ABSTRACT

DAS, LALITENDU. Catalytic Valorization of Lignin into Value Added Chemicals. (Under the direction of Dr. Praveen Kolar).

The goal of this research was to oxidize lignin into aromatic chemicals via catalytic oxidation. The objectives were to: (1) investigate niobium-based catalysts for oxidation of lignin (2) test the activity of the catalysts during oxidization of lignin into aromatic chemicals (3) optimize the process parameters, and (4) investigate mechanism involved in the breakdown of lignin. The research was carried out in three phases. In the first phase, batch experiments were carried out using niobium oxalate catalyst via central composite design at 95 °C using 4-12 g/100 mL of lignin, 3-7 mL/100 mL of H_2O_2, and 0.5-1.0 g/100 mL of catalyst. Results indicated that, a yield of 65.58 mg g^{-1} of vanillin and 23.12 mg g^{-1} of syringaldehyde were produced under optimum conditions of 3mL of H_2O_2, 0.5 g of catalyst and 7.26 g of lignin. Effect of temperature illustrated that production of aldehydes were dependent on temperature in the range of 85ºC-100ºC with 100ºC significantly ($p=0.001$) different from the other two temperatures.

Second phase experiments were performed using niobium oxide catalyst. Results indicated that under optimum conditions of temperature at 90 °C, and catalyst loading of 0.5 g, 137.194 mg L^{-1} of vanillin and 30.290 mg L^{-1} of acetovanillone were produced. Niobium oxide eliminated the dependency of oxidants, since lattice oxygen present in the catalyst was the driving force for the oxidation process. Effects of oxidants were also investigated by employing H_2O_2 and $KMnO_4$ as oxidants. Results indicated that for production of vanillin, no oxidant was significantly ($p=0.0046$) different from H_2O_2 but is not significantly ($p=0.1527$) different from $KMnO_4$, whereas production of acetovanillone was independent of oxidants.

Studies on effect of mixing (no mixing, 50 rpm, 150 rpm and 200 rpm) revealed that production of both vanillin and acetovanillone were not dependent on mixing.

In the third phase, oyster shell and carbon rod supported niobium (2%, 5% and 8% loading) catalyst were synthesized and tested for lignin oxidation. Lignin oxidation resulted in formation of vanillin, acetovanillone, syringaldehyde and homovanillic acid. Oyster shell supported niobium (5%) catalyst produced a maximum of 86.25 mg L^{-1} of vanillin whereas carbon rod supported niobium (2%) produced a maximum of 139.39 mg L^{-1} of vanillin. Role of oxidants were compared to that of the catalyst by adding 0.5 mL 100 mL^{-1} of hydrogen peroxide to the system. It was observed that both catalysts (all loading concentrations) performed equally well. Overall lignin oxidation mechanism was explained by breaking of α and β-aryl ether bonds of lignin.

Catalytic Valorization of Lignin into Value Added Chemicals

by
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DEDICATION

To my Parents Shri Narendranath Das & Smt Mrugaja Das.

BIOGRAPHY

Lalitendu was born in Kalahandi, Orissa, India. He completed his B.Tech in Agricultural Engineering at Orissa University of Agriculture and Technology and graduated in 2005. In 2010, he moved to North Carolina State University to pursue his Masters in Biological and Agricultural Engineering. He graduated with a MS degree in the fall of 2012 and soon after started working on his doctoral studies in Biological and Agricultural Engineering at North Carolina State University.

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In this wonderful journey I would foremost like to acknowledge to god and the contribution of my family. I am indebted to them for their blessing that made me fulfill my dreams. I would like to thank Dr. Praveen Kolar, for his continuous guidance and support during my stay at NC state university. I would also like to thank Drs. Sharma, Classen and Osborne for being on my committee and for their constant feed-back to accomplish my thesis work. My gratitude for the completion of my work is extended to Rachel Huie in Environmental Analysis Lab in the department, Drs Dhana Savithri and Debra Clare in flex laboratories. I would like to mention my friends for their constant support, Rajat Sharma, Kamal Kanta Sahoo and Pankaj Pandey. A special thanks to Veronica Mbaneme for helping me in all possible ways. I would like to thank my lab mates Yane, Yiying and Han.

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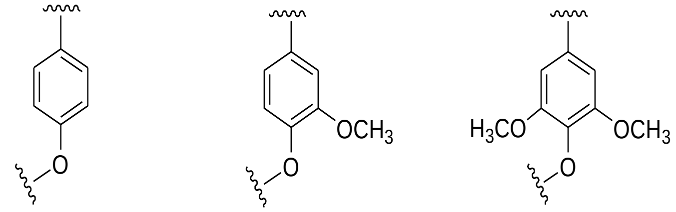
CHAPTER 1

INTRODUCTION

The last decade has witnessed huge upsurge in research on biomass as a potential candidate for renewable energy. Currently most of the biomass conversion processes are focused on breakdown of cellulose and hemicelluloses for production of fuels and bio-based products, whereas lignin is usually underutilized. Lignin is made of three monomers (fig 1.1), including *p*-coumaryl (H), coniferyl (G), and sinapyl (S) alcohols (Pinto et al., 2012).



H **G** **S**

Figure 1.1: Lignin Monomers

In general, in the lignocellulosic matrix, lignin accounts for 15% -30% by weight. Despite being a major fraction of lignocellulosic material, lignin is still considered as waste product and burnt as low-value fuel (Das et al., 2012). Lignin, being one of the nature's most abundant aromatic compounds and a promising renewable source for platform chemicals is being underutilized of its potential. Conversion of lignin to chemicals and materials has been investigated for long time, but until now most of the studies remained at the laboratory scale. The major setback in the effort to increase value of lignin is due to its complex molecular structure along with highly recalcitrant chemical nature. The most crucial and challenging part in lignin depolymerization is the selective break down to low molecular weight compounds, preferably to monoaromatic compounds (Chakar and Ragauskas, 2004). Hence, the goal of this research is to utilize lignin to produce aromatic aldehydes (Fig 1.2).

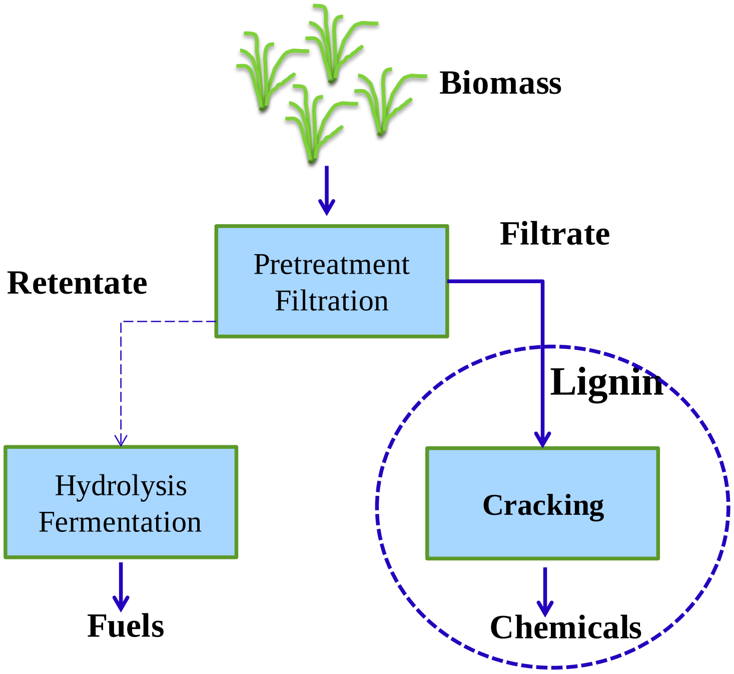


Figure 1.2: Utilization of lignin form biomass

To achieve the goal of selective deconstruction of lignin many process such as chemical, thermal, and biological could be implemented. However, among all these routes catalytic oxidation process is considered suitable for producing wide range of chemicals (Bozell et al., 2007). In this research the approach was to utilize selective catalyst in presence of an oxidant for partial oxidation of lignin to produce aromatics (Fig 1.3). Figure 3 illustrates that lignin and oxidant will react on the surface of the catalyst forming products which will be adsorbed on the surface of the catalyst, subsequently will be released to the liquid phase which can be recovered for further downstream processing.

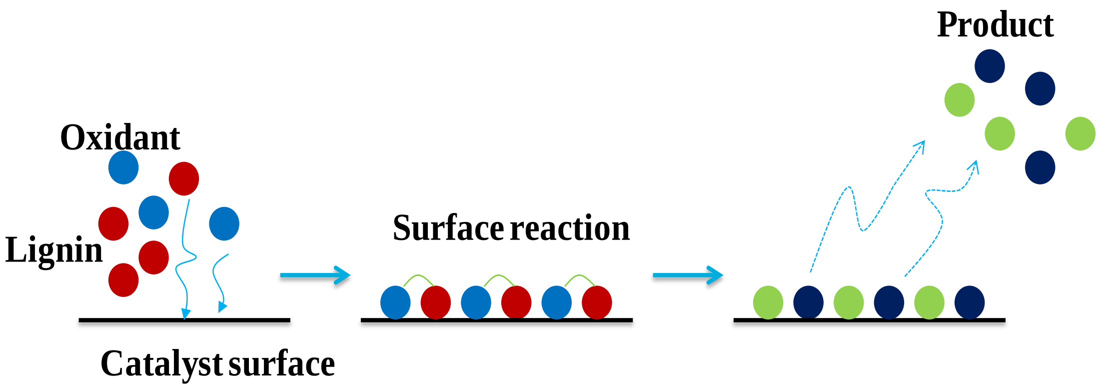


Figure 1.3: Selective catalytic oxidation

Hypothesis

- Highly active transition metal catalysts coupled with advanced oxidants will facilitate the selective catalytic oxidation process.
- Presence of lattice oxygen in the metal catalyst will not require additional oxidants in the system for lignin depolymerization.

Objective

Lignocellulosic biomass is the most abundant renewable source of energy. In order to utilize the biomass to its fullest, sustainable biorefinery technologies must be implemented to maximize the output of fuels and chemicals. Lignin being a major component of lignocellulosic matrix is constantly being underutilized. Unique chemical structure of lignin as an aromatic building block has excited many researchers and chemical industries to explore lignin more in detail. Depolymerization of lignin to produce desired chemicals depend on the source of lignin, pulping, recovery processes, process to break down lignin (chemical, catalytic or biological), and severity of process parameters. Catalytic oxidation process has been widely used for deconstruction of lignin into lower molecular weight compounds, but most of the studies involved higher temperature coupled with high pressure and molecular oxygen to achieve desired products. Hence this research is focused on exploring metal catalyst containing lattice oxygen to react with lignin at lower temperature and atmospheric pressure. Specifically, this dissertation investigated the following general objectives.

1. Exploring niobium-based catalysts for oxidation of lignin into lower molecular weight compounds.
2. Optimize the process parameters of lignin oxidation, and
3. Investigate mechanism involved in the breakdown of lignin.

The objectives outlined above were accomplished in three parts. In first part, a homogenous catalyst, niobium oxalate was employed along with H_2O_2 as oxidant to produce aldehydes. Effects of lignin concentration, catalyst loading, temperature and concentration of

H_2O_2 were studied. In the second phase of the research, a niobium oxide, a heterogeneous catalyst was tested and effects of temperature and catalyst loading were studied. In addition, the effect of oxidants and rate of mixing were also investigated. It was observed that lattice oxygen in the metal catalyst acted as an oxidant. Results obtained from parts 1 and 2 were utilized as guideline for synthesis of a solid heterogeneous catalyst that was studied in the third part. Results obtained for the study can be used to improve the utilization of lignin and add value to the biorefinery process.

Results obtained as a part of this dissertation were also presented in various professional meetings and conferences (Table1.1). In addition, the data also resulted in four manuscripts, of which two have already been published in refereed journals (Table 1.2), while others are in various stages of publication.

Table 1.1 Conferences resulted from the dissertation.

Conference	**Title**	**Year**	**Type**
IAB, Raleigh, NC	Catalytic oxidation of lignin into value-added aromatics	2012	Oral
IBE, Raleigh, NC	Catalytic oxidation of lignin into value added chemicals	2013	Oral
IAB, Rapid city, SD	Catalytic oxidation of lignin into value-added products	2013	Poster
ASABE, Montreal, Canada	Selective oxidation of lignin into aromatic aldehydes using niobium oxalate	2014	Poster
N. C. Biotechnology Summit, Raleigh	Selective valorisation of lignin into aromatics	2014	Poster
ASABE, New Orleans, LA	Exploring Novel Catalysts for Selective Valorization of Lignin to Aromatics	2015	Oral

IAB- Industry Advisory Board

IBE- Institute of Biological Engineers

ASABE- American Society of Agricultural and Biological Engineers

Table 1.2 Refereed journals resulted from the dissertation.

Chapter	**Title**	**Submission**	**Status**
Two	Heterogeneous catalytic oxidation of lignin for value added chemicals	*Biofuels*	Published
Three	Selective Oxidation of Lignin into Aromatic Aldehydes using Niobium Oxalate	*Transaction of ASABE*	Accepted
Four	Oxidative Conversion of Lignin to Vanillin using Niobium Oxide	*Bioresource Technology*	In Preparation
Five	Depolymerization of Lignin using Niobium Oxalate Supported solid Catalyst	*Chemical Engineering Journal*	In Preparation

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CHAPTER 2

HETEROGENEOUS CATALYTIC OXIDATION OF LIGNIN INTO VALUE ADDED CHEMICALS

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***This chapter “HETEROGENEOUS CATALYTIC OXIDATION OF LIGNIN INTO VALUE ADDED CHEMICALS” has been published in the journal *Biofuels*.**

Summary

Of late there is significant interest in establishing biorefineries for total utilization of lignocellulosic biomass components to produce energy, chemicals and value-added products. Lignin is an abundant and yet underutilized constituent of lignocellulosic biomass that accounts for up to 40% of the energy content. Among several approaches towards value addition of lignin, catalytic oxidation appears to be promising. Hence, the purpose of this report is to provide background information on catalytic oxidation and to update the reader about current research on heterogeneous catalytic oxidation of lignin into value-added products. Additionally, some thoughts are presented to stimulate discussion on lignin oxidation.

Defined key terms: (Lignin, Catalytic oxidation, Advanced oxidation process, Heterogeneous catalysis)

(1) Lignin: A complex polymer that constitutes a significant portion of plant biomass.

(2) Catalytic oxidation: Liquid or gas phase oxidation reaction between a reactant (usually an organic compound) and an oxidant (usually oxygen) in presence of a catalyst.

(3) Advanced oxidation processes: Oxidation of organic compounds using free radicals formed as a result of reaction between catalyst/ozone, ozone/H_2O_2, and Ozone/UV, etc.

(4) Heterogeneous catalysis: A chemical reaction occurring between gases or liquids on the surface of a solid cataly

1. Introduction

Continuous burning of fossil fuels has resulted in increased green house gas emissions and climate change (www.eia.gov). For example, Parikka, 2004 estimated that 80% of CO_2 emissions are due to burning of fossil fuels. Additionally, due to increased oil demand from emerging countries and unrest in oil producing nations, the demand and price of crude oil is on the rise. Hence, countries around the world are exploring alternative and renewable sources of energy, fuels, and chemicals (Bridgewater, 2003). One such renewable source is biomass that is expected to make significant contribution to renewable energy (Demribas, 2001). It is estimated that about 75% of the world's production (of total 421 billion tons) of woody biomass may be used for producing biofuels (Parikka, 2004). Research has shown that use of biofuels will not only reduce GHG emissions but also improves local economies (Huber et al., 2006). However, despite its merits, the use of biofuels is limited to about 3.5% in developed countries such as USA (www.eia.gov). Hence the US biomass research and development (R&D) technical advisory committee, created as a part of the biomass R&D act of 2000, has mandated that by the year 2030, 5% of the nation's power, 20% of transportation fuel, and 25% of chemicals be produced from biomass (Perlack et al., 2005). This target has opened up opportunities for R&D on novel and practical technologies for conversion of biomass into energy and platform chemicals (Corma, et al., 2008).

To achieve the target, strong emphasis is being placed on establishing biorefineries that can utilize locally/regionally available biomass to produce energy and an array of products (Carolan et al., 2007). Similar to a petroleum-based refinery, a biorefinery is a facility that produces a variety of products from lignocellulosic and other carbonaceous materials, which may include crop residues, hardwood, softwood, herbaceous biomass, cellulose, and municipal solid wastes (FitzPatrick et al., 2010; Sanchez and Cardona, 2008; Zakzeski et al., 2010). For biorefineries to be economically viable, every component of the biomass must be utilized optimally (Ragaukkas et al., 2006).

However, most of the biomass-to-energy research (via a biochemical pathway) is focused on conversion of cellulose and hemicelluloses from lignocellulosic materials into ethanol (and/or butanol) and biobased products (Zazo et al., 2011). Lignin, the remaining component of biomass is not being used optimally. Most of the world's lignin production of 40 million tons is burnt as fuel (Haber, 1997), despite the fact that lignin accounts for up to 40% of the energy value of the biomass (Zakzeski et al., 2011).

2. Lignin

Lignin is one of the most abundantly available carbonaceous materials. It is an irregular, heterogeneous, and amorphous 3D polymer consisting of methoxylated phenylpropane structures (Pearl, 1967; Goring, 1989; Furusawa et al., 2007). The repeatable (monomeric) unit in lignin is phenylpropane unit (or C9-unit) of the *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) types.

Considering the unique structure and chemistry of lignin, there is a great potential for catalytically transforming lignin into a wide range of chemicals (Figure 2.1). Some of the currently available routes for lignin cracking include thermochemical, biochemical, and catalytic processes (Fargues et al., 1996; Hocking, 1997; Zakzeski et al., 2010). Thermochemical processes involve breaking and rearranging carbon-hydrogen bonds in the presence of heat and pressure and were recently reviewed by Pandey and Kim, 2011. Similarly biochemical approaches involve use of microorganisms and enzymes to break down lignin into simpler compounds. The third and most versatile approach involves chemical catalysis to preferentially breakdown lignin into fine chemicals. Catalysis allows two options: catalytic reduction and catalytic oxidation. However, there has been a general consensus that catalytic oxidation allows for transforming lignin into chemicals with a broad range of functionalities which can directly be used as fine chemicals or can further be processed into secondary chemicals (Stark, et al., 2010).

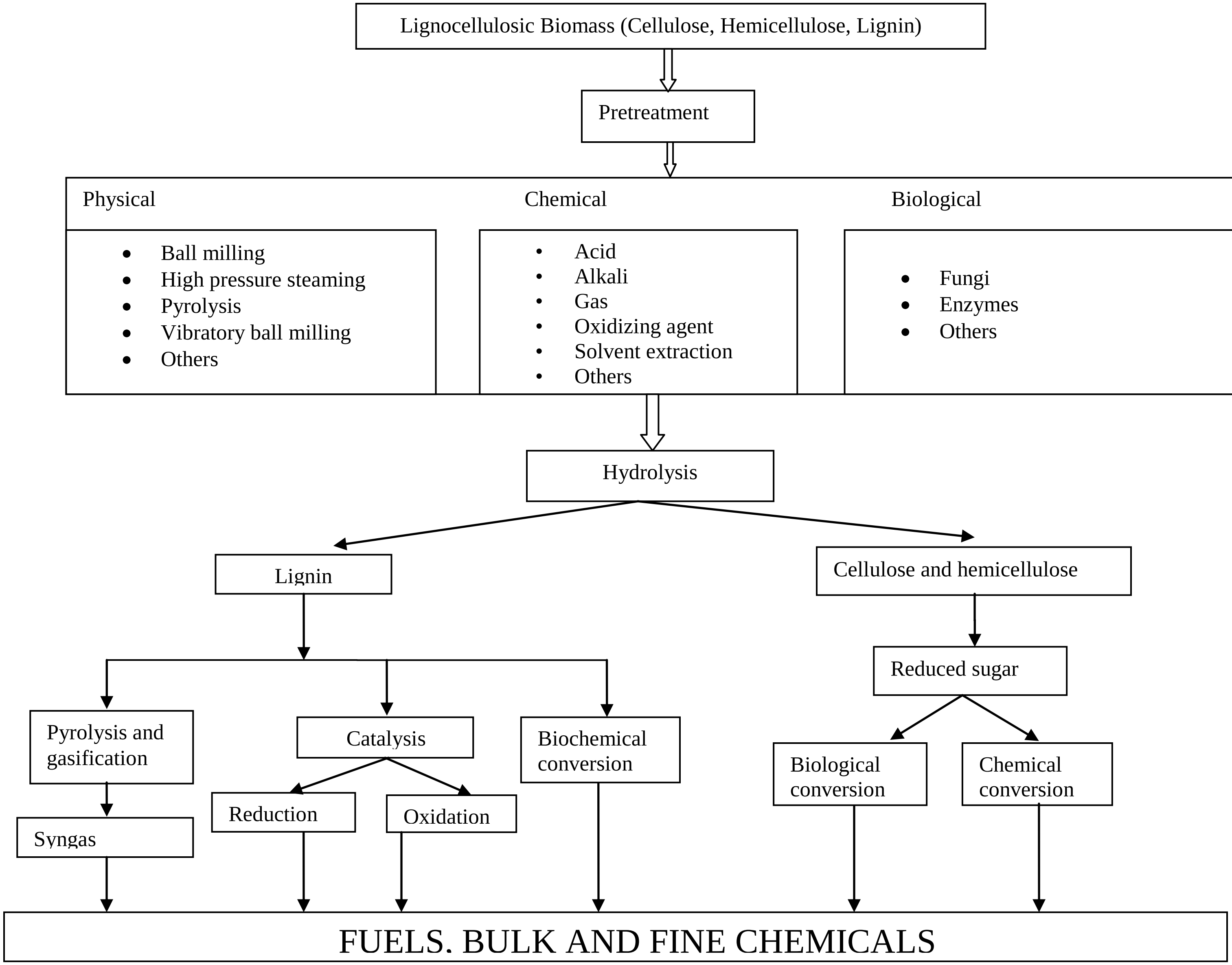

Figure 2.1. Lignin obtained from lignocellulosic biomass may be transformed into several chemicals.

