CATALYTIC PYROLYSIS OF CELLULOSE, HEMICELLULOSE AND LIGNIN MODEL COMPOUNDS

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Thesis submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Biological Systems Engineering

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January 25, 2010

Blacksburg, Virginia

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ABSTRACT

The effect of HZSM-5 catalyst and NaOH pretreatment on the product distribution and bio oil properties from pyrolysis of cellulose, hemicellulose and lignin model compounds was investigated at 450 ^{o}C. NaOH pretreated and untreated cellulose was pyrolyzed on sand and the HZSM-5 catalysts; VPISU001 HZSM-5, BASF HZSM-5, and Sud-Chemie HZSM-5. The pyrolysis of cellulose on BASF and Sud-Chemie HZSM-5 catalysts increased the yields of the organic liquid fraction, total liquid and char while decreasing the gas yields. However the catalyst decreased the organic and char yields while increasing the water yields but there was no change in gas yields. The NaOH treatment caused a decrease in the organic and total oil yields relative to the control but the char yield increased. The change in gas yields was not significant. The characterization of the oils using FTIR and ^{13}C–nmr showed that, the VPISU001 HZSM-5 with and without NaOH pretreatment caused elimination of the levoglucosan fraction while increasing the aromatic fraction. The NaOH pretreated cellulose pyrolyzed on sand reduced the levoglucosan groups while increasing the aromatic fraction of the bio oil. In the hemicellulose studies, birchwood xylan and NaOH treated xylan samples were pyrolyzed on sand and VPISU001 HZSM-5 catalyst. The organic liquid yields were very low and ranged from 3.3 wt% to 7.2 wt%, the water yields ranged from 17.8-25.7 wt%, the char yield were 17.8-25 wt% and gas yield were 40.9-49.6 wt%. The HZSM-5 catalysts increased the water and gas yields and

produced the lowest char yield. NaOH pretreatment produced the lowest water yield while the char yield was the highest. The combined effect of NaOH pretreatment and HZSM-5 produced the lowest organic yield and highest char yield. The FTIR and ^{13}C-nmr analyses of the organic liquids showed that the HZSM-5 catalyst promoted the formation of aromatic products, while the NaOH pretreatment promoted the formation of aliphatic hydrocarbons. The combined effect of NaOH pretreatment and HZSM-5 catalyst seem to promote the formation of anhydrosugars. The main gases evolved were CO, CO_2 and low molecular weight hydrocarbons. The HZSM-5 catalyst promoted CO formation while NaOH pretreatment promoted CO_2. The HZSM-5 catalyst produced the highest yield of low molecular weight hydrocarbon gases. The lignin and model compounds studies involved using low molecular weight kraft lignin, guaiacol, and syringol which were pyrolyzed on sand and VPISU001 HZSM-5 catalyst at 450 ^{o}C. The kraft lignin pyrolysis produced low liquid and gas yields and high char yields. The HZSM-5 catalysts increased the water yield and decreased the organic liquid yield. NaOH pretreatment increased the char yield and decreased the liquid products. NaOH and the HZSM-5 catalyst together decreased the char and increased the gas yields. The ^{13}C-nmr and FTIR analysis showed that NaOH pretreatment promoted the formation of mainly guaiacol while the HZSM-5 catalyst formed different aromatic components. NaOH pretreatment promoted the formation of more CO_2 than CO whilst HZSM-5 catalyst promoted the formation of more CO than CO_2. Methane formation was enhanced by NaOH pretreatment. Other hydrocarbon gases were however enhanced by the HZSM-5 catalysts. Pyrolysis of the model compounds on the HSZM-5 catalyst showed an increase in pyrolytic water. The HZSM-5 catalyst promoted demethylation in syringol pyrolysis as compared to guaiacol.

DEDICATION

This research work is dedicated to my family, for their unconditional support and love especially my father Mr. Bernard Atadana for his support in every step of my education. I also dedicate this work to Jennifer Przybyla and Lola Przybyla for their love and support. Finally I dedicate this work to all my lab mates for their help and suggestions throughout my research work.

ACKNOWLEDGEMENTS

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CHAPTER ONE

INTRODUCTION

1.1 Background

Throughout history biomass has been used as an energy source and remains an important component of the national energy supplies in several countries (Hall et al. 1982.; Gercel 2002; Jones 1989). Biomass constitutes the fourth largest source of energy in the world, accounting for about 14–15% of the world's primary energy consumption and about 38–43% of the primary energy consumption in developing countries (Hall et al. 1982. ; Scurlock et al. 1993.; Demirbas 2001; Chen et al. 2003). Biomass energy is becoming a particularly important issue in developed nations due to their burning of fossil fuels which is the primary suspect responsible for global warming. If the harvesting and use of biomass is done in a sustainable way, this renewable energy source is nearly CO_2 neutral (Liang and Kozinski 2000).

Biomass is a polymer of hemicellulose, cellulose, lignin, and minor amounts of other organics which pyrolyze or degrade at different rates and by different mechanisms and pathways (Bridgwater et al. 1999). Cellulose is a polymer of glucose that can be broken down by hydrolysis reactions with water catalyzed by cellulase enzymes or acids. Glucose units are tightly held together by hydrogen bonds forming a crystalline structure. Hemicellulose is an amorphous chain consisting of a mixture of sugars made up of arabinose, galactose, glucose, mannose, and xylose. Hemicellulose chains are more readily broken down to their monomeric units than cellulose. Lignin, unlike the others, is not a sugar based structure but a heterogeneous substance based on phenol-propene backbone (Wyman 1999).

Biomass conversion methods can be divided into two broad pathways: biological (fermentation and anaerobic digestion) and thermochemical (combustion, gasification, and pyrolysis). Among the various thermochemical conversion processes, pyrolysis is considered to be an emerging technology for liquid oil (bio crude) production (Islam and Beg 2004; Mohan et al. 2006). Char and gas are additional by-products of the pyrolysis process.

Pyrolysis is a very complex process that is influenced by many factors such as the nature of the biomass, water content, reactor configuration, inherent minerals, heating rates, and additives (Wang et al. 2006.). Due to the intricacy and potential of this process to produce bio fuel, it becomes essential to understand the fundamentals of the pyrolysis process. Previous studies have shown that biomass pyrolysis can be separated into four phases: moisture evolution, hemicellulose decomposition, cellulose decomposition, and lignin decomposition (Raveendran et al. 1996; Yang et al. 2004). The overall rate of biomass pyrolysis is suggested to be sum of the individual rates of the three major components hemicellulose, cellulose, and lignin (Kuofopanos et al. 1989; Srivastava and Jalan 1994; Raveendran et al. 1996; Miller and Bellan 1997; Rao and Sharma 1998; Orfao et al. 1999; Manya et al. 2003). The yield of volatiles, gases, and char from pyrolysis has been shown to be proportional to the three components in virgin biomass (Srivastava and Jalan 1994; Raveendran et al. 1996). Therefore it is vital to identify the pyrolysis characteristics of the three main components in order to better understand biomass pyrolysis. So far, numerous studies on the three main components have been carried out with an emphasis on developing kinetic models for predicting behavior of biomass pyrolysis (Orfao et al. 1999; Manya et al. 2003; Yang et al. 2004; Yan et al. 2005). Additional studies were focused on the

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prediction of biomass pyrolysis behavior from a thermogravimetric analysis (TGA) of the three components (Yang et al. 2006).

Catalytic pyrolysis can yield desired product yields or selectivity by using appropriate additives (Wang et al. 2006). Obtaining the appropriate catalyst for biomass that exists not only in large varieties but also with different structural composition is a herculean task. Studies regarding catalysts have been conducted and findings published (A.E. Borgund and T. Barth 1999; Williams and Nugranad 2000; Ates¸ F. et al. 2006). Researchers (Wang et al. 2006) have used thermal analysis, which provides a fast and preliminary evaluation of catalytic effects of additives on biomass pyrolysis, to study the effects of six inorganic catalysts (Na_2OH, Na_2CO3, $NaCl$, Na_2SiO_3, TiO_2, and HZSM-5) on pyrolysis of three different kinds of biomass. Sodium based catalysts caused a reduction in the pyrolysis temperature but increased the amount of char formed in order of their increasing basicity. TiO_2 and HZSM-5 tend to decrease the char formed in order of increasing acidity. Additional studies examined the effect of mineral mater on palm oil waste using thermal analysis to study the catalytic effect of mineral matter on the individual biomass components (cellulose, hemicelluloses, and lignin) as well as a synthetic biomass made from the components and the natural biomass (Haiping et al. 2006).

Catalysts used in pyrolysis can be divided into two distinct groups. The first group of catalysts, primary catalysts, is added directly to the biomass before the experiments. The addition of catalyst is done by wet impregnation of the raw material or by dry mixing the catalyst with the raw material. Primary catalysts are usually non-renewable (in-bed mode) and are exposed to the same operating temperature of the reactor as the biomass. This enables the immediate contact of

the evolved pyrolysis vapors with the catalyst. The second group of catalysts is placed in a secondary reactor located downstream from the pyrolysis reactor (Samolada and Vasalos 2000; Sutton 2001). Using catalysts enhances the cracking reactions of heavy molecules in pyrolysis products leading to the production of less viscous bio-oil, reduces the formation of carboxylic acids making bio-oil less corrosive, and enhances the formation of more valuable products like hydrocarbons that can increase the heating value of the bio-oil produced (Pattiya and Bridgwater.). Currently there is insufficient research on the catalytic effect of additives on yields from the pyrolysis of lignocellulosic biomass and determining the effect of the catalyst on the three individual components: lignin, cellulose, and hemicellulose.

The purpose of this research is to study the effect of catalysts on the components of wood; cellulose, hemicellulose and lignin, examining the effect of catalysts on the yield and characteristics of the pyrolytic products. In this study a primary catalysts a liquid catalyst of NaOH solution, will be used to pre-treat the samples by impregnation and a solid catalyst, zeolite HZSM-5, will be mixed with the sample in the fluidized bed pyrolysis reactor to serve as the fluidized medium.

1.2 Project Objectives

1. Pyrolyze treated and untreated cellulose on H-ZSM5 catalyst.
2. Pyrolyze treated and untreated hemicellulose on H-ZSM5 catalyst.
3. Pyrolyze low molecular weight kraft lignin, guaiacol and syringol.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Composition of Wood

Wood is primarily composed of composite plant material constructed from oxygen containing organic polymers; cellulose, hemicellulose, lignin and extractives (Rowell, 1984). Each of these components contributes to fiber properties, which ultimately impact product properties (Sjostrom1993).

2.1.1 Cellulose

Cellulose provides wood's strength and comprise approximately between 40-50 wt% of dry wood (Rowell, 1984). Chemically cellulose is a high-molecular-weight (10^6 or more) linear polymer of β-(1 ⟶ 4)-D-glucopyranose units in the $^4C_1$ conformation . The basic repeating unit of the cellulose polymer consists of two glucose anhydride units, called a cellobiose unit. Glucose anhydride is formed via the removal of water from each glucose unit. This is polymerized into long cellulose chains that contain 5000-10000 glucose units. The fully equatorial conformation of β-linked glucopyranose residues stabilizes the chair structure, minimizing flexibility (Mohan et al. 2006).

Each D-anhydroglucopyranose unit possesses hydroxyl groups at C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols. The molecular structure of cellulose gives it, its characteristics properties: hydrophylicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of hydroxyl groups. Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by

the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies (Klemn et al 2005).

The crystalline structure resists thermal decomposition better than hemicelluloses (Mohan et al., 2006). Besides this the presence of crystalline cellulose, with regions of less order and the size of the elementary fibrils work together to produce interesting combination of contrary properties such as stiffness and rigidity on one side and flexibility on the other (Wagberg and Annergren 1997). Crystalline cellulose has very limited accessibility to water and chemicals thus attack by chemicals are primarily expected to occur at the amorphous cellulose and crystalline surface. Cellulose degradation occurs at 240-350 °C to produce anhydrocellulose and levoglucosan (Mohan et al. 2006). Levoglucosan is produced when the glucosan radical is generated without the bridging oxygen from the preceding monomer unit.

2.1.2 Hemicellulose

Hemicellulose also called polyose constitute about 25-35% by mass of dry wood(Rowell 1984). Hemicellulose is a heteropolysaccharide made up of monosaccharide such as glucose, mannose, galactose, xylose, arabinose,4-*O*-methyl glucuronic acid and galacturonic acid residues and unlike cellulose hemicellulose have a lower degree of polymerization(between 50-300) with some containing side groups on the chain molecules and are essentially amorphous. The types of hemicellulose found in wood depend on the type of wood and they vary in structure and amount. In soft wood the main types of hemicellulose present are galactoglucomannans (10-15 wt%) and arabinoglucoronoxylan (7-10 wt%) while in hardwood it's the partially acetylated glucuronoxylan (20-35 wt%) and a small percentage of galactomannan (2-5 wt%) in hardwood

(Sjostrom 1993). Table 2.3 summarizes the main structural features of hemicellulose appearing in both soft and hardwood. Xylan is different from glucomannan in the sense that it contains acidic groups (glucuronic acid) and has a molecular structure similar to cellulose when their side branches are removed from xylan. This makes xylan combine with cellulose in more ordered structure after kraft pulping (Mitikka and Vourinene 1995).Glucomannan is more sensitive to kraft cooking conditions than xylan (Wagberg and Annergren 1997). Hemicellulose in hardwood pulp are dominated by xylan however in soft wood kraft pulps the amount of xylan present becomes almost the same as that of glucomannan though glucomannan is higher in content in softwood due to its chemical resistant nature.

2.1.3 Lignin

Lignin is the third major wood component. In soft wood it accounts for 23%-33% of the mass while in hardwood it accounts for 16%-25% by mass of hardwood(Bridgwater 2004). Structurally Lignin is a three-dimensional, highly branched, polyphenolic substance that consists of an irregular array of variously bonded "hydroxy-" and "methoxy-"substituted phenylpropane units (McCarthy and Islam 2000). Lignin is an amorphous cross-link resin with no exact structure, functionally serving as a binder for the agglomeration of fibrous cellulosic components while also serving as a shield against rapid microbial or fungal destruction of the cellulosic fibers. The p-coumeryl, coniferyl and sinapyl structures are exhibited by these three general phenyl propane units, which undergo radical dimerization and further oligomerisation, eventually polymerize and cross linking to form lignin. Softwood mostly contains guaiacyl lignin formed from the polymerization of a higher fraction of coniferyl phenyl propane units. In hardwood the type of lignin found is the guaiacyl-syringyl a copolymer of both the coniferyl and synapyl phenyl propane units where the fraction of synapyl units is higher than that in soft wood lignin.

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Lignin possesses an amorphous in structure enabling a large number of possible interlinkages between individual units. This is due to the fact that the radical reactions that results in lignin formation are nonselective random condensations (Mohan et al. 2006). Interms of bond linkages between units, ether bonds predominate among lignin units whilst in cellulose and hemicellulose the acetyl functional group predominates. Besides this the carbon-to-carbon linkages also exist in lignin. Lignin is linked to the polysaccharides by covalent bonds (Fengel and Wegner 1984). Lignin isolation from the polysaccharides results in a modified and partially degraded product. The chemical and physical properties of lignin differ depending on the extraction or isolation method used (Mohan et al. 2006).

2.1.4 Extractives

The extractives found in wood are organic in nature. Functionally they serve as intermediates in metabolism as energy reserves and as defense against microbial and insect attack. Example extractives include fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils. They can be extracted from wood by using solvents like water methylene chloride and alcohol or non polar solvents like toluene or hexane (Mohan et al. 2006).

2.1.5 Inorganic Minerals

Woody biomass contains a small amount of mineral content that ends up in the pyrolysis ash. Calcium and potassium are the most abundant elements found in woody biomass. Sulfur, chlorine and heavy metals are present in trace amounts. These elements do not produce energy during combustion but they do affect the energy content of woody biomass. On average hardwoods have a higher concentration of these mineral elements than soft woods. The amount

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of the minerals found vary according to the location of growth rather than the species, size or age of the wood (www.forestencyclopedia.net)

2.2 Energy Conversion Methods for Wood

Energy conversion methods can be divided into two broad pathways; biochemical which include fermentation and anaerobic digestion (Wyman 1999). The other is thermochemical which involves combustion gasification and pyrolysis (Islam and Beg 2004). Pyrolysis is regarded central in the thermochemical conversion processes (Antal 1983). Pyrolysis is a complex process whose product output proportions and make up are influenced by factors such as the type of pyrolysis process employed, nature of the biomass, water content, reactor configuration, inherent minerals, heating rates, residence time and additives (Wang et al. 2006)The pyrolysis technology falls into two main types, slow and fast pyrolysis depending on the operating conditions employed (Maschio and Lucchesi 1992).

2.3 Slow Pyrolysis

This technology has been in existence over thousands of years employed mainly for the production of charcoal. The process involves heating the biomass to ~500 $^{\circ}$C. The heating rate in conventional pyrolysis (slow pyrolysis) is much slower than that employed in fast pyrolysis. The vapor residence time varies from 5min to 30min (Bridgewater 1990; Bridgewater 1994; Bridgwater et al. 2001). The vapors do not escape as rapidly as they do in fast pyrolysis this allows the components in the vapor phase to continue to react with each other as the solid char and liquid are being formed (Mohan et al. 2006).

2.4 Fast Pyrolysis

Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. This produces mostly vapors and aerosols and char .After cooling and condensation dark brown mobile liquid is formed which has heating value about half that of conventional fuel oil (Bridgwater et al. 2001). Fast pyrolysis processes produce 60-75 wt% of liquid bio-oil, 15-25 wt% of solid char and 10-20wt% of noncondensable gases, depending on the feedstock used. No waste is generated, because the bio oil and solid char can each be used as a fuel and the gas can be recycled back into the process. There are four essential features of a fast pyrolysis process; very high heating and heat transfer rates are used which requires finely ground biomass feed. Secondly, a carefully controlled pyrolysis temperature usually between 425-500 ^{o}C. Thirdly short residence times are used typically between 0.5-5s. Finally the pyrolysis vapors and aerosols are rapidly cooled to give bio-oil (Demirbas 2005). Rapid heating and quenching results in intermediate pyrolysis liquid products which condense before further reactions break down higher-molecular-weight species into gaseous products. The rate and extent of decomposition of the components of biomass depends on the process parameters of reactor, reactor configuration temperature, nature of biomass (composition of minerals, proportions of lignin and the carbohydrates), biomass treatment (e.g. storage conditions, size reduction, e.t.c) use of catalyst biomass heating rate and pressure (Bridgwater 1994; Agblevor and Besler 1995; Agblevor et al. 1996; Bridgwater et al. 1999). The degree of secondary reaction of the gas/vapor products depends on the time temperature history to which they are subjected before collection which affects the proportions of product yields oil. High reaction rates minimize char formation and under some conditions no char is formed. The major product of pyrolysis is gas at higher fast pyrolysis temperature (Mohan et al. 2006).

2.4.1 Fast Pyrolysis Reactors

Research over the years has led to the development of different reactor configuration for the purpose of fast pyrolysis. The fluidized bed reactor, the circulating fluid bed reactor, entrained, rotating cone, ablative and vacuum reactor. Each of these reactors possesses its inherent advantages in the area of heat supply, heat transfer, feed preparation and complexity of operation. The ablative reactor where the wood is pressed against a heated surface and rapidly moved causing the wood to melt leaving an oil film behind which evaporates has the advantage of accommodating larger wood size particle and being a compact and intensive reactor which does not require a carrier gas. However these attributes result in disadvantages of limited heat transfer to the reactor and being a surface area controlled system and moving parts at high temperatures (Bridgwater et al. 1999). The fluidizing bed and circulating fluid bed makes use of a mix of convection and conduction heat to transfer heat from source to the biomass. The heat transfer limitation here is the wood particle itself thus these reactors have the limitations of requiring very small particle size less than 3mm to produce good oil yields. Also they require inert gas for fluidization and transport (Bridgwater et al. 1999). Finally the vacuum pyrolysis reactor where the pyrolysis occurs under reduced pressure and slow heating rates has the advantage of also using larger particle size. However its limited by its higher equipment cost and low oil yields (Bridgwater et al. 1999; Mohan et al. 2006).

2.5 Bio Oil

Bio oil is a dark brown, free-flowing organic liquid that are compromised of highly oxygenated compounds (Peacocke et al. 1994; Czernik and Bridgewater 2004). Bio-oil can be considered a microemulsion in which the continuous phase is an aqueous solution of holocellulose decomposition products and small molecules from lignin decomposition. The continuous liquid

phase stabilizes a discontinuous phase that is largely composed of pyrolytic lignin macromolecules (Piskorz and Radlien 1998). The stabilization of the microemulsion is achieved by hydrogen bonding and nanomicelle and micromicelle formation. Bio oil formed by rapidly and simultaneously depolymerization and fragmenting cellulose, hemicellulose, and lignin with a rapid increase in temperature. Rapid quenching "freezes" in the intermediate products of the fast degradation of hemicellulose, cellulose and lignin this prevents products which would further react if the residence time at high temperature was extended (Mohan et al. 2006). In terms of chemical composition bio oil is a complex mixture of pyrones, syringols catechols, guaiacols, water, vanillin, furancarboxaldehydes, isoeugenol, acetic acid, formic acid and other carboxylic acids (Piskorz and Radlien 1998). Besides these Hydroxyaldehydes hydroxyketones, sugars, carboxylic acids and phenolics are the other major compounds groups present. Some oligomeric compounds present in bio oil are derived from cellulose but majority of these are from lignin. These oligomers form part of the aerosols. Free water in the biomass explosively vaporizes upon fast pyrolysis. It shreds the feed particles and aids in heat transfer. Cellulose and hemicellulose also loose water which contributes to the process. Oligomeric species may not be vaporized but simply blown apart into aerosols as decomposition occurs rapidly. The heating rate, residence time, particle size, temperature and biomass type used determine the molecular weight distribution of bio oil produced (Mohan et al. 2006).

2.5.1 Chemical Properties of Bio-Oil

Bio oil is a complex mixture of oxygenated hydrocarbons. In terms of elemental composition bio oil approximates biomass (Bridgwater 1996). Most of the original oxygen is retained in the fragments that collectively comprise the bio oil. The rest go into CO_2, CO and water formed. Oxygen is present in most of the more than 300 compounds that have been identified in bio-oil

(Soltes and Elder 1981). The compounds found in bio oil have been classified into the following five broad categories: 1. hydroxyaldehydes, 2. hydroxyketones, 3. sugars and dehydrosugars, 4. carboxylic acids, and 5. phenolic compounds. The phenolic compounds derived from lignin are present as monomeric units and oligomers derived from the coniferyl and syringols building blocks of lignin. The oligomers molecular weights range from several hundreds to as much as 5000 or more depending on the process conditions used for pyrolysis. Piskorz et. al. and Amen-Chen et. al (Piskorz and Radlien 1998; Amen-Chen et al. 2001) gave a more detailed classification of the compounds found in the bio oil as: acids, alcohols, aldehydes, esters, phenols, ketones, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds, and miscellaneous oxygenates. Changing the thermal conditions of the process or employing catalysts in the pyrolysis process the chemistry of bio-oils can be manipulated. Increasing the cracking severity (time-temperature relationship) lowers the molecular weight distribution in the resulting oils and produces more gas. At very high temperatures, dehydrogenation/aromatization reactions can eventually lead to larger polynuclear aromatic hydrocarbons and, eventually, increases in carbonization (Mohan et al. 2006). The relationship between the types of compounds in the products and the temperature to which the vapors were exposed before quenching were described following relationship shown in table 2.1. That relationship is described as, with increase in temperature, alkyl groups cleave from aromatic compounds. Eventually, the aromatic compounds condense into polycyclic aromatic hydrocarbons (PAHs) at the higher temperatures.

Table 2.1: Temperature of Exposure before Quenching Relationship with Products Formed.

Temperature (^{o}C)	Groups of Components Present
400	Mixed oxygenates
500	Phenolic ethers
600	Alkyl phenolics
700	Heterocyclic ethers
800	Polycyclic PAH
900	Larger PAH

2.5.2 Chemical Characterization Methods.

The bio-oil contains higher-molecular-weight species, including degradation products of pentoses, hexoses, and lignin, this makes complete chemical characterization of bio-oil difficult. Analysis is especially difficult because complex phenolic species from lignin decomposition can have molecular weights as high as approximately 5000 amu. Besides this a variety of these fragmented oligomeric products exist with varying numbers of acidic phenolic and carboxylic acid hydroxyl groups as well as aldehyde, alcohol, and ether functions only a portion of the bio-oil can be detected via Gas Chromatography (GC), even using robust columns and high-temperature programs. In addition, the bio oil contains polar, nonvolatile components that are only accessible by High Performance Liquid Chromatography (HPLC) or Gel Permeation Spectroscopy (GPC) analysis (Gerdes et al. 2002). Whole pyrolysis liquids can be analyzed by GC-MS (volatile compounds), HPLC and HPLC/electrospray MS (nonvolatile compounds), Fourier transform infrared (FTIR) spectroscopy (functional groups), gel permeation spectroscopy

(GPC) (molecular weight distributions), and nuclear magnetic resonance (NMR) (types of hydrogens or carbons in specific structural groups, bonds, area integrations) (Mohan et al. 2006).

2.6 Fast Pyrolysis of Woody Biomass

Though some studies have been done on the individual components of biomass most applied and larger scale work has focused on whole biomass as the cost of pre-separation is deemed too high (Bridgwater et al. 1999). Emmons and Atreya (1982) estimated that more than 200 intermediate products formed during pyrolysis of biomass. Beaumont (1999) described the qualitative and quantitative composition of the volatile portion of pyrolytic oil from fast pyrolysis of beech wood. The pyrolytic oil contained more than 50 compounds, the products that formed were compared to the pyrolytic products of cellulose. This study showed the origin of the product formed from wood pyrolysis (Beaumont 1999). Murwanashyaka et. al (2001) to monitor the evolution of phenols, from woody biomass conducted both stepwise and one-step vacuum pyrolysis of birch sapwood and birch bark. Guaiacol derivative occurred at low temperatures, followed by syringol derivatives. The evolution of phenolic groups was determined to occur in the following order: methyl guaiacol, ethylguaiacol, guaiacol, propenylsyringol, phenol, and catechol. Their transformation to pyrocatechols occurred at high temperature. The maximum rate of evolution was observed between 275-350 ^{o}C. The methoxylated phenolics were converted to catechols by demethylation of the methoxy groups from 350-450 ^{o}C. Using the yield, heating value and water content as evaluation criteria Luo et al.(2004) found from the fast pyrolysis of *Pterocarpus indicus*, *Cunninghamia lanceolata*, and *Fraxinus mandshurica* and rice straw in a fluidized-bed reactor with an inert nitrogen atmosphere that the best bio oil was obtained from *Pterocarpus indicus* followed by *Cunninghamia lanceolata* and *Fraxinus mandshurica*

respectively with rice straw giving the worst bio oil. The maximum bio oil production was obtained at 500 ^{o}C.

2.6.1 Fast Pyrolysis of Individual Wood Components and Model Compounds

In order to understand the phenomenon of fast pyrolysis an understanding of the role played by the individual components of wood is essential. Extensive studies (Kuofopanos and Lucchesi 1989; Srivastava and Jalan 1994; Antal and Varhegyi 1995; Caballero et al. 1995; Raveendran et al. 1996; Blasi and Lanzetta 1997; Miller and Bellan 1997; Pasquali and Herrera 1997; Varhegyi and Szabo 1997; Rao and Sharma 1998; Groni and Varhegyi 1999; Orfao et al. 1999; Stenseng et al. 2001; Manya et al. 2003) based on one or all the components of biomass have been carried out to distinguish the behavior of the three components in order to understand the biomass pyrolysis process.

2.6.1.1 Pyrolysis of Cellulose and Model Compounds

Anhydrocellulose and levoglucosan are the decomposition products of cellulose pyrolysis. Cellulose degradation occurs between 240-350 °C (Mohan et al. 2006). Pyrolysis of cellulose is believed to follow the Broido-Shafizadeh model. The first step in the model is the formation of active cellulose (AC), followed by two competing reaction pathways: one producing char and gases and the other producing volatiles, mainly levoglucosan, through a transglycosylation reaction (Shafizadeh 1982). Levoglucosan can further be dehydrated to forming levoglucosenone and 1,4:3,6-dianhydro-α-D-gluco-pyranose (DPG). Fission and disproportional reactions can further transform levoglucosan into furans and low-molecular-mass acids (Atte et al. 2008). Luo et. al (2004) proposed a modified Broido-Shafizadeh (B-S) where they suggest that degradation of AC would proceed along three competing reaction pathways. AC was believed to degrade into levoglucosan and to char and gases, as in the B-S model. A new competing pathway was

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suggested for the formation of hydroxy-acetaldehyde and 1-hydroxy-2-propanone from AC. Levoglucosan is produced when the glucosan radical is generated without the bridging oxygen from the preceding monomer unit (Mohan et. al, 2006). Atte et.al (2008) pyrolyzed microcrystalline cellulose to produce mainly levoglucosan, 1,4:3,6-dianhydro-α-D-gluco-pyranose and 2-furanmethanol.

