the surface area of the FCC catalyst after steam treatment at 732 °C and 788 °C respectively. The non-phosphorus based ZSM-5 additive lost about 15% of its surface area after mild steaming at 732 °C. However, the phosphorus impregnated ZSM-5 additive was not affected at both steaming conditions. The hydrothermal treatment of the catalysts influenced the catalytic product distribution and the quality of the bio-oil. The steamed FCC catalyst produced higher organic liquid and gas yields and decreased the formation of coke and water. The viscosity and the density of the bio-oils produced from the steamed FCC catalyst were lower than those produced with the fresh FCC catalyst. In the case of the ZSM-5 additives, the steam treatment affected only the organic liquid and gas yields. The organic liquid yield increased and the gas yield decreased. Steaming of the ZSM-5 additive did not show any effect on the char/coke yield as was seen with the FCC catalyst due to the lower tendency of ZSM-5 to form coke. The GC analysis of the product gases suggested that steam treatment influenced the catalyst selectivity in the formation of CO, CO₂, H₂, CH₄ and C₂-C₅

hydrocarbons. The ^{13}C -NMR spectra of the bio-oil showed generally that steaming of the FCC catalyst increased the selectivity for the production of aromatic hydrocarbons.

3.1. Introduction

Petroleum refineries in the future would be under economic pressure to consider processing readily available alternative feedstocks due to limited oil sources, soaring petroleum prices, potential instabilities in Middle-East politics and climbing demand due to increases in industrialization and population. Catalytic pyrolysis of biomass is one of the emerging promising technologies that converts biomass into bio-oil for further processing into biobased gasoline, diesel and jet fuel using existing infrastructure [1-10]. Catalytic pyrolysis of biomass, in contrast to conventional pyrolysis seeks to increase the usability and compatibility of bio-oils with petroleum feedstocks by cracking oxygenated functionalities such as, carbohydrates, guaiacyl and syringyl groups, aldehydes, ketones and carboxylic acids into hydrocarbon fractions. In essence, catalytic pyrolysis of biomass vapors is analogous to fluid catalytic cracking (FCC), an important downstream process used to convert heavy feedstocks (Atmospheric gas oil (AGO) and Vacuum gas oil (VGO)) into more valuable products such as naphtha, liquefied petroleum gases (LPG) and FCC gas oil. Thus, there is an opportunity for introducing biomass intermediates in petroleum refinery process streams and this would in fact present new market demands in FCC catalyst formulations.

The evaluation of the reactivity of traditional FCC catalyst towards biomass intermediates will provide essential direction for FCC catalyst formulation and design for co-cracking of biomass derived feed and hydrocarbon fractions such as VGO. The FCC catalyst which belongs to the faujasite zeolite family has been shown to be effective at deoxygenating biomass derived molecules [3-5, 9-18]. However, the FCC catalyst when used to crack biomass pyrolysis vapors deactivates reversibly due to

high amount of coke [4, 10, 19-22]. This implies that, the FCC catalyst would have to be regenerated rapidly to maintain catalytic activity in a continuous operation.

In the oil refinery, FCC units (FCCUs) are operated in such a way that a portion of the spent catalyst is continuously removed and regenerated in order to maintain activity throughout the process. During the regeneration cycles, the FCC catalyst is exposed to high temperatures (650 – 800 °C) and steam for about 15 mins [23]. The catalyst under such conditions suffers irreversible deactivation due to dealumination/decomposition of the zeolite and collapse of the matrix surface [23-26]. These structural changes that occur during catalyst regeneration affect the catalyst activity and selectivity [24, 26-28].

To evaluate FCC catalyst regeneration during the catalytic pyrolysis of biomass, the fresh catalyst was pretreated with steam. Hydrothermal catalyst pretreatment is an important step that precedes the evaluation of the FCC catalyst. The primary goal of the pretreatment is to artificially deactivate a fresh catalyst to realistically simulate what will be observed in a commercial unit. Hydrothermal pretreatment of the fresh FCC catalyst is performed in the presence of steam at temperatures ranging from 538 °C to 927 °C for a period of 2 to 24 hours [29] and depending on the pretreatment condition the activity and selectivity of the FCC catalyst is altered. There exist many steaming philosophies for deactivating the FCC catalyst, but to achieve a reasonable catalyst activity, temperatures in the range of 730 – 790 °C with 100% steam are recommended [30].

In the present work the effect of steam pretreatment of FCC catalyst and ZSM-5 additives on product yields and the physical property of the bio-oil from the fractional catalytic pyrolysis of hybrid poplar wood was investigated.

3. 2. Materials and methods

3.2.1. Biomass Feedstock

Hybrid poplar wood samples were air dried and ground to pass a 1-mm screen in a Wiley mill prior to all experiments. The moisture content was determined using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). The elemental composition and calorific value of the hybrid poplar wood are shown in Table 2. 1.

3.2.2. Steam treatment of FCC Catalyst

A commercial fluid cracking catalyst (FCC) and two commercial ZSM-5 FCC based additives were supplied and characterized by BASF Catalysts LLC (Iselin, NJ, USA). The fresh FCC catalyst and ZSM-5 additives were pretreated with 100% steam at 732 °C (1350 °F) and 788 °C (1450 °F) for 4 h in a fluidized bed reactor. Multipoint BET method was used to determine the total surface areas of the various catalysts after steam treatment. The measurements were based on isothermal adsorption of nitrogen according to the procedure described in ASTM D3663 using a Micrometrics TriStar instrument. The samples prior to measurements were degassed at 300 °C for 4 h. Relative pressures (P/P_0) of 0.08, 0.11, 0.14 and 0.17 were used. The data from the multipoint determination was used to calculate the matrix surface area using the t-plot method. The difference between the BET surface area and the matrix surface was considered to be the zeolite surface area. The characteristics of the FCC and the ZSM-5 based additives are shown in Table 3.1

3.2.3. Fractional catalytic pyrolysis

The fractional catalytic pyrolysis of hybrid poplar wood with both fresh and steam treated catalysts were conducted in a 50 mm bench scale bubbling fluidized bed reactor (Figure 2.1) at 475 °C and a weight hourly space velocity (WHSV) of 2 h⁻¹. A detailed description of the pyrolysis unit and the

fractional catalytic process used has been given in chapter 2. The catalytic pyrolysis tests were performed at apparent average vapor residence times of 6.5 s and 3 s. The apparent average vapor residence time was defined as the total volume of fluidized catalyst divided by gas flow rate at reactor conditions. The non-condensable gases were analyzed every 3.25 minutes online using a Varian 490 micro GC (Agilent Technologies, Inc. Santa Clara, CA USA). The micro GC was equipped with two modules, a 10 m Molsieve (MS) 5Å column and a 10 m porous polymer (PPU) column. Each module had a thermal conductivity detector. The MS column was used to analyze hydrogen, methane and carbon monoxide. Carbon dioxide and C₁-C₅ gases were analyzed by the PPU column. The bio-oil and the char yields were determined gravimetrically and the yield of the non-condensable gas was calculated by difference. Each experiment was replicated 3 times and the average yields were expressed in percentage on a moisture free basis.

Table 3.1. Catalytic properties of Catalyst

Catalyst Properties	FCC	ZSM5-Additive A	ZSM5-Additive B
Al ₂ O ₃ , wt.%	38.86	30.36	17.37
RE ₂ O ₃ , wt.%	5.54	-	-
P ₂ O ₅ , wt.%	0.08	15.28	0.09
BET surface area, m ² /g	516	112	141
Micropore Volume, cm ³ /g	0.258	0.0234	0.077
Average Particle size, μm	86	91	75

3.2.4 Bio-oil Analysis

The bio-oils were analyzed for C, H, N, O, and S on a Thermo Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Cambridge, UK). The higher heating values (HHV) of the oils

were determined using IKA C2000 basic bomb calorimeter (IKA® Works, Inc, NC, and U.S.A.) according to ASTM D2015. The pH was measured using a Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The pH data were obtained after 5-10 min stabilization of the mechanically stirred oil. The viscosity and density of the bio-oils were measured at 40 °C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were equivalent to viscosities determined by ASTM D445 method. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used. 50 mL of methanol was placed in the titration vessel and conditioned. About 60-100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass was recorded. The ^{13}C -NMR spectrum was recorded on a JOEL 300 MHz NMR spectrometer (JEOL Ltd, Tokyo, Japan). 1.0 g of bio-oil was dissolved in 0.7 mL of dimethyl sulfoxide- d_6 in a 5 mm sample tube. The NMR solvent, DMSO- d_6 [99.9 atom % D, contain 1% (v/v) tetramethylsilane (TMS)] was obtained from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The observing frequency for the ^{13}C nucleus was 100.58 MHz. The pulse width was 10 μs , the acquisition time was 1.58 s, and the relaxation delay was 2 s. The spectra were obtained with 4000 scans and a sweep width of 20.0 KHz. All the analyses of the bio-oils were done in 3 replicates.

3.3. Results and Discussion

3.3.1. Hydrothermal treatment of FCC catalyst

Due to the importance of hydrothermal stability of the zeolite crystal in fluid catalytic cracking, the FCC catalyst is usually stabilized with rare earth oxides [31, 32] and the ZSM-5 additive is stabilized

with phosphorus [33]. In this study, the FCC catalyst contained 5 wt.% rare earth oxides and the ZSM-5 additive A tested was stabilized with 15 wt.% phosphorus. The ZSM-5 additive B had no phosphorus added. The micropore surface area measurements in Table 3.2 showed that the hydrothermal treatment resulted in loss of catalyst surface areas. During hydrothermal treatment, the catalyst was exposed to high temperatures and steam partial pressure which may have resulted in decomposition of the zeolite and collapse of the matrix.

Table 3.2. Effect of steam treatment on catalyst surface area

Catalyst Properties	Catalyst Pretreatment conditions		
	Fresh	Steamed at 732 °C for 4 h	Steamed at 788 °C for 4 h
<u>FCC</u>			
BET surface area, m ² /g	516	391	339
<u>ZSM5-Additive A</u>			
BET surface area, m ² /g	112	124	127
<u>ZSM5-Additive B</u>			
BET surface area, m ² /g	141	120	

The FCC catalyst degraded with increase in pretreatment severity. The FCC catalyst lost 24 % of the surface area when steamed at 732 °C for 4 hours and 34% when steamed at 788 °C for 4 hours. In the case of ZSM-5 additive A, there was “apparent” increase in the total surface area of the catalyst. However, there was a loss of about 15% of the total surface area of ZSM-5 additive B which contained no phosphorus. The observed increase in the surface area of the ZSM-5 additive A after steam treatment suggests that the impregnation of 15 wt.% of phosphorus led to some initial pore blockage which perhaps reduced N₂ adsorption. However, during steaming, the pores and some of the ZSM-5 channels

which had been initially blocked by the matrix become free as a result of the collapse of matrix micropores. This consequently increased the accessibility of nitrogen to the ZSM-5 pores and therefore, higher micropore surface area was measured. For the non-phosphorus additive B, there was no occurrence of channel blockage and the ZSM-5 was fully accessible. Thus, the hydrothermal treatment degraded the ZSM-5 additive B more than that of ZSM-5 additive A which was stabilized by phosphorus

3.3.2. Effect of hydrothermal treatment of FCC catalyst on the product yields

The effect of hydrothermal treatment of the various catalysts on the product distribution from the catalytic pyrolysis of biomass was examined. The various catalysts tested were tagged as follows in the remaining sections of this paper for simplicity; Fresh FCC (FCC1), FCC steamed at 732 °C (FCC2), FCC steamed at 788 °C (FCC3), fresh ZSM-5 additive A (PZSM5-1), ZSM-5 additive A steamed at 732 °C (PZSM5-2), ZSM-5 additive A steamed at 788 °C (PZSM5-3), fresh ZSM-5 additive B (ZSM5-1) and ZSM-5 additive B steamed at 732 °C (ZSM5-2). Since catalytic cracking is also influenced by process conditions such as contact time, temperature and turn over frequency, each catalyst used was tested at two different vapor residence times. The first set of experiments was conducted with a vapor residence time of 3 s and the second set of experiments was performed at a vapor residence time of 6.5 s. From the product yields shown in Table 3.3, it is evident that catalyst steaming severity and vapor residence time affected the catalytic product distribution. The effects were dependent on the type of catalyst.

For the FCC catalysts tests at vapor residence of 3 s, the organic liquid fraction (OLF) ranged from 20.6-25.0 wt. % and the char/coke yield was between 20.6-25.2 wt.% depending on the catalyst pretreatment severity. The OLF yield decreased in the order FCC3 > FCC1 > FCC2 and the char/coke yield decreased in the order FCC1 > FCC2 > FCC3. The FCC1 produced slightly higher water yield and FCC2 produced the highest gas yield. When the FCC catalysts were run at a vapor residence of 6.5 s, the OLF decreased while water, char/coke and gas yields increased. The decrease in the OLF and the increase in

the char/coke yield at a vapor residence time of 6.5 s were attributed to longer contact time which enhanced the catalytic cracking of the pyrolysis vapors into water, coke and gas. However, it appeared from the results that the influence of hydrothermal treatment of the FCC catalyst on the product distribution followed a similar trend for each vapor residence time with the exception of water yield at a vapor residence of 6.5 s where the FCC2 catalyst had the highest yield. In terms of the OLF, catalyst steaming at 788 °C had the most significant effect. The FCC3 catalyst produced respectively 21% and 42% more organics at vapor residence time of 3 s and 6.5 s compared to FCC1. The increase in the organic liquid yield was attributed to the decrease in the surface area of the micropore after steam treatment. As already mentioned, pretreatment of the FCC catalyst at 788 °C produced a catalyst with a BET surface area of 34% lower than the fresh catalyst.

The catalyst surface area is one of the important properties of the catalyst that is used to monitor the activity and stability of the catalyst. A loss in catalyst surface area mirrors a loss in catalytic activity. The results therefore suggest that an FCC catalyst with lower total surface area potentially produces higher OLF. The hydrothermal treatments of the FCC catalyst affected the catalyst selectivity and both FCC2 and FCC3 made less coke and more gas. It is also worth mentioning that the char/coke yield decreased by 18.28% and 20% respectively at vapor residence of 3 s and 6.5 s after steam treatment at 788 °C. Generally, the 3-dimensional large pore network and large cavity characteristic of the highly acidic FCC catalyst promotes coke forming reactions during the catalytic pyrolysis of biomass. The biomass pyrolysis vapors contain a considerable amount of aromatic species from the decomposition of lignin. These aromatics depending of the catalytic property of the FCC catalyst can either undergo side chain cracking to produce unsubstituted aromatics and olefins or go through transalkylation to different alkylaromatics. Additionally, the aromatics can undergo dehydrogenation/condensation reactions to form polyaromatics which can further dehydrogenate and

condense to form coke. These coke formation reactions on the FCC catalyst usually involve hydrogen transfer which is controlled by the acid site density [34]. Studies have shown that when the FCC catalyst undergo hydrothermal treatment, migration of aluminum atoms from the zeolite framework to the outer surfaces of the crystallites occur which consequently cause migration of silicon atoms into the vacancies to heal the structure [25-28, 35]. As a result, the number of Bronsted acid sites on the framework decreases and the framework Si/Al ratio increase. This probably explains why the steam treated FCC catalysts produced lower amount of char/coke yields compared with the fresh catalyst.

The product distributions from the ZSM-5 based additives were different from those produced from the FCC catalyst. Higher OLF, lower char/coke and lower water yields were achieved compared to the FCC catalyst. The ZSM-5 based additives contain ZSM-5 zeolite crystal which is a member of the pentasil family of high-silica zeolites with small pore size (5.5 Å) relative to the larger pore size Y-zeolite (7.4 Å) in the FCC catalyst. Studies have shown that ZSM-5 is capable of performing shape selective reactions in the conversion of methanol and biomass compounds into aromatics and olefins [20, 21, 36-43]. Additionally, due to its restricted narrow pore, ZSM-5 has limited coking tendencies. The organic liquid ranged between 24.1 – 35.4 wt.% for PZSM5 catalysts and between 23.9 – 37.1 wt.% for ZSM5 catalyst depending on catalyst steam treatment and vapor residence time. The char/coke yield did not show much variation and was between 16.65 – 18.66 wt.% . Steam treatment of the PZSM5 catalyst at 788 °C for four hours resulted in about 18% increase in OLF and 12% decrease in gas yield at both vapor residence times. Conversely, the effect of steam treatment on the non-phosphorous based ZSM5 at 732 °C had a negative effect on the OLF yields. It should be noted that the fresh form of the ZSM5 (141 m²/g) gave the highest OLF yield. After steam treatment, the surface area of the ZSM5 reduced and caused the organic liquid yield to decrease by 11.0% and the gas yield to increase by 22 % at a vapor residence of 3s.

Table 3.3. Production distribution of fractional Catalytic pyrolysis of hybrid poplar

Type of Catalyst	Product Distribution (wt.%)			
	Organics	Water	Char/Coke	Gas
Catalytic pyrolysis at a vapor residence of 3.0 s				
FCC-1	20.6±1.5	23.6±1.9	25.2±1.7	30.9±2.4
FCC-2	20.4±1.8	22.9±0.3	21.9±0.7	33.9±2.1
FCC-3	25.0±0.8	21.5±0.7	20.6±0.6	32.9±1.3
PZSM-5-1	29.8±0.8	19.1±1.0	17.0±0.4	34.0±2.1
PZSM-5-2	32.9±2.5	19.0±1.8	16.3±0.8	31.8±0.1
PZSM-5-3	35.4±2.2	18.1±1.5	16.7±1.0	29.8±2.4
ZSM-5-1	37.1±2.3	19.6±0.7	17.0±1.3	26.3±2.5
ZSM-5-2	33.2±1.7	19.0±0.3	16.0±0.3	32.1±1.7
Catalytic pyrolysis at a vapor residence of 6.5 s				
FCC-1	13.8±0.9	26.8±2.1	26.5±0.49	32.8±2.6
FCC-2	12.4±0.3	29.1±1.1	22.5±1.0	36.1±0.4
FCC-3	19.5±0.6	24.8±0.8	21.2±0.3	34.6±0.7
PZSM-5-1	24.1±0.8	22.1±1.0	18.2±0.4	35.5±1.1
PZSM-5-2	25.3±1.5	23.5±1.8	18.6±0.8	32.6±0.8
PZSM-5-3	28.4±1.1	22.2±1.0	18.0±1.1	31.5±1.4
ZSM-5-1	26.8±1.3	23.7±1.7	18.7±0.5	30.9±1.5
ZSM-5-2	23.9±1.0	22.5±1.2	18.3±0.8	35.2±1.1

From the product yields, it appeared that the influence of catalyst steaming on the PZSM5 additive differed from the ZSM5 additive. In the case of PZSM-5, the OLF yields increased with increase in steaming severity but the OLF yield for the ZSM5 decreased and the gas yield increased after

steaming. The difference in the effect of hydrothermal treatment of PZSM5 and ZSM5 was attributed to their catalytic properties. The PZSM5 was impregnated with 15 wt.% phosphorous and the ZSM5 on the other hand contained no phosphorous. The presence of phosphorus in FCC additive is known to stabilize the acidity and shape selectivity of the catalyst by preventing dealumination of the zeolite [33, 44] during hydrothermal treatment. This study showed that the P-stabilized ZSM5 (PZSM5) retained the total surface area of the micropore after steaming at 788 °C for four hours whilst the non-P-stabilized ZSM5 lost about 15% of its surface area

3.3.3. Gas Analysis

The compositions of the gases produced from the catalytic pyrolysis of hybrid poplar wood using various catalysts were determined using a Varian 490-GC micro gas chromatograph. The gas analysis was performed online at a sampling time interval of 3.5 min throughout the one hour run time. This means that for a 1 hour run, the gases were sampled at least 16 times. The nitrogen free compositional analysis by weight of the gaseous product reported in Table 3.4 is an average of the gas concentrations taken every 3.5 minutes from the catalytic pyrolysis at a vapor residence time of 6.5 s. The gases identified included H₂, CH₄, CO, CO₂, and C₂-C₅ hydrocarbon gases. The CO and CO₂ accounted for over 80% of the total gas yields in all the catalytic pyrolysis experiments. The predominant gas produced from the catalytic pyrolysis was CO. CO₂ was the second highest gas generated and CO/CO₂ ratio ranged between 1.17 - 1.60. For all the FCC catalyst tested, CH₄ was the third highest single component followed by C₄ hydrocarbon gases. H₂ formed the lowest fraction of the gases, it accounted for less than 1% and the highest concentration was produced by FCC3 catalyst. In comparing the two types of catalyst, the FCC catalyst produced higher amounts of H₂ and CH₄ and the ZSM-5 based additives produced higher fractions of C₂-C₅ hydrocarbons.

The hydrothermal treatment influenced the selectivity of FCC catalyst especially in the case of H_2 and the light hydrocarbon gases. The H_2 and the C_2 - C_5 hydrocarbons increased in the order $FCC1 < FCC2 < FCC3$ and CH_4 decreased in the order $FCC1 > FCC2 > FCC3$. The production of H_2 , CO , CO_2 , lower molecular weight hydrocarbons and coke in catalytic cracking of biomass derived molecules is believed to be formed through reactions such as cracking, dehydration, hydrogen-consuming, hydrogen producing and Diels-Alder/aldol condensation [9, 45]. These catalytic reactions are strongly influenced by the FCC catalyst acid site (type, strength, concentration and distribution) [34]. The Y-zeolite FCC catalyst is known to contain Bronsted and Lewis acid sites. The Bronsted acid sites are predominantly within the Y-zeolite pore structure and are due to the acidic hydroxyl groups attached to the framework [46, 47] whilst Lewis acidity is normally attributed to the non-framework aluminum species [47].

However, studies have shown that catalyst steaming causes destruction of the zeolite structure and removal of framework aluminum ions [27, 28, 34, 35]. As a result, new non-frameworks Al atoms are generated. The decrease in the framework aluminum atoms have been demonstrated to correspond to increases in Lewis acid concentration and framework SiO_2/Al_2O_3 ratio [27, 28, 35]. This could explain the reason why the formation of H_2 and C_4 hydrocarbons increased whilst the production of CH_4 decreased with increase in steaming severity. One of the obvious effects of steaming the FCC catalyst was the marked reduction in coke. It is proposed that coke formation involves the transferring of hydrogen from coke species to other dehydrated species. This also implies that hydrogen-consuming reactions such as hydrogen transfer decreased with hydrothermal treatment of the catalyst and favored the formation of C_4 hydrocarbons and H_2 while decreasing coke formation. It is worth noting that decarboxylation and decarbonylation reactions were also influenced. Table 3.4 shows that the CO/CO_2 ratio increased in the order of $FCC3 < FCC1 < FCC2$. This suggests that the effect of steaming on some of

the reactions are nonlinear since the steaming at 732 °C generated relatively higher CO and lower CO₂ gases compared to steaming at 788 °C which produced rather lower CO and higher CO₂ yields.

The gas composition of the ZSM-5 based additives showed that the selectivity of phosphorous impregnated additive (PZSM5) was not appreciably affected by the hydrothermal treatment since the gas compositions were about the same for all the PZSM5-1, PZSM5-2 and PZSM5-3 catalyst. However, it can be concluded that the treatment influenced the catalyst activity since increase in steam treatment severity decreased the overall gas yield. The non-phosphorus ZSM5 additive on the other hand was affected by the mild steam treatment at 732 °C. There was increase in the content of some of the hydrocarbon gases. The C₄ gases increased by 46.0%, C₅ gases increased by 41.8% and C₃ increased by 28%. The amount of CO₂ also decreased and H₂ gas slightly increased. It appeared also that the activity of the non-P ZSM-5 increased after steaming despite the loss of 15% of the total surface area. This inference was drawn from the increase in gas yields and decrease in OLF after hydrothermal treatment. A study conducted by Lago et al.[6] found that mild steaming of ZSM-5 zeolite leads to increased catalytic activity. Beyerlein et al.[9] suggested that the high activity observed from mild steaming of zeolites is a synergistic interaction between Bronsted and dispersed Lewis acid sites. As discussed above, hydrothermal treatment had some effect on the activity /selectivity of the catalyst. Nevertheless, there is no linear correlation to explain its exact influence as observed in the study.

Table 3.4. Nitrogen free compositional analysis by weight of the gaseous product from the catalytic pyrolysis of hybrid poplar at a vapor residence of 6.5 s

Gas Composition	Effect of steaming treatment of the catalyst							
	FCC1	FCC2	FCC3	PZSM5-1	PZSM5-2	PZSM5-3	ZSM5-1	ZSM5-2
H ₂	0.71	0.74	0.81	0.37	0.39	0.40	0.43	0.54
CH ₄	6.86	6.48	5.70	4.22	4.14	4.10	3.89	4.01
CO	45.10	46.07	43.81	51.26	51.64	51.39	46.59	46.79
CO ₂	38.46	36.64	38.83	31.82	32.24	32.53	37.30	35.49
C ₂	1.42	1.46	1.34	1.84	1.74	1.71	2.16	1.54
C ₃	2.03	2.10	1.91	2.64	2.51	2.46	3.10	2.22
C ₄	3.03	3.54	4.77	3.43	3.81	3.72	3.54	5.17
C ₅	2.38	2.97	2.83	4.42	3.49	3.69	2.99	4.24
C ₂ -C ₅	8.86	10.07	10.85	12.34	11.50	11.58	11.79	13.17
CO/CO ₂	1.17	1.26	1.13	1.61	1.60	1.58	1.25	1.32

3.3.4. Physical properties of bio-oils

Table 3.5 shows the moisture content, pH, density, viscosity, HHV and elemental composition of the bio-oils produced at a vapor residence of 6.5 s. All the steamed catalysts produced bio-oils with properties that differed from the fresh catalyst but there was no clear correlation between catalyst steaming and the characteristic of the bio-oils. Among the FCC catalyst tested, the bio-oils produced with FCC2 had the highest HHV (30.89 MJ/kg), pH (3.15) and the lowest density (1.12 g/cm³). The elemental analysis also showed that the FCC2 bio-oils had higher carbon (71.56%), higher hydrogen (6.83%) and lower oxygen (21.62 %) contents. Both steamed catalysts, FCC2 and FCC3 produced bio-oils

that had relatively lower viscosity, density and higher pH compared to those from FCC1. It appeared that, mild steam treatment at 732 °C altered the catalytic properties of the FCC catalyst such that it was able to perform much better than the fresh catalyst. The severe steam treatment at 788 °C did not have much effect on the catalytic property since the oils produced with FCC2 were similar to those produced with FCC1 catalyst.

The ZSM-5 additives were affected differently by the steam treatment, the fresh catalyst of each type of additive produced bio-oils with higher HHVs and lower densities and viscosities relative to the steamed equivalents. The organic elemental analysis also showed that steamed catalyst produced bio-oils with lower carbon and hydrogen contents relative to the unsteamed catalyst. However, it is worth noting that the bio-oils produced with PZSM5-2 and PZSM5-3 had similar physical properties. This implied that severe treatment of PZSM5 additive at 788 °C did not have any effect because of the strong stability impacted by the phosphorous.

Table 3.5. Physical Properties of the bio-oil fractions produced at a vapor residence of 6.5 s

Property	Bio-oils (ESP)							
	FCC1	FCC2	FCC3	PZSM5-1	PZSM5-2	PZSM5-3	ZSM5-1	ZSM5-2
Moisture (wt%)	3.23	4.01	3.86	4.10	3.90	4.05	4.01	3.78
pH	2.76	3.15	3.04	3.07	3.11	3.06	3.05	2.95
Density (g/cm ³)	1.17	1.12	1.15	1.15	1.15	1.15	1.15	1.16
HHV (MJ/kg)	28.49	30.89	28.45	28.31	27.96	27.72	28.48	27.0
Kinematic viscosity, at 40°C(cSt)	82.2	54.6	53.7	52.2	48.9	50.5	63.2	80.6
Elemental composition, wt% (moisture free)								
C	67.78	71.56	67.45	66.10	64.36	64.02	66.93	64.94
H	6.54	6.83	6.34	6.49	6.26	6.18	6.48	6.28
N	0.18	0.19	0.18	0.15	0.19	0.17	0.15	0.16
O	25.50	21.62	26.03	27.26	29.2	29.2	26.44	28.62

3.3.5. ¹³C-NMR spectrometry of bio-oils

The relative compositions of the various functional groups in the bio-oils produced with the various catalysts at a vapor residence of 6.5 s were determined using ¹³C-NMR spectrometry. The ¹³C-NMR technique was used because it offers the advantage of analyzing the whole bio-oil for oxygenated functionalities which are of great interest in catalytic cracking of pyrolysis vapors. Semi quantitative analysis was performed by integrating the chemical shifts of the various functional groups. The ¹³C-NMR spectra in Figures 3.1, 3.2 and 3.4 represent the bio-oil fraction from FCC, PZSM5 and ZSM5 catalysts. The chemical shift region between 180-220 ppm was attributed to aldehydes and ketones. The signals between 160 and 180 ppm were assigned to carboxylic acids and their derivatives. The signals in the chemical shift of 140-160 ppm and 105-125 ppm were assigned to aromatic carbons in phenol, and methoxylated phenols related to guaiacyl and syringyl lignin. Carbons in alcohols and carbohydrate decomposition products were assigned to the region between 105 and 50 ppm with the exception of the intense signal at 56.2 ppm which was assigned to methoxyl carbon in guaiacyl and syringyl motifs. The group of signals at 65.3, 72, 73.9, 74.1, 76.9 and 102.6 ppm were assigned to levoglucosan from the decomposition of cellulose. Lastly, alkyl hydrocarbon side chains were assigned to chemical shift from 50 to 1 ppm. The NMR solvent signal, DMSO-*d*₆ was at 39 ppm.

From the ¹³C- NMR analysis, it was evident that hydrothermal treatment of the catalyst influenced the chemical composition of the bio-oils. From the relative analysis of the chemical groups, it was found that the FCC catalyst that was hydrothermally treated at 788 °C (FCC3) produced bio-oils that contained more oxygenated compounds. The bio-oil from FCC3 catalyst had relatively higher amount of alcohols, sugars (levoglucosan), methoxylated phenols, phenols, carboxylic groups, aldehydes and ketones. The relatively high concentrations of oxygen-containing compounds suggest that the FCC3 catalyst was not effective at deoxygenating the pyrolysis vapors through reactions such as

decarboxylation, decarbonylation and demethoxylation. The ineffectiveness of the FCC3 catalyst compared to the other two FCC catalysts in cracking the oxygenated compounds was attributed to reduction in catalyst activity because of the severe steam treatment at 788 °C. This also explains why the OLF yield from the FCC3 was the highest. Conversely, the FCC catalyst that was mildly steam treated at 732 °C (FCC2) produced bio-oil fraction that was rich in aromatic hydrocarbons and poor in oxygenated compounds. From the spectra in Figure 3.1, it can be seen that the spectrum of the oil fraction from FCC2 showed extensive cracking of the carbohydrate degradation products, carboxylic groups and methoxylated phenols. The FCC2 catalyst in comparison to FCC3 was capable of performing cracking, demethoxylation, decarboxylation and decarbonylation reactions. It implies that, the FCC2 catalyst still had sufficient catalyst activity after steaming at 732 °C.

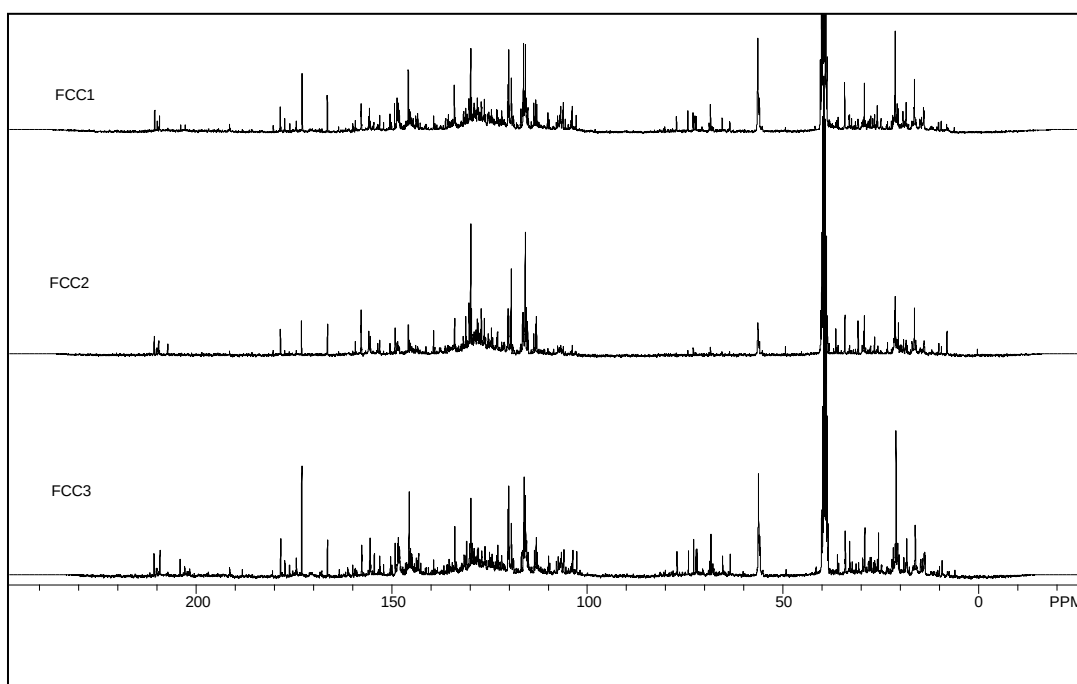


Figure 3.1 ^{13}C -NMR spectra of bio-oil produced with FCC catalyst at vapor residence of 6.5 s

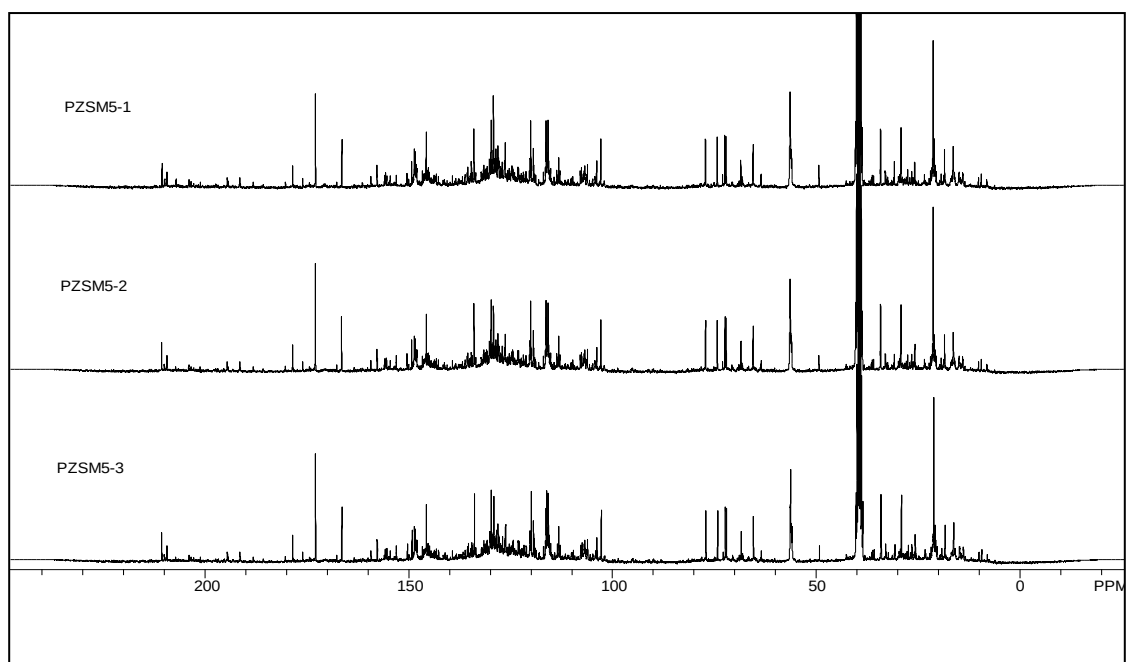


Figure 3.2. ^{13}C -NMR spectra of bio-oil produced with PZSM-5 additive at vapor residence of 6.5 s

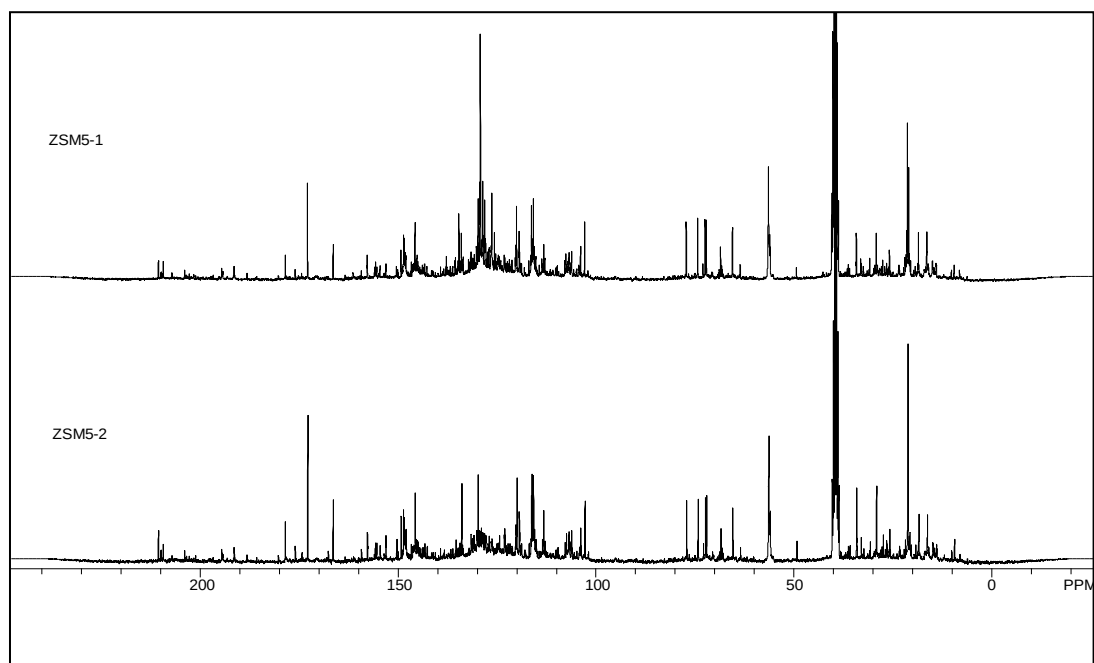


Figure 3.3. ^{13}C -NMR spectra of bio-oil produced with ZSM-5 additive at vapor residence of 6.5 s

A comparison between the bio-oil fraction from FCC1 and FCC2 suggest that the activity of the FCC2 catalyst was enhanced if we assume that higher catalyst activity produces bio-oil with lower oxygenated compounds. However, the suggestion of FCC2 having higher catalyst activity than FCC1 would be false if the activity is based on the total micropore surface area given that the FCC2 catalyst had a surface area lower than FCC1. Nonetheless, some literatures on the cracking of petroleum crude using FCC catalyst reported higher catalyst activity after steam treatment due to the generation of non-framework aluminum species (Lewis acid sites) as a result of zeolite dealumination [48-51]. It has also been shown that the catalytic effect of non-framework aluminum species is dependent on the amount of non-framework species per unit cell [27, 52]. Thus, the notable effect of FCC2 catalyst suggests that mild steaming of the FCC catalyst at 732°C enhanced catalytic activity whilst treatment at 788 °C reduced the catalytic activity.