3. General principles of Heterogeneous Catalytic Oxidation

In a heterogeneous system, reaction between an organic compound (e.g lignin) and an oxidant (usually oxygen and its associated products) occurs on the surface of the catalyst. The reaction generally proceeds in a step-wise manner starting with adsorption and activation of reactants followed by reaction between the adsorbed species and finally desorption of products (Cullis, 1967). When O is adsorbed on the catalyst surface it is converted into several reactive oxygen species such as O_2^-, O^-, M=O and so on (Panov et al., 2006). Some oxygen species are bound to the metal surface (M) as lattice oxygen (e.g., M-O-M) and others exist as radicals (e.g., O^-) (Hermans et al., 2009). The exact nature of the adsorbed oxygen species depends on the electronic properties of the surfaces. As classified by Bielanski and Haber, 1979, electron-rich surfaces of metal oxides (p-type semiconductors, e.g., oxides of Ni, Co and so on) activate oxygen by donating electrons to form radical oxygen (O^-). The availability of electrons on the surfaces of n-type semiconductors, (e.g., oxides of Zn) is rather limited and hence the adsorbed oxygen takes the form of O_2^-. Certain metal oxides (oxides of niobium) on the other hand do not allow adsorption of oxygen; however, these oxides serve as a source of lattice oxygen needed for partial oxidation. Catalytic activities of metal oxides based on electrical conductivities were also described by Spivey, 1987. P-type oxides adsorb oxygen easily while n-type oxides adsorb oxygen only at selected sites making p-type oxides suitable for complete oxidation.

Depending on the nature of the oxygen species on the surface, the reaction can result in either complete oxidation to obtain CO_2 and water or partial oxidation to obtain desired intermediate products. For example, a catalyst surface dominated with electrophilic species (O^-) tends to favor complete oxidation while nucleophilic oxygen (e.g., M-O-M) is believed to participate in partial oxidation reactions. The electrophilic species potentially abstract hydrogen from the organic molecules resulting in highly unstable active free radicals that initiate a chain reaction which, under certain conditions will result in complete oxidation (Haber, 1997). Alternatively, some electrophilic species may attack the C=C bond resulting in complete oxidation (Bielanski and Haber, 1979). Partial oxidation, on the other hand involves hydrogen(s) abstraction from the organic molecule and inclusion of nucleophilic oxygen into the structure resulting in desirable oxygenated products (Haber, 2003; Vedrine, 2003). Additionally, the metal-oxygen bond strength may also influence the extent of oxidation. Weakly bonded oxygen leads to over oxidation while extremely strongly bonded oxygen will under oxidize the molecule (Grasselli, 2002). Further, as Callahan and Grasselli, 1963 explained, the surface density of the oxygen atoms surrounding the active site could significantly influence the extent of oxidation. Presence of higher than stoichiometric requirement of oxygen can lead to over oxidation while presence of isolated oxygen species will result only in an inactive site.

Physical properties of the surface also play a role in catalysis (Cullis, 1967). If the catalyst consists of an extensive pore structure, the intermediate products tend to get oxidized during their transport within the pores. Hence, when highly porous catalysts are used, the possibility of over oxidation of the desirable intermediate products is fairly high. Similarly modifying surfaces with certain materials capable of serving as lattice oxygen donors will enhance the activity of the catalyst via oxygen spillover effect (Delmon, 1996).

Complete catalytic oxidation is preferred in environmental applications while partial oxidation is commonly adopted to synthesize platform molecules. Excellent summaries on selective and complete oxidation of organic compounds on different types of catalysts have been provided by (Grasselli, 2002; Haber and Witko, 2003; Panov et al., 2006; Spivey, 1987) and others and the reader is encouraged to refer for additional information.

3.1. General Mechanisms of Heterogeneous Catalytic Oxidation

Several models have been proposed to describe catalytic oxidation using oxygen. In one of his excellent reviews, Spivey, 1987 described catalytic oxidation using two approaches: a simple empirical power law and a more complex mechanistic approach that provides insight into the reaction mechanism. A power law describes oxidation rate as a function of a rate constant and the concentration of the reactants.

$$-r = kC_C^n C_{O_2}^m \qquad (1)$$

where r is the rate of reaction, and C_C and C_{O_2} are concentrations of organic molecule and oxygen, n and m are orders of reaction, and k is the reaction rate constant.

A power law model, although mathematically simple and useful in industrial reactor designs, does not allow for an understanding of the reaction mechanism. Hence, additional mechanistic models have been proposed to obtain an understanding of catalytic oxidation processes. For example, oxidation of styrene using manganese (Mn) oxide-Fe oxide was studied by Tseng and Chu, 2001**.** The authors described two mathematical models (shown below as equations 2 and 3) based on Langmuir-Hinshelwood mechanism: reaction between adsorbed styrene and adsorbed molecular oxygen (Figure 2.2A, and equation 2) and reaction between adsorbed styrene and adsorbed atomic oxygen (O) (Figure 2.2B, and equation 3) by assuming that the products do not irreversibly adsorb on the catalyst surface.

$$-r_S = k_S \left(\frac{K_S C_S \, K_O \, C_O}{\left(1 + K_S C_S + K_O C_O\right)^2} \right) \quad (2)$$

$$-r_S = k_S \left(\frac{K_S C_S \sqrt{K_O \, C_O}}{\left(1 + K_S C_s + \sqrt{K_O C_O}\right)^2} \right) \quad (3)$$

where $-r_S$ is the oxidation rate of styrene, C_S and C_O are the concentrations and K_S and K_O are the adsorption equilibrium constants of styrene and oxygen and k_S is the overall oxidation rate constant.

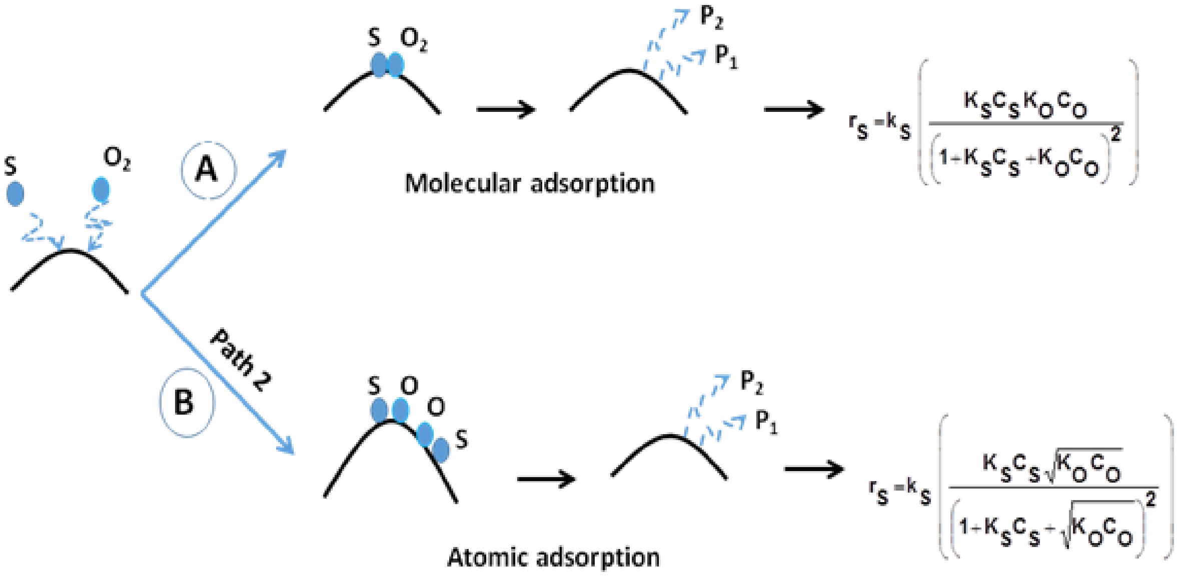

Figure 2.2. Proposed Langmuir-Hinshelwood reaction mechanism for oxidation of styrene via (A) molecular oxygen and (B) atomic oxygen. Data from (Tseng and Chu, 2001).

Gangawal et al. 1998 described a redox model originally proposed by Mars and Van-krevelen, 1954 and Grasselli, 2002 for oxidizing benzene and n-hexane over Ni-Pt/γ-Alumina (Al_2O_3) catalyst using molecular oxygen. After adsorption on the surface, benzene (and n-hexane) was believed to react with the oxygen present in the lattice of the catalyst to form the product and a reduced (deactivated) site (Figure 2.3). Subsequently, the bulk oxygen that was adsorbed on the surface reactivated the site for the next cycle through acceptance of four electrons from the metal oxide surface to form $2O^{2-}$ (Vedrine, 1997).

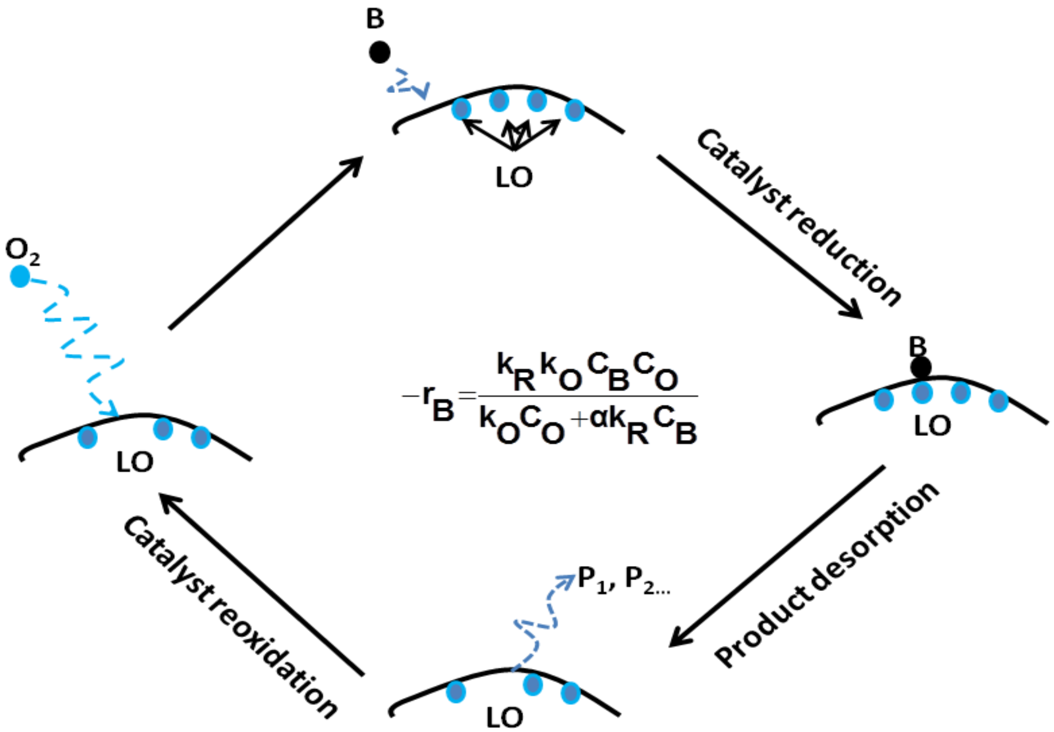

Figure 2.3: Proposed redox reaction mechanism for oxidation of benzene via lattice oxygen (based on Gangwal et al., 1988).

Further, by assuming that oxidation rate of the organic molecules is proportional to number of organic molecules and reoxidation of catalyst is proportional to the oxygen pressure in the bulk phase and the number of available reduced active sites, following relation was provided by (Gangwal et al., 1988).

$$-r_B = \frac{k_R k_O C_B C_O}{k_O C_O + \alpha k_R C_B} \quad (4)$$

where $-r_B$ is the rate of oxidation of the organic compound, C_B and C_O are the concentrations of benzene and oxygen respectively, k_R and k_o are the rate constants for reduction and oxidation of the catalyst respectively, and α is the stoichiometric ratio of oxygen to benzene for completion of the reaction.

4. Catalytic Oxidation of Lignin

4.1. Oxidants

Various types of oxidants have been used for oxidizing lignin. Villar et al. differentiated the oxidants based on their oxidative strengths and the location of attack (Holladay, 2007). Some of the commonly used oxidants include: oxygen, hydrogen peroxide (H_2O_2), ozone, nitrobenzene, permanganate, metals such as Cu, Ag. Each oxidant has certain advantages and disadvantages with respect to activity and selectivity. Table 2.1 briefly summarizes salient features of oxidants for lignin oxidation:

Table 2.1. Oxidants used for oxidation of lignin

Oxidant	Advantages	Disadvantages	References
Oxygen	Inexpensive and green Aromatic ring is preserved	Nonselective, possibility of over oxidation -Requires high temperature for oxygen activation	(Mathias and Rodrigues, 1995)
Ozone	Somewhat selective	Requires on-site generation	(Ragelt and Clark, 2000)
H_2O_2	Efficient Inexpensive and green Yield water after reduction	Aromatic rings disrupted; yields acids	(Maziero et al., 2012)
Nitrobenzene	Effective Aromatic ring is preserved	Non volatile and possible carcinogen	(Masingale et al., 2009; Villar et al., 2001)
Metal ions (Cu, Fe)	Effective	Difficult to separate after the reaction Heavy metal	(Deng et al., 2010)

4.2 Wet Oxidation

Wet oxidation is a chemical reaction between organic compounds and oxygen under high temperatures and pressures (Luck, 1996). The reaction typically proceeds via formation of oxygen-generated free radicals (Luck, 1999) and their subsequent reaction with organic compounds to yield simpler compounds (Imamura, 1999). Details of the basic chemistry and mechanism of wet oxidation are available in reviews provided by (Bhargava, et al., 2007; Imamura, 1999; Kolaczkowski, 1999; Luck, 1996; Luck, 1999; Levec and Pintar, 2007) and others. Due to the use of molecular oxygen, wet air oxidation is regarded as one of the easier and greener technologies for oxidation of complex organic compounds (Levec and Pintar, 2007). Rodrigues's group has extensively studied oxidation of lignin using molecular oxygen. For example Fargues et al., 1996 studied the oxidation of Kraft lignin for synthesis of vanillin. An autoclave reactor (500 mL, 1150 rpm) was used to investigate the effects of oxygen (pO_2 = 0.12-0.51), lignin (30-120 g/L), and temperature (110-154 °C) on vanillin yields. Under the most favorable experimental conditions (~130 °C, pO_2 = 0.28), the authors reported an optimal vanillin yield of 10.8%. The rate of vanillin synthesis was expressed as a power law model with the orders of reaction for oxygen and lignin as 1.75 and 1, respectively. Additionally, it was also suggested that alkaline pH was needed to minimize further oxidation of vanillin synthesized during oxidation (Fargues et al., 1996. Araújo et al., 2010, evaluated and modeled kraft lignin oxidation in a flow through reactor (0.7m x 0.1 m Φ) packed with Mellapak^R (carbon steel) packing using 50% oxygen as an oxidant. Under similar experimental conditions, presence of packing in the reactor enhanced the production of vanillin by 23% due to increased transport of oxygen. It was noted that lignin oxidation into vanillin was determined by oxygen transfer into the liquid phase. Further, computer simulation of the process predicted a yield of 1.8 g/L of vanillin by increasing the flow rate, temperature, partial pressure, gas flow rate, and mass transfer coefficient to 0.167 L/min, 433 K, 10 bar, 40 Standard LPM, and 0.0015/s. In a recent study, Pinto et al., 2011 screened eight lignins and selected two softwood (pine and spruce) and one hardwood (beech) lignin for oxidation. The experiments were conducted in 1-L process-controlled autoclave reactor (total pressure 9.7 bar) at 120 °C at constant oxygen pressure of 3 bar for a period of 60-120 min. The predominant oxidation products of softwood lignin were vanillin followed by vanillic acid whereas syringaldehyde followed by vanillin were the main reaction products for hardwood lignin. Based on the structural identification of lignin via nitrobenzene oxidation, the authors attributed formation of vanillin from softwood lignin to significantly high proportion of guaiacyl type phenylpropane units in the structure. Similarly, as hardwood lignin was composed of syringyl and guaiacyl type phenylpropane units, syringaldehyde and vanillin were formed as a result of oxidation.

In spite of its efficiency, wet oxidation involves high temperature and pressure, making the process expensive to scale up (Bhargava et al., 2007). One approach to reduce the reaction temperature is using catalysts along with wet oxidation (also called as catalytic wet oxidation) (Levec and Pintar, 2007). The presence of a catalyst in the reaction media not only provides alternate pathways and increases the oxidation rates but also enhances product selectivity (Akolekar, 2002). Both homogeneous and heterogeneous catalysts have been used in wet oxidation; however heterogeneous catalysts allow for easier separation and repeated reuse (Zhang et al., 2009). Hence this section focuses on the use of heterogeneous catalysts for lignin oxidation.

4.3 Transition Metals

In one of their earlier studies, Wu et al., 1994 tested catalytic oxidation of steam-exploded hardwood lignin in a magnetically stirred autoclave reactor (2000 rpm at 170 °C) using pure oxygen as an oxidant and Cu sulfate and ferric chloride as catalysts (Table 2). The authors reported that addition of catalysts significantly enhanced oxidation of lignin into syringaldehyde, hydroxybenzaldehydes, and vanillic aldehyde when compared to a non-catalytic process. In addition, the reaction was also affected by oxygen and pH. Higher oxygen pressure during the initial period of the reaction resulted in faster lignin oxidation and lower pressure in the reactor during the later stages of the reaction, which limited further oxidation of the aldehydes. Higher pH (10.5-12) facilitated the ionization of hydroxyl groups associated with lignin structure. Based on the results, it was proposed that formation of phenoxy radical by electron deficient Cu^{+2} and increased oxygen levels due to Fe^{+3}-lignin complex enhanced the rate of lignin oxidation.

Villar et al., 2001 studied oxidation of lignin derived from eucalyptus liquor in an autoclave reactor that was maintained at 150 °C for 120 min using oxides of Cu, Co, and Al_2O_3-supported platinum (Pt) catalysts. While oxidation resulted in production of vanillin, vanillic acid syringaldehyde, and syringic acid, the addition of catalysts did not enhance the product yield. On the contrary, except for Cu oxide catalyst, the yields of the aforementioned products decreased when compared to a non-catalytic oxidation. The authors suggested that the decreased yields are a result of either over oxidation of lignin or formation of certain products that could not be detected.

Akolekar et al., 2002 investigated the efficiencies of single metal, such as Cu, Mn, and palladium (Pd) and supported dual-metal catalysts such as Mn supported Cu and Pd-supported Cu during the oxidation of pulp waste liquor. The catalysts were tested in a stirred-tank reactor (0.6 L) while maintaining a constant oxygen partial pressure of 500 kPa. Effects of catalyst type, catalyst mass (0-8.3 g), reaction pH (11.3-14), and temperature (145-190 °C) on the substrate's (pulp liquor) oxidation efficiency were studied. The authors reported that presence of catalysts increased oxidation efficiency of the substrate by 20-167% (on a relative basis) when compared to a non-catalytic reaction. Of all the catalysts tested, Pd-supported Cu was found to be the most active (fractional removal of 78.8%), with fractional conversion of the pulp liquor increasing with an increase in catalyst loading up to 3 g but remained constant beyond 3 g (equivalent to a mass loading of 5 g/L). It was also reported that oxidation efficiency (fractional conversion) was inversely correlated with pH of the reaction mixture perhaps due to loss of metal and formation of intermediate recalcitrant products. As expected when the reaction temperature was increased from 145 to 190 °C, fractional conversion of the substrate increased from about 34 to 56% in presence of Mn-supported Cu catalyst. In a recent study by Bhargava et al., 2007 catalytic oxidation of lignin (ferulic acid), was studied using Cu-based catalyst supported on Al_2O_3, kaolin, and Mn in an autoclave reactor maintained at 100 °C for 2 hours using an oxygen pressure of 172 kPa. The synthesis was performed via precipitation-co-precipitation methods to obtain, single, dual, and multi-metal catalysts that included combinations of Cu, Co, Fe, Mn, Ni and cerium (Ce). Al_2O_3-supported Cu-Ni-Ce and Al_2O_3-supported Cu-Mn were found to be the best catalysts. However, despite providing a higher fractional removal (81 %) than Al_2O_3-supported Cu-Mn catalyst (75%), Al_2O_3-supported Cu-Ni-Ce suffered excessive leaching (20%) of Cu into the reaction media suggesting that presence of Mn as a co-metal may minimize leaching of Cu. The authors found that heterogeneous multi-metal Cu-Mn-Fe catalyst possessed limited activity perhaps due to a limited surface area. It was also reported that despite leaching of Cu into the solution, the catalytic activity of Al_2O_3-supported Cu-Ni-Ce was predominantly heterogeneous and catalyst was reused successfully for four times.