2.6.1.2 Pyrolysis of Hemicellulose and Model Compounds

Hemicellulose decomposes at temperatures from 200-260 °C, giving rise to more volatiles, less tars, and less chars than cellulose (Soltes and Elder 1981). Most hemicelluloses do not yield significant amounts of levoglucosan. Much of the acetic acid liberated from wood during pyrolysis is attributed to deacetylation of the hemicellulose. Xylan, though it may possess different physical and chemical properties, has been widely used as a representative of hemicellulose in pyrolysis processes (Kuofopanos and Lucchesi 1989; Rao and Sharma 1998; Orfao et al. 1999). Haiping et. al(2006) found from the pyrolysis of xylan as a model compound for hemicellulose that hemicellulose decomposition falls in the range of 220-315°C. Acetic acid, 2-furanmethanol, and levoglucosan were the main compound present in the bio oil from the fluidized bed fast pyrolysis of galactoglucomannan model compound representing softwood hemicellulose by Atte et al (2008). The acetic acid formed was suggested to be formed by the removal of O-acetyl groups from mannose units present in the galactoglucomannan structure.

2.6.1.3 Pyrolysis of Lignin and Model Compounds

Studies by Nguyen, et. al and Kuofopanos et. al (1989) have shown that lignin is the most heat resistant component in wood. Maximum rate loss for lignin has been observed between 360 ^{o}C and 407 ^{o}C (Faix et al. 1988a; Faix et al. 1988b). The weight loss profile is dependent on the lignin isolation method (Gardner et al. 1985) and the nature of the wood species (Faix et al. 1987). From their (Gardner et al. 1985) studies they observed that lignin isolated from different wood species using hydrochloric acid, Klason, enzymatic and steam exploded methods behaved differently in their thermal degradation. The Klason lignin was more heat resistant than the other lignin fractions and exhibited a broad DTA peak while the steam exploded and the enzymatic lignin exhibited sharper peaks. Klason lignin pyrolysis yielded considerably less guaiacol, methylguaiacol, syringol and syringaldehyde than HCL-lignin from the same wood species. Fenner and Lephardt(1981) studied the pyrolysis vapors from Kraft lignin pyrolysis using TG-FTIR and they observed formic acid, formaldehyde, sulphur dioxide, carbon dioxide, methanol, methane and water among the volatile components. Faix et al.(1988a) observed from their thermal dehydration of milled-wood lignin from beech and spruce species by TG-MS that dehydration of aliphatic HO- groups was most likely the source of pyrolytic water as proposed by Fenner and Lephardt. They suggested that the demethylation of methoxy groups in guaiacyl and syringyl groups occurs at about 450 ^{o}C while the alkyl chains decompose at about 600 ^{o}C. Formaldehyde and acetaldehyde were also detected among the volatile compounds. The pyrolysis of single model compounds like methoxyphenols has been studied as an essential approach to determine the thermal stability of the intermediate products formed during lignin pyrolysis (Amen-Chen et al. 2001). Catechol, methane, phenol and carbon monoxide were the main products of pyrolysis from guaiacol pyrolysis at 350°C by Klein (1981). Catechol and methane yields were in almost stoichiometric amounts as well as phenol and carbon monoxide

yields. Catechol was produced from demethylation of guaiacol. Catechol yield was five times higher at 450 ^{o}C than 300 ^{o}C. A free radical reaction and a concerted reaction was suggested for the pyrolysis of guaiacol pyrolysis at 350-400 ^{o}C and reaction times from 0.5-4 h(Vuori and Brendenberg 1987). Schlosberg et. al (1983) established a possible pathway for the production of benzyaldehyde, toluene and phenol from anisole. Phenol was produced from CH_3-O bond scission and further H-abstraction from an anisole molecule. The free radical produced from the anisole was also suggested to undergo rearrangement to form benzaldehyde or stabilization to benzylalcohol which may further decompose to form toluene and water. the pyrolysis of dimethoxy-phenols in a batch reactor from 250-325 ^{o}C and reaction times 2-6 h by Masuku (1991) observed that syringol mainly yielded 2,3-dihydroxyanisole, 2,3-dimethoxyphenol and small amounts of guaiacol and methylguaiacol at 250 ^{o}C. Product composition was considerably more complex as the temperature increased. The reactivity of the model compounds studied followed the order of: 2,3-dimethoxyphenol, 2,6- dimethoxyphenol and 3,5-dimethoxyphenol. Methylguaiacol was suggested as likely to be formed by rearrangement of one of the methoxyl groups. The production of guaiacol was explained as the direct cleavage of the methoxyl C-O bond via a catechol intermediate as suggested also by Klein (1981) and Vuori and Brendenberg (1987).

2.7 Influence of Additives on the Pyrolysis of the Individual Components of Wood

2.7.1Influence of Metal Ions and Salts

Metal ions can be used to alter or tailor the products produced by biomass pyrolysis. The presence of alkaline cations in biomass is known to affect the mechanism of thermal decomposition during the fast pyrolysis. These cations cause fragmentation of the monomers that comprise the natural polymer chains, rather than the predominant depolymerization that occurs in their absence (Pan and Richards 1989; Richards and Zeng 1991; Piskorz and Scott 1994; Piskorz and Radlien 1998; Scott et al. 2000; Dobele et al. 2005). Potassium and calcium are the major cations present in wood, along with minor amounts of sodium, magnesium, and other elements. Richards and Zeng (1991) purposely incorporated several different metal ions, individually, into cottonwood via ion exchange and then investigated the products of vacuum pyrolysis. The cations K^+, Li^+, and Ca^{2+} induced high char and low tar yields. The tar was very low in levoglucosan. In contrast, all of the other ions investigated, especially the transition metals, gave increased yields of levoglucosan (as much as 15.8% from wood exchanged with ferrous ions). This corresponds to a 32% conversion of cellulose to levoglucosan. When salts were absorbed into the wood (instead of ion-exchanged), smaller, but significant, levoglucosan increases were again obtained, when indigenous salts in the wood were first removed by acid washing. The effect of the anion on pyrolysis was investigated with absorbed salts. Chlorides (especially copper chlorides and iron chlorides) increased the levoglucosan yield. Low levels of absorbed $FeSO_4$ catalyzed the formation of both levoglucosan and levoglucosenone. The principal effect of removing alkaline or alkaline-earth cations, followed by fast pyrolysis is the production of anhydrous liquid that is rich in levoglucosan and anhydropentoses (Piskorz and Scott 1994).

2.7.2 Influence of Catalysis

The use of catalyst can alter greatly the pyrolytic product distribution. The main catalyst that has been used in this area includes zeolite catalyst, basic catalyst (NAOH) and transition metal catalyst (eg. Nickel). Studies by Atuxta et. al (2005) using HZSM-5 catalyst to pyrolyze sawdust observed that the gas yields increased significantly while, the liquid yields decreased significantly and the char yields decrease slightly with increase in catalyst amount used. Catalyst use caused the bio-oil composition to undergo a drastic change. The heavy organic fraction was proposed to be partially transformed to the aqueous fraction due to cracking, whereas the aqueous liquid fraction was hypothesized to undergo dehydration, decarboxylation, and decarbonylation. Williams et. al (1994) from their pyrolysis of pine subjected the oil obtained to downstream catalytic upgrading and observed that oils were highly oxygenated before catalysis. After catalysis, the oils had markedly less oxygenated species present, a higher aromatic content, and an increase in biologically active polynuclear aromatic (PAHs) species. The gases that evolved during the biomass pyrolysis were CO_2, CO, H_2, CH_4, C_2H_4, C_3H_6, and minor amounts of other hydrocarbons. The amounts of CO_2 and CO increased during catalysis. Oxygen in the oxygenated compounds was catalytically converted mainly to H_2O at lower catalyst temperatures and CO_2 and CO at high catalyst temperatures. The amounts of PAHs increased as the catalyst temperature increased. The oxygenated compounds remaining in the oil formed over the ZSM-5 bed were mainly phenols and carboxylic acids. Exposure to ZSM-5 progressively decreased the concentration of phenolics and acids as the bed temperature increased. Adam et al aslo conducted pyrolysis of spruce wood in the presence of Al-MCM-41-type mesoporous catalysts. Four Al-MCM-41- type catalysts were tested. The catalytic properties of Al-MCM-41 were modified by both pore enlargement, which allows the processing of larger molecules, and the introduction of Cu cations into the structure. The catalysts were used for further conversion of

the pyrolysis vapors from spruce wood to attempt to improve bio-oil properties. Spruce wood pyrolysis was performed at 500 °C, and the products were analyzed via PY-GC/MS. Levoglucosan was completely eliminated, whereas acetic acid, furfural, and furans become important cellulose pyrolysis products over an unmodified Al-MCM-41 catalyst. The quantity of higher-molecular-mass phenolic compounds was strongly reduced in the lignin-derived products. The increase in acetic acid and furan and the decrease of large methoxyphenols were both somewhat repressed over catalysts with enlarged pores. The copper-modified catalyst performed similarly to the enlarged pore catalyst in converting the wood pyrolysis vapors, although its pore size was similar to the unmodified Al-MCM-41. Borgund and Barth used Sodium hydroxide (NaOH) as a basic catalyst to increase oil yield and decrease coke generation from the pyrolysis of a pure thermomechanical pulp (TMP) from softwood (Norwegian spruce) that was comprised of 46.6 % carbon, 6.2 % hydrogen, and 47.2 % oxygen. The TMP was dried at 100 °C to a constant weight. The addition of a catalyst caused a decrease in coke formation, along with an increase in the extractable organic matter. Polar compounds dominated in the extracted matter. The amount of water present in the biomass had the largest effect on yields. The temperature and the amount of starting material exerted minor effects.

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CHAPTER THREE

PYROLYSIS OF CELLULOSE

ABSTRACT

Catalytic and non catalytic pyrolysis of cellulose was carried out in a fluidized bed reactor at 450 ^{o}C to study the effect of catalysis on cellulose pyrolysis product distribution and bio oil properties. NaOH pretreated and untreated cellulose was pyrolyzed on sand and HZSM-5 catalysts. The pyrolysis of cellulose on BASF and Sud-Chemie HZSM-5 catalysts increased the yields of organic liquid fraction, total liquid and char while decreasing the gas yields. However the VPISU001 HZSM-5 catalyst decreased the organic and char yields while increasing the water yields but there was no change in gas yields. The NaOH treatment caused a decrease in the organic and total oil yields relative to the control but the char yield increased. The change in gas yields was not significant. The characterization of the oils using FTIR and ^{13}C–nmr showed that, the VPISU001 HZSM-5 with and without NaOH pretreatment caused elimination of the levoglucosan fraction while increasing the aromatic fraction. The NaOH pretreated cellulose pyrolyzed on sand reduced the levoglucosan groups while increasing the aromatic fraction of the bio oil.

3.1 Introduction

Fossil fuels currently serve the majority of our needs, both energetically and chemically (Bozell 2001). However, burning fossil fuel is believed to be responsible for approximately three quarters of the anthropogenic emissions of CO_2 (IPCC 2001), a major greenhouse gas that contributes to global warming (Ramaswamy 2001). The possibility of reduced fossil fuel supplies in the future, either through geo-political conflicts, or through reaching a ''Hubbert Peak'' are also strong drivers for a search for alternatives (Hayes 2008). Governments around the world have recognized this and have implemented minimum targets for the implementation of alternative fuels in the future, with the expectation that biofuels will play a major role in these targets. For example, the European Union (EU) has set targets of 5.75 % renewable energy substitution by 2010 (EC 2003) and a mandatory target of 10 % by 2020 while in the USA the Energy Independence and Security Act of 2007 mandates the production of 36 billion gallons of renewable fuels by 2022 (US Congress 2007).

Fast pyrolysis is an emerging technology for converting biomass into liquid fuel. In this process the biomass is heated to 400-600 ^{o}C in the absence of oxidizing agents and short resident times (less than one minute) to produce liquids, gases and solid products. Pyrolysis oils from wood and herbaceous biomass are complex, acidic, viscous, reactive and thermally unstable. These properties of bio-oil result in several significant problems during its use as fuel in standard equipment such as boilers and engines. Poor volatility, high viscosity, corrosiveness and long term instability have limited the range of bio-oil applications (Czernik and Bridgwater, 2004). Hydrotreatment (Baldauf and Balfanz 1991; Laurent et al. 1994) and catalytic cracking (Sharma and Bakhshi 1991; Williams and Horne 1995; Samolada and Vasalos 1998) are employed to

upgrade and improve the quality of the bio oil. However these methods are limited by the cost in additional equipment requirement and process cost.

Catalytic biomass pyrolysis is an emerging technology for overcoming the costly condensation and re-evaporation procedures for bio-oil upgrading, but this approach is still in its development stages (Samolada and Vasalos 2000). Several catalysts have been tested and studied in detail in order to understand the mechanisms and identify the most promising products.

Zeolites (Nokkosmaki et al. 1998; Williams and Nugrand 1998) and basic catalytic materials were studied on various biomass feedstock's (Nokkosmaki and Kuopala 1998). However it's difficult to understand the reactions taking place because biomass is composed of three complex biopolymers each of which behaves independently. Thus it is important to understand the effect of catalysis on the individual component of biomass.

Cellulose pyrolysis without catalyst has been studied by several researchers in the past (Shafizadeh 1982; Antal et al. 1985; Julien et al. 1991; Soares et al. 1995; Banyasz et al. 2001). Shafizadeh proposed a simple model, where the primary decomposition step is the formation of active cellulose, which then produces char and gases by one decomposition pathway or the formation of volatiles by another route. The primary volatiles resemble cellulose monomeric units, and include levoglucosan (Ebringerova et al. 2005), levoglucosenone and 1,4:3,6-dianhydro-β-D-glucopyranose . The levoglucosan yields obtained from the pyrolysis of different celluloses varied from 20 % to 60 % (Pouwels et al. 1989). Carbon dioxide, methane, water, acetone and acetic acid, formaldehyde, glycolaldehyde, butanone, 2-furaldehyde, 5-

hydroxymethyl-2-furaldehyde and furan derivatives are also produced from cellulose pyrolysis (Piskorz et al. 1986).

The presence of minerals in cellulose promotes char and gas formation while the tar yield decreases (Antal et al. 1985; Soares et al. 1995; Pappa et al. 2003). Using mild acid pretreatment, Julien et al (1991) showed that pretreated cellulose (low metal content) produced higher yield of levoglucosan (33.1 %) compared to 3.7 % for the untreated cellulose and the amount of hydroxyacetaldehyde was reduced from 11.1 % to 0 %.

The catalytic pyrolysis of biomass has been studied for different feedstocks (Horne and Williams 1996; Atutxa et al. 2005; Huber et al. 2008; Lappas and Vasalos 2002; Adam et al. 2006). Cellulose, glucose, xylitol and cellobiose were catalytically pyrolyzed with ZSM-5 catalyst producing mainly aromatics, CO, CO_2 and coke (Huber et al. 2008). It was observed that the selectivity for the desired products depended on selecting the proper catalyst, using high heating rates and using high catalysts to feed ratio. Gayubo et al. (2004) studied the effect of operating conditions, such as, temperature, space time (amount of catalyst divided by the amount of reactant) and time on stream, on the transformation of the aqueous fraction of biomass pyrolysis oil into hydrocarbons using an HZSM-5 zeolite with a Si/Al ratio of 24. Their main conclusions were that by increasing the space time and temperature the transformation of the reactants towards the desired products was increased. The non catalytic and catalytic pyrolysis of rice husks with ZSM-5 showed that the influence of the catalyst was to convert the bio oil largely to H_2O at the lower catalyst temperature and largely to CO and CO_2 at the higher catalyst temperatures and the catalytic oils were markedly increased in single ring and poly aromatic

compounds (PAH) compared with the non-catalytic biomass pyrolysis oils (Williams and Nugranad 2000). In this section the effect of HZSM-5 catalyst and NaOH pretreatment of cellulose on product distribution, was investigated.

3.2 Materials and Methods

3.2.1 Materials

Microcrystalline cellulose was purchased from Alfa Aesar (Alfa Aesar, Ward hill, MA), the catalysts; the VPISU001 HZSM-5 catalyst (proprietary) was formulated in our lab and the other HZSM-5 catalysts were purchased from Sud-Chemie (Sud-Chemie Inc. Colton, CA) and BASF (BASF Inc, Florham Park, NJ) and the NaOH and white silica sand were purchased from Fischer Scientific (Fischer Scientific, Pittsburg PA).

3.2.2 Cellulose Pretreatment and Characterization

The cellulose was pretreated to 1 wt% of NaOH by dissolving 1 g of NaOH in 250 ml distilled water and mixing the solution with 100 g of cellulose powder and thoroughly mixing to ensure all the powder were mixed with the water. The slurry was dried at 75 ^{o}C to constant mass.

The moisture content of the pretreated and untreated samples was determined using a Metler Toledo halogen moisture analyzer (Metler Toledo Inc. Polaris Parkway, Columbus, OH). About 1.00 g of the sample was weighed into the moisture analyzer and the moisture content was determined at 105 ^{o}C.

The treated and untreated microcrystalline samples were analyzed thermogravimetrically on TA Instruments Q600 SDT (TA Instruments Inc. Newcastle Delaware). About 20 mg sample was placed in an alumina crucible and analyzed. The carrier gas was nitrogen at 20 ml/min and the sample was heated from 25 ^{o}C to 700 ^{o}C at a heating rate of 5 ^{o}C/min. The thermograms were analyzed using TA universal analysis software.

3.2.3 Catalyst Preparation and Characterization

The Sud-Chemie (HMF-I90) 1/16 inch pellets were ground with mortar and pestle and sieved to 63-297 μm to match the BASF particle size of 75-297μm. The catalyst of appropriate size and mass were then weighed and activated overnight at 575 ^{o}C in a muffler furnace.

3.2.4 Pyrolysis Experiments

3.2.4.1 Catalytic Pyrolysis

The fast pyrolysis unit (Figure 3.1) used for the studies consisted of a K-Tron volumetric feeder (K-Tron International, Inc. Pitman, NJ) with twin screw feeding system, 50 mm bubbling fluidized bed reactor equipped with a 100 μm porous metal gas distributor, hot gas filter (HGF), two chilled water condensers, an electrostatic precipitator, a coalescing filter, a packed column and an SRI gas chromatograph (GC) instrument (SRI Instruments, Torrance, CA). The reactor was heated with a three-zone electric furnace (Thermcraft, Winston-Salem, NC) while the HGF was heated with a single zone electric furnace (Applied Systems Inc, Butler PA).

About 100 g of catalyst was used as the fluidized bed and was fluidized with nitrogen using 8 L/min of nitrogen. 100 g of the pretreated and untreated cellulose samples were pyrolyzed at 450 ^{o}C at feeding rate of 100 g/h to give a weight hourly space velocity (WHSV) of 1. About 3-4 L/min of nitrogen gas was used to entrain the feed through a jacketed air-cooled feeder tube into the fluidized bed. The reactor temperature, feed rate, and fluidizing gas were kept constant for each experiment. During pyrolysis, the mixture of char, gases and vapors that exited from the reactor were separated by a hot gas filter maintained at 400 ^{o}C. The separated gases and vapors were then passed through two condensers connected in series and maintained at -9 ^{o}C with a 50/50 cooling mixture of ethylene glycol and water. The condensers were cooled with a Haake A82 refrigerated circulating bath (Haake, Karlsruhe, Germany). The condensates were drained

from the base of the condensers. Any condensable gases and aerosols that escaped from the condenser were captured by an electrostatic precipitator (ESP) kept at 16-20 kV. Any condensable vapors that escaped the ESP were trapped by a coalescing filter, a packed column of glass beads and a packed glass wool column. The non-condensable gases were sampled periodically and analyzed on an SRI gas chromatograph (SRI Instruments Torrance CA, USA). Samples of the gases were also stored in gas bags for duplicate analysis.

3.2.4.2 Non-Catalytic Pyrolysis

The same pyrolysis unit was used for the non-catalytic pyrolysis. However, because silica sand was used as the heat transfer medium the fluidizing gas flow rates were modified. The nitrogen fluidizing gas flow rate was 12 L/min and 6 L/min of nitrogen was used to entrain the feed into the reactor.
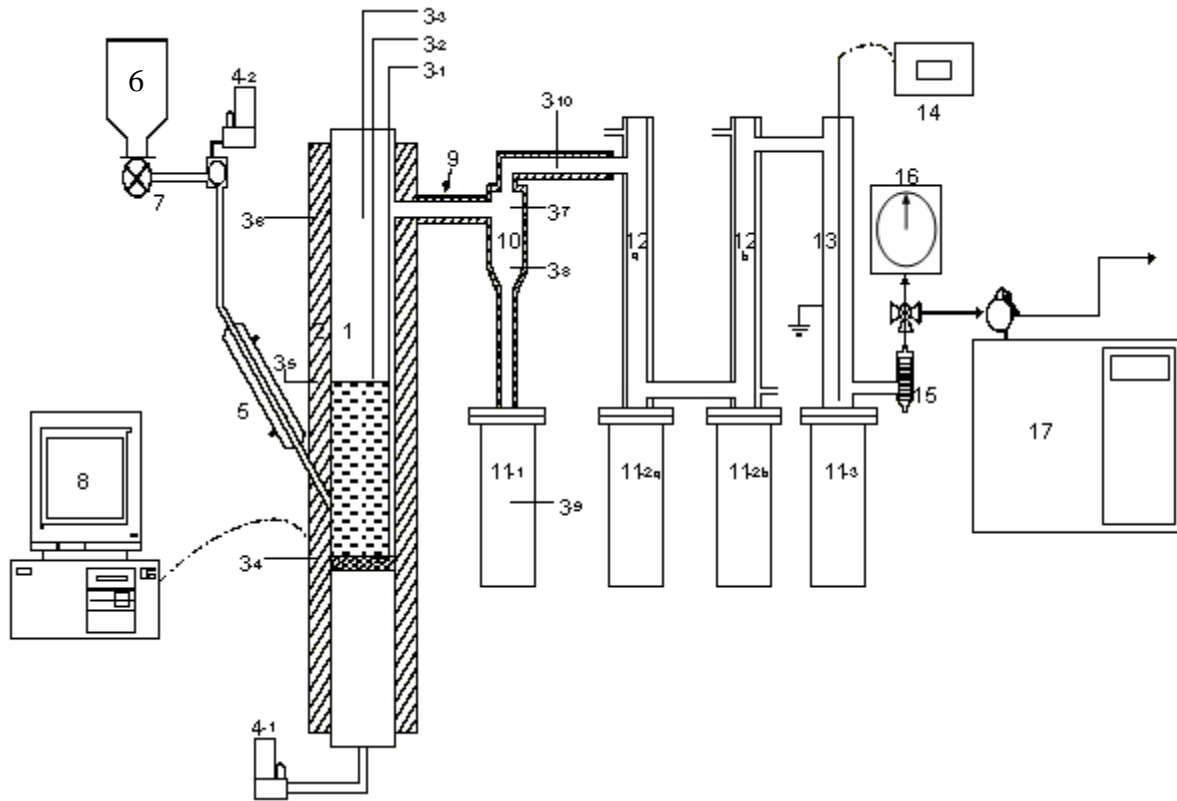
Figure 3.1 Schematic diagram of the fluidized bed pyrolysis reactor unit

(1-Fluidized bed reactor, 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)

3.2.5 Characterization of Pyrolysis Oils

The masses of the pyrolysis oils produced were determined gravimetrically by weighing the condensers, electrostatic precipitator and the packed column before and after each experiment and the difference was used to calculate the yields of pyrolysis oils. The mass of char was determined gravimetrically by weighing the hot gas filter and the reactor before and after each pyrolysis experiment and the mass difference was used in calculating the yields of char. The gas yield was determined by difference. All the yields were calculated on moisture-free biomass basis.

The moisture contents of the pyrolysis oils were determined using the Karl Fischer titration method. Metrohm 701KF Titrino (Brinkmann Instruments, Inc, New York, NY U.S.A) and a 703 titration stand setup were used for the titration. About 40 ml methanol was measured into the titration vessel and a blank titration was carried out using Hydranal Composite 5 reagent (Sigma Aldrich Inc, St Louis, MO). About 1.0 ml oil sample was loaded into a hypodermic plastic syringe and weighed. A portion of the sample was injected into the titration solvent and the syringe was weighed again. The mass of the sample used was determined by difference. The mixture was stirred to dissolve the oil and the water content was titrated automatically and the water content determined.

The Fourier-Transform Infrared (FTIR) spectra of the pyrolysis oil samples were acquired on 100 mg samples. The spectra were obtained over a range of 4000-650 cm^{-1} using Nicolet Avatar 370 DTGS instrument (Thermo Electron Corporation, Waltham, MA) equipped with a multi-bounce accessory with a ZnSe cell. 32 scans at 4 cm^{-1} resolution and a background gain of 4.0

were used. Data analyses were performed using the OMNIC 7.3 (Thermo Electron Corporation) software package.

The ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectra of the pyrolysis oils were acquired using a Varian Unity 400 MHz spectrometer (Varian Inc, Palo Alto, CA). About 1.0 g of pyrolysis oil was dissolved in 1.5 mL of deuterated dimethyl sulfoxide (DMSO) in a 10 mm sample probe and the ^{13}C-NMR spectra were acquired on a Varian Unity 400 MHz spectrometer. The observing frequency for the ^{13}C nucleus was 100.58 MHz. The pulse width was 11.00 µs, the acquisition time was 1.31s, and the recycle delay was 1s. The spectra were obtained with 1392 scans and a sweep width of 25000.0s. Data analysis was performed with NutsPro-NMR Utility Transform Software – Professional (Acorn NMR, 1993-2005, Livermore, CA).

3.2.6 Analysis of Pyrolysis Gases

The composition of the pyrolysis gases were determined using an SRI multiple gas analyzer #2 gas chromatograph (SRI Instruments Torrance CA, USA) equipped with a Thermal Conductivity Detector (TCD), Flame Ionization Detector (FID) with a Methanizer. A 10-port gas sampling valve and Dual Loops6 channel Peak Simple Data System. The columns consisted of Molecular Sieve 13X & HayeSep-D packed columns, MTX capillary column. The injection temperature was 40 ^{o}C and the detector temperature was 380 ^{o}C. The ultra pure helium was used as carrier gas at a flow rate of 20 ml/min and the oven was kept at 40 ^{o}C for 10 min and heated from 40 to 200 ^{o}C at a heating rate of 10 ^{o}C/min.

3.3 Results and Discussion

3.3.1 Catalyst Characteristics

The acid strength and acid type are the key properties of zeolites. These play important roles in the activity and selectivity of zeolites. The acid strength of zeolites is mainly dependent on the Silica/Alumina ratio (Shourong 2002).The lower this ratio (i.e. higher Alumina content) the more acidic the HZSM-5 catalyst and also the higher its surface area (Shirazi et al. 2008). The Sud-Chemie was an HMFI-90 type of HZSM-5 with a total SiO_2/Al_2O_3 ratio of 90. The BASF belongs to the 5000-10000 series of HZSM-5 catalyst with alumina and silica wt% composition range of 0-25 %. Thus its highest possible SiO_2/Al_2O_3 would be less than that of Sud-Chemie. While the SiO_2/Al_2O_3 of VPISU001 ranged between that of Sud-Chemie and BASF.