In contrast to the FCC catalyst, the ZSM-5 additives produced bio-oil fractions containing more oxygenated species as seen by the marked intensities of the carbohydrate decomposition products. The ¹³C-NMR analysis of the bio-oil fractions showed that steam treatment affected the phosphorous impregnated ZSM-5 (PZSM5) to some extent and the non-phosphorous ZSM5 to a greater extent (See Figures 3.2 and 3.3). In both cases, the steaming affected the selectivity of the catalyst in producing aromatic hydrocarbons as their relative amounts decreased after steaming. It is worth noting that the severity of steam treatment did not affect the chemical composition of the phosphorus impregnated ZSM5 additive. Both PZSM5-2 and PZSM5-3 showed a similar spectrum of their respective bio-oil fractions and had about the same relative amount of carbon distribution. The possible reason for the minor effect of steam treatment on PZSM-5 catalyst could be that the framework of the ZSM-5 zeolite was preserved by the phosphorus and any occurrence of framework dealumination after steaming would be less relative to the non-phosphorus based additive.

From Figure 3.3, it can be seen that the steam treatment of the non-phosphorus based ZSM-5 additive considerably affected the production of aromatic hydrocarbons as shown by 125 and 140 ppm intensities. In fact, it is also important to recall that the organic liquid yield decreased and more gas was produced after the ZSM-5 with phosphorus was steam treated at 732 °C.

3.4. Conclusion

From this study, it can be concluded that irreversible deactivation of the FCC catalyst and ZSM-5 additives due to steaming influenced both the product distribution and the quality of the bio-oil produced from the fractional catalytic pyrolysis of wood. Severe steaming at 788 °C increased the organic fractions and decreased the coke yields for FCC catalyst and the phosphorus impregnated ZSM-5. Steam treatment of the non-phosphorus ZSM-5 reduced the organic liquid fraction and favored the formation of gas. Mild steam treatment at 732 °C for 4 hours improved the catalytic property of the FCC catalyst and consequently produced bio-oils with improved quality and had lesser oxygenated compounds. The steamed forms of the ZSM-5 additives produced bio-oils that contained higher amount of oxygenated compounds than the fresh catalyst. The effect of steaming on the catalyst was different for the Y-zeolite FCC catalyst and the ZSM-5 based additives. The presence of phosphorus in the PZSM-5 additive stabilized the catalyst and prevented any substantial detrimental effect on the product distribution and bio-oil quality.

3.5 REFERENCES

1. Agblevor, F.A., S. Beis, O. Mante, and N. Abdoulmoumine, *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood*. Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.
2. Agblevor, F.A., O. Mante, N. Abdoulmoumine, and R. McClung, *Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis*. Energy & Fuels, 2010. **24**(7): p. 4087-4089.
3. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
4. Lappas, A.A., S. Bezergianni, and I.A. Vasalos, *Production of biofuels via co-processing in conventional refining processes*. Catalysis Today, 2009. **145**(1-2): p. 55-62.
5. Lappas, A.A., M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, and I.A. Vasalos, *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
6. Williams, P.T. and N. Nugranad, *Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks*. Energy, 2000. **25**(6): p. 493-513.
7. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading*. Biomass and Bioenergy. **In Press, Corrected Proof**.
8. Carlson, T.R., Y.-T. Cheng, J. Jae, and G.W. Huber, *Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust*. Energy & Environmental Science, 2011. **4**(1): p. 145-161.
9. Corma, A., G.W. Huber, L. Sauvanaud, and P. O'Connor, *Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst*. Journal of Catalysis, 2007. **247**(2): p. 307-327.
10. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
11. Mante, O., F. Agblevor, and R. McClung, *Fluid catalytic cracking of biomass pyrolysis vapors*. Biomass Conversion and Biorefinery, 2011. **1**(4): p. 189-201.
12. Zhang, H., R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.

13. Adam, J., E. Antonakou, A. Lappas, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, and G. Øye, *In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials*. Microporous and Mesoporous Materials, 2006. **96**(1-3): p. 93-101.
14. Graça, I., F.R. Ribeiro, H.S. Cerqueira, Y.L. Lam, and M.B.B. de Almeida, *Catalytic cracking of mixtures of model bio-oil compounds and gasoil*. Applied Catalysis B: Environmental, 2009. **90**(3-4): p. 556-563.
15. Lee, K.-H., S.-G. Jeon, K.-H. Kim, N.-S. Noh, D.-H. Shin, J. Park, Y. Seo, J.-J. Yee, and G.-T. Kim, *Thermal and catalytic degradation of waste high-density polyethylene (HDPE) using spent FCC catalyst*. Korean Journal of Chemical Engineering, 2003. **20**(4): p. 693-697.
16. Lee, K.-H. and D.-H. Shin, *A comparative study of liquid product on non-catalytic and catalytic degradation of waste plastics using spent FCC catalyst*. Korean Journal of Chemical Engineering, 2006. **23**(2): p. 209-215.
17. Li, H., B. Shen, J.C. Kabalu, and M. Nchare, *Enhancing the production of biofuels from cottonseed oil by fixed-fluidized bed catalytic cracking*. Renewable Energy, 2009. **34**(4): p. 1033-1039.
18. Samolada, M.C., W. Baldauf, and I.A. Vasalos, *Production of a bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking*. Fuel, 1998. **77**(14): p. 1667-1675.
19. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(1): p. 39-61.
20. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways*. Fuel Processing Technology, 1995. **45**(3): p. 185-202.
21. Carlson, T., G. Tompsett, W. Conner, and G. Huber, *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
22. Aho, A., N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D.Y. Murzin, *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.
23. Peters, A.W., *Instrumental Methods of FCC Catalyst Characterization*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 183-221.
24. Cerqueira, H.S., G. Caeiro, L. Costa, and F. Ramôa Ribeiro, *Deactivation of FCC catalysts*. Journal of Molecular Catalysis A: Chemical, 2008. **292**(1-2): p. 1-13.

25. Rawlence, D.J. and K. Gosling, *FCC catalyst performance evaluation*. Applied Catalysis, 1988. **43**(2): p. 213-237.
26. Rawlence, D.J. and K. Gosling, *Irreversible deactivation of fcc catalysts*. Catalysis Today, 1991. **11**(1): p. 47-59.
27. Beyerlein, R.A., C. Choi-Feng, J.B. Hall, B.J. Huggins, and G.J. Ray, *Effect of steaming on the defect structure and acid catalysis of protonated zeolites*. Topics in Catalysis, 1997. **4**(1): p. 27-42.
28. Tonetto, G.M., M.L. Ferreira, J.A. Atias, and H.I. de Lasa, *Effect of steaming treatment in the structure and reactivity of FCC catalysts*. AIChE Journal, 2006. **52**(2): p. 754-768.
29. Moorehead, E.L., J.B. McLean, and W.A. Cronkright, *Microactivity Evaluation of FCC Catalysts in the Laboratory: Principles, Approaches and Applications*, in *Studies in Surface Science and Catalysis*1993, Elsevier. p. 223-255.
30. Young, G.W., *Realistic Assessment of FCC Catalyst Performance in the Laboratory*, in *Studies in Surface Science and Catalysis*1993, Elsevier. p. 257-292.
31. de la Puente, G. and U. Sedran, *Conversion of methylcyclopentane on rare earth exchanged Y zeolite FCC catalysts*. Applied Catalysis A: General, 1996. **144**(1-2): p. 147-158.
32. de la Puente, G. and U. Sedran, *Evaluation of hydrogen transfer in FCC catalysts. A new approach for cyclohexene as a test reactant*. Chemical Engineering Science, 2000. **55**(4): p. 759-765.
33. Degnan, T.F., G.K. Chitnis, and P.H. Schipper, *History of ZSM-5 fluid catalytic cracking additive development at Mobil*. Microporous and Mesoporous Materials, 2000. **35-36**: p. 245-252.
34. Scherzer, J., *Correlation Between Catalyst Formulation and Catalytic Properties*, in *Studies in Surface Science and Catalysis*1993, Elsevier. p. 145-182.
35. Biaglow, A.I., D.J. Parrillo, G.T. Kokotailo, and R.J. Gorte, *A Study of Dealuminated Faujasites*. Journal of Catalysis, 1994. **148**(1): p. 213-223.
36. Chang, C.D. and A.J. Silvestri, *The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts*. Journal of Catalysis, 1977. **47**(2): p. 249-259.
37. Weisz, P.B., W.O. Haag, and P.G. Rodewald, *Catalytic Production of High-Grade Fuel (Gasoline) from Biomass Compounds by Shape-Selective Catalysis*. Science, 1979. **206**(4414): p. 57-58.
38. Weisz, P.B. and J.F. Marshall, *High-Grade Fuels from Biomass Farming: Potentials and Constraints*. Science, 1979. **206**(4414): p. 24-29.

39. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts*. Fuel Processing Technology, 1995. **45**(3): p. 161-183.
40. Gayubo, A.G., B. Valle, A.s.T. Aguayo, M. Olazar, and J. Bilbao, *Olefin Production by Catalytic Transformation of Crude Bio-Oil in a Two-Step Process*. Industrial & Engineering Chemistry Research, 2009. **49**(1): p. 123-131.
41. Pütün, E., B.B. Uzun, and A.E. Pütün, *Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor*. Energy & Fuels, 2009. **23**(4): p. 2248-2258.
42. Vitolo, S., M. Seggiani, P. Frediani, G. Ambrosini, and L. Politi, *Catalytic upgrading of pyrolytic oils to fuel over different zeolites*. Fuel, 1999. **78**(10): p. 1147-1159.
43. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. Biomass and Bioenergy, 1994. **7**(1-6): p. 223-236.
44. Blasco, T., A. Corma, and J. Martínez-Triguero, *Hydrothermal stabilization of ZSM-5 catalytic-cracking additives by phosphorus addition*. Journal of Catalysis, 2006. **237**(2): p. 267-277.
45. Huber, George W. and A. Corma, *Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass*. Angewandte Chemie International Edition, 2007. **46**(38): p. 7184-7201.
46. Jacobs, P.A., H.E. Leeman, and J.B. Uytterhoeven, *Active sites in zeolites : I. Cumene cracking activity of NH₄Y zeolites after different reactor pretreatments*. Journal of Catalysis, 1974. **33**(1): p. 17-30.
47. Scherzer, J. and J.L. Bass, *Infrared spectra of ultrastable zeolites derived from type Y zeolites*. Journal of Catalysis, 1973. **28**(1): p. 101-115.
48. Katada, N., Y. Kageyama, K. Takahara, T. Kanai, H. Ara Begum, and M. Niwa, *Acidic property of modified ultra stable Y zeolite: increase in catalytic activity for alkane cracking by treatment with ethylenediaminetetraacetic acid salt*. Journal of Molecular Catalysis A: Chemical, 2004. **211**(1-2): p. 119-130.
49. Narbeshuber, T.F., A. Brait, K. Seshan, and J.A. Lercher, *The influence of extraframework aluminum on H-FAU catalyzed cracking of light alkanes*. Applied Catalysis A: General, 1996. **146**(1): p. 119-129.

50. Wang, Q.L., G. Giannetto, and M. Guisnet, *Dealumination of zeolites III. Effect of extra-framework aluminum species on the activity, selectivity, and stability of Y zeolites in n-heptane cracking*. Journal of Catalysis, 1991. **130**(2): p. 471-482.
51. Williams, B.A., S.M. Babitz, J.T. Miller, R.Q. Snurr, and H.H. Kung, *The roles of acid strength and pore diffusion in the enhanced cracking activity of steamed Y zeolites*. Applied Catalysis A: General, 1999. **177**(2): p. 161-175.
52. Humphries, A., D.H. Harris, and P. O'Connor, *The Nature of Active Sites in Zeolites: Influence on Catalyst Performance*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 41-82.

CHAPTER 4

Fractional catalytic pyrolysis of biomass: The use of ZSM-5 based additive as co-catalyst to FCC catalyst

4.0 Abstract

The catalytic pyrolysis of biomass with Y-zeolite based FCC catalyst produce considerable amounts of coke and significantly less bio-oil than ZSM-5 based catalyst. Studies have shown that the product slate from catalytic pyrolysis of biomass can be considerably changed by varying the characteristics or functionality of the catalyst. In this study, fractional catalytic pyrolysis of hybrid poplar wood was performed with FCC catalyst and blends containing 25, 50, 75 wt.% of ZSM-5 additives at 475 °C and a weight hourly space velocity of 2 h⁻¹. The influence of reactor configuration was also investigated using a 1-stage and a 2-stage bench scale bubbling fluidized bed reactor. The hybrid catalysts containing ZSM-5 additive were more selective compared to the pure FCC catalyst. It was shown that ZSM-5 additive increased the organic liquid fraction and decreased the coke/char yields. The increase in ZSM-5 additive also decreased the formation of CO₂, CH₄, and H₂ gases and increased the generation of C₅ hydrocarbons. The FCC/ZSM-5 hybrid catalysts produced bio-oils with relatively lower viscosity and higher pH values. ¹³C-NMR spectrometry analysis of the whole bio-oil showed that, the addition of ZSM-5 to the FCC catalyst enhanced the formation of aromatic hydrocarbons. Reactor configuration was found to influence the process in terms of product distribution and the physico-chemical properties of the bio-oils. The use of ZSM-5 additive as co-catalyst was effective in improving the overall fractional catalytic pyrolysis with FCC catalyst.

4.1. Introduction.

Over the past three decades, a wide range of catalysts (ZSM-5, faujasities, mordenite and aluminosilicates) and different process configurations are being pursued for the conversion of biomass into hydrocarbon rich bio-oils and chemicals [1-30]. It is considered by many research laboratories and organizations that adaptation of the fluid catalytic cracking (FCC) process for the conversion of biomass intermediates will facilitate the introduction of marketable biofuels [30-34]. The FCC technology is the heart of petroleum refinery and is widely used to convert heavy fractions of crude oil into gasoline, diesel and liquefied petroleum gas (LPG) [35, 36]. The Y-zeolite is used as the primary cracking component [35, 37-39] of the FCC catalyst and is characteristically known to be highly acidic and hydrothermally stable [37, 40-42].

Currently, there is emergent interest in extending the application of FCC catalyst to the conversion of biomass feedstocks into bio-oils and chemicals. Studies have shown that the FCC catalyst is effective at rejecting oxygen from biomass derived molecules [10, 11, 18, 28, 33, 43-49]. However, the removal of oxygen is not optimal because it favors dehydration reactions and consequently results in poor liquid yields due to its strong acidity [1, 3, 5, 11, 24, 43]. The FCC catalyst also forms high amount of coke and gas in cracking biomass molecules due to the large pore size of the Y-zeolite [1, 3, 5, 18, 25, 30, 44]. Nevertheless, it is envisioned that the catalytic pyrolysis of biomass with FCC catalyst can be enhanced by the use of additives that have a lesser tendency to form coke but active enough to crack the oxygenated molecules from biomass. The use of additives in conjunction with FCC catalyst is a standard practice in the petroleum refinery industry. With the use of additives, the FCC process has responded to changing feedstock (Resid cracking), product requirement (High octane number) and environmental regulations (NO_x and SO_x control). The most widely used additive in FCC process is

Mobil's patented ZSM-5. The ZSM-5 based FCC additive is a 10-membered sieve containing channel openings of 5.1 to 5.6 Å in a non-active matrix of silica/alumina.

The ZSM-5 additive is mainly used in the fluid catalytic cracking of atmospheric gas oil (AGO) and vacuum gas oil (VGO) to increase olefins production for alkylation and boost gasoline research and motor octane number [50-56]. The ZSM-5 based additive can either be incorporated into the FCC catalyst, or added as a separate additive [53]. The latter offers the advantage of higher flexibility since the ratio of the additive to the FCC catalyst can be changed with ease. In a typical FCC unit, the amount of ZSM-5 ranges from 0.8 to 12 wt.% of the total catalyst inventory [57]. The concept of adding additives to FCC catalyst has been recently adapted in the production of biofuels [45, 50]. Studies by Chew and Bhatia[50] showed that the addition of HZSM-5 to Rare earth-Y (REY) catalyst increased the conversion and organic liquid product in the cracking of palm oil. Graca et al.[45] also used an FCC equilibrium catalyst (E-CAT) and a mixture of ECAT/ZSM-5 additive to study the catalytic cracking of model bio oil compounds with standard gasoil under FCC conditions. Their results however, showed that ZSM-5 was less effective in the presence of acetic acid, hydroxyacetone and phenol.

In this study, the effect of ZSM-5 based additive as a co-catalyst to FCC catalyst in the fractional catalytic pyrolysis of hybrid poplar on the product distribution was investigated. Two different types of reactors were used to examine the influence of reactor configuration on the catalytic process. The first set of experiments involved the use of a 1-stage fluid bed reactor and the second set of experiments were carried out in a 2-stage fluid bed reactor.

4. 2. Materials and methods

4.2.1. Biomass Feedstock

The biomass used in the study was hybrid poplar wood. The samples were air dried and ground to pass a 1-mm screen in a Wiley mill prior to all experiments. The moisture content was determined using an HG53 Halogen Moisture analyzer (Mettler Toledo, Greifensee, Switzerland). The elemental composition and calorific value of the hybrid poplar wood are shown in Table 2. 1.

4.2.2. FCC Catalyst and ZSM-5 additive

The catalyst used for the tests were commercially available fluid cracking catalysts (FCC) and ZSM-5 based additives. The catalysts were supplied and characterized by BASF Catalysts LLC (Iselin, NJ, USA). The catalysts were mildly steamed at 732.2 °C with 100% steam for 4 h in a fluidized bed reactor to stimulate a commercial deactivation process so that its performance was representative of an equilibrium catalyst. Both fresh and steamed forms of the catalyst were tested. The multipoint BET method was used to determine the total surface areas of the various catalysts. The measurements were based on the isothermal adsorption of nitrogen according to the procedure described in ASTM D3663 using a Micrometrics TriStar instrument. The data from the multipoint determination was used to calculate the matrix surface area using the t-plot method. The difference between the BET surface area and the matrix surface was considered to be the zeolite surface area. The characteristics of the FCC catalyst and the ZSM-5 based additive are shown in Table 4.1. The ZSM-5 additive was blended with the FCC catalyst at 25 wt%, 50 wt% and 75 wt% level. The FCC catalyst had higher BET surface area than the ZSM-5 additive. The steamed FCC catalyst contained about 40% of Y-zeolite and the ZSM-5 additive had about 13% ZSM-5 zeolite. Hence the addition of ZSM-5 to FCC catalyst will decreases the BET surface area and consequently lowers the aggregate activity of the blend catalyst.

Table 4.1. FCC Catalyst description

Type of catalyst	TSA ₂ (m ² /g)	MSA ₂ (m ² /g)	ZSA ₂ (m ² /g)	APS (μm)
Fresh FCC	516	112	404	108
Steamed FCC	391	104	287	102
Fresh ZSM-5 additive	141	45	96	91
Steamed ZSM-5 additive	120	27	93	86

4.2.3. Fractional catalytic pyrolysis

The fractional catalytic pyrolysis of hybrid poplar was carried out using a bench scale pyrolysis unit (see Figure 2.1 in chapter 2). The unit consisted of a K-Tron volumetric feeder (K-Tron Process Group, Pitman, NJ), a fluidized bed reactor, hot gas filter, two chilled ethylene glycol condensers, an electrostatic precipitator and a coalescing filter. The -1-stage fluid bed reactor (Figure 4.1a) is a 50 cm tall 316 stainless steel pipe, 5 cm (D_1) in diameter and a reactor height (L_1) of 30 cm. The 2-stage fluid bed (Figure 4.1b) reactor was constructed also from 316 stainless steel pipe consisting of a small diameter section of 2 cm (D_1) and large diameter section of 6.5 cm (D_2). The reactor height of the small section is 5.5-in (L_1) and that of the large section is 14 cm (L_2). The reactors were equipped with 100 μm distribution plate. Each reactor was externally heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC) and the temperatures were measured and controlled by three K-thermocouples inserted into a thermal well in the reactors. 250 g of biomass was charged into the feed hopper and was continuously fed for an hour into a hot bed of FCC catalyst and blends containing 25, 50, 75 wt.% ZSM-5 additives at 475-500 °C. The weight hourly space velocity (WHSV) for each experiment was 2.0 h⁻¹. The catalytic media was fluidized with 6.5 L/min of nitrogen gas to ensure intimate and uniform contact between the feed and the catalyst throughout the reactor as well as to minimize the losses of fine catalyst into the hot gas filter. The apparent average total vapor residence time was approximately 6 s

for the single stage and 6.5 s for the two-stage reactor. The apparent average total vapor residence time was defined as the total volume of fluidized catalyst divided by gas flow rate at reactor conditions.

The mixture of char, entrained catalyst, gases and vapors that exited the reactor was separated by a hot gas filter maintained at 380 °C. The separated gases and vapors were then passed through two condensers connected in series. The condensers were maintained at average temperature of -8 °C with a 50/50 cooling mixture of ethylene glycol and water from an 18-L refrigerated circulating bath (Haake, Karlsruhe, Germany). Any condensable gases and aerosols that escaped from the condenser were captured by an electrostatic precipitator (ESP) kept at 16–20 kV. The temperatures across the reactor, hot gas filter and the condensers were controlled and monitored using the OMB-Multiscan 1200 acquisition system (Omega Engineering, Inc.) with TempView 2.1 program. The nitrogen gas flow rate was controlled by a mass flow controller and the total non-condensable gas that exited the coalescing filter was measured with a totalizer. The evolved gases were analyzed every 3.25 minutes online using a Varian 490 micro GC (Agilent Technologies, Inc. Santa Clara, CA USA). The micro GC was equipped with two modules, a 10 m Molsieve (MS) 5Å column and a 10 m porous polymer (PPU) column. Each module had a thermal conductivity detector. The MS column was used to analyze hydrogen, methane and carbon monoxide. Carbon dioxide and C₁-C₅ gases were analyzed by the PPU column. The mass of char/coke was determined gravimetrically by weighing the hot gas filter and the reactor before and after each pyrolysis experiment. The total mass of bio-oil was also determined gravimetrically by weighing the condensers and electrostatic precipitator before and after each experiment. The total mass of the non-condensable gas was calculated from the average gas composition and the total volume of the non-condensable gases. Each experiment was replicated 3 times and the average yields were expressed in percentage on a moisture free basis.

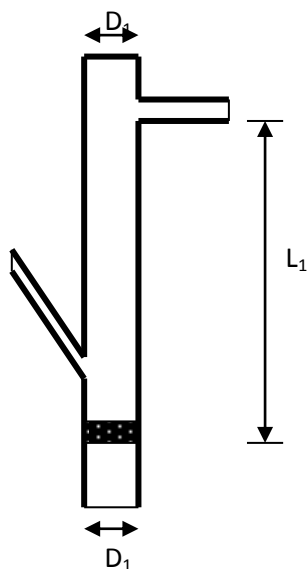


Figure 4.1a. 1-Stage fluid bed reactor

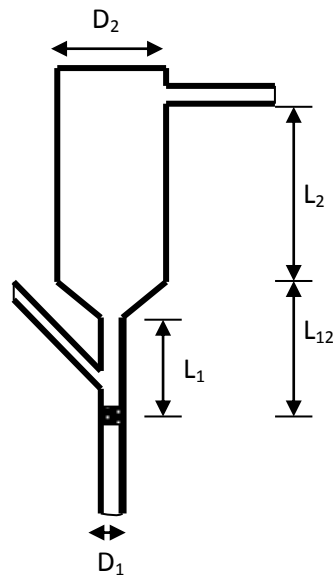


Figure 4.1b. 2-Stage fluid bed reactor

4.2.4. Bio-oil Analysis

A Thermo Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Cambridge, UK) was used to determine the C, H, N, O, and S of the bio-oil fraction. The higher heating values (HHV) were determined using IKA C2000 basic bomb calorimeter (IKA® Works, Inc, NC, and U.S.A.) according to ASTM D2015. The pH was measured using a Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The pH data were obtained after 15 min stabilization of the mechanically stirred oil. The viscosity and density of the bio-oils were measured at 40 °C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were equivalent to viscosities determined by the ASTM D445 method. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent and 50 ml of methanol were used. About 60-100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass was recorded.

The ^{13}C NMR spectra were recorded on a JOEL 300 MHz NMR spectrometer (JEOL Ltd, Tokyo, Japan). 1.0 g of oil was dissolved in 0.7 mL of dimethyl sulfoxide- d_6 in a 5 mm sample tube. The NMR solvent, DMSO- d_6 [99.9 atom % D, contain 1% (v/v) tetramethylsilane (TMS)] was obtained from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The observing frequency for the ^{13}C nucleus was 100.58 MHz. The spectra were obtained with 4000 scans and a sweep width of 20.0 KHz. All the analyses of the bio-oils were done in 3 replicates.

4.3. Results and Discussion

4.3.1. Reactor configuration

The influence of reactor configuration on the fractional catalytic pyrolysis process was investigated using 1-stage and 2-stage fluid bed reactors. The 1-stage had the same fluidizing bed diameter across the length of reactor but the 2-stage reactor was designed with varying fluidizing bed diameters. The 2-stage reactor configuration would allow pyrolysis to occur at a shorter contact-time in the first stage of the reactor since the gas velocity in the small diameter section will be relatively higher. The large section of the 2-stage reactor would experience lower gas velocity and catalytic cracking would predominately be expected to occur in that section at a longer time.

The plots shown in Figures 2a and 2b respectfully represents a typical temperature and gas flow profile for the 1-stage and the 2-stage reactor. The temperature profile depicts the different types of reactions that were occurring over the period of the experiment. Each reactor was equipped with three thermocouples for measuring temperatures at the bottom, middle and top of the reactor. For the 2-stage reactor, the bottom thermocouple (T_1) measured the temperature in the small section and both middle (T_2) and top thermocouples (T_3) measured the temperature across the large section of the

reactor. The temperature program for T_1 and T_2 of the reactor were set to 500 °C and T_3 at 475 °C to prevent further cracking of the vapors.

From the profiles, it can be seen that the temperature behavior in the 1-stage reactor was different from that of the 2-stage reactor. For a well-mixed bed, it is expected that at least two of the three thermocouples will indicate about the same temperature. The fluidizing gas flow rate of 6.5 L/min corresponded to about $12U_{mf}$ in the 1-stage reactor. The 2-stage reactor had gas velocities of $87.5U_{mf}$ and $7.9U_{mf}$ in the small and large sections respectively. For the 1-stage reactor, a uniform sinusoidal pattern for the T_1 and T_2 thermocouples that measured the bottom and middle part of the reactor was observed. However, the 2-stage reactor showed separate temperature profiles for the thermocouples in the small and large sections. The T_1 thermocouple showed a lower temperature profile when compared to T_2 which showed a relatively higher temperature profile. This suggests that, the small and large sections were operating at different reaction regimes. It appeared that endothermic reactions primarily occurred in the first stage of the reactor and exothermic reactions took place in the second stage. This may also imply that the initiation reaction which is pyrolytic/thermal was decoupled from the catalytic (heterogeneous) reaction to some extent in the 2-stage reactor. It is worth noting that these different reaction regimes shown by the temperature profiles observed in the 2-stage reactor were not evident in the single reactor. Nevertheless, the temperature profile for T_1 of the 1-stage reactor and T_1 of the 2-stage reactor were of similar sinusoidal patterns.

The reactor configuration also played a role in the loss of catalyst into the hot gas filter during the experiment. Table 4.2 shows the change in reactor content after the experimental runs. The values that exceed 100 % implies that there was an increase in the reactor content due to accumulation of larger char particles and values less than 100 % suggest the loss of catalyst. It is clear from Table 3 that the 2-stage reactor experienced up to 30 % loss of catalyst.

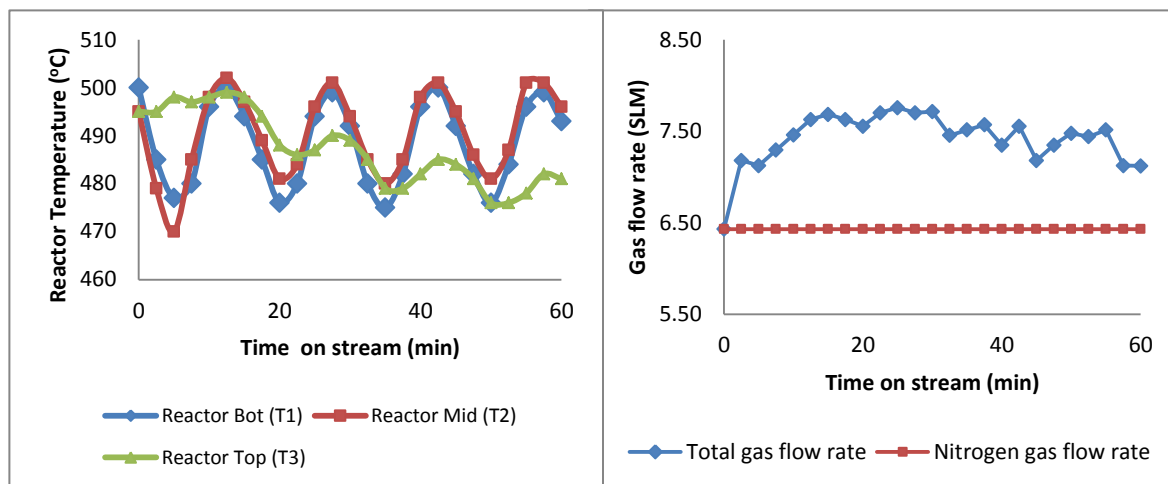


Figure 4.2a. Typical temperature and gas flow profiles for the 1-stage reactor

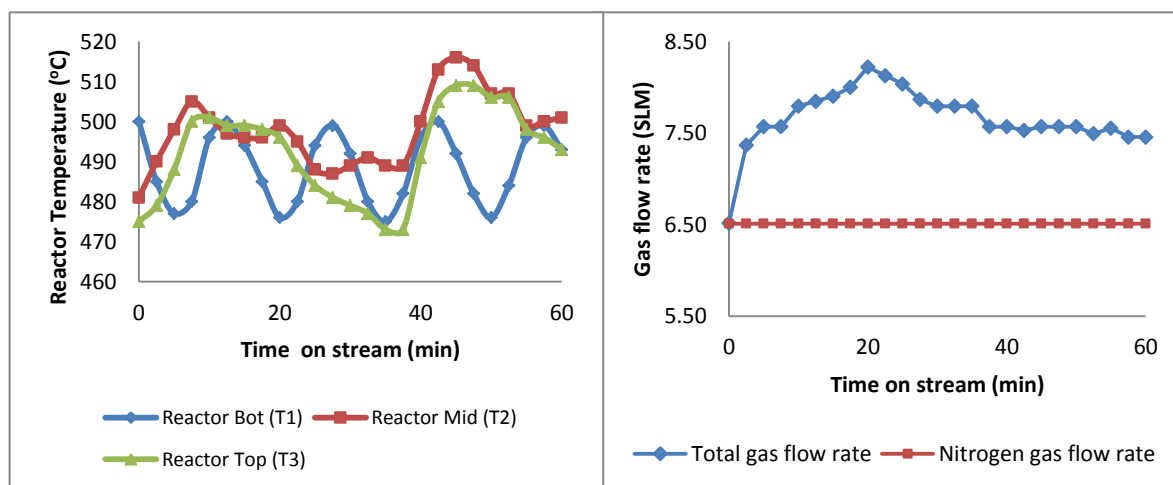


Figure 4.2b. Typical temperature and gas flow profiles for the 2-stage reactor

The nature of the fluidized bed (bubbling, turbulent and spouting) obviously depends on the superficial gas velocity in the reactor. The superficial gas velocity in the 1-stage reactor was approximately 0.049 m/s and the gas velocities in the 2-stage reactor were 0.35 m/s (small section) and 0.0315 m/s (large section). Higher superficial velocity in the reactor will increase catalyst entrainment and result in catalyst carry over into the hot gas filter. Therefore, it appeared that the higher gas velocity

(0.35 m/s) in the small section of the 2-stage reactor may have caused entrainment of catalyst fines such that the lower gas velocity in the large section was insufficient to prevent catalyst losses.

Table 4.2. Effect of catalyst configuration on catalyst losses

Type of Catalyst	Change in reactor content after run (%)	
	1-stage reactor	2-stage reactor
FCC	112.6	75.5
75% FCC & 25% ZSM-5	113.0	69.2
50% FCC & 50% ZSM-5	109.0	71.6
25% FCC & 75% ZSM-5	102.0	69.5
ZSM-5	101.5	69.8

4.3.2. Product Yield Analysis

The product distribution plots in Figure 4.3 show the effect of the addition of ZSM-5 additive to the base FCC catalyst in the fractional catalytic pyrolysis of hybrid poplar wood. In the 1-stage reactor experiment using fresh catalyst, the base FCC catalyst produced an organic liquid yield of 13.8 wt%, that increased to 19.4 wt% when the blend catalyst had 50 wt% of ZSM-5 additive. The char/coke yield consequently decreased from 26.6 wt% to 21.0 wt%. The addition of ZSM-5 at 50 wt% level resulted in about 40% increase in organic liquid fraction (OLF) and 21% decrease in char/coke yields. The results from the 1-stage reactor using steamed catalyst showed similar trends in the product distribution. However, the steamed catalyst produced relatively higher yields of organic liquid and lower yields of char/coke. The organic liquid yield increased from 15.5 wt% to 24.2 wt% and the char/coke yield decreased from 24.1 wt% to 19.7 wt% at 50 wt% level of ZSM-5 additive. A further increase in the ZSM-5 additive to 75 wt% level in the blend catalyst did not result in any appreciable effect. The increase in organic liquid yield at a 50 wt% and 75 wt% additive levels relative to the base FCC catalyst were respectfully 56.7% and 63.1%. It appeared that the influence of ZSM-5 additive at higher addition levels

on the organic liquid yields was subdued by the contributing effect of catalyst steaming. A Similar effect was observed in the char/coke yield. The addition of 25 wt% ZSM-5 additive to the base FCC catalyst resulted in about 22% decrease in char/coke yields. Nonetheless, a further increase of ZSM-5 additive at 50-75 wt% levels accounted for an additional 4% decrease. These results again indicate that steaming of the catalyst had confounding effect on the product yields at high ZSM-5 additive levels. Steaming typically reduces the catalyst activity which consequently decreases the intrinsic coke forming tendency of the catalyst.