Microwave-assisted oxidation of 4-hydroxy-1-phenylpropane was investigated by Gu et al., 2010 using lanthanum impregnated mesoporouos silica catalyst (La/SBA-15) and H_2O_2. Experiments were performed by mixing 4-hydroxy-1-phenylpropane (dissolved in acetonitrile), H_2O_2, and catalyst and heating in microwave (200 W for 40 min). Identical experiments were conducted separately in round bottom flasks (60 °C for 24 h) to test the efficacy of the microwave system. No reaction occurred in experiments without the catalyst and oxidant, while limited conversion occurred in the presence of H_2O_2 and SBA-15. The highest activity was obtained from La/SBA-15, suggesting that the interaction between lanthanum and silica played a significant role in catalysis. Fractional conversion of 4-hydroxy-1-phenylpropane was significantly higher with microwave heating (70.5%) when compared to that of conventional heating (14.3%) and the reaction yielded p-hydroxybenzaldehyde, p-hydroxybenzoic acid, and p-hydroxybenzoquinone as end products.

4.4 Perovskite Type Metal Oxides

Lin's group tested perovskite type mixed metal oxide catalysts for oxidation of lignin obtained from corn stalk. In one of their studies, $LnMnO_3$ catalyst was synthesized and was tested in a slurry reactor that was maintained at 120 °C and a total pressure of 20 bar (O_2 = 5 bar) (Deng et al., 2008). It was observed that presence of $LnMnO_3$ yielded higher amounts of vanilladehyde, syringaldehyde, and p-hydroxybenzaldehyde when compared to a non-catalytic reaction. The authors also tested $LaCl_3$ and $MnSO_4$ as catalysts to investigate the individual role of La and Mn in lignin oxidation. The authors found that $LaCl_3$ was inactive and $MnSO_4$ possessed little activity, suggesting that the chemisorbed oxygen on $LnMnO_3$ catalyst was responsible for its catalytic activity. In addition, the catalyst was stable and maintained activity for five consecutive runs. $LaCoO_3$ catalyst was also tested in oxidation of lignin derived from corn stalk using the experimental conditions described in Deng et al., 2008. Although lignin was oxidized to vanilladehyde, syringaldehyde, and p-hydroxybenzaldehyde as expected, it was also found that the reaction time needed to obtain maximum yields of products was longer for the catalytic process than non-catalytic process (Deng et al., 2009). Similar results were reported by Zhang, 2008 when $LaFe_{1-n}Cu_nO_3$ ($0<n<0.2$) catalysts were tested for lignin oxidation. The catalysts were synthesized by systematically adding Cu to $LaFeO_3$ via sol-gel method and tested in a slurry reactor maintained at 120 °C and a total pressure of 20 bar (O_2 = 5 bar). The authors reported that addition of copper to $LaFeO_3$ enhanced the catalytic activity of lignin oxidation and formation of vanilladehyde, syringaldehyde, and p-hydroxybenzaldehyde. The increased activity of copper loaded $LaFeO_3$ was attributed to formation of quinone methide radical initiated by oxygen-lignin-Fe complex and increased amounts of Cu-oxygen species. Recently Deng et al., 2010 investigated Cu-Co-lanthanum perovskite-type catalysts for lignin oxidation. Lignin was obtained from steam explosion of corn stalk and the catalysts were synthesized via standard sol-gel process by varying the proportion of Co and Cu on the mixture. The authors observed that presence of Cu enhanced the catalytic activity towards formation of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde, which was related to a positive interaction between Co and Cu cation species on the surface. Additionally, it was found that increase in Cu content also increased the production of end products perhaps due to increased adsorption of oxygen species on the surface.

In a separate study, Bin and Zhu, 2011 investigated oxidation of straw-derived alkaline lignin using $LaMnO_3$ doped with strontium and Cu of varying proportions. The catalysts were prepared via sol-gel method and all oxidation experiments were performed in a batch reactor maintained at 140 °C (0.5 MPa O_2). *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde were found to be the main products of the reaction. Relative yield of the products indicated that doping of strontium and Cu increased the yields of aldehydes which were attributed to enhanced oxygen vacancies formed due to presence of the dopants.

4.5 Organometal and Other Catalysts

Polystyrene and poly 4-vinylpyridine supported methyl trioxorhenium catalysts were explored by Crestini et al., 2006 to oxidize several lignin model compounds and real lignin obtained from hydrolysis of sugar cane and red spruce kraft lignin using H_2O_2 as an oxidant. The catalytic activity tests indicated that heterogeneous MTO catalysts inhibit further oxidation of the products. Based on the analysis of the reaction products and significant reduction of aliphatic OH groups and increase in carboxylic groups, it was proposed that oxidation of lignin proceeded via opening of the aromatic ring structure pathway (Crestini et al., 2010). Extensive details about the lignin compounds tested, mass balances, and product yields are provided in Crestini et al., 2006.

Metal organic frame works have generated significant interest as catalysts for oxidation of lignin partly due to their structural stabilities and ordered porosities (Masingale et al., 2009). Recently Zakzeski et al., 2011 synthesized a novel heterogeneous catalyst, zeolitic imidazolate frameworks (ZIF) for oxidation of several lignin-derived aromatics. The catalyst was prepared by reacting Co nitrate with benzimidazole to obtain Co-zeolitic imidazolate framework. The catalytic activity towards oxidation of selected lignin-derived aromatics was tested in a high pressure slurry reactor in presence of NaOH using toluene as solvent and oxygen (0.5 MPa) as an oxidant. The authors reported that the catalyst exhibited excellent selectivity towards oxidation of phthalan into phthalide, veratryl alcohol into veratraldehyde, vanillin alcohol into vanillin. It was observed that the presence of NaOH significantly increased the conversion suggesting that hydroxyl group was able to activate the surface oxygen. Additionally, the catalytic activity was found to be stable and consistent after three consecutive runs.

4.6 Noble Metals

Noble metals especially Pt and Pd have also been tested for catalytic oxidation of lignin. Oxidation of hardwood kraft lignin was studied by Villar et al., 2001 using commercial Al_2O_3-supported Pt catalysts in a temperature and pressure-controlled reactor maintained at 150 °C and 7 atm. The results indicated that presence of Pt- Al_2O_3 catalysts (when compared to a non-catalytic reaction) did not increase production of aldehydes or acids. On the contrary, the yields decreased significantly. The authors proposed that the Pt-Al_2O_3 was probably over oxidizing lignin into smaller molecules or CO_2.

Pd impregnated on γ-Al_2O_3 was investigated as a catalyst for wet oxidation of lignin obtained from sugarcane bagasse (Sales et al., 2004). Pd/ γ-Al_2O_3 was synthesized via wet impregnation to obtain a Pd loading of 2.85%. A multi-phase fluidized bed reactor was used to test the effects of catalyst loading (2.5-5%), reaction temperature (100-140 °C), and oxygen concentration (2-10 bar). It was observed that increase in temperature and pressure resulted in higher conversion rates of lignin into vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde. Based on their assumed pseudo-first order model, presence of the catalyst (Pd/γ-Al_2O_3) increased the rates of lignin conversion by 1.7 times, vanillin by 13 times, syringaldehyde by 44 times, and *p*-hydroxybenzaldehyde by 10 times. Based on these results, Sales et al., 2006 proposed that aldehyde production occurred after initial hydrolysis of lignin and the aldehydes were further oxidized into acids and finally into CO_2 as end product. In a related work Sales et al., 2007 compared the activity of the Pd/ γ-Al_2O_3 in batch and continuous systems.

Table 2.2 Oxidation products produced from various lignin sources

Lignin source	Oxidant	Catalyst	Products	Yield (%)	references
Sugarcane	Oxygen	Pd/γ-Alumina	p-hydroxybenzaldehyde	2-8*	(Sales et al., 2006
			Vanillin		
			Syringaldehyde		
Straw	Oxygen	$LaMnO_3$,	p-hydroxybenzaldehyde	3.8-5.5	(Bin and Zhu, 2011)
		$La_{0.8}Sr_{0.2}MnO_3$,	Vanillin	3.0-6.1	
		$LaCu_{0.2}Mn_{0.8}O_3$,	Syringaldehyde	4.9-11.2	
4-hydroxy-1-phenylpropane	H_2O_2	La/SBA-15	p-hydroxybenzaldehyde,	26	(Gu et al., 2010)
			p-hydroxybenzoic acid,	4.5	
			and p-hydroxybenzoquinone	7	
Phthalan	Oxygen	Co-ZIF	Phthalide, Phthalaldehyde	89, 8	(Zakzeski et al., 2011)
Vanillyl alcohol			Vanillin	NA	
Cinnamyl alcohol			Cinnamaldehyde	30	
Veratryl alcohol			veratraldehyde	46	
Corn stalks	Oxygen	$LaMnO_3$	p-hydroxybenzaldehyde	2.03	(Deng et al., 2008)
			Vanillin	4.32	
			Syringaldehyde	9.32	
Cornstalks	Oxygen	LaFe0.8Cu0.2O3	p-hydroxybenzaldehyde	2.49	(Zhang et al., 2009)
			Vanillin	4.56	
			Syringaldehyde	11.51	
Cornstalks	Oxygen	LaCoCuO3	p-hydroxybenzaldehyde	2.23	(Deng et al., 2010)
			Vanillin	4.55	
			Syringaldehyde	9.99	
Steam-exploded hardwood lignin	Oxygen	$FeCl_3$ and $CuSO_4$	Syringaldehyde	9.5	(Wu et al., 1994)
			vanillic aldehyde	4.7	
Sugarcane bagasse	Oxygen	Pd/γ-Al_2O_3	Vanillin	1.9	(Sales et al., 2004)
			syringaldehyde	1.7	

- Depending on oxygen concentration and temperature

It was observed that continuous operation resulted in 11 times higher yields of vanillin, 23 times those of syringaldehyde when compared to a batch system. Additionally, syringaldehyde was found to be very reactive while *p*-hydroxybenzaldehyde was relatively inert.

4.7 Photo & Electro-Catalysts

Ma et al., 2008 tested titanium oxide impregnated with Pt as a photocatalyst to oxidize pure lignin dissolved in sodium hydroxide. The catalyst was synthesized by depositing a Pt salt followed by drying (150 °C) and calcination (400 °C in hydrogen) to obtain reduced platinum on the surface. Effects of catalyst dosage, loading, and pH on lignin oxidation were tested in a 400 mL stirred batch reactor enclosed by UV lighting. The results indicated that Pt-deposited TiO_2 exhibited higher activity than UV and TiO_2. The authors suggested that Pt/TiO_2 increased the formation of hydroxyl radicals thereby enhancing lignin oxidation. Oxidation of lignin was also affected by the pH of the reactants. Increase in pH decreased the catalytic activity suggesting that acidic environment increased the density of OH radicals in the system that initiated lignin oxidation.

Parpot et al., 2000 studied electrochemical oxidation of kraft lignin (dissolved in 1M NaOH) using several anodes such as Ni, Pt, Cu, oxygen evoluting dimensionally stable anode and lead oxide, as working electrodes in a three-electrode electrolytic cell. The authors reported that vanillin was the main product of oxidation and its yield was dependent on the rate of oxygen evolution, which was directly related to the applied current. It was also observed that use of Cu anode resulted in a significantly higher rate of vanillin production than Ni and Pt. However, in order to prevent further oxidation of vanillin into vanillinic acid and others, continuous extraction of vanillin was recommended.

Recently, an electrochemical approach for oxidation of lignin using iridium oxide electrodes was demonstrated by Tolba et al., 2010. The authors prepared iridium oxide electrodes that were coated with oxides of Ti, Ta, Ru, and Sn. The activity of the electrodes was tested via UV/vis spectroscopy using 100 mg/L lignin obtained from a paper and pulp facility. Among all the combinations tested, Ti-RuO_2-IrO_2 was found to possess highest activity. Their analysis also indicated that the rate of lignin oxidation (in NaOH) followed a pseudo first-order reaction and lower activation energies, suggesting a free-radical oxidation reaction. The research was continued by Tian et al., 2010, by combining photo- and electro-chemical techniques to oxidize lignin derived from paper pulp into vanillin and vanillic acid. Experiments were conducted using a three-electrode system coupled with UV light. The results indicated that about 92% lignin was oxidized using iridium oxide electrodes and UV while only 66% lignin was oxidized using the iridium oxide electrodes alone confirming the synergistic effect of photoelectrochemical technique.

5. Potential Products From Lignin Oxidation

If selectively oxidized, lignin provides an excellent opportunity to produce various industrial chemicals. Depending on the nature of lignin, extent of oxidation, and the catalyst selectivity, several value added products may be realized (Table 2). For example, mild oxidation could yield vanillin and vanillic acid (Clark et al., 2006). Moderate oxidation is expected to yield aldehydes (vanillin and syrigaldehyde), ketones (syringanone vanillone), and carboxylic acids (oxalic, formic, succinic, vanillic acids) (Xiang and Lee, 2001). Stronger oxidation processes on the other hand will yield, for example, benzoic, acetic acids (Holladay et al., 2007), due to rupture of phenolic rings (Maziero et al., 2012). Partial oxidation (gasification) under high temperatures (500-700 °C) will crack lignin into a mixture of H_2 and CO, which could be combusted for energy or further catalytically transformed into methanol (Pandey and Kim, 2011). Further, Collinson and Thielemans, 2010 suggested that oxidized lignin may serve as a flocculant that may significantly impact wastewater treatment processes. In addition, as a significant carbon source, lignin could also serve as catalyst support and an adsorbent (Sushas et al., 2007). For example, Zazo et al., 2011 synthesized activated carbon-supported iron catalysts by impregnating iron chloride on kraft lignin followed by activation in nitrogen atmosphere. The catalysts so obtained had surface areas between 300-805 m^2/g and were active in oxidation of phenol using peroxide. Similarly, Cotoruelo et al., 2011 prepared highly active adsorbents by carbonizing and activating eucalyptus kraft lignin for adsorption of aromatics.

6. Future Perspective

In the above works, oxygen was used as an oxidant and oxidation generally occurred between 120-200°C. In order to be economically competitive, oxidation of lignin should be performed at lower temperatures preferably ambient, or slightly above ambient. One approach towards lowering the reaction temperature is to use highly active catalysts in combination with advanced oxidation processes. In our opinion future research on lignin oxidation should be focused on the following areas:

6.1 Catalysis:

Majority of the research on lignin oxidation is focused on simply testing various catalysts and determining the reactivity rather than designing catalysts based on the actual oxidation mechanism. Synthesizing catalysts is an iterative process. First, model catalysts are tested and fundamental understanding of the mechanism is obtained. Next, based on the fundamental analysis, the catalysts are modified to expedite the slowest reactions. This process is repeated until the catalysts perform in a desired and predictable manner. As emphasized by Zakzeski et al., 2011, we also reiterate the need for additional research on designing selective catalysts to oxidize actual lignin into high value chemicals. For instance, Bhargava et al., 2007 demonstrated that presence of Mn-minimized leaching of Cu into the solution. Additional research to investigate the role of Mn as a co-catalyst is needed. Similarly, oxysalts of transition metals may also be explored as selective oxidation catalysts. Further, to evaluate catalysts, using a single biomass feed stock is recommended. This is especially important because lignin can be quite heterogeneous. Utilizing a common feedstock to develop and test different catalysts will provide valuable insight on the working mechanism and actual role of the catalysts in oxidation processes.

6.2 Emerging Feedstock:

At present, extensive research is underway to utilize lignocellulosic materials as feed stock for ethanol production. Among all the available plant based biomass, perennial grasses such as switchgrass and miscanthus sp., have enormous potential due to their faster growth and high yield (Fike et al., 2006; Pyter et al., 2008). As the lignocellulosic ethanol industry matures, it is expected that significant quantity of lignin will be generated as byproduct (Hanson et al., 2010).

Additionally, as analyzed by Yan et al., 2010, switchgrass possesses all three *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, which upon oxidation are expected to yield hydroxybenzaldehydes, vanillin, syringaldehyde, and their corresponding acids and ketones depending on the degree of oxidation. At the present time, limited information is available on the technical and economic feasibility of converting lignin derived from switchgrass and miscanthus sp. Hence, research into catalytic oxidation of lignin derived from switchgrass and miscanthus species is recommended.

6.3 Oxidants:

Most of the research on lignin oxidation and cracking has been conducted using molecular oxygen at higher temperature. One proposed approach is to use ozone as an oxidant because it can catalyze selective oxidation even at lower temperatures under certain conditions (Rafelt et al., 2000). Additionally, after the completion of the reaction, oxidants such as ozone can easily be converted into molecular oxygen relatively easily (Quesada et al., 1998). At present catalytic ozonation is being used to oxidize organic compounds in aqueous and gas-phase systems (Legube and Leitner, 1999; Li et al., 2009)**.** But the focus of catalytic ozonation has been on complete oxidation rather than partial oxidation. Considering the size, complexity, and heterogeneity of lignin molecules, it may be possible to selectively control catalytic ozonation to partially crack lignin into smaller, stable, and intermediate products with high economic value; for example, organic acids. Research into technical feasibility of controlled catalytic oxidation of lignin at significantly lower temperature is suggested.

7. Executive Summary:

Lignin

- Biomass-derived-lignin possesses unique structural chemistry and hence can potentially serve as feedstock for production of chemicals and value-added products.

Heterogeneous catalytic oxidation

- Catalytic oxidation offers one of the routes to transforming lignin into intermediate chemicals or chemicals that can further be processed into secondary chemicals.
- Previous research on heterogeneous catalytic oxidation of lignin using transition metal, Perovskite type oxides**,** noble metals, and photo & electrocatalysts resulted in diverse end products.

Future perspective

- For value addition of lignin on an industrial scale, intensive research on evaluating emerging feedstocks, preparing active and selective catalysts, and evaluating novel oxidants is needed.

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CHAPTER 3

SELECTIVE OXIDATION OF LIGNIN INTO AROMATIC ALDEHYDES USING NIOBIUM OXALATE

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***This chapter "SELECTIVE OXIDATION OF LIGNIN INTO AROMATIC ALDEHYDES USING NIOBIUM OXALATE" has been accepted for publication in Transaction of ASABE**

ABSTRACT

There is a strong interest in utilizing lignin as a precursor for synthesis of value-added chemicals such as aromatic aldehydes. Among all the existing processes for converting lignin into aromatic aldehydes, catalytic oxidation appears to be promising. In this research, we explored niobium oxalate as a selective oxidation catalyst and hydrogen peroxide as an oxidant for oxidizing lignin into vanillin and syringaldehyde. Research objectives were to 1) determine the effect of catalyst mass, lignin concentration, and H_2O_2 concentration on synthesis of aromatic aldehydes, (2) study effect of reaction temperature and 3) optimize of the reaction parameters. Batch experiments were performed via central composite design at 95 °C using 4-12 g/100 mL of lignin, 3-7 mL/100 mL of H_2O_2 and 0.5-1.0 g/100 mL of catalyst. Results indicated that under optimum conditions of 3mL of H_2O_2, 0.5 g of catalyst, and 7.26 g of lignin, 65.58 mg g^{-1} of vanillin and 23.12 mg g^{-1} of syringaldehyde were produced. In addition, production of aldehydes showed dependency on temperature in the range of 85ºC-100ºC with 100ºC producing highest product concentrations. It is theorized that perhydroxyl anion (HOO^-), being a strong nucleophile and most active agent in alkaline hydrogen peroxide breaks α and β- aryl ether bonds of lignin to produce corresponding aldehydes. It is suggested that niobium is a potential catalyst for selective oxidation of lignin.

Keywords.

Aldehydes, Catalytic oxidation, Hydrogen Peroxide, Lignin, Niobium oxalate

1. Introduction

Increase in oil demand and depletion of fossil fuels across the globe have led to the exploration of renewable and alternatives sources of energy (Demribas, 2001). Biomass is an important renewable source for the production of fuels, energy, and chemicals. Fuels derived from biomass decrease greenhouse gas emissions and improve local economy (Das et al., 2012). As a result, the United States targeted to produce 30% of transportation fuel and 25% of chemicals from biomass and its derivatives by 2030 (Perlack et al., 2005). The trend is similar in Europe, the Americas, and Asia, where the use of biomass-derived fuels is highly encouraged. Considering this target, several research groups are focused on converting biomass into fuel and chemicals

Currently most of the biomass conversion processes are focused on breakdown of cellulose and hemicelluloses for production of fuels and bio-based products whereas lignin is underutilized (Bozell et al., 2007). Lignin, a cross–linked racemic three dimensional methoxylated phenylpropane structured macromolecule, is a vital component of plant material that binds the cellulose and hemicelluloses together in the lignocellulosic matrix. As a result, it is considered as one of the most abundantly available organic polymers next only to cellulose (Chakar and Ragauskas, 2004; Pearl, 1967). Generally lignin accounts for 15% - 30% by weight and 40% by energy content of biomass. However, only 2% of the lignin from pulp and paper industry is used commercially and around 40 million tons world's lignin is burnt as low-value fuel (Gosselink et al., 2004).