3.3.2 Thermogravimetric Analysis of Microcrystalline Cellulose

The thermogram and the differential thermogram of treated (na-mcc) and untreated (mcc) microcrystalline cellulose are shown in fig 3.1a and fig 3.1b respectively.   The thermogram for the mcc showed two weight loss regimes. There was a minor weight loss between 25 and 75 ^{o}C which was attributed to the adsorbed moisture on the surface of the mcc. The major weight loss for the mcc started at 305 ^{o}C and continued until 373 ^{o}C. The maximum weight loss occurred at 351 ^{o}C (Fig 3.1b). About 89 % of the material was lost between room temperature and 373 ^{o}C. Beyond 373 ^{o}C, the weight loss was very gradual but after 450 ^{o}C, there was no further weight loss and the solid residue was 6.9 wt%. The maximum temperature observed in this analysis was similar to those reported by (Kim and Agblevor 2007). The thermogram of the na-mcc showed three weight loss regimes. The first weight loss regime was similar to that of the mcc and this was attributed to the moisture adsorbed on the surface of the na-mcc. The second weight loss regime occurred between 201 ^{o}C and 275 ^{o}C with a small maximum occurring at 231 ^{o}C (fig 3.1b). This second maximum was not observed for the mcc.   The second maximum could be attributed to the decomposition of the amorphous fraction created by the NaOH treatment of the microcrystalline cellulose. It is known that the maximum weight loss temperature is a function of the crystallinity of the cellulose (Weinstetn and Broido 1970) and treatment of cellulose with NaOH is also known to reduce the crystallinity of the cellulose (Lin et al. ; Jackson 1977; Isogai and Atalla 1998). The third weight loss regime occurred between 275 ^{o}C and 365 ^{o}C with a maximum occurring at 329 ^{o}C. The third maximum was attributed to the decomposition of the crystalline fraction of the mcc. Clearly, it appears the NaOH treatment lowered the maximum weight loss temperature of the mcc which is in agreement with data published in literature (Saafan 1989). The maximum decomposition temperature of cellulose is a function of the degree of crystallinity of the cellulose, so this implies that part of the cellulose was still crystalline, but

its degree of crystallinity was lower than that of the original mcc. Beyond 365 ^{o}C, the weight loss was very gradual until after 450 ^{o}C when there was no further weight loss. The solid residue for the na-mcc was 18.7 wt% compared to the 6.9 wt% for the mcc. However, it must be noted that the 18.7 wt% residue included some of the NaOH used in the treatment of the sample.
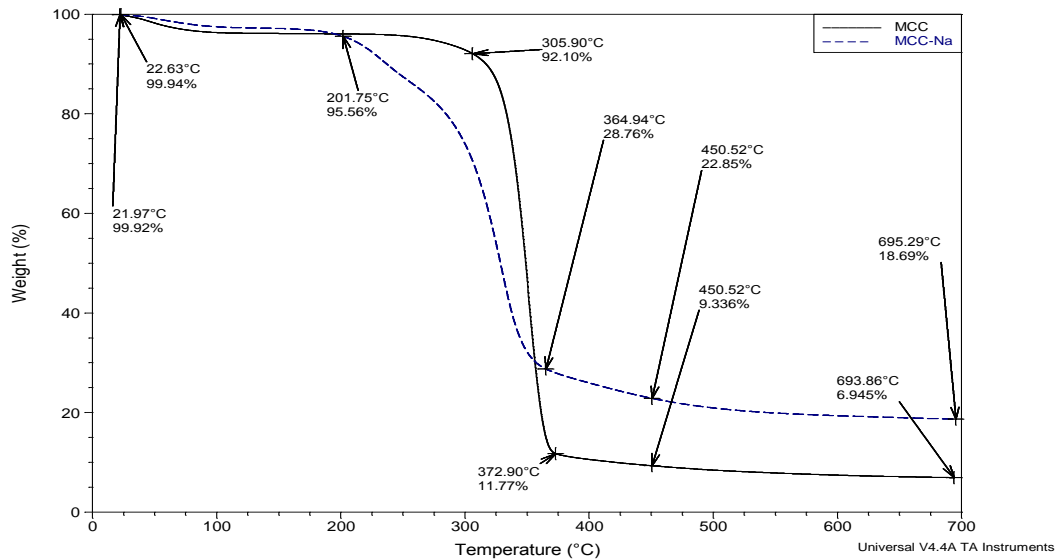
Figure 3.1a: TG curves of untreated microcrystalline cellulose (mcc) and NaOH pretreated microcrystalline cellulose (na-mcc)
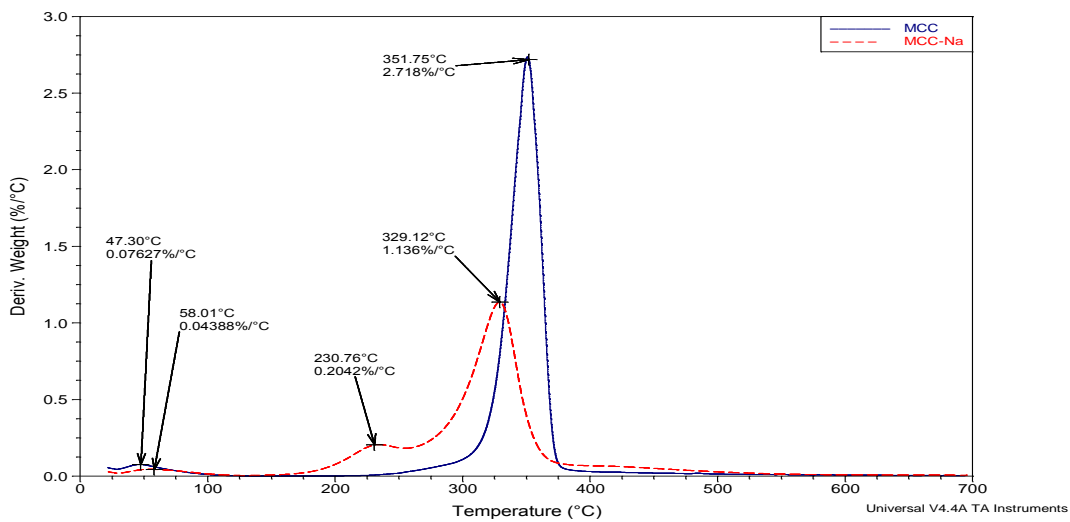
Figure 3.1b: DTG curves of untreated microcrystalline cellulose (mcc) and NaOH pretreated microcrystalline cellulose (na-mcc)

3.3.3 Fluidized Bed Pyrolysis of Microcrystalline Cellulose

The yields of various pyrolysis products from microcrystalline cellulose pyrolysis using sand and various HZSM-5 catalysts medium are shown in Table 3.2 and Figure 3.2 The total liquid yield using the sand pyrolysis medium was 38.4 wt% but 8 wt% was water and the difference was organic liquid fraction. The char yield was 11.5 wt% which was similar to the residue obtained from the thermogravimetric studies suggesting that perhaps the two pyrolysis pathways were similar. The gas yield was very high and constituted 50 wt% of the products. The pyrolysis of mcc using Sud-Chemie HZSM-5 (Sud-Chemie) was quite different from the sand pyrolysis. The total liquid yield was 56% higher than that from the sand pyrolysis and the organic liquid fraction was 58% higher than that from the sand mcc pyrolysis. The char yield was also 49% higher than that produced from the sand pyrolysis. However, the gas yield was 54.4% lower than the gas yield from the sand pyrolysis. The BASF HZSM-5 (BASF) product yield distribution was different from the Sud-Chemie and the sand pyrolysis. The total liquid yield was less than that from the Sud-Chemie but it was only 40.6 % higher than the mcc pyrolysis using the sand. The organic liquid fraction was only 28.8 % higher than the sand pyrolysis because the BASF catalyst produced much higher water than both the Sud-Chemie and the sand. The gas yield for the BASF was less than that of the sand but was similar to Sud-Chemie. The char yield from the BASF was 100 % higher than that produced from the sand. The pyrolysis of the mcc using the VPISU001 HZSM-5 (VPISU001) catalyst was the most interesting. It produced the lowest yields of total liquids, organic liquid fractions, and char. The water yield was 158 % higher than that produced using the sand but the gas yield was similar to that of the sand. The char yield was 31 % less than char produced from the sand pyrolysis. This char yield was several times lower than those produced using the BASF and Sud-Chemie (Table 3.2) Thus, it appears most of the organic liquid fraction and some of the char were cracked to produce

mostly water. Thus, this catalyst is unique in its catalysis of the cellulose pyrolysis. A similar

unique behavior was also observed when this catalyst preparation was used for the pyrolysis of

various whole wood samples (Agblevor et al. 2009).

Table 3.2 Summary of Pyrolysis Results Showing the Effect of the HZSM-5Catalysts

Sample	Product Yields wt %				
	Organics	Water	Total Liquid	Char	[q]Gas
mcc-sand	30.2±0.13	8.2±0.6	38.4±0.5	11.5±0.4	50.0±0.2
mcc-Sud-Chemie	47.8±1.4	12.3±2.2	60.0±0.7	17.2±0.9	22.8±0.1
mcc-BASF	38.9±1.2	15.2±1.2	54.0±2.4	23.0±0.7	23.0±1.6
mcc-VPISU001	20.2± 2.9	21.2±0.1	41.8±2.6	7.9±1.9	50.3±2.5

[q] Calculated by difference
mcc-sand: untreated microcrystalline cellulose pyrolyzed on sand
mcc-Sud-Chemie: untreated microcrystalline cellulose pyrolyzed on Sud-Chemie HZSM-5catalyst
mcc-BASF: untreated microcrystalline cellulose pyrolyzed on BASF HZSM-5catalyst
mcc-VPISU001: untreated microcrystalline cellulose pyrolyzed on VPISU001catalyst
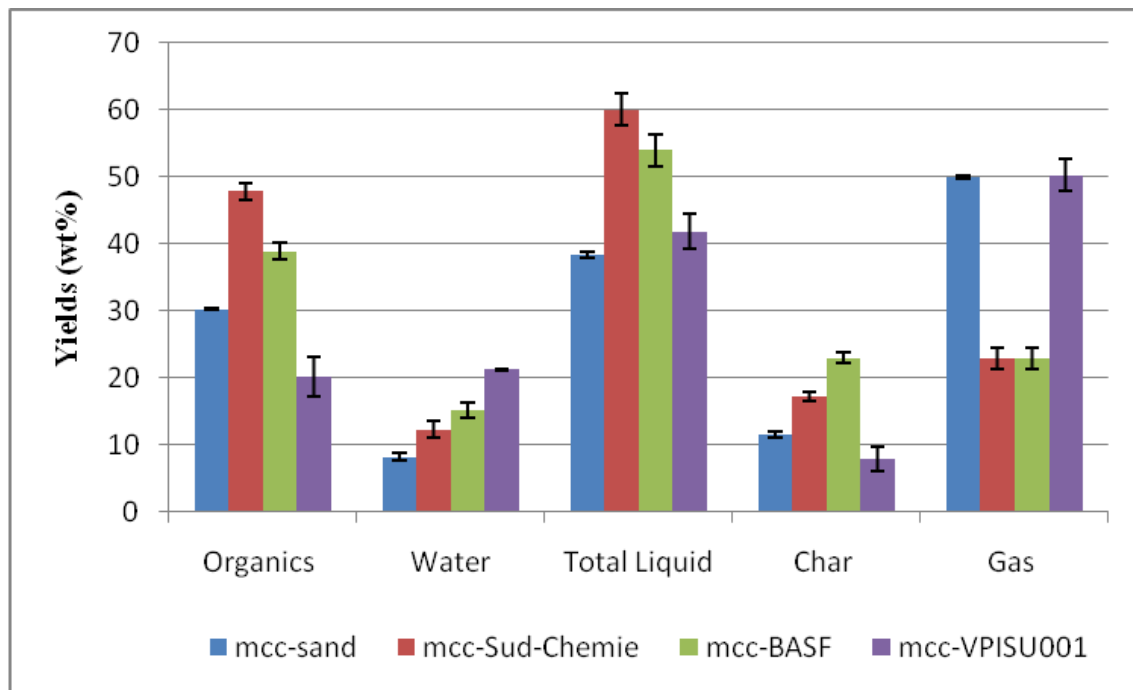
Figure 3.2: Pyrolysis products distribution of untreated microcrystalline cellulose

Table 3.3 Test of Significant Effect of the HZSM-5 Catalysts on the Pyrolytic Yields of Microcrystalline Cellulose using Turkey-Kramer HSD Significance Test.

Level	Pyrolysis Yields wt %				
	Organics	Water	Total Liquid	Char	^{q}Gas
mcc-sand	30.2^C	8.2^D	38.4^C	11.5^C	50.0^A
mcc-Sud-Chemie	47.8^A	12.3^C	60.0^A	17.2^B	22.8^B
mcc-BASF	37.6^B	16.5^B	54.0^B	23.0^A	23.0^B
mcc-VPISU001	20.2^D	21.2^A	41.8^C	7.9^D	50.3^A

Levels not connected by the same letter are significantly different at 0.05 alpha level (Ott and   Longnecker, 2001).

3.3.4 Fluidized Bed Pyrolysis of NaOH Treated Microcrystalline Cellulose

The pyrolysis product yields of various products of NaOH treated microcrystalline cellulose (na-mcc) pyrolyzed in the fluidized bed reactor are shown in Table 3.4. In addition to the na-mcc data, the mcc data on sand was also included for comparison. For the untreated sample, the total liquid yield was 38.4 wt% and the char and gas yields were 11 wt% and 50.6 wt% respectively. After sodium hydroxide treatment and similar pyrolysis conditions, the total liquid yield were reduced by 19.5 % while the char yield increased by 58.3 % relative to the untreated cellulose. The gas yield after NaOH treatment was almost the same. The NaOH treatment appeared to have promoted both char and water formation from the cracking of the organic liquid fraction. Clearly, the sodium hydroxide treatment promoted the conversion of the organic fraction into char and water. The organic fraction was reduced by 37.7 % while the water yield increased by 43.9 % and the char increased by 58.3 %. The changes in the yields were statistically significant for the char and the total liquids but were insignificant for the water and gas yields (Table 3.5).

The increase in the char yield is in agreement with Tanczos et al (2003) who also reported increase in the pyrolysis char yields when they treated cellulose with sodium hydroxide.

The pyrolysis products distributions of the na-mcc using the three HZSM-5 catalysts are also shown in Table 3.4 and Figure 3.3. The product distribution showed opposite trends compared to the pyrolysis products of mcc using these same catalysts. The organic liquid yield for the Sud-Chemie catalyst decreased by 44.7 % relative to the pyrolysis on the sand and it was also 65 % lower than mcc pyrolysis on the same catalyst. The water yield increased by 150 %, the char yield increased by 59 %, but the gas yield decreased by 9.8 % relative to the pyrolysis on the sand. It is interesting to note that the char yield relative to the mcc pyrolysis increased only slightly (6 %). In contrast gas yield increased by 98 % and the water yield increased by 66.7 % relative to the mcc pyrolysis using the Sud-Chemie. The products distribution of the BASF followed a similar trend as those observed for the Sud-Chemie catalyst Fig 3.3. However, the effect of NaOH treatment on the VPISU001 catalyst was quite different. The char yield increased by 138% and organic liquid yield decreased by 112.6% relative to mcc pyrolysis on this catalyst. However, the water (17.9%) yield increased minimally and gas (6.6%) decreased slightly. Thus, it appeared the NaOH treatment of the microcrystalline cellulose promoted the conversion of a large fraction of the organic liquid into water and gaseous products and a slight amount of char when the BASF and Sud-Chemie catalysts were used, but the exact opposite occurred for the VPISU001 catalyst. A detailed analysis of the data in Tables 3.3 and 3.4 showed very interesting trends. NaOH treatment of microcrystalline cellulose suppressed the organic liquid formation whiles Sud-Chemie and BASF catalysts promoted organic liquid formation, but VPISU001 suppressed liquid formation. Two different types of acid sites are

usually observed in HZSM-5 zeolites: Bronsted and Lewis acid sites. Bronsted acid sites are related to aluminum located in the framework of the zeolites, while the Lewis acids sites are related to the extra-framework aluminum (EFAL) or distorted aluminum in the framework (Shourong 2002). Since NaOH is a strong base and HZSM-5 is a Bronsted-Lewis acid, it appeared that some of the active catalytic sites that promoted organic liquid formation were poisoned by the NaOH during the pyrolysis process and hence the suppression of organic liquid formation. However, since gas formation increased relative to the untreated sample, and NaOH treatment does not promote gas formation, it appeared that the active site responsible for gas formation was still active in these catalysts and therefore more gas was produced from this reaction. Since a Bronsted acid is proton-rich and a Lewis acid is electron-rich, it appeared that the Bronsted acid sites were poisoned by the NaOH treatment whiles the Lewis acid sites were preserved. Similar observation was made by Katikaneni (1996) where the Bronsted acid sites were decreased with potassium impregnation while the Lewis acid sites were enhanced. The poisoning effect of the NaOH appeared to be more severe for the BASF than the Sud-Chemie catalyst because char formation increased by 6% for the Sud-Chemie compared to 16% for the BASF catalyst. In case of the VPISU001 catalyst, the poisoning effect of NaOH appeared to be more severe because the char yield increased by 138%. Since the NaOH treatment tends to promote char formation on sand medium, it appeared that all the Bronsted acid sites in the VPISU001 catalyst were completely poisoned and therefore those sites were behaving like sand and forming more char. This phenomenon could be used to control the selectivity of the HZSM-5 catalysts towards specific products.

Table 3.4 Summary of Pyrolysis Results Showing the Effect of HZSM-5Catalyst and NaOH Treatment

Sample	Pyrolysis Yields wt %				
	Organics	Water	Total Liquid	Char yield	[q]Gas yield
mcc-sand	30.2±0.1	8.2±0.6	38.4±0.5	11.5±0.4	50.0±0.2
na-mcc-sand	18.8±1.5	11.8±2.5	30.9±1	18.2±0.4	51.0±1.2
na-mcc-Sud-Chemie	16.7±1.5	20.5±4.1	36.6±2.7	18.3±0.6	45.1±2.8
na-mcc-BASF	17.3±0.3	22.3±4.0	36.8±.9	26.7±5.3	36.5±6.1
na-mcc-VPISU001	9.5±1.5	25.0±1.4	34.3±2.9	18.8±1.3	47.0±1.7

[q] Calculated by difference

mcc-sand: untreated microcrystalline cellulose pyrolyzed on sand
na-mcc-Sud-Chemie: NaOH pretreated microcrystalline cellulose pyrolyzed on Sud-Chemie catalyst
na-mcc-BASF: NaOH pretreated microcrystalline cellulose pyrolyzed on BASF catalyst
na-mcc-VPISU001: NaOH pretreated microcrystalline cellulose pyrolyzed on VPISU001catalyst
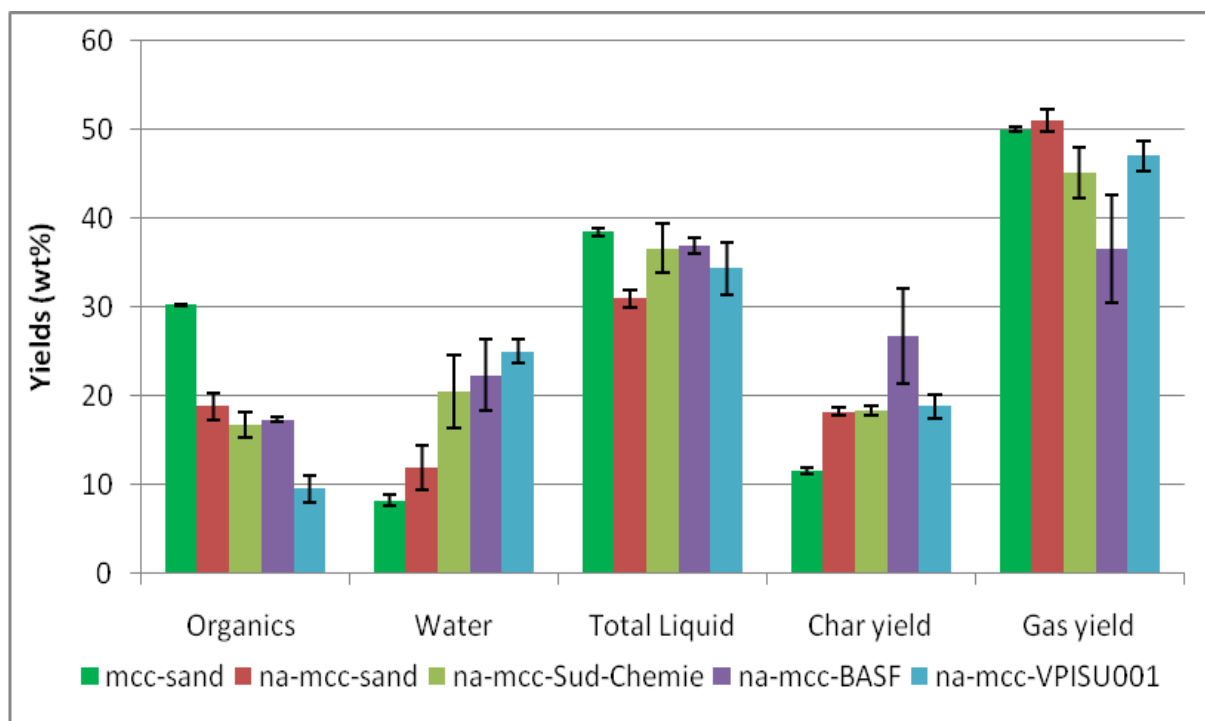
Figure 3.3: pyrolysis products distribution of NaOH treated microcrystalline cellulose

Table 3.5 Test of Significant Effect of NaOH Pretreatment and the HZSM-5Catalysts on the Pyrolytic Yields of Microcrystalline Cellulose Using Turkey-Kramer HSD Significance Test

Sample	Pyrolysis Yields wt %				
	Organics	Water	Total Liquid	Char	[q]Gas
mcc-sand	30.2[A]	8.2[B]	38.4[A]	11.5[C]	50.0[A]
na-mcc-sand	18.8[B]	11.7[B]	30.9[B]	18.2[B]	51.0[A]
na-mcc-Sud-Chemie	16.7[B]	20.5[A]	36.6[A]	18.3[B]	45.1[A]
na-mcc-BASF	17.3[B]	22.3[A]	36.8[A]	26.7[A]	36.5[B]
na-mcc-VPISU001	9.5[C]	25.0[A]	34.3[AB]	18.8[B]	47.0[A]

Levels not connected by the same letter are significantly different at 0.05 alpha level (Ott and Longnecker, 2001).

3.3.5 Characterization of Untreated Cellulose Pyrolysis Oils.

The pyrolysis oils collected from the ESP had lower moisture content than the condenser oils and were used for these studies. The untreated microcrystalline cellulose ESP pyrolysis oils from sand and catalysts all appeared brownish, acidic (Table 3.6), and had strong smoky smell. The condenser oils were also acid and the color varied from deep brown for sand, pale brown for the individual catalysts and pale yellow for the VPISU001 catalysts. The ESP oils were characterized using ^{13}C-nmr and FTIR spectroscopy.

The ^{13}C-nmr spectra of the various pyrolysis oils are shown in Figure 3.4. From 0- 55ppm the aliphatic hydrocarbons are the class of compounds found. From 8-30 ppm there is the primary long chain unbranched alkane region (methyl, -CH_3), 15-55 ppm secondary branched alkane region (methylene, -CH_2-) , 20-60 ppm tertiary branched alkane region (tertiary, methyne, C-H) and from 30-40 ppm quaternary branched alkane region(-c-) (Silverstein and Webster 1997).

Carbohydrate sugars, ethers, phenolic methoxy and alcohols groups of compound are found from 55- 104 ppm (Silverstein and Webster 1997; Mullen et al. 2009). From 95-165 ppm the aromatic classes of compound are found. Aromatic compounds with polar substituents are found within the entire range while those with hydrogen or alkyl substituents show intense peaks from 120-150 ppm (Silverstein and Webster 1997). Olefins also show up from 80-170 ppm (Silverstein and Webster 1997; Mullen et al. 2009). Esters and carboxylic acids show up from 160- 185 ppm and finally ketones and aldehydes groups of compounds show up from 180-220 ppm(Silverstein and Webster 1997). Table 3.7 summarizes the class of compounds identified and their functional groups.

The oil from sand was rich in the carbohydrate sugar levoglucosan (Figure 3.5 and Table 3.6) relative to the other class of compounds. The oil samples from Sud-Chemie and BASF under the same pyrolysis conditions showed similar trends. This suggests that both catalysts did not influence the production of the levoglucosan groups. The VPISU001 catalyst on the other hand showed interesting results. The levoglucosan groups were drastically reduced, suggesting that the VPISU001 catalysts was more selective in the breakdown of these groups and also clearly explains the fact that the levoglucosan groups were the main organic liquid components cracked to form more water as seen from Figure and the pale yellowish nature of the condenser oils.

In the aromatic region (95-165 ppm) there was drastic increase in the peaks associated with these regions with the use of VPISU001 catalyst while there were fewer of these groups with the BASF and Sud-Chemie catalysts relative to sand. Careful analysis of the spectra from Sudchemie and BASF oils showed that there was a drastic decrease in alkyl substituted aromatics

(120-150 ppm) relative to sand as evidenced by the decrease in alkyl side chain peaks from 5-30 ppm. In contrast the use of the VPISU001 HZSM-5 catalysts resulted in an increase in polar aromatic (95-160 ppm) and alkyl (120-150 ppm) substituted aromatic groups with a corresponding increase in the alkyl side chains 5-30 ppm relative to sand. The 56 ppm corresponding to methoxyl groups was present in all samples but with low intensity, showing that methoxylated aromatic compounds were present but in low quantities.

In the 165- 180 ppm corresponding to the esters and carboxylic acid groups there was a slight reduction in the peaks present with the use of Sud-Chemie while the BASF and the VPISU001 HZSM-5 catalysts caused a slight increase in the groups present. The ketones and aldehydes group region from 180 to 215 ppm saw a slight reduction in the peaks in from 200-205 ppm regions with the use of all catalyst but however there was a new peak observed at 188 ppm with use of BASF and Sud-Chemie catalysts, with Sud-Chemie producing the more intense peak. From these results its can be inferred that the VPISU001 catalyst is effective in breakdown of the carbohydrate sugars, while enhancing the formation of aromatic compound in the oil.

Figure 3.7 compares the FTIR spectra oil obtained with catalytic pyrolysis of untreated cellulose on the HZSM-5 catalysts with the control oil from the noncatalytic pyrolysis on sand. The broad absorbance peak between 3100 and 3600 cm^{-1} represents bonded O-H stretching vibration indicating the presence alcohols, water and phenols (Silverstein and Webster 1997; Putun et al. 2001; El-barbary et al. 2009). The C-O stretching vibration between 1260-1000 cm^{-1} and the O-H in plane bending vibration between 1420 and 1330 cm^{-1} complements the presence of alcohols

and phenols (Silverstein and Webster 1997). The functional group composition of the oils in these regions appears similar for all the oils.

The presence of methyl and methylene groups of alkanes in pyrolysis oils are indicated by the C-H stretching vibrations between 2800 and 3000 cm^{-1} and C-H deformation vibrations between 1350 and 1470 cm^{-1} (El-barbary et al. 2009). The use of VPISU001 caused a distinct increase in the absorbance in the 3000-2800 cm^{-1} and a 1470-1350 cm^{-1} region respectively regions. This was confirmed by the increase in the peaks in the acyclic regions on the ^{13}C-nmr spectra in Figure 3.4. In contrast Sud-Chemie catalyst as observed in the ^{13}C-nmr spectra saw a drastic reduction in the absorbance in this regions especially the C-H deformation stretch region 1470-1350 cm^{-1}. BASF also caused a similar trend but not as drastic as observed in Sud-Chemie.

The absorbance peak from C=O (carbonyl) stretching vibrations between 1650 and 1750 cm^{-1} together with the presence of O-H absorbance peak are indicative of the presence of carboxylic acids and their derivatives (Silverstein and Webster 1997). The presence of aldehydes and ketones groups are also indicated by the C=O stretching vibrations in these region (Putun et al. 2001). Sud-Chemie pyrolysis oils appeared to have a pronounced decrease in the absorbance peaks found in these regions; reducing the pronounced 1703 cm^{-1} relative to sand pyrolytic oil drastically and forming a new peak at 1665 cm^{-1}. This observation corresponds with the reduction of the peaks in the ketone and aldehyde region and formation of a new distinct peak at 188ppm from its [13]C- nmr spectra. BASF and the VPISU001 catalyst however did not affect these absorbance regions significantly as seen in the [13]C- nmr analysis. These results suggest that Sud-Chemie appear to suppress the formation of compounds with carbonyl functionalities.

Aromatic compounds are indicated by the out of plane C-H bending vibrations between 900-675 cm^{-1}. These are complemented by the C=C skeletal vibrations from 1600-1584 cm^{-1} and 1500-1400 cm^{-1} and in-plane C-H bending bands between 1300 and 1585 cm^{-1}(Silverstein and Webster 1997). Sud-Chemie and BASF catalysts did not appear to influence these groups. Interestingly however the pyrolysis oil from the VPISU001 catalyst was very rich in aromatic groups relative to sand pyrolytic oil as confirmed by the ^{13}C- nmr spectra.

The C-O-C pyranose ring skeletal vibrations from 1076-1023 cm^{-1} indicate the presence of levoglucosan (Sun et al. 2004). The BASF and Sud-Chemie catalysts did not cause any appreciable change in these regions as observed in C-13NMR spectra. In contrast however the VPISU001 HZSM-5 catalysts resulted in drastic break down of these groups as confirmed by the ^{13}C- nmr spectra. Thus it's clear that the major oxygenated group in untreated cellulose pyrolysis that is deoxygenated by the VPISU001 HZSM-5 catalysts is the levoglucosan groups.