The product distribution from the 2-stage reactor using the steamed catalyst was quite different. In comparison, the FCC catalyst produced higher organic liquid yield (17.4 wt%) in the 2-stage reactor than in the 1-stage reactor (13.45 wt%). The organic liquid yield from the 2-stage reactor was expected to be lower since secondary vapor cracking could occur as a result of the high temperature and relatively longer vapor residence time in the larger section of the reactor. However, the observed effect was contradictory to what was presumed. The possible reason for the higher organic liquid yield and lower char/coke yield produced by the steamed FCC catalyst in the 2-stage could be as a result of the relative lower concentration of catalyst in the reactor. It was shown in Table 4.2 that the use of the 2-stage reactor resulted in about 30% loss of catalyst into the hot gas filter. The increase in catalyst losses during the experiment decreases the catalyst concentration in the reactor and subsequently reduces the cumulative catalytic effect. This also implies that the actual WHSV in the 2-stage reactor would be higher. In comparison to the 1-stage reactor, there was negligible loss of catalyst. Hence, the relative catalytic effect would be higher (lower WHSV). This explains the lower organic yield and higher char/coke yield produced with the base FCC catalyst in the 1-stage reactor compared with the 2-stage reactor. The effect of the blend catalyst on the product yields from the 2-stage reactor also followed similar trends as seen with the 1-stage experiment. The organic liquid yields increased and the

char/coke yields decreased with increase in ZSM-5 additive level. The water and gas yields were not much affected by the ZSM-5 addition. However, the increase in ZSM-5 additive showed a gradual decrease in gas yields whilst there was no observed trend in the water yield. It is worth noting that the effect of the ZSM-5 additive in the 2-stage reactor was not as intense in the 1-stage reactor. For instance, at a 75 wt% ZSM-5 additive level, the organic liquid yield increased by 29% and 63.1% respectively for the 2-stage and the 1-stage reactor. Additionally, the same catalyst blend caused 11.5% decrease in char/coke for the 2-stage reactor compared to a decrease of 24.6% in the char/coke yield for the 1-stage reactor. The difference in the measure of influence by the ZSM-5 additive on the product distribution between the two reactors was attributed partly to process conditions due to reactor configuration and different reaction regimes experienced in the reactors.

Generally, the product slate for the fractional catalytic pyrolysis of hybrid poplar wood was dependent on the type of catalyst and the reactor configuration. The effect of the ZSM-5 additive was predominantly on the organic liquid and char/coke yields. The decrease in the char/coke yield with the use of ZSM-5 additive was attributed to the reduction in coke formation. The decrease in the formation of coke was due to the characteristic narrow pore size of the ZSM-5 zeolite in the catalyst blends. The Y-zeolite in the FCC catalyst is considered to be highly active due to its acidity and large pore size [37, 40-42] whilst the ZSM-5 zeolite is known to be selective because of its narrow pores [1, 2, 5, 14, 22, 24, 58, 59]. The pore channels of the ZSM-5 zeolite are small such that it is difficult for coke precursors such as polyaromatics products to form [1, 25, 58]. The Y-zeolite on the other hand allows larger coke precursors to enter the pore structure leading to coke formation. Thus, the increase of ZSM-5 additive and the decrease of FCC catalyst in the blend resulted in a gradual reduction of coke and contributed to higher organic liquid yields.

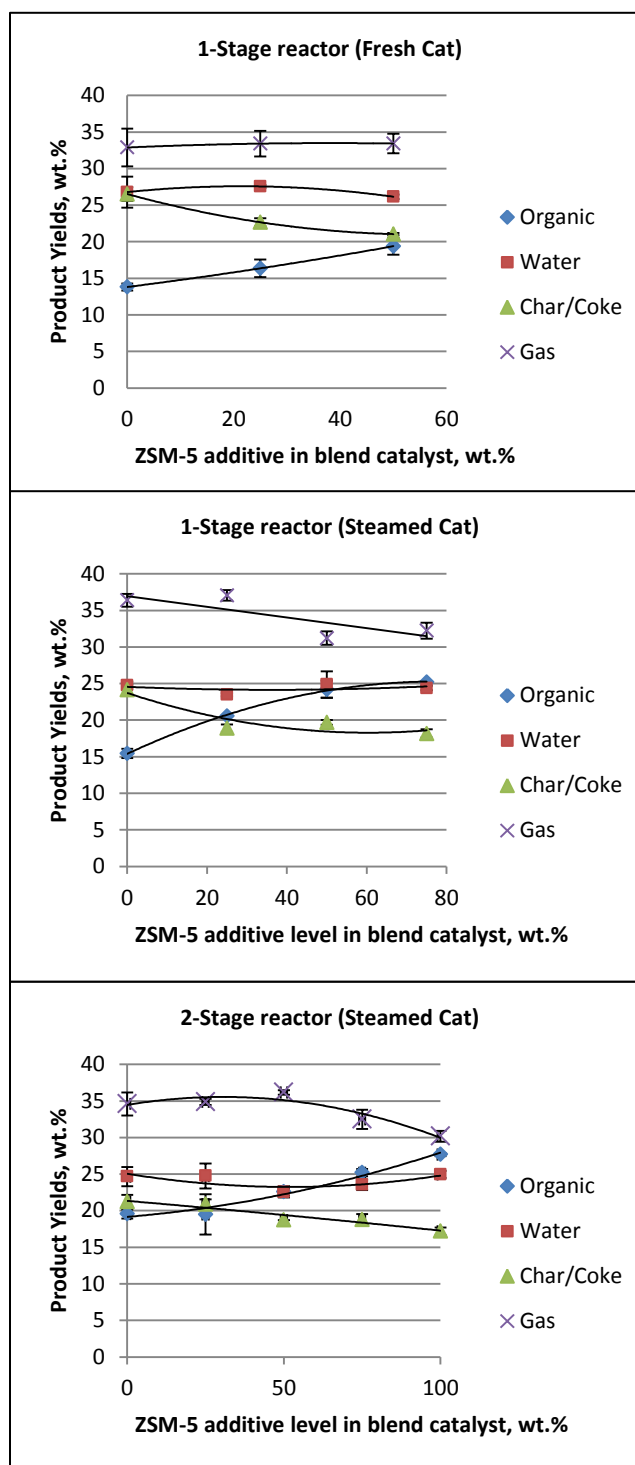


Figure 4.3. Effect of blending ZSM-5 additive with FCC catalyst on organic, water, char/coke and gas yields

4.3.3. Gas Yield Analysis

The gas yield distribution shown in Table 4.3 was determined by a gas flow totalizer and gas chromatograph. The use of a micro gas chromatograph allowed timely analysis of the composition of the non-condensable gases during the experiment. The identified gases were H_2 , CH_4 , CO, CO_2 and C_2 - C_5 hydrocarbons. CO_x gases were mainly produced in the catalytic vapor cracking of the oxygenated compounds and they constituted over 80% of the gas yields. The individual gas yields were influenced by the catalyst system and reactor configuration. Typical yields of CO were in the range of 13-15 wt% and that of CO_2 were between 9 -13 wt.%. The C_1 - C_5 hydrocarbons yields ranged between 5 – 6.2 wt% and H_2 was less than 0.5 wt.%.

The FCC catalyst had higher selectivity for H_2 , CH_4 and CO_2 and the ZSM-5 additive had higher selectivity for C_4 and C_5 hydrocarbons. Catalytic cracking of the vapors in the 2-stage reactor showed that the steamed FCC catalyst produced higher CO_x yield (27.86 wt%) compared with the steamed ZSM-5 additive (24.08 wt%). The most abundant light hydrocarbon gas produced with the FCC catalyst was CH_4 which accounted for about 40% of the total hydrocarbons. For ZSM-5-based additive and FCC/ZSM-5 additive blends, C_5 s hydrocarbons were dominant.

The results from each reactor configuration evidently showed that the addition of ZSM-5 additive linearly decreased the selectivity for H_2 , CH_4 and CO_2 . The increase in ZSM-5 additive level in the FCC/ZSM-5 blend catalyst was found to specifically increase the selectivity for C_4 and C_5 hydrocarbons. The formation of CO was not affected by the addition of ZSM-5 and did not also follow any particular trend. It can be inferred from the data that the ZSM-5 additive decreased decarboxylation reactions and increased reaction pathways for the production of C_4 and C_5 hydrocarbons.

The experiment with the FCC/ZSM-5 additive blend in the 2-stage reactor suggests interaction effect between the base FCC catalyst and the ZSM-5 additive on the formation of C_4 and C_5 hydrocarbons. Higher yields of C_5 hydrocarbons were generated with the FCC/ZSM-5 blends than the base FCC catalyst and the pure ZSM-5 additive. The highest yield of C_5 hydrocarbons was produced with the 25 % FCC and 75% ZSM-5 blend in the 1-stage reactor and the 50% FCC and 50% ZSM-5 blend in the 2-stage reactor. This suggests that the pure ZSM-5 additive was unable to convert some of the oxygenated compounds into C_4 and C_5 hydrocarbons due to its restricted small pore size. The presence of the large pore Y-zeolite (FCC catalyst) in the FCC/ZSM-5 blend probably cracked oxygenated compounds into smaller fragments and increased the amount of small hydrocarbons that could diffuse into the pore of the ZSM-5 additive for conversion into C_4 and C_5 hydrocarbons. Hence, higher yields were relatively produced with the blend catalysts.

It is also important to note that the concentrations of the individual gases were affected by the reactor configuration as well as steaming of the catalyst. In the case of reactor configuration, it can be seen that most of the steamed catalyst blends gave slightly higher yields of H_2 , CH_4 , CO , CO_2 , C_4 and C_5 hydrocarbons in the 2-stage reactor than in the 1-stage reactor. However, the C_2 and C_3 hydrocarbon gases were not markedly influenced. The higher gas yields reported for the 2-stage reactor were probably due to extensive cracking of the pyrolysis vapors since the average temperature in the second section of the 2-stage reactor was slightly higher than what was experienced in the 1-stage reactor. Studies on zeolite catalytic cracking have shown generally that higher temperature increases the yield of the gas products due to the occurrence of secondary cracking reactions [26, 60-64]. From the results, the most widely influenced gases were H_2 and C_4 hydrocarbons. Depending of the catalyst system, the yields of H_2 and C_4 hydrocarbons from the 2-stage reactor were respectively 17–53% and 6–64 % higher than those generated from the 1-stage reactor.

Table 4.3. Individual gas yields, wt% of biomass

Gases	100% FCC	75% FCC & 25% ZSM-5	50% FCC & 50% ZSM-5	25% FCC & 75% ZSM-5	100% ZSM-5
1-Stage Reactor (Fresh catalyst blends)					
H ₂	0.13±0.01	0.09±0.01	0.10±0.01		
CH ₄	1.76±0.26	1.66±0.19	1.49±0.25		
CO	13.40±0.23	13.68±0.15	14.97±0.52		
CO ₂	10.02±0.41	8.99±0.14	9.40±0.41		
C ₂ S	0.41±0.017	0.40±0.02	0.47±0.02		
C ₃ S	0.59±0.024	0.57±0.027	0.67±0.03		
C ₄ S	0.80±0.12	1.07±0.08	1.08±0.1		
C ₅ S	0.90±0.27	2.06±0.1	2.06±0.37		
C ₂ -C ₅	2.70±0.44	4.10±0.05	4.28±0.25		
1-Stage Reactor (Steamed catalyst blends)					
H ₂	0.23±0.02	0.16±0.01	0.12±0.01	0.13±0.011	
CH ₄	2.22±0.18	1.59±0.14	1.44±0.21	1.43±0.09	
CO	14.56±0.21	13.71±0.11	13.62±0.09	13.72±0.15	
CO ₂	12.42±0.2	10.01±0.16	9.31±0.03	9.41±0.14	
C ₂ S	0.46±0.002	0.44±0.008	0.43±0.003	0.41±0.007	
C ₃ S	0.66±0.006	0.63±0.02	0.61±0.003	0.58±0.02	
C ₄ S	0.98±0.03	1.26±0.03	1.38±0.08	1.27±0.06	
C ₅ S	0.77±0.05	1.59±0.1	1.63±0.07	1.95±0.1	
C ₂ -C ₅	2.87±0.11	3.92±0.15	4.05±0.13	4.21±0.21	
2-Stage Reactor (Steamed catalyst blends)					
H ₂	0.27±0.019	0.24±0.016	0.22±0.019	0.20±0.02	0.18±0.014
CH ₄	1.92±0.102	1.86±0.123	1.66±0.042	1.52±0.13	1.25±0.06
CO	14.77±0.17	14.96±0.02	14.73±0.23	14.43±0.029	13.57±0.19
CO ₂	13.09±0.15	12.08±0.03	11.29±0.16	10.88±0.05	10.51±0.10
C ₂ S	0.45±0.007	0.44±0.003	0.44±0.005	0.44±0.006	0.43±0.008
C ₃ S	0.65±0.01	0.66±0.005	0.62±0.008	0.62±0.008	0.61±0.011
C ₄ S	1.61±0.1	1.55±0.05	1.47±0.05	1.41±0.024	1.36±0.056
C ₅ S	0.95±0.07	1.58±0.08	1.98±0.10	1.69±0.105	1.60±0.03
C ₂ -C ₅	3.66±0.13	4.23±0.11	4.51±0.16	4.16±0.13	4.00±0.10

Furthermore, results from the 1-stage reactor where both steamed and fresh catalyst were used showed that steaming of the catalyst influenced its selectivity and consequently increased the individual gas yields for H₂, CO CO₂ and C₄ hydrocarbons. Among the carbon oxides, CO₂ was affected

the most. This suggests that the steamed FCC catalyst increased the selectivity for decarboxylation and hydrogen producing reactions. The influence on the gas yields was attributed to catalyst modification as result of the decomposition of the zeolite and collapse of the matrix during steaming. Steam treatment of FCC catalyst generates non-framework aluminum species (Lewis acid sites) [65-68] which affects the activity and selectivity of the catalyst [69, 70].

The complete chain of reactions that leads to the generation of non-condensable gases in catalytic cracking of oxygenated compounds is still unclear. Nonetheless, Corma et al. [33] proposed that H_2 , CO and CO_2 are generated from reactions such as dehydration, decarbonylation, dehydrogenation, water-gas shift (WGS) and steam reforming of dehydrated species. They suggested that, light hydrocarbons were formed through repeated dehydrogenation/hydrogenation or hydrogen transfer reactions. As already seen from the results, the FCC catalyst and the ZSM-5-based additive generated different gas yields and the variations in the gas composition can be attributed to their catalytic properties. One of the major differences between the FCC catalyst and ZSM-5 additive is the catalyst pore size and structure. The Y-zeolite crystal in FCC catalyst has parallel channels with large openings (7.4 Å) and is able to allow large molecules to diffuse into and crack [37, 39, 42]. The ZSM-5 zeolite has three-dimensional system of intersecting channels with a medium pore size opening (5.5 Å) and admits selectively smaller molecules for conversion into mainly light hydrocarbon (olefins) and aromatics[1, 3, 5, 18, 25, 44].

The Y-zeolite of the FCC catalyst and the ZSM-5 also differ in their mechanisms for cracking hydrocarbons. Primarily, there are two main types of mechanisms that govern acid catalyzed cracking of hydrocarbons [71, 72]. They are namely bimolecular (classical) cracking which involves hydride transfer reactions[73] and monomolecular cracking which occur by formation of carbonium ions[74]. The monomolecular (non-classical) cracking proposed by Haag and Dessau [74] extensively occurs in medium

pore shape selective zeolites (ZSM-5) [75-77] since bimolecular reaction intermediates cannot be formed in the narrow pores. However, both monomolecular and bimolecular cracking reactions occur in the Y-zeolite of the FCC catalyst due to its relatively large pore size[78]. In short, the FCC catalyst mainly catalyzes cracking and hydrogen transfer reactions [40, 77, 79-82] and the ZSM-5 additive promotes isomerization and shape selective cracking reactions [81].

The exact determination of the contribution of these cracking mechanism in the catalytic pyrolysis of biomass is impossible since most of the reactants are more than four carbons [72]. However, the relatively higher yields of H_2 and CH_4 produced by the FCC catalyst compared to the ZSM-5 additive suggest that protolytic cracking (monomolecular mechanism) of oxygenated compounds was dominant in the FCC catalyst [72, 75]. The higher yields of C_5 hydrocarbons produced from the FCC/ZSM-5 hybrid catalysts also suggest that isomerization and shape selective cracking were enhanced and both hydrogen transfer reactions and bimolecular reactions were minimized in the presence of ZSM-5 additive.

4.3.4 Physico-chemical Analysis of Bio-oils

The physical properties of the bio-oils in Tables 4.4-4.6 show that the addition of ZSM-5 additive affected the properties of the bio-oil. The viscosity of the bio-oil was the most influenced physical property. The addition of ZSM-5 additive decreased the viscosity of the bio-oil. The increases in pH and higher heating value (HHV) were minimal. The elemental analysis of the bio-oils showed slight increase in carbon content and decrease in oxygen content with the addition of ZSM-5 additive. The decrease in the viscosity of the bio-oils was attributed to increases in the formation of smaller molecular weight compounds promoted by the presence of ZSM-5 additive. The slight increase in pH of the bio-oils caused by addition of the ZSM-5 additive suggests that some of the oxygenated functionalities contributing to the acidity of the bio-oil were cracked by the ZSM-5 additive.

Table 4.4. Physical properties of bio-oil produced from single stage reactor using fresh catalyst blends

Property	Bio-oils		
	FCC	75% FCC & 25% ZSM-5	50% FCC & 50% ZSM-5
Moisture (wt%)	3.23	2.87	2.90
pH	2.76	3.16	3.08
Density (g/cm ³)	1.172	1.162	1.158
Kinematic viscosity, at 40 °C(cSt)	82.2	66.8	62.24
Elemental composition, wt% (moisture free)			
C	67.78	70.28	68.67
H	6.54	6.18	6.20
N	0.178	0.231	0.254
O	25.50	23.31	24.88
HHV (MJ/kg)	28.49	29.24	28.66

It is worth noting that the some of the bio-oils produced with the FCC/ZSM-5 hybrid catalysts had higher pH, HHV and carbon content as well as lower viscosities than the bio-oils produced with the pure FCC catalyst or ZSM-5 additive. For instance, the catalytic pyrolysis in the 1-stage reactor with the fresh hybrid catalyst blend (75 wt% of FCC and 25 wt% of ZSM-5) produced the highest quality bio-oil (see Table 4.4). That bio-oil had relatively higher carbon content (70 wt%), lower oxygen content (23 wt%), higher HHV (29.24 MJ/kg), lower viscosity (66.8 cSt) and higher pH (3.16) compared to the other bio-oils produced. This observation suggests a synergistic effect of the FCC catalyst and the ZSM-5 additive on the physical properties.

The bio-oils produced from the catalytic pyrolysis with the steamed catalyst in the 1-stage reactor showed that higher levels of ZSM-5 additive could decrease the carbon content and consequently lower the HHV (Table 4.5). The bio-oil produced with the hybrid catalyst containing 75

wt% of ZSM-5 additive had carbon and oxygen content of 65.6 % and 28.0% respectively compared to 68.1% and 25.3% for bio-oil produced with the hybrid catalyst containing 50 wt% of ZSM-5 additive.

Nonetheless, the results from the 2-stage reactor did not show such effect and the properties of the bio-oils produced with the FCC/ZSM-5 hybrid catalyst were comparable (Table 4.6). This again is suggestive of the fact that reactor configuration plays a role in the catalytic pyrolysis. The most obvious physical property that was influenced by the usage of the 2-stage reactor was viscosity. The viscosities of the bio-oils produced with the 2-stage reactor were higher than the bio-oils generated in the 1-stage reactor. The higher viscosities reported for the bio-oils from the 2-stage reactor could partly be as a result of the relatively higher temperature experienced by the vapors in the upper section of the reactor and the loss of catalyst. At higher temperatures, polymerization reactions could be enhanced which may increase the viscosity of the bio-oil.

Table 4.5. Physical properties of bio-oil produced from 1- stage reactor using steamed catalyst blends

Property	Bio-oils			
	FCC	75% FCC & 25% ZSM-5	50% FCC & 50% ZSM-5	25% FCC & 75% ZSM-5
Moisture (wt%)	2.80	2.70	3.00	3.30
pH	2.73	2.95	3.12	3.06
Density (g/cm ³)	1.17	1.16	1.16	1.16
Kinematic viscosity, at 40 °C(cSt)	67.6	55.0	49.8	52.4
Elemental composition, wt% (moisture free)				
C	67.36	67.27	68.14	65.61
H	6.52	6.39	6.40	6.20
N	0.21	0.18	0.19	0.18
O	25.91	26.16	25.27	28.01
HHV (MJ/kg)	27.41	27.27	27.68	26.32

Table 4.6. Physical properties of bio-oil produced from the 2- stage reactor using steamed catalyst

blends

Property	Bio-oils				
	FCC	75% FCC & 25% ZSM-5	50% FCC & 50% ZSM-5	25% FCC & 75% ZSM-5	ZSM-5
Moisture (wt%)	2.01	2.26	3.10	2.90	3.05
pH	2.78	3.15	3.09	3.13	3.09
Density (g/cm ³)	1.17	1.16	1.16	1.16	1.16
Kinematic viscosity, at 40 °C(cSt)	172	146	120	128	144
Elemental composition, wt% (moisture free)					
C	66.97	67.29	67.44	67.61	66.63
H	6.33	6.41	6.47	6.50	6.44
N	0.19	0.20	0.18	0.19	0.17
O	26.50	26.10	25.91	25.69	26.76
HHV (MJ/kg)	27.95	28.45	28.18	28.36	28.35

The carbon-13 nuclear magnetic resonance (¹³C-NMR) spectra of the bio-oils produced from the 2-stage reactor in Figure 4.4 show the effect of ZSM-5 additive on the various functional groups in the bio-oil. The integration of the spectra regions of the whole bio-oil (Table 4.7) showed that the aliphatic hydrocarbon carbon content (0-50 ppm) was higher in bio-oil produced with the FCC catalyst (26.43%) compared to the bio-oil produced with ZSM-5 additive (19.03%). Conversely, the aromatic hydrocarbons (125-160 ppm) were higher in the bio-oil produced with the pure ZSM-5 additive (38.47%) than the bio-oil produced with the FCC catalyst (25.34%).

The findings agree with the knowledge that FCC catalyst favors the formation of aliphatics due to hydrogen transfer reactions and ZSM-5 zeolite produces more aromatics and olefins via isomerization, Diels-Alder and aldol condensation [33]. The sugars and anhydrosugars (57-105 ppm) from the decomposition of carbohydrates were lower in the FCC catalyst bio-oil (7.9%) and relatively higher in the ZSM-5 additive bio-oil (9.5%). This suggests that the FCC catalyst cracks more of the

pyrolysis dehydration product of cellulose (levoglucosan). The methoxyl groups (55-57 ppm) and the guaiacyl/syrigyl aromatics (105-125 ppm) which indicate methoxylated phenols were higher in the bio-oil produced with the FCC catalyst. Additionally, the carbonyls (160-180 ppm) belonging to carboxylic acids (e.g. formic, acetic, propionic, etc.) and carbonyl (180-220 ppm) due to ketones and aldehydes were found to be less in the bio-oil fraction produced from the ZSM-5 additive.

The effect of ZSM-5 additive on the carbon distribution of the various chemical functionalities was reflective in the bio-oils produced with the FCC/ZSM-5 additive hybrids (see Table 4.7 and 4.8). The increase in ZSM-5 additive corresponded to a gradual increase in aromatic hydrocarbons and a decrease in the aliphatic hydrocarbons for bio-oils produced in both 1-stage and 2-stage reactors. Also, the increase in ZSM-5 additive resulted in decrease of the methoxylated compounds in bio-oils produced with the 2-stage reactor and increase in bio-oils produced with the 1-stage reactor. Furthermore, the increase in ZSM-5 additive levels decreased carboxylic acids, aldehydes and ketones in bio-oils from the 2-stage reactor. However, it appeared that the carbonyl functionalities in the bio-oils produced from the 1-stage reactor were not influenced by the addition of ZSM-5 additive. From the results, it is clear that the influence of ZSM-5 additive is dependent on the reactor configuration. Hence, the differences between the chemical compositions of the bio-oils produced in the 1-stage and the 2-stage is suggestive that some of the reactions that occurred in the reactors were dissimilar.

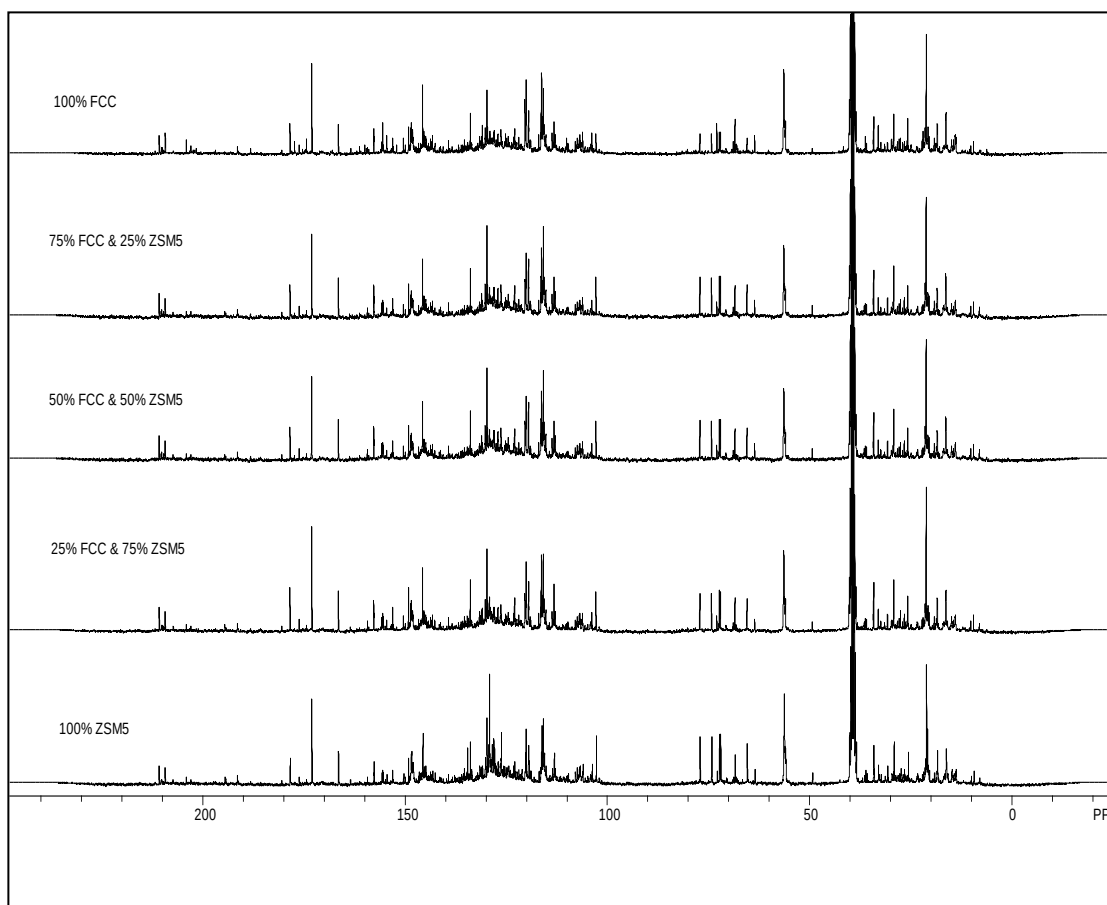


Figure 4.4. ^{13}C -NMR spectra of various whole bio-oil from two- stage reactor using steamed catalyst blends

Table 4.7. ¹³C-NMR Integration of whole bio-oil from 2- stage reactor using steamed catalyst blends

Chemical Shift region (ppm)	Type of Carbon	FCC	75% FCC & 25% ZSM-5	50% FCC & 50% ZSM-5	25% FCC & 75% ZSM-5	ZSM-5
0 - 50	Aliphatic hydrocarbon	26.43	24.29	24.81	23.76	19.03
55 - 57	Methoxyl	9.48	7.29	7.22	7.76	7.91
57 - 105	Levoglucosan, anhydrosugars, ethers, alcohols	7.97	8.67	8.62	8.52	9.47
105 - 125	Aromatic (guaiacyl, syringyl)	22.40	23.57	23.29	21.81	21.13
125 - 160	General Aromatic	25.34	29.34	29.39	32.50	38.47
160 - 180	Carbonyl (Carboxylic acids and derivatives)	5.55	4.35	4.22	3.95	3.51
180 - 220	Carbonyl (Aldehydes, Ketones)	2.83	2.48	2.45	2.47	1.61

Table 4.8. ¹³C-NMR Integration of whole bio-oil from 1- stage reactor using steamed catalyst blends

Chemical Shift region (ppm)	Type of Carbon	FCC	75% FCC & 25% ZSM-5	50% FCC & 50% ZSM-5	25% FCC & 75% ZSM-5
0 - 50	Aliphatic hydrocarbon	27.32	25.81	23.42	20.76
55 - 57	Methoxyl	7.54	7.95	8.17	9.56
57 - 105	Levoglucosan, anhydrosugars, ethers, alcohols	6.24	5.17	6.67	5.37
105 - 125	Aromatic (guaiacyl, syringyl)	23.09	22.91	23.10	23.29
125 - 160	General Aromatic	29.15	31.78	32.71	33.43
160 - 180	Carbonyl (Carboxylic acids and its derivatives)	3.94	3.94	3.58	3.29
180 - 220	Carbonyl (Aldehydes, Ketones)	2.72	2.43	2.36	2.13

4.4. CONCLUSION

Catalytic pyrolysis of biomass with FCC catalyst results in large amount of coke and lower organic liquid yields. In the present study, ZSM-5 based additive was investigated as a co catalyst to the FCC catalyst in the fractional catalytic pyrolysis of hybrid poplar wood in 1-stage and 2-stage reactors. From the experimental results reported, the increase in ZSM-5 additive increased the yield of bio-oil and decreased coke formation. The ZSM-5 additive influenced the composition of the non-condensable gases as well. The formation of H_2 , CH_4 and CO_2 decreased whilst the generation of C_4 - C_5 hydrocarbons increased with increasing levels of ZSM-5 additive. The results from the 1-stage and 2-stage fluid bed reactors showed that reactor configuration potentially influences fractional catalytic pyrolysis process.

The physical characteristics of the bio-oil fractions showed that the FCC/ZSM-5 hybrid catalyst produced bio-oils with improved oil properties when compared to the FCC catalyst. There was a decrease in acidity and viscosity as well as an increase in the HHV. The elemental analysis of the bio-oils showed that the fresh catalyst blend of 75 wt% of FCC and 25 wt% of ZSM-5 produced bio-oils with higher carbon content. The physical properties of the bio-oils and the non-condensable gas composition suggest synergistic effect of the FCC catalyst and the ZSM-5 additive. Under the experiments of the study, the ^{13}C -NMR spectrometric analysis of the whole bio-oil fractions showed that ZSM-5 additive decreased aliphatic hydrocarbon and increased the aromatic hydrocarbon content. The effect of ZSM-5 on the cracking of levoglucosan, carbonyl functionalities and methoxylated compounds from the decomposition of lignin were dependent on the configuration of the reactor. The bio-oils produced with the 2-stage reactor showed that ZSM-5 additive decreased the amount of methoxylated phenols and carbonyl groups belonging to carboxylic acids, ketones and aldehydes.

4.5 REFERENCES

1. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways*. Fuel Processing Technology, 1995. **45**(3): p. 185-202.
2. Agblevor, F.A., S. Beis, O. Mante, and N. Abdoulmoumine, *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood*. Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.
3. Aho, A., N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D.Y. Murzin, *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.
4. Chen, N.Y., D.E. Walsh, and L.R. Koenig, *Fluidized-Bed Upgrading of Wood Pyrolysis Liquids and Related Compounds*, in *Pyrolysis Oils from Biomass* 1988, American Chemical Society: Washington, DC. p. 277-289.
5. Carlson, T., G. Tompsett, W. Conner, and G. Huber, *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
6. Ates, F., A.E. Pütün, and E. Pütün, *Fixed bed pyrolysis of Euphorbia rigida with different catalysts*. Energy Conversion and Management, 2005. **46**(3): p. 421-432.
7. Ates, F., A.E. Pütün, and E. Pütün, *Catalytic pyrolysis of perennial shrub, Euphorbia rigida in the water vapour atmosphere*. Journal of Analytical and Applied Pyrolysis, 2005. **73**(2): p. 299-304.
8. Iliopoulou, E.F., E.V. Antonakou, S.A. Karakoulia, I.A. Vasalos, A.A. Lappas, and K.S. Triantafyllidis, *Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts*. Chemical Engineering Journal, 2007. **134**(1-3): p. 51-57.
9. Lappas, A.A., D.K. Iatridis, and I.A. Vasalos, *Production of Liquid Biofuels in a Fluid Catalytic Cracking Pilot-Plant Unit Using Waxes Produced from a Biomass-to-Liquid (BTL) Process*. Industrial & Engineering Chemistry Research, 2010.
10. Adam, J., E. Antonakou, A. Lappas, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, and G. Øye, *In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials*. Microporous and Mesoporous Materials, 2006. **96**(1-3): p. 93-101.

11. Lappas, A.A., M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, and I.A. Vasalos, *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
12. Li, H.-y., Y.-j. Yan, and Z.-w. Ren, *Online upgrading of organic vapors from the fast pyrolysis of biomass*. Journal of Fuel Chemistry and Technology, 2008. **36**(6): p. 666-671.
13. Peng, J., P. Chen, H. Lou, and X. Zheng, *Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol*. Bioresource Technology, 2009. **100**(13): p. 3415-3418.
14. Pütün, E., B.B. Uzun, and A.E. Pütün, *Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor*. Energy & Fuels, 2009. **23**(4): p. 2248-2258.
15. R. K. Sharma, N.N.B., *Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals*. The Canadian Journal of Chemical Engineering, 1991. **69**(5): p. 1071-1081.
16. Radlein, D.S.A.G., S.L. Mason, J. Piskorz, and D.S. Scott, *Hydrocarbons from the catalytic pyrolysis of biomass*. Energy & Fuels, 1991. **5**(5): p. 760-763.
17. Ramesh K. Sharma, N.N.B., *Catalytic upgrading of fast pyrolysis oil over hzsm-5*. The Canadian Journal of Chemical Engineering, 1993. **71**(3): p. 383-391.
18. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
19. Sharma, R.K. and N.N. Bakhshi, *Conversion of non-phenolic fraction of biomass-derived pyrolysis oil to hydrocarbon fuels over HZSM-5 using a dual reactor system*. Bioresource Technology, 1993. **45**(3): p. 195-203.
20. Srimat T. Srinivas, A.K.D.N.N.B., *Thermal and catalytic upgrading of a biomass-derived oil in a dual reaction system*. The Canadian Journal of Chemical Engineering, 2000. **78**(2): p. 343-354.
21. Vitolo, S., B. Bresci, M. Seggiani, and M.G. Gallo, *Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading-regenerating cycles*. Fuel, 2001. **80**(1): p. 17-26.
22. Vitolo, S., M. Seggiani, P. Frediani, G. Ambrosini, and L. Politi, *Catalytic upgrading of pyrolytic oils to fuel over different zeolites*. Fuel, 1999. **78**(10): p. 1147-1159.
23. Williams, P.T. and H.M. Chishti, *Two stage pyrolysis of oil shale using a zeolite catalyst*. Journal of Analytical and Applied Pyrolysis, 2000. **55**(2): p. 217-234.

24. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. Biomass and Bioenergy, 1994. **7**(1-6): p. 223-236.
25. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(1): p. 39-61.
26. Williams, P.T. and N. Nugranad, *Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks*. Energy, 2000. **25**(6): p. 493-513.
27. Zhang, H., R. Xiao, H. Huang, and G. Xiao, *Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor*. Bioresource Technology, 2009. **100**(3): p. 1428-1434.
28. Zhang, H., R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.
29. Zhang, Q., J. Chang, Wang, and Y. Xu, *Upgrading Bio-oil over Different Solid Catalysts*. Energy & Fuels, 2006. **20**(6): p. 2717-2720.
30. Mante, O., F. Agblevor, and R. McClung, *Fluid catalytic cracking of biomass pyrolysis vapors*. Biomass Conversion and Biorefinery, 2011. **1**(4): p. 189-201.
31. de Miguel Mercader, F., M.J. Groeneveld, S.R.A. Kersten, N.W.J. Way, C.J. Schaverien, and J.A. Hogendoorn, *Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units*. Applied Catalysis B: Environmental, 2010. **96**(1-2): p. 57-66.
32. Domine, M.E., A.C. van Veen, Y. Schuurman, and C. Mirodatos, *Coprocessing of Oxygenated Biomass Compounds and Hydrocarbons for the Production of Sustainable Fuel*. ChemSusChem, 2008. **1**(3): p. 179-181.
33. Corma, A., G.W. Huber, L. Sauvanaud, and P. O'Connor, *Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst*. Journal of Catalysis, 2007. **247**(2): p. 307-327.
34. Stöcker, M., *Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials*. Angewandte Chemie International Edition, 2008. **47**(48): p. 9200-9211.
35. Huber, George W. and A. Corma, *Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass*. Angewandte Chemie International Edition, 2007. **46**(38): p. 7184-7201.
36. de la Puente, G. and U. Sedran, *Conversion of methylcyclopentane on rare earth exchanged Y zeolite FCC catalysts*. Applied Catalysis A: General, 1996. **144**(1-2): p. 147-158.

37. Hosseinpour, N., Y. Mortazavi, A. Bazyari, and A.A. Khodadadi, *Synergetic effects of Y-zeolite and amorphous silica-alumina as main FCC catalyst components on triisopropylbenzene cracking and coke formation*. Fuel Processing Technology, 2009. **90**(2): p. 171-179.
38. Fogassy, G., N. Thegarid, G. Toussaint, A.C. van Veen, Y. Schuurman, and C. Mirodatos, *Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units*. Applied Catalysis B: Environmental, 2010. **96**(3-4): p. 476-485.
39. Tonetto, G.M., M.L. Ferreira, J.A. Atias, and H.I. de Lasa, *Effect of steaming treatment in the structure and reactivity of FCC catalysts*. AIChE Journal, 2006. **52**(2): p. 754-768.
40. Al-Khattaf, S., *The influence of Y-zeolite unit cell size on the performance of FCC catalysts during gas oil catalytic cracking*. Applied Catalysis A: General, 2002. **231**(1-2): p. 293-306.
41. Dight, L.B., Leskiewicz, Mark A., Bogert, David C., *High zeolite content FCC catalysts and method for making them.*, 1990, ENGELHARD CORP (US).
42. Tonetto, G., J. Atias, and H. de Lasa, *FCC catalysts with different zeolite crystallite sizes: acidity, structural properties and reactivity*. Applied Catalysis A: General, 2004. **270**(1-2): p. 9-25.
43. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
44. Lappas, A.A., S. Bezergianni, and I.A. Vasalos, *Production of biofuels via co-processing in conventional refining processes*. Catalysis Today, 2009. **145**(1-2): p. 55-62.
45. Graça, I., F.R. Ribeiro, H.S. Cerqueira, Y.L. Lam, and M.B.B. de Almeida, *Catalytic cracking of mixtures of model bio-oil compounds and gasoil*. Applied Catalysis B: Environmental, 2009. **90**(3-4): p. 556-563.
46. Lee, K.-H., S.-G. Jeon, K.-H. Kim, N.-S. Noh, D.-H. Shin, J. Park, Y. Seo, J.-J. Yee, and G.-T. Kim, *Thermal and catalytic degradation of waste high-density polyethylene (HDPE) using spent FCC catalyst*. Korean Journal of Chemical Engineering, 2003. **20**(4): p. 693-697.
47. Lee, K.-H. and D.-H. Shin, *A comparative study of liquid product on non-catalytic and catalytic degradation of waste plastics using spent FCC catalyst*. Korean Journal of Chemical Engineering, 2006. **23**(2): p. 209-215.
48. Li, H., B. Shen, J.C. Kabalu, and M. Nchare, *Enhancing the production of biofuels from cottonseed oil by fixed-fluidized bed catalytic cracking*. Renewable Energy, 2009. **34**(4): p. 1033-1039.

49. Samolada, M.C., W. Baldauf, and I.A. Vasalos, *Production of a bio-gasoline by upgrading biomass flash pyrolysis liquids via hydrogen processing and catalytic cracking*. Fuel, 1998. **77**(14): p. 1667-1675.
50. Chew, T.L. and S. Bhatia, *Effect of catalyst additives on the production of biofuels from palm oil cracking in a transport riser reactor*. Bioresource Technology, 2009. **100**(9): p. 2540-2545.
51. Adewuyi, Y.G., D.J. Klocke, and J.S. Buchanan, *Effects of high-level additions of ZSM-5 to a fluid catalytic cracking (FCC) RE-USY catalyst*. Applied Catalysis A: General, 1995. **131**(1): p. 121-133.
52. Buchanan, J.S., *The chemistry of olefins production by ZSM-5 addition to catalytic cracking units*. Catalysis Today, 2000. **55**(3): p. 207-212.
53. Degnan, T.F., G.K. Chitnis, and P.H. Schipper, *History of ZSM-5 fluid catalytic cracking additive development at Mobil*. Microporous and Mesoporous Materials, 2000. **35-36**: p. 245-252.
54. Dzikh, I.P., J.M. Lopes, F. Lemos, and F. Ramôa Ribeiro, *Mixing effect of USHY+HZSM-5 for different catalyst ratios on the n-heptane transformation*. Applied Catalysis A: General, 1999. **176**(2): p. 239-250.
55. Zhao, X. and T.G. Roberie, *ZSM-5 Additive in Fluid Catalytic Cracking. 1. Effect of Additive Level and Temperature on Light Olefins and Gasoline Olefins*. Industrial & Engineering Chemistry Research, 1999. **38**(10): p. 3847-3853.
56. Li, X., B. Shen, Q. Guo, and J. Gao, *Effects of large pore zeolite additions in the catalytic pyrolysis catalyst on the light olefins production*. Catalysis Today, 2007. **125**(3-4): p. 270-277.
57. Schipper, P.H., F.G. Dwyer, P.T. Sparrell, S. Mizrahi, and J.A. Herbst, *Zeolite ZSM-5 in Fluid Catalytic Cracking: Performance, Benefits, and Applications*, in *Fluid Catalytic Cracking* 1988, American Chemical Society. p. 64-86.
58. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts*. Fuel Processing Technology, 1995. **45**(3): p. 161-183.
59. Gayubo, A.G., B. Valle, A.s.T. Aguayo, M. Olazar, and J. Bilbao, *Olefin Production by Catalytic Transformation of Crude Bio-Oil in a Two-Step Process*. Industrial & Engineering Chemistry Research, 2009. **49**(1): p. 123-131.
60. Evans Robert, J. and T. Milne, *Molecular-Beam, Mass-Spectrometric Studies of Wood Vapor and Model Compounds over an HZSM-5 Catalyst*, in *Pyrolysis Oils from Biomass* 1988, American Chemical Society. p. 311-327.

61. Mathews, J.F., M.G. Tepylo, R.L. Eager, and J.M. Pepper, *Upgrading of aspen poplar wood oil over HZSM-5 zeolite catalyst*. The Canadian Journal of Chemical Engineering, 1985. **63**(4): p. 686-689.
62. Sharma, R.K. and N.N. Bakhshi, *Upgrading of wood-derived bio-oil over HZSM-5*. Bioresource Technology, 1991. **35**(1): p. 57-66.
63. Carlson, T.R., Y.-T. Cheng, J. Jae, and G.W. Huber, *Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust*. Energy & Environmental Science, 2011. **4**(1): p. 145-161.
64. Encinar, J.M., J.F. González, G. Martínez, and S. Román, *Catalytic pyrolysis of exhausted olive oil waste*. Journal of Analytical and Applied Pyrolysis, 2009. **85**(1-2): p. 197-203.
65. Katada, N., Y. Kageyama, K. Takahara, T. Kanai, H. Ara Begum, and M. Niwa, *Acidic property of modified ultra stable Y zeolite: increase in catalytic activity for alkane cracking by treatment with ethylenediaminetetraacetic acid salt*. Journal of Molecular Catalysis A: Chemical, 2004. **211**(1-2): p. 119-130.
66. Narbeshuber, T.F., A. Brait, K. Seshan, and J.A. Lercher, *The influence of extraframework aluminum on H-FAU catalyzed cracking of light alkanes*. Applied Catalysis A: General, 1996. **146**(1): p. 119-129.
67. Wang, Q.L., G. Giannetto, and M. Guisnet, *Dealumination of zeolites III. Effect of extra-framework aluminum species on the activity, selectivity, and stability of Y zeolites in n-heptane cracking*. Journal of Catalysis, 1991. **130**(2): p. 471-482.
68. Williams, B.A., S.M. Babitz, J.T. Miller, R.Q. Snurr, and H.H. Kung, *The roles of acid strength and pore diffusion in the enhanced cracking activity of steamed Y zeolites*. Applied Catalysis A: General, 1999. **177**(2): p. 161-175.
69. Beyerlein, R.A., C. Choi-Feng, J.B. Hall, B.J. Huggins, and G.J. Ray, *Effect of steaming on the defect structure and acid catalysis of protonated zeolites*. Topics in Catalysis, 1997. **4**(1): p. 27-42.
70. Humphries, A., D.H. Harris, and P. O'Connor, *The Nature of Active Sites in Zeolites: Influence on Catalyst Performance*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 41-82.
71. Corma, A., P.J. Miguel, and A.V. Orchillés, *Product selectivity effects during cracking of alkanes at very short and longer times on stream*. Applied Catalysis A: General, 1996. **138**(1): p. 57-73.
72. Corma, A. and A.V. Orchillés, *Current views on the mechanism of catalytic cracking*. Microporous and Mesoporous Materials, 2000. **35-36**: p. 21-30.

73. Greensfelder, B.S., H.H. Voge, and G.M. Good, *Catalytic and Thermal Cracking of Pure Hydrocarbons: Mechanisms of Reaction*. Industrial & Engineering Chemistry, 1949. **41**(11): p. 2573-2584.
74. Haag, W.O. and R.M. Dessau. in *Proceedings of the 8th International Congress on Catalysis*. 1984. Berlin: Verlag Chemie, Weinheim.
75. Jentoft, F.C. and B.C. Gates, *Solid-acid-catalyzed alkane cracking mechanisms: evidence from reactions of small probe molecules*. Topics in Catalysis, 1997. **4**(1): p. 1-13.
76. Jolly, S., J. Saussey, M.M. Bettahar, J.C. Lavalley, and E. Benazzi, *Reaction mechanisms and kinetics in the n-hexane cracking over zeolites*. Applied Catalysis A: General, 1997. **156**(1): p. 71-96.
77. Corma, A., F.V. Melo, L. Sauvanaud, and F. Ortega, *Light cracked naphtha processing: Controlling chemistry for maximum propylene production*. Catalysis Today, 2005. **107-108**(0): p. 699-706.
78. den Hollander, M.A., M. Wissink, M. Makkee, and J.A. Moulijn, *Synergy effects of ZSM-5 addition in fluid catalytic cracking of hydrotreated flashed distillate*. Applied Catalysis A: General, 2002. **223**(1-2): p. 103-119.
79. Scherzer, J., *Correlation Between Catalyst Formulation and Catalytic Properties*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 145-182.
80. Zhao, X. and R.H. Harding, *ZSM-5 Additive in Fluid Catalytic Cracking. 2. Effect of Hydrogen Transfer Characteristics of the Base Cracking Catalysts and Feedstocks*. Industrial & Engineering Chemistry Research, 1999. **38**(10): p. 3854-3859.
81. Dwyer, F.G. and T.F. Degnan, *Chapter 13 Shape Selectivity in Catalytic Cracking*, in *Studies in Surface Science and Catalysis*, S.M. John and M.M. Maurice, Editors. 1993, Elsevier. p. 499-530.
82. de la Puente, G. and U. Sedran, *Evaluation of hydrogen transfer in FCC catalysts. A new approach for cyclohexene as a test reactant*. Chemical Engineering Science, 2000. **55**(4): p. 759-765.

CHAPTER 5

A Response Surface Methodology Study on Fractional Catalytic Pyrolysis of Biomass with FCC Catalyst

5.0. Abstract

A response surface methodology was used to investigate the influence of temperature, weight hourly space velocity (WHSV) and vapor residence time on the fractional catalytic pyrolysis of hybrid poplar wood using FCC catalyst in a 50 mm bubbling fluidized bed reactor. The levels of the independent variables were: temperature (400 - 600 °C), WHSV (1 - 3 h⁻¹), and vapor residence time (3 - 6 s). The Box-Behnken experimental design was used and a total number of 15 experimental runs including 3 center runs were generated. The responses were organic liquid yield, char/coke yield, water yield, CO concentration, CO₂ concentration, H₂ concentration, CH₄ concentration, carbon content, oxygen content, viscosity and pH. The analysis of variance (ANOVA) at 95 % confidence interval was performed with Minitab 16 software and reduced models were generated for the prediction of the responses. The reaction temperature was the most influential significant independent variable on char/coke yield, concentration of non-condensable gases, carbon content, oxygen content, pH and viscosity of the bio-oils. The WHSV was found to be the most important significant independent variable that affected the yield of organic liquid and water. The models for the prediction of the responses with the exception of viscosity were adequate and statistically significant.

5.1. Introduction

In the quest to attain a potential marketplace acceptance of bio-oils from biomass, catalytic pyrolysis technology is being developed as one of the routes to produce high grade bio-oils which are stable, high in energy content, less viscous and less acidic[1, 2]. In the catalytic pyrolysis of biomass, an acid catalyst or zeolite is used to promote deoxygenation and cracking of the primary vapors into hydrocarbons and small oxygenates. However, the yield of the bio-oil reduces as a result of carbon rejection (CO_2 and CO), hydrogen consumption (H_2O) and coke formation in the presence of a catalyst. One of the major research challenges in catalytic pyrolysis is how to increase the yield while improving the quality of the bio-oil.

In order to enhance the catalytic pyrolysis process, the reaction conditions for the production of by-products (coke, CO , H_2O , and other non-condensable hydrocarbon gases) must be controlled since the process does not always use the optimal pathway. The product stream directed by a particular kind of catalyst in catalytic pyrolysis is governed by operating conditions and the composition of the primary vapors (feedstock). The various compounds in primary vapors including anhydrosugars, ketones, aldehydes, carboxylic acids, furfural and alcohols from carbohydrate decomposition [3, 4] as well as methoxylated phenols from lignin decomposition [5] present another challenge in controlling reaction pathways when using monofunctional catalysts.

Studies on the conversion of oxygenated molecules over ZSM-5 catalyst showed that the reaction mechanism for alcohols, carboxylic acids, esters, ketones and aldehydes were different [6-11]. It was reported that the rejection of oxygen was dependent on the type of oxygenated compound. Hydroxyl and methoxyl groups rejected oxygen in the form of water [6, 11], carboxyl groups rejected oxygen as carbon dioxide and water [7] while carbonyl groups rejected oxygen largely as carbon monoxide[12]. Gayubo et al. [13-15] investigated the reactivity and reaction pathways of model bio-oil compounds using zeolite. They also found that alcohols, phenols, aldehydes, ketones and acids reacted

with HZSM-5 catalyst at different temperatures. Alcohols were converted into higher olefins at 250 °C, then to paraffins and aromatics at 350 °C. Acetone was converted to C5+ olefins with less reactivity at temperatures above 350 °C. The acetic acid was first converted to acetone above 400 °C and then to olefins and aromatics. Acetaldehyde, phenol and 2-methoxyphenol were reported to have low reactivity to hydrocarbons with a noticeable deactivation caused by coke deposition.

Generally, the type of catalyst [16-23] and operating conditions such as reaction temperature, vapor residence time and weight hour space velocity (WHSV) [17, 19, 22, 24-42] affect the product distribution from the catalytic pyrolysis of biomass. Milne et al.[24] used a partial factorial Box-Behnken experimental design to study the effects of temperature (400, 475, 550 °C), WHSV (1, 3.5, 6) and volume percent (4, 8, 12) of wood vapor on the characteristics of the liquid yield. They reported that high WHSV increased the hydrocarbon yields and low WHSV increased the formation of CO and CO₂. Maximum yield of hydrocarbons were produced at 500 °C with WHSV of 6 and 4% volume of wood vapor. Another study by Evans and Milne[43] showed that higher reaction severity (lower WHSV or higher temperature) increased the formation of aromatic hydrocarbons and intermediate products (e.g. benzofuran) at lower reaction temperature. The highest organic liquid yield was achieved at 495 °C and WHSV of 4.0. Williams and Nugranad [25] also studied the catalytic pyrolysis of rice husks over ZSM-5 catalyst at 400-600 °C. They reported that the oil yield, coke yield, oxygen content, and molecular weight distribution of the oils decreased with increasing catalyst temperature while the formation of polycyclic aromatic species increased. Lappas et al[27] showed that increase in feed/catalyst ratio resulted in higher fractions of water and gas in the study of biomass pyrolysis using FCC catalyst and ZSM-5 additive in a circulating fluidized bed reactor. In a study by Thring et al.[26], solvolysis lignin was used to produce gasoline range hydrocarbons over HZSM-5 catalyst at 500 °C- 650 °C and weight hourly space velocities of 2.5 -7.5 h⁻¹. The highest liquid yield was achieved with a WHSV of 5 h⁻¹ at 550 °C. Ates et al.[36] found that 500 °C was the optimum temperature in maximizing bio-oil yield from the catalytic pyrolysis of *Euphobia rigida*

and sesame stalk in a fixed-bed reactor using commercial catalysts. In another study by Ates and Isikdag [36], it was reported that maximum oil yield occurred at 600 °C and higher temperatures decreased the oil yield and increased gas yield in the catalytic pyrolysis of corncob with alumina catalyst. Encinar et al[37] worked on the catalytic pyrolysis of exhausted olive oil waste with dolomite and showed that increasing temperature and catalyst amount decreased the liquid yield and increased both the yield and higher heating value of the gases. A study by Carlson et al[31] on the production of green aromatic and olefins from the catalytic fast pyrolysis of wood with ZSM-5 catalyst showed that temperature and WHSV can be used to control the selectivity and yield of aromatics. In another work by Carlson et al[19], they found that coke yield increased and aromatic yield decreased with decrease in catalyst-to-feed ratio in the catalytic fast pyrolysis of cellulose.

The influence of operating conditions such as temperature and WHSV on the product distribution and quality of the bio-oil in the catalytic pyrolysis of biomass have been well documented in the literature as described above. However, most of the work reported focused mainly on ZSM-5 catalyst using the one-factor-at-a-time approach with less emphasis on Y-zeolite based FCC catalyst. The Y-zeolite in comparison to ZSM5 produces lower bio-oil yield and higher amounts of coke in the catalytic pyrolysis of biomass due to its larger pore sizes (7.4µm) and higher BET surface area [16-21, 28, 44-46].

The objective of this paper is to investigate the effect of temperature, vapor residence time and WHSV on the fractional catalytic pyrolysis of hybrid poplar with FCC catalyst using response surface methodology (RMS). The RMS is a statistical modeling technique for multiple regression analysis and is effective for studying complex processes with more than 2 important factors [47-50]. A Box-Behnken design will be used since it offers some advantage in requiring fewer treatment combinations than the central composite design employed in cases involving 3 factors. The operational variables that will be

investigated are as follows: temperature (400, 500, and 600 °C), vapor residence time (3, 4.5, and 6 s) and WHSV (1, 2, and 3 h⁻¹).

5. 2. Material and methods

5.2.1. Biomass Feedstock

Hybrid poplar wood samples were air dried and ground to pass a 1-mm screen in a Wiley mill prior to all experiments. The ultimate composition and calorific value of the wood are shown in Table 2.1

5.2.2. FCC Catalyst

The catalyst used was a commercially available fluid cracking catalysts (FCC) supplied and characterized by BASF Catalysts LLC (Iselin, NJ, USA). The multipoint BET method was used to determine the total surface areas of the various catalysts. The measurements were based on the isothermal adsorption of nitrogen in accordance to the procedure described in ASTM D3663 using a Micrometrics TriStar instrument. The data from the multipoint determination was used to calculate the matrix surface area using the t-plot method. The difference between the BET surface area and the matrix surface was considered to be the zeolite surface area. The characteristics of the FCC catalyst are shown in Table 5.1.

Table 5.1 . Catalytic properties of FCC Catalyst

Catalyst Properties	FCC
Al ₂ O ₃ , wt.%	38.86
RE ₂ O ₃ , wt.%	5.54
BET surface area, m ² /g	516
Zeolite Area (m ² /g)	404
Matrix Area (m ² /g)	112
Micropore Volume, cm ³ /g	0.258
Average Particle size, μm	86

5.2.3. Design of Experiments (DOE)

The RSM was first developed by Box and Wilson[51] and is described as a collection of mathematical and statistical techniques for developing, improving and optimizing processes by finding the true relationship between the response and a set of independent variables[52]. The response surface methodologies consist of sequential experimentation. Before fitting a response surface model, screening and steepest ascent experiments are performed to identify important factors and assess if the main effects can be improved. In this study, 3-factors [temperature (A), WHSV (B), vapor residence time (C)] were identified as important factors that influence the catalytic pyrolysis of biomass. A Box-Behnken design which can be considered as a 3-level incomplete factorial design [53] was used. The Box-Behnken design is a class of rotatable or nearly rotatable second-order design and requires fewer treatment combinations than a central composite design in cases involving 3 factors. A total number of 15 experimental runs including 3 center runs were generated. Table 5.2 shows the factor levels in the natural units and the coded units for each measured response. The responses of interest in the study were organic liquid yield, char/coke yield, water yield, CO concentration, CO₂ concentration, H₂ concentration, CH₄ concentration, carbon content, oxygen content, viscosity and pH (see table 5.2).

A second-order regression model was used to approximate the responses based on a second-order Taylor series approximation of the form below [52]

$$y_i = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \cdots + \beta_k x_{ik} + \beta_{11} x_{i1}^2 + \beta_{22} x_{i2}^2 + \cdots + \beta_{kk} x_{ik}^2 + \beta_{12} x_{i1} x_{i2} + \beta_{13} x_{i1} x_{i3} + \cdots + \beta_{k-1,k} x_{i,k-1} x_{ik} + \epsilon_i$$

$$y_i = \beta_0 + \sum_{j=1}^k \beta_j x_{ij} + \sum_{j=1}^k \beta_{jj} x_{ij}^2 + \sum_{j=1}^{k-1} \sum_{j'=j+1}^k \beta_{jj'} x_{ij} x_{ij'} + \epsilon_i$$

The model above contains the $k + 1$ terms from the strict first-order model, the k pure quadratic (x^2_i) terms, and the $\binom{k}{2}$ two-factor interactions. Therefore, the regression model contains a total of $(k + 1) + k + \binom{k}{2} = \frac{(k+1)(k+2)}{2}$ terms.

This means that for given k value of 3, the regression model contains 10 terms which consist of 4 coefficients for main effects, 3 coefficients for pure quadratic main effects and 3 coefficients for two factor interaction effects. In the equation above, y_i is the response, β_0 is the constant coefficient, β_j , β_{jj} and $\beta_{jj'}$ are the coefficients for the linear, quadratic and interaction effects, x_{ij} and $x_{ij'}$ are the factors and ϵ_i is the error.

5.2.4. Statistical Analysis

The ANOVA analysis of the Box-Behnken design was used to determine the statistically significant terms and also estimate the fitness of the regression models. In order to determine significant second-order models that fit the experimental responses and the independent variables, analysis of variance (ANOVA) was performed at an alpha level of 0.05 using the Minitab 16 software package (Minitab Inc., State College, PA). Letters *A*, *B*, and *C* were used to denote temperature, WHSV and vapor residence time in the models respectively. The model coefficients, *F*-values, significant probabilities and R^2 -values were evaluated. The *F* statistic and the lack-of-fit test were used to examine whether the regression models were adequate to describe the observed data. The probability of the lack-of-fit was required to be insignificant (p value > 0.05) for all the fitted models. For most of the responses, the quadratic model was manually modified by eliminating the insignificant terms to obtain a better model. No transformation was performed in any instance to produce an insignificant lack of fit. The *R*-squared statistics was also analyzed for the percentage variability of the optimization parameter that is explained by the model. Finally, the normal probability plots of the residuals and the plots of the

residuals versus the predicted responses were checked for the adequacy of the model. Contour plots were used to show how a response variable relates to two factors based on a model equation.

5.2.3. Fractional catalytic pyrolysis

The fractional catalytic pyrolysis of hybrid poplar wood with FCC catalyst was conducted in a 50 mm bench scale bubbling fluidized bed reactor (Figure 2.1). The reactor was externally heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC) and the temperatures were controlled and monitored using the OMB-Multiscan 1200 acquisition system (Omega Engineering, Inc.) with TempView 2.1 program. The operational variables investigated were temperature (400, 475, 550 °C), WHSV (1, 2, 3 h⁻¹) and vapor residence time (3, 4.5, 6 s). The biomass was fed continuously for an hour at a rate of 100, 200, and 300 g/h from a feed hopper using a twin-screw feeder into a 100 g of fluidized FCC catalyst. The nitrogen gas flow rate was used to control the vapor residence time. The vapor residence time was defined as the total volume of fluidized catalyst divided by gas flow rate at reactor conditions. The mixture of char, entrained catalyst, gases and vapors that exited the reactor were separated by a hot gas filter maintained at 380 °C. The separated gases and vapors were then passed through two condensers connected in series, an electrostatic precipitator and a coalescing filter.

The non-condensable gases (NCG) were analyzed every 3.25 minutes online using a Varian 490 micro GC (Agilent Technologies, Inc. Santa Clara, CA USA). The micro GC was equipped with two modules, a 10 m Molsieve (MS) 5Å column and a 10 m porous polymer (PPU) column. Each module had a thermal conductivity detector. The MS column was used to analyze hydrogen, methane and carbon monoxide. Carbon dioxide and C₁-C₅ gases were analyzed by the PPU column. The mass of char/coke was determined gravimetrically by weighing the hot gas filter and the reactor before and after each pyrolysis experiment. The total mass of bio oil was determined gravimetrically by weighing the

condensers, electrostatic precipitator and the coalescing filter before and after each experiment. The total mass of the NCG was calculated by difference and the yields expressed in weight percentage of the biomass.

5.2.4. Bio-oil Analysis

The bio-oils were analyzed for carbon and oxygen content on a Thermo Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Cambridge, UK). The pH data were obtained after 15 min stabilization of the mechanically stirred oil. The viscosities of the bio-oils were measured at 40 °C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were equivalent to viscosities determined by the ASTM D445 method. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Karl Fischer titration. Hydranal[®] Composite 5 reagent was used and 50 mL of methanol were used as solvent. About 60-100 mg of oil sample was loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated and the resulting mass recorded.

5.3. Results and Discussion

5.3.1. Summary

The Box-Behnken design, product yields, organic liquid properties and composition of the pyrolysis gases are shown in Table 5.2. The organic liquid yield ranged from 9.72 wt% to 27 wt% and the char/coke yield was from 14.6 wt% to 32.52 wt%. The highest organic liquid yield (27.17 wt.%) was achieved at (500 °C, 3 h⁻¹, 3 s) and the lowest organic liquid yield was produced at (600 °C, 1 h⁻¹, 4.5 s). For char/coke, the highest yield was at (400 °C, 1 h⁻¹, 4.5 s) and the lowest yield occurred at (600 °C, 3 h⁻¹, 4.5 s). The composition of the NCG on weight basis showed that CO centration was highest at (600 °C, 3 h⁻¹, and 4.5 s) and lowest at (400 °C, 2 h⁻¹, 3 s). CO₂ concentration was highest at (400 °C, 3 h⁻¹, 4.5 s) and lowest at (600 °C, 3 h⁻¹, 4.5 s) while H₂ concentration was highest at (600 °C, 1 h⁻¹, 4.5 s) and lowest at (500 °C, 3 h⁻¹, 6 s). In the case of hydrocarbons, CH₄ concentration was highest at (600 °C, 1 h⁻¹, 4.5 s) and lowest at (400 °C, 2 h⁻¹, 6 s). For C₂-C₅, the highest concentration was produced at (500 °C, 3 h⁻¹, 3.0 s) and the lowest occurred at (600 °C, 2 h⁻¹, 3.0 s). The elemental analysis of the bio-oils produced showed that the highest carbon content and the lowest oxygen content was produced at (600 °C, 1 h⁻¹, 4.5 s) and the bio-oil with the lowest carbon content and highest oxygen content was produced at (500 °C, 3 h⁻¹, 3.0 s). The physical properties of the bio-oils also showed that the most acidic but less viscous bio-oil was produced at (400 °C, 2 h⁻¹, 6.0 s) and the most viscous but less acidic bio-oil was produced at (600 °C, 2 h⁻¹, 3.0 s). The results showed that the responses measured were influenced by the various levels of the independent variables (temperature, WHSV and vapor residence time).

Table 5.2. Box-Behnken Experimental design

Design Pattern	A (Temperature) (°C)	B (WHSV) (h ⁻¹)	C (Vapor Residence, s)	Organic (wt.%)	Char (wt.%)	H ₂ O (wt.%)	NCG Composition (w/w %)					Physical property of bio-oil			
							CO	CO ₂	H ₂	CH ₄	C ₂ -C ₅	C	O	Viscosity	pH
-0-	400	2	3.0	23.50	25.18	23.65	50.65	36.38	0.43	4.40	8.14	62.48	31.20	77	2.28
0-+	500	1	6.0	11.87	27.87	28.3	59.69	23.76	0.45	8.36	7.74	67.14	26.45	232	2.70
+0+	600	2	6.0	16.65	16.44	22.16	63.47	18.43	0.97	9.78	7.35	70.65	22.90	320	2.89
000	500	2	4.5	20.91	21.66	23.79	57.83	25.24	0.39	8.23	8.31	63.55	30.86	170	2.62
++0	600	3	4.5	23.32	14.60	22.3	68.88	11.49	0.90	9.44	9.29	64.18	29.35	201	2.85
--0	400	1	4.5	13.89	32.52	28.19	57.00	28.00	0.42	2.90	11.68	63.22	30.53	218	2.31
0+-	500	3	3.0	27.17	17.39	21.57	60.10	21.94	0.32	7.86	9.78	58.88	34.79	102	2.65
-+0	400	3	4.5	24.80	25.00	24.62	52.58	37.20	0.32	3.68	6.22	61.92	31.53	75	2.23
+0-	600	2	3.0	19.40	15.10	23.91	63.79	16.70	0.96	9.74	8.81	67.87	25.75	545	3.03
-0+	400	2	6.0	19.53	28.17	24.6	51.00	36.33	0.32	2.65	9.70	62.54	30.96	61	2.20
000	500	2	4.5	19.90	21.28	25.64	57.66	24.96	0.38	8.36	8.64	63.68	29.85	145	2.57
000	500	2	4.5	21.50	20.90	23.33	58.50	24.00	0.39	8.50	8.61	63.55	30.06	155	2.61
+ -0	600	1	4.5	9.72	19.90	25.52	68.50	11.50	1.15	9.91	8.94	74.84	18.78	419	2.85
0--	500	1	3.0	12.19	23.58	26.03	60.00	23.58	0.40	7.72	8.30	66.13	26.51	403	2.66
0++	500	3	6.0	18.98	20.14	24.7	59.31	24.86	0.29	7.83	7.71	61.63	32.07	144	2.49
<i>Repeated runs</i>															
000	500	2	4.5	20.12	21.83	25.54									
000	500	2	4.5	21.25	21.04	25.03									

5.3.2. Organic liquid production

The analysis of variance at 95% confidence level (Table 5.3) showed that the reduced model below (Equation 1) for the organic liquid yield was significant, adequate and explained most of the variability in the data obtained.

$$\text{Organic liquid yield} = 20.61 - 1.58 A + 5.83 B - 1.9 C - 2.53 B^2 - 0.69 C^2 + 0.37 AB - 1.97 BC \quad (1)$$

For a reliable model, the experimental data must be predicted with reasonable accuracy as shown in Figure 5.1. The high R^2 value of 0.99 indicated a good fit and the model accounted for more than 99% of the observed variability. The statistically significant F -value for the regression model (p -value less than $\alpha=0.05$) and the statistically insignificant lack-of-fit (p -value > 0.05) further justified the adequacy of the model. This suggests that the organic liquid yield depends on at least one of the factors. The individual t -tests indicated that the coefficients of the main effects of A , B , C and the second-orders (B^2 and C^2) were significant (p -value < 0.001). The coefficients of the interaction terms (AB and BC) were also significant. The normal probability plots of the residuals and the plots of the residuals versus the predicted response further confirmed the adequacy of the model.

Table 5.3. Analysis of Variance Table for Organic liquid yield at 95% confidence level

Term	Sum of squares	DF	Mean of squares	F value	Prob > F
model	367.5	7	52.5	116.9	0.0001 ^a
A	19.9	1	19.9	44.4	0.000 ^a
B	271.4	1	271.4	604.1	0.000 ^a
C	28.9	1	28.9	64.53	0.000 ^a
B^2	27.8	1	26.9	60.0	0.000 ^a
C^2	2.0	1	2.0	4.45	0.000 ^a
AB	1.8	1	1.8	4.03	0.064 ^b
BC	15.5	1	15.5	34.5	0.076 ^b
Lack- of- fit	2.1	5	0.41	0.85	0.577
Pure error	2.0	4	2.0		
Corrected total	371.6	16			
$R^2=0.989$, adj $R^2=0.981$, pred $R^2=0.953$ RMSE = 0.670, Mean = 19.1					

^a significant term. ^b Taken as significant term

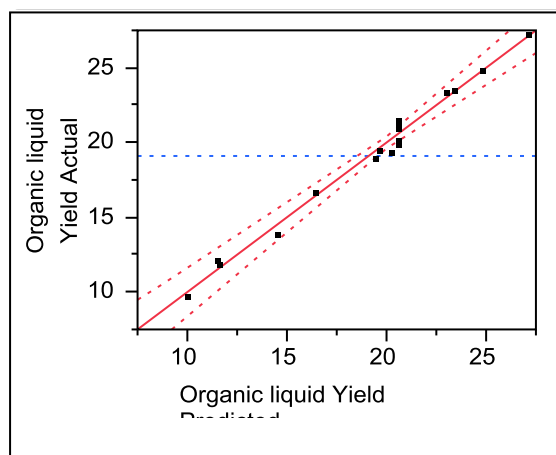


Figure 5.1. Plot of actual yield versus predicted yield of organic liquid

In the organic liquid model (Equation 1), the negative coefficients of A , B^2 , C^2 and BC imply that when these parameters increase the organic liquid yield decreases. Likewise, the positive coefficients of B and AB indicate that the organic liquid yield increases with increase in these independent variables. Hence, increase in temperature and vapor residence time decreases the organic liquid yield. Conversely, a higher level of WHSV increases the organic liquid yield and a lower level of WHSV decreases the organic liquid yield. From the model, WHSV had both the largest positive linear term coefficient and the largest negative quadratic term coefficient. This suggests that WHSV was the most important factor that significantly affected the organic liquid yield.

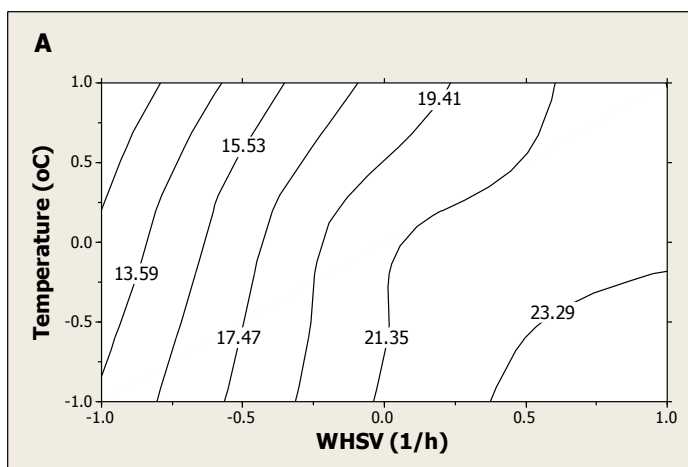


Figure 5.2a. Contour Plot of temperature versus WHSV in coded units showing interaction effect on the organic liquid yield.