At present, a small portion of high molecular weight lignin is used in carbon fibers, polymer modifiers and adhesives. However, considering its unique chemistry and structure, it is possible to convert lignin into platform chemicals (Zakzeski et al., 2011). Currently available approaches for valorization of lignin are depicted in fig.3.1.

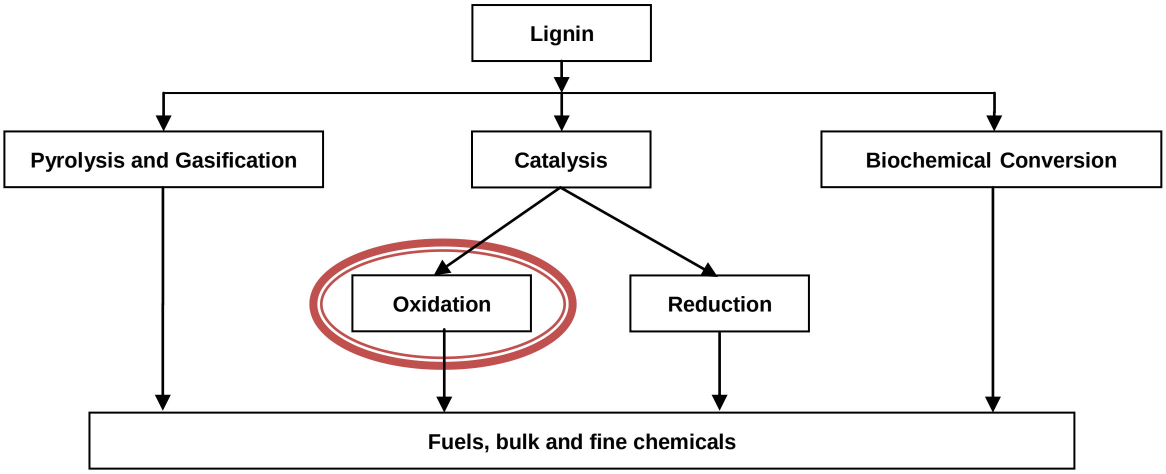

Figure 3.1. Possible pathways for conversion of lignin into fuels and chemicals.

Among all these processes, catalytic oxidation for lignin valorization can produce a wide range of value-added chemicals (Das et al., 2012). Among the available approaches for conversion of lignin into chemicals, oxidative processes for synthesis of aromatic aldehydes are considered to be promising due to ease of operation and the possibility of production of high-value chemicals such as aldehydes. Presently, there is a great demand for aromatic aldehydes and their derivatives in food, cosmetics, and pharmaceutical industries. For example, vanillin produced from lignin is an environmentally friendly product that has widespread application as a flavoring agent in the food industry (Hocking, 1997). Similarly, syringaldehyde is used as a precursor for other fine chemicals in the pharmaceutical industry (Bjorsvik and Liguori, 2002). With the expected increase in worldwide food production and processing, the demand for these aldehydes is expected to increase substantially.

Production of vanillin, aromatic aldehydes, and acids from lignin via alkaline oxidation using O_2 and H_2O_2, with and without catalysts, has been studied by many researchers (Pinto et al., 2011; Sales et al., 2006; Alves et al., 2003; Xiang and Lee, 2001; Bin and Zhu, 2011). Yield of these above mentioned compounds depended on the choice of raw materials, type of catalysts, nature of oxidants, and operational conditions including temperature, pressure, and pH. Most of the prior studies with molecular oxygen employed high temperatures (120ºC – 200ºC), as higher temperatures were needed for activation of oxygen. Along with higher temperature, the process also utilized high pressure which made the process expensive and energy intensive. Hence the goal of this research is to convert lignin into aromatic aldehydes at relatively lower temperatures (85ºC -100ºC) and atmospheric pressure using selective catalytic oxidation. Niobium oxalate is known for its selectivity and to the best of our knowledge it has not been used for lignin oxidation. Therefore we explored niobium oxalate as a catalyst for lignin oxidation. Our objectives were to (1) study the effects of catalyst mass, lignin concentration, and H_2O_2 concentration on synthesis of aromatic aldehydes from lignin, 2) study the effect of reaction temperature and 3) optimize of the reaction parameters.

2. Experimental Methods

2.1 Materials

Solid Niobium oxalate ($C_{10}H_5NbO_{20}$) obtained from Alfa Aesar, Inc., was used as a homogeneous catalyst, while hydrogen peroxide (50% purity, Fisher Scientific, Inc.) was used as an oxidant. Alkaline lignin (Kraft) and methylene chloride (99.99%) were obtained from Tokyo Chemical Industry Inc., and Fisher Scientific, Inc., respectively. Standards for 4-hydroxybenzaldehyde (99%), 4-hydroxy-3-methoxybenzaldehyde (98%) and 4-hydroxy-3,5-dimethoxybenzaldehyde (99%) were procured from Sigma Aldrich.

2.2 Experimental Design

To study the effects of catalyst loading, hydrogen peroxide concentration, and lignin mass on synthesis of aromatic aldehydes (vanillin and syringaldehyde), we employed a central composite design (CCD) approach. The experimental design consisted of 2^3 factorial levels, 2×3 axial levels, and 6 center points. An unreplicated 2×2×2 complete factorial design, with 6 axial points denoted by α and factorial points, coded as +1 and -1 was employed (table 3.1). Levels for these three independent variables, viz., catalyst (X_1), lignin (X_2) and H_2O_2 (X_3) were set in the range of 0.5-1 g, 4-12 g and 3-7 mL, respectively. The data were then fit to the following second order polynomial equation in Eq. (1) (Giesbrecht and Gumpertz, 2004).

$$\hat{Y} = \beta_0 + \sum_{i}^{n} \beta_i x_i + \sum_{ii}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j \qquad (1)$$

where $\hat{Y}$ is the response, β_0 is the intercept, β_i the linear coefficients, β_{ii} the quadratic coefficients, β_{ij} the interaction coefficients and $x_i x_j$ are the coded values.

Table 3.1. Experimental factors and their coded levels of independent variables for central composite design.

Factors	**Code**	**Coded variable levels**				
		-α	-1	0	1	+α
Catalyst (g)	X_1	0.33	0.5	0.75	1	1.17
Lignin (g)	X_2	1.27	4	8	12	14.73
H_2O_2 (mL)	X_3	1.64	3	5	7	8.36

2.3 Batch Experimentation and Analytical Method

Batch experiments for lignin oxidation were performed in a 500-mL three-neck round bottom flask. A 100 mL aliquot of aqueous solution containing predetermined (from the CCD design) amount of lignin, catalyst, and H_2O_2 was added to the round bottom flask and mixed on a hot plate. The reaction mixture was agitated at150 rpm using a magnetic stirrer. The reaction was carried out at 95°C for 60 min and samples were drawn (1.5 mL) every 5 min (fig. 3.2). Subsequently, these samples were mixed with 2 mL of methylene chloride and stored in a refrigerator at 4 °C. Further, the samples were analyzed via a high performance liquid chromatography (HPLC) (Shimadzu, LC-20AT) with a C18 column and ultra-violet (UV) detector (Shimadzu, SPD-20A) set to a wave length of 280 nm (fig. 3.3). Products were separated using elution gradient with acetonitrile and water with formic acid as mobile phase.

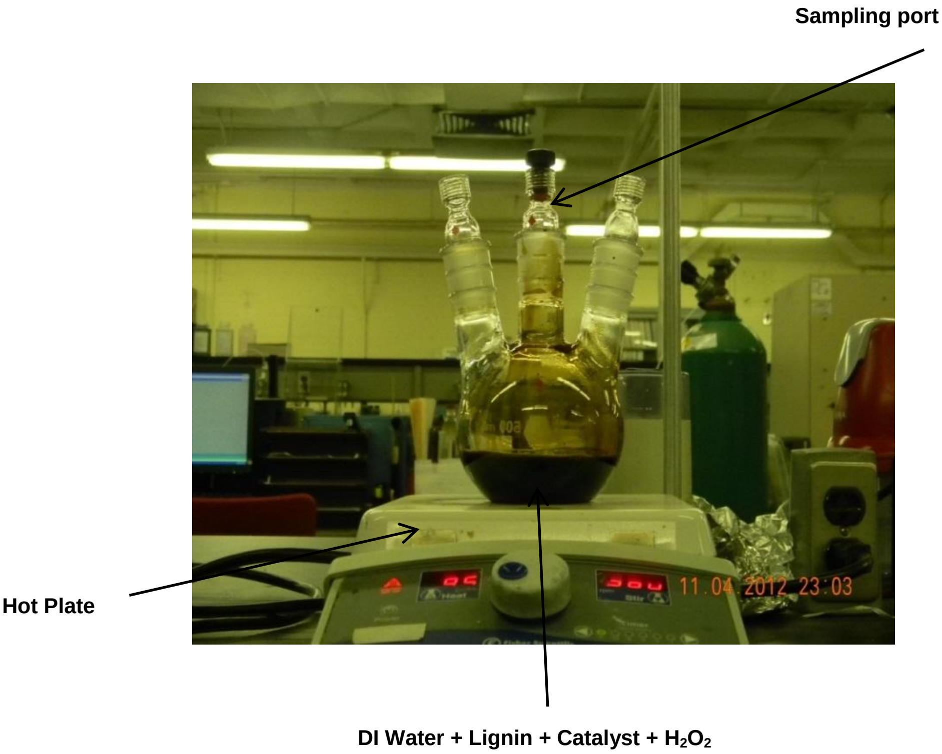

Figure 3.2. Batch experimental setup for oxidation of lignin.

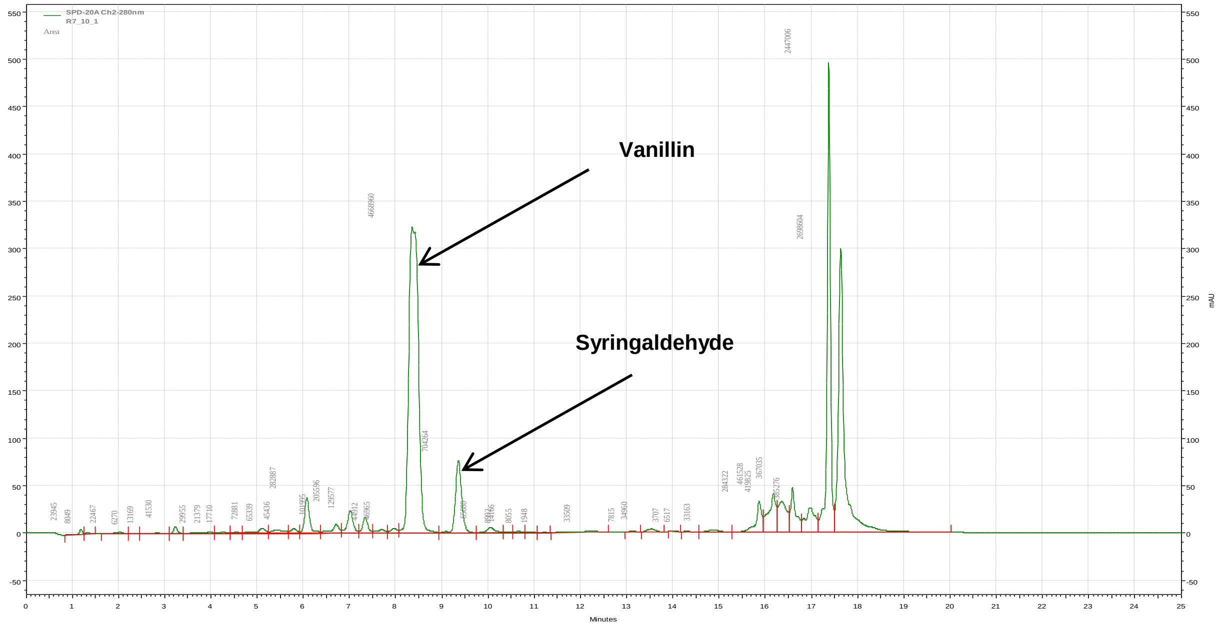

Figure 3.3. Representative chromatogram obtained from HPLC during oxidation of lignin.

3 Results and Discussion

3.1 Development of Model Equation

Results from the batch experiments indicated that concentration of vanillin and syringladehyde was found in the range of 21.56 – 113.34 mg g^{-1} of lignin and 15.13 – 36.97 mg g^{-1} of lignin respectively (table 3.2). In addition, a polynomial model was developed from experimental data collected via central composite design (fig. 3.4) to describe the formation of vanillin and syringaldehyde from lignin using JMP 10.0 (Cary, NC, USA). Suggested quadratic regression models for vanillin and syringaldehyde were as below:

$$\hat{Y}v = 58.957 + 10.626X_1 + 7.849X_2 + 0.472X_3 + 8.382X_1^2 - 6.677X_2^2 - 1.477X_3^2 + 10.801X_1X_2 + 10.256X_1X_3 + 1.331X_2X_3 \quad (2)$$

$$\hat{Y}s = 18.807 + 2.236X_1 + 3.975X_2 + 0.152X_3 + 3.628X_1^2 - 1.642X_2^2 + 0.873X_3^2 + 2.587X_1X_2 + 2.560X_1X_3 - 0.220X_2X_3 \quad (3)$$

where X_1, $X_{2,}$ and X_3 are catalyst, lignin and H_2O_2 respectively. The coefficients with one factor (X_1, X_2, X_3) represent linear effects of each factor, while the coefficients with two factors (X_1X_2, X_1X_3, X_2X_3) and those with second-order terms (X_1^2, X_2^2, X_3^2) represent the interaction between the two factors and quadratic effect respectively.

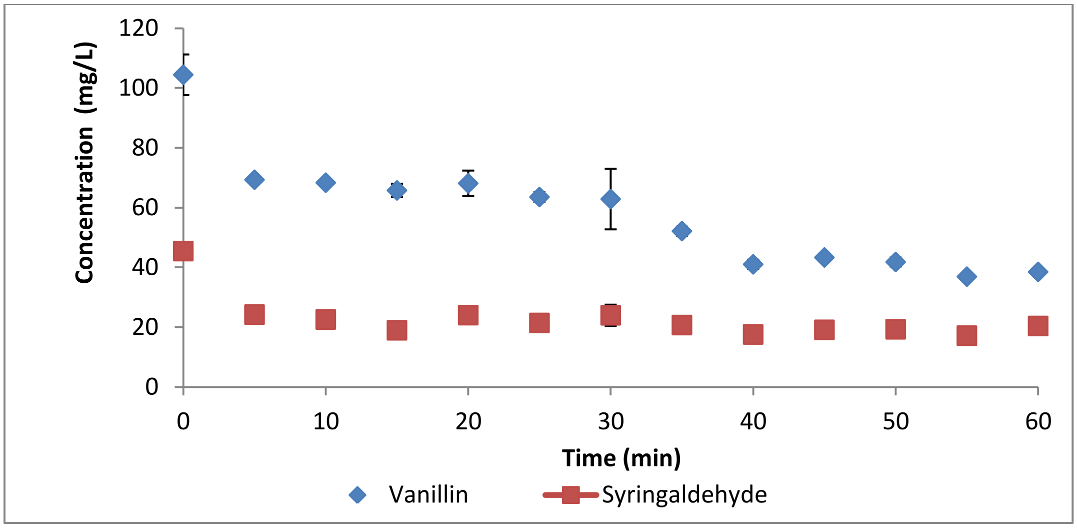

Figure 3.4. Representative plot for oxidation of lignin (Experimental conditions: Lignin - 8 g/100mL, Catalyst - 0.329 g /100mL, and H_2O_2 -5 mL /100mL at 95 ºC)

Table 3.2. Experimental conditions and corresponding concentrations of **V**anillin and **S**yringaldehyde.

*Pattern	Lignin (g)	Catalyst (g)	H_2O_2 (mL)	Vanillin (mg g^{-1})	Syringaldehyde (mg g^{-1})
0a0	8	0.33	5	69.32	24.22
000	8	0.75	5	58.49	18.95
−−−	4	0.5	3	45.86	16.44
+−−	12	0.5	3	52.04	26.03
000	8	0.75	5	58.29	18.57
a00	1.27	0.75	5	25.03	8.40
−+−	4	1	3	45.10	15.29
+−+	12	0.5	7	21.56	15.13
000	8	0.75	5	58.01	18.60
00a	8	0.75	1.64	74.55	24.03
000	8	0.75	5	58.29	18.89
+++	12	1	7	105.03	34.58
−−+	4	0.5	7	57.21	20.19
−++	4	1	7	50.32	15.53
A00	14.73	0.75	5	72.44	22.98
00A	8	0.75	8.36	52.34	21.57
000	8	0.75	5	58.69	18.90
000	8	0.75	5	58.98	18.39
++−	12	1	3	47.33	21.47
0A0	8	1.17	5	113.34	36.97

*Pattern: [a]Range of the factors which is coded as $-\alpha$ in table1 (Lignin-1.27g, Catalyst-0.33g and H_2O_2-1.64mL), [A]Range of the factors which is coded as $+\alpha$ in table1 (Lignin-14.73g, Catalyst-1.17g and H_2O_2-8.36mL), [0]Middle value of the factors which is coded as 0 in table1 (Lignin-8g, Catalyst-0.75g and H_2O_2-5mL), [−]Lower value of the factors which is coded as -1 in table1 (Lignin-4g, Catalyst-0.5g and H_2O_2-3mL) and [+]Higher value of the factors which is coded as 1 in table1 (Lignin-12g, Catalyst-1.0g and H_2O_2-7mL)

3.2 Optimization of Reaction Parameters

Reaction parameters used in this research were optimized using JMP 10.0 (Cary, NC). However a single optimized solution for vanillin and syringaldehyde could not be achieved as the solution obtained was a saddle point. The reason for not achieving a single point solution may be attributed to the narrow range of the independent variable. Among all experimental conditions, only catalyst had significant effect on vanillin production ($p=0.0404$) whereas lignin ($p=0.0036$) and quadratic (catalyst * catalyst) effect of catalyst ($p=0.0053$) had significant effect on syringaldehyde (fig. 3.5). The absence of an optimum solution led to the selection of parameters that provided with a maximum yield of vanillin and syringaldehyde, which was found to be 65.58 mg g^{-1} of lignin and 23.12 mg g^{-1} of lignin, respectively, at H_2O_2 concentration of 3 mL, catalyst loading of 0.5 g and 7.26 g of lignin in 100 mL of solution.

3.3 Effect of H_2O_2

Fig. 3.5 C & D illustrate the effects of H_2O_2 and lignin on vanillin and syringaldehyde, while Fig. 3.5 E & F demonstrate the effects of H_2O_2 and catalyst on syringaldehyde and vanillin production. From the figures as well as ANOVA (table 3.3 & 3.4) it is evident that H_2O_2 did not have any significant effect ($p= 0.9188$ and $p= 0.8877$). Similar results were reported by Xiang and Lee (Xiang and Lee, 2000) who found that doubling the concentration of hydrogen peroxide has minor effect on the production of aromatic aldehydes and their corresponding acids. It was suggested that hydrogen peroxide, being a very weak acid, dissociates to hydroxyl radicals and super oxide ions under alkaline condition (Agnemo et al., 1979), and most of hydrogen peroxide was perhaps decomposed without reacting with lignin. It may also be possible that hydroxyl radicals and superoxide ions produced during the reaction were inactive at 85-95ºC for degradation of lignin. Additionally, lack of hydrogen peroxide activating agents such as acetic acid or formic acid or metalloporphyrins in the reaction mixture may have negatively impacted degradation of lignin.