The peaks between 1300-950 cm^{-1} are due to the presence of primary, secondary and tertiary alcohols (Das et al. 2004). The absorbance in these regions appeared more pronounced in the pyrolytic oils from untreated cellulose from VPISU001 HZSM-5 catalysts relative to that from sand.

Finally there was also a more pronounced increase in the 1300-900 cm^{-1} region corresponding to the primary, secondary and tertiary alcohols with the use of the VPISU001 catalyst than Sud-Chemie and BASF catalysts. Hence from the FTIR the use of the VPISU001 catalyst had a more

pronounced effect on the decomposition products of the catalytic pyrolysis than the individual catalysts.

Table 3.6: pH of Pyrolytic Oils

SAMPLE	PH
mcc-sand	2.35
mcc-BASF	1.86
mcc-Sud-Chemie	2.00
mcc-VPISU001	2.10

MCC-SAND

1-1

MCC-SUD-CHEMIE

2-2

MCC-BASF

3-3

MCC-VPISU001

4

200   150   100   50   0
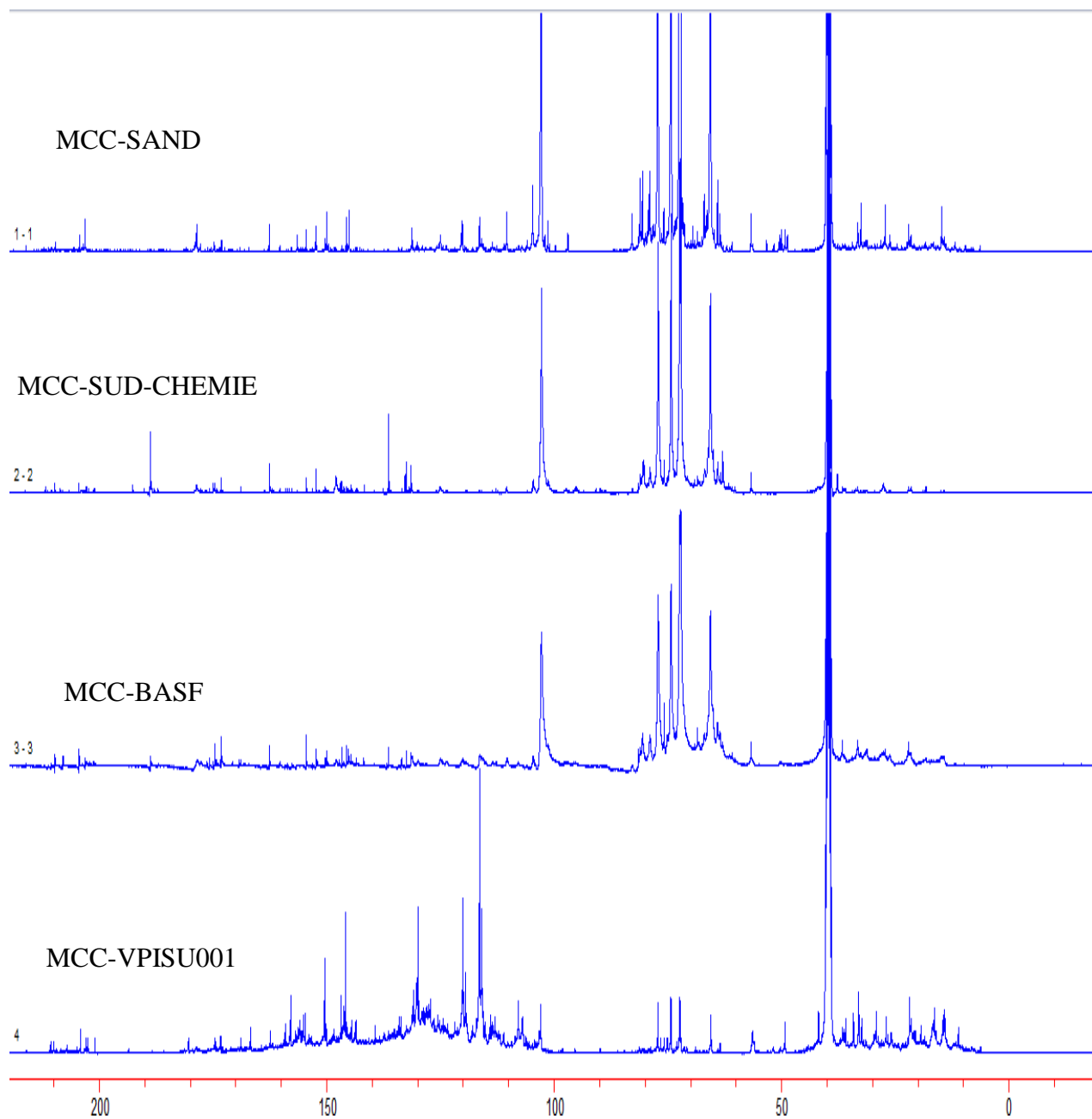
Figure 3.4: ^{13}C-nmr showing the effect of HZSM-5catalysts used
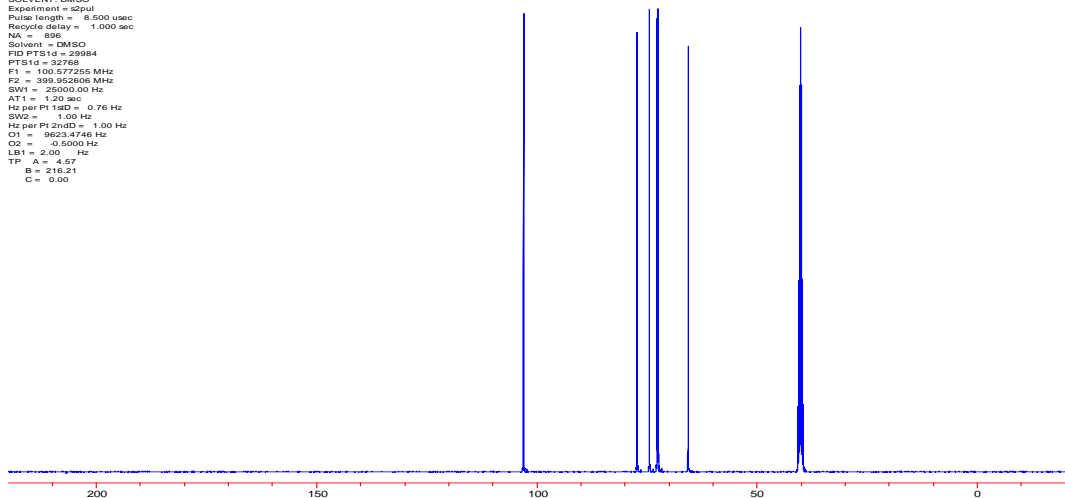
Figure 3.5: ^{13}C-nmr of pure levoglucosan in d$_6$-DMSO solvent

Table 3.7: Peak positions in levoglucosan structure

Carbon	PPM
C_1	102.8
C_2	77.1
C_3	74.2
C_4	72.3
C_5	72.1
C_6	63.9
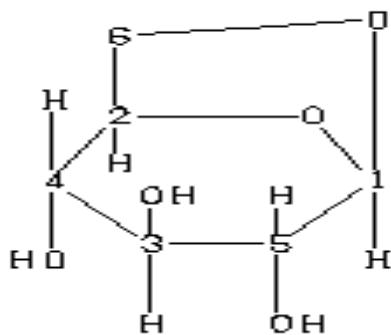
Figure 3.6: Structure of levoglucosan showing the carbon signals in the ^{13}C-nmr spectrum

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Table 3.8: Class of Compounds and their Regions of Identification

Type of Carbon	Chemical Shift (ppm)
Aliphatic Hydrocarbons	0-55
Carbohydrate Sugars, Alcohols, Ethers,	55-104
Phenol Methoxy(-OCH$_3$)	55-56
Levoglucosan C	64,72,74,77,103
Aromatics	95-165
Phenolic C	115,121,130,155
Carboxylic acids and Esters	165-180
Aldehydes and Ketones	180-215
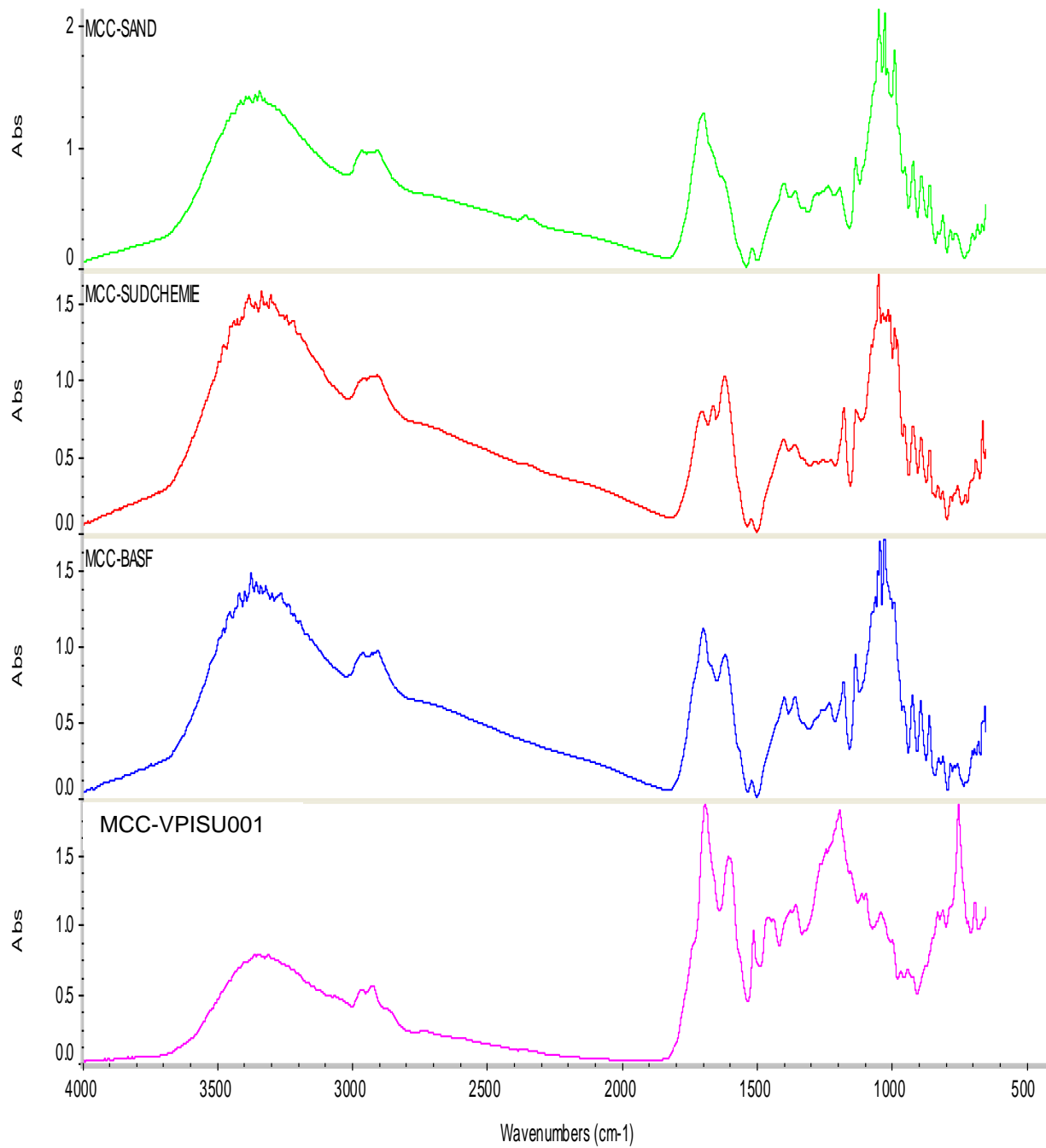
Figure 3.7: FTIR spectra showing the effect of HZSM-5catalysts used

3.3.6 Characterization of NaOH Treated Cellulose Pyrolysis Oils.

The ESP oils from NaOH treated cellulose pyrolyzed on sand and the HZSM-5 catalysts were used for characterization. All the oils appeared brownish, acidic, and had strong smoky smell. The condenser oils were also acidic and appeared from deep brown for sand, pale brown for the individual catalysts and pale yellow for the VPISU001 catalyst. The ESP oils were characterized using ^{13}C-nmr and FTIR spectroscopy.

Figure 3.8 is the ^{13}C-nmr showing the effect of NaOH treatment and HZSM-5 catalysts on cellulose pyrolysis. The assignments of peaks are similar to those done in the previous section. NaOH treatment appeared to decrease the intensity of the levoglucosan peaks relative to the untreated sample pyrolyzed on sand. According to Barker and Drews (1985), inorganic bases act to catalyze the pyrolytic degradation of cellulose so that it occurs at a temperature below the minimum required for the conformational interconversion necessary for levoglucosan formation. From the DTG curve Figure 3.1b NaOH pretreatment reduced the decomposition temperature of cellulose thus it's likely that NaOH treatment caused the decomposition of cellulose to occur at a temperature below the minimum for the formation of levoglucosan.

In the aromatic region from 95-105 ppm, NaOH treatment under the same pyrolysis conditions appeared to significantly increase these classes of compounds and their side alkyl chains (5-40 ppm) relative to the untreated sample pyrolyzed on sand. The peak at 56 ppm indicates some of the aromatics groups were methoxylated. The carboxylic acids and esters (165-180 ppm) and ketones and aldehydes (180-215) appeared to increase slightly relative to the untreated cellulose pyrolyzed on sand. From these observations it can be inferred that NaOH pretreatment of

cellulose significantly reduces the carbohydrate sugars (levoglucosan) and increases the aromatic and aliphatic hydrocarbon components.

NaOH treated cellulose pyrolyzed on BASF and Sudchemie HZSM-5 catalysts showed similar trends as sand. When the spectra of the untreated cellulose samples pyrolyzed on the same catalysts are compared to the treated samples, the treated samples shows significant increase and decrease in the aromatic and levoglucosan groups respectively. Thus it appeared that NaOH treatment plays a major role in breakdown of levoglucosan decomposition and formation of aromatic groups than the individual HZSM-5 catalysts.

The pyrolysis of the treated cellulose over the VPISU001 HZSM-5 catalysts showed interesting results. The levoglucosan groups were almost completely decomposed relative untreated sample pyrolyzed on sand. The aromatic groups increased significantly relative to sand. Comparison of the oil sample from the untreated and treated samples pyrolyzed on the same catalyst under similar conditions showed that the treated sample produced mainly phenolic group of aromatics. The dominant peaks at 115, 121, 130 and 155 ppm comes from the phenols present in the oil sample. These results suggest that NaOH treatment enhances the cracking of levoglucosan on the VPISU001 HZSM-5 catalysts and also the selectivity of phenols as the main aromatic class of compounds. The increase in aliphatic groups relative to sand and the intensity of alkyl substituted aromatics (120-150 ppm) suggests also that alkyl substituted groups of aromatic were also produced. The presences of the methoxyl peak at 56 ppm also suggest the presence of methoxylated aromatic groups. The carboxylic acids and esters (164-180 ppm), ketones and

aldehydes (180-215 ppm) peaks decreased in intensity in the pyrolytic oils from NaOH treated cellulose on this catalysts relative to the untreated cellulose pyrolytic oils from sand.

Figure 3.9 shows the FTIR spectra representing functional group compositional analysis from NaOH pretreated cellulose pyrolytic oils from sand and the VPISU001 HZSM-5 catalysts. The O-H stretching vibration indicating the presence alcohols, water and phenols (3100 and 3600 cm$^-$^{1}) did not appear different in the oils from NaOH treated cellulose pyrolyzed on sand.

The NaOH pretreated cellulose pyrolytic oils from sand was rich in aliphatic hydrocarbons (2800 and 3000 cm^{-1} and C-H deformation vibrations between 1350 and 1470 cm^{-1}) relative to the untreated pyrolytic oils from sand under the same conditions. This observation is confirmed by the production of more aliphatic hydrocarbon peaks in the ^{13}C-nmr spectra of the NaOH pretreated sample in Figure 3.9.

Analysis of the aromatics peaks showed that NaOH treated cellulose pyrolysis oils was richer in aromatic compounds relative to untreated pyrolysis oils from sand. C=C skeletal vibrations from 1500-1400 cm^{-1} and in-plane C-H bending bands between 1300 and 1585 cm^{-1} and the in plane C-H stretch vibrations peaks 900-650 cm^{-1} were intense relative those from untreated cellulose.

The C-O-C pyranose ring skeletal vibration of levoglucosan (1076-1023 cm^{-1}) showed weaker intensity in the NaOH pretreated cellulose pyrolytic oils relative to the untreated sample. This observation was confirmed in the ^{13}C-nmr from Figure 3.9.

Clearly from these results NaOH pretreatment of cellulose enhances the production of aromatic products while decreasing the levoglucosan products.

The pyrolysis of the NaOH treated cellulose on BASF and Sud-Chemie catalysts produced similar results as in sand. The VPISU001 HZSM-5 catalysts on the other were richer in the aromatic moieties relative to sand. Again interestingly as indicated by the ^{13}C-nmr spectra of the VPISU001 HZSM-5 catalytic oil the FTIR spectra showed strong presence of phenols. The out of plane C-H bend, at 810 cm^{-1} and 751 cm^{-1}, the out of plane C=C bend at 690 cm^{-1}, the C-O stretch at 1195 cm^{-1}, the C=C stretch at 1597, 1511, 1453 cm^{-1}, the aromatic C-H stretch at 3046 cm^{-1}, the in-plane O-H bend at 1360 cm^{-1} and the broad O-H stretch 3371 cm^{-1} all together indicate strong presence of phenols. Thus its clear when both the ^{13}C-nmr and FTIR spectra of untreated and treated oil samples from the VPISU001 HZSM-5 catalysts are compared, NaOH treatment promotes the catalytic activity towards mainly phenolic aromatic compounds.

MCC-SAND

NA-MCC-SAND

NA-MCC-BASF

NA-MCC-SUDCHEMIE

NA-MCC-VPISU001
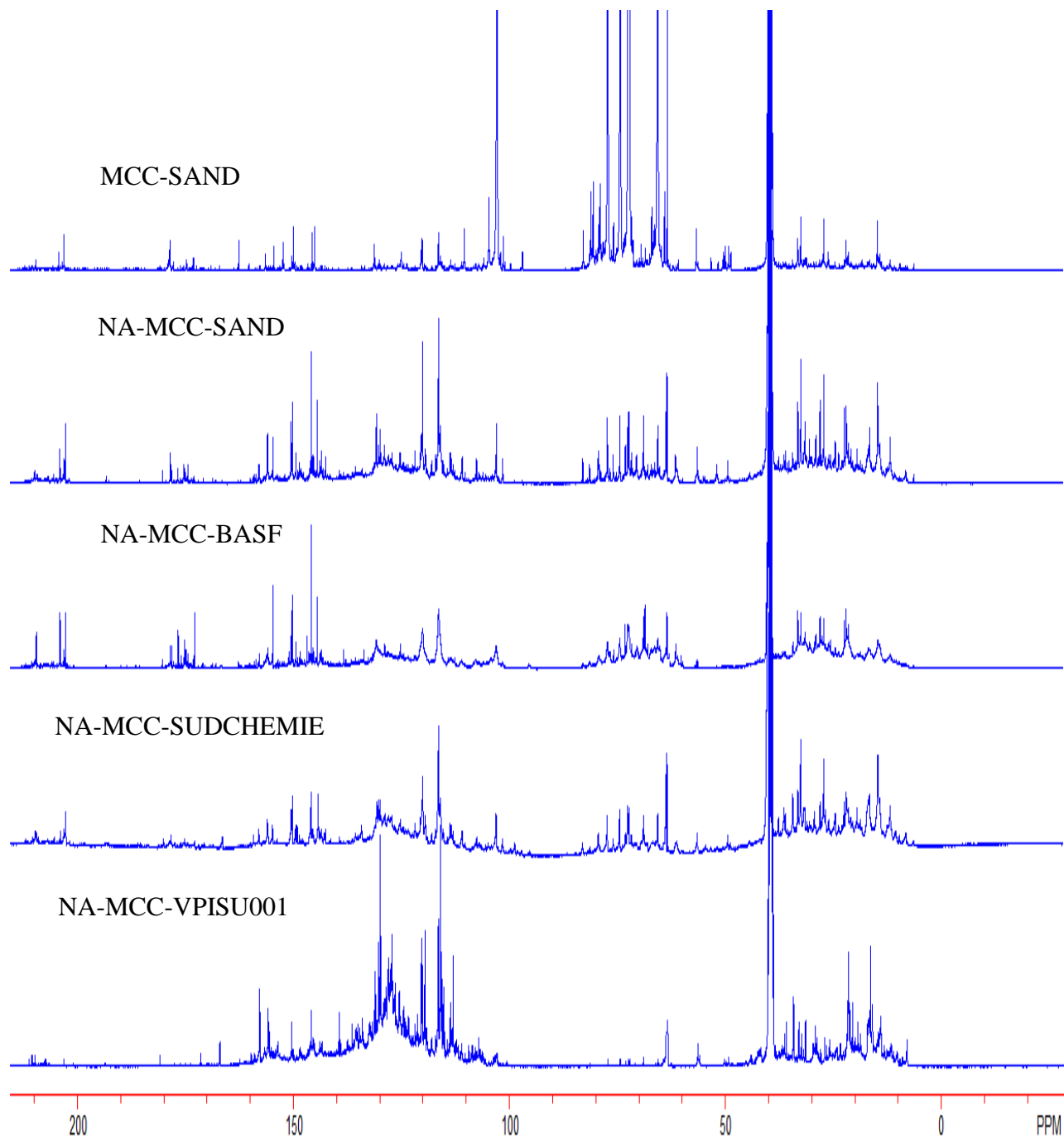
Figure 3.8: ^{13}C- nmr showing the effect of NaOH treatment and HZSM-5 catalysts
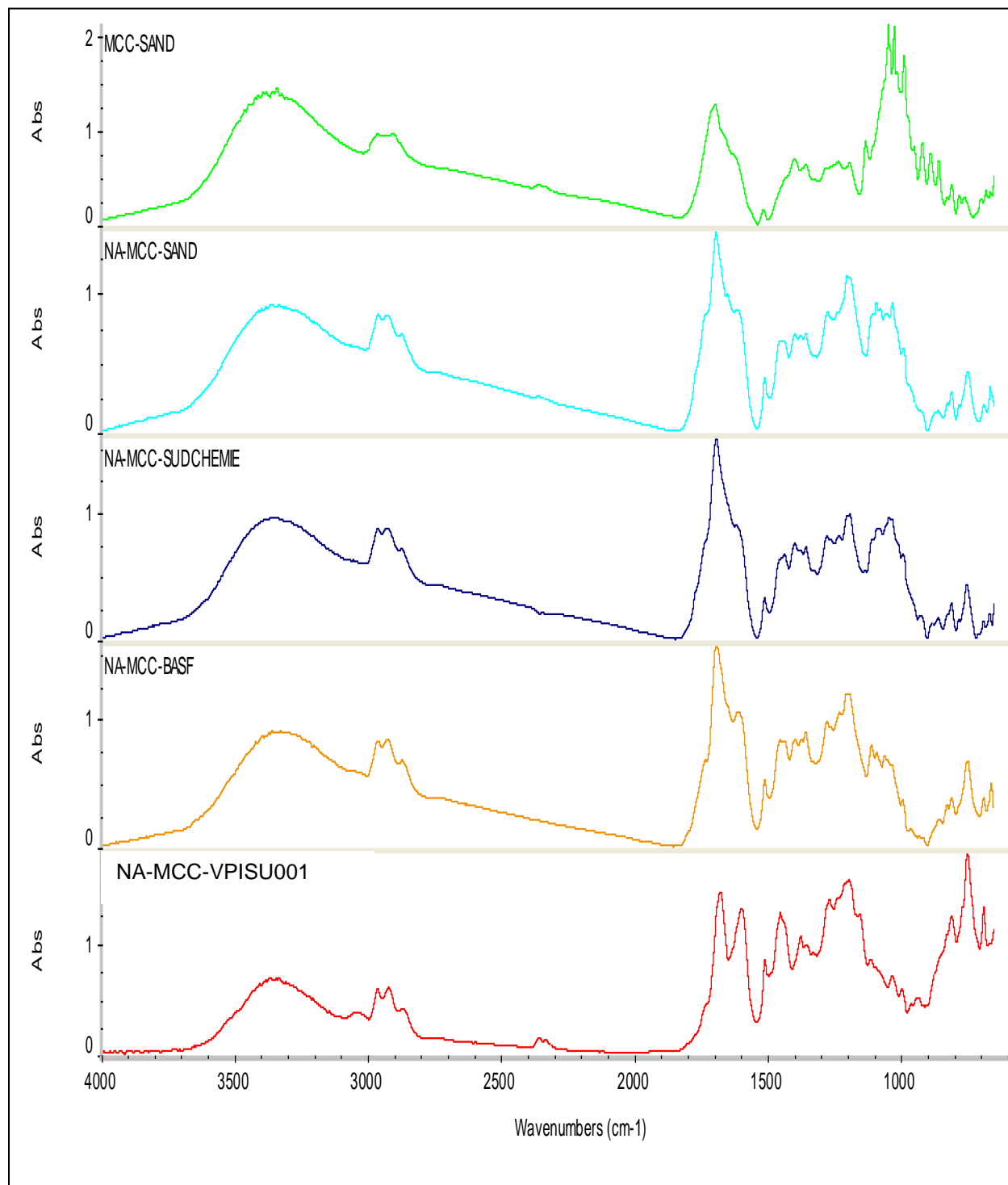
Figure 3.9: FTIR spectra showing the effect of HZSM-5catalysts and NaOH pretreatment

3.3.7 Gaseous Products Characterization

3.3.7.1 Effect of HZSM-5 Catalysts

From table 3.9 Sud-Chemie decreased the CO and CO_2 gas yields. The CO yields reduced significantly from 34.0 to 20.1 %, CO_2 from 29.4 to 8.8 % and the hydrocarbon yield increase doubled from 5.0 to 10.1 %. The low yield of CO and CO_2 may result from the catalyst favoring liquid production and char production as seen from the significant increase in the organic, total oil yield and char yields, and a reduction in the gas yield. Besides this its ineffectiveness in deoxygenating the pyrolysis vapors may also contribute to the low yield of CO and CO_2 as seen from the presence of oxygenated carbohydrate sugars in the FTIR and ^{13}C-nmr spectra of Sud-Chemie catalyzed oil. The increase in the hydrocarbon amount may be due to catalytic cracking effect of the pyrolysis vapors to form these hydrocarbon gases.

The use of BASF also saw similar trends in CO, CO_2 and the Hydrocarbon yields. The CO yield reduced significantly from 34.0 to 20.2 %, while CO_2 yield reduced marginally from 29.4 to 25.1 %.The hydrocarbon yield increased from 5.0 to 9.56 %. These results imply BASF had a greater deoxygenating effect and favored the production of liquid products to a lesser extent than Sud-Chemie producing more CO and CO_2 than Sud-Chemie, as seen in the significantly lower oil yield and higher char yields than Sud-Chemie.

With the VPISU001 catalyst the CO yield reduced significantly from 34.0 to 23 %, while CO_2 yields reduced marginally from 29.0 to 28.3 %. The greatest difference however was in the hydrocarbon yields which increased drastically from 5.0 to 46.5 %. These observed results may be due to the extensive catalytic cracking of the pyrolysis vapors. This may explain the low

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organic yield with the use of the VPISU001 HZSM-5catalysts and the drastic break down of the carbohydrate sugars (levoglucosan) as observed in the ^{13}C-nmr and FTIR spectra.

Table 3.9: The Effect of HZSM-5 Catalyst on Gas Product Composition

SAMPLE	CO	CO$_2$	Hydrocarbons	Unknown
MCC-SAND	34	29.4	5	31.6
MCC-SUDCHEM	20.1	8.8	10.1	60.9
MCC-BASF	20.2	25.1	9.56	45.14
MCC-VPISU001	23	28.3	46.5	2.2

3.3.7.2 Effect of NaOH Pretreatment

From table 3.10 NaOH pretreated cellulose pyrolyzed on sand produced more CO, CO_2 and hydrocarbon gases as compared to the untreated cellulose sample. The CO, CO_2 and hydrocarbon gases increased from 34 to 36%, 29.4 to 39.4% and 5 to 6% respectively. The increase in % area of these gases indicates that NaOH pretreatment of cellulose resulted in deoxygenation and further cracking of the pyrolysis vapors to produce these gases.