The contour plot (Figure 5.2a) suggests that higher organic liquid yields are achievable at higher WHSV levels and at low to moderate temperatures (400 -500 °C). The higher temperatures and lower WHSV levels showed lower organic liquid yields. In the catalytic pyrolysis of biomass, primary organic vapors are produced first before they are catalytically cracked by diffusion into the catalyst pore and adsorption on to the active sites. As a result, the yield of the liquid products, water, coke and light gases are dependent on the number of molecules that react per active site per unit time, the rate of conversion of the primary vapors, the rate of desorption of the formed product as well as temperature. The decrease in the organic liquid yield at higher reaction temperatures suggests that the primary vapors underwent extensive cracking. It is also worth noting that the highest organic liquid was produced at 500 °C, with a higher WHSV (3 h^{-1}) and a lower vapor residence time (3 s). It appeared that at 500 °C, the devolatilization of the biomass into primary vapors was enhanced and the use of lower vapor residence time prevented extensive cracking of the primary vapors. Also it is possible that at WHSV of 3 h^{-1} , the catalyst reached a saturation state due to high concentration of primary vapors. Thus, some of the primary vapors escaped catalytic cracking or experienced less cracking severity and

contributed to higher organic liquid yield. The lowest organic liquid yield produced at 600 °C, WHSV of 1 h⁻¹ and vapor residence time of 4.5 s was attributed to severe cracking of the primary vapors. At such high temperature and low WHSV (600 °C, 1 h⁻¹, 4.5 s), the reaction severity is high and extensive cracking of the vapors is favored, hence lower organic liquid yield is produced. The contour plot of WHSV versus vapor residence time (Figure 5.2b) also suggests that shorter reaction time is essential in producing higher organic liquid yields. At shorter residence time, there is reduced contact time between the catalyst and the primary vapors. Thus, the vapors suffer less thermal/catalytic cracking. However, the organic liquid yield at lower WHSV level was not influenced by the vapor residence time. This means that the reaction at the lower WHSV was very rapid and kinetically controlled; whereas at the higher WHSV, the reaction appeared to be mass transfer controlled and catalyst surface appeared to be saturated.

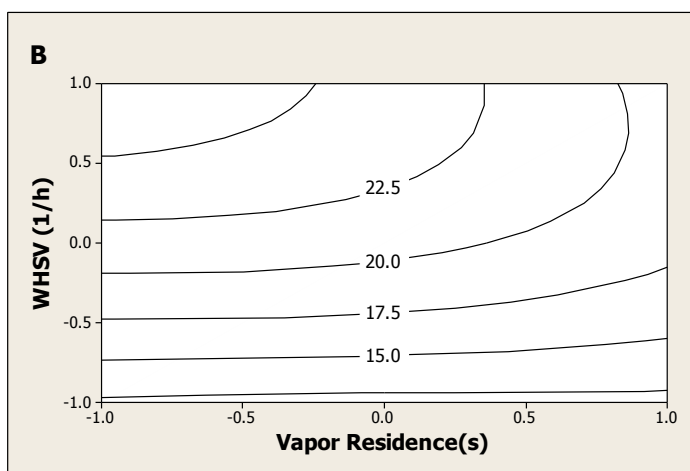


Figure 5.2b. Contour Plot of WHSV versus vapor residence time in coded units showing interaction effect on the organic liquid yield.

5.3.3. Char/Coke Production

The catalytic pyrolysis of the hybrid poplar wood with FCC catalyst produced char and coke. The char was mainly from the pyrolysis of the biomass and the coke which formed on the catalyst surface

was primarily produced through the catalytic cracking of the vapors. In this paper, the char and the spent catalyst were mixed together in such a way that the determination of the separate yield for char and coke was difficult. Hence, the effect of the independent variables was reported on the combined yield (char/coke). The reduced model for the char/coke yield (Equation 2) was significant at 95% confidence level as shown by the analysis of variance in Table 5.4.

$$\text{Char/coke yield} = 21.29 - 5.60 A - 3.34 B + 1.42 C + 1.34 B^2 + 0.56 AB \quad (2)$$

From the ANOVA table, the overall *F*-test for the model was significant (*p*-value <0.001) and the *p*-value for the lack-of-fit was insignificant. Hence, the model was adequate and provided enough statistical evidence that at least one of the coefficients is not zero.

Table 5.4. Analysis of Variance Table for Char/Coke yield with 95% of confidence level

Term	Sum of squares	DF	Mean of squares	F value	Prob > F
model	365.55	5	73.11	185.20	0.000 ^a
A	251.22	1	251.22	636.37	0.000 ^a
B	89.38	1	89.38	226.41	0.000 ^a
C	16.16	1	16.16	40.93	0.000 ^a
B ²	7.56	1	7.56	19.15	0.001 ^a
AB	1.23	1	1.23	3.12	0.105
Lack- of- fit	3.71	7	0.53	3.37	0.129
Pure error	0.63	4	0.16		
Corrected total	369.89	16			
R ² =0.988, adj R ² = 0.983, pred R ² =0.963 RMSE = 0.628, Mean = 21.92					

^a significant term

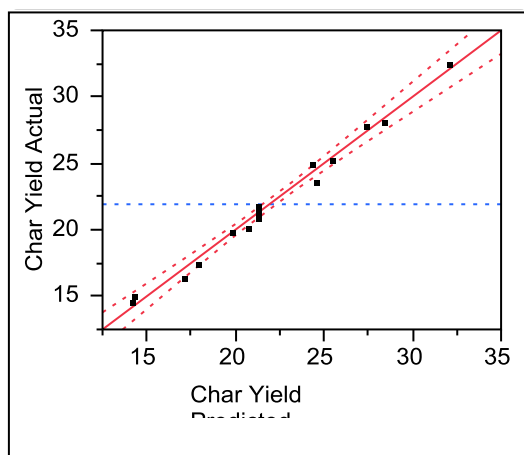


Figure 5.3. Plot of actual yield versus predicted yield for char/coke

The plot of actual yield versus predicted yields in figure 4 showed that the model had a good fit. The R^2 value accounted for more than 98% of the observed variability and the adjusted R^2_{adj} was 0.96. Examination of the plot of residuals against the predicted values suggested that no biases were present. The coefficients of the main effects of A , B , C and B^2 in the model were all significant (p -value < 0.001). However, the coefficient of the interaction term AB in the model was insignificant.

From the model, temperature (A) had the largest negative regression coefficient followed by WHSV (B). The vapor residence time (C) and second-order term (B^2) had about the same positive regression coefficient. For char/coke yield, temperature appeared to be the most important factor that significantly affected the response. The main effects of the independent variables can be inferred from the coefficients of the linear regression terms in the model. Increase in temperature and WHSV decreased the char/coke yield whereas increase in vapor residence time increased the char/coke yield. The contour plot (Figure 5.4) showed that char/coke formation were enhanced at lower temperatures and lower WHSV and vice versa. It is also important to mention that, the analysis of the interaction plot between temperature and WHSV (Figure not shown) appeared to suggest that for a constant

temperature, the decrease in char/coke yield with increase in WHSV was stronger for values between 1 and 2 h^{-1} . The effect of WHSV on the char yield was weaker for values above 2 h^{-1} .

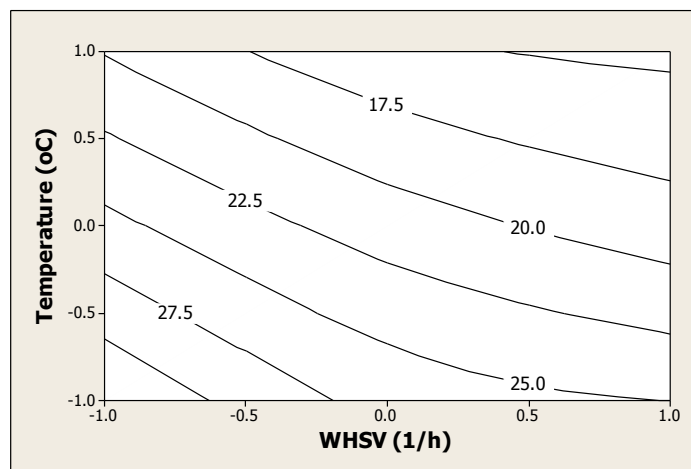


Figure 5.4 . Contour Plot of temperature versus WHSV in coded units showing interaction effect on the char/coke yield.

The reduction of coke production in the catalytic pyrolysis of biomass with FCC catalyst is of great interest since the FCC catalyst has a higher tendency in promoting coke forming reactions [54]. The coke is formed through extensive dehydration and dehydrogenation of polycyclic aromatics compounds [19]. The active ingredient (Y-zeolite) in the FCC catalyst has been shown to promote such reactions compared to medium pore size catalyst [18-21, 44, 46, 54]. The Y-zeolite is made up of a three dimensional faujasite structure, 1.2 -1.3 nm supercage, 12-ring channel system [19, 21, 44] and contains strong acid sites (mainly Bronsted) [55] favorable for cracking and hydrogen transfer reactions [56]. Aho et al. [18] studied the catalytic cracking of biomass at 450°C with the proton form of Y-zeolite and reported char/coke yield of 23.2 wt.%. Zhang et al. [57] also reported char/coke yields between 26-34 wt.% in the catalytic cracking of corn cobs in a fluidized bed at 550°C with 30% each of fresh and spent FCC catalyst. A study by William et al.[21] showed that the Y-zeolite used for catalytic cracking of biomass in a fluidized bed reactor at 500°C produced char/coke yield of 36.6 wt%. Adam et al. [16]

reported as high as 42 wt.% of coke yield for an equilibrium FCC catalyst when used at 500 °C in a fixed bed catalytic upgrading of biomass derived fast pyrolysis vapors.

From the experimental data in this study, the char/coke yield ranged from 14.60 wt.% to 32.52 wt.% with the highest and lowest yields occurring at (400 °C, 1 h⁻¹, 4.5 s) and (600 °C, 3 h⁻¹, 4.5 s) respectfully. The results suggest that the independent variables influenced the production of char and the formation of coke on the catalyst. The increase in char/coke yield at the lower WHSV could be attributed to the enhancement in dehydration and dehydrogenation of polycyclic aromatic compounds which lead to coke formation. The effect of WHSV on coke formation in the study is in agreement with other studies [28, 58, 59] where increase in catalyst/feed ratio increased coke yields and vice versa. Also, the increase in char/coke yield with increase in vapor residence time was attributed to the promotion of charring and coke forming reactions which seem to be favored at longer vapor residence times.

Furthermore, at higher temperatures, potential coke precursors such as phenolic compounds and heavy molecular weight oxygenated compounds [15, 41, 60] could decompose and result in lower concentrations which prevent extensive coking. Similar result was reported by Williams and Nugranad [25] in the study of catalytic pyrolysis of rice husks. They found that coke formation on the catalyst decreased as the temperature increased from 400 °C to 600 °C. Temperature also affects char formation. At a higher temperature, the char yield could either reduce as a result of the enhancement in devolatilization of the biomass or decomposition through secondary reactions. Studies show that during pyrolysis of wood, the hemicellulose component breaks down first between 200 to 260 °C, cellulose follows at 240 to 350 °C, with lignin being the last component to decompose over a wider temperature range of 280 to 500 °C [61-63]. Hence, at the lower temperature (400 °C), there would be an incomplete thermal degradation of the lignin component contributing to a relatively higher char yield. However, at

the higher temperature (600 °C), most of the lignin fraction would have degraded to produce lower char yields and also the remaining char in the reactor could have possibly undergone gasification reactions and as a result lower the char content [64]. It can therefore be concluded that, to minimize char/coke yield, the catalytic pyrolysis with FCC catalyst should be performed at higher temperature, higher WHSV and lower vapor residence time.

5.3.4. Non-condensable gas (NCG) production.

The models for the concentrations of H₂, CH₄, CO and CO₂ in Equations 3 - 6 were all statistically significant at 95 % confidence level. However, the model for the concentration of C₂-C₅ hydrocarbons was insignificant and hence was not considered. The ANOVA analysis in Table 5.5 showed that the models had significant *F*-test and insignificant lack-of-fit test. The plots of actual yield versus predicted yields in Figure 5.5 showed that the model fit well to the experimental data. All the *R*² values were high and accounted for 97% of the observed variability. Further adequacy of the models was checked by analysis of the residuals and they appeared adequate for predicting the responses. Below are the models for H₂, CH₄, CO and CO₂.

$$\text{H}_2 \text{ concentration} = 0.37 + 0.31 A - 0.074 B + 0.31 A^2 - AB - (3)$$

$$\text{CH}_4 \text{ concentration} = 8.12 + 3.16 A - 0.14 C - 1.56 A^2 + 0.45 AC - (4)$$

$$\text{CO concentration} = 58.36 + 6.68 A - 0.54 B - 0.13 C + 3.1 B^2 - 1.41 C^2 + 1.2 AB - (5)$$

$$\text{CO}_2 \text{ concentration} = 24.96 - 9.97 A + 1.08 B + 0.6 C - 3.08 B^2 - 1.83 C^2 + 2.30 AB - (6)$$

The individual t-test indicated that the coefficients of *A*, *B* and *A*² in the H₂ concentration model were significant and the interaction term *AB* was insignificant. For CH₄ concentration, the coefficients of *A* and *A*² were significant and that of *C* and *AC* were insignificant. The coefficients of *A*, *B*², *C*² and *AB* were significant and that of *B* and *C* were insignificant in the CO concentration model. In the CO₂ model,

A , B^2 and AB were significant terms and B , C and C^2 was insignificant. Temperature was the most influential factor that significantly affected the composition of the non-condensable gases. Increase in the reaction temperature decreased the concentration CO_2 and increased the concentration of H_2 , CH_4 and CO . The increase in WHSV increased CO_2 and decreased H_2 and CO formation. The formation of CH_4 and $\text{C}_2\text{-C}_5$ were not affected significantly by WHSV. The vapor residence time appeared not to influence the concentration of gases significantly. The second-order term of temperature (A^2) had a positive effect on H_2 and a negative effect on CH_4 . The quadratic term of WHSV (B^2) influenced CO positively and CO_2 negatively. The quadratic term of the vapor residence time (C^2) showed a stronger influence than its linear (C) effect on CO and CO_2 .

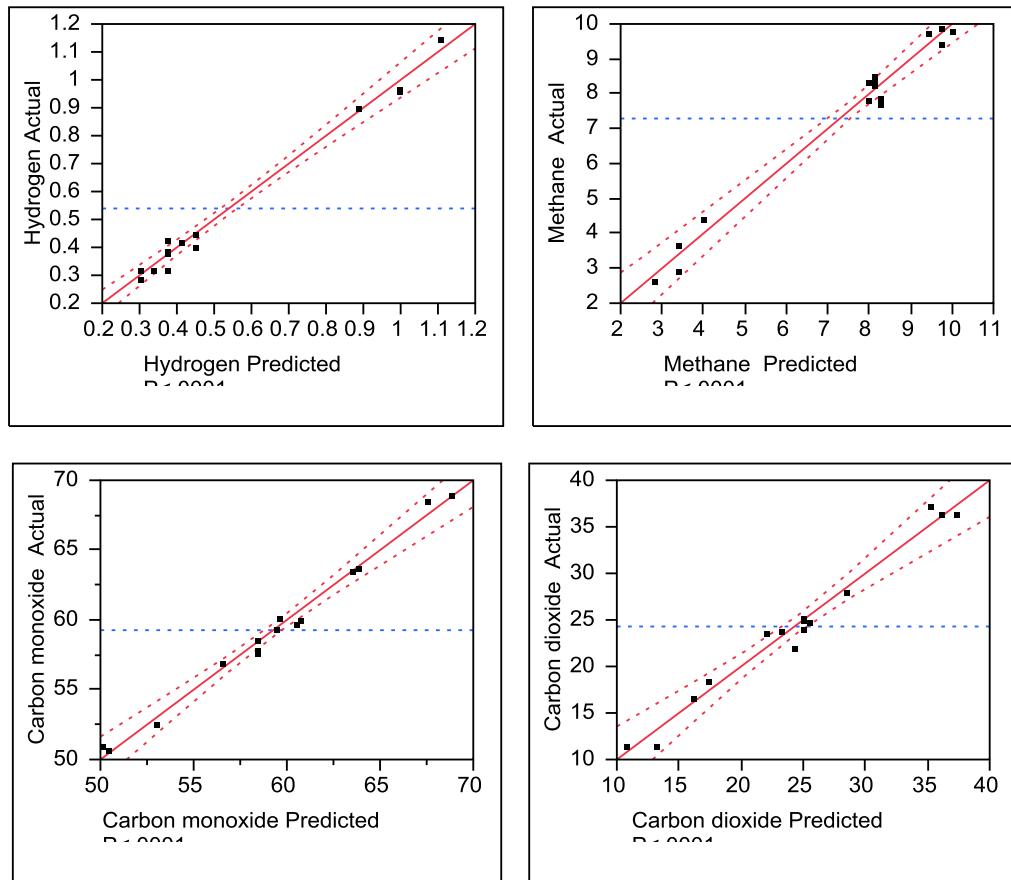


Figure 5.5. Plot of actual yield versus predicted yield for concentrations of H_2 , CH_4 , CO and CO_2

Table 5.5. Analysis of Variance Table for the concentrations of H₂, CH₄, CO and CO₂ with 95% of confidence level

Source	Sum of Squares	DF	Mean Square	F value	Prob > F
Hydrogen Concentration (% w/w)					
Model	1.18	4	0.30	213.9	0.000 ^a
A	0.78	1	0.78	561.2	0.000 ^a
B	0.043	1	0.043	31.5	0.000 ^a
A ²	0.36	1	0.36	258.9	0.000 ^a
AB	0.0056	1	0.0056	4.07	0.071
Lack of fit	0.006	4	0.0015	1.13	0.424
Pure error	0.008	6	0.0013		
Total	1.195	14			
R ² =0.988, adj R ² = 0.984, pred R ² =0.968 RMSE = 0.037, Mean = 0.54					
Methane concentration (% w/w)					
Model	89.67	4	22.41	136.7	0.000 ^a
A	79.63	1	79.63	485.5	0.000 ^a
C	0.15	1	0.15	0.92	0.360
A ²	9.09	1	9.09	55.42	0.000 ^a
AC	0.80	1	0.80	4.88	0.052
Lack of fit	1.04	4	0.26	2.59	0.143
Pure error	0.60	6	0.10		
Total	91.31	14			
R ² =0.982, adj R ² = 0.975, pred R ² =0.947 RMSE = 0.405, Mean = 7.29					
Carbon Monoxide Concentration (% w/w)					
Model	410.5	6	68.4	124.1	0.000 ^a
A	356.6	1	356.6	646.8	0.000 ^a
B	2.33	1	2.33	4.23	0.074
C	0.14	1	0.14	0.26	0.624
B ²	38.24	1	35.68	64.72	0.000 ^a
C ²	7.42	1	7.42	13.45	0.000 ^a
AB	5.76	1	5.76	10.45	0.012 ^a
Lack of fit	4.02	6	0.67	3.39	0.245
Pure error	0.39	2	0.20		
Total	414.88	14			
R ² =0.989, adj R ² = 0.981, pred R ² =0.942 RMSE = 0.743, Mean = 59.26					
Carbon dioxide concentration (% w/w)					
Model	880.2	6	146.7	62.48	0.000 ^a
A	795.8	1	795.8	338.91	0.000 ^a
B	9.35	1	9.35	3.98	0.081 ^b
C	2.86	1	2.86	1.22	0.302
B ²	38.58	1	35.32	15.04	0.005 ^a
C ²	12.42	1	12.42	5.29	0.050
AB	21.21	1	21.21	9.03	0.017 ^a
Lack of fit	17.94	6	2.99	7.07	0.129
Pure error	0.85	2	0.42		
Total	899.0	14			
R ² =0.979, adj R ² = 0.963, pred R ² =0.874 RMSE = 1.53, Mean = 24.29					

^a significant term ^b taken as significant term

The non-condensable gases produced in catalytic pyrolysis are formed through a series of complicated reactions involving molecular species and intermediate radicals during the thermal decomposition of the building blocks of biomass (cellulose, hemicellulose and lignin) and the catalytic cracking of the primary vapors (e.g. levoglucosan, anhydrosugars, ketones, aldehydes, carboxylic acids, furfural methoxylated phenolics, etc.). Literature reports on some of the reaction pathways in the thermal degradation of woody biomass during pyrolysis [61, 65-73] and mechanisms in the catalytic cracking of oxygenated compounds [23]. Based on the gaseous products, it can be generalized that the CO, CO₂, H₂, CH₄ and light hydrocarbons produced in the process were generated by dehydration, decarboxylation, decarbonylation, demethoxylation, dehydrogenation, water-gas shift (WGS) and steam reforming of dehydrated species. From the data, temperature and WHSV strongly affected these reactions.

The interaction effect of temperature and WHSV shown in the contour plots (Figure 5.6) indicates that H₂ concentration was higher at a higher temperature and lower WHSV and lower at a higher WHSV and a lower temperature. In the contour plot (Figure 5.6) for CO, it can be seen that at a lower temperature (400 °C), the use of a lower WHSV (1 h⁻¹) produced higher amounts of CO than the use of a higher WHSV (3 h⁻¹). However, at a higher temperature (600 °C), the concentration of CO was higher at both low WHSV (1 h⁻¹) and high WHSV (3 h⁻¹). This suggests that cracking of the primary vapors was predominant at higher reaction temperature and contributed to the increased concentration of CO. It is known that the degradation of lignin increases the evolution of CO, CH₄ and H₂ [61, 64]. Other studies have reported that the formation of CO is highly influenced by secondary reactions of low molecular weight products (ring-opened intermediates) at higher temperatures [72, 73]. This in part may explain why the concentrations of CO were higher at 600 °C. Also, possible occurrence of char decomposition or reactions of char/coke with CO₂ (Boudouard reaction) at 600 °C could have contributed to the increased concentration of CO. In a study by Westerhof et al.[74] on the

conventional pyrolysis of pine wood using sand, they showed that increase in pyrolysis temperature increased the concentrations of CO, CH₄ and H₂ but decreased the concentration of CO₂. This suggests that the evolution of CO, CH₄ and H₂ in the pyrolysis of biomass can be due to thermal or catalytic reactions.

Additionally, it can be seen that higher concentrations of CO₂ was produced at a higher WHSV and a lower temperature whereas lower CO₂ concentrations occurred at a higher temperature with both high and low WHSV. The formation of CO₂ is reported to be produced primarily in the early stage reactions of cellulose[73] and from the decarboxylation reaction of O-acetyl groups linked to the xylan chain [72, 74]. The lower concentration of CO₂ suggests that reactions of the primary vapors with the FCC catalyst did not follow decarboxylation pathways. For CH₄, the interaction plot showed that at a lower temperature, increase in vapor residence time decreased the concentration. However, the vapor residence time did not have much effect on the concentration at higher temperatures. The significant increase in the concentration of CH₄ with increasing temperature was attributed to cracking of the vapors. Interestingly, none of the conditions had any significant effect on the C₂-C₅ concentration. However, the data showed that increase in temperature from 400 °C to 500 °C and vapor residence time from 3 to 4.5 s did not affect the concentration. Conversely, above 500 °C and at a vapor residence time of 4.5 s, the concentration decreased. On the other hand, the increase in WHSV above 1 h⁻¹ decreased the C₂-C₅ concentration through a minimum at 2 h⁻¹ and then increased at 3 h⁻¹.

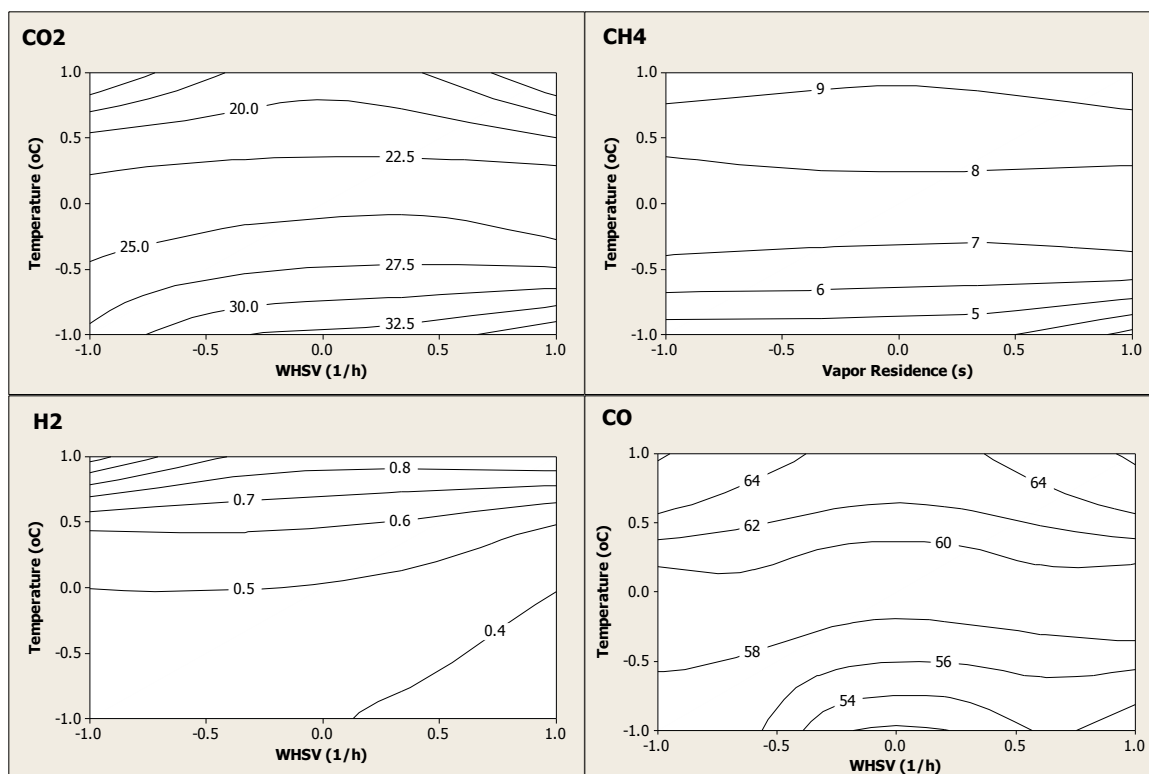


Figure 5.6. Contour Plot showing interaction effect of AB on CO₂, H₂, CO, and AC on CH₄ concentrations

5.3.5. Water production

The statistical analysis in Table 5.6 on the yield of H₂O formed during the catalytic pyrolysis with FCC catalyst showed that the coefficients of A , B and B^2 were significant. The reduced model had relatively lower R^2 and adjusted R^2 values. The model accounted for over 80 % of the observed variability. The lack-of-fit was insignificant and the overall F -test indicated a significant model. The yield of water can be predicted with the model in equation 7.

$$\text{H}_2\text{O yield} = 23.52 - 1.02 A - 1.98 B + 1.51 B^2 - (7)$$

The weight hourly space velocity was the most influential variable that affected the yield of water. The coefficient of the main effects indicated that the increase in WHSV and temperature decreased the formation of H₂O. The effect of vapor residence time was insignificant. However, the experimental data showed that increase in vapor residence time promoted the formation of water. The quadratic term of

WHSV also had a positive effect on the yield of H₂O. The H₂O produced during catalytic pyrolysis of biomass is primarily from dehydration. As can be seen from the results, dehydration reactions were less favorable at higher temperatures and predominant at lower temperatures. Additionally, higher WHSV decreased such reactions. It can be inferred that, at lower WHSV and higher temperature, deoxygenation of the primary vapors in the form of H₂O was not a preferred route. It could also be that water gas-shift reaction was enhanced at a higher temperature and a lower WHSV. The analysis on the composition of the non-condensable gases supports this explanation because the rejection of oxygen in the form of CO was enhanced over CO₂ at those conditions. A study by William and Horne[75] also found that the rejection of oxygen as H₂O was favored at lower temperature (400 °C) while the removal of oxygen as CO and CO₂ were the main deoxygenation routes at higher catalyst temperature (550 °C). The reaction pathways (decarboxylation, decarbonylation and dehydration) for deoxygenation of the primary vapors in catalytic pyrolysis of biomass is of great importance since it has significant effects on the yield of the bio-oil produced. Complete decarboxylation reaction would be the best route for deoxygenation of the vapors because less carbon will be used to reject the oxygen and hydrogen would be conserved, hence higher yield of liquid product would be produced. In decarbonylation, more carbon is utilized for the removal of the oxygen and as a result decreases the oil yield. Also, dehydration reactions may not be preferred since it is accompanied with coke formation.

Table 5.6. Analysis of Variance Table for water yield with 95% of confidence level

Term	Sum of squares	DF	Mean of squares	F value	Prob > F
Model	49.43	3	16.48	18.03	0.000 ^a
A	8.34	1	8.34	9.13	0.010 ^a
B	31.40	1	31.40	34.36	0.000 ^a
B ²	9.68	1	9.68	10.59	0.006 ^a
Lack- of- fit	2.08	5	0.42	0.34	0.876
Pure error	9.81	8	1.23		
Corrected total	61.31	16			
R ² =0.806, adj R ² = 0.765					

^a significant term.

5.3.6. Carbon and Oxygen content of the bio-oil

The effect of temperature, WHSV and vapor residence time on the carbon and oxygen content of the bio-oil were investigated. The analysis of variance in Table 5.7 showed that the models generated in Equations (8) and (9) were significant and they fit the experimental results well.

$$\text{Carbon content} = 63.60 + 3.42 A - 3.1 B + 0.83 C + 2.53 A^2 - 0.15 C^2 - 2.34 AB + 0.68 AC + 0.44 BC \quad (8)$$

$$\text{Oxygen content} = 30.1 - 3.43 A + 3.18 B - 0.73 C - 2.46 A^2 + 2.40 AB - 0.65 AC - 0.67 BC \quad (9)$$

The plots of actual versus predicted for carbon and oxygen content (Figure 5.7) indicated also that the models fit well. The R^2 values showed that the models accounted for 98 % of the observed variability. The adjusted R^2 values indicated that the models were well-specified. The models were found to be adequate for prediction within the range of variable used in the study. They had insignificant lack-of-fit and significant overall F -test. The terms with significant coefficients in the models for carbon and oxygen content were A , B , C , A^2 , AB , AC , and BC . Temperature and WHSV were found to be the most important independent variables. The increase in temperature increased the carbon and decreased the oxygen content. However, the increase in WHSV decreased the carbon content and increased the oxygen content of the bio-oil. For vapor residence time, the increase resulted in a decrease in oxygen and increase in carbon content.

The contour plots (Figure 5.8a and 5.8b) indicated that the carbon content of the bio-oil was higher at a higher temperature and a lower WHSV and was lower at higher WHSV and a lower temperature. For a constant temperature, increasing WHSV decreased the carbon content of the bio-oil. However, the effect of WHSV was greater at a higher temperature than at a lower temperature. In the case of oxygen, the highest oxygen content was in the region of higher WHSV and low to moderate temperatures. The increase in WHSV at constant temperature indicated increase in oxygen content. Similarly, the effect of WHSV on the oxygen content was greater at a higher temperature. From the results, it can be inferred that the removal of oxygen was higher at higher temperatures and lower

WHSV due to extensive cracking. The gas composition analysis showed that decarbonylation which was identified as the main route for the removal of oxygen by the FCC catalyst was more favorable at lower WHSV and higher temperatures. It is important to note that regardless of the temperature, higher WHSV decreased the carbon content and increased oxygen content. Additionally, the interaction between WHSV and vapor residence time also indicated that at a constant vapor residence time, the increase in WHSV decreased the carbon content and increased the oxygen content. This is because at higher WHSV, the vapors were less cracked and as result the rejection of oxygen from the primary vapors was ineffective.

The contour plot for temperature and vapor residence time shows that the carbon content increased and the oxygen content decreased with increasing vapor residence time. This can be explained by the fact that at a higher residence time, the contact time between the primary vapors and the catalyst was relatively longer causing the vapors to experience extensive catalytic cracking which enhanced the rejection of oxygen. Moreover, at a lower temperature, the effect of the vapor residence time was negligible. However, at a higher temperature, the vapor residence had a profound effect on the carbon and oxygen content. This is because at such conditions, extensive cracking of the vapors are favored resulting in a decrease in oxygen and subsequent increase in carbon content of the bio-oil.

From the study, it can be concluded that, the catalytic pyrolysis with FCC catalyst must be conducted at higher temperatures ($> 550\text{ }^{\circ}\text{C}$) and lower WHSV (≤ 2) to produce bio-oil high in carbon and low in oxygen content. However, it should be noted that catalytic pyrolysis at lower temperatures (e.g $400\text{ }^{\circ}\text{C}$) with high WHSV and shorter contact times may not significantly increase the carbon or decrease the oxygen content of the bio-oil.

Table 5.7. Analysis of Variance Table for carbon and oxygen content with 95% of confidence level

Source	Sum of Squares	DF	Mean Square	F value	Prob > F
Carbon content (% w/w)					
Model	222.6	8	27.8	776.0	0.000 ^a
A	93.7	1	93.7	2613.1	0.000 ^a
B	76.4	1	76.4	2130.1	0.000 ^a
C	5.4	1	5.4	151.8	0.000 ^a
A ²	22.2	1	22.2	618.2	0.000 ^a
C ²	0.09	1	0.09	2.4	0.173
AB	21.9	1	21.9	610.8	0.000 ^a
AC	1.9	1	1.9	51.6	0.000 ^a
BC	0.8	1	0.8	21.1	0.004 ^a
Lack of fit	0.20	4	0.051	9.05	0.102
Pure error	0.01	2	0.006		
Total	222.8	14			
R ² =0.999, adj R ² = 0.9974, pred R ² =0.990, RMSE = 0.189, Mean = 64.82					
Oxygen Content (% w/w)					
Model	228.5	7	32.64	153.87	0.000 ^a
A	94.11	1	94.11	443.72	0.000 ^a
B	81.09	1	81.01	382.30	0.000 ^a
C	4.31	1	4.31	20.31	0.003 ^a
A ²	22.58	1	22.58	106.45	0.000 ^a
AB	22.89	1	22.89	107.94	0.000 ^a
AC	1.70	1	1.70	8.03	0.025 ^a
BC	1.77	1	1.77	8.34	0.023 ^a
Lack of fit	0.92	5	0.18	0.65	0.700
Pure error	0.57	2	0.28		
Total	229.95	14			
R ² =0.994, adj R ² = 0.987, pred R ² =0.969, RMSE = 0.406, Mean = 28.77					

^a significant term.