Table 3.3. ANOVA and lack of fit test for Vanillin

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**	**Prob > F**
Model	9	6047.939	671.993	2.414	0.093
Error	10	2783.260	278.326		
C. Total	19	8831.199			
Lack Of Fit	5	2782.677	556.535	4767.945	<.0001*
Pure Error	5	0.584	0.117		
Total Error	10	2783.260			

Parameter Estimates

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	58.957	6.804176	8.66	<.0001*
Lignin(4,12)	7.8485	4.514416	1.74	0.1127
Catalyst(0.5,1)	10.626	4.514416	2.35	0.0404*
H_2O_2(3,7)	0.472	4.514416	0.10	0.9188
Lignin*Catalyst	10.802	5.898369	1.83	0.0970
Lignin* H_2O_2	1.331	5.898369	0.23	0.8260
Catalyst* H_2O_2	10.256	5.898369	1.74	0.1127
Lignin*Lignin	-6.677	4.394662	-1.52	0.1596
Catalyst*Catalyst	8.382	4.394662	1.91	0.0856
H_2O_2* H_2O_2	-1.477	4.394662	-0.34	0.7437

Table 3.4. ANOVA and lack of fit test for Syringaldehyde

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**	**Prob > F**
Model	9	645.823	71.7581	4.7661	0.0114*
Error	10	150.559	15.0559		
C. Total	19	796.382			
Lack Of Fit	5	150.296	30.0592	572.4192	<.0001*
Pure Error	5	0.262	0.0525		
Total Error	10	150.559			

Parameter Estimates

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	18.807102	1.582529	11.88	<.0001*
Lignin(4,12)	3.9749007	1.049972	3.79	0.0036*
Catalyst(0.5,1)	2.2356682	1.049972	2.13	0.0591
H_2O_2 (3,7)	0.1520408	1.049972	0.14	0.8877
Lignin*Catalyst	2.5873625	1.371855	1.89	0.0886
Lignin* H_2O_2	-0.220212	1.371855	-0.16	0.8757
Catalyst* H_2O_2	2.5604125	1.371855	1.87	0.0915
Lignin*Lignin	-1.642081	1.022119	-1.61	0.1392
Catalyst*Catalyst	3.6278446	1.022119	3.55	0.0053*
H_2O_2* H_2O_2	0.8728859	1.022119	0.85	0.4131

3.4 Effect of Lignin Concentration

Combined effects of catalyst mass and H_2O_2 on lignin concentration for production of vanillin and syringaldehyde are illustrated in Fig. 3.5 A, B, C, D. It appears that vanillin formation is independent of lignin (p=0.1127) concentration whereas lignin concentration has significant (p=0.0036) effect on syringaldehyde production. Similar results were reported by Pinto *et al.* (Pinto et al., 2012) using O_2 as oxidant where the authors observed a decrease in vanillin yield from 10% to 3% as they increased lignin concentration from 30-120 g L^{-1}.

Lignin used in this research was softwood kraft lignin which primarily contained guaiacyl (G) units and hence enhanced production of vanillin (65.58 mg g^{-1} lignin) when compared to syringaldehyde (23.12 mg g^{-1} of lignin).

3.5 Effect of Catalyst Loading

Fig. 3.5 A & B depict effects of catalyst and lignin on vanillin and syringaldehyde formation whereas Fig.3.5 E & F illustrate combined effect of H_2O_2 and catalyst on syringaldehyde and vanillin production. Catalyst loading had a significant ($p=0.0404$) effect on production of vanillin and catalyst*catalyst has significant ($p=0.0053$) effect on syringaldehyde in the range of 0.5-1.0 g. With increase in catalyst loading it appeared that more active sites became available for reactions, which perhaps further reacted with products (aldehydes) to form corresponding acids and eventually to carbon dioxide and water.

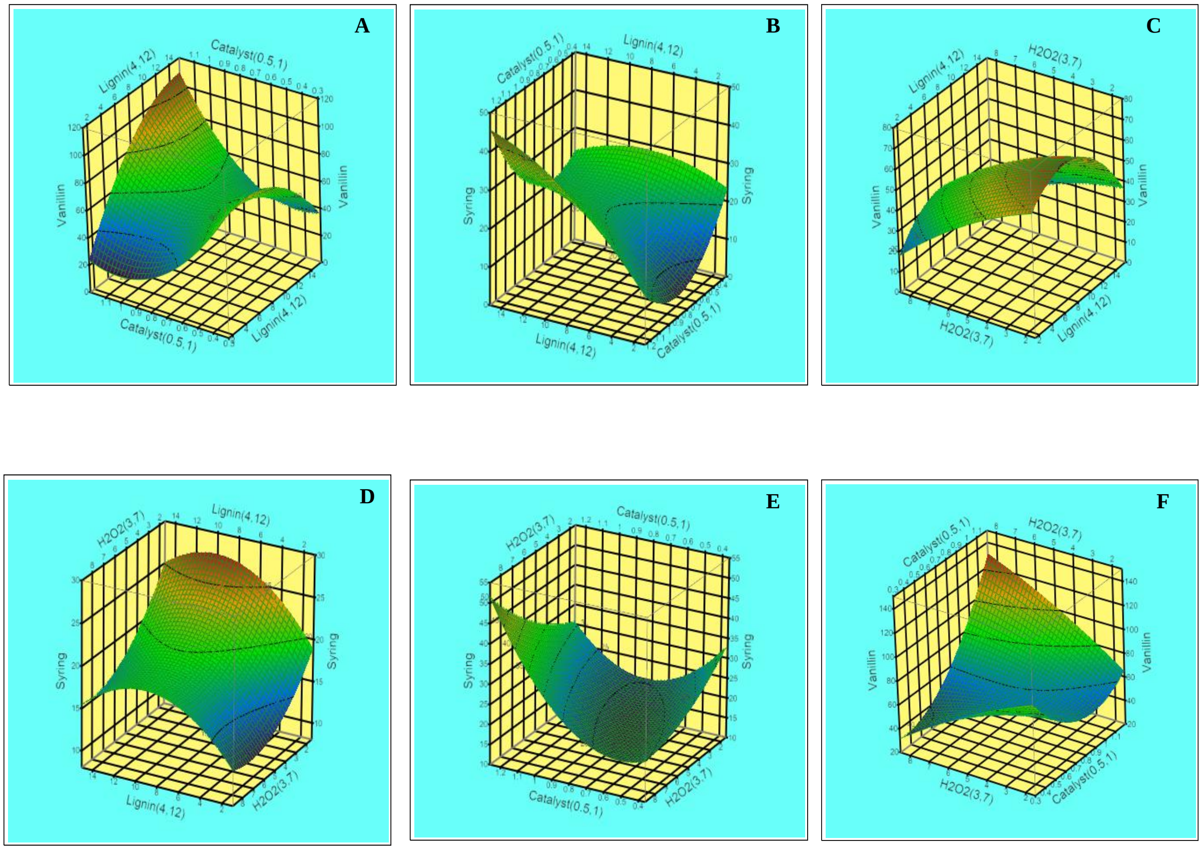

Figure 3.5. Surface response plots describing the effects of (A) & (B) Catalyst and Lignin (C) & (D) H_2O_2 and Lignin (E) & (F) H_2O_2 and Catalyst on Vanillin and Syringaldehyde.

3.6 Effect of Reaction Temperature

Additional experiments were performed (based on the optimal conditions for the CCD design to investigate the effect of temperature on production of vanillin and syringaldehyde. Briefly, 7.26 g of lignin, 0.5 g of catalyst and 3 mL of H_2O_2 in a 100 mL of aqueous solution were allowed to react at temperatures 85, 95 and 100 ºC in the three-neck flask. These experiments were performed for 5 min and aliquots were drawn every 1 min, samples were analyzed by HPLC as explained previously. A multiple comparison (Duncan) test was performed on the effect of temperature using SAS 9.3 (Cary, N.C. USA).

Figures 3.6 and 3.7 illustrate the production of vanillin and syringaldehyde respectively, which, indicated that the yields of vanillin and syringaldehyde at 100ºC were significantly (p=0.001) different from the other two temperatures**.** One possible reason for low production of aldehydes at temperatures 85ºC-95ºC could be formation of hydroxyl radicals and superoxide ions during disintegration of hydrogen peroxide, which probably were not very active. Similar results were reported by Xiang and Lee (Xiang and Lee, 2000) and Pinto *et al.* (Pinto et al., 2012) where they observed higher yields of aldehydes but at the same time these aldehydes were vulnerable to rapid degradation as well.

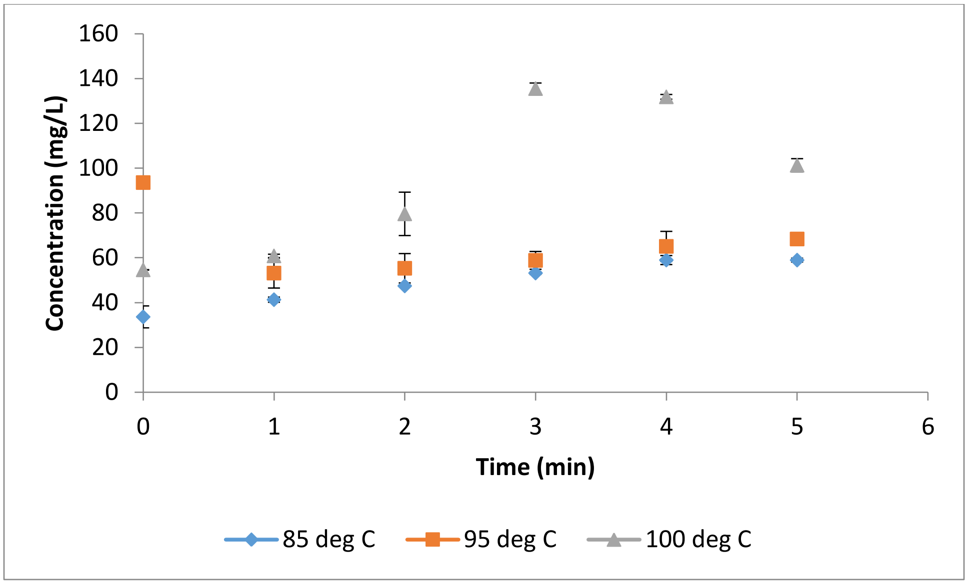

Figure 3.6. Effect of temperature on Vanillin production from lignin (Experimental conditions: Lignin - 7.26 g/100mL, Catalyst - 0.5 g /100mL, and H_2O_2 - 3 mL /100mL)

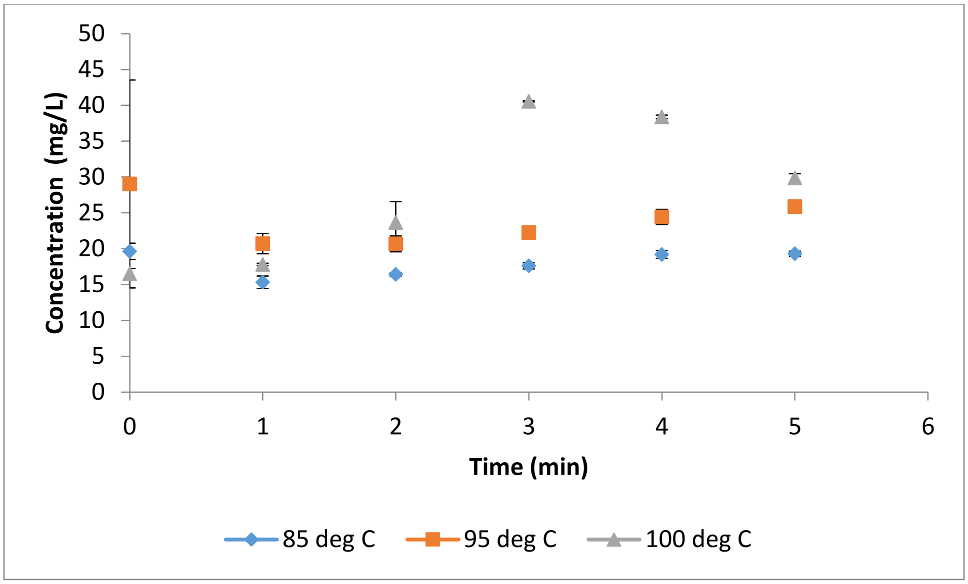

Figure 3.7. Effect of temperature on Syringaldehyde production from lignin (Experimental conditions: Lignin - 7.26 g/100mL, Catalyst - 0.5 g /100mL, and H_2O_2 - 3 mL /100mL)

3.7 Plausible Lignin Oxidation Mechanism

Based on the results from this study and previous literature available on reaction between hydrogen peroxide with model and real lignins, we propose a possible reaction mechanism that corroborates with earlier studies. Lignin used in this study produced higher amount of vanillin than syringaldehyde; this is expected given the source of the lignin is from softwood and overall lower yields of aldehydes implied that the lignin was from conifers (Taraban'ko et al., 1995). Yield of phenolics from lignin is dependent on its structure which is actually influenced by the source of lignin, pulping, and recovery processes (Villar et al., 2001; Va´zquez et al., 1997; Robert et al., 1984). Wood pulping is an intensive process which leads to the alteration of inter-unit linkages and frequency of functional groups of lignin that facilitates formation of phenolic aldehydes when further treated under oxidizing agents (Gellerstedt and Gustafsson, 1987).

Under alkaline conditions, hydrogen peroxide dissociates into hydroxyl radicals and superoxide ions, and may react with each other or with hydrogen peroxide resulting in oxygen and water as final products according to equation (4 and 5) (Agnemo et al., 1979). Decomposition of hydrogen peroxide occurs through disproportionation reaction which attains its maximum rate at the pH of its pKa (11.6) (Agnemo and Gellerstedt, 1979)

$$\mathrm{H_2O_2} + \mathrm{HO_2^-} \rightarrow \mathrm{HO^{\cdot}} + \mathrm{O_2^{\cdot}}^- + \mathrm{H_2O} \qquad (4)$$

$$\mathrm{H_2O_2} + \mathrm{OH^-} \rightarrow \mathrm{H_2O} + \mathrm{HOO^-} \qquad (5)$$

Hydrogen peroxide by itself does not react with lignin. But the decomposed products from hydrogen peroxide react with lignin. Perhydroxyl anion ($\mathrm{HOO^-}$) being a strong nucleophile and most active agent in alkaline hydrogen peroxide breaks α and β-aryl ether bonds of lignin to produce corresponding benzaldehydes which are susceptible to subsequent oxidation (Kadla and Chang, 2001) (fig. 3.8). In this study we observed very low amount of aldehydes produced as compared to other studies which may be due to either over oxidation of aldehydes by hydrogen peroxide leading to formation of carbon dioxide and water or due to strong condensation degree (C-C linkages) of lignin which probably suppressed production of monomers.

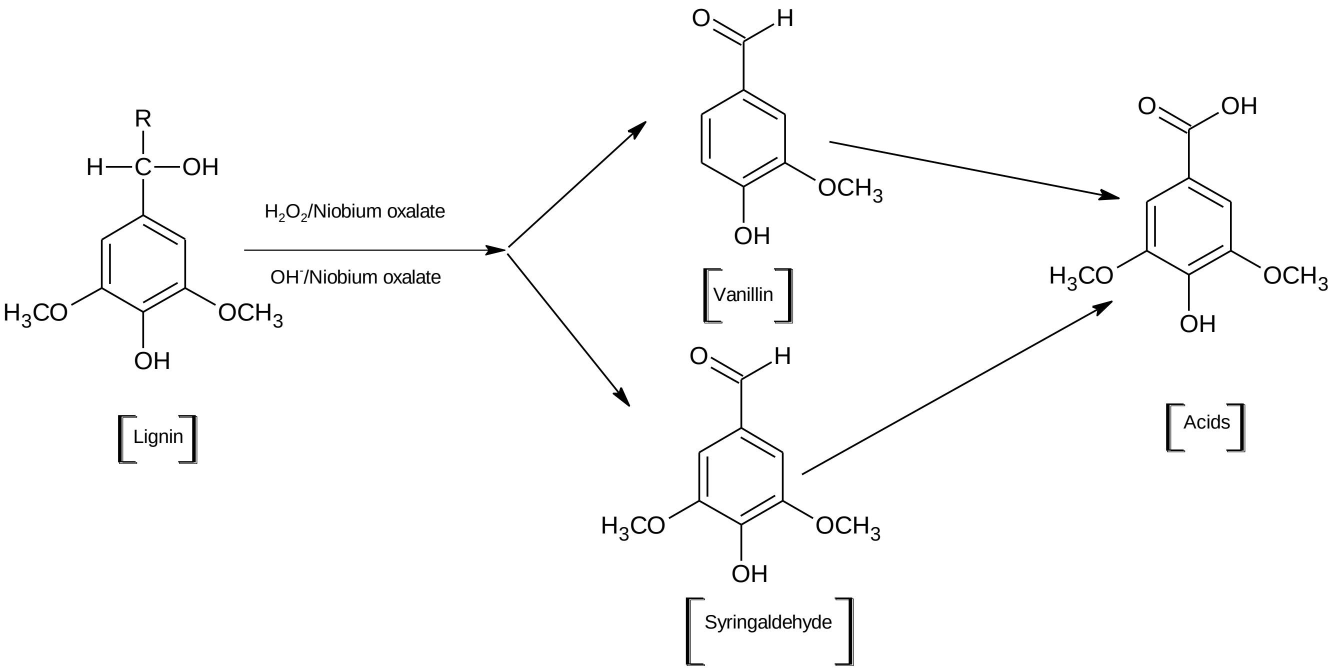

Figure 3.8. Proposed oxidation reaction steps under alkaline condition.

3.8 Future Direction

Our study focused on oxidation of lignin to aromatic aldehydes using a homogeneous niobium oxalate catalyst by studying the effects of catalyst, oxidant, and lignin loadings. Current findings from this study indicated that aldehydes produced are being over oxidized perhaps due to abundance of niobium ions in the reaction solution. Hence efforts are underway to synthesize a heterogeneous catalyst by depositing niobium on inert supports such as activated carbon and alumina. It is expected that such heterogeneous catalysts will be more selective, provide higher yields, and facilitate catalyst reusability. It is also noted that agitation of reaction mixture may play a role in the yield of products by minimizing mass transfer limitations. Therefore additional studies are underway to determine the effect of mixing on the yield of vanillin and syringaldehyde.

4 Conclusion

Based on the experimental data following inferences may be drawn:

- As hypothesized, niobium oxalate was selective in degrading lignin to vanillin and syringaldehyde and trace amounts of acids.
- Catalyst had significant effect on vanillin production (p=0.0404) whereas lignin (p=0.0036) and catalyst (p=0.0053) had significant effect on syringaldehyde formation. Formation of products was not affected by concentration of H_2O_2 in the reaction.
- Maximum production of vanillin and syringaldehyde (65.58 mg g^{-1} of lignin 23.12 mg g^{-1} of lignin) are expected to be obtained at 3 mL H_2O_2, 0.5 g catalyst loading, and 7.26 g/100 mL lignin.
- Temperature had substantial impact on oxidation of lignin. Maximum product concentrations were produced at 100ºC which indicated higher activity of hydroxyl radicals and superoxide ions.
- Further investigations on (1) depositing niobium on inert supports to enhance selectivity of desired products and (2) effect of mixing are underway.

Acknowledgement

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CHAPTER FOUR

OXIDATIVE CONVERSION OF LIGNIN USING NIOBIUM OXIDE

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Abstract

There is a significant interest in valorization of lignin into chemicals. In this research, niobium oxide was tested as a catalyst for partial oxidation of lignin. Research objectives were to: 1) study the effect of temperature and catalyst loading on synthesis of aromatics from lignin, 2) study the effect of oxidants and rate of mixing on lignin oxidation, and 3) determine the reaction kinetics. Batch experiments were performed via a factorial design with catalyst loading (0.1-0.3 g) and temperature (70-90 °C) as two factors. Results indicated that under optimal conditions of temperature of 90 °C, and catalyst loading of 0.5 g, 137.194 mg L^{-1} of vanillin and 30.290 mg L^{-1} of acetovanillone were produced. Oxidant type was found have a significant effect for vanillin production but not for acetovanillone. In addition, production of both vanillin and acetovanillone were independent of mixing. It is theorized that formation of aceto derivatives and vanillin under alkaline conditions were due to retroaldol cleavage of the α-hydroxy-γ-carbonyl structure of the lignin.

Keywords.

Vanillin, Catalytic oxidation, Lattice oxygen, Lignin, Niobium oxide

1. Introduction

The depletion of fossil fuel reserves and increasing concern over global warming due to emission of greenhouse gases have led to the investigation of renewable and cleaner alternative energy sources (Corma et al., 2007). Lignocellulosic biomass being the world's most abundant feedstock has promising characteristics to be the sustainable alternative for fuel and chemical production (Demribas, 2001, Ragauskas et al., 2014). Lignocellulosic biomass consists of cellulose, hemicellulose, and lignin which are bonded together to form a rigid complex matrix. In recent years production of bio-ethanol from cellulose and hemicellulose is becoming increasingly important, leaving aside lignin as a waste product. Lignin accounts for 15 -30% by weight and 40% by energy content of biomass (Gosselink et al., 2004). The U.S. energy security and independence act of 2007 mandates annual production of 79 billion liters of second generation biofuels by 2022. In light of these projections, the U.S. alone is expected to produce 62 million tons of lignin (Ragauskas et al., 2014).

Lignin is the second most abundant terrestrial polymer after cellulose which consists of highly branched (600-15000 kDa) methoxylated phenylpropane units (Kleinert and Barth, 2008). It is made of three monomers, namely, *p*-coumaryl (H), coniferyl (G), and sinapyl (S) alcohols which vary depending on the plant species. Lignin content in soft woods is 25-35% dry weight whereas in hardwoods it is 18-25% (Araujo et al., 2010).