Table 3.10: Showing the Effect of NaOH Pretreatment on Gas Products Distribution

SAMPLE	CO	CO_2	Hydrocarbons	Unknown
MCC-SAND	34	29.4	5.0	31.6
NA-MCC-SAND	36	39.4	6.0	18.6

3.3.7.3 Effect of NaOH Pretreatment and HZSM-5 Catalysts

From table 3.11 NaOH pretreated cellulose pyrolyzed on Sud-Chemie resulted in a significant decrease and increase in CO and hydrocarbon gases respectively. The CO decreased from 34.0 to 19.0 % respectively and the hydrocarbons increased from 5.0 to 22.3 %. The CO_2 yield on the other hand increased marginally from 29.4 to 33.2 %. In comparison with NaOH pretreatment on sand the main effect of the Sud-Chemie was to increase the hydrocarbon yields significantly. This means that Sud-Chemie enhances the cracking of the organic vapors more than just NaOH pretreatment alone as seen in the lower organic and higher water yields.

The use of BASF saw a significant increase in CO from 34.0 to 42.8 % the CO_2 marginally from 29.4 to 30.0 % and the hydrocarbons marginally from 5.0 to 5.9 %. Comparing to NaOH pretreated cellulose on sand BASF increased CO from 36.0 to 42.8 % and decreased CO_2 from 39.4 to 30.0 % and insignificant effect on the hydrocarbon yield. This may be due to BASF presence favoring removal of oxygen through CO than CO_2.

NaOH pretreated cellulose pyrolyzed on the VPISU001 catalyst decreased the CO and CO_2 yields marginally from 34.0 to 30.5 % and 29.4 to 24.54 % respectively while increasing the hydrocarbon yields significantly from 5.0 to 48.1 %. Comparing to the CO CO_2 and hydrocarbon yields of 36.0 39.4 and 6.0 % from Just NaOH pretreated cellulose pyrolyzed on sand the obvious influence of the VPISU001 catalyst was a huge increase in the hydrocarbon gases produced, marginal decrease in CO and a significant decrease in CO_2 produced. The relative decrease in CO and CO_2 may be due to the extensive cracking of the pyrolysis vapors producing huge amounts of hydrocarbons thus reducing the concentration of the CO and CO_2 gases. The complete breakdown of the carbohydrate sugars from the ^{13}C-nmr and FTIR of this oil shows the

effective catalytic ability of VPISU001 catalyst to deoxygenate and crack the pyrolysis vapors to produce more hydrocarbon gases. This may also explain significant decrease in the organic liquid yields and significant increase in the water yield.

Table 3.11: Showing the Effect of NaOH pretreatment and HZSM-5Catalyst on Gas Products Distribution

SAMPLE	CO	CO_2	Hydrocarbons	Unknown
MCC-SAND	34	29.4	5	31.6
NA-MCC-SAND	36	39.4	6	18.6
NA-MCC-SUDCHEM	19	33.2	22.3	25.5
NA-MCC-BASF	42.8	30	5.9	21.3
NA-MCC-VPISU001	30.5	24.54	48.1	2.2

3.4 Conclusions

In this experiment it was found that NaOH treatment by itself and the use of Zeolites catalyst either by themselves or both caused varying results in the products distribution and oil properties. NaOH treatment by itself decreased the total oil produced affecting mainly the organics with no appreciable increase in water production while increasing char yields significantly in all experiments. NaOH treatment also affects the chemical nature of the oil by reducing the formation of levoglucosan while increasing the aromatic compounds production as observed from the ^{13}C-nmr and FTIR analysis. NaOH treatment by itself produced more gas than all the others giving the highest CO and CO_2 yields in the process. The VPISU001 catalyst was the most effective in breakdown of the levoglucosan regions either with, or without NaOH treatment, producing aromatics and acylic hydrocarbons in the process. But it produced more water in the process and less amounts of organics and char. However the NaOH treatment saw an increase in the char yields. Hence it's possible that the increase in the water production and aromatics formation results mainly from the breakdown of the carbohydrate sugars by deoxygenation to produce water, CO_2, CO and more hydrocarbon gases.

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CHAPTER FOUR

PYROLYSIS OF XYLAN

ABSTRACT

Birchwood xylan and NaOH treated xylan samples were pyrolyzed on sand and HZSM-5 catalysts. The organic liquid yields were very low and ranged from 3.3 wt% to 7.2 wt%, the water yields ranged from 17.8-25.7 wt%, the char yield were 17.8-25 wt% and gas yield were 40.9-49.6 wt%. The HZSM-5 catalysts produced the highest water and gas yields and the lowest char yield. NaOH pretreatment produced the lowest water yield while the char yield was the highest. The combined effect of NaOH pretreatment and HZSM-5 produced the lowest organic yield and highest char yield. The FTIR and ^{13}C-NMR analyses of the organic liquids showed that catalysis affected the pyrolysis products distribution significantly. The HZSM-5 catalyst promoted the formation of aromatic products, while the NaOH pretreatment promoted the formation of aliphatic hydrocarbons. The combined effect of NaOH pretreatment and HZSM-5 catalysts seem to promote the formation of anhydrosugars. The main gases evolved were CO, CO_2 and low molecular weight hydrocarbons. The GC analysis of these gases showed that the HZSM-5 catalyst promoted CO formation while NaOH pretreatment promoted CO_2 formation instead of CO. The HZSM-5 catalyst produced the highest yield of low molecular weight hydrocarbon gases.

4.1 Introduction

Pyrolysis is a promising technology for biomass conversion as alternate source of energy to supplement the dwindling sources of fossil fuels (Haipang et al. 2007). However, biomass pyrolysis products are very complex and the pathways of products formation cannot be easily followed. In order to understand the pyrolysis products distribution, the major components of the biomass should be studied independently.

Hemicellulose which constitutes 20-35 wt% of the biomass (Mohan et al. 2006) is a polymer of several monosaccharides such as :xylose, mannose, galactose, arabinose glucose and other saccharides. Compared to cellulose, few studies have been conducted on hemicellulose pyrolysis behavior. Xylan polysaccharides and model compounds have been used to study the pyrolytic behavior of hemicellulose and the decomposition temperature falls between 200-250°C (Varhegyi et al. 1989). The overall decomposition mechanism of hemicellulose pyrolysis under conditions of low heating rates and atmospheric pressure consists of competing reactions. Below 250 ^{o}C low temperature depolymerization occurs to form char, carbon monoxide, carbon dioxide and water. Between 250-350 ^{o}C, the polysaccharides decompose to form volatile anhydrosugars and related monomeric compounds (Nowakowski and Jones 2008).

The effect of additives on the decomposition behavior of hemicellulose has been investigated (Shafizadeh et al. 1972; Nowakowski and Jones 2008). Shafizadeh (1972) studied the effect of NaOH and zinc chloride ($ZnCl_2$) on hemicellulose pyrolysis using the model compounds such as methyl-β-D-xylopyranoside and D-xylose in addition to O-acetyl-4-O-methylglucuroxylan and 4-O-methylglucuroxylan extracted from cotton wood. Carbon dioxide, carbon monoxide, water, char and tar were the products. The $ZnCl_2$ catalyzed the dehydration reactions producing 2-

furaldehyde, water and char. While the NaOH catalyzed the fragmentation and rearrangement reactions producing low molecular weight products.

Huber (2009) studied the effect of zeolites (ZSM-5) catalyst on the aromatic production from cellulose, glucose, cellubiose and using xylitol (a hemicellulose derived model compound) in a pyroprobe analytical pyrolyzer. The major products were aromatics, CO, CO_2 and coke. The xylitol feed gave the highest aromatic product yield.

The goal of this chapter is to study the effect of HZSM-5 catalysts and NaOH treatment on the pyrolysis products distribution of xylan.

4.2 Materials and Methods

4.2.1 Materials

Birchwood xylan (a yellow powder) with xylose residues greater than 90% was purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO) to represent hemicellulose. The catalysts used was VPISU001 HZSM-5 catalyst. The NaOH and white silica sand were purchased from Fischer Scientific (Fischer Scientific, Pittsburg PA).

4.2.2 Xylan Pretreatment and Characterization

The xylan was pretreated with 1 wt% of NaOH by dissolving 1g of NaOH in 125 ml distilled water and mixing the solution with 50 g of xylan powder and thoroughly mixing to ensure all of the powder were soaked in the water and the resulting paste was dried at 75 ^{o}C to a constant mass.

The moisture content of the pretreated and untreated xylan samples was determined using a Metler Toledo halogen moisture analyzer (Metler Toledo Inc. Polaris Parkway, Columbus, OH). About 1 g of the sample was weighed into the moisture analyzer and the moisture content determined at 105 ^{o}C.

Samples of xylan and NaOH treated xylan were analyzed thermogravimetrically using TA Instruments Q600 SDT following a similar methodology as described in Chapter 3 materials and methods section.

4.2.3 Pyrolysis Experiments

The xylan pyrolysis experiment was conducted in the same pyrolysis unit as that used for the cellulose pyrolysis described in Chapter 3. The pyrolysis temperature was maintained at 450 °C, 50 g of xylan was used for both catalytic and non catalytic experiments. The amount of catalyst used was 50 g to give a WHSV of 1 the same amount of sand was used in the non catalytic process.

4.2.4 Pyrolysis Product Characterization

The pyrolysis oils were recovered by washing the electrostatic precipitator (ESP) and condensers with methanol because the quantities of oils produced were very low. The methanol was then evaporated in a rotary vacuum evaporator at 40 °C. About 200 mg of the methanol recovered oil was dissolved in 0.7 ml deuterated dimethyl sulfoxide (d_6-DMSO) in a 5 mm sample probe. The ^{13}C-NMR spectra were recorded on a Varian Inova 400 MHz NMR spectrometer (Varian Inc, Palo Alto, CA). The observing frequency for the ^{13}C nucleus was 100.58 MHz. The pulse width was 9.6 μs, the acquisition time was 1.36 s, and the recycle delay was 1s. The spectra were obtained with 2000 scans and a sweep width of 24140 s. Data analysis was performed with NutsPro - NMR Utility Transform Software – Professional (Acorn NMR, 1993-2005,Livermore, CA).

FTIR analysis was also performed on the pyrolysis oils using similar analysis conditions as those used for the cellulose pyrolysis oils described in Chapter 3.

The gas composition was determined using similar analysis conditions as those described in Chapter three.

4.3 Results and Discussion

4.3.1Thermogravimetric (TG) and Differential Thermogravimetric Analysis (DTG) Showing the Effect of NaOH Pretreatment on Xylan Pyrolysis

The thermograms of the birchwood xylan samples are shown in Figure 4.1a (TG) and 4.1b (DTG). The decomposition temperature for the treated and untreated samples ranged from 25 ^{o}C to 700 ^{o}C. The pretreated and untreated sample had similar weight loss pattern and with two maxima. The first maximum weight loss occurred at 235 ^{o}C and 229 ^{o}C respectively for the treated and untreated xylan samples and was a small shoulder (Fig 4.1b). The NaOH treatment appeared to have increased the maximum weight loss temperature for this peak. The second maximum and the most intense weight loss occurred at 288 ^{o}C. This maximum was almost identical for the treated and untreated samples (Fig 4.1b). The NaOH pretreatment did not influence the maximum decomposition temperature but decreased the amount of material lost. At 220 ^{o}C (fig 4.1a) the untreated xylan sample showed slow weight loss compared to the pretreated sample. At 320 ^{o}C however the residue was the same (41 wt %) for both samples. At the pyrolysis temperature of interest (450 ^{o}C) and final temperature of 700 ^{o}C the residue were about 31 wt% and 26 wt% respectively for both treated and untreated samples (Fig 4.1a). Thus it appears that the NaOH treatment has minimal effect on the decomposition temperature of the birchwood xylan which is in contrast with the microcrystalline cellulose samples which showed considerable lowering of the maximum weight loss temperature (see Chapter 3).
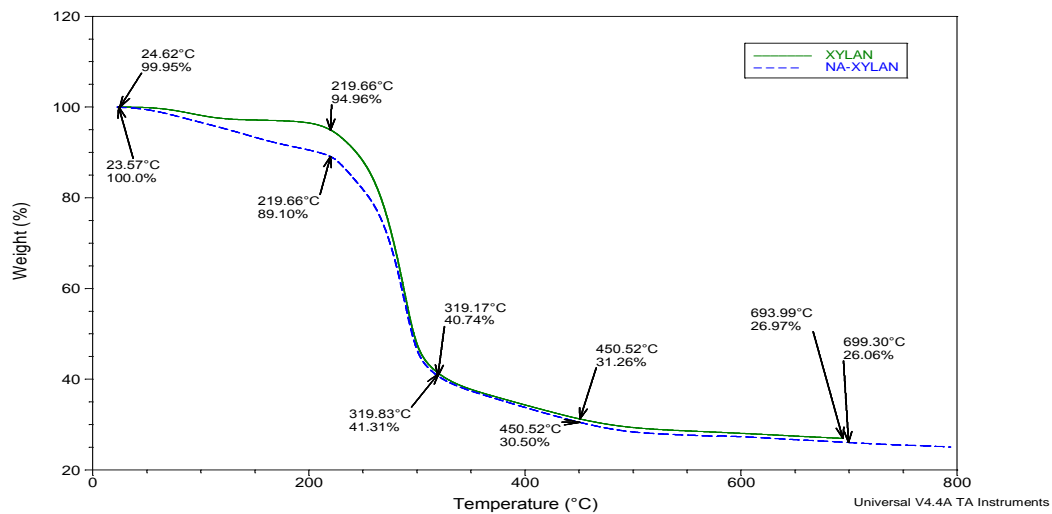
Figure 4.1a: TG plot of NaOH pretreated and untreated birchwood xylan
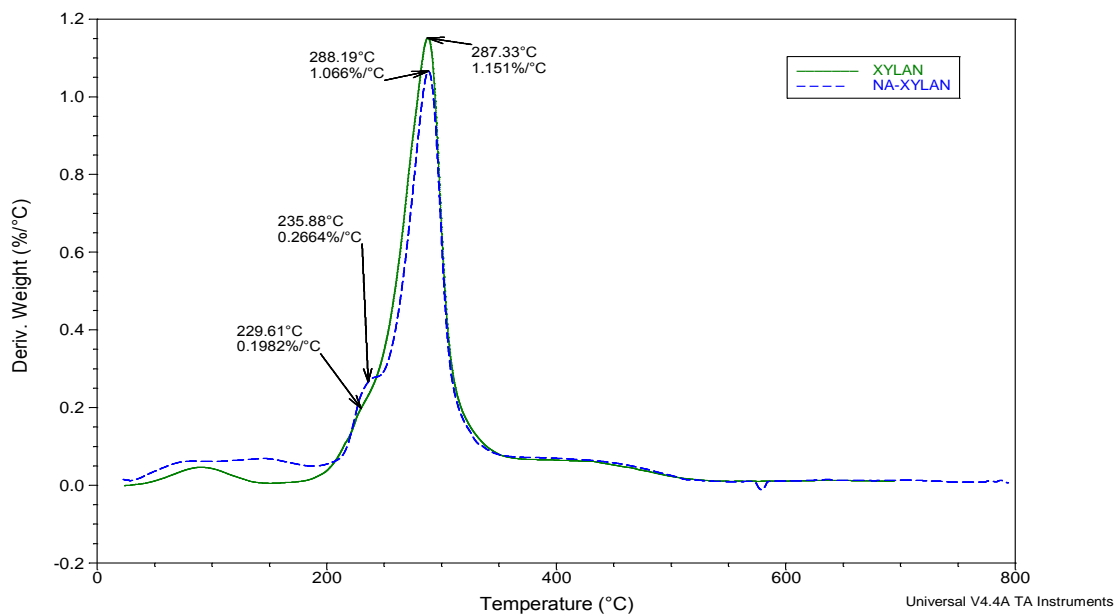
Figure 4.1b: D TG plot of NaOH pretreated and untreated birchwood xylan

4.3.2 Xylan Fluidized Bed Pyrolysis Products Distribution

Unlike the cellulose which was easily fed into the reactor and pyrolyzed readily, the pyrolysis of the xylan was very difficult. It appeared that at the interphase of the fluidizing medium and the xylan feed, the xylan decomposed and formed foams which mixed with the fluidizing medium to form a cake that sometimes blocked the feeding tube. This behavior of the xylan appeared to have influenced the pyrolysis process considerably and probably affected the total liquid yields.

The yields of the pyrolysis products are shown in Table 4.1 and Figure 4.2 although the total liquid yields were comparable to those obtained for the cellulose pyrolysis, most of the liquid was water for all the samples investigated. The pyrolysis of the untreated birchwood xylan on sand produced the highest yield of organic liquid (7.2 wt%) which decreased by 36 % when the xylan was treated with NaOH and pyrolyzed on sand. The water fraction after the NaOH treatment also decreased by 24 % and the total liquid yield decreased by 27.5 %. In contrast both the char and gaseous products increased after the NaOH treatment and pyrolysis on sand (Table 4.1). Thus it appears that the organic fraction was mostly converted into char and small fraction into gas after the NaOH treatment. The increase in the char yield was similar to that observed for the cellulose treatment, but unlike the cellulose, there was a slight increase in the gas yield (Chapter 3).

The pyrolysis of the untreated birchwood xylan on HZSM-5 catalyst also showed a 33 % decrease in the organic liquid fraction yield relative to the pyrolysis on sand. The decrease in the yield was similar to that obtained when the NaOH treated sample was pyrolyzed of the xylan and pyrolysis on sand (Figure 4.2). However, the water yield from the HZSM-5 pyrolysis did not change relative to the untreated sample pyrolyzed on the sand. The char yield decreased by 17.6

% relative to sample pyrolyzed on sand. The gas fraction increased considerably suggesting that the catalyst converted most of the organic fraction into gases without forming char.

The pyrolysis of the NaOH treated xylan on the HZSM-5 catalyst showed a considerably different result (Table 4.2). The loss of organic liquid fraction was highest and there was some increase in the water yield. Whereas there was an increase in the char yield, the gas yield decreased. This suggests that the combination of the NaOH treatment with the HZSM-5 pyrolysis suppressed gas evolution but promoted both water and char formation from the organic liquid fraction of the pyrolysis products.

Table 4.1: Summary of Pyrolytic Yields

Sample	Pyrolysis Products Yields (wt %)				
	Organics	Water	Total Liquid	Char	^{q}Gas
xylan-sand	7.2±0.3	23.6±0.9	30.9±1.2	26.1±1.5	43.0±1.2
na-xylan-sand	4.6±0.3	17.8±0.2	22.4±0.1	30.8±1.2	46.8±1.1
xylan-VPISU001	4.8±0.4	24.2±1.0	28.9±1.4	21.5±0.7	49.6±0.7
na-zylan-VPISU001	3.3±0.2	25.7±0.2	29.0±1.1	30.1±0.9	40.9±0.9

q: calculated by difference
xylan-sand: Untreated birchwood xylan pyrolyzed on sand
na-xylan-sand: NaOH pretreated birchwood xylan pyrolyzed on sand
xylan-VPISU001: Untreated birchwood xylan pyrolyzed on VPISU001catalysts
na-xylan-VPISU001: NaOH birchwood xylan pyrolyzed on VPISU001catalysts
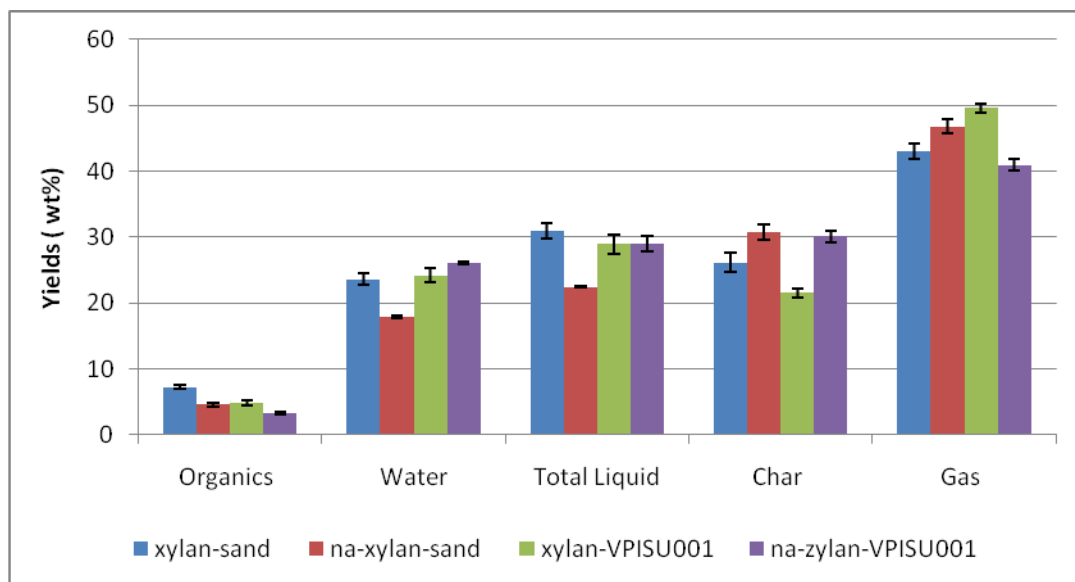
Figure 4.2: Effect of NaOH treatment and HZSM-5 catalysts on pyrolytic product distribution

Table 4.2: Test of Significant Effect of NaOH Treatment and HZSM-5 Catalysts on the Pyrolytic Yields of Microcrystalline Cellulose Using Turkey-Kramer HSD Significance Test.

Level	Pyrolysis Yields wt %				
	Organics	Water	Total Liquid	Char yield	[q]Gas yield
xylan-sand	7.2[A]	23.6[B]	30.9[A]	26.1[B]	43.0[C]
na-xylan-sand	4.6[B]	17.8[C]	22.4[B]	30.8[A]	46.8[B]
xylan-VPISU001	4.8[B]	24.2[AB]	28.9[A]	21.5[C]	49.6[A]
na-xylan-VPISU001	3.3[C]	25.7[A]	29.0[A]	30.1[A]	40.9[C]

Levels not connected by the same letter are significantly different 0.05 alpha level (Ott and Longnecker. 2001)

4.3.3 Characterization of Pyrolysis Oils

The pyrolysis oils were characterized using both ^{13}C-nmr and FTIR methods. The FTIR spectra of the pyrolysis oils of the treated and untreated xylan samples pyrolyzed on sand and HZSM-5 catalyst are shown in Fig 4.3.

The O-H vibrations of hydroxyl groups indicating the presence of water, phenolic or alcoholic group are represented by the absorbance peak between 3600 and 3100 cm^{-1}. The C-O stretching vibration between 1260-1000 cm^{-1} and the O-H in plane bending vibration between 1420 and 1330 cm^{-1} complements the presence of alcohols and phenols (Silverstein and Webster 1997). The functional group composition of the oils in this region of the spectra were similar for all the oils.

The presence of methyl and methylene groups of alkanes are shown by the absorbance peak of C-H stretching vibrations between 3000 and 2800 cm^{-1} and the C-H deformation vibrations between 1470 and 1350 cm^{-1} (El-barbary et al. 2009). The intensity of the alkane functional groups in the pyrolysis oil of the untreated xylan and NaOH treated sample were similar.

The C=O stretch vibrations between 1760 and 1650 cm^{-1} show the presence of carbonyl functional groups (carboxylic acids, aldehydes and ketones). The treatment of the xylan with NaOH and pyrolysis on sand did not appear to influence the intensity of the carbonyl functional groups.

Aromatic compounds are indicated by out of plane bending of C-H bonds between 900-675 cm^{-1} and these are complemented by skeletal C=C ring stretching vibrations in the 1600 - 1585 cm^{-1} and 1500 and 1400 cm^{-1} regions, the in-plane C-H bending bands between 1300 and 1000 cm^{-1}

and C-H stretching bands between 3100 and 3000 cm^{-1} (Silverstein and Webster 1997).The aromatic functional groups composition of both the NaOH treated and untreated samples pyrolyzed on the sand were similar. Thus, the FTIR did not show any significant difference in the functional composition of the two pyrolysis oils.

The FTIR spectra of the pyrolysis oils obtained from HZSM-5 catalytic pyrolysis of untreated birchwood xylan was clearly different from the untreated xylan pyrolyzed on the sand. The major differences between the oils appear in the aromatic (3100-3000 cm^{-1}, 1600- 1650 cm^{-1} and 900-675 cm^{-1}) and the aliphatic hydrocarbon (2800-3300 cm^{-1}) regions. The pyrolysis oils from the sand pyrolysis were richer in aliphatic hydrocarbons than the corresponding HZSM-5 pyrolyzed catalysts. These data are complemented by the ^{13}C-nmr (Fig 4.4) which show relatively more intense peaks in the aliphatic hydrocarbon region (0-30 ppm). The HZSM-5 pyrolysis oils also appear to be very rich in aromatic components as shown by the strong peak at the 1600 cm^{-1} due to aromatic skeletal vibration, the pronounced peak at 747 cm^{-1} from C-H out of planed bend and the 3053 peak from the aromatic C-H stretching bands. The ^{13}C-nmr spectrum also complements this assertion because it showed relatively more intense peaks in 110-150 ppm region that are typical of aromatic compounds.

The FTIR spectra of the pyrolysis oils obtained after treatment with NaOH and pyrolysis on HZSM-5 were similar to those obtained without NaOH treatment except in the intensity of the peaks in the 1100 to 1000 cm^{-1} region and the 756 cm-1 region. The NaOH treatment appeared to have reduced the intensity of the 1600 cm^{-1} and 1453 cm^{-1} skeletal aromatic hydrocarbon ring vibration. In contrast, the peaks in the 1100 to 1000 cm^{-1} which are typical of anhydrosugars

appeared to have increased intensity. The ^{13}C-nmr spectra showed increase intensity of peaks typical of levoglucosan whereas the aromatic hydrocarbon peaks appeared to have reduced intensity.

The ^{13}C-nmr spectra of the various oils are shown in Fig 4.4. The assignment of peaks is similar to those done in chapter three for the cellulose pyrolysis. The treatment of the xylan with NaOH appeared to increase the intensity of the aromatic hydrocarbon peaks (110-150 ppm) relative to the untreated xylan when they were both pyrolyzed on sand. Both oils were relatively rich in aliphatic hydrocarbon moieties and there were hardly any levoglucosan components.

The HZSM-5 pyrolysis of the untreated xylan had a more pronounced effect on the composition of the pyrolysis oil. The HZSM-5 pyrolysis increased the relative intensity of peaks in the aromatic region as well as anhydrosugars region (60-103 ppm) region. The anhydrosugars peaks are similar to those observed for levoglucosan suggesting that under pyrolysis conditions, HZSM-5 is able to produce a small fraction of the levoglucosan. This has to be verified with further analysis of the pyrolysis products.

The relatively intense aromatic hydrocarbon peaks in the 110-150 ppm region suggests that the HZSM-5 catalyst is capable of converting some of the xylan degradation products to aromatic compounds similar to those observed for the cellulose pyrolysis on this catalyst. There appeared to be a small methoxyl carbon signal at 56 ppm suggesting that some of the carbon ring was methoxylated. The intensity of the peaks in the aliphatic hydrocarbon region appeared to have

decreased relative to oil samples produced on the sand. Thus, some of the aliphatic compounds produced on the sand were probably aromatized on the HZSM-5 catalyst.

The treatment of the xylan before the pyrolysis on the HZSM-5 catalyst appeared to have some very interesting effect on the pyrolysis oil composition as shown by the ^{13}C-nmr spectra. The relative peak intensities in the aromatic carbon region appeared strongly reduced and appeared to be similar to those produced on the sand. However, the intensity of the peaks in the region assigned to the anhydrosugars appeared to be more intense. This suggests that the NaOH treatment promotes the formation of levoglucosan from xylan decomposition products on this catalyst. However, this treatment suppresses the formation of aromatic hydrocarbons probably because some of the acidic sites that promoted aromatization had been neutralized by the NaOH. This is an interesting observation because it clearly shows that the catalytic activity of this catalyst is due to separate sites. Each site produces a specific group of compounds.