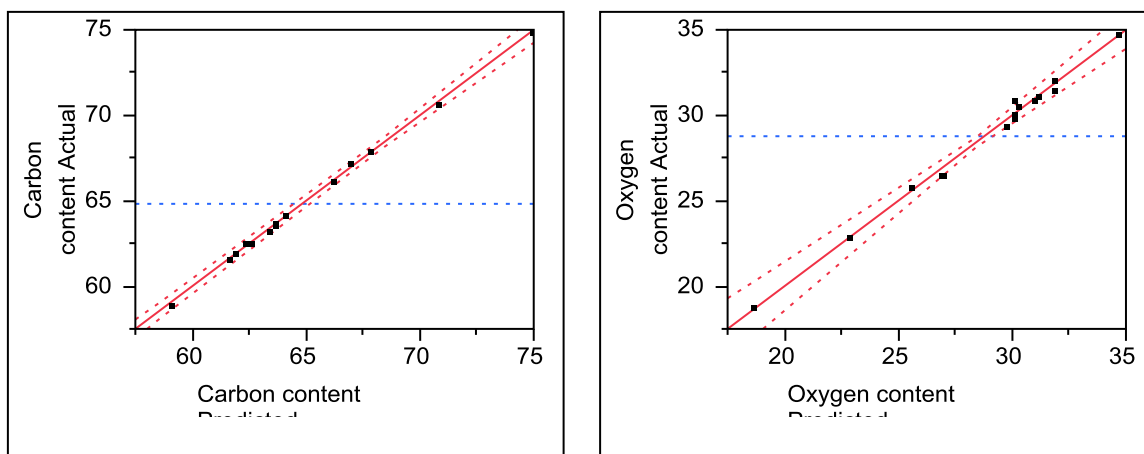


Figure 5.7. Plot of actual yield versus predicted for carbon and oxygen content of the bio-oil

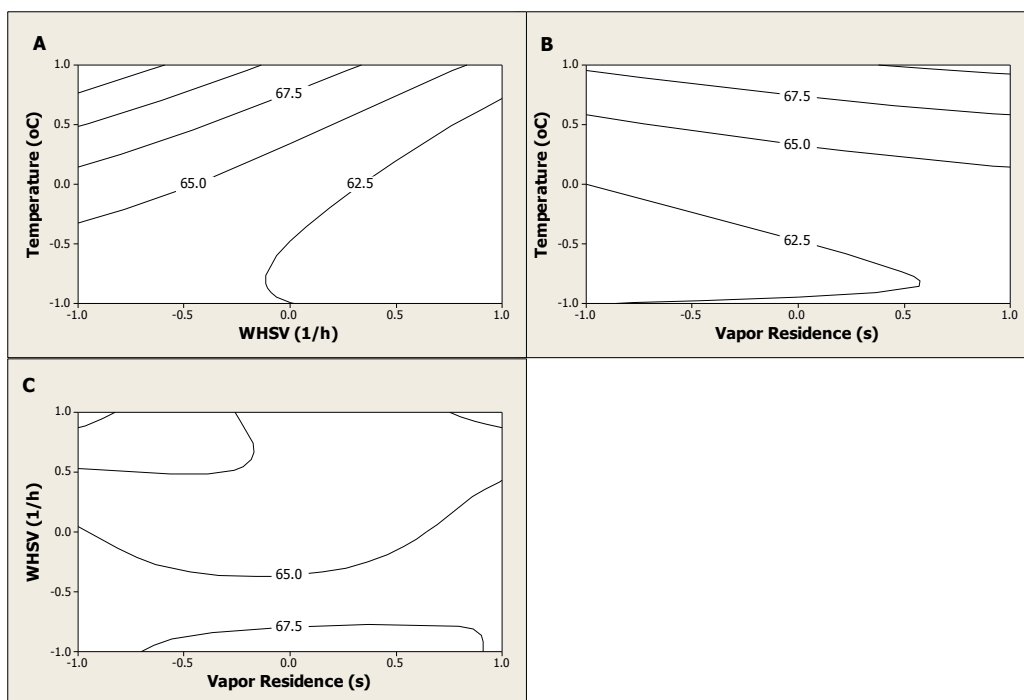


Figure 5.8a. Plot of actual yield versus predicted for carbon and oxygen content of the bio-oil

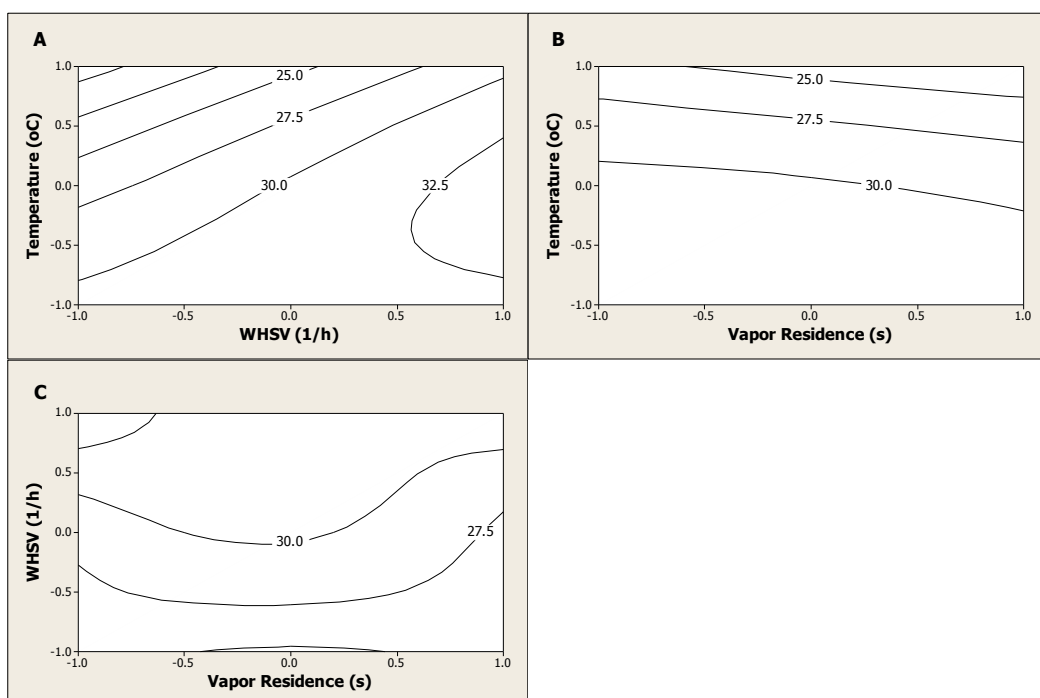


Figure 5.8b. Plot of actual yield versus predicted for carbon and oxygen content of the bio-oil

5.3.6. pH and viscosity of the bio-oil

The experimental data showed that all the bio-oils produced with the FCC catalyst had acidic pH. The pH values of the bio-oils ranged from 2.20 to 3.05 depending on the levels of the independent variables. The analysis of variance at 95% confidence level showed that the regression model was significant (Table 5.8). The linear coefficients of *A*, *B*, *C* and the interaction coefficient of *BC* were significant. Temperature had a positive effect whiles WHSV and vapor residence time had negative effects on the pH values. The predicted response fit well with the experimental data and the R^2 value showed that the model accounted for 98% of the observed variability. The predicted and adjusted R^2 were reasonably high. The significant overall *F*-test and the insignificant lack-of-fit indicated that the model was adequate for prediction. Nonetheless, the model did not contain any second-order terms. The reduced model for the pH is shown below in Equation (9).

$$\text{pH} = 2.61 + 0.35 A - 0.28 B - 0.051C + 0.028 AB - 0.020 AC - 0.038 BC \quad - (9)$$

The pH of the bio-oil is influenced by the presence of carboxylic acids which are primarily produced from the hemicellulose fractions of the biomass. Acetic acid which is one of the main carboxylic acids is produced from the elimination of O-acetyl groups in hemicellulose [63, 72]. Other organic acids such as formic and propionic acid are formed from the degradation of xylan [76, 77]. The increase in temperature consequently increased the pH of the bio-oil. It implies that at higher temperatures some of the acidic compounds responsible for the pH were cracked and hence decreased their concentration in the bio-oil. However, the increase in WHSV and vapor residence decreased the pH of the bio-oil (Figure 5.9). The results indicate that lower WHSV and shorter contact times are therefore required for the cracking of some of the organic acid vapors to reduce the acid concentration.

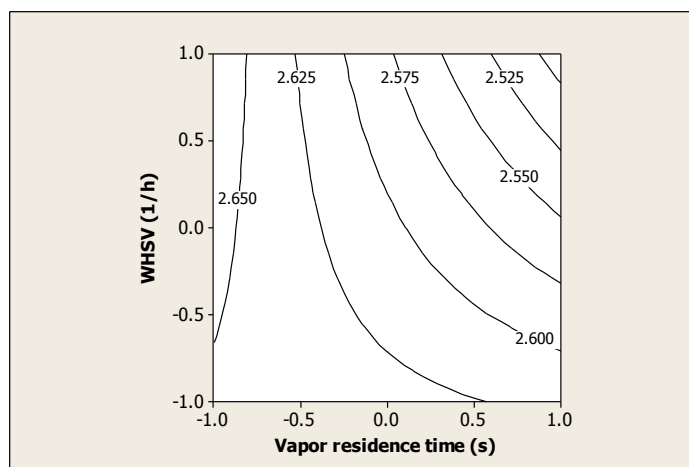


Figure 5.9. Contour Plot of WHSV versus vapor residence time in coded units showing interaction effect on the pH of the bio-oil.

Table 5.8. Analysis of Variance Table for the pH and viscosity of the bio-oil at 95% of confidence level

Source	Sum of Squares	DF	Mean Square	F value	Prob > F
pH					
Model	1.01	6	0.168	215.59	0.000 ^a
A	0.97	1	0.97	1245.79	0.000 ^a
B	0.0061	1	0.0061	7.75	0.024 ^a
C	0.0210	1	0.0210	26.90	0.001 ^a
AB	0.0030	1	0.0030	3.87	0.085
AC	0.0016	1	0.0016	2.05	0.190
BC	0.0056	1	0.0056	7.20	0.028 ^a
Lack of fit	0.00485	6	0.00081	1.15	0.533
Pure error	0.00140	2	0.0007		
Total	1.01657	14			
$R^2=0.994$, adj $R^2 = 0.989$, pred $R^2=0.973$ RMSE = 0.189, Mean = 64.82					
Viscosity (cSt)					
Model	228440	4	57110	11.44	0.001 ^a
A	134940	1	134940	27.04	0.000 ^a
B	70313	1	70313	14.09	0.004 ^a
C	15753	1	15753	3.16	0.106
A ²	7435	1	7435	1.49	0.250
Lack of fit	49593	8	6199	39.15	0.025
Pure error	317	2	158		
Total	278350	14			
$R^2=0.821$, adj $R^2 = 0.749$, pred $R^2=0.551$					

^a significant term.

The viscosity of the bio-oil was also influenced by temperature, WHSV and vapor residence time. The reduced model (Equation 10) was inadequate for prediction and had a significant lack-of-fit even though the overall F -test was significant (see Table 5.8). The R^2 accounted for about 82% of the observed variability. The adjusted R^2 and the predicted R^2 were insufficient and accounted for 75 % and 55% respectively. The coefficients of A and B were significant and C was insignificant at 95% confidence level. The main effect of temperature on the viscosity was positive and that of WHSV was negative. This indicates that increase in temperature increased the viscosity whereas increase in WHSV caused a decrease in viscosity of the bio-oil. The insignificant negative coefficient of C in the model also suggests that an increase in vapor residence time resulted in a decrease in the viscosity. Overall, the model for the prediction of viscosity (Equation 10) below was concluded to be a poor fit for the experimental data.

$$\text{Viscosity} = 193 + 130 A - 93.8 B - 44.4 C + 44.6 A^2 \quad (10)$$

The viscosity appeared to be a physical property that was complex to model with the process parameters used in the study. This could be because the viscosity depends also on other factors such as the molecular weight of the various compounds present in the bio-oil [78, 79] and the moisture content [80, 81]. The bio-oils produced in this study had about the same water content. The Karl Fischer titration analysis showed that the moisture content of the bio-oils measured for viscosity ranged between 2.0 - 3.5 wt%. Thus, the variations seen in the viscosities were attributed mainly to the differences in the molecular weight of the compounds present in the bio-oils.

The increase in viscosity with temperature as seen in this study suggests that at higher temperatures, polymerization/condensation reactions resulting in the formation of high molecular weight compounds were dominant. Additionally, the decrease in viscosity due to increase in WHSV suggest that the polymerization reactions were promoted by the FCC catalyst. It is not known if such reactions occurred in the pore of the Y-zeolite or on the surface of the catalyst. However, it is most likely

that the reactions took place on the surface of the catalyst since pore cracking of the vapors would potentially reduce the molecular weight of the resulting products. Nonetheless, it is possible that the cracked products could polymerize and increase the molecular weight of the final product upon condensation. It also has to be noted that at longer vapor residence times, the viscosity of the bio-oil decreased. This is because cracking of the vapors are enhanced at longer residence times and as a result reduce the formation of high molecular weight compounds. The increase in viscosity of the bio-oils at higher temperatures could also be as a result of uncracked lignin derived oligomers which are known to have high molecular weight [82-84]. In a work by Agblevor et al.[85], they found that the increase in temperature of the pyrolysis of starter turkey (mostly pine wood) from 450 °C to 550 °C increased the viscosity of the biocrude oil. Another study by Westerhof et al.[74] also reported that the increase in the pyrolysis temperature from 330 °C to 530 °C of pine wood increased the viscosity of the bio-oil as well as the average molecular weight. Generally, the effect of temperature on the viscosity of the bio-oils is still not clear. From the literature, some studies on conventional pyrolysis of biomass reported increase in viscosity with increase in temperature[74] and others reported decrease in viscosity with increase in temperature above 450 °C [86, 87]. The dissimilarities in the effect of temperature on the viscosities of the bio-oil as reported in literature can be attributed to differences in process conditions, reactor configuration as well as biomass feedstock.

5.4.0. CONCLUSION

The response surface methodology shows that temperature, WHSV and vapor residence time affect the product yields and quality of the bio-oils. The analysis of variance (ANOVA) at 95 % confidence showed that the reaction temperature was the most influential significant independent variable on char/coke yield, concentration of non-condensable gases and the carbon content, oxygen content, pH and viscosity of the bio-oils. The WHSV was found to be the most important significant independent variable that affected the yield of organic liquid and water. The increase in temperature decreased char/coke yield, CO₂ concentration and oxygen content of the bio-oil. However, the carbon content, pH and viscosity as well as the concentrations of H₂, CH₄ and CO increased with increasing temperature. The increase in WHSV increased the organic liquid yield and decreased the water yield. The reduced models for the prediction of the responses were all adequate and statistically significant with the exception of the model for viscosity of the bio-oil. The following were concluded from the study;

1. To produce high organic liquid fraction, higher levels of WHSV ($> 1 \text{ h}^{-1}$) with shorter vapor residence time and moderate temperatures ($500 \leq \text{Temperature} < 600$) would have to be used.
2. To minimize char/coke formation, the catalytic pyrolysis with FCC catalyst should be performed at a higher temperature and WHSV.
3. The catalytic pyrolysis with FCC catalyst at high temperatures ($> 500 \text{ }^{\circ}\text{C}$) and long residence time will enhance cracking of the primary vapors and increase the concentrations of CO, H₂ and CH₄.
4. Operation at higher temperatures ($> 500 \text{ }^{\circ}\text{C}$) and lower WHSV ($\leq 2 \text{ h}^{-1}$) produce bio-oil high in carbon and low in oxygen content.
5. Higher WHSV and longer vapor residence time produces bio-oil with lower pH value. Higher reaction temperature increases the pH of the bio-oil
6. The viscosity of the bio-oil is higher at higher temperatures and lower at higher WHSV.

5.5 REFERENCES

1. Agblevor, F.A., S. Beis, O. Mante, and N. Abdoulmoumine, *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood*. Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.
2. Agblevor, F.A., O. Mante, N. Abdoulmoumine, and R. McClung, *Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis*. Energy & Fuels, 2010. **24**(7): p. 4087-4089.
3. Adam, J., M. Blazsó, E. Mészáros, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, and G. Øye, *Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts*. Fuel, 2005. **84**(12-13): p. 1494-1502.
4. Carlson, T.R., J. Jae, Y.-C. Lin, G.A. Tompsett, and G.W. Huber, *Catalytic fast pyrolysis of glucose with HZSM-5: The combined homogeneous and heterogeneous reactions*. Journal of Catalysis, 2010. **270**(1): p. 110-124.
5. Faix, O., I. Fortmann, J. Bremer, and D. Meier, *Thermal degradation products of wood*. European Journal of Wood and Wood Products, 1991. **49**(5): p. 213-219.
6. Chang, C.D. and A.J. Silvestri, *The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts*. Journal of Catalysis, 1977. **47**(2): p. 249-259.
7. Chantal, P.D., S. Kaliaguine, and J.L. Grandmaison, *Reactions of Phenolic Compounds over H-ZSM5*. Applied Catalysis, 1985. **18**(1): p. 133-145.
8. Chen, N.Y., T.F.J. Degnan, and L.R. Koenig, *Liquid fuel from carbohydrates*. CHEMTECH, 1986. **16**(8): p. 506-511.
9. Diebold, J.P.L., CO), Evans, Robert J. (Lakewood, CO), *Process for producing furan from furfural aldehyde*, 1988, The United States of America as represented by the United States (Washington, DC): United States.
10. Haniff, M.I. and L.H. Dao, *Deoxygenation of carbohydrates and their isopropylidene derivatives over ZSM-5 zeolite catalysts*. Applied Catalysis, 1988. **39**(0): p. 33-47.
11. Hanniff, M.I. and L.H. Dao. *Conversion of Biomass Carbohydrates into Hydrocarbon Products*. in *Proceedings of IGT/CBETS Conference on Energy from Biomass and Wastes X*. 1986. Washington, D.C.
12. Diebold, J. and J. Scahill, *Biomass to Gasoline*, in *Pyrolysis Oils from Biomass*, E.J. Soltes and T.A. Milne, Editors. 1988, American Chemical Society: Washington, DC. p. 264-276.

13. Gayubo, A.G., A.T. Aguayo, A. Atutxa, R. Aguado, and J. Bilbao, *Transformation of Oxygenate Components of Biomass Pyrolysis Oil on a HZSM-5 Zeolite. I. Alcohols and Phenols*. Industrial & Engineering Chemistry Research, 2004. **43**(11): p. 2610-2618.
14. Gayubo, A.G., A.T. Aguayo, A. Atutxa, R. Aguado, M. Olazar, and J. Bilbao, *Transformation of Oxygenate Components of Biomass Pyrolysis Oil on a HZSM-5 Zeolite. II. Aldehydes, Ketones, and Acids*. Industrial & Engineering Chemistry Research, 2004. **43**(11): p. 2619-2626.
15. Gayubo, A.G., A.T. Aguayo, A. Atutxa, B. Valle, and J. Bilbao, *Undesired components in the transformation of biomass pyrolysis oil into hydrocarbons on an HZSM-5 zeolite catalyst*. Journal of Chemical Technology & Biotechnology, 2005. **80**(11): p. 1244-1251.
16. Adam, J., E. Antonakou, A. Lappas, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, and G. Øye, *In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials*. Microporous and Mesoporous Materials, 2006. **96**(1-3): p. 93-101.
17. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
18. Aho, A., N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D.Y. Murzin, *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.
19. Carlson, T., G. Tompsett, W. Conner, and G. Huber, *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
20. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
21. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(1): p. 39-61.
22. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts*. Fuel Processing Technology, 1995. **45**(3): p. 161-183.
23. Corma, A., G.W. Huber, L. Sauvanaud, and P. O'Connor, *Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst*. Journal of Catalysis, 2007. **247**(2): p. 307-327.
24. Milne, T.A., J. Evans R., and F. J., *Molecular Beam Mass Spectrometric Studies of HZSM-5 Activity during wood Pyrolysis Product Conversion*, in *Research in Thermochemical Biomass Conversion*,

- A.V. Bridgwater and J.L. Kuester, Editors. 1988, Elsevier Applied Science: London and New York. p. 910-926.
25. Williams, P.T. and N. Nugranad, *Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks*. Energy, 2000. **25**(6): p. 493-513.
 26. Thring, R.W., S.P.R. Katikaneni, and N.N. Bakhshi, *The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst*. Fuel Processing Technology, 2000. **62**(1): p. 17-30.
 27. Lappas, A.A., M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, and I.A. Vasalos, *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
 28. Pütün, E., B.B. Uzun, and A.E. Pütün, *Rapid Pyrolysis of Olive Residue. 2. Effect of Catalytic Upgrading of Pyrolysis Vapors in a Two-Stage Fixed-Bed Reactor*. Energy & Fuels, 2009. **23**(4): p. 2248-2258.
 29. Zhang, H., R. Xiao, H. Huang, and G. Xiao, *Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor*. Bioresource Technology, 2009. **100**(3): p. 1428-1434.
 30. Gayubo, A.G., B. Valle, A.s.T. Aguayo, M.n. Olazar, and J. Bilbao, *Attenuation of Catalyst Deactivation by Cofeeding Methanol for Enhancing the Valorisation of Crude Bio-oil*. Energy & Fuels, 2009. **23**(8): p. 4129-4136.
 31. Carlson, T.R., Y.-T. Cheng, J. Jae, and G.W. Huber, *Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust*. Energy & Environmental Science, 2011. **4**(1): p. 145-161.
 32. Atutxa, A., R. Aguado, A.G. Gayubo, M. Olazar, and J. Bilbao, *Kinetic Description of the Catalytic Pyrolysis of Biomass in a Conical Spouted Bed Reactor*. Energy & Fuels, 2005. **19**(3): p. 765-774.
 33. Mathews, J.F., M.G. Tepylo, R.L. Eager, and J.M. Pepper, *Upgrading of aspen poplar wood oil over HZSM-5 zeolite catalyst*. The Canadian Journal of Chemical Engineering, 1985. **63**(4): p. 686-689.
 34. Natalie G. Wilson, P.T.W., *Investigation into the potential of a novel superacid catalyst for the catalytic upgrading of pyrolytic bio-oil*. International Journal of Energy Research, 2003. **27**(2): p. 131-143.
 35. Ates, F., A.E. Pütün, and E. Pütün, *Pyrolysis of two different biomass samples in a fixed-bed reactor combined with two different catalysts*. Fuel, 2006. **85**(12-13): p. 1851-1859.

36. Ates, F. and M.A. Islkdag, *Influence of temperature and alumina catalyst on pyrolysis of corncob*. Fuel, 2009. **88**(10): p. 1991-1997.
37. Encinar, J.M., J.F. González, G. Martínez, and S. Román, *Catalytic pyrolysis of exhausted olive oil waste*. Journal of Analytical and Applied Pyrolysis, 2009. **85**(1-2): p. 197-203.
38. Pütün, E., *Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst*. Energy, 2010. **35**(7): p. 2761-2766.
39. Li, H.-y., Y.-j. Yan, and Z.-w. Ren, *Online upgrading of organic vapors from the fast pyrolysis of biomass*. Journal of Fuel Chemistry and Technology, 2008. **36**(6): p. 666-671.
40. Adjaye, J.D., S.P.R. Katikaneni, and N.N. Bakhshi, *Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution*. Fuel Processing Technology, 1996. **48**(2): p. 115-143.
41. Sharma, R.K. and N.N. Bakhshi, *Upgrading of wood-derived bio-oil over HZSM-5*. Bioresource Technology, 1991. **35**(1): p. 57-66.
42. Vitolo, S., M. Seggiani, P. Frediani, G. Ambrosini, and L. Politi, *Catalytic upgrading of pyrolytic oils to fuel over different zeolites*. Fuel, 1999. **78**(10): p. 1147-1159.
43. Evans Robert, J. and T. Milne, *Molecular-Beam, Mass-Spectrometric Studies of Wood Vapor and Model Compounds over an HZSM-5 Catalyst*, in *Pyrolysis Oils from Biomass* 1988, American Chemical Society. p. 311-327.
44. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways*. Fuel Processing Technology, 1995. **45**(3): p. 185-202.
45. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. Biomass and Bioenergy, 1994. **7**(1-6): p. 223-236.
46. Lappas, A.A., S. Bezergianni, and I.A. Vasalos, *Production of biofuels via co-processing in conventional refining processes*. Catalysis Today, 2009. **145**(1-2): p. 55-62.
47. Abnisa, F., W.M.A. Wan Daud, and J.N. Sahu, *Optimization and characterization studies on bio-oil production from palm shell by pyrolysis using response surface methodology*. Biomass and Bioenergy, 2011. **35**(8): p. 3604-3616.
48. Ghosh, D. and P.C. Hallenbeck, *Response surface methodology for process parameter optimization of hydrogen yield by the metabolically engineered strain Escherichia coli DJT135*. Bioresource Technology, 2010. **101**(6): p. 1820-1825.

49. Sahu, J.N., J. Acharya, and B.C. Meikap, *Optimization of production conditions for activated carbons from Tamarind wood by zinc chloride using response surface methodology*. Bioresource Technology, 2010. **101**(6): p. 1974-1982.
50. Mante, O.D. and F.A. Agblevor, *Parametric study on the pyrolysis of manure and wood shavings*. Biomass and Bioenergy, 2011. **35**(10): p. 4417-4425.
51. Box, G.E.P. and K.B. Wilson, *Experimental attainment of optimum conditions*. Journal of the Royal Statistical Society, 1951. **13**(1): p. 1-45.
52. Myers, R.H., D.C. Montgomery, and C.M. Anderson-Cook, *Response Surface Methodology, in Process and Product Optimization Using Designed Experiments* 2009, John Wiley & Sons, Inc.
53. Box, G.E.P. and D.W. Behnken, *Some New Three Level Designs for the Study of Quantitative Variables*. Technometrics, 1960. **2**(4): p. 455-475.
54. Mante, O., F. Agblevor, and R. McClung, *Fluid catalytic cracking of biomass pyrolysis vapors*. Biomass Conversion and Biorefinery, 2011. **1**(4): p. 189-201.
55. Ward, J.W., *The nature of active sites on zeolites : III. The alkali and alkaline earth ion-exchanged forms*. Journal of Catalysis, 1968. **10**(1): p. 34-46.
56. Scherzer, J., *Correlation Between Catalyst Formulation and Catalytic Properties*, in *Studies in Surface Science and Catalysis* 1993, Elsevier. p. 145-182.
57. Zhang, H., R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.
58. Boxiong, S., W. Chunfei, G. Binbin, W. Rui, and Liangcai, *Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts*. Applied Catalysis B: Environmental, 2007. **73**(1-2): p. 150-157.
59. Meng, X., C. Xu, and J. Gao, *Coking behavior and catalyst deactivation for catalytic pyrolysis of heavy oil*. Fuel, 2007. **86**(12-13): p. 1720-1726.
60. Sharma, R.K. and N.N. Bakhshi, *Conversion of non-phenolic fraction of biomass-derived pyrolysis oil to hydrocarbon fuels over HZSM-5 using a dual reactor system*. Bioresource Technology, 1993. **45**(3): p. 195-203.
61. Mohan, D., C.U. Pittman, and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review*. Energy & Fuels, 2006. **20**(3): p. 848-889.
62. Soltes, E.J. and E.J. Elder, *Pyrolysis*, in *Organic Chemicals from Biomass*, I.S. Goldstein, Editor 1981, CRC Press: Boca Raton, FL. p. 63-95.

63. Hon, D.N.-S. and N. Shiraishi, *Wood and Cellulosic Chemistry* 1990, New York, NY: Marcel Dekker Inc.
64. Buttermann, H.C. and M.J. Castaldi, *Influence of CO₂ Injection on Biomass Gasification*. Industrial & Engineering Chemistry Research, 2007. **46**(26): p. 8875-8886.
65. A, D., *Mechanisms of liquefaction and pyrolysis reactions of biomass*. Energy Conversion and Management, 2000. **41**(6): p. 633-646.
66. Murwanashyaka, J.N., H. Pakdel, and C. Roy, *Step-wise and one-step vacuum pyrolysis of birch-derived biomass to monitor the evolution of phenols*. Journal of Analytical and Applied Pyrolysis, 2001. **60**(2): p. 219-231.
67. Wittkowski, R., J. Ruther, H. Drinda, and F. Rafiei-Taghanaki, *Formation of Smoke Flavor Compounds by Thermal Lignin Degradation, in Flavor Precursors* 1992, American Chemical Society. p. 232-243.
68. Orfão, J.J.M., F.J.A. Antunes, and J.L. Figueiredo, *Pyrolysis kinetics of lignocellulosic materials—three independent reactions model*. Fuel, 1999. **78**(3): p. 349-358.
69. Fenner, R.A. and J.O. Lephardt, *Examination of the thermal decomposition of kraft pine lignin by Fourier transform infrared evolved gas analysis*. Journal of Agricultural and Food Chemistry, 1981. **29**(4): p. 846-849.
70. Kawamoto, H., M. Murayama, and S. Saka, *Pyrolysis behavior of levoglucosan as an intermediate in cellulose pyrolysis: polymerization into polysaccharide as a key reaction to carbonized product formation*. Journal of Wood Science, 2003. **49**(5): p. 469-473.
71. Shen, D.K. and S. Gu, *The mechanism for thermal decomposition of cellulose and its main products*. Bioresource Technology, 2009. **100**(24): p. 6496-6504.
72. Shen, D.K., S. Gu, and A.V. Bridgwater, *Study on the pyrolytic behaviour of xylan-based hemicellulose using TG-FTIR and Py-GC-FTIR*. Journal of Analytical and Applied Pyrolysis, 2010. **87**(2): p. 199-206.
73. Li, S., J. Lyons-Hart, J. Banyasz, and K. Shafer, *Real-time evolved gas analysis by FTIR method: an experimental study of cellulose pyrolysis*. Fuel, 2001. **80**(12): p. 1809-1817.
74. Westerhof, R.J.M., D.W.F. Brilman, W.P.M. van Swaaij, and S.R.A. Kersten, *Effect of Temperature in Fluidized Bed Fast Pyrolysis of Biomass: Oil Quality Assessment in Test Units*. Industrial & Engineering Chemistry Research, 2009. **49**(3): p. 1160-1168.

75. Williams, P.T. and P.A. Horne, *Analysis of aromatic hydrocarbons in pyrolytic oil derived from biomass*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(0): p. 15-37.
76. Beaumont, O., *Flash Pyrolysis Products From Beech Wood*. Wood and Fiber Science, 1985. **17**(2): p. 228-239.
77. Güllü, D. and A. Demirbas, *Biomass to methanol via pyrolysis process*. Energy Conversion and Management, 2001. **42**(11): p. 1349-1356.
78. Adjaye, J.D., R.K. Sharma, and N.N. Bakhshi, *Characterization and stability analysis of wood-derived bio-oil*. Fuel Processing Technology, 1992. **31**(3): p. 241-256.
79. Czernik, S., D.K. Johnson, and S. Black, *Stability of wood fast pyrolysis oil*. Biomass and Bioenergy, 1994. **7**(1-6): p. 187-192.
80. Soltes, E.J. and T.A. Milne, *Pyrolysis Oils from Biomass: Producing, Analyzing, and Upgrading*. ACS SYMPOSIUM SERIES 376, ed. M.J. Comstock 1988, Washington, DC: American Chemical Society.
81. Nolte, M.W. and M.W. Liberatore, *Viscosity of Biomass Pyrolysis Oils from Various Feedstocks*. Energy & Fuels, 2010. **24**(12): p. 6601-6608.
82. Pandey, K.K., *A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy*. Journal of Applied Polymer Science, 1999. **71**(12): p. 1969-1975.
83. Scholze, B., C. Hanser, and D. Meier, *Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): Part II. GPC, carbonyl groups, and ¹³C-NMR*. Journal of Analytical and Applied Pyrolysis, 2001. **58-59**: p. 387-400.
84. Scholze, B. and D. Meier, *Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC/MS, FTIR, and functional groups*. Journal of Analytical and Applied Pyrolysis, 2001. **60**(1): p. 41-54.
85. Agblevor, F.A., S. Beis, S.S. Kim, R. Tarrant, and N.O. Mante, *Biocrude oils from the fast pyrolysis of poultry litter and hardwood*. Waste Management, 2010. **30**(2): p. 298-307.
86. He, R., X.P. Ye, B.C. English, and J.A. Satrio, *Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties*. Bioresource Technology, 2009. **100**(21): p. 5305-5311.
87. Garcia-Perez, M., X.S. Wang, J. Shen, M.J. Rhodes, F. Tian, W.J. Lee, H. Wu, and C.Z. Li, *Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products*. Industrial & Engineering Chemistry Research, 2008. **47**(6): p. 1846-1854.

CHAPTER 6

The Influence of Recycling Non-Condensable Gas in the fractional catalytic pyrolysis of biomass.

6.0 Abstract

Fractional catalytic pyrolysis of biomass produces considerable amount of non-condensable gases (NCG). The NCG which is a mixture of CO, H₂, CO₂ and low molecular weight hydrocarbons can be used as fluidizing gas or combusted to fuel the pyrolysis process. However, the catalytic pyrolysis process could be potentially influenced by the NCG if used as a fluidizing gas instead of an inert gas. In this study, the effect of recycling the NCG in the catalytic pyrolysis of hybrid poplar using FCC catalyst was investigated. A 50 mm bench scale bubbling fluidized bed reactor at 475 °C with a weight hourly space velocity (WHSV) of 2 h⁻¹ and a gas recycling capability was used for the studies. Model fluidizing gas mixtures of CO/N₂, CO₂/N₂, CO/CO₂/N₂ and H₂/N₂ were used to determine their independent effects. Recycling of the NCG in the process was found to potentially increase the liquid yield and decrease char/coke yield. All the model fluidizing gases increased the liquid yield and CO₂/N₂ fluidizing gas had the lowest char/coke yield. The ¹³C-NMR spectrometric analysis of the bio-oils showed that recycling of NCG increases the aromatic fractions and decreases the methoxyl, carboxylic and sugar fractions. The CO₂/N₂ was found to produce the highest fraction of aromatics and CO/N₂ enhanced demethoxylation of the lignin decomposition products. Recycling of NCG increased the higher heating value and the pH of the bio-oil as well as decreased the viscosity and density. The bio-oils produced with NCG recycle contained relatively less amount of oxygen and higher contents of carbon and hydrogen. The concept of recycling the NCG in the catalytic cracking of biomass vapors with FCC catalyst improved the overall process.

6.1. Introduction

Catalytic fast pyrolysis technology is one of the thermochemical platforms that are used to produce high quality bio-oil and chemicals from biomass feedstocks [1-7]. The process involves the rapid heating of biomass under inert atmosphere in the presence of a suitable catalyst. The technology has been extensively reviewed in literature by Bridgwater[8], Park et al. [9], Huber et al.[10] and Taarning et al.[11]. In catalytic pyrolysis, a large fraction of the biomass is converted into non-condensable gases (NCG) at the expense of the liquid product. The gas product yield obtained on a dry biomass feed is about 20-50% depending on the type of catalyst used [3, 6, 12-16]. It mainly consists of carbon oxides, methane, hydrogen and minor hydrocarbons [10, 12]. These gases can be usefully recycled back into the reactor to assist in fluidization or could be combusted to provide process heat for large scale operations. The concept of recycling the NCG helps to reduce operational cost and eliminates further downstream processes of the gas stream. Studies have shown that with efficient condensation systems and compressors, the NCG can be effectively recycled back to replace the initial inert fluidizing gas [4, 17, 18].

Theoretically, recycling the NCG for fluidization could possibly influence the catalytic pyrolysis of biomass as these gases are capable of acting as co-reactants in the process. Studies have shown that the reductive gas stream (CO , H_2 , and hydrocarbons) and mild oxidative gas (CO_2) affect the thermal decomposition of biomass [7, 19-29]. Zhang et al.[20] investigated the effect of N_2 , CO_2 , CO , CH_4 and H_2 as carrier gases on the fast pyrolysis of concomb in a fluidized bed reactor. They reported that the liquid yield was dependent on the type of gas used and more oxygen was converted to CO_2 and H_2O in the presence of CO and H_2 . Meesuk et al.[21] also reported that lower liquid yields were achieved in H_2 atmosphere from the fast pyrolysis of rice husk in a fluidized bed reactor with or without the use of

CoMo/Al₂O₃ and Ni/LY catalyst. A study by Thangalazhy-Gopakumar[22] also reported a reduction in carbon yield when the thermogravimetric studies of pine wood chips under He was changed to H₂.

However, they did not observe any significant change in the yield when the experiment was conducted with a ZSM-5 zeolite catalyst. Studies by Carlson et al.[30] on the production of green aromatics and olefins from wood sawdust via catalytic fast pyrolysis using ZSM-5 zeolite, showed that co-feeding light hydrocarbons (C₂-C₃) with wood increases gasoline yields. An earlier work by Scahill and Diebold [19] also explored the effect of recycling olefins over HZSM-5 zeolite catalyst in the upgrading of pyrolysis vapors from wood. Most of the literature reports are on only the effect of individual gases on the pyrolysis of biomass. Currently, there are no reported findings on the influence of recycling the pyrolysis gas on catalytic pyrolysis of biomass.

In this study, the effect of recycling the NCG from the fractional catalytic pyrolysis of hybrid poplar wood using FCC catalyst on the product yields and properties of the bio-oils was investigated. The FCC catalyst which contains Y-zeolite has been shown to have a different effect on the catalytic pyrolysis of wood when compared with ZSM-5 zeolite catalyst [7, 12, 31-34]. The FCC catalyst typically produces lower bio-oil yields and forms large amounts of coke due to its pore size and acidity [6, 7, 15, 32, 33, 35, 36]. It is therefore hypothesized that recycling of the NCG with the FCC catalyst would enhance the catalytic process. Two sets of experiments were conducted to understand the effect of recycling the NCG. In the first trial, the NCG was recycled continuously throughout the run. The second experiment focused on the effect of the individual gases (CO, CO₂ and H₂) on the product distribution and bio-oil composition.

6.2. Materials and methods

6.2.1. Materials

The hybrid poplar wood samples were prepared in accordance to the method described in chapter 2. The ultimate composition and calorific value of the wood are shown in Table 2.1. The commercial FCC catalyst, water gas shift catalyst (FeCrCu) and the CoMo/Al₂O₃ catalyst used for the experiments were supplied and characterized by BASF Catalysts LLC (Iselin, NJ, USA). The FeCrCu and the CoMo/Al₂O₃ were added to the FCC catalyst at 20 wt% level.

6.2.3. Fractional catalytic pyrolysis of hybrid poplar

The catalytic pyrolysis of hybrid poplar at 475 °C and a weight hourly space velocity (WHSV) of 2 h⁻¹ was carried out using the experimental setup in Figure 6.1. The bench scale pyrolysis unit consisted of a K-Tron volumetric feeder (K-Tron Process Group, Pitman, NJ), a fluidized bed reactor, hot gas filter, two chilled water condensers, an electrostatic precipitator, coalescing filter and a compressor. The reactor was externally heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC) and the temperatures were measured and controlled by three K-thermocouples inserted into a thermal well in the reactor. The temperatures across the reactor, hot gas filter and condensers were controlled and monitored using the OMB-Multiscan 1200 acquisition system (Omega Engineering, Inc.) with TempView 2.1 program. The nitrogen gas flow rate was controlled with a mass flow controller. A total of 6.5 L/min of N₂ gas was used to fluidize the catalyst bed and entrain the biomass into the reactor. The catalytic cracking experiments were performed at apparent average vapor residence times of 3 s and 6.5 s. The apparent average vapor residence time was defined as the total volume of fluidized catalyst divided by gas flow rate at reactor conditions. For all recycling experiments, the NCG that exited the coalescing

filter was continuously returned to the reactor using an oil-less diaphragm compressor/pump (GAST WLS71272 pump). The initial flow rate of the N₂ fluidizing gas was reduced appropriately to maintain the same vapor residence time. For the gas chromatography analysis, a stream of non-condensable gases from the coalescing filter at flow rate of 0.1 L/min was connected to a Varian 490 micro GC (Agilent Technologies, Inc. Santa Clara, CA USA) to determine the concentration of the gases during the run. The gases were automatically analyzed online every 3.25 minutes for the duration of the experiment. The micro GC was equipped with two modules, a 10 m Molsieve (MS) 5Å column and a 10 m porous polymer (PPU) column. Each module had a thermal conductivity detector. The MS column was used to analyze hydrogen, methane and carbon monoxide. Carbon dioxide and C₁-C₅ gases were analyzed by the PPU column. The model gas experiments were conducted with the following synthetic gas mixtures: 10 mol% CO in N₂; 10 mol% CO₂ in N₂; 5 mol% H₂ in N₂; and 4.5 mol% CO + 7 mol% CO₂ in N₂. Each experiment was replicated 3 times and the average yields were expressed in percentage on a moisture free basis.