Presently, lignin is still an underutilized feedstock for synthesis of fuels and chemicals. The major reasons for this are: i) lignin's structural stability makes it difficult to break down to desired products, ii) degradation of lignin generates very high amount of sulfur residues,

iii) readily available petroleum derived monomers for production value-added chemicals. Despite these adversities, over the years several researches have focused on depolymerization of lignin. Various methods have been reported for production of phenols from lignin, such as hydrolysis, hydrogenolysis, pyrolysis, catalytic oxidation, catalytic reduction and biochemical conversion. Due to presence of hydroxyl groups in lignin, catalytic oxidation is a suitable process for formation of valued chemicals (Xiang and Lee, 2000). The oxidation of lignin produces a wide range of chemicals from aromatic aldehydes to aromatic acids depending on the process parameters (Xiang and Lee, 2001). Fargues et al., 1996 investigated production of vanillin from kraft lignin at 130 ºC, an oxygen partial pressure of 3 bar, and a total pressure of 9 bar. In a separate study, Sales et al., 2006 used palladium catalyst supported on γ-alumina for production of syringaldehyde, p-hydroxybenzaldehyde and vanillin from 60 kg m^{-3} lignin of sugarcane bagasse via oxidation at 100-136 ºC, total pressure 20 bar, partial pressure of O_2 2-10 bar, and 2 mol L^{-1} NaOH. Deng et al., 2008 reported successful testing of perovskite-type oxide $LaMnO_3$ via wet aerobic oxidation. They reported formation of syringaldehyde, p-hydroxybenzaldehyde and vanillin at 120 ^{o}C, and 15-20 bar total pressure.

One of the most important aspects of partial oxidation of organic molecules including lignin is the choice of catalyst. Since the goal is to minimize secondary oxidation reactions that result in intermediate products, the catalyst should be selective. In addition, it should possess a low to medium surface area to discourage the adsorption and retention of intermediate products on the catalyst’s surface which tend to get oxidized further.

One such potential selective oxidation catalyst is niobium oxide (Nb_2O_5). Niobium oxide (a) is stable and can form strong metal support interaction (Wachs et al., 2000; Ziolek, 2003) (b) possesses higher number of specific surface active sites, and c) exhibits much higher Tamman temperature thereby making the surface more suitable for liquid phase reactions. Niobium oxide has been used as a catalyst in several reactions including oxidative dehydrogenation of alkanes, oxidative coupling of methane, oxidation and ammoxidation, hydrogenation, esterification, and hydrolysis (Tanabe, 2003). However, to the best of our knowledge its potential has not been investigated for lignin oxidation. Considering the chemistry of niobium oxide, we hypothesize that niobium oxide can catalyze oxidation of lignin. Hence the goal of this research is to investigate the efficacy of niobium oxide as a selective oxidation catalyst for lignin oxidation. Specific objectives were to (1) study the effect of temperature and catalyst loading on oxidation of lignin and product formation, (2) investigate the effect of oxidants and mixing on product formation, and (3) determine the kinetics of the reaction.

2. Experimental Methods

2.1. Materials

Niobium oxide (Nb_2O_5) (99.3% metal basis) obtained from Alfa Aesar, Inc., was used as a catalyst. Alkaline lignin (Kraft) and methylene chloride (99.99%) were obtained from Tokyo Chemical Industry Inc., and Fisher Scientific, Inc., respectively. Standards for 4-hydroxy-3-methoxybenzaldehyde (99%) and 4-Hydroxy-3-methoxyacetophenone (98%)

were procured from Acros Organics, while hydrogen peroxide (50% v/v) and $KMNO_4$ (99.3%) were obtained from Fisher Scientific.

2.2. Batch experiments and analytical method

Degradation of lignin was carried out in a 500-mL three-neck round bottom flask. A 100 mL aliquot of aqueous solution containing 8 g 100 mL^{-1} of lignin, and a predetermined amount of catalyst were mixed on a hot plate with predesigned temperatures. The mixture was agitated at150 rpm using a magnetic stirrer. The reaction was carried out for 120 min and samples (1.5 mL) were drawn every 20 min. Subsequently, these samples were mixed with 2.5 mL of methylene chloride and stored in a refrigerator at 4 °C. The samples were further analyzed via a gas chromatograph equipped with a mass selective detector (GC-MS) (Agilent Technologies, 7890 A) and a DB-5 MS UI column (30 m x 0.25 mm x 0.25μm) using Helium as a carrier gas. Data was acquired using an oven temperature of 100 °C (2 min hold time) with ramping to 200° C @ 15° C min^{-1} (2 min hold time) and 200° C with ramping to 270° C @ 10° C min^{-1} (2 min hold time) with a split ratio of 150:1 (1.2 mL min^{-1}) The injector and detector were maintained at 300° C.

2.3. Experimental design and statistical analysis

To study the effects of catalyst loading and temperature on formation of products, we employed a 3^2 factorial design with three center points. Levels for these two experimental factors, catalyst (X_1), and temperature (X_2) were set in the range of 0.1-0.5 g and 70-90 °C, respectively. Center points were included to enable estimation of experimental error variance and experimental sequence was randomized to minimize the effects of uncontrolled errors.

2.4. Depolymerization of Lignin

Lignin depolymerization analysis was carried via batch experiments. Lignin used in this study was found to be sulfite lignin. Similar lignin was used by Yoshikawa et al., (2014) and the monomer associated with this lignin was found to be 2-methoxy-4-(2,3-dihydorxy-1-sulfo)-propylphenol. The recovery of vanillin was determined by using the following equation (Yoshikawa et al. 2014):

$$Recovery\ \%\ of\ vanillin = \frac{mols\ of\ aromatic\ ring\ in\ vanillin\ produced}{mols\ of\ aromatic\ ring\ in\ lignin} \times 100 \quad (1)$$

Moles of aromatic ring in vanillin produced and moles of aromatic ring in lignin were estimated using equations 2 & 3.

$$Moles\ of\ aromatic\ ring\ in\ vanillin\ produced$$
$$= \frac{Carbon\ mol\ of\ the\ produced\ vanillin}{Carbon\ numbers\ in\ a\ unit\ molecule\ of\ vanillin} \qquad (2)$$

$$Moles\ of\ aromatic\ ring\ in\ lignin$$
$$= \frac{Weight\ of\ lignin\ used\ in\ the\ batch\ experiment}{Molecular\ weight\ of\ the\ constituent\ lignin\ monomer} \qquad (3)$$

2.5 Effect of Oxidants

Additional experiments were performed to investigate the effect of various oxidants including H_2O_2 and $KMnO_4$ on degradation of lignin. Based on the optimal conditions obtained by the factorial design, temperature 90 ºC and catalyst loading 0.5 g were allowed to react with 1mL 100 mL^{-1} of H_2O_2 and 1mL 100 mL^{-1} of $KMnO_4$ separately in the three-neck flask. A multiple comparison (Tukey) test was performed on the effect of oxidants using SAS 9.4 (Cary, N.C. USA).

2.6 Rate of Mixing

In addition to the effect of oxidants, additional experiments were performed to investigate the effect of mixing on degradation of lignin. Based on the optimal conditions identified from results of the factorial design study, a temperature of 90 ºC and a catalyst loading of 0.5 g were mixed at 50, 150, and 250 rpm to determine role of mixing. Separate experiments were also performed separately without mixing to serve as control.. Batch experiments and sample analyses were similar to those mentioned in previous sections. A multiple comparison (Tukey) test was performed on the effect of mixing using SAS 9.4 (Cary, N.C. USA).

3. Results and Discussion

3.1. Product analysis

Products obtained via catalytic oxidation of lignin were determined via a gas chromatograph. As shown in Figure 4.1, vanillin (A) and acetovanillone (B) were main products obtained as a result of oxidation of lignin. Concentration of vanillin and acetovanillone were in the range of 11.50 – 137.19 mg L^{-1} and 1.49– 30.29 mg L^{-1} respectively (Table 4.1). Catalyst loading (niobium oxide) had a significant effect ($p=0.0288$) on vanillin production, whereas vanillin production was found to be plausibly independent of reaction temperature ($p=0.507$). For production of acetovanillone both reaction temperature and catalyst loading were not significant. Analysis using JMP 10.0 (Cary, NC, USA) suggested that optimum levels for reaction conditions were temperature 90 °C and a catalyst loading of 0.5 g corresponding with predicted yields of 136.75 mg L^{-1} with 95% confidence interval (C.I of [75.29 mg L^{-1}, 198.22 mg L^{-1}]) and 25.09 mg L^{-1} with 95% C.I of [8.23 mg L^{-1}, 41.96 mg L^{-1}] for vanillin and acetovanillone, respectively. Additionally, recovery of vanillin (as determined by using equations 1, 2, 3) under optimum conditions was 0.02%.

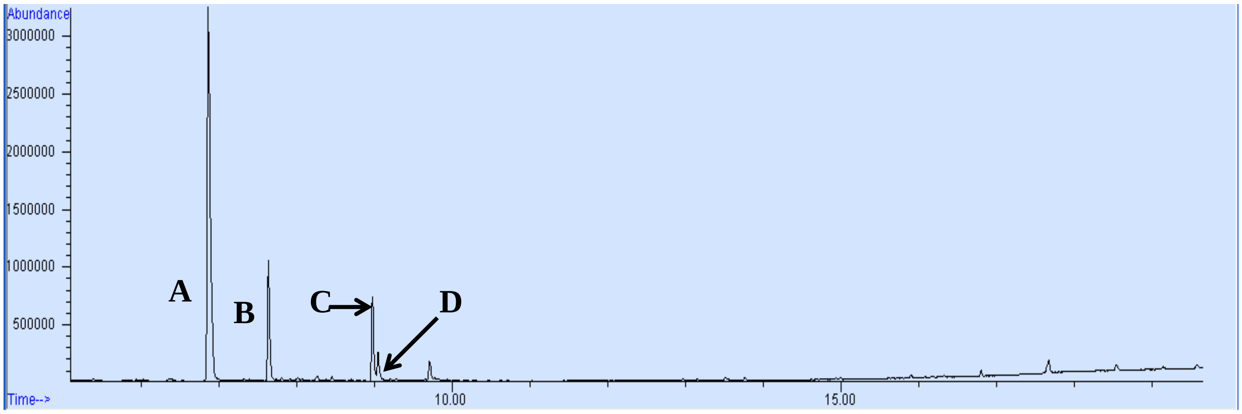

Figure 4.1: Products identified by gas chromatogram via catalytic oxidation (A) 4-hydroxy-3-methoxybenzaldehyde, (B) 1-(4-hydroxy-3-methoxyphenyl)-ethanone, (C) 4-hydroxy-3-methoxy benzenacetic acid, (D) 4-hydroxy-3,5-dimethoxybenzaldehyde

Table 4.1: Experimental conditions and corresponding observed and predicted concentrations of vanillin and acetovanillone

Pattern	**Temp (°C)**	**Catalyst (g)**	**Vanillin (mg L^{-1})**	**Acetovanillone (mg L^{-1})**	**Predicted Vanillin (mg L^{-1})**	**Predicted Acetovanillone (mg L^{-1})**
32	90	0.3	22.169	1.487	78.835	14.259
31	90	0.1	11.500	2.247	20.913	3.420
21	80	0.1	51.208	6.760	34.136	6.799
11	70	0.1	22.616	4.361	47.358	10.179
23	80	0.5	102.411	5.406	105.038	18.175
12	70	0.3	34.331	7.233	60.338	10.716
13	70	0.5	58.426	11.800	73.318	11.253
00	80	0.3	99.991	17.417	69.587	12.487
22	80	0.3	99.487	21.901	69.587	12.487
00	80	0.3	98.535	20.694	69.587	12.487
00	80	0.3	97.171	20.253	69.587	12.487
33	90	0.5	137.194	30.290	136.757	25.098

3.2. Effect of Catalyst Loading

Figures 4.2 A & B illustrate the effects of catalyst loading and reaction temperature on vanillin and acetovanillone formation. Catalyst loading had a significant (p=0.0288) effect on production of vanillin, whereas production of acetovanillone is independent (p=0.158) of catalyst loading in the range of 0.1-0.5 g. With an increase in catalyst loading, concentration of vanillin increased, Plausible explanation for this increase in vanillin concentration may be due to i) formation of more active sites containing lattice oxygen. ii) moderate metal-oxygen (M-O) bond strength, which favors partial oxidation of lignin, and iii) availability of spatially isolated reactive surface lattice oxygen for selective conversion lignin to vanillin. Similar results were reported by Wu et al., (1994), who tested $CuSO_4$ and $FeCl_3$ with molecular oxygen for catalytic oxidation of steam exploded hard wood lignin at 170 °C. The authors reported that increase in catalyst loading from 0-0.5 g increased the yield of vanillin by 0.4% but decreased the yield of total aldehyde. In another study Villar et al., (2001) investigated $CuSO_4$, $CoCl_2$, and Co(II) salen in the presence of oxygen for oxidation of hard wood kraft lignin in alkaline medium. The authors also observed that increase in copper (II) and cobalt (II) loading did not increase aldehyde yield, due to subsequent oxidation of aldehydes into lower molecular weight products (acids).

3.3. Effect of Temperature

Figures 4.2 A & B illustrate the effects of catalyst loading and reaction temperature on vanillin and acetovanillone formation. The effect of temperature on yields of vanillin and acetovanillone was not significant ($p=0.507$, $p=0.641$) in the range of 70-90 °C. The reason for low production of vanillin may be due to i) inactiveness of the catalyst at lower temperature (<100 ºC), ii) vanillin concentration being close to the equilibrium, i.e., formation of subsequent vanillin leading to degradation to carbon dioxide and water. Our results were somewhat different from those reported by Pinto et al. (2012) and Pacek et al., (2013) where the authors observed increased yields of aldehydes with increase in reaction temperature but at the same time overall yield of these aldehyde were low as they were vulnerable to rapid degradation as well.

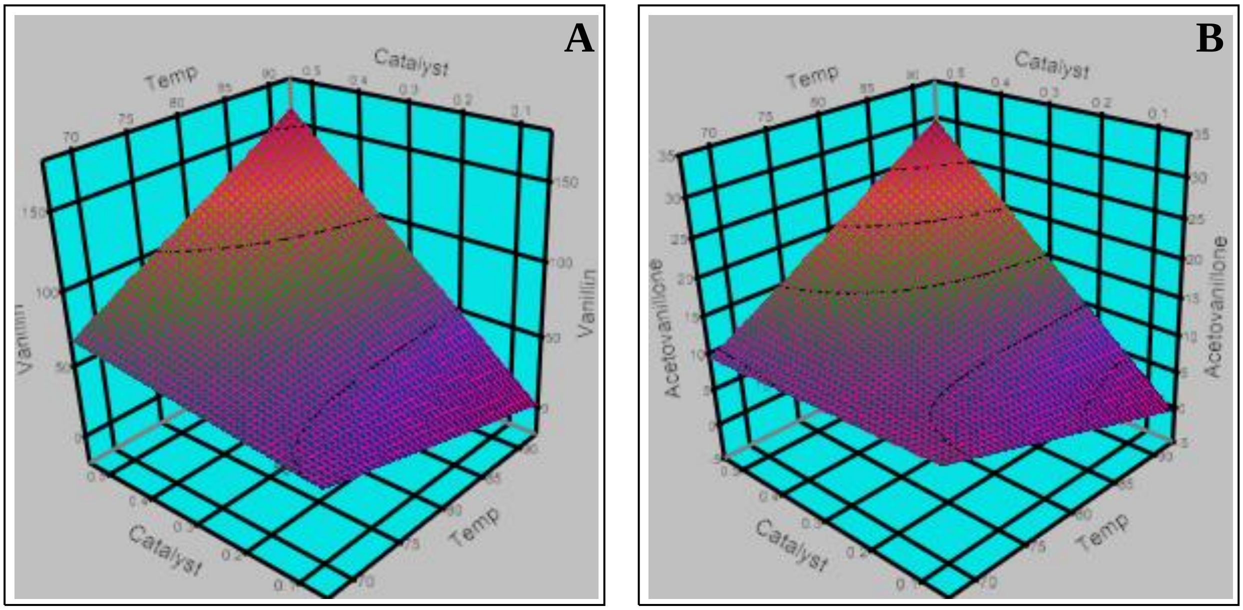

Figure 4.2: Surface response plots describing the effects of catalyst loading and reaction temperature on (A) Vanillin and (B) Acetovanillone.

3.4. Effect of Oxidants

Figures 4.3 A&B illustrate the effect of oxidants on production of vanillin and acetovanillone respectively. Analysis of data using Tukey's test suggested that for production of vanillin without an added oxidant (only niobium oxide) was significantly (p=0.0124) different from H_2O_2, but was not significantly different from $KMnO_4$ (p=0.2787). However, it appeared that for production of acetovanillone there was no significant difference between the oxidants when compared to the niobium oxide (no oxidant) catalyst.

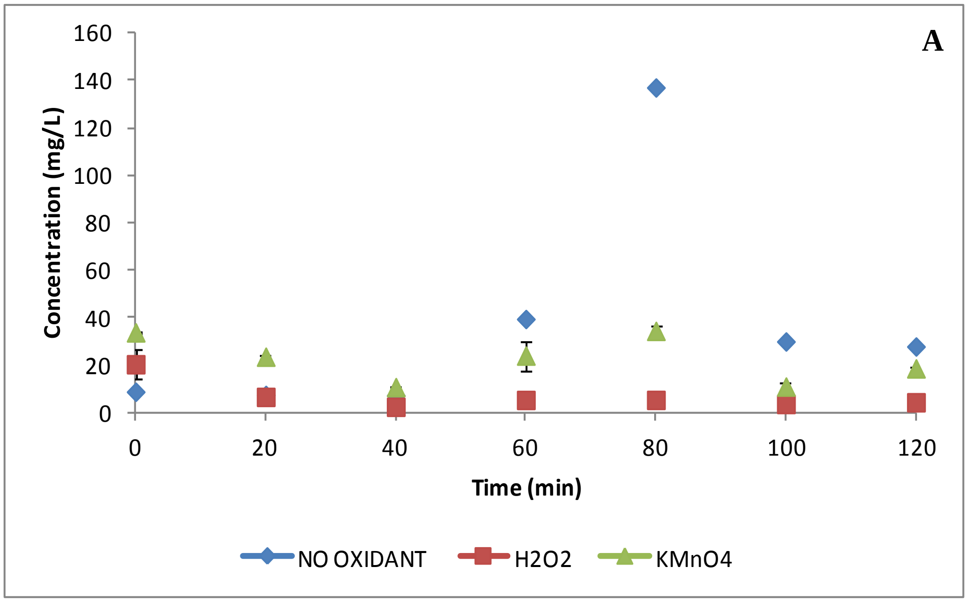

Figure 4.3A. Effect of oxidant on vanillin production from lignin (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 0.5 g 100 mL^{-1}, and temperature 90 ^{o}C)

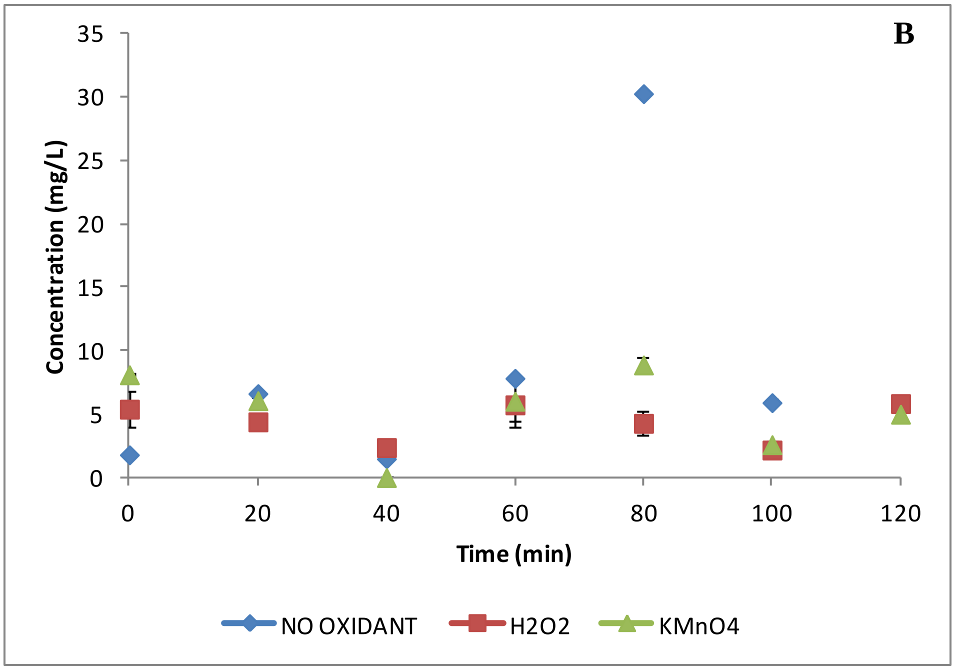

Figure 4.3B. Effect of oxidant on acetovanillone production from lignin (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 0.5 g 100 mL^{-1}, and temperature 90 ^{o}C)

When only niobium oxide was present in the batch reactor (no oxidant) the system yielded maximum product concentration due to reaction of lattice oxygen with lignin. Callahan and Grassellie, (1963) proposed that lattice oxygen from a reducible metal oxide acts as a more selective oxidizing agent than gaseous oxygen. Further the authors explained that lattice oxygen reacts with the reactant by creating an anion vacancy at the surface of the solid metal oxide. This vacancy is filled by the migration of surrounding lattice oxygen and subsequent reoxidation of the solid metal oxide by oxygen from the gaseous phase to complete the cyclic reaction and bringing back the solid metal oxide to its original fully oxidized state. This cyclic process may take place simultaneously (eq. 4, 5) or in separate steps depending on the suitability of the metal oxide (Grassellie, 2002).

$$M^{x+}O^{2-}_{1/2(x-y)} + Lignin \rightarrow M^{(x-y)+}O^{2-}_{1/2(x-y)} + product + H_2O + CO_2 \tag{4}$$

$$M^{(x-y)+}O^{2-}_{1/2(x-y)} + O_{2(g)} \rightarrow M^{x+}O^{2-}_{1/2(x-y)} \tag{5}$$

where *x*=valence of the metal and *y*=no. of lattice oxygen removed. From our data it seems that the catalytic oxidation process took place in two different stages, because the concentration of product suddenly increased at 80 min which discards the possibility of simultaneous reaction. Successful completion of the redox cycle also depends on the metal-oxygen (M-O) bond strength and structure of the host (Grassellie, 2001). Possible reasons for the low concentration of the product may be due to i) may be weak M-O strength leading to over oxidation of products to CO_2 and H_2O ii) probably weak host structure incapable of rapid electron transfer between vacant sites and lattice oxygen iii) combination of both the factors.