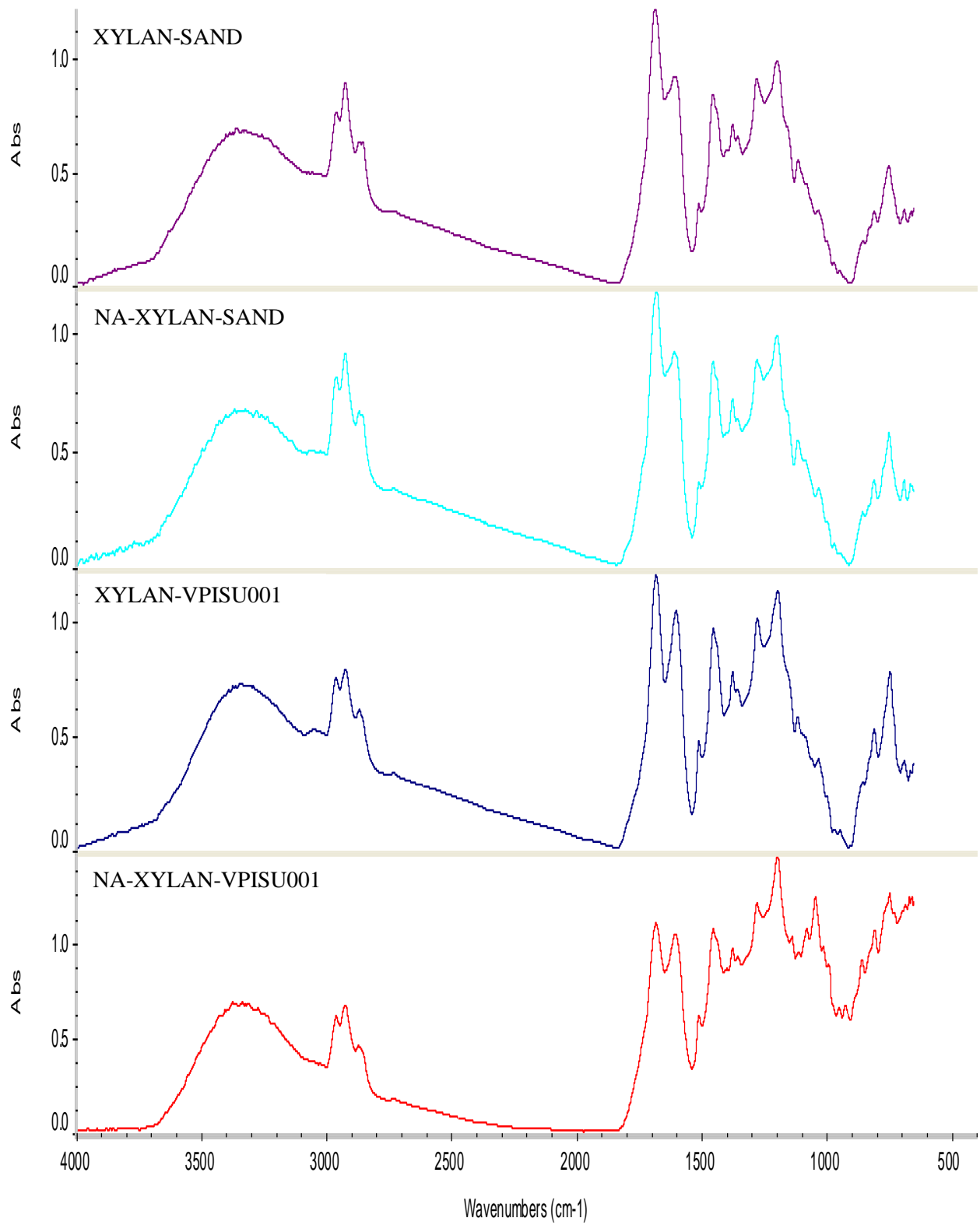Figure 4.3: FTIR spectra showing the effect of catalysis on xylan pyrolytic oil
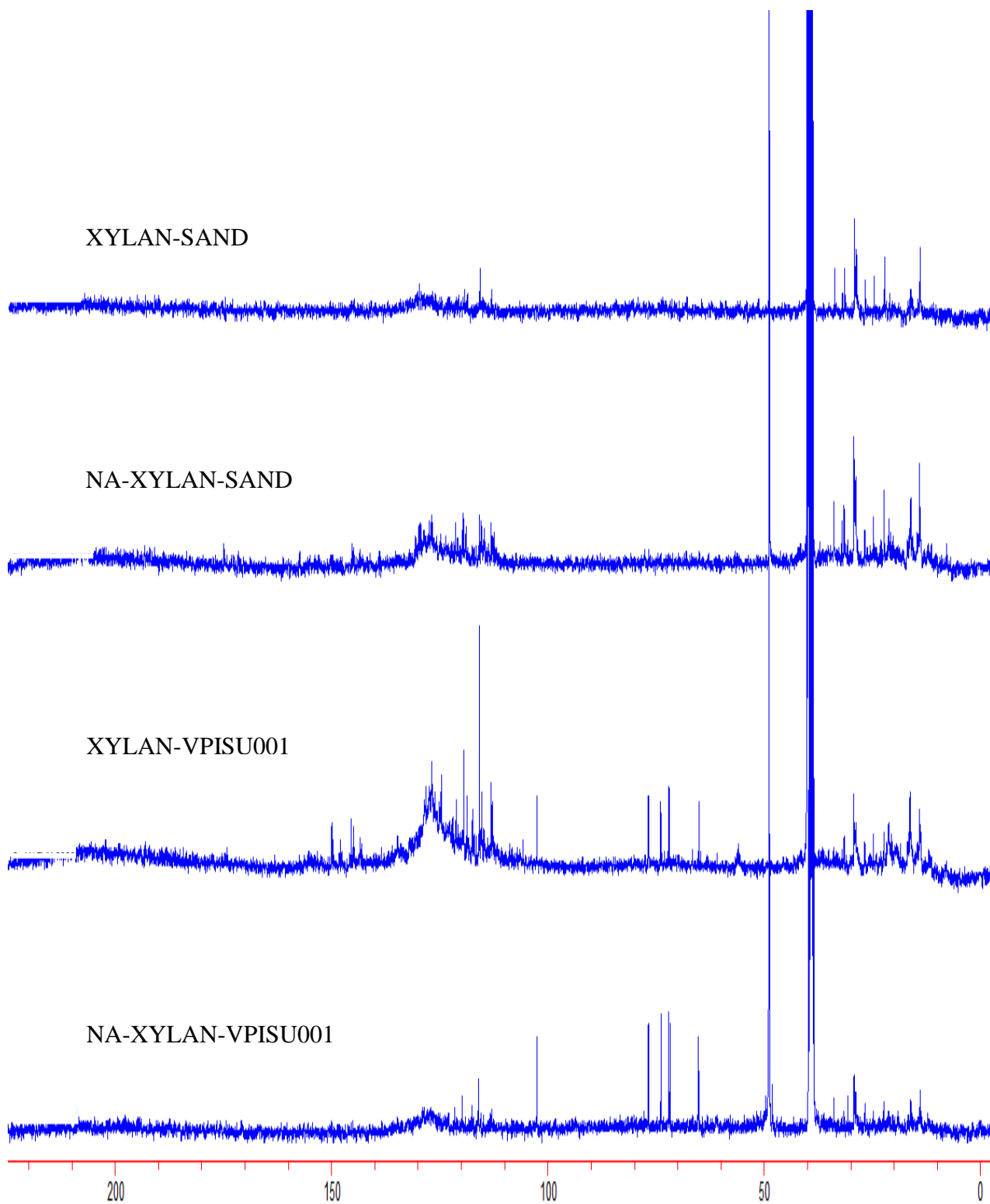
XYLAN-SAND

NA-XYLAN-SAND

XYLAN-VPISU001

NA-XYLAN-VPISU001

| 200 | 150 | 100 | 50 | 0 |

Figure 4.4: ^{13}C-nmr spectra showing the effect of catalysis on xylan pyrolytic oil

4.3.4 Effect of Catalysis on Gas Composition

The CO yield NaOH pretreated xylan pyrolyzed on sand and the VPISU001 HZSM-5 catalysts resulted in a significant decrease in the CO yield, from 27.0 to 18.8 and 2.3 % respectively and the untreated sample pyrolyzed on the VPISU001 HZSM-5 catalysts resulted in a significant decrease in gas yield from 27.0 to 7.0 %. The relatively low % values of CO with the HZSM-5 catalysts presence may be due to the relatively high amount of unknown components produced (71.8 % for na-xylan-VPISU001 and 61.6 % for xylan-VPISU001). The composition of the xylan pyrolysis gases are shown in table 4.3.

The CO_2 yield decrease with all catalysts forms tested. NaOH pretreatment resulted in decrease in the CO_2 from 53.0 to 42.4%, NaOH pretreated xylan pyrolyzed on a VPISU001 HZSM-5 catalysts decreased the gas yield further to 7.1 % whilst the untreated xylan sample pyrolyzed on a VPISU001 HZSM-5 catalysts decreased the gas yield further to 3.9 %. The relatively low % values CO_2 with the HZSM-5 catalysts may again be due to the relatively high amounts of unknown components produced.

The CO/CO_2 ratio helps to indicate the preferred path of catalysis since the oxygen is removed from the pyrolysis vapor through CO, CO_2 and H_2O. But the water goes into the liquid yield whilst the activity of catalyst which results in CO and CO_2 goes into the gas products. Thus the CO/CO_2 ratio relative to the uncatalyzed pyrolysis would help explain the preferred path of oxygen removal with catalysis. CO and CO_2 are formed from decarboxylation and decarbonylation reactions. CO from hemicellulose mainly comes from the breakdown of the C=O and C-O-C functional groups and CO_2 from the cracking of the C=O and COOH functionalities (Haipang et al. 2007). From table 4.3 CO/CO_2 ratios for untreated xylan pyrolyzed

on sand, was 0.52 meaning in the absence of catalysis the CO_2 is more favored. With NaOH

pretreatment this ratio was decreased further to 0.44, implying NaOH pretreatment favored CO_2

production route than CO. From the FTIR analysis of Figure 4.3 since NaOH pretreatment

resulted in slight increase in the C=O absorbance peak relative the untreated sample, may be due

to more CO_2 being produced from this functional group than CO. With the presence of both

NaOH pretreatment and the HZSM-5 catalyst this ratio decreased further to 0.32. This may mean

the catalyst and pretreatment combined effect promoted more CO_2 production than CO. This was

evident from the FTIR in Figure 4.3 the C-O-C vibrations absorbance peak between 1076 and

1023 cm^{-1} was intense implying there were fewer breaks down of the C-O-C bonds to form CO

thus decreasing the ratio. In the absence of NaOH pretreatment and with the presence of the

HZSM-5 catalysts however the CO/CO_2 ratio increased to 1.8 meaning the catalyst by itself

favored the CO route than $CO_2.$ From the FTIR spectra in Figure 4.3 C-O-C absorbance peak was

drastically reduced in comparison to the presence of NaOH and the intensity of the C=C

aromatic peak at 1600 cm^{-1} was almost close to that of the C=O absorbance at 1694 cm^{-1}

implying the CO came from both C-O-C and C=O cracking and this route promotes the

production of aromatic compounds.

The hydrocarbon gas yields saw an increase in all the catalysts forms. NaOH pretreatment

increased the hydrocarbons from 8.3 to 15.3%, NaOH pretreated xylan pyrolyzed on the

VPISU001 HZSM-5 catalysts increased the gas yield further to 19.9% whilst the untreated xylan

sample pyrolyzed on a VPISU001 HZSM-5 catalysts increased the gas yield further to 27.5%.

The high hydrocarbon gas yields with untreated xylan sample in the presence of HZSM-5 may

be due to the cracking path used. With the release of CO preferable to CO_2 it meaning this path

promoted the formation of more hydrocarbon gases than the others. Besides this since NaOH

pretreatment by itself and in the presence of the HZSM-5 catalyst favored the CO_2 route more,

hence if the cracking is extensive in this direction then it is expected that the hydrocarbon yield

would increase, hence the increases observed. This may explain the low yield of organic liquid

yields with catalysis.

Table 4.3: Composition of Xylan Pyrolysis Gases

SMPLE	CO	CO_2	CO/ CO_2	Hydrocarbons	Unknown
XYLAN-SAND	27.0	52.3	0.52	8.3	12.4
NA-XYLAN-SAND	18.8	42.4	0.44	15.3	23.5
NA-XYLAN-VPISU001	2.3	7.1	0.32	18.8	71.8
XYLAN-VPISU001	7.0	3.9	1.79	27.5	61.6

xylan-sand : untreated xylan pyrolyzed on sand
na-xylan-sand: NaOH pretreated xylan pyrolyzed on sand
na-xylan-VPISU001: NaOH pretreated xylan pyrolyzed on VPISU001 catalysts

xylan-VPISU001: NaOH pretreated xylan pyrolyzed on VPISU001 catalysts

4.4 Conclusion

The catalytic pyrolysis of xylan from birch wood (representing hemicellulose) generally resulted in low organic liquid yields. NaOH pretreatment and the HZSM-5 zeolite catalysts by themselves reduced this yield further significantly with no difference among them significantly. However their combined effect reduced the yield further significantly.

The water yield increased significantly with the combined effect of NaOH pretreatment and the HZSM-5 catalysts. NaOH pretreatment by itself decreased the water yield significantly while HZSM-5 though caused an increase but was not significant

The char yield increased significantly with NaOH pretreatment in the presence and absence of HZSM-5 catalysts. The HZSM-5 catalysts by themselves however decreased the char yield significantly

NaOH pretreatment and the HZSM-5 catalysts independently increased the gas yield significantly, with the HZSM-5 giving the more significant yield. However their combined effect decreased the gas yields but was not significant.

The ^{13}C-nmr and FTIR analysis showed that the HZSM-5 catalyst promoted the formation of aromatics whilst NaOH pretreatment by itself promoted the formation of aliphatic alkanes. Their combined effect however seemed to suggest the formation of carbohydrate sugar groups or groups with alcoholic functionalities.

The gas analysis showed that the main gases evolved were CO, CO_2 and Hydrocarbons. NaOH pretreatment independently and in the presence of the HZSM-5 catalysts seemed to favor more CO_2 formation than CO. Whilst the HZSM-5 catalyst independently favored more CO formation than CO_2. The hydrocarbon gases increased with each catalysis experiment with the HZSM-5 giving the highest yield.

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CHAPTER FIVE

PYROLYSIS OF KRAFT LIGININ AND LIGNIN MODEL COMPOUNDS

ABSTRACT

Low molecular weight kraft lignin, guaiacol, and syringol were pyrolyzed on sand and HZSM-5 catalysts at 450 ^{o}C. The kraft lignin pyrolysis produced low liquid and gas yields and high char yields. The HZSM-5 catalysts increased the water yield and decreased the organic liquid yield. NaOH pretreatment increased the char yield and decreased the liquid products NaOH and the HZSM-5 catalysts together decreased the char and increased the gas yields. The ^{13}C-nmr and FTIR analysis showed that NaOH pretreatment promoted the formation of mainly guaiacol while the HZSM-5 catalyst formed different aromatic components. NaOH pretreatment promoted the formation of more CO_2 than CO whilst HZSM-5 catalysts promoted the formation of more CO than CO_2. Methane formation was enhanced by NaOH pretreatment. Other hydrocarbon gases were however enhanced by the HZSM-5 catalysts. Pyrolysis of the model compounds on the HSZM-5 catalysts showed an increase in pyrolytic water. The HZSM-5 catalysts promoted demethylation in syringol pyrolysis as compared to guaiacol.

5.1 Introduction

Biomass is a renewable and alternative source for the production of low sulphur and nitrogen fuels and chemicals (Amen-Chen, Hooshang et al. 2001). Biomass derived pyrolysis oils are highly oxygenated and unstable and need further upgrading to improve their properties. Rao et al. (1998) and Varhegyi et. al (1997) have indicated the importance of understanding the role the various components of biomass play in pyrolysis.

Wood is made up of cellulose, hemicellulose, lignin, minerals and extractives. Lignin is the next dominant component after the carbohydrates polymers (cellulose and hemicellulose) (Bridgwater 2004). Lignin is a three-dimensional, amorphous polyphenolic compound. Lignin is extracted from wood as a byproduct from black liquor, produced in the pulping of lignocellulosic materials. The chemical and physical properties of lignin vary depending on the starting biomass and the method of isolation used (Abd-Alla, El-Shakhaway et al. 1998; Mohan, Pittman et al. 2006).

Volatile products from lignin pyrolysis are liberated over a wide range of temperature (200-600 ^{o}C) (Nunn, Howard et al. 1985; Jakab , Faix et al. 1993; Britt, Buchmann et al. 1995; Caballero, Font et al. 1995; Sharma and Hajaligol 2003). The pyrolytic behavior and product distribution of lignin vary depending on the pyrolysis conditions, type of lignin and the isolation method (Nunn, Howard et al. 1985; Jakab , Faix et al. 1993; Caballero, Font et al. 1997). Lignin from different wood species were isolated separately by hydrochloric acid, Klason, steam exploded and enzymatic methods to study the effect of the lignin isolation method on their thermal degradation behavior (Gardner, Schultz et al. 1985). Klason lignin was more heat-resistant than the other lignin fractions, exhibiting broad DTA peak. Enzymatic and steam exploded lignin exhibited

broad sharper DTA peaks. Evans (1986) established a relationship between the lignin isolation procedure and the volatile phenolic composition. Monolignols were predominant in native or milled wood lignin, while guaiacol, syringol and lighter phenols were important in more severe lignin isolation methods like kraft.

The other major products from lignin pyrolysis are carbon monoxide, carbon dioxide, water, light hydrocarbons, acetic acid, acetaldehyde, methanol and formaldehyde (Nunn, Howard et al. 1985; Caballero, Font et al. 1997). The aliphatic OH group content was correlated with the yields of formaldehyde and water (Jakab , Faix et al. 1993) and the free OH groups was also shown to promote the scission of COOH groups from acetylation of lignin (Jakab , Faix et al. 1997). A free radical mechanism was proposed for pyrolytic lignin decomposition (Britt, Buchmann et al. 1995).Fenner and Lephardt (1981) studied the pyrolysis of kraft lignin from ambient temperature to 850 ^{o}C. Formic acid, formaldehyde, methanol, carbon dioxide, carbon monoxide and water was identified among the volatile compounds released.

Pyrolysis of lignin model compound is important to understand the thermal stability of different bonds in lignin, the origin of pyrolysis products, and the stability of the intermediate compounds formed (Amen-Chen, Hooshang et al. 2001). Klien (1981) studied the pyrolytic behavior of monomeric compounds guaiacol and syringol between 300 and 500 ^{o}C. Catechol, methane, phenol and carbon monoxide were the main products. Demethylation resulted in the production of catechol and methane while demethoxylation resulted in the production of phenol and carbon monoxide.

The effect of catalysis has been studied on the decomposition of lignin by some researchers. Enkvist (1975) found that catechol and its alkyl derivatives were produced on heating kraft black liquor at 310 ^{o}C with NaOH under N_2 at atmospheric pressure. Domburg (1976) also studied the effect of basic additives; NaOH, K_2CO_3 and Na_2CO_3 on lignin thermal reactivity, phenolic composition and pyrolytic oil yields. NaOH addition to wood increased the thermal reactivity, with vapors evolving earlier and at higher yields at lower temperatures but at temperatures higher than 470 ^{o}C charring reactions were predominant in the alkaline samples. Yields of some specific phenols such as guaiacol, syringol and their vinyl derivatives were considerably increased with NaOH addition but the total phenolic yield was not improved. Thring et al (2000) studied zeolite upgrading of lignin with HZSM-5 at 500-650 ^{o}C and 2.5-7.5 h^{-1} WHSV. Toluene, benzene and xylene were the major liquid components. The highest liquid yield was 43%, and the coke char yields were 15 -50 %. The gas yields increased with temperature and the char and liquid yields decreased.

In this chapter the effect of NaOH pretreatment and zeolite catalysts (HZSM-5) would be assessed on lignin pyrolysis products distribution and properties.

5.2 Materials and Methods

5.2.1 Materials

Low molecular weight kraft lignin (Curan 100) was purchased from Borregaard Ligno-Tech, (Backhammer, Sweden). The catalysts used were the VPISU001 HZSM-5 catalysts. NaOH and white silica sand were purchased from Fischer Scientific (Fischer Scientific, Pittsburg PA). The model compounds guaiacol and syringol were purchased from Sigma-Aldrich (Sigma-Aldrich, Co. St. Louis, MO).

5.2.2 Low Molecular Weight Kraft Lignin Pretreatment and Characterization

The NaOH pretreatment of the Curan 100, moisture content determination and TGA/DTG analysis of feed was performed in a similar manner as described in the cellulose characterization section chapter three.

5.2.3 Catalyst Preparation and Characterization

The catalysts were prepared as described in the catalysts characterization section chapter three

5.2.4 Pyrolysis of Low Molecular Weight Kraft Lignin

The catalytic and non catalytic experiments on Curan 100 lignin were performed in a similar manner as described in chapter three.

5.2.5 Pyrolysis of Syringol

The same pyrolysis unit and process parameters was used except that in both catalytic and non catalytic experiment 25 g of the syringol was mixed with 25g of fine ground sand to facilitate feeding of the syringol (paste like in nature) and prevent clogging of the inlet into the reactor. In the catalytic experiment the sample was fed into the reactor with a nitrogen flow of 6 L/min at 100 g/h (to achieve a WHSV of 1) and 100 g of the VPISU001 HZSM-5 catalyst was used and

fluidized with 8 L/min of nitrogen flow. In the non catalytic experiment 12 L/min of nitrogen flow was used to fluidize the sand bed.

5.2.6 Pyrolysis of Guaiacol

Guaiacol was liquid at room temperature and was fed using a KDS-100 infusion syringe pump (KD Scientific Inc. Holliston, MA). In the catalytic experiment 25 g of the sample was fed at 100g/h (to achieve a WHSV of 1) and entrained into the reactor using 4 L/min of nitrogen flow. 100 g of the VPISU001 HZSM-5 catalyst was used and fluidized with 8 L/min of nitrogen flow. In the non catalytic experiment 25 g of the sample was fed at 100 g/h and entrained into the reactor with 4 L/min of nitrogen flow and the 100 g sand bed fluidized with 12 L/min of nitrogen flow.

5.2.7 Pyrolysis Products Characterization

The pyrolysis product yields, the moisture contents of the bio oils, FTIR analysis and GC analysis were all performed in a similar manner as described in chapter three. The ^{13}C-nmr analysis was performed using 200 mg of fresh ESP oil dissolved in 0.7 ml dimethyl sulfoxide (d$_6$-DMSO) in a 5 mm sample probe. The ^{13}C- NMR spectra were recorded on the Varian Inova 400 MHz NMR Robot spectrometer. The observing frequency for the ^{13}C nucleus was 100.58MHz. The pulse width was 9.6 μs, the acquisition time was 1.36s, and the recycle delay was 1s. The spectra were obtained with 14000 scans and a sweep width of 24140s. Data analysis was performed with NutsPro-NMR Utility Transform Software – Professional.

5.2.8 Gas Chromatography Mass Spectroscopy (GC-MS) Analysis

The GC-MS analyses of the syringol and guaiacol pyrolysis products were performed by the

Virginia Tech Chemistry Mass Spectrometry laboratory Lab.

5.3 Results and Discussion

5.3.1 Thermogravimetric Analysis of Low Molecular Weight Kraft Lignin

The thermograms of the treated and untreated Curan 100 lignin showed three maxima weight loss regimes (fig 5.1a and 5.1b). The first maximum weight loss occurred between 60 and 70 ^{o}C where there was about 10% loss in weight. For the untreated Curan 100 lignin, the first maximum occurred at 60 ^{o}C whereas the maximum occurred at 70 ^{o}C for the treated Curan 100. The NaOH treatment appeared to have increased the decomposition temperature of this component of the lignin.

The second maximum weight loss was very broad and occurred between 275 and 370 ^{o}C. For both treated and untreated Curan 100, the temperatures for maximum weight loss were similar. However, there was more weight loss from the untreated Curan 100 than the treated sample.

The third maximum weight loss was also very broad and occurred between 600 and 700 ^{o}C. The NaOH treatment of the Curan 100 also appeared to have increased the temperature of maximum weight loss.

The char yield from the untreated Curan 100 was 43% compared to 50% for the NaOH treated sample. However, it is important to note that the treated char residue also contain some NaOH. Thus, the overall effect of the NaOH treatment of the Curan 100 lignin was an increase in the maximum weight loss temperature for some fractions of the lignin and a slight increase in the char residue.
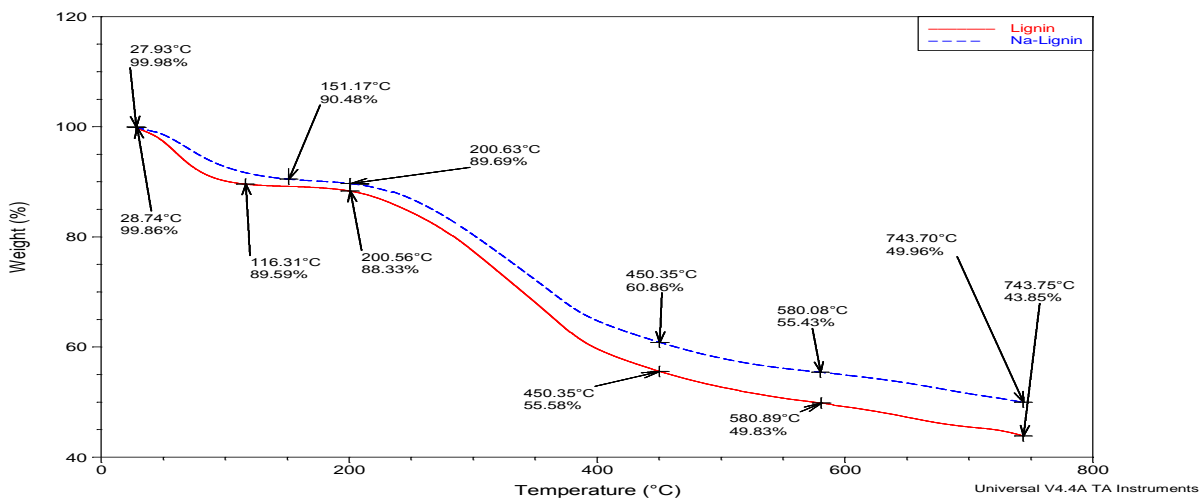
Figure 5.1a: Thermogram of NaOH treated and untreated low molecular weight kraft lignin (Curan 100).
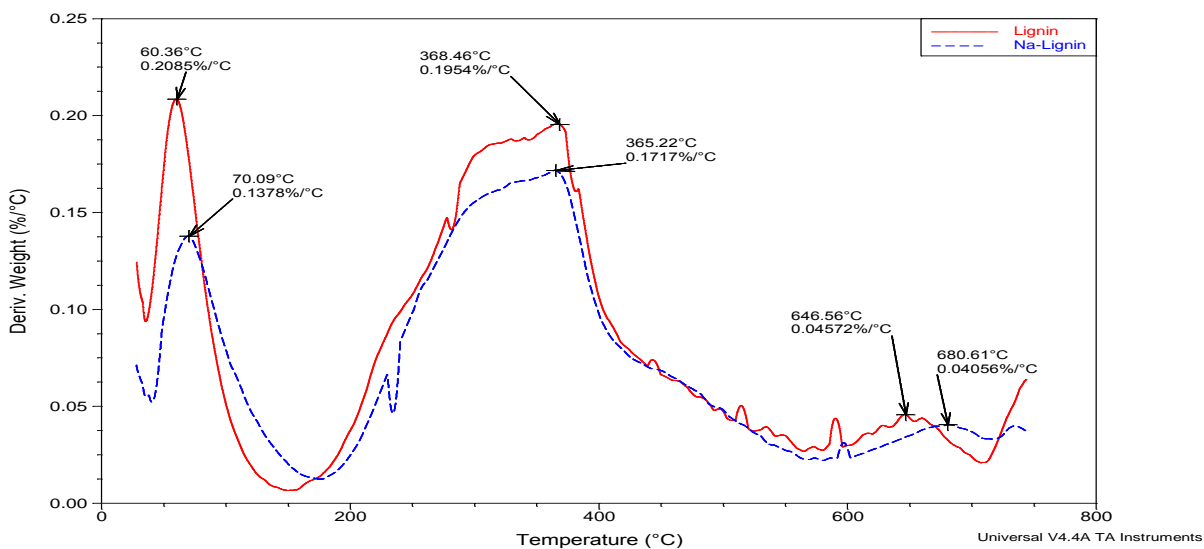

Figure 5.1b: Differential thermogram of NaOH treated and untreated low molecular weight kraft lignin (Curan 100)

5.3.2 Pyrolysis of Low Molecular Weight Kraft Lignin (Curan 100)

The yields of pyrolysis products of Curan 100 lignin pyrolyzed under several different conditions and pretreatment are shown Table 5.1. The pyrolysis of Curan 100 lignin on sand produced a large fraction of water and a small amount of organic product. The char yield was very high and the gas yield was moderate.