6.2.4. Bio-oil Analysis

A Thermo Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Cambridge, UK) was used to determine the C, H, N, O, and S of the bio-oil fraction. The higher heating values (HHV) were determined using IKA C2000 basic bomb calorimeter (IKA® Works, Inc, NC, and U.S.A.) according to ASTM D2015. The pH was measured using a Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The pH data were obtained after 5-10 min stabilization of the mechanically stirred oil. The viscosity and density of the bio-oils were measured at 40 °C with a SVM 3000 Stabinger viscometer (Anton Parr, Graz, Austria). The results were consistent with viscosities determined by the ASTM D445 method. A Metrohm 701KF Titrino (Brinkmann Instruments, Inc, N.Y, U.S.A) and a 703 titration stand setup were used for the Volumetric Karl Fischer titration. Hydranal® Composite 5 reagent was used. 50ml of methanol was placed in the titration vessel and conditioned. About 60-100 mg of oil sample was

loaded into a hypodermic plastic syringe and weighed. The sample was injected into the titration solvent and the syringe was weighed again. The water content was titrated volumetrically and the resulting mass was recorded. The ^{13}C -NMR spectra were recorded on a JOEL 300 MHz NMR spectrometer (JEOL Ltd, Tokyo, Japan). 1.0 g of oil was dissolved in 0.7 ml of dimethyl sulfoxide- d_6 in a 5mm sample tube. The NMR solvent, DMSO- d_6 [99.9 atom % D, containing 1% (v/v) tetramethylsilane (TMS)] was obtained from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA). The observing frequency for the ^{13}C nucleus was 100.58MHz. The pulse width was 10 μs , the acquisition time was 1.58 s, and the relaxation delay was 2 s. The spectra were obtained with 4000 scans and a sweep width of 20.0 KHz. All the analyses of the bio-oils were done in 3 replicates.

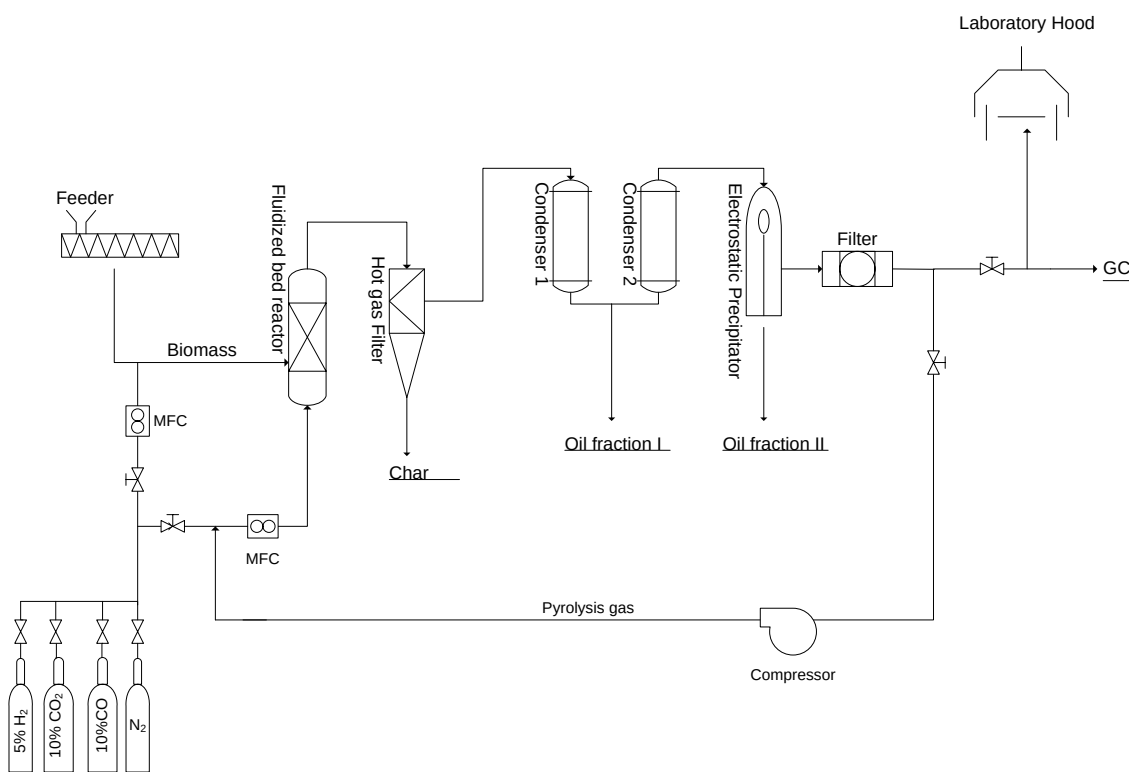


Figure 6.1. Schematic diagram of the fluidized bed pyrolysis reactor unit

6.3. Results and Discussion

6.3.1 Product yields

The product distribution in terms of organic, water, gas and char/coke from the fractional catalytic cracking of hybrid poplar pyrolysis vapors are shown in Table 6.1. From the results, it can be seen that the product distribution varied depending on catalytic conditions such as fluidizing gas stream, vapor residence time and the type of catalyst. Generally, the catalytic cracking at vapor residence of 6.5s produced lower organic yield and higher char/coke yield whilst cracking at 3.0 s produced higher organic and lower char/coke yields. The lower organic yield and the higher char/coke yield produced at a vapor residence of 6.5 s was attributed to extensive cracking of the pyrolysis vapors at that condition. The product distribution was also affected when the NCG was recycled back into the reactor for fluidization. The FCC catalyst produced organic yield of 13.8 wt.% and a char/coke yield of 26.5 wt.% at vapor residence of 6.5s. However, when the NCG was recycled in the process, the organic yield increased to 15.7 wt% and the char/coke yield decreased to 22.4 wt.%. The char/coke yield was highly influenced relative to the other products. The char/coke decreased by 15.5% upon recycling the NCG. Similarly, the organic yield increased from 14.3 wt.% to 15.9 wt% and the char/coke yield decreased from 19.0 wt.% to 17.2 wt% when the NCG was recycled in the catalytic cracking with FCC/FeCrCu/CoMo catalyst blend at vapor residence of 6.5 s. The quantitative changes in the product distribution due to recycling of the NCG suggest that the pyrolysis gas is a reactive gas stream and could potentially improve the yields from the fractional catalytic cracking of the pyrolysis vapors.

It is also worth noting that the addition of either 20% FeCrCu or 20% CoMo/Al₂O₃ to the FCC catalyst resulted in a significant increase in the gas yield and a decrease in the char/coke. The increase in the gas yield for the FCC/FeCrCu catalyst was attributed to the additional production of CO₂ and H₂ via water gas shift reaction as will be shown in the gas analysis. The observed increase in the gas yield for

FCC/CoMo was plausibly due to the promotion of hydrocracking reactions. The selectivity of FeCrCu and CoMo/Al₂O₃ towards the production of higher gas fraction was evident in the gas yield (43.4 wt%) in the catalytic cracking with FCC/FeCrCu/CoMo blend catalyst. The lower char/coke yield (18.3-19.3 wt%) for blend catalyst systems when compared with FCC catalyst (26.5 wt.%) may arise from the relatively lower amount of FCC in the blend catalyst.

The results from the model fluidizing gas studies using CO/N₂, CO₂/N₂, and H₂/N₂ confirmed the effect seen in recycling of the NCG (see Table 6.1). The results from the catalytic cracking of the pyrolysis vapors at a residence time of 3 s showed that more organics and less char/coke were produced in the presence of CO₂. The organic yield decreased in the order of CO₂/N₂ > CO-CO₂/N₂ > N₂ > CO/N₂ and the char/coke yield decreased in the order of N₂ > CO/N₂ > CO-CO₂/N₂ > CO₂/N₂. The water yield was about the same for all the gases but CO/N₂ produced the highest gas yield. For the experiments conducted at a vapor residence of 6.5 s, all the fluidizing gases except N₂ gave relatively higher organic and water yield. The organic yield decreased in the order of CO/N₂ > CO₂/N₂ > H₂/N₂ > N₂ and water yield decreased in the order of H₂/N₂ > CO/N₂ > CO₂/N₂ > N₂. The results suggest that CO, CO₂, and H₂ fluidizing gases enhanced the devolatilization and thermal decomposition of hybrid poplar wood. It has been shown by thermogravimetric analysis that CO₂ atmosphere influences the thermal decomposition of biomass by lowering the apparent activation energy [26]. A study by Butterman et al[24] showed that cellulose degrades at a relatively lower temperature in the presence of CO₂.

Table 6.1. Production distribution of fractional Catalytic cracking of hybrid poplar

Type of Catalyst	Fluidizing gas	Product Distribution (wt.%)			
		Organics	Water	Char/Coke	Gas
Catalytic cracking at a vapor residence of 6.5 s					
FCC	N ₂	13.8±0.9	26.8±2.1	26.5±0.49	32.8±2.6
FCC with recycle	NCG/N ₂	15.7±0.8	28.0±0.7	22.4±1.55	33.9±1.9
FCC/FeCrCu	N ₂	17.2±2.1	24.3±1.	19.3±1.6	39.6±0.4
FCC/CoMo	N ₂	16.1±2.5	27.1±1.3	18.3±1.4	38.5±0.7
FCC/FeCrCu/CoMo	N ₂	14.3±1.0	23.3±0.5	19.0±0.2	43.4±1.3
FCC/FeCrCu/CoMo with recycle	NCG/N ₂	15.9±2.5	25.9±0.1	17.2±0.5	40.9±2.1
FCC	CO/N ₂	17.4±1.8	31.5±0.3	21.2±0.7	29.9±2.3
FCC	CO ₂ /N ₂	17.1±0.9	30.9±0.7	19.3±0.5	32.6±1.8
FCC	H ₂ /N ₂	16.2±2.1	32.5±0.9	20.5±1.1	31.1±1.6
Catalytic cracking at a vapor residence of 3.0 s					
FCC	N ₂	20.6±1.5	23.6±1.9	25.2±1.7	30.9±2.4
FCC	CO/N ₂	18.9±0.2	23.9±0.8	23.5±0.2	33.3±1.1
FCC	CO ₂ /N ₂	24.1±1.0	23.7±0.5	20.8±0.3	31.4±1.3
FCC	CO/CO ₂ /N ₂	22.5±1.1	24.1±0.7	22.3±1.5	31.1±2.6

The char/coke yield was similarly affected and the fluidizing gases (CO/N₂, CO₂/N₂, and H₂/N₂) had lower yields compared with N₂. The CO₂/N₂ fluidizing gas produced the lowest char/coke yield followed by CO/N₂ for catalytic cracking at a vapor residence of 6.5 s. The decrease in char/coke particularly under CO₂/N₂ atmosphere suggests that CO₂ either minimizes the formation of coke

precursors or it reacts via Boudouard reaction with carbon deposits on the catalyst and char. A study by Zhang et al.[20] on conorb fast pyrolysis found that the char yield under CO₂ atmospheres was the lowest and they attributed the effect to char and CO₂ reactions. Jindarom et al.[26] reported a reduction in solid yield when the thermochemical decomposition of sewage sludge was performed under CO₂ instead of inert atmosphere (N₂). Other studies have also shown that char/carbon oxidation occurs in the presence of CO₂ through Boudouard reactions but at relatively higher temperatures [23-25, 27]. However, it is possible for Boudouard reactions to occur at lower temperature in the presence of a catalyst [37].

The catalytic cracking at a vapor residence of 6.5 s with CO/N₂ fluidizing gas also produced relatively lower char/coke yield. The explanation of that effect could be that CO reacts with coke precursors or minimizes their formation. One of the main coke precursors are phenolic compounds [6, 38] and a study by Kubiak [39] suggested the possibility of CO reacting with phenolics over a transition metal catalyst to form aromatics. However, this phenomenon cannot be substantiated in our present work using the FCC catalyst. In summary, the model fluidizing gas studies confirm that reductive gas streams (CO and H₂,) and mild oxidative gas (CO₂) have an effect on the fractional catalytic pyrolysis using FCC catalyst. Also, the results were indicative that their influence on the product yields was dependent on other process conditions such as vapor residence time.

6.3.2 Gas Analysis

The composition of the non-condensable gas was measured and monitored by a micro-GC during the experiment at a time interval of 3.5 min. This means that for a 60 min run, the gases were sampled at least 15 times. In the recycling experiment, the concentration of the evolution gases (Figure 2a and 2b) represents both the generated and that of the recycled NCG that exited the coalescing filter.

6.3.2.1. Effect of Recycling

Figure 6.2a and 6.2b respectively represent the gas evolution plots for the catalytic cracking with FCC catalyst and FCC/FeCrCu/CoMo blend catalyst. From the gas evolution plots, it can be seen that the concentration of the individual gases increased with time and the fluidizing gas stream was enriched continuously with NCG during each recycling experiment. It is worth mentioning that, the type of catalyst influenced the concentration of the individual gases. In the NCG recycle run with FCC catalyst, CO was the predominant gas followed by CO₂ from the start of the experiment to the end. Conversely, CO₂ concentration was about the same as CO for the first 35 minutes of the NCG recycle run with FCC/FeCrCu/CoMo blend catalyst.

The average molar composition (Table 6.2) of the NCG without recycle from the catalytic cracking using FCC catalyst at a vapor residence of 6.5 s constituted about 51.5% CO, 23.8% CO₂, 12.1% CH₄, 6% H₂ and 5.8% light hydrocarbons (C₂-C₅). However, the composition of the NCG upon recycling showed that, CO concentration and C₂-C₅ hydrocarbons decreased and H₂, CO₂ and CH₄ increased (See Table 6.2). The small increase in CO₂ and H₂ suggest that recycling of the NCG may have enhanced WSG reactions (CO+H₂O→CO₂+H₂). Furthermore, the monotonic increases in the molar ratios of CO₂/CO and H₂/CO during the recycling corroborate WGS reactions due to NCG recycle. The reduction in the concentration of the light hydrocarbons (C₂-C₅) implies that they underwent reactions and were consequently consumed. It is also worth noting that H₂ was not consumed evidently in the recycling process. It appeared therefore that catalytic cracking over FCC without hydrotreating catalyst did not favor hydrogen consuming reactions.

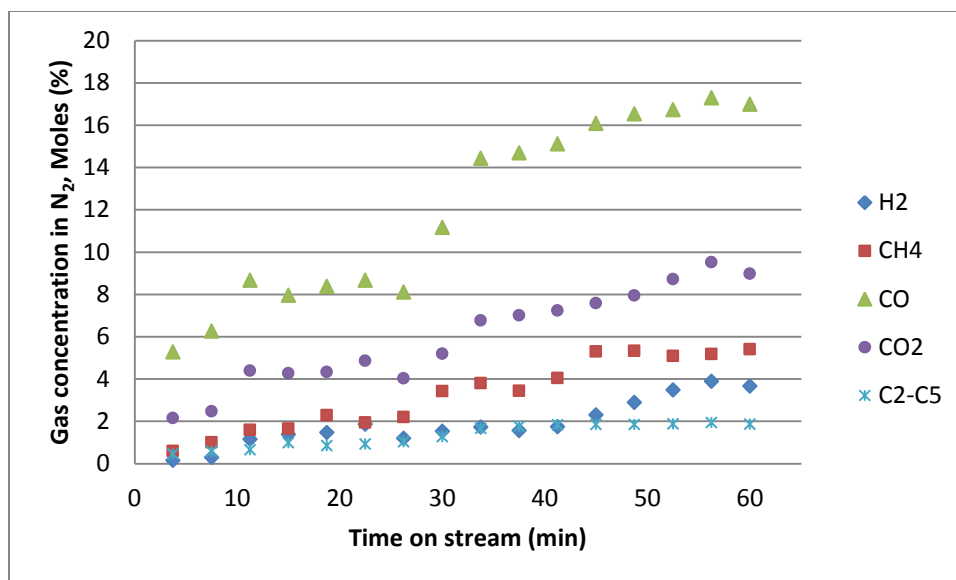


Figure 6.2a. Gas evolution plot showing the actual mole concentration of the gases during the recycling of the non-condensable gases in catalytic cracking of hybrid polar wood vapors using FCC catalyst at a vapor residence time of 6.5 s

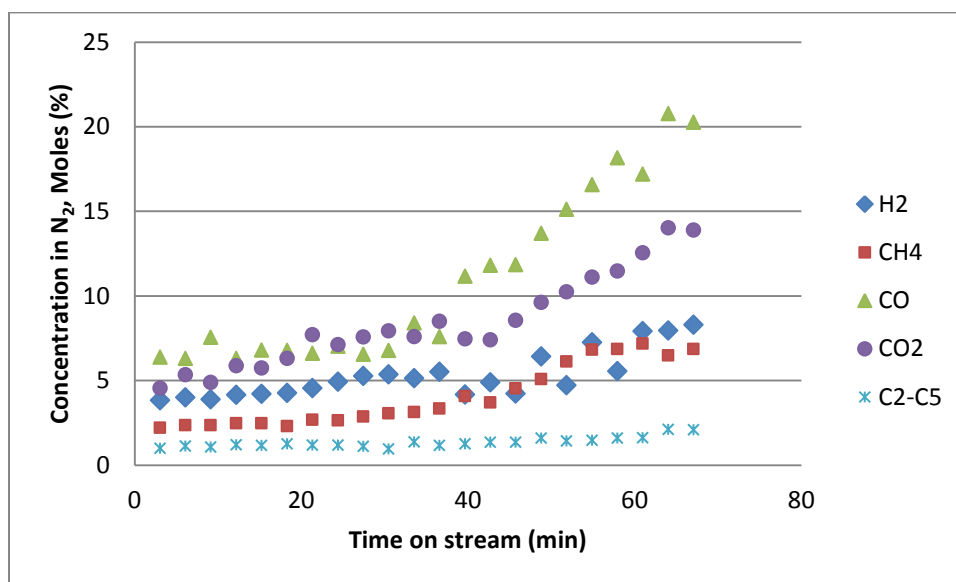


Figure 6.2b. Gas evolution plot showing the actual mole concentration of the gases during the recycling of the non-condensable gases in catalytic cracking of hybrid polar wood vapors using FCC/FeCrCu/CoMo catalyst blend at a vapor residence time of 6.5 s

In the NCG recycle experiment with FCC/FeCrCu/CoMo, it was observed that the molar concentration of H₂ and CH₄ increased and that of CO and C₂-C₅ hydrocarbons decreased when compared with the experiment without NCG recycle (Table 6.2). For this particular run, the FeCrCu catalyst was added to promote WGS reactions with CO and consequently generate more H₂ for utilization in hydrogen consuming reactions promoted by CoMo/Al₂O₃ catalyst. The addition of the FeCrCu to FCC catalyst undoubtedly performed as expected and increased the concentration of H₂ and CO₂ via WGS reaction. The H₂, CO₂ and CO produced from the catalytic cracking using FCC/FeCrCu constituted respectively 16.9 %, 28.4 % and 39.9% of the NCG. These correspond to 144% increase in H₂, 22% decrease in CO and 18% increase in CO₂. The results therefore show that more H₂ was formed and some of the CO was converted to CO₂. This observation shows that the conditions for the FCC catalytic cracking were equally suitable for the WGS catalyst. Hence, the process can be advantageously used to generate H₂ *in-situ*.

Nevertheless, the composition of the NCG from the catalytic cracking with FCC/CoMo showed that the CoMo/Al₂O₃ catalyst did not behave as expected. The FCC/CoMo blend catalyst produced relatively higher concentration of H₂ (14.2%) and CH₄ (12.6%) and lower concentration of CO (44.1%) compared with the FCC catalyst. From the results, it was evident that CoMo/Al₂O₃ did not catalyze hydrogen consuming reactions; instead it enhanced cracking reactions that lead to the generation of more H₂ and CH₄ species. From the product yield distribution, it was obvious that the addition of FeCrCu and CoMo/Al₂O₃ at 20 wt% level to the FCC catalyst significantly increased the gas yield by 21–34 %.

The CoMo/Al₂O₃ catalyst did not promote hydrogen consuming reactions probably due to the lack of suitable operating conditions such as high pressure, turnover frequency and long residence time [40, 41]. Most of the reported literatures on hydrolysis were conducted under high hydrogen pressure and low space velocities [40, 42-49]. Hydrolysis of wood and bagasse by Rocha et. al[42] in

a fixed bed reactor using NiMo/ γ -Al₂O₃ catalyst at 400 °C showed that increasing hydrogen pressure from 2.5 to 10 MP improved the process and resulted in the decrease in bio-oil oxygen content from 20 to 10% (w/w). Pindoria et al.[45] also studied the effect of hydrogen pressure and samples configuration in hydropyrolysis of Eucalyptus. They reported that increasing pressure significantly produced less oxygenated oils. Other studies have however, shown that it is possible to perform hydropyrolysis at atmospheric pressure. Takarada et al[50] was able to pyrolyze coal in H₂ at atmosphere pressure using CoMo/Al₂O₃ catalyst and produced aromatic hydrocarbons. A recent study by Meesuk et al[21] on fast pyrolysis of rice husk found that higher deoxygenation of the pyrolysis vapors was achievable with CoMo/Al₂O₃ catalyst at atmospheric pressure in the presence of H₂ than in an inert atmosphere (N₂). Nevertheless, it appeared from this study that the catalytic cracking conditions were not optimal for hydrodeoxygenation with the CoMo/Al₂O₃ catalyst. It should be noted that, the concept of generating H₂-rich NCG by WGS catalyst and recycling the gas over FCC/hydrodeoxygenation catalyst has potential advantages over conventional hydrodeoxygenation since it prevents the cost associated with hydrogen generation, purification and recovery. Studies by Wang et al[51] showed that syngas could replace pure hydrogen in hydropyrolysis of biomass. Future studies would have to be conducted to determine suitable conditions (temperature, reactor configuration, catalysts ratios and residence time) for the process.

6.3.2.2 Model gas studies

The model fluidizing gas studies with FCC catalyst confirmed that CO, CO₂ and H₂ influence the formation of the evolved gas species in the catalytic cracking of hybrid poplar wood. As such, the product distributions from the catalytic cracking under the different reactive gas streams compared to the products from the inert atmosphere (N₂) were found to be different.

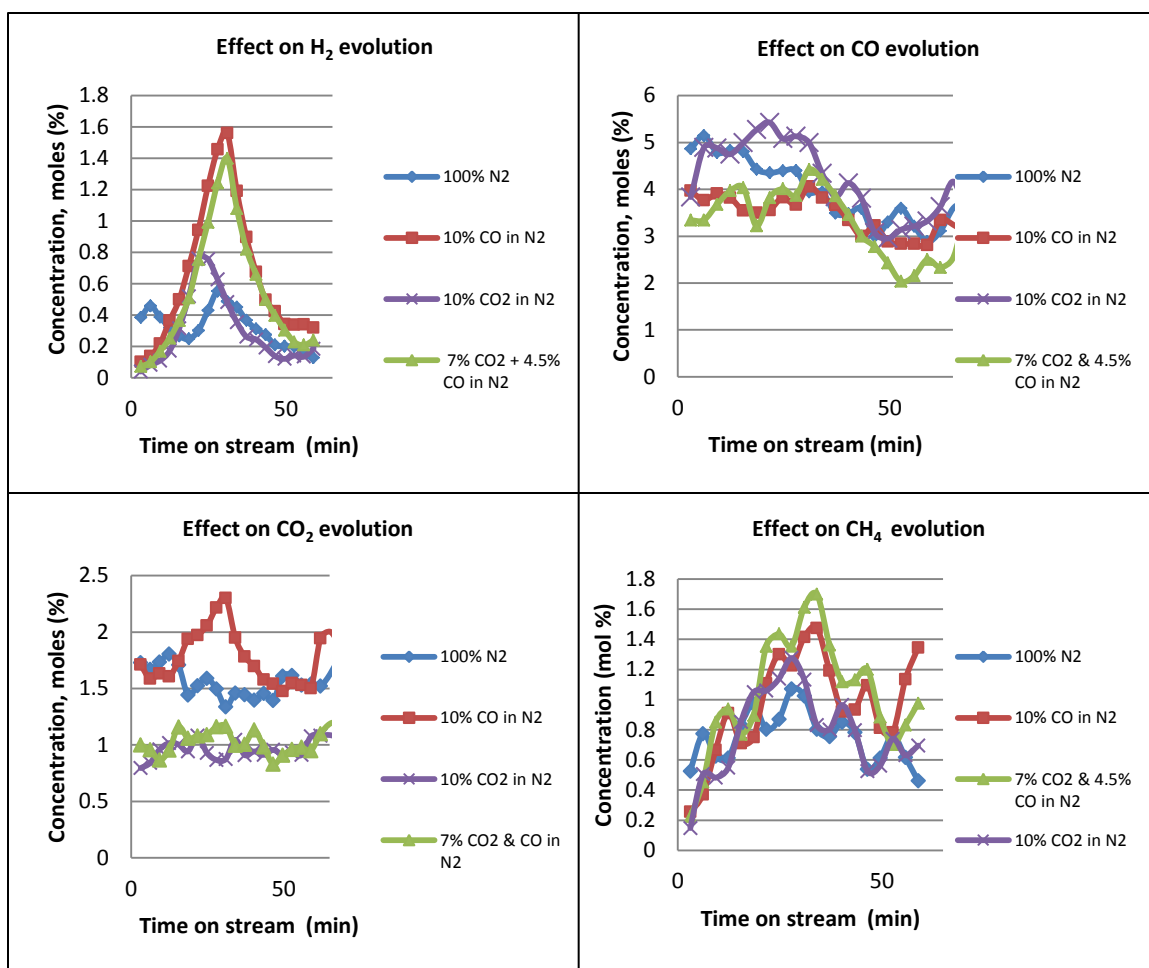


Figure 6.3. Gas evolution plot showing the effect of the various model gas mixtures on the concentration of H₂, CO₂, CO and CH₄ in catalytic cracking of hybrid polar wood vapors using FCC catalyst at a vapor residence time of 3 s

For catalytic cracking at a vapor residence of 3.0 s, the fluidizing gas mixtures of CO/N₂, CO₂/N₂ and CO-CO₂/N₂ were all found to promote some reactions. The CO/N₂ fluidizing gas consistently resulted in the evolution of higher concentrations of H₂, CO₂ and CH₄ (Figure 6.3). The enhancement in the concentration of CO₂ and H₂ was attributed to the promotion of WGS reaction in the presence of CO. Also the increase in CH₄ evolution was probably through direct hydrogenation reaction ($\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$) [24]. The molar ratios (CO₂/CO and H₂/CO) plot in figure 4 show the effect of the various

fluidizing gas mixtures on the concentration of the evolved gases during the experiment. The selectivity of CO_2 and H_2 species with respect to CO increased when CO/N_2 fluidizing gas was used. Furthermore, the actual concentrations of the evolved CO_2 during the run suggest the occurrence of WGS reaction (see Figure 6.3). This also explains why the average composition of the recycle gas had higher concentration of H_2 and CO_2 as the FCC catalyst predominantly produced CO. A Study by Zhang et al.[20] also found that fast pyrolysis of concomb under CO atmosphere produced the highest CO_2 concentration. Their findings are in agreement with the results from this work.

The catalytic cracking with FCC catalyst at vapor residence of 6.5 s with CO_2/N_2 fluidizing gas had a remarkable effect on the concentration of the evolved gases. CO_2 has been shown to affect the thermal decomposition of cellulose and lignin [24]. The presence of CO_2 in the fluidizing gas stream enhanced the pathway for the evolution of CO at the expense of CO_2 (Figure 6.3). This indicates that reaction such as decarboxylation leading to the evolution of CO_2 was suppressed and decarbonylation reaction that results in CO was enhanced in the presence of higher levels of CO_2 . Furthermore, the higher concentration of CO suggests the possible occurrence of reverse water gas shift reaction due to the presence of higher levels of CO_2 in the fluidizing gas. The WGS reaction in the presence of high levels of CO_2 can cause a shift to the left and in so doing generate more CO and consume H_2 . This also explains why the concentration of H_2 was relatively lower than CO. Also, the addition of CO_2 generated relatively lower concentrations of CH_4 when compared with CO.

Table 6.2. Average molar composition of the non-condensable pyrolysis gas sample at a time interval of 3.5 mins during the catalytic cracking of hybrid polar wood vapors

Type of Catalyst	Fluidizing medium	Gas composition (moles, %)				
		H ₂	CH ₄	CO	CO ₂	C ₂ -C ₅
Catalytic cracking at a vapor residence of 6.5 s						
FCC	N ₂	6.9±0.2	11.9±0.3	51.33±0.2	24.1±0.4	5.8±0.1
FCC with recycle	NCG	8.8±1.5	13.5±0.1	47.0±1.1	25.5±1.7	5.2±0.2
FCC/FeCrCu	N ₂	16.9±.8	9.2±0.1	39.9±0.5	28.4±0.6	5.5±0.4
FCC/CoMo	N ₂	14.2±0.2	12.6±0.5	44.1±0.2	24.3±0.8	4.9±0.1
FCC/FeCrCu/CoMo	N ₂	16.0±0.4	11.2±0.1	38.1±0.2	29.1±0.1	5.7±0.2
FCC/FeCrCu/CoMo with recycle	NCG	17.9±1.6	13.4±1.9	36.1±2.1	28.1±1.7	4.6±0.3
FCC	CO/N ₂	9.5±.6	13.6±0.3	43.9±0.5	26.9±0.9	6.3±0.1
FCC	CO ₂ /N ₂	7.68±0.5	15.0±0.8	58.9±1.4	11.4±1.9	7.0±0.3
FCC	H ₂ /N ₂	5.5±0.3	14.1±1.0	51.1±1.2	23.2±1.6	6.1±0.6
Catalytic cracking at a vapor residence of 3.0 s						
FCC	N ₂	4.9±1.4	10.2±0.8	51.8±0.8	25.5±1.6	7.6±0.2
FCC	CO/N ₂	8.7±1.5	12.1±0.8	43.7±3.1	28.2±0.8	7.3±0.2
FCC	CO ₂ /N ₂	4.3±1.1	11.3±1.9	58.7±1.1	18.2±1.5	7.5±2.3
FCC	CO/CO ₂ /N ₂	7.4±1.1	14.2±1.7	45.9±1.4	21.8±1.3	11.4±21.8

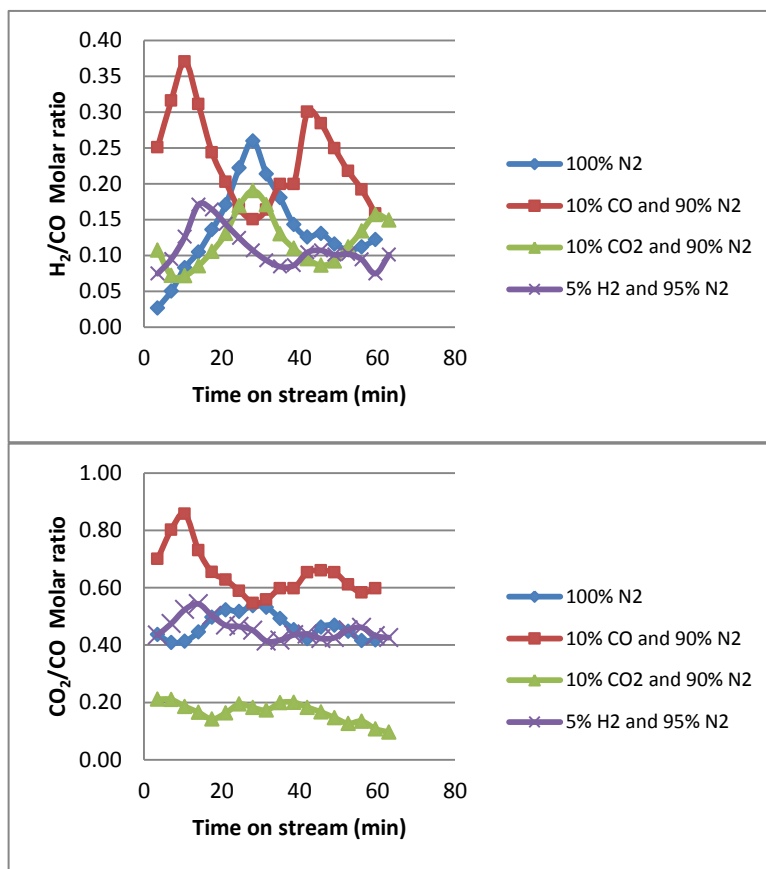


Figure 6.4. A plot showing the effect of the model gas mixtures on the variation in the in the mole ratio of CO₂/CO and H₂/CO in catalytic cracking of hybrid polar wood vapors using FCC catalyst at a vapor residence time of 6.5 s

A study by Buttermann and Castaldi [23] found that the injection of CO₂ as a cofeed in biomass gasification depressed the evolution of H₂ and CH₄. They reported that the depression of H₂ in the presence of CO₂ caused a reduction in CH₄ evolution due to a decrease in the availability of H₂ for possible methanation reactions. It is also believed that CO₂ promotes oxidative reactions and is reactive with carbon. Therefore, the marked increase in CO concentration could be as a result of Boudouard reaction ($\text{CO}_2 + \text{C} \leftrightarrow 2\text{CO}$) where the CO₂ is reduced to CO by reacting with carbon residues in the

reactor. Actually, the reduction in the char/coke yields when CO₂/N₂ was used as fluidizing gas suggests such phenomenon.

The CO/CO₂/N₂ gas mixture also had a different effect on the evolution of hydrocarbon gases (Figure 3). The gas mixture generated higher concentrations of CH₄ and C₂-C₅ hydrocarbons. It appeared therefore that the CO/CO₂/N₂ fluidizing gas was more reactive and favored the cracking of the pyrolysis vapors into light hydrocarbons. The H₂/N₂ gas stream was also found to increase the evolution of CH₄. It is known that the evolution of CH₄ from woody biomass could occur via molecular methanation reactions where methyl and methoxy radicals react with H₂ [23]. Thus, it appears that the H₂/N₂ fluidizing gas favored such reaction. Generally, the H₂/N₂ fluidizing gas had comparable effect as N₂ and their molar gas compositions of the non-condensable gas were similar (Table 6.2). The H₂/N₂ gas stream did not seem to be reactive and that could be due to the process conditions. The short vapor residence time and the lack of pressure and suitable catalyst may have prevented the hydrogen from undergoing some reactions [21, 22].

6.3.3. Spectrometric Analysis of bio-oils

The bio-oils were analyzed using ¹³C-NMR spectrometry and their relative carbon distribution determined by integration (Table 6.3). Figure 6.5 shows the spectra for the bio-oil fraction produced from FCC without recycle (A), FCC with gas recycle (B), FCC/FeCrCu/CoMo without recycle (C) and FCC/FeCrCu/CoMo with gas recycle (D). The various compounds in the bio-oil were categorized into six main functional groups according to their chemical shifts (δ, ppm). The groups were aliphatic hydrocarbons (0-55 ppm); methoxyl (-OCH₃) in lignin (55-57 ppm); levoglucosan, anhydrosugars, alcohols, ethers (57-105 ppm); total aromatics including olefins and phenolics (105 -160 ppm); C=O in carboxylic acids and derivatives (160 -180 ppm) and C=O in aldehydes and ketones (180 -220 ppm).