Hydrogen peroxide appeared to be the least effective oxidant. The reason for this could be probably formation of inactive hydroxyl radicals and superoxide ions due to disintegration of hydrogen peroxide at lower temperatures (70-90 ^{o}C). Perhydroxyl anion (HOO^{-}) is the most active agent in alkaline hydrogen peroxide which facilitates the breakdown of the α and β-aryl ether bonds of lignin to produce desired aldehydes, but at the same time these aldehydes are prone to further degradation (Kadla and Chang, 2001). Results from our research are consistent with the previous studies.

Degradation of lignin using potassium permanganate was discussed by Gellerstedt, 1992. The author reported that major products formed during chemical degradation of lignin via potassium permanganate are acids due to cleavage of β-aryl ether bonds. However these finding are different from the results obtained in the current study, where aldehydes are produced instead of its corresponding acids. This deviation may be explained due to over oxidation of the aldehydes to carbon dioxide and water, whereas formation of aldehydes can be associated with the lattice oxygen from the niobium oxide catalyst.

3.5. Rate of Mixing

Figures 4.4A and B illustrate the effect of mixing on production of vanillin and acetovanillone respectively. Tukey’s test revealed that production of vanillin (p=0.5307) and acetovanillone (p=0.2413) were independent of rate of mixing. It may be noted that at lower mixing speed, the reaction rate is low due to limited mass transfer of reagents. Increasing the mixing speed may result in the formation of increased contact surface area; which may make the catalyst well-dispersed in the interface and that could lead to accelerated reaction. However, at very high mixing speeds whirlpool effect could be formed in the system leading to inadequate surface contact thereby reducing the rate of oxidation.

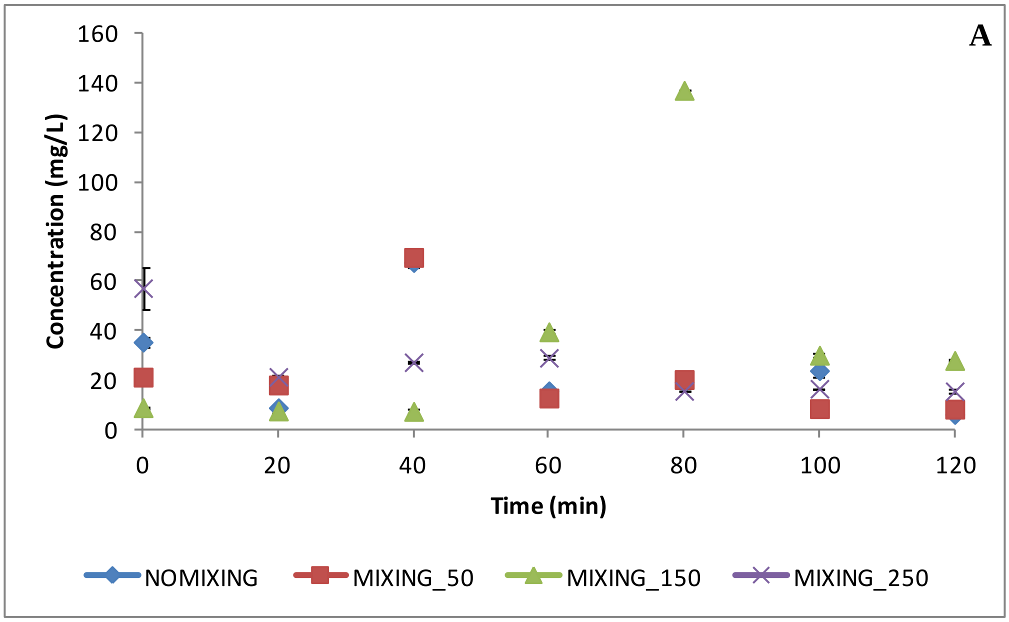

Figure 4.4A. Effect of mixing (rpm) on vanillin production from lignin (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 0.5 g 100 mL^{-1}, and temperature 90 ^{o}C)

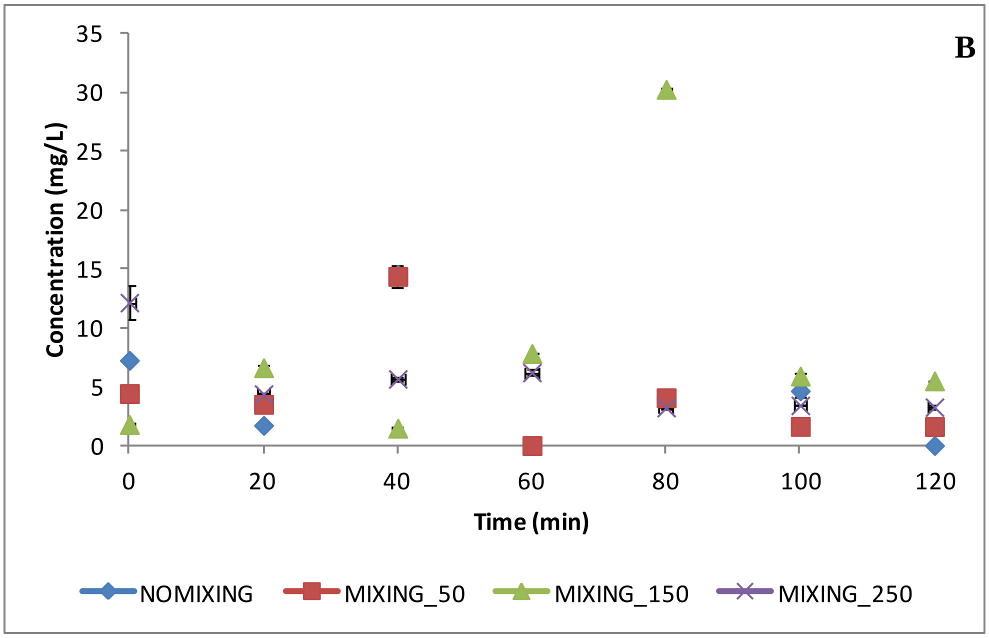

Figure 4.4B. Effect of mixing (rpm) on acetovanillone production from lignin (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 0.5 g 100 mL^{-1}, and temperature 90 ^{o}C)

3.6. Kinetic Evaluation of Lignin Oxidation

The kinetic experiments were carried with temperature 90 ºC and catalyst loading 0.5 g. This and with varying lignin concentrations of 2-12 mg, similar to that of the batch experiments described previously. Samples were drawn periodically and analyzed using the same protocol as mentioned in previous sections. The reaction mechanism of catalytic oxidation leading to formation of aldehydes is a complex process. In a catalytic oxidation system it is considered that lignin is depolymerized to aromatic aldehydes and these aldehydes are subjected to further degradation leading to other products such as acids, water and carbon dioxide (Mathias and Rodrigues, 1994).

In our experiment since lattice oxygen from the catalyst played the role for lignin degradation, it is assumed that lignin was oxidized on the catalyst surface and the aldehydes are produced due to adsorption of lignin on the catalyst (eq 6).

$$\text{Lignin (L)} \overset{r_1}{\rightarrow} \text{Adsorbed aldehyde(V)} \overset{r_2}{\rightarrow} \text{ODC} \qquad (6)$$

Where ODC represents other decomposed compounds such as acids, CO_2 and H_2O. The oxidation reaction of lignin *Rate* is represented by power low (eq 7).

$$Rate \ = k_1 C_{O_2}^{a} C_L^{b} \qquad (7)$$

where C_{O_2} is the concentration of oxygen dissolved in the liquid, C_L is the lignin concentration, K_1 is the rate constant, *a* and *b* are the reaction orders with respect to oxygen and lignin respectively. Since oxygen was always available, mass transfer of oxygen to the liquid is not rate controlling hence its concentration was assumed to be constant. Equation (7) may now be be transformed into

$$Rate \ = K C_L^{b} \qquad (8)$$

Non-linear regression analysis was used for fitting the experimental data. The coefficient of determination (R^2) was 0.63, K=0.082 $(mg/L)^{0.15}$ $min^{-1}$and *b* is 1.15 (first order approximately).

In addition, the experimental data was also fitted to Mars-van Krevelen model which is appropriate for selective oxidation via lattice oxygen. This mechanism involves two reaction stages. In the first stage lattice oxygen from the catalyst oxidizes lignin and in the second stage reoxidation of partially reduced catalyst by molecular oxygen (Makwana et al., 2002) The rate of lignin oxidation is given as

$$R_1 = k_1[Lignin]^{\theta} \quad (9)$$

Where θ is the degree of catalyst surface occupied by lignin.

The rate of reoxidation of the catalyst surface is proportional to the surface area not occupied by oxygen and can be represented as

$$R_2 = k_2[O_2]^m(1-\theta) \quad (10)$$

At equilibrium R_1 and R_2 would be equal, hence

$$\gamma k_1[Lignin]^{\theta} = k_2[O_2]^m(1-\theta) \text{ (Makwana et al., 2002)} \quad (11)$$

Where γ=1 is the stoichiometric coefficient for O_2. Equation 11 can be solved to get the final rate expression

$$Rate = \frac{1}{\frac{1}{k_1[Lignin]} + \frac{1}{k_2[O_2]^m}} \quad (12)$$

Where k_1 and k_2 are the rate constants from two reaction steps. Using the previous argument of oxygen not being rate controlling, hence concentration of oxygen is constant. Equation (12) can be rearranged to

$$Rate = \frac{a[Lignin]}{b + c[Lignin]} \quad (9)$$

The model parameters were again estimated by non-linear regression. The coefficient of determination (R^2) was 0.62. This result suggested that both the models were equally explaining the mechanism for lignin oxidation.

3.7. Proposed Reaction Pathway

The mechanism of oxidation of lignin (with and without catalyst) has been hypothesized by many researchers, but to date its exact path is still not completely clear. Tomlinson and Hibbert, (1936) proposed a mechanism for vanillin formation, where the authors reported that under alkaline conditions and in the absence of oxidizing agent, vanillin and acetovanillone were formed due to retroaldol cleavage of the α-hydroxy-γ-carbonyl structure of the lignin.

Tarabanko et al. (2004) proposed a mechanism (Fig. 4.5) which suggested the formation of aceto derivatives and vanillin under alkaline conditions. As illustrated in Fig 4.5 the reaction starts with detachment of one electron from phenoxyl anion to form phenoxyl radical. The quinonemethide is formed from phenoxyl radical either by proton detachment or disproportionation and subsequent oxidation. Coniferaldehyde is formed with the addition of hydroxide ion to the quinonemethide and finally formation of vanillin from coniferaldehyde due to retroaldol cleavage. In our research apart from vanillin we also detected acetovanillone as a secondary byproduct, which corroborates the pathway proposed by Tarabanko et al. (2004).

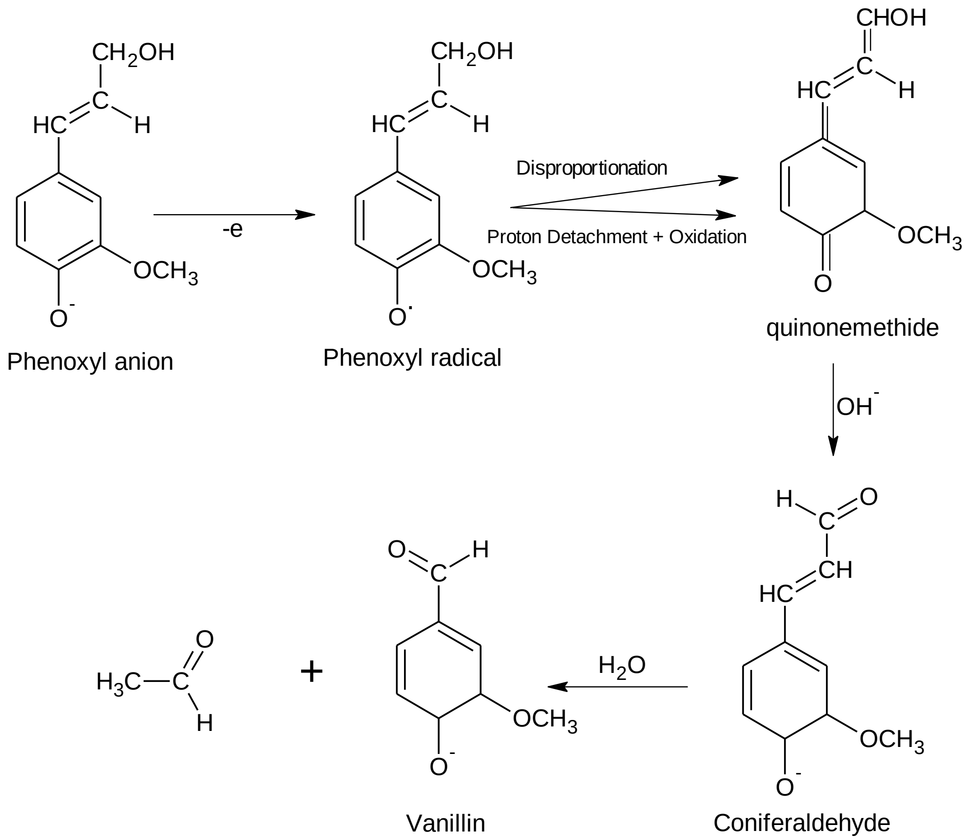

Figure 4.5: Reaction path way for lignin oxidation

4. Conclusion

Form our experimental data the following inferences may be drawn:

- Results suggest that niobium oxide is a selective oxidation catalyst which successfully converts lignin to vanillin, acetovanillone, syringaldehyde and homovanillic acid.
- Catalyst loading had a significant ($p=0.0288$) effect on production of vanillin, whereas production of acetovanillone is plausibly independent ($p=0.158$) of catalyst loading in the range of 0.1-0.5 g.

- Effect of temperature on yields of vanillin and acetovanillone was not significant (p=0.507, p=0.641) effect in the range of 70-90 °C.
- Under optimum conditions of temperature of 90 °C, and catalyst loading of 0.5 g yielded 137.194 mg L^{-1} of vanillin and 30.290 mg L^{-1} of acetovanillone.
- Lattice oxygen was believed to responsible for the oxidation process.
- Production of both vanillin and acetovanillone were independent of mixing.

Acknowledgement

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CHAPTER 5

DEPOLYMERIZATION OF LIGNIN USING NIOBIUM OXALATE SUPPORTED SOLID CATALYSTS

(A SHORT COMMUNICATION)

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Abstract

Valorization of lignin into chemicals has driven researchers for decades. In this research, niobium oxalate was deposited on oyster shell (OSNC) and carbon rods (CRNC) to investigate the depolymerization of lignin. Research objectives were to (1) characterize the catalyst and (2) test the activity of OSNC and CRNC for lignin depolymerization. Catalysts (2%, 5% and 8% loading) were synthesized via wet impregnation. Batch experiments were performed at 95 °C, 8 g of lignin, and 1 g of catalyst. Maximum vanillin concentration for OSNC was 86.25 mg L^{-1} at 5% Nb whereas as for CRNC, maximum vanillin concentration was 139.40 mg L^{-1} at 2% Nb loading. Addition of hydrogen peroxide into the batch reactor decreased the concentration of vanillin production.

Keywords: Catalytic oxidation, Carbon rod, Oyster shell, Lignin, Niobium oxalate

1. Introduction

Considering the recent ongoing research and future demands, it will not be an exaggeration to say that lignicellulosic biomass would be the dominating source of some of the fine or platform chemicals (Long et al., 2014; Zakzeski et al., 2010). Depolymerization of lignin into value-added aromatics is one of the most important route in the biomass conversion process (Nanayakkara et al, 2014). The use of lignin as a source of high valued chemicals has been extensively studied (Cherubini and Strømman, 2011). However, it is of significant challenge to effectively deconstruct lignin into low molecular weight compounds because of its highly complex molecular structure (Ragauskas et al., 2014). The pulp and paper industry is a major source for lignin production, but most of its lignin produced is utilized for burning to counter balance the energy requirement of the industry (Tomani et al., 2011).

Lignin is biosynthesized via oxidative coupling of monomers i.e., sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol into a heavily branched polymer (Azarpira et al., 2014). The branched structure of the lignin and its monomers is dependent on the plant type. The complexity of the lignin structure is due to cross coupling of monomers with other phenolic units. These inter-unit linkages are combination of carbon-oxygen and carbon-carbon bonds which vary based on the plant type. The most common linkages are β-O-4, β-β, β-5, 5-5 and 5-O-4.

Several lignin degradation methods such as hydrolysis, hydrogenolysis, pyrolysis, oxidation, reduction, and biochemical conversion produce an array of chemical compounds. However, oxidation of lignin results in compounds with moderate yield. The major chemicals from lignin oxidation are mainly simple aldehydes or acids, such as vanillin, syringaldehyde, p-hydroxybenzaldehyde, vanillic acid and syringic acid (Crestini et al., 2010; Azarpira et al., 2014).

Several studies have focused on oxidative degradation of lignin using hydrogen peroxide, oxygen, and other chemical oxidants with or without catalyst. Crestini et al. (2005, 2006) used CH_3ReO_3 catalyst in presence of H_2O_2 at room temperature for oxidation of lignin model compounds, sugar cane lignin, and red spruce kraft lignin. Their study showed that hydrolytic sugar cane lignin, red spruce kraft lignin and hardwood organosolvent lignin produced aliphatic OH, syringol OH, guaiacyl OH, p-hydroxy phenyl OH and COOH with a yield ranging from 0.29%-1.51%. Similarly Herrmann et al. (2000) also used CH_3ReO_3 catalyst in presence of H_2O_2 for oxidation of trans-ferulic acid and isoeugenol at 60 ºC for 10 h to produce vanillin. Sales and co-workers (2007) investigated the effect of Pd/Al_2O_3 (2.85% wt) catalyst for lignin form sugar cane bagasse in presence of O_2 in a slurry and continuous fluidized bed reactors. Experimental results illustrated that from the batch reactor 0.56 g of vanillin and 0.50 g of syringaldehyde were produced from 60 g L^{-1} of lignin at 120 ºC and 5.00 bar pressure after 2 h of reaction, similarly from the fluidized bed reactor 6.5 g vanillin and 11.4 g of syringaldehyde were obtained from 30 g L^{-1} of lignin under the same operating conditions.

Catalytic oxidation requires a selective catalyst that would minimize secondary oxidation reactions. One such selective catalyst is niobium oxalate. Niobium compounds are known to exhibit the characteristics of supporter as well as promoter. Niobium compounds when supported on other oxides increase the catalytic activity significantly (Tanabe, 2003; Ziolek, 2003). Hence, solid supported niobium catalyst have been used several reactions such as hydrogenation, methylisobutyl ketone synthesis, metathesis, hydrotreating reactions etc. (Tanabe, 2003). However, to best of our knowledge solid supported niobium catalyst has not been investigated for lignin oxidation. Considering the supporter effect of niobium compounds, the goal of the present research was to investigate niobium oxalate impregnated on on oyster shell and carbon rods as catalysts. Hence the goal of this study was to (1) characterize the catalyst (2) test the activity of oyster shell and carbon rod supported niobium catalyst.

2. Experimental Methods

2.1. Materials

Solid Niobium oxalate ($C_{10}H_5NbO_{20}$) obtained from Alfa Aesar, Inc. Alkaline lignin (Kraft) and methylene chloride (99.99%) were obtained from Tokyo Chemical Industry Inc., and Fisher Scientific, Inc., respectively. Oyster shells were procured from local restaurant whereas carbon rods were obtained from Fisher Scientific. Hydrogen peroxide (50% v/v) was obtained from Fisher Scientific. Standards for 4-hydroxy-3-methoxybenzaldehyde (99%) and 4-Hydroxy-3-methoxyacetophenone (98%) were procured from Acros.