The NaOH pretreatment of the Curan 100 before pyrolysis on the sand influenced the products distribution. The yield of organic fraction was similar to the untreated sample but the water yield decreased by 35% compared to the untreated sample. Thus there was an overall decrease in the total liquid yield because of the NaOH treatment of the Curan 100. There were only slight increases in the gas (11.7%) and char (9.4%) yields compared to the untreated Curan 100.

The pyrolysis of the untreated Curan 100 on VPISU001 HZSM-5 catalyst resulted in a 58.9% decrease in the organic fraction yield compared to similar pyrolysis on sand; however, the total liquid yield was similar to that obtained for the sand. In the HZSM-5 pyrolysis, a major pyrolysis product was water which increased by 12% relative to the sand pyrolysis. The yield of both char and gases were similar to those obtained for the pyrolysis on the sand. This clearly showed the organic fraction was almost selectively converted into water. This result is in contrast to the cellulose and xylan reactions where the organic fractions were converted into all three products (water, char and gas).

The pretreatment of the Curan 100 with the NaOH before pyrolysis on the HZSM-5 appeared to have a synergistic effect. Although there was a decrease in the organic fraction yield this was only 30 % compared to the 58.9 % reduction when the untreated material was pyrolyzed on the

HZSM-5. The water fraction increased as expected, but a more interesting result was the increase in the gas yield and the decrease in the char yield. The char yield decreased by 17.5% compared to the pyrolysis on the sand without treatment. It is interesting to note that NaOH treatment and pyrolysis on the sand increased the char yield whiles pyrolysis on the HZSM-5 decreased the char yield. Another important observation was the large increase in the gas yield (62.6%) compared to the untreated Curan 100 pyrolyzed on the sand. Thus the combination of NaOH treatment and HZSM-5 appeared to have some positive effect on the pyrolysis of the lignin in that it reduces char and water formation and promotes gas formation. It appears the gas was produced from both the cracking of the organic and char fractions.

Table 5.1 Summary of Results Showing the Effect of HZSM-5 Catalysts and NaOH Treatment

Sample	Pyrolysis Yields wt %				
	Organics	Water	Total Liquid	Char yield	^{q}Gas yield
KL-sand	5.6±1.1	21.8±0.7	27.2±1.5	51.0±1.9	22.2±1.0
Na-KL-Sand	5.4±0.6	14.0±0.1	19.4±0.7	55.8±0.2	24.8±0.9
KL-VPISU001	2.3±0.6	24.5±0.1	26.8±0.6	50.5±0.2	22.7±0.8
Na-KL-VPISU001	3.9±0.1	17.9±1.3	21.8±1.3	42.1±0.7	36.1±0.7

q Calculated by difference

KL-sand: untreated kraft lignin pyrolyzed on sand
na-KL-sand: NaOH pretreated kraft lignin pyrolyzed on Sud-Chemie catalyst
KL-VPISU001: untreated kraft lignin pyrolyzed on VPISU001 HZSM-5 catalysts
na-KL-VPISU001: NaOH pretreated kraft lignin pyrolyzed on VPISU001 HZSM-5 catalysts
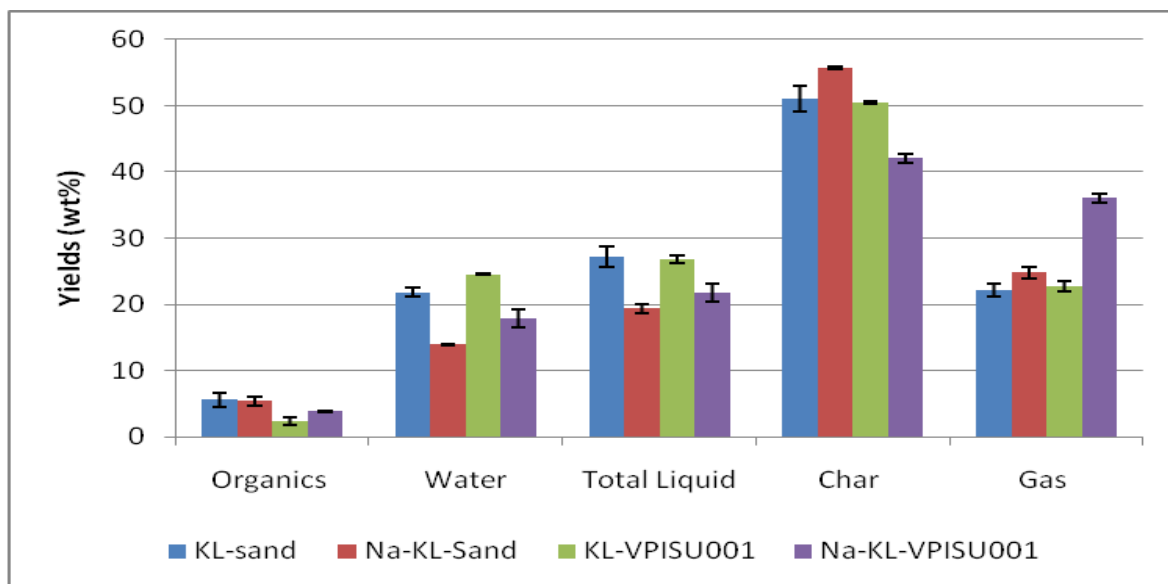
Figure 5.2: Product distribution of treated and untreated low molecular kraft lignin pyrolyzed on sand and HZSM-5 catalysts

Table 5.2 Test of Significant Effect of NaOH Pretreatment and HZSM-5 Catalysts on Products Distributions

Sample	Pyrolysis Yields wt %				
	Organics	Water	Total Liquid	Char yield	[q]Gas yield
KL-sand	5.6[A]	21.8[B]	27.2[A]	51.0[B]	22.2[C]
Na-KL-Sand	5.4[A]	14.0[D]	19.4[B]	55.8[A]	24.8[B]
KL-VPISU001	2.3[B]	24.5[A]	26.8[A]	50.5[B]	22.7[BC]
Na-KL-VPISU001	3.9[AB]	17.9[C]	21.8[B]	42.1[C]	36.1[A]

Levels not connected by the same letter are significantly different at 0.5 alpha level(Ott and Longnecker. 2001)

5.3.3 Characterization Curan 100 Pyrolysis Oils.

The oils obtained from the pyrolysis of Curan 100 were brownish and had a strong pungent phenolic smell. Because the yields were very low, the pH of the oils were not measured and neither were other physical properties, such as viscosity, and density measured. However, the oils were characterized by both FTIR and ^{13}C-nmr spectroscopy. FTIR spectra of all the four samples produced under different conditions are shown in Fig 5.1. All the four oil samples showed almost identical spectra with exception of a small difference in the 2800-2900 cm^{-1} region of the untreated Curan 100 pyrolyzed on HZSM-5. The CH and CH$_2$ peaks typical of aliphatic side chains were absent from the untreated Curan 100 HZSM-5 produced pyrolysis oil. All four oil samples show spectra typical of phenolic compounds. The O-H in plane bending vibrations between 1420 and 1330 cm^{-1} and C-O stretching vibration between 1260 and 1000cm^{-1} are complementary peaks showing the presence of alcohols and phenols.

The C-H stretching band between 3100 and 3000 cm^{-1} , the in plane bands between 1300-1000 cm^{-1}, the C=C skeletal vibrations in the 1600-1585 cm^{-1} and 1500-1400 cm^{-1} regions and the C-H out of plane bending vibration between 900-675 cm^{-1} all indicate the presence of aromatic compounds (Gunzler and Bock 1975; Silverstein and Webster 1997). There was not much difference in the absorbance among the various oils in these regions. The C-H out of plane bending vibration between 900-675 cm^{-1} could help explain the type of phenolic derivatives and their substitution patterns of the aromatic ring in the mixture present (Guillen, Manzanos et al. 1995). Aromatic rings with five or four neighboring hydrogen atoms show the most intense bands at 770-730 cm^{-1}. Phenol (746 cm^{-1}), guaiacol (748 cm^{-1}) and 2-methylphenol (747 cm^{-1}) belong to this group (Guillen, Manzanos et al. 1995). The NaOH pretreated Curan 100 pyrolyzed on sand and the HZSM-5 catalyst showed intense peaks at 747 cm^{-1} and 744 cm^{-1} respectively

which suggests the presence of guaiacol as the major phenolic compound. The untreated Curan

pyrolyzed on sand and the HZSM-5 showed intense peaks at 745 and 746 cm^{-1} respectively

which suggests the presence of phenols or phenol with a single substituted group. These data are

in agreement with results from pyrolysis of pine kraft lignin between 300-480°C which produced

guaiacol and 2-methoxy-4-alky-substituted phenol as major products (Fenner and Lephardt

1981). Domburg (1976) showed that increasing the NaOH concentration in lignin favored the

production of guaiacol, syringol and their vinyl derivatives. Aromatic compounds with three

adjacent hydrogen atoms such as syringol, 2,6-dimethylphenol show one intense absorption band

between 810 and 750 cm^{-1} (Guillen, Manzanos et al. 1995). Figure 5.3 did not show any strong

absorbance in this range for the all the samples. This suggests very low concentrations of these

compounds in the pyrolysis oils. The aromatic compounds with two adjacent or isolated

hydrogen atoms show bands from 900-800 cm^{-1} . Aromatic compounds such as 2-methoxy-4-

ethylphenol (808-816 cm-l), 2-methoxy-4-(2-propenyl) phenol (817-802 cm^{-1}), 2,6-dimethoxy-4-

(2-propenyl) phenol (827 -802 cm^{-1}), and 2,6-dimethoxy-4-methylphenol(818-794 cm^{-1}) absorb in

this range(Guillen, Manzanos et al. 1995). All the samples showed small absorbance peaks in

this region, suggesting the low presence of these types of aromatics.

The ^{13}C-nmr spectra of the four pyrolysis oils are shown in Fig 5.2. These spectra reveal some

interesting information about the oils. The spectrum of the oil of untreated Curan 100 pyrolyzed

on sand showed the presence of carbohydrate degradation products in the oil. The peaks at 72 to

102 ppm are typical resonances of levoglucosan indicating that the lignin sample was

contaminated with cellulose. The phenolic compounds produced from the untreated Curan 100

using the sand contained minimal amounts of methoxylated phenols as shown by the low intensity of the methoxyl carbon signal at 56 ppm.

The treatment of the Curan 100 with NaOH and pyrolysing on the sand produced both methoxylated and simple phenol (115,121,129 and 155 ppm) and thus increasing the peak intensities due to phenolic compounds in the 110-160 ppm region of the spectrum. The methoxyl signal at 56 ppm was very intense which were complemented by other phenolic signals in the 110 to 160 ppm region of the spectrum. It appeared major phenolic compound was guaiacol (see spectrum of pure guaiacol in Fig 5.3.). It is interesting to note the absence of the levoglucosan peaks that were observed in the untreated Curan 100 sample. As shown in the cellulose pyrolysis oil in Chapter 3, the treatment of cellulose with NaOH suppresses the formation of levoglucosan and promotes the formation of aromatic compounds and thus in this case also, the levoglucosan formation pathway of the cellulose was probably suppressed. The two spectra also contain low intensity peaks due to aliphatic side chains (0-40 ppm).

The ^{13}C-nmr spectrum of the pyrolysis oils from untreated Curan 100 pyrolyzed on HZSM-5 did not contain any of the levoglucosan peaks and had the least number of peaks occurring in the aromatic region 100-160 ppm. The intensity of the methoxyl carbon peak had increased relative to the one from the sand pyrolysis. This suggests that this oil was dominant in methoxylated aromatic compounds. This oil also had some aliphatic hydrocarbon side chains as shown in 0-40 ppm region of the spectrum.

The pyrolysis oil spectrum obtained from the NaOH treatment of the Curan 100 and pyrolyzing on the HZSM-5 was the most interesting (Fig 5.2). The spectrum appeared to show synergistic effect of the NaOH and the HZSM-5. The spectrum appeared to be the sum of the spectra of NaOH treated Curan 100 pyrolyzed on sand plus untreated Curan 100 pyrolyzed on HZSM-5 (Fig 5.2). It appeared that the HZSM-5 and the NaOH were acting independently on the lignin pyrolysis products. The intensity of the phenolic carbon, the ring carbons and the methoxyl carbon had all increased. The phenol also appeared to be a guaiacol and substituted guaiacols as indicated by the increase in the intensity of the aliphatic hydrocarbon side chain peaks.
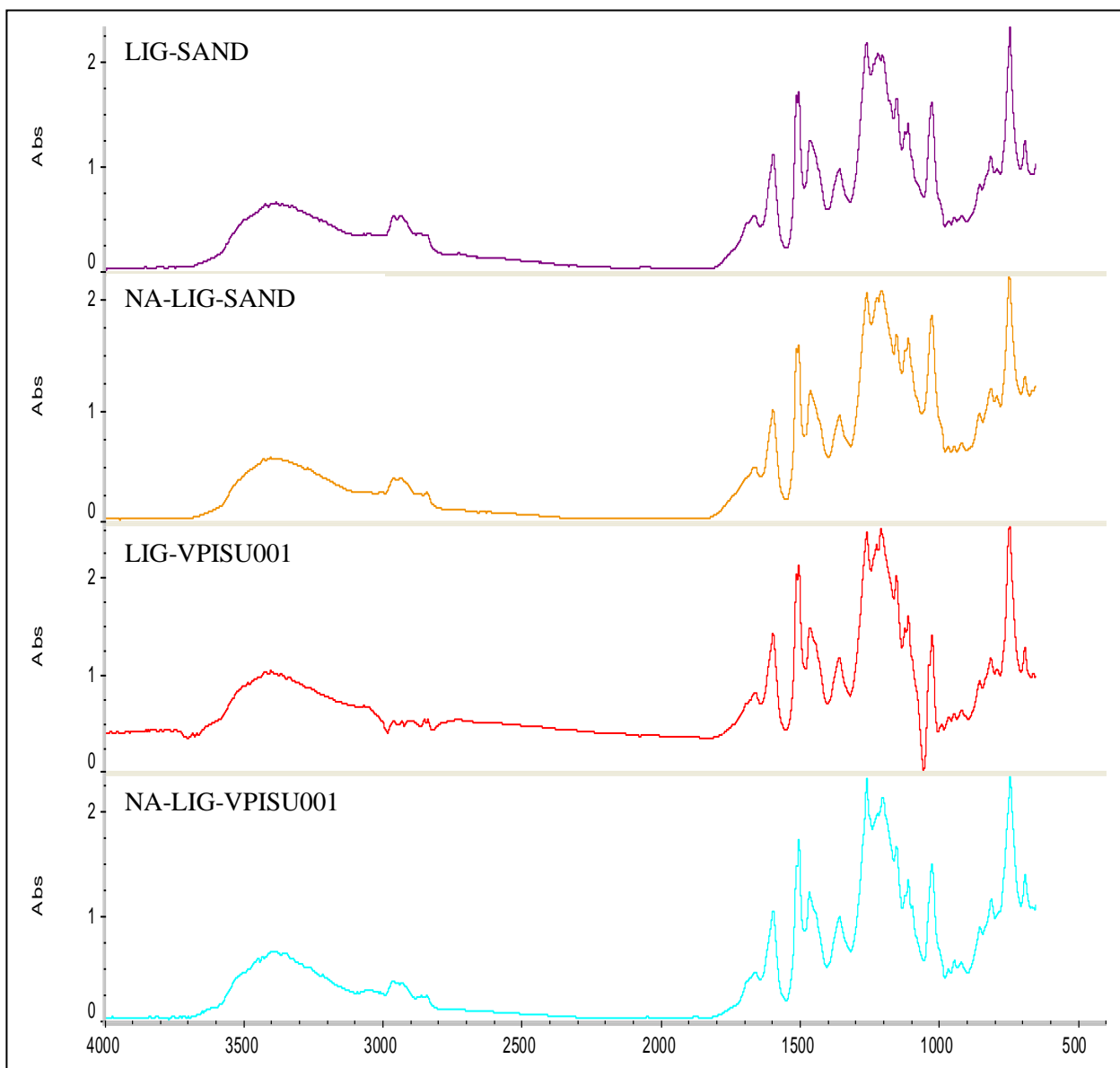
Figure 5.3: FTIR spectra showing the effect of NaOH pretreatment and HZSM-5 catalysts
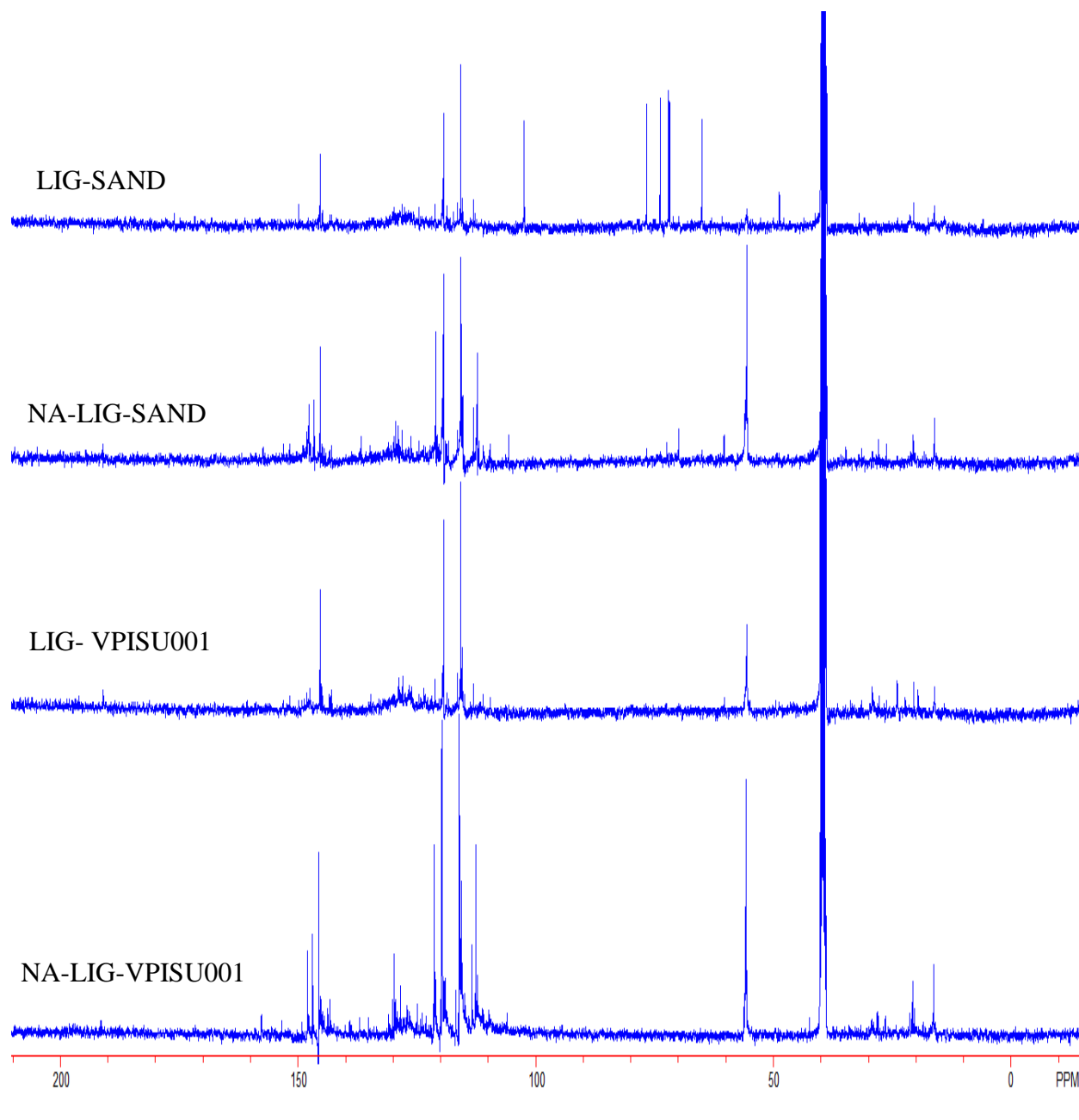
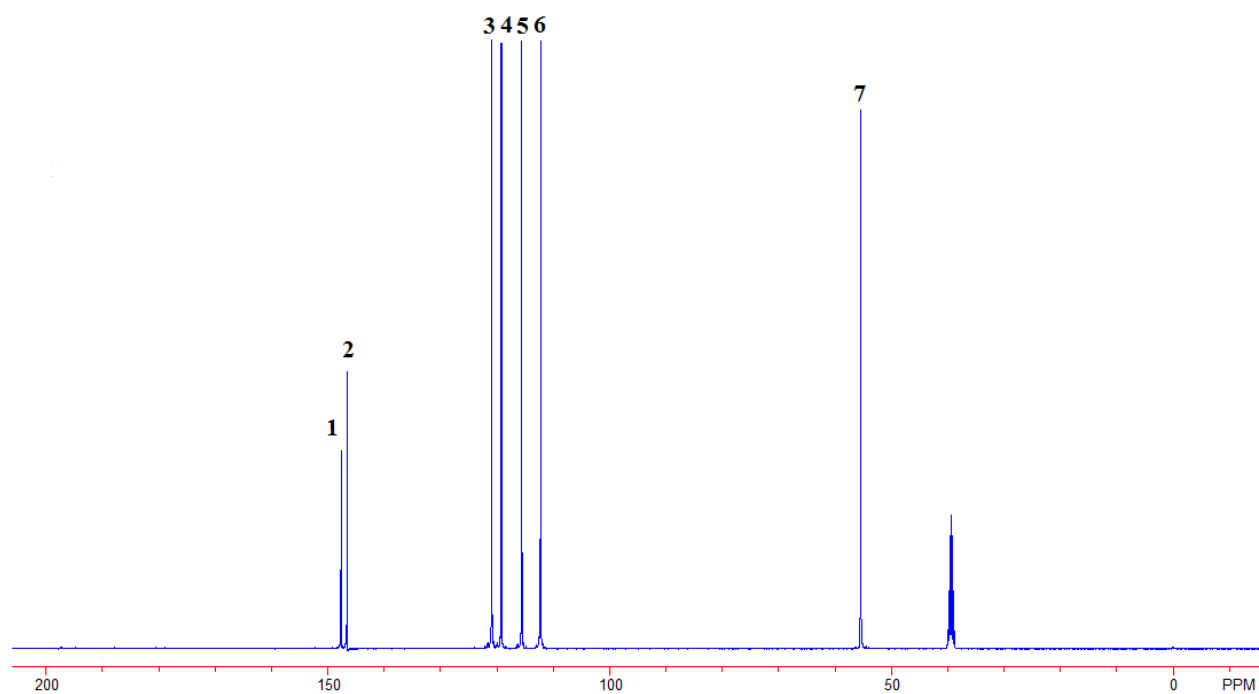Figure 5.4: ^{13}C-nmr spectra showing the effect of NaOH pretreatment and HZSM-5 catalysts

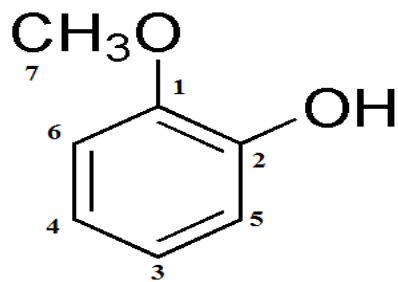Figure 5.5: ^{13}C-nmr spectrum of pure guaiacol in d$_6$-DMSO solvent

Figure 5.6: Structure of guaiacol relating the carbon positions in the ^{13}C-nmr spectrum

5.3.4 Pyrolysis Gases

The pyrolysis gases were analyzed using the SRI multiple gas analyzer #2. The major pyrolysis gas components in Table 5.3 show a wide compositional variation depending on the pyrolysis conditions. The untreated Curan 100 pyrolyzed on sand had a relatively high level of CO, other hydrocarbons and a relatively large unknown compound. The amount of CO_2 was relatively low and thus the CO/CO_2 ratio was relatively high. However, NaOH treatment of the Curan 100 before pyrolysis on the sand changed the gas composition drastically. In this case, the CO_2 became the dominant gas constituting 47 % of the total gas and the unknown gas content appeared to have been considerably reduced and the other hydrocarbons were also reduced. It appeared that some of the unknowns were either converted into CO_2 or the pathway producing these compounds were suppressed by the NaOH treatment. It is also interesting to note that the CH_4 content of the gases have also doubled and CO production was considerably suppressed. Thus, it appears the production of CO_2 is strongly associated with CH_4 production and the suppression of the production of the other hydrocarbons.

The composition of the gases produced from pyrolysis of the untreated Curan 100 on the HZSM-5 appeared to be almost identical to those produced from the pyrolysis of the similar sample on the sand (Table 5.3). However, the composition of the gases after NaOH treatment of the Curan 100 and pyrolysing on the HZSM-5 appeared to follow a similar trend as the NaOH treated sample and pyrolyzed on the sand except in the case of the CH_4 and other hydrocarbon fractions. The CH_4 produced in this case was less than 50% that produced on the sand and the other hydrocarbons were twice as much as those produced on the sand. It appeared that HZSM-5 and NaOH were acting independently on different components of the lignin. The suppression of the CO production and increase CO_2 production appeared to follow the same trend as the NaOH

treated Curan 100 pyrolyzed on sand, while the production CH_4 and other hydrocarbons appeared to follow the trend of the HZSM-5 pyrolytic pathway. The gas compositional trend of these samples appear to follow what was observed in the ^{13}C-nmr of the pyrolysis oils and the distribution of the products as shown in Table 5.1.

In the case of NaOH treated sample, the rejection of oxygen from the lignin pyrolysis products appeared to be through the rejection of CO_2 and less through water. However, in the case of the HZSM-5, the predominant pathway for oxygen rejection was through formation of water and CO. Thus, it appears these two pathways are parallel and compete when the Curan was treated with NaOH and pyrolyzed on the HZSM-5. Alternatively, it could be inferred that since HZSM-5 is a Bronsted-Lewis acid, the NaOH poisons one acidic site but the other was left intact and thus the catalytic reaction was only taking place on one site. This is very interesting because it appeared that the NaOH did not poison all the active catalyst sites. This method provides an insight of the catalytic activity of this catalyst.

Table 5.3: The Effect of NaOH and HZSM-5 Catalysts on Gas Composition from Lignin Pyrolysis

SMPLE	CO	CO_2	CH_4	CO/ CO_2	Other Hydrocarbons	Unknown
LIGNIN-SAND	25.7	9.4	6.1	2.7	26.6	32.2
NA-LIGNIN-SAND	12.6	47.4	12.8	0.27	13.2	14.0
LIGNIN-VPISU001	24.2	7.8	5.2	3.1	27.8	35.0
NA-LIGNIN-VPISU001	10.9	41.0	5.8	0.27	30.9	11.9

5.3.5 Pyrolysis of Model Compounds

Guaiacol and Syringol are dominant intermediate compounds formed during lignin pyrolysis especially lignin isolated by kraft and organosolv lignin methods (Evans, Milne et al. 1986; Amen-Chen, Hooshang et al. 2001). The methoxy groups (Figure 5.4 and 5.5) present in these compounds contribute to the total oxygen content of lignin derived bio oils. Thus in this study it was desired to test the deoxygenating property of the VPISU001 HZSM-5 catalyst through its ability to break down these methoxy groups. The effects of the catalyst on these groups were analyzed from their product distribution, ^{13}C-nmr, GC and GC-MS analysis, which would be discussed in these sections.
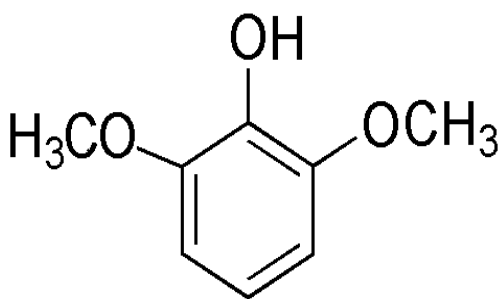

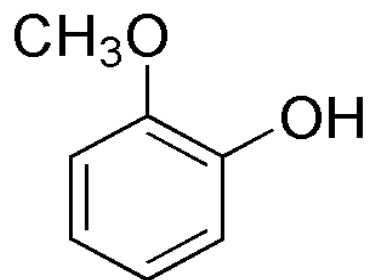Figure 5.7: Structure of Syringol

Figure 5.8: Structure of Guaiacol

5.3.5.1 Pyrolysis of Guaiacol

The pyrolysis of guaiacol produced only liquid and gas product but no char (Table 5.4). The yield of gas and liquid products was the same 67.1 and 32.9 wt % respectively. However there was a difference in the organic liquid and water yields. The organic liquid yield reduced from 65.7 % to 63.7 % in the presence of the catalysts. While the water yield increased from 1.4 % to 3.4 % representing an increase of 143 %. These results suggest that the catalyst was able to dehydrate the guaiacol to produce water.