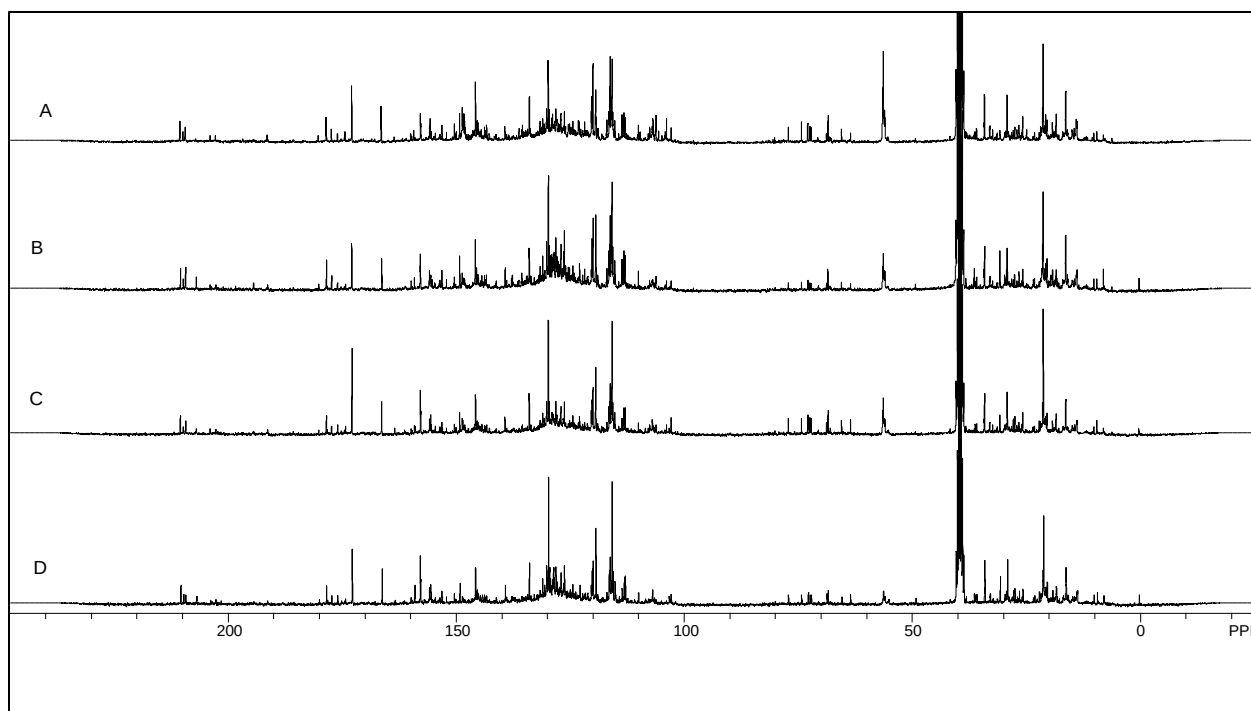


Figure 6.5. ^{13}C -NMR spectra of bio-oils showing the effect of fluidizing gas (A) FCC; (B) FCC-recycle (C) FCC/FeCrCu/CoMo; (D) FCC/FeCrCu/CoMo-Recycle

The relative carbon content of the chemical groups in the bio-oil varied depending on the catalyst used and the process conditions. The relative carbon distribution (see Table 6.3) for a typical bio-oil produced from conventional pyrolysis of hybrid poplar (non-catalytic) is about 22% aliphatic hydrocarbons, 6.5% methoxyls, 26.3% sugars, 38.5% aromatics, 5.4% carboxylic and 2% carbonyls. However, the bio-oil produced from the fractional catalytic pyrolysis of hybrid poplar with FCC catalyst under the process conditions used in this work has a relative carbon distribution of 21.6% aliphatics, 3.7% methoxyls, 6.0% sugars, 61.1% aromatics, 4.9% carboxylics and 2.7% carbonyls. It can be seen that the catalyst cracked about 77% of the sugars (particularly levoglucosan) and produced more aromatics which resulted in over 50% increase in the relative carbon content. The other functional groups that decreased in relative content due to the presence of FCC catalyst included methoxyls and carboxylics. The relative content of the carbonyls conversely increased. The increase in carbonyls has been reported

in literature to be typical of FCC catalyst [13, 34]. It appeared therefore that the catalytic cracking produced relatively more ketones or aldehydes. In general, catalytic cracking produces bio-oils which are highly aromatic in nature as result of the formation of aromatic hydrocarbons and monofunctional phenolics [1-3, 5-7, 52].

Table 6.3. ^{13}C NMR of biocrude oils produced from complete recycle of non-condensable gas (Percentage carbon total)

	Chemical Shift, δ (ppm)	Bio-oils			
		FCC	FCC- Recycle	FCC/FeCrCu/CoMo	FCC/FeCrCu/CoMo - Recycle
Aliphatic hydrocarbons	0-55	21.63	22.61	22.20	22.17
Methoxyl (-OCH ₃) in lignin	55-57	3.68	2.19	2.38	1.29
Levoglucosan, anhydrosugars, alcohols ,ethers	60-105	6.01	3.71	7.00	3.37
Total aromatics including olefins and phenolics	105-160	61.09	66.08	62.84	68.49
C=O groups (carboxylic acids and derivatives)	160-180	4.94	3.64	4.59	3.89
Aldehydes, ketones	180-220	2.65	1.76	0.99	0.79

Recycling of the NCG in the catalytic cracking of the pyrolysis vapors was found to further decrease the relative carbon content of sugars, methoxyls and carboxylics as well as increase primarily the carbon content of the aromatics. Interestingly, the relative content of the carbonyls decreased after NCG recycle. It can be inferred from the results that, the presence of CO, CO₂, H₂, CH₄ and C₁-C₄ hydrocarbon in the recycle gas promoted reactions that enhanced the cracking of levoglucosan and depolymerization/demethoxylation of the lignin fragments. The reduction in both the carboxylics and

carbonyl relative contents suggest that decarboxylation and decarboxylation reactions were also enhanced by the gas recycle. The effect was evident in both catalytic processes with FCC catalyst and the FCC/FeCrCu/CoMo blend catalyst. Nevertheless, NCG recycle in the catalytic cracking process with FCC/FeCrCu/CoMo produced bio-oil that was highly aromatic and contained relative lower carbon content of sugars, methoxyls, carboxylics and carbonyls. This suggests that, the presence of the FeCrCu and the CoMo/Al₂O₃ catalyst promoted more deoxygenation reactions.

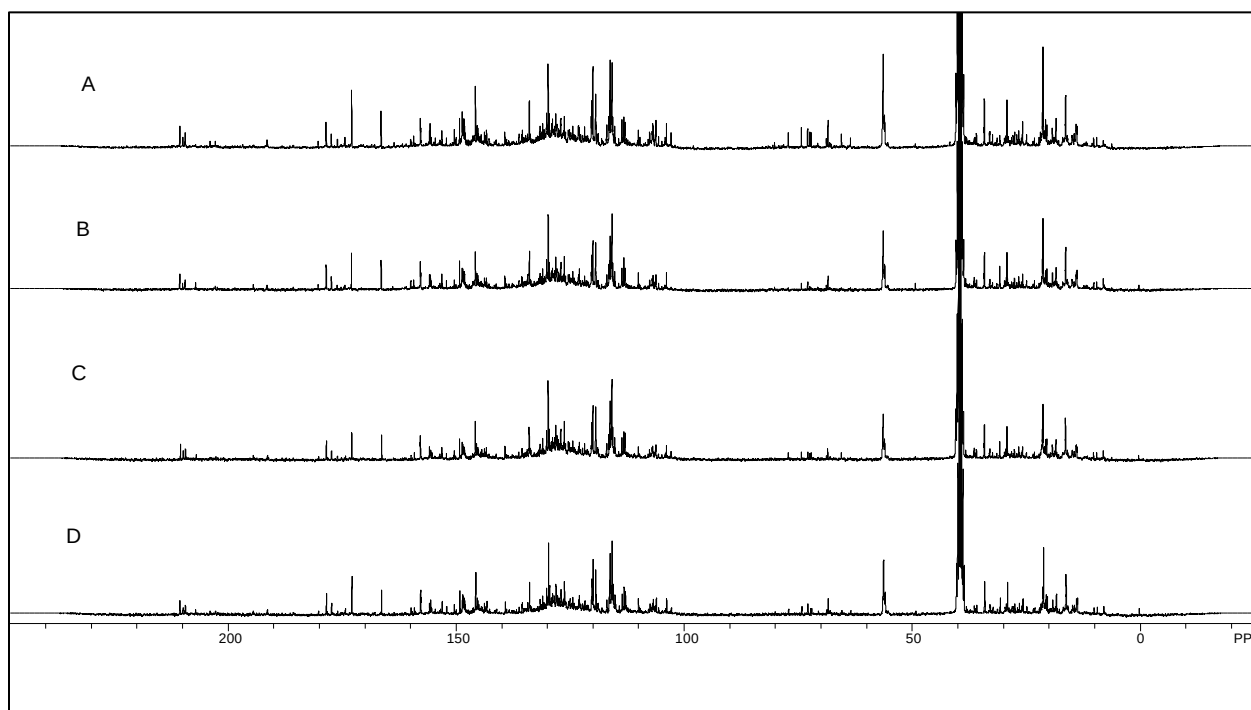


Figure 6.6. ¹³C-NMR spectra of bio-oils showing the effect of fluidizing gas (A) 100% N₂; (B) CO₂/N₂; (C) CO/N₂ and (D) H₂/N₂

The model fluidizing gas studies in comparison with the FCC cracking under the inert atmosphere (N₂) showed that all the gas mixtures (CO/N₂; CO₂/N₂ and H₂/N₂) increased deoxygenation reactions and resulted in a further reduction of the relative contents of methoxyls, sugars, carboxylics and carbonyls. Consequently, the relative aromatic content increased in the presence of these gas mixtures. The CO/N₂ gas in particular was found to crack more sugars and demethoxylate lignin

decomposition products. From Table 6.4, it can be seen that the bio-oil produced with the CO₂/N₂ was the most aromatic. It had a relative carbon content of 69.07% which corresponded to 13% more aromatics than the bio-oil produced with N₂. Furthermore it was found to produce the least carboxylic and carbonyl carbons. The CO₂/N₂ gas was found to enhance dextoxygenation reactions. This could plausibly be due to the fact that the catalyst lifetime was improved in the presence of CO₂/N₂ as a result of the suppression of coke formation or the reduction in carbon deposits on the catalyst. Thus, the catalyst was fairly active and performed relatively better. The char/coke yield at least suggests that less coke was formed with CO₂/N₂ fluidizing gas. Ohnishi et al[53] studied the catalytic dehydrocondensation of methane with CO and CO₂ on Mo/HZSM5-5 and Fe/Co-modified Mo/ZSM-5. They reported that the addition of a few percent of CO and CO₂ to methane feed promoted benzene production and significantly improved the catalyst by minimizing coke formation.

Table 6.4. ¹³C NMR of biocrude oils produced under N₂, CO/N₂, CO₂/N₂ and H₂/N₂ gas mixtures.

(Percentage carbon total)

Carbon Type	Chemical Shift, δ (ppm)	Bio-oils			
		N ₂	CO/N ₂	CO ₂ /N ₂	H ₂ /N ₂
Aliphatic hydrocarbons	28-5	21.63	25.10	20.87	19.26
Methoxyl (-OCH ₃) in lignin	55-57	3.68	2.37	3.02	3.26
Levoglucosan, anhydrosugars, alcohols,ethers	105-60	6.01	3.71	4.44	5.21
Total aromatics including olefins and phenolics	160-105	61.09	64.16	69.07	66.43
C=O groups (carboxylic acids and derivatives)	180-160	4.94	3.94	2.50	3.99
Aldehydes, ketones	180-220	2.65	0.80	0.1	1.84

From the results, CO/N₂ and NCG were found to relatively enhance demethoxylation of lignin decomposition products. During thermal degradation of lignin, the phenolic phenylpropanoid polymer undergoes extensive cleavage of β -aryl ether and C-C linkages into phenolics and aromatics. Normally the phenols, aromatics and their alkyl derivatives are formed via recombination, cyclization and Aldol condensation reactions[54]. In the absence of a suitable catalyst, most of the phenolics and the aromatics are methoxylated (guaiacol, syringols and its derivatives)[13, 55]. Nevertheless, the use of a catalyst produces primarily phenols, catechols and alkylated phenols via demethoxylation reactions[3]. The formations of these products via demethoxylation are preceded with cleavages of the methyl C-O bond, aromatic C-O bond and the side chain C-C bond [54]. Assuming demethoxylation occurred by the cleavage of the aromatic C-O bond, then the methoxy radical can react with CO to form CO₂ and the generated methyl radical could either recombine (methylation) to the phenol cresol to form methyl substituted phenol or react with H₂ to form CH₄ [54]. It is presumed that this reaction route is facilitated in the presence of CO/N₂ and the NCG. This could explain why the methoxyl content was relatively lower in these bio-oils. The increase in the actual concentration of CH₄ and CO₂ evolution with CO/N₂ fluidizing gas substantiates this phenomenon (see figure 6.3). The observed effect of CO/N₂ in producing less methoxylated phenols is in agreement with studies by Zhang et al[20]. They reported increase in monofunctional phenols and a decrease in methoxyl-containing compounds in the presence of CO and CO₂ atmosphere. This also explains why the methoxyl content decreased upon recycling the non-condensable gas.

6.3.4. Physical properties of bio-oils

The physical properties of the bio-oils showed that non-condensable gas recycle in the catalytic cracking of the hybrid poplar wood did not only affect the yield of the products but also changed the

bio-oil qualitatively. The higher heating value (HHV) and pH increased whilst the viscosity and density decreased. (Table 6.5). Additionally, the carbon content increased and the oxygen content decreased with NCG recycle. The improvement in the properties of the bio-oils were attributed to the enhancement in cracking and deoxygenation reactions such as decarboxylation, decarbonylation and demethoxylation by the presence of the reductive gas stream (CO, H₂, and hydrocarbons) and mild oxidative gas (CO₂) in the recycle gas. The carbon and oxygen contents for the bio-oil from FCC without NCG recycle was 67.78% and 25.50% respectively compared with the bio-oil from FCC with recycle which was 70.50% and 22.62%. The bio-oil from the FCC/FeCrCu/CoMo also had an increase in carbon from 67.5% to 71.63% and a decrease in oxygen content from 25.82% to 21.43% upon recycling the NCG. The increase in the HHV was due to the increase in carbon content and a decrease in the oxygen content. The decrease in the viscosity and density suggest that the bio-oils produced with gas recycling contained more compounds with lower molecular weight.

Table 6.5. Physical properties of bio-oils produced from complete recycle of non-condensable gas

Property	Bio-oils			
	FCC	FCC Recycle	FCC/FeCrCu/CoMo	FCC/FeCrCu/CoMo – Recycle
Moisture (wt%)	3.23	3.15	3.10	2.90
pH	2.76	3.25	2.70	3.33
Density (g/cm ³)	1.17	1.12	1.16	1.16
Kinematic viscosity, at 40°C (cSt)	82.2	53.96	74.9	63.58
HHV (MJ/kg)	28.49	30.13	28.65	31.27
Elemental Composition				
C	67.78	70.50	67.5	71.63
H	6.54	6.74	6.52	6.81
N	0.18	0.14	0.16	0.13
O	25.50	22.62	25.82	21.43

Tables 6.6 and 6.7 show respectively the properties of the bio-oils produced with the various gas mixtures at vapor residence of 3 s and 6.5 s. The bio-oils produced at a vapor residence of 6.5 s showed much difference in their properties as a result of enhanced catalytic cracking at that condition. The results evidently showed that the CO/N_2 , CO_2/N_2 , and H_2/N_2 influenced the properties of the bio-oil. Again, the HHV and pH of the bio-oils produced with the model gases were higher and their viscosities were lower when compared with the bio-oil produced in the inert atmosphere. From Table 6.7, it can be seen that the quality of the bio-oil produced under the various gas mixtures was in the order $\text{CO}_2/\text{N}_2 > \text{CO}/\text{N}_2 > \text{H}_2/\text{N}_2 > \text{N}_2$. The bio-oil from CO_2/N_2 had the highest HHV (29.59), pH (3.10) and carbon content (70.71%) as well as the lowest oxygen content (22.65%). The improvement in the property of the bio-oil as seen with the CO_2/N_2 gas mixture was attributed to extensive deoxygenation of the pyrolysis vapors. Nonetheless, it is worth mentioning that the bio-oils produced with the recycling of the complete pyrolysis gas (CO , CO_2 , CH_4 , H_2 , $\text{C}_2\text{-C}_5$ hydrocarbons and N_2) were of much higher quality. It suggests therefore that CH_4 and $\text{C}_1\text{-C}_5$ hydrocarbons contributed to the observed improvement in the physical properties of the bio-oil.

Table 6.6. Physical properties of bio-oils produced at vapor residence of 3 s under N₂, CO/N₂, CO₂/N₂ and CO/CO₂/N₂ gas mixtures.

Physical Properties	Bio-oils			
	N ₂	CO/N ₂ ,	CO/CO ₂ /N ₂	CO ₂ /N ₂
Moisture, wt%	4.69	2.77	3.04	4.40
Kinematic Viscosity at 40 °C , cSt	48.22	57.42	50.25	54.50
Density, g/cm ³	1.179	1.162	1.166	1.178
pH	2.81	2.61	2.58	2.61
Higher Heating Value (HHV), MJ/kg	26.10	27.74	26.91	26.02
Elemental composition, wt% (moisture free)				
C	62.23	66.54	65.11	62.89
H	6.33	6.45	6.44	6.47
N	0.13	0.13	0.13	0.13
O	31.31	27.01	28.32	30.51

Table 6.7. Physical properties of bio-oils produced at vapor residence of 6.5 s under N₂, CO/N₂, CO₂/N₂ and H₂/N₂ gas mixtures.

Physical Properties	Bio-oils			
	N ₂	CO/N ₂	CO ₂ /N ₂	H ₂ /N ₂
Moisture, wt%	3.23	3.10	3.56	3.80
Kinematic Viscosity at 40 °C , cSt	82.0	62.0	65.10	59.20
Density, g/cm ³	1.17	1.16	1.16	1.17
pH	2.76	3.06	3.10	2.91
Higher Heating Value (HHV), MJ/kg	28.49	29.13	29.59	29.41
Elemental composition, wt% (moisture free)				
C	67.78	69.23	70.71	68.88
H	6.54	6.61	6.51	6.47
N	0.18	0.13	0.13	0.13
O	25.50	24.03	22.65	24.52

6.4. CONCLUSIONS

The NCG was successfully recycled in the catalytic cracking of pyrolysis vapors from hybrid poplar using FCC catalyst and FCC/FeCrCu/CoMo/Al₂O₃ catalyst. The recycling of the NCG in the catalytic cracking evidently influenced the product yield distribution and the quality of the bio-oil. NCG recycle can potentially increase the total liquid yield and decrease the char/coke yield. The model fluidizing gas study showed that CO₂ and CO reduces char/coke formation as well as increases the organic yield. The FeCrCu catalyst was capable of promoting WGS reactions and more hydrogen was generated in-situ at the catalytic cracking conditions. The lack of suitable conditions prevented CoMo/Al₂O₃ catalyst from performing hydrodeoxygenation reactions. Recycling of NCG enhanced deoxygenation reactions and produced bio-oil with higher aromatic fraction and lower fractions of methoxyls, carboxylics and sugars. The quality of the bio-oil improved after NCG recycle. The higher heating value and the pH of the bio-oil increased whilst the viscosity and density decreased. The elemental analysis of the bio-oils showed that carbon and hydrogen increased and oxygen content decreased upon NCG recycle. The model fluidizing gas study with CO, CO₂ and H₂ confirmed the effect of recycling the NCG in the catalytic cracking process.

6.5 REFERENCES

1. Weisz, P.B., W.O. Haag, and P.G. Rodewald, *Catalytic Production of High-Grade Fuel (Gasoline) from Biomass Compounds by Shape-Selective Catalysis*. Science, 1979. **206**(4414): p. 57-58.
2. Diebold, J. and J. Scahill, *Biomass to Gasoline*, in *Pyrolysis Oils from Biomass*1988, American Chemical Society. p. 264-276.
3. Agblevor, F.A., S. Beis, O. Mante, and N. Abdoulmoumine, *Fractional Catalytic Pyrolysis of Hybrid Poplar Wood*. Industrial & Engineering Chemistry Research, 2010. **49**(8): p. 3533-3538.
4. Agblevor, F.A., O. Mante, N. Abdoulmoumine, and R. McClung, *Production of Stable Biomass Pyrolysis Oils Using Fractional Catalytic Pyrolysis*. Energy & Fuels, 2010. **24**(7): p. 4087-4089.
5. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts*. Fuel Processing Technology, 1995. **45**(3): p. 161-183.
6. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**(1): p. 39-61.
7. Carlson, T., G. Tompsett, W. Conner, and G. Huber, *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
8. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading*. Biomass and Bioenergy. **In Press, Corrected Proof**.
9. Park, H., J.-K. Jeon, D. Suh, Y.-W. Suh, H. Heo, and Y.-K. Park, *Catalytic Vapor Cracking for Improvement of Bio-Oil Quality*. Catalysis Surveys from Asia, 2011: p. 1-20.
10. Huber, George W. and A. Corma, *Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass*. Angewandte Chemie International Edition, 2007. **46**(38): p. 7184-7201.
11. Taarning, E., C.M. Osmundsen, X. Yang, B. Voss, S.I. Andersen, and C.H. Christensen, *Zeolite-catalyzed biomass conversion to fuels and chemicals*. Energy & Environmental Science, 2011. **4**(3): p. 793-804.
12. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. Biomass and Bioenergy, 1994. **7**(1-6): p. 223-236.
13. Zhang, H., R. Xiao, D. Wang, Z. Zhong, M. Song, Q. Pan, and G. He, *Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.

14. Mante, O., F. Agblevor, and R. McClung, *Fluid catalytic cracking of biomass pyrolysis vapors*. Biomass Conversion and Biorefinery, 2011. **1**(4): p. 189-201.
15. Lappas, A.A., S. Bezergianni, and I.A. Vasalos, *Production of biofuels via co-processing in conventional refining processes*. Catalysis Today, 2009. **145**(1-2): p. 55-62.
16. Pütün, E., *Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst*. Energy, 2010. **35**(7): p. 2761-2766.
17. Bridgwater, A.V., *Principles and practice of biomass fast pyrolysis processes for liquids*. Journal of Analytical and Applied Pyrolysis, 1999. **51**(1-2): p. 3-22.
18. Bridgwater, A.V. and G.V.C. Peacocke, *Fast pyrolysis processes for biomass*. Renewable and Sustainable Energy Reviews, 2000. **4**(1): p. 1-73.
19. Scahill, J. and J. Diebold, *Engineering Aspects of Upgrading Pyrolysis Oil Using Zeolites*, in *Research in Thermochemical Biomass Conversion*, A.V. Bridgwater and J.L. Kuester, Editors. 1988, Elsevier Applied Science ; Sole distributor in the USA and Canada, Elsevier Science Pub. Co.: London; New York; New York, NY, USA. p. 927-940.
20. Zhang, H., R. Xiao, D. Wang, G. He, S. Shao, J. Zhang, and Z. Zhong, *Biomass fast pyrolysis in a fluidized bed reactor under N₂, CO₂, CO, CH₄ and H₂ atmospheres*. Bioresource Technology, 2011. **102**(5): p. 4258-4264.
21. Meesuk, S., J.-P. Cao, K. Sato, Y. Ogawa, and T. Takarada, *Fast Pyrolysis of Rice Husk in a Fluidized Bed: Effects of the Gas Atmosphere and Catalyst on Bio-oil with a Relatively Low Content of Oxygen*. Energy & Fuels, 2011. **25**(9): p. 4113-4121.
22. Thangalazhy-Gopakumar, S., S. Adhikari, R.B. Gupta, M. Tu, and S. Taylor, *Production of hydrocarbon fuels from biomass using catalytic pyrolysis under helium and hydrogen environments*. Bioresource Technology, 2011. **102**(12): p. 6742-6749.
23. Butterman, H.C. and M.J. Castaldi, *Influence of CO₂ Injection on Biomass Gasification*. Industrial & Engineering Chemistry Research, 2007. **46**(26): p. 8875-8886.
24. Butterman, H.C. and M.J. Castaldi, *CO₂ as a Carbon Neutral Fuel Source via Enhanced Biomass Gasification*. Environmental Science & Technology, 2009. **43**(23): p. 9030-9037.
25. Butterman, H.C. and M.J. Castaldi, *Syngas Production via CO₂ Enhanced Gasification of Biomass Fuels*. Environmental Engineering Science, 2009. **26**(4): p. 703-713.
26. Jindarom, C., V. Meeyoo, T. Rirksomboon, and P. Rangsunvigit, *Thermochemical decomposition of sewage sludge in CO₂ and N₂ atmosphere*. Chemosphere, 2007. **67**(8): p. 1477-1484.

27. Osvalda, S., *Kinetics of pyrolysis, combustion and gasification of three biomass fuels*. Fuel Processing Technology, 2007. **88**(1): p. 87-97.
28. Minkova, V., S.P. Marinov, R. Zanzi, E. Björnbom, T. Budinova, M. Stefanova, and L. Lakov, *Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide*. Fuel Processing Technology, 2000. **62**(1): p. 45-52.
29. Susanto, H. and A.A.C.M. Beenackers, *A moving-bed gasifier with internal recycle of pyrolysis gas*. Fuel, 1996. **75**(11): p. 1339-1347.
30. Carlson, T.R., Y.-T. Cheng, J. Jae, and G.W. Huber, *Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust*. Energy & Environmental Science, 2011. **4**(1): p. 145-161.
31. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
32. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways*. Fuel Processing Technology, 1995. **45**(3): p. 185-202.
33. Aho, A., N. Kumar, K. Eränen, T. Salmi, M. Hupa, and D.Y. Murzin, *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.
34. Lappas, A.A., M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, and I.A. Vasalos, *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
35. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
36. Mante, O., F. Agblevor, and R. McClung, *Fluid catalytic cracking of biomass pyrolysis vapors*. Biomass Conversion and Biorefinery: p. 1-13.
37. Marquez-Montesinos, F., T. Cordero, J. Rodríguez-Mirasol, and J.J. Rodríguez, *CO₂ and steam gasification of a grapefruit skin char*. Fuel, 2002. **81**(4): p. 423-429.
38. Sharma, R.K. and N.N. Bakhshi, *Conversion of non-phenolic fraction of biomass-derived pyrolysis oil to hydrocarbon fuels over HZSM-5 using a dual reactor system*. Bioresource Technology, 1993. **45**(3): p. 195-203.

39. Kubiak, C.P., *Preconversion catalytic deoxygenation of phenolic functional groups. Quarterly technical progress report, January 1, 1995--March 31, 1995, in Other Information: PBD: 19951995*. p. Medium: ED; Size: 6 p.
40. Rocha, J.D., S.D. Brown, G.D. Love, and C.E. Snape, *Hydropyrolysis: a versatile technique for solid fuel liquefaction, sulphur speciation and biomarker release*. Journal of Analytical and Applied Pyrolysis, 1997. **40-41**(0): p. 91-103.
41. Singh, N.R., W.N. Delgass, F.H. Ribeiro, and R. Agrawal, *Estimation of Liquid Fuel Yields from Biomass*. Environmental Science & Technology, 2010. **44**(13): p. 5298-5305.
42. Dilcio Rocha, J., C.A. Luengo, and C.E. Snape, *The scope for generating bio-oils with relatively low oxygen contents via hydropyrolysis*. Organic Geochemistry, 1999. **30**(12): p. 1527-1534.
43. Gerçel, H.F., A.E. Pütün, and E. Pütün, *Hydropyrolysis of Extracted Euphorbia rigida in a Well-Swept Fixed-Bed Tubular Reactor*. Energy Sources, 2002. **24**(5): p. 423-430.
44. Pindoria, R.V., I.N. Chatzakis, J.Y. Lim, A.A. Herod, D.R. Dugwell, and R. Kandiyoti, *Hydropyrolysis of sugar cane bagasse: effect of sample configuration on bio-oil yields and structures from two bench-scale reactors*. Fuel, 1999. **78**(1): p. 55-63.
45. Pindoria, R.V., J.-Y. Lim, J.E. Hawkes, M.-J. Lazaro, A.A. Herod, and R. Kandiyoti, *Structural characterization of biomass pyrolysis tars/oils from eucalyptus wood waste: effect of H₂ pressure and sample configuration*. Fuel, 1997. **76**(11): p. 1013-1023.
46. Pindoria, R.V., A. Megaritis, A.A. Herod, and R. Kandiyoti, *A two-stage fixed-bed reactor for direct hydrotreatment of volatiles from the hydropyrolysis of biomass: effect of catalyst temperature, pressure and catalyst ageing time on product characteristics*. Fuel, 1998. **77**(15): p. 1715-1726.
47. Pütün, A.E., H.F. Gerçel, Ö.M. Koçkar, Ö. Ege, C.E. Snape, and E. Pütün, *Oil production from an arid-land plant: fixed-bed pyrolysis and hydropyrolysis of Euphorbia rigida*. Fuel, 1996. **75**(11): p. 1307-1312.
48. Pütün, A.E., Ö.M. Koçkar, S. Yorgun, H.F. Gerçel, J. Andresen, C.E. Snape, and E. Pütün, *Fixed-bed pyrolysis and hydropyrolysis of sunflower bagasse: Product yields and compositions*. Fuel Processing Technology, 1996. **46**(1): p. 49-62.
49. Marker, T., L. Felix, M. Linck, and M. Roberts. *Integrated Hydropyrolysis and Hydroconversion Process (IH₂) for Production of Gasoline and Diesel Fuel From Wood, Algae, Cornstover, Lemna,*

- and Bagasse Feedstocks*. in *Spring Meeting & 7th Global Congress on Process Safety*. 2011. Chicago, IL.
50. Takarada, T., T. Tonishi, Y. Fusegawa, K. Morishita, N. Nakagawa, and K. Kato, *Hydropyrolysis of coal in a powder-particle fluidized bed*. *Fuel*, 1993. **72**(7): p. 921-926.
 51. Wang, G., W. Li, B. Li, and H. Chen, *TG study on pyrolysis of biomass and its three components under syngas*. *Fuel*, 2008. **87**(4-5): p. 552-558.
 52. Diebold, J. and J. Scahill, *Biomass to Gasoline*, in *Pyrolysis Oils from Biomass*, E.J. Soltes and T.A. Milne, Editors. 1988, American Chemical Society: Washington, DC. p. 264-276.
 53. Ohnishi, R., S. Liu, Q. Dong, L. Wang, and M. Ichikawa, *Catalytic Dehydrocondensation of Methane with CO and CO₂ toward Benzene and Naphthalene on Mo/HZSM-5 and Fe/Co-Modified Mo/HZSM-5*. *Journal of Catalysis*, 1999. **182**(1): p. 92-103.
 54. A, D., *Mechanisms of liquefaction and pyrolysis reactions of biomass*. *Energy Conversion and Management*, 2000. **41**(6): p. 633-646.
 55. Mohan, D., C.U. Pittman, and P.H. Steele, *Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review*. *Energy & Fuels*, 2006. **20**(3): p. 848-889.

CHAPTER 7

7.0 CONCLUSION

The overall goal of this work is to enhance existing knowledge and understanding of the use of commercially available FCC catalyst for the production of high quality bio-oil. This dissertation investigated the production of upgraded bio-oil from hybrid poplar wood. The research work focused on the following:

1. The effect of Y-zeolite content in the FCC catalyst
2. The influence of steam treatment of the FCC catalyst
3. The use of ZSM-5 additives as co-catalyst to FCC catalyst
4. The effect of temperature, WHSV and vapor residence time
5. Recycling of the non-condensable gases produced during the fractional catalytic pyrolysis

The Y-zeolite content of the FCC catalyst is an important characteristic that influences the product distribution and quality of bio-oil from the catalytic pyrolysis of biomass. The Y-zeolite content can be used to control the formation of organic liquid, water, coke and gas. FCC catalyst with high amounts of Y-zeolite (> 40 wt.%) is highly active towards biomass feedstocks and extensively cracks the primary vapors into higher fractions of coke and water. The zeolite content also affects the rate of catalyst deactivation. FCC catalyst with higher Y-zeolite content deactivates quickly relative to FCC catalyst with lower Y-zeolite content due to high formation of coke on the catalyst. FCC catalyst with total BET surface areas less than 200 m²/g would be appropriate for the catalytic pyrolysis of biomass. It must be noted that higher zeolite FCC catalyst produces bio-oil with higher carbon content, lower oxygen content, higher HHV, lower viscosity and relatively higher pH value. Matrix design can also be

used to improve upon the overall catalytic pyrolysis of biomass especially in FCC catalyst with relatively lower Y-zeolite content.

Steam treatment of the FCC catalyst influences the catalytic pyrolysis of the biomass. The product distribution and the quality of the bio-oil are dependent on the steaming conditions. Severe steaming of the FCC catalyst at 788 °C caused the organic liquid fraction to increase and coke yield to decrease. Mild steaming at 732 °C improved the catalytic activity of the FCC catalyst and consequently produced more gas and less amount of coke. Steaming of the FCC catalyst produces bio-oils with lower viscosity and density. The hydrothermal treatment affects the selectivity of the FCC catalyst in the formation of CH_4 , H_2 , C_2 - C_5 hydrocarbon and the production of aromatic hydrocarbons. The change in the activity and selectivity of the FCC catalyst as a result of steam treatment is attributed to zeolite destruction and the presence of nonframework aluminum (NFA) species. The evidence from this study suggests that steaming of the catalyst can be considered a pretreatment step for altering the activity and selectivity of the FCC catalyst to minimize coke formation, enhance organic liquid yield and improve the quality of the bio-oil.

With ZSM-5 based additive as a co-catalyst to FCC catalyst in the catalytic pyrolysis of biomass, organic liquid yield increases and coke formation decreases. The formation of CO_2 , CH_4 , and H_2 gases decreases and the generation of C_5 hydrocarbons increases with increase in ZSM-5 additive. The productions of bio-oils that are less viscous, less acidic and relatively high in energy are achievable with a blend of FCC catalyst and ZSM-5 additive. ZSM-5 additive increases the aromatic hydrocarbons and decreases the aliphatic fractions in the bio-oil. The effect of ZSM-5 additive is attributed to its characteristic shape selectivity in cracking of the vapors. Reactor configuration affects the product distribution and physico-chemical properties of the bio-oils. This was evident in the use of a 2-stage reactor. Overall, the results obtained from the use of ZSM-5 additive as a co-catalyst to the FCC catalyst

contribute additional evidence that suggests the role of Y zeolite in the formation of the catalytic pyrolysis products.

The findings from the response surface methodology study suggest that temperature, weight hourly space velocity (WHSV) and vapor residence time are important factors that affect the catalytic pyrolysis of biomass with FCC catalyst. The study showed that different conditions are required to increase organic yield, decrease char/coke yield and improve the quality of the bio-oil (i.e decrease viscosity, increase carbon content and pH value). The WHSV was found to be the most influential significant factor that affects the yield of organic liquid and water. Reaction temperature was the most important significant factor that influence char/coke yield, concentration of non-condensable gases, carbon content, oxygen content, pH and viscosity of the bio-oils. To increase organic liquid yield and decrease coke/char yield, higher levels of WHSV ($>2 \text{ h}^{-1}$) and moderate temperatures ($500 \text{ }^{\circ}\text{C} \leq A < 600 \text{ }^{\circ}\text{C}$) at shorter vapor residence time ($\leq 4.5 \text{ s}$) would be suitable. The concentrations of H_2 , CH_4 and CO increase with increasing temperature whereas the concentration of CO_2 increases with decreasing temperature. Higher temperatures promote extensive cracking reactions which results bio-oils with lower oxygen content and higher carbon content. Higher reaction temperatures also increase the pH and viscosity of the bio-oils. Among all the three factors studied, vapor residence time is the least influential. The current results add to a growing body of literature on the influence of process conditions in the catalytic pyrolysis of biomass with zeolites.

Recycling of the non-condensable gases produced in the catalytic pyrolysis of biomass can potentially increase the total liquid yield and decrease the char/coke yield. The results from the model fluidizing gas study show that CO_2 and CO promotes reactions that reduce char/coke formation and increases organic yields. Additionally, deoxygenation reactions are enhanced in the presence of the non-condensable gases resulting in the production of bio-oils with higher aromatic fraction and lower

fractions of methoxyls, carboxylics and sugars. The HHV and the pH value of the bio-oils produced with recycling are higher whilst the viscosity and density are lower. The results provide additional evidence that process conditions can be used to improve the overall catalytic pyrolysis process using Y-zeolite based FCC catalyst.

Future work needs to be done to establish the influence of recycling the non-condensable gases on product yields and quality of the bio-oil in fractional catalytic pyrolysis of biomass. Specifically, experiments would have to be conducted to determine the effect of the lower molecular weight hydrocarbons. Also, investigation on suitable conditions (temperature, catalysts ratios and residence time) for the recycling process is recommended. There is also the need to improve on the design of the 2-Stage reactor to avoid spouting of the catalyst bed and minimize catalyst losses. Further experimental investigations are needed to understand the role of matrix, unit cell size and rare earth content of the FCC catalyst.