Table 5.4 Product Distribution of Catalytic and Non Catalytic Pyrolysis of Guaiacol

Sample	Oil yield	Organics	Water	Gas
	wt %	wt %	wt %	wt %
Guaiacol-sand	67.1±1.2	65.7±0.6	1.4±0.2	32.9±1.3
Guaiacol-VPISU001	67.1±0.6	63.7±0.1	3.4±0.7	32.9±0.9

5.3.5.1.1 Characterization of Guaiacol Pyrolysis Liquid

The pyrolysis oil from guaiacol pyrolysis on sand and the VPISU001 HZSM-5 catalysts were brownish and had strong phenolic smell. Both ESP and condenser oils were similar in color and smell. The ESP oils were used for characterization and ^{13}C-nmr analysis was employed to study the effect of the HZSM-5 on the liquid oils. The ^{13}C-nmr spectra of pure guaiacol, esp oils from guaiacol pyrolyzed on sand and HZSM-5 catalysts are shown in Figure 5.6. The various carbons present in pure guaiacol (fig 5.5) show up in its spectra as follows: C_1 resonates at 148ppm, C2 resonates at 147 ppm, C_3 at 121 ppm, C_4 at 120 ppm, C_5 at 116 ppm, C_6 at 112 ppm and the methoxyl carbon C_7 at 56 ppm. The ^{13}C-nmr spectra of the oil from sand showed that the guaiacol peaks were still dominant. This suggests that most of the original guaiacol was captured in the final product and the pyrolysis conditions did not promote the decomposition of guaiacol. In contrast Experiments by Klein (1981) on guaiacol pyrolysis at 350 ^{o}C showed that phenols and catechols were the main decomposition products. The peaks belonging to phenol 155 ppm 130 ppm 121 ppm and 115 ppm (NAIST Spectral Database) were very low in intensity. Klein (1981) proposed that demethoxylation of guaiacol resulted in mainly phenol production and demethylation results in catechol production. Thus it appeared pyrolysis of guaiacol on sand resulted in minimal demethoxylation to produce phenols. The presence of methyl (-CH$_3$) aliphatic groups from 15-25 ppm suggests the presence of methylated aromatic components. The peak at 192 ppm in the ketone and aldehyde region (180-215 ppm) indicates the presence of aromatic groups with a ketone or aldehyde substituent.

Pyrolysis of Guaiacol on VPISU001 HZSM-5 showed similar characteristics as sand. This indicates that there selectivity of the catalysts for this reactant was low or the pyrolysis condition was not favorable for catalytic activity.
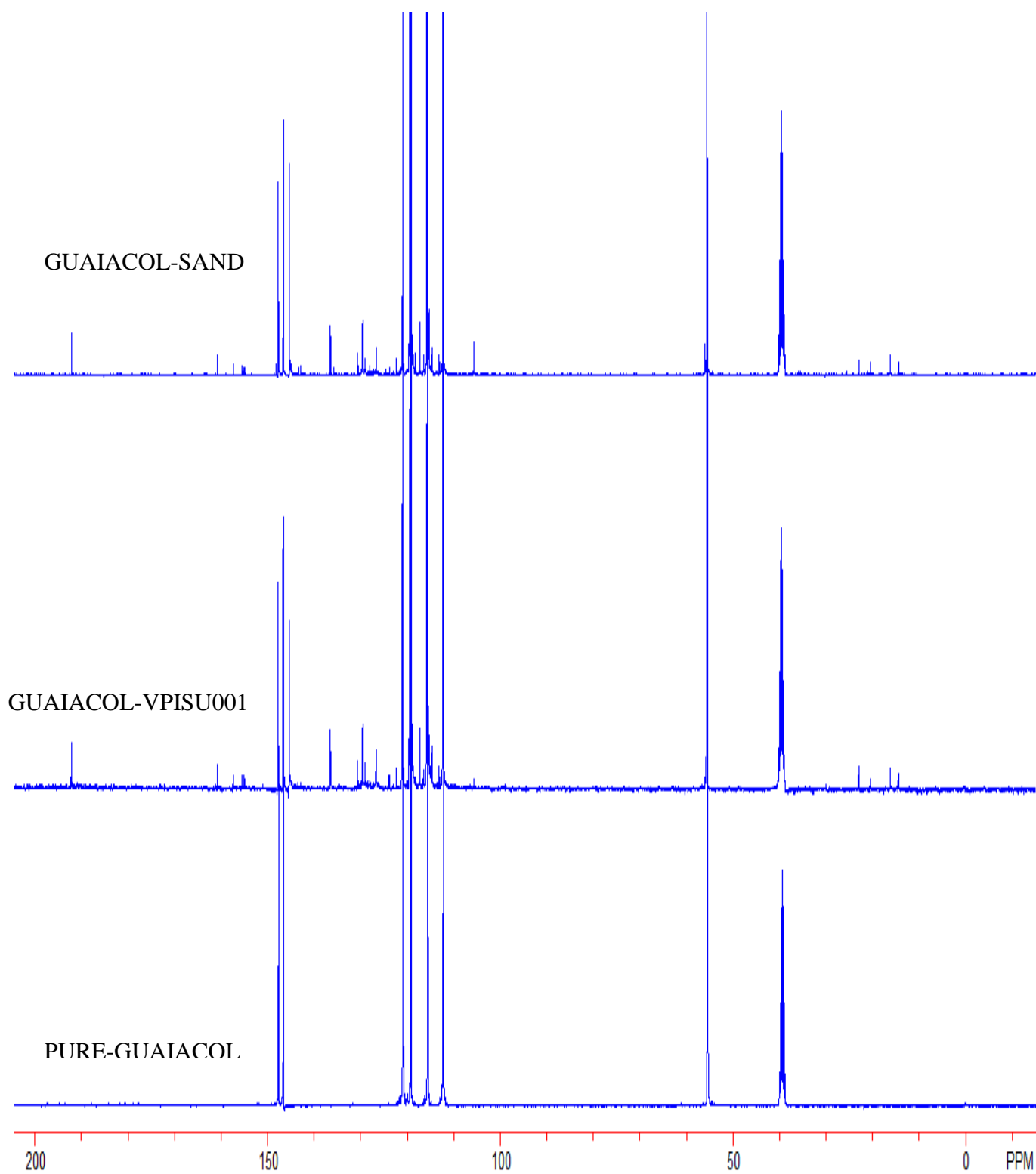
130

Figure 5.9: ^{13}C-nmr Spectra showing the effect of HZSM-5 catalysts on guaiacol pyrolysis

5.3.5.1.2Gas Composition Analysis

Table 5.1 shows the % area composition of gas obtained from catalytic and non catalytic lignin pyrolysis of guaiacol. Guaiacol pyrolysis on sand produced more CO and methane than in the presence of the HZSM-5 catalyst (table 5.5). Pyrolysis on sand yielded 31.1 % CO this reduced to 29.7 % in the presence of the catalysts. CO_2 yields were generally low 13.2 % in the presence of the catalysts and 5.7 % when pyrolyzed on sand. This gave a CO/CO_2 ratio of 5.5 and 2.3 when the pyrolysis took place on sand and the VPISU001 HZSM-5 catalyst respectively. The main gas products form guaiacol pyrolysis is methane and carbon monoxide (Klein 1981). Methane yield decreased from 20.4 % to 12.3 % when the VPISU001 HZSM-5 catalyst was used. Carbon monoxide is produced by demethoxylation of guaiacol while demethylation of guaiacol produces methane (Klein 1981). The production of more CO and methane on sand than in the presence of the catalyst suggests that the VPISU001 HZSM-5 catalyst does not promote the demethoxylation and demethylation of guaiacol.

The yield of the other hydrocarbon gases however was higher in the presence of the VPISU001 HZSM-5 catalysts than in the presence of sand. The amount of hydrocarbon produced increased from 4 % in the presence of sand to 10.9 % in the presence of the catalysts. This increase may be due to the catalytic activity of the HZSM-5 catalyst.

Table 5.5 Gas Composition of Catalytic and Non Catalytic Pyrolysis of Guaiacol

SMPLE	CO	CO_2	CH_4	CO/CO_2	Other Hydrocarbons	Unknown
GUAIACOL-SAND	31.1	5.7	20.4	5.5	4	38.8
GUAIACOL-VPISU001	29.7	13.2	12.3	2.3	10.9	33.9

5.3.5.2 Pyrolysis of syringol

The pyrolysis of the syringol produced liquid and gas product but no char (table 5.6). The yield of total liquid products was 66. 9 % when syringol was pyrolyzed on sand but increased to 68.4 % in the presence of the VPISU001 HZSM-5 catalysts. The increase in the total liquid yield was attributed to the increased water yield from 2.0 % to 9.9 % and a decrease in the organic liquid yield from 64.9 % to 58.5 %.These results suggests that the catalyst was dehydrating the syringol to produce water and gas. The gas yield decreased from 33.1 % to 31.6 %

Table 5.6 Product Distribution of Catalytic and Non Catalytic Pyrolysis of Syringol

Sample	Oil yield	Organics	Water	Gas
Syringol-sand	66.9±0.2	64.9±1.1	2.0±0.5	33.1±1.2
Syringol-VPISU001	68.4±0.7	58.5±0.1	9.9±0.2	31.6±0.7

5.3.5.2.1 Characterization of Syringol Pyrolysis Oil

The pyrolysis oil from syringol pyrolysis on sand and the VPISU001 HZSM-5 catalyst were also brownish and had strong phenolic smell. Both ESP and condenser oils were similar in color, smell. The ESP oils were characterized by ^{13}C-nmr and GC-MS. From Figure 5.7 the peak at 149 ppm represents the point of attachment of the two methoxy (-H$_3$CO) groups to the aromatic ring on the pure syringol (Figure 5.4). The point of attachment of the OH group to the aromatic group is at 136 ppm the peaks at 119 ppm and two overlapping peaks at 106 ppm represent the three remaining C-H carbons in the aromatic ring (NAIST Spectral Database). The methoxy (-H$_3$CO) groups appear at 56 ppm.

Similar to the guaiacol pyrolysis the peaks representing syringol remained dominant after pyrolysis on both sand and the VPISU001 HZSM-5 catalyst. This suggests that the pyrolysis conditions did not favor complete conversion of syringol. The development of new peaks in the both catalytic and non catalytic pyrolysis was similar in the aromatic and acyclic hydrocarbon regions. The peaks derived from the catalytic pyrolysis were more prominent than in the non catalytic process. The peaks in the 15-25 ppm acyclic region indicates the presence of alky substituent on the aromatic groups produced (Silverstein and Webster 1997). The peak produced in the 100-120 ppm region in the aromatic range indicates the presence of aromatic groups with alkyl or hydrogen substituent which show up in the acyclic hydrocarbon region. The region between 120 and 150 ppm region indicates the presence of aromatic groups with polar substituent. Since these groups were more intense in the oil obtained from the catalytic pyrolysis, the HZSM-5 catalysts enhanced the production of these groups. The peaks belonging to simple phenol 155 ppm 130 ppm 121 ppm and 115 ppm (NAIST Spectral Database)was present in both

catalytic and non catalytic oils but in low intensity. The catalytic oil appeared to be richer in the phenolic groups relative to sand.

Besides these the catalytic pyrolysis resulted in the production of aldehyde substituent on the aromatic group which appeared in the 190-200 ppm range as determined by the GC-MS analysis.

GC-MS analysis was performed on the VPISU001 HZSM-5 pyrolytic oil as it showed more promise of catalytic activity to identify the specific compounds produced. The major product was syringol 61.3 % as suggested by the C-13 spectra (Table 5.7). This confirms the assertion that the pyrolytic conditions (temperature, residence time and catalyst condition) did not facilitate the conversion of majority of syringol components.

The main products of syringol decomposition was 2-methoxyresorcinol (9.4 %), 2-ethyl-phenol (4.2 %), 2-methyl-phenol (4.2 %), 2-hydroxy-3-methoxy-benzyldehyde (2.7 %) 4-ethylcatechol (2.1 %), catechol (1.6 %), 1,2-benzenediol (1.4 %) 2-methoxy-6-methylphenol and mequinol (1.3 %). The phenol amount produced as indicated by the ^{13}C-nmr was low (0.75 %). Thus the main aromatic compounds produced were methoxylated phenols and alkylated phenols. Pyrolysis of syringol by Masuku (1991) produced mainly 2,3-dihydroxyanisole, 2,3-dimethoxyphenol and small amounts of guaiacol and methylguaiacol . The product composition became more complex with increasing temperature. Studies by Klein (1981) on syringol pyrolysis also showed that syringol decomposed in a similar way as guaiacol producing mainly catechol and phenols. From Table 5.7 phenol yield was 0.75 % and catechol yield was 1.64 %. Their low yields indicate that the HZSM-5 catalysts did not promote the demethoxylation and

demethylation of syringol under the pyrolysis conditions. Besides since the yield of catechol was more than twice that of phenol it implies the demethylation of syringol to form catechol was promoted more than demethoxylation to form phenols.
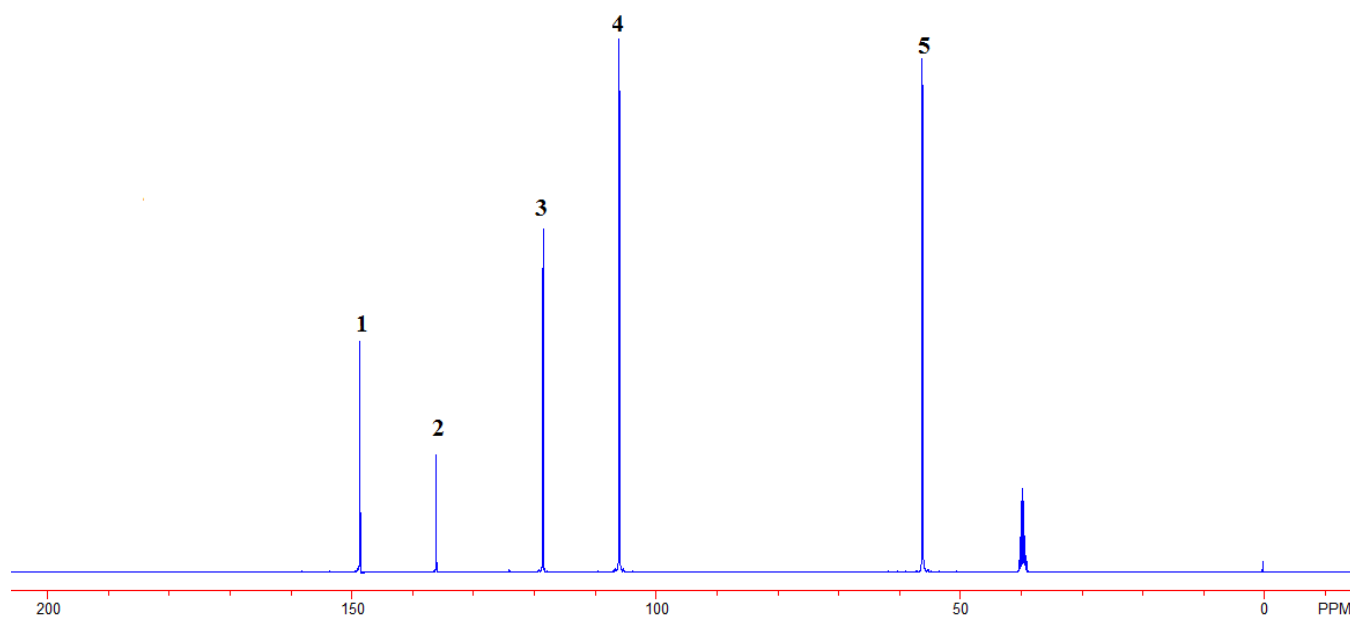

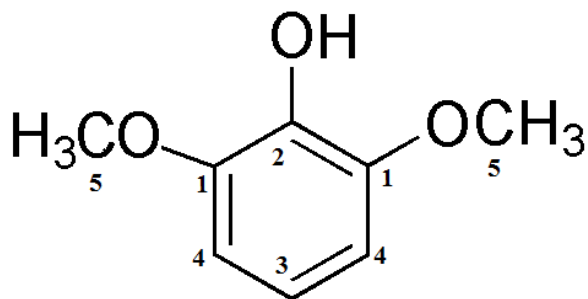Figure 5.10: ^{13}C-nmr spectrum of pure syringol in d$_6$-DMSO solvent

Figure 5.11: Structure of syringol relating the carbon positions in the ^{13}C-nmr spectrum
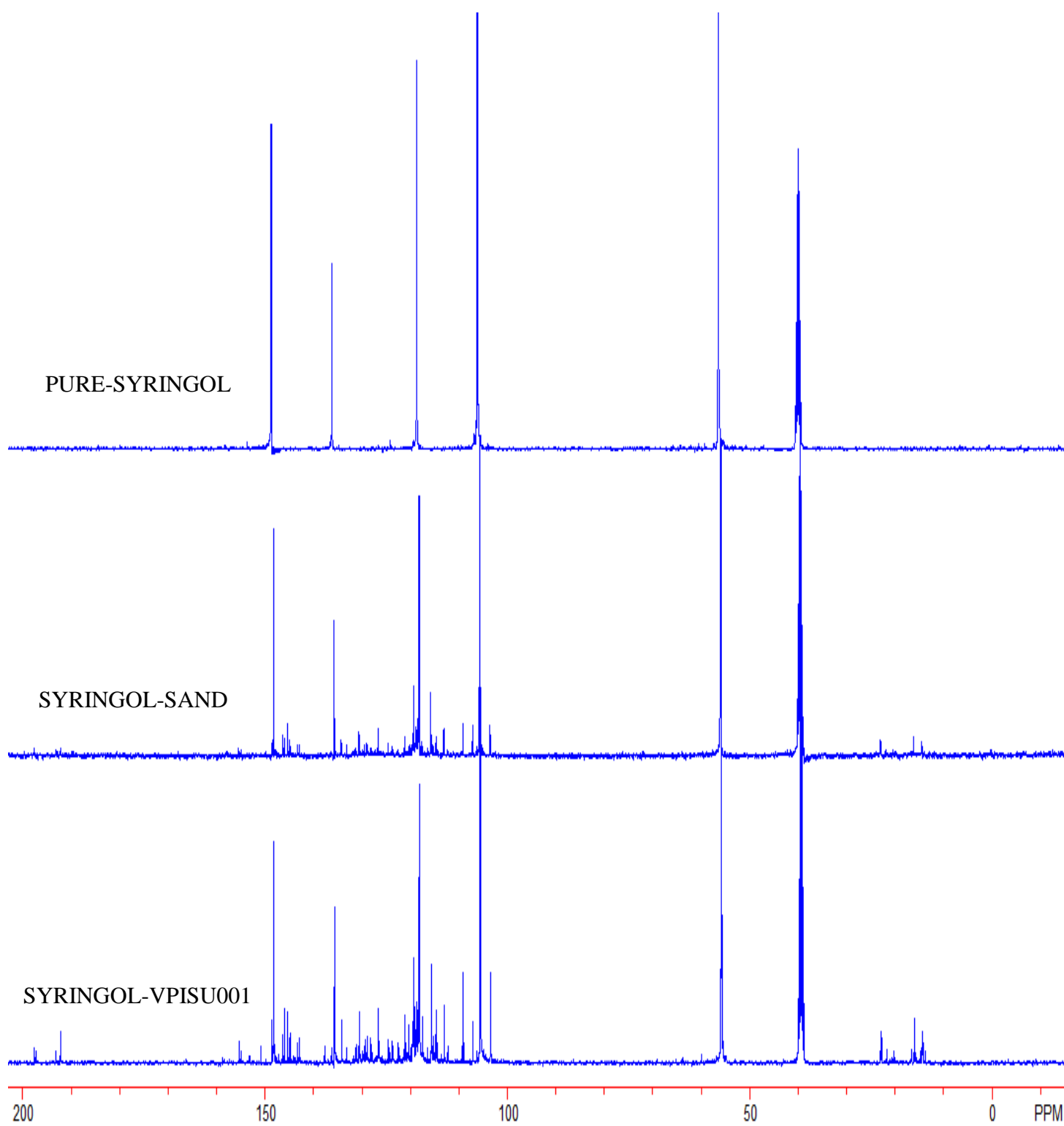
Figure 5.12: ^{13}C-nmr Spectra showing the effect of HZSM-5 catalysts on syringol pyrolysis
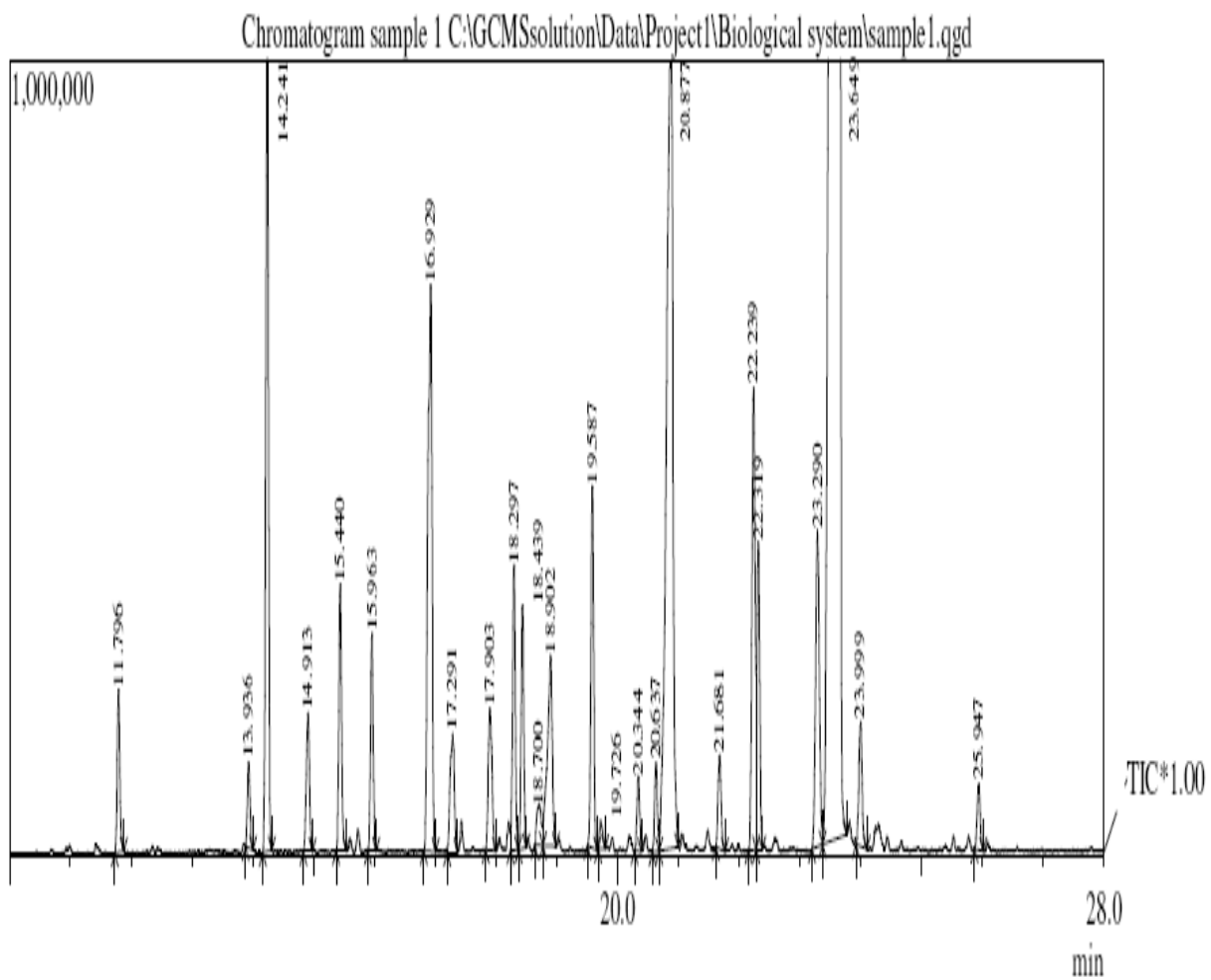
PURE-SYRINGOL

SYRINGOL-SAND

SYRINGOL-VPISU001

Figure 5.13: GC-MS Chromatogram of VPISU001 HZSM-5 syringol pyrolytic oil

Table 5.7: Product Composition of VPISU001 HZSM-5 Syringol Pyrolytic Oil

Peak	% Area	Compound
1	0.75	Phenol
2	0.40	2-Hydroxybenzyldehyde
3	4.17	2-Methyl-phenol
4	0.77	2-Methyl-phenol
5	1.28	Mequinol
6	0.99	2,6-Dimethyl-phenol
7	4.17	2-Ethyl-phenol
8	0.86	2,5-Dimethyl-phenol
9	0.93	3-Methoxy-6-methylphenol
10	1.36	2-Methoxy-6-methylphenol
11	1.14	2-Ethyl-6-methyl-phenol
12	0.34	5-Methylene-4,5,6,6a-tetrahydro-3ah-pentalen-1-one
13	1.64	Catechol
14	1.78	2,3,4,6-tetramethyl-phenol
15	0.14	3,4,5-trimethyl-phenol
16	0.36	2,6-dimethoxy-phenol
17	0.43	2,5-Diethylphenol
18	9.38	2-Methoxyresorcinol
19	0.52	1,2-Benzenediol, 4-methyl
20	2.67	2-Hdroxy-3-methoxy-benzaldehyde
21	1.45	1,2,3-Trimethoxybenzene
22	2.08	4-Ethylcatechol
23	61.34	Syringol
24	0.70	1,2,3-Benzenetriol
25	0.35	2-hydroxy-2,5-cyclohexadiene-1,4-dione
	100.00	

5.3.5.2.2 Gas composition Analysis

From Table 5.8 syringol pyrolysis on sand produced 38.3 % CO which reduced to 29.3 % in the presence of the HZSM-5 catalysts. The CO_2 yield however increased from 8.1 % to 10.2 %. This resulted in a CO/CO_2 ratio of 4.7 and 2.9 respectively for syringol pyrolyzed on sand and the VPISU001 HZSM-5. As suggested by Klien(1981) demethoxylation of syringol resulted in CO and phenol production hence the low CO and phenol (from the GCMS) analysis suggest that the pyrolysis conditions was not optimal for demethoxylation of syringol.

In contrast the methane yield increased from 11.4 % when syringol was pyrolyzed on sand to 19.7 % when syringol was pyrolyzed on the VPISU001 HZSM-5 catalyst. The increase in CH_4 production and the presence of relatively high catechol in the liquid suggests that the catalyst promoted demethylation of syringol.

The other hydrocarbon yields increased from 5.2 to 6.1 %. This increase may be due to the catalytic cracking activity of the zeolite catalysts.

Table 5.8 Gas Composition of Catalytic and Non Catalytic Pyrolysis of Syringol

SMPLE	CO	CO$_2$	CH$_4$	CO/ CO$_2$	Other Hydrocarbons	Unknown
SYRINGOL-SAND	38.3	8.1	11.4	4.7	5.2	32.3
SYRINGOL-VPISU001	29.3	10.2	19.7	2.9	6.1	34.7

5.4 Conclusions

The pyrolysis of low molecular kraft lignin (Curan 100) resulted in low liquid and gas yields and high char yields. The char yield was enhanced by NaOH pretreatment. NaOH pretreatment and the HZSM-5 catalysts had a combined effect of reducing the char yield and increase in the gas yields. NaOH pretreatment decreased the water yields but did not affect the organic liquid yields. The HZSM-5 catalysts significantly decreased the organic liquid yield and increased the water yields. The combined effect of NaOH pretreatment and zeolite catalysts decreased the water and organic liquid yields.

The ^{13}C-nmr and FTIR analysis showed that pyrolysis of untreated Curan 100 on sand produced mainly aromatic and levoglucosan groups from cellulose contaminants. HZSM-5 produced similar aromatic groups but with a methoxy group s. The NaOH pretreated Curan 100 pyrolyzed on sand and the VPISU001 produced mostly guaiacol.

Untreated Curan 100 pyrolyzed on sand produced more CO than CO_2. The presence of HZSM-5 catalysts increased the CO/CO_2 ratio and reduced the methane yield while increasing the amount of other hydrocarbons produced. NaOH pretreatment produced more CO_2 than CO and increased the methane yield. The other hydrocarbon gases were however reduced. The combined effect of NaOH pretreatment and the zeolite catalysts also produced more CO_2 than CO and increased the amount of other hydrocarbon gases produced. However the methane produced was reduced.

Pyrolysis of the guaiacol and syringol model compounds on sand and the HZSM-5 catalysts caused demethylation of guaiacol and syringol to produce phenol, catechol and methane.

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The HZSM-5 catalysts also promoted water formation through the dehydration of the organic fractions.

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