2.2. Catalyst Synthesis

Oyster shells obtained from local restaurant were washed thoroughly in water and then calcined at 400 °C for 2 h. After calcination, shells were broken to the size of 1-2 mm. These broken shells were then treated with 2%, 5%, and 8% of Niobium oxalate in an aqueous solution of oxalic acid and were subsequently recalcined at 1000 °C for 4 h and were named as oyster shell supported niobium catalyst (OSNC).

Carbon rods purchased from fisher scientific were broken to 2-3 mm size and were treated (2%, 5%, and 8%) of Niobium Oxalate in an aqueous solution of oxalic acid which were then calcined at 200 °C for 5 h and were called as carbon rod supported niobium catalyst (CRNC).

2.3. Catalyst Testing and Analytical Methods

Catalyst testing for oxidation of lignin was carried out in a 500-mL three-neck round bottom flask. A 100 mL aliquot of aqueous solution containing 8 g 100 mL^{-1} of lignin, 1 g 100 mL^{-1} of catalyst was added to the round bottom flask and mixed on a hot plate at temperature of 95 °C. The reaction mixture was mixed thoroughly at150 rpm using a magnetic stirrer. Role of oxidant were determined by adding 0.5 mL 100 mL^{-1} of H_2O_2 to the batch experiments. For OSNC reaction was carried out for 60 min whereas for CRNC, the reaction was continued for 180 min. Samples (1.5 mL) were drawn every 10 min and 20 min for OSNC and CRNC respectively. Subsequently, these samples were mixed with 2.5 mL of methylene chloride and stored in a refrigerator at 4 °C for further analysis. The samples were analyzed via a gas chromatograph equipped with a mass selective detector (GC-MS) (Agilent Technologies, 7890 A) and a DB-5 MS UI column (30 m x 0.25 mm x 0.25μm) with Helium as carrier gas. Sample identification was achieved by maintaining oven temperature of 100 °C (hold for 1 min) to 200 °C @ 20° C min^{-1} (2 min hold) and 200 °C to 270 °C @ 15 °C min^{-1} (hold for 2 min) with a split ratio of 150:1 (1.2 mL min^{-1}) while injector and detector were maintained at 300 °C. .

2.4. Depolymerization of Lignin

Yield of vanillin is defined as the ratio of vanillin produced to the amount of lignin used. Sulfite lignin was the lignin used for this study and the monomer associated with this is 2-methoxy-4-(2, 3-dihydorxy-1-sulfo)-propylphenol (Yoshikawa et al., 2013). The recovery of vanillin was obtained by using following equations:

$$Recovery\ \%\ of\ vanillin = \frac{X}{Y} \times 100 \tag{1}$$

$$X = \ moles\ of\ aromatic\ ring\ in\ vanillin\ produced$$

$$Y = \ moles\ of\ aromatic\ ring\ in\ lignin$$

Moles of aromatic ring in vanillin produced and mols of aromatic ring in lignin were estimated using equations 2 & 3.

$$X = \frac{Carbon\ moles\ of\ the\ produced\ vanillin}{Carbon\ numbers\ in\ one\ molecule\ of\ vanillin} \tag{2}$$

$$Y = \frac{Weight\ of\ lignin\ used\ in\ the\ batch\ experiment}{molecular\ weight\ of\ the\ constituent\ lignin\ monomer} \tag{3}$$

3. Results and Discussion

3.1. Catalyst Testing and Oxidation Products

Product analysis and quantification were performed using a gas chromatogram attached to a mass spectroscope. Identified products were vanillin, acetovanillone and homovanillic acid (Fig. 5.1). Results from the batch experiment illustrated that concentrations of vanillin for OSNC at 2%, 5% and 8% loading were 40.08 mg L^{-1}, 86.25 mg L^{-1}, and 39.01 mg L^{-1} respectively. However, for the same catalyst loading, when hydrogen peroxide (0.5 mL) was introduced to the system, the concentrations were 37.63 mg L^{-1}, 34.53 mg L^{-1}, and 36.77 mg L^{-1} respectively. Similarly for CRNC, concentrations of vanillin at 2%, 5% and 8% loading were 139.40 mg L^{-1}, 95.97 mg L^{-1}, and 75.16 mg L^{-1} respectively, and 88.18 mg L^{-1}, 86.78 mg L^{-1}, and 84.75 mg L^{-1} respectively, with addition of hydrogen peroxide.

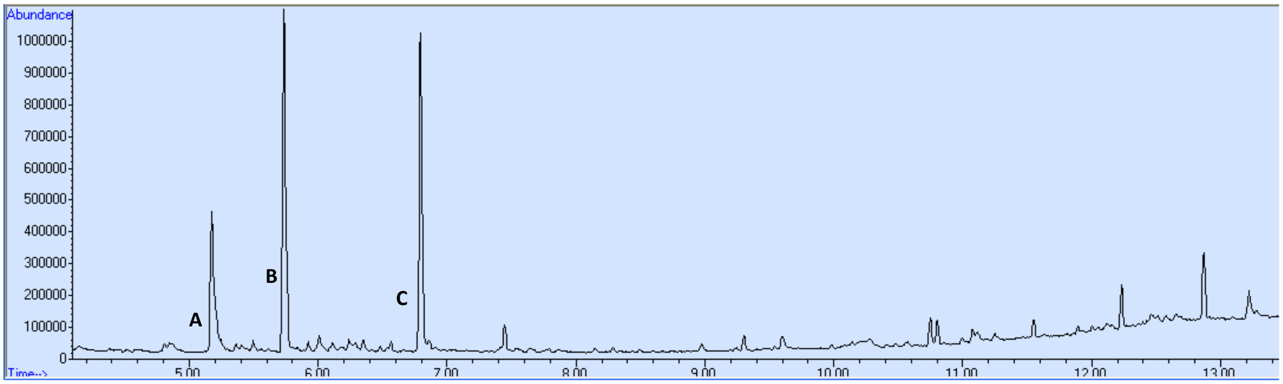

Figure 5.1: Products identified by gas chromatogram via catalytic oxidation (A) 4-hydroxy-3-methoxybenzaldehyde, (B) 1-(4-hydroxy-3-methoxyphenyl)-ethanone, (C) 4-hydroxy-3-methoxy benzenacetic acid

3.2. Oyster Shell Supported Niobium Catalyst

Oyster shell was used as a support to deposit niobium oxalate to synthesize OSNC. Figures 5.2 and 5.3 demonstrate the product concentrations of vanillin and acetovanillone at different catalyst loading and without using H_2O_2 in the system. Catalyst with 5% loading had highest concentration of 86.25 mg L^{-1} at 10 min after which the concentration decreased with advancement of time whereas concentrations of vanillin and acetovanillone were same at 10 min for both 2% & 8%. Highest Concentration of 9.50 mg L^{-1} acetovanillone was achieved at 8% loading at 10 min. The yield of vanillin for 5% loading at 10 min was determined by using equations 1, 2, & 3 which was 0.01%. The oyster shell mainly consists of $CaCO_3$. Equations 4 & 5 represent oyster shell decomposition under heat and subsequent breakdown in aqueous solution (Ok et al., 2010).

$$CaCO_3 \xrightarrow{Calcination} CaO + CO_2 \tag{4}$$

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \tag{5}$$

Oxygen in the system is provided from niobium oxalate and hydroxyl ion from calcined oyster shell. The oxygen is the driving force behind product formation. At 2% loading, lower vanillin concentration was noticed than 5%, which may be due to inadequate amount of niobium oxalate for reaction. Similarly at 8% loading lower vanillin concentration was noticed than 2% loading which may be due to excess niobium blocking the pore entrance of the catalyst thereby making the surface reaction difficult. From Fig 5.2 it is evident that after 30 min vanillin concentration reduced to zero which may be due to over oxidation of the produced vanillin to CO_2. Our results with niobium oxide supported oyster shell catalysts are similar to those obtained by other researchers like Sancho et al., 2013 investigated the effect MCM-41-supported niobium-oxide catalyst for dehydration of xylose to furfural. They reported a conversion of 74.5% and a furfural yield of 36.5% at a catalyst loading of 16 wt% of Nb_2O_5 but the yield decreased when catalyst loading was increased to 33 wt% as was observed in our research.

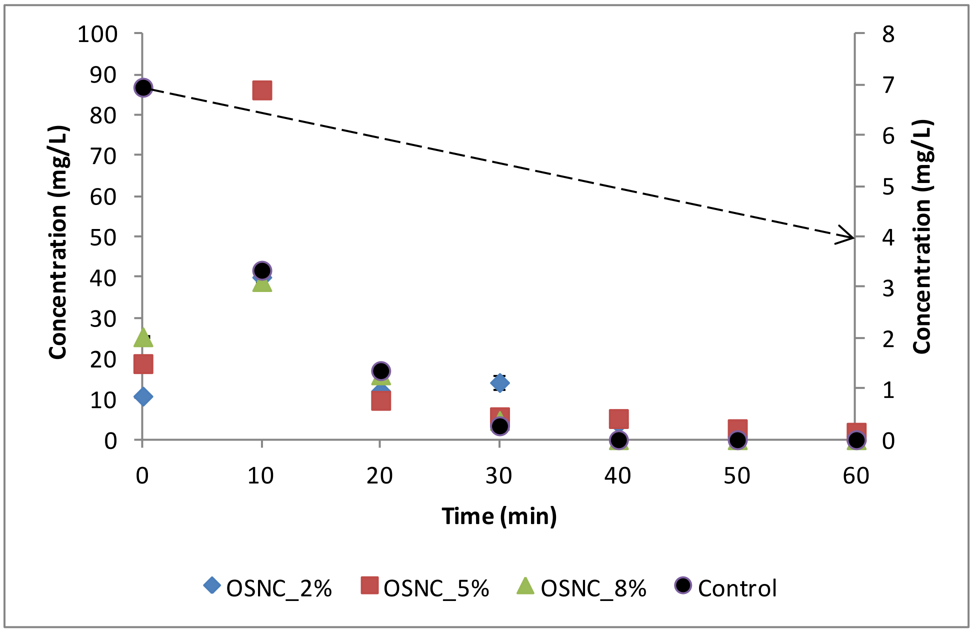

Figure 5.2: Vanillin Production using OSNC without H_2O_2 (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

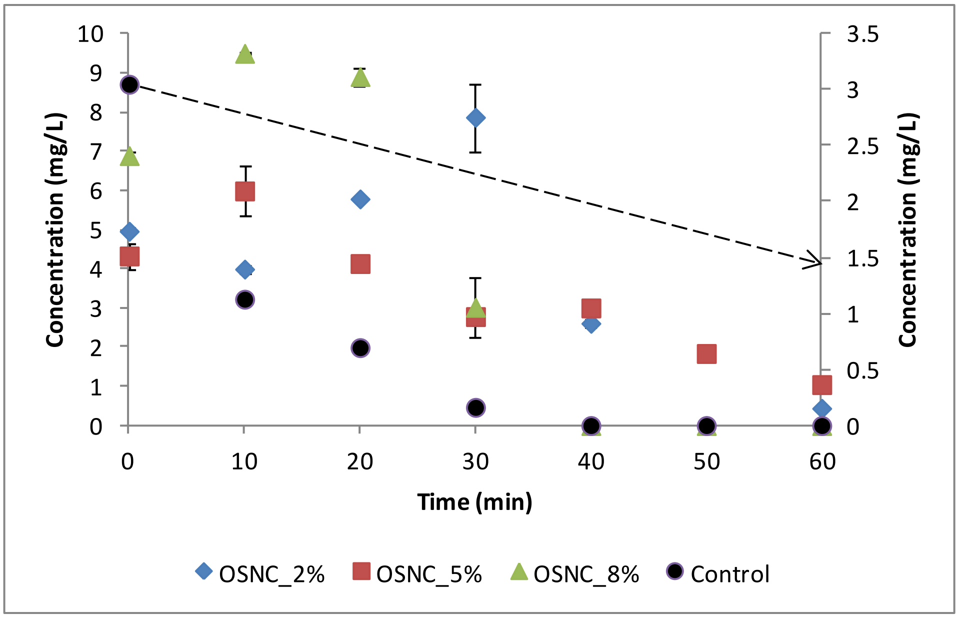

Figure 5.3: Acetovanillone Production using OSNC without H_2O_2 (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

To investigate the effect of oxidant, H_2O_2 (0.5 mL) was added to the system. Figures 5.4 and 5.5 illustrate the role H_2O_2 in producing vanillin and acetovanillone. The results indicate that reactions for all loadings were instantaneous and concentration of products decreased immediately after time zero. Similar results were reported in our previous study where we niobium oxalate catalyst in presence of H_2O_2 (Das et al., 2015). The reason for this fast reaction may be due to reaction of hydroxyl ion produced from decomposition of CaO in aqueous phase and subsequent reaction with H_2O_2 to form perhydroxyl anion. These anions are most active agents that facilitates the deconstruction of α and β-aryl ether bonds of lignin to aldehydes, but at the same time produced aldehydes are vulnerable to further oxidation (Kadla and Chang, 2001)

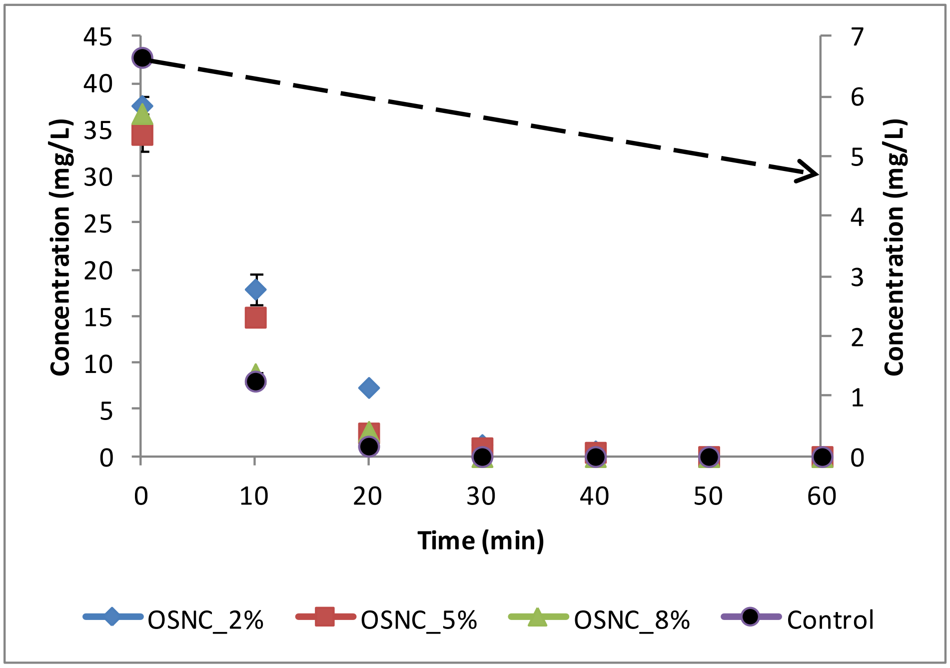

Figure 5.4: Vanillin Production using OSNC (Experimental conditions: Lignin - 8 g 100 mL^{-1}, H_2O_2- 0.5 mL, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

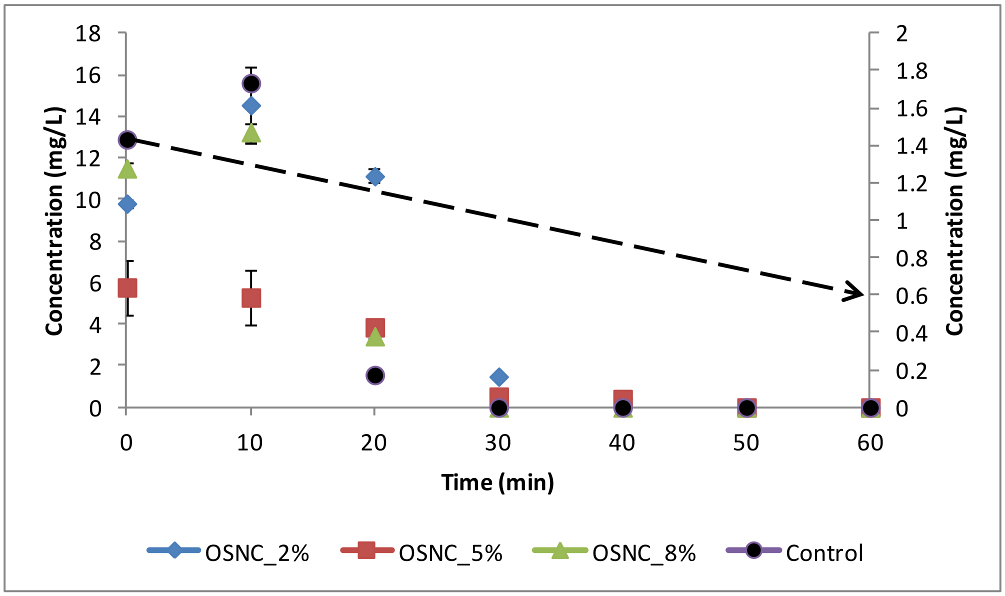

Figure 5.5: Acetovanillone Production using OSNC (Experimental conditions: Lignin - 8 g 100 mL^{-1}, H_2O_2 – 0.5 mL, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

3.3. Carbon Rod Supported Niobium Catalyst

Carbon supported niobium catalyst (CSNC) was synthesized and tested for depolymerization of lignin. Deposition of niobium increased the vanillin concentration significantly. Maximum vanillin concentration of 139.40 mg L^{-1} was obtained at 2% loading and reaction time of 120 min. The yield of vanillin at 2% loading was 0.02% which was estimated by using equations 1, 2, &3. Concentration of vanillin decreased from 95.97 mg L^{-1}, to 75.16 mg L^{-1} as loading was increased from 5% to 8%. Figures 5.6 and 5.7 represent the concentration of vanillin and acetovanillone with respect to different loadings of niobium oxalate. Maximum acetovanillone concentration of 39.88 mg L^{-1} was observed at 2% loading and time of 100 min.

In our research, the product concentration decreased with increase niobium loading may be due to: (1) high loading percent of niobium blocking the pore structure of the carbon surface which may hinder the surface reaction and (2) strong metal-oxygen bond strength decreasing the efficacy of the catalyst to react.

Additional experiments were performed to test the effect H_2O_2 as oxidizing agent. In a separate batch experiment, 0.5 mL H_2O_2 was added to the system to investigate the lignin deploymerzation. Figures 5.8 and 5.9 illustrate the role H_2O_2 in producing vanillin and acetovanillone. The results indicated that reactions for all loadings, concentration of vanillin did not change much i.e for 2%, 5% and 8% loading were 88.18 mg L^{-1}, 86.78 mg L^{-1}, and 84.75 mg L^{-1} respectively at time of 20 min.

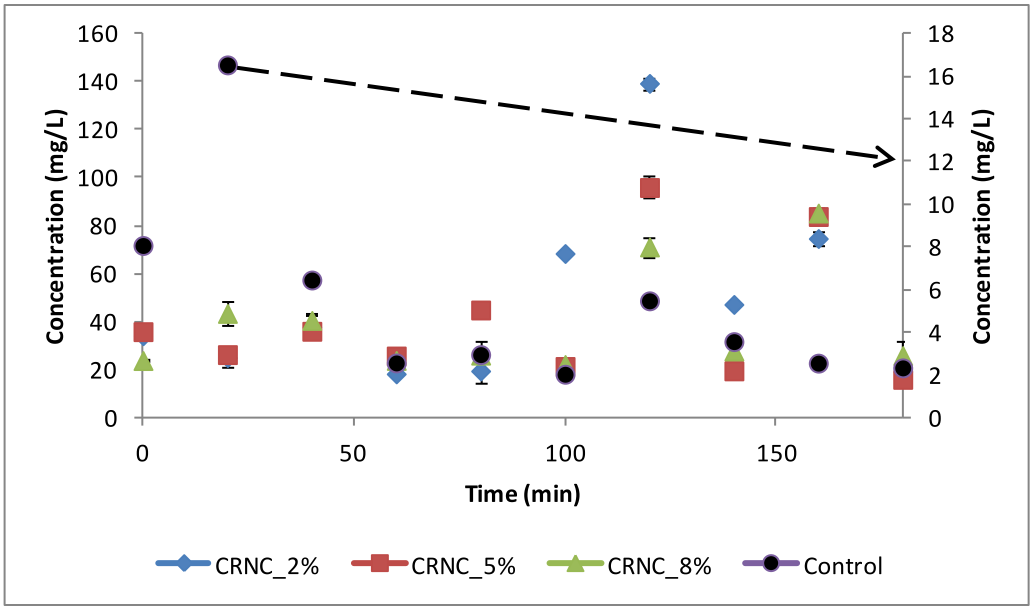

Figure 5.6: Vanillin Production using CRNC without H_2O_2 (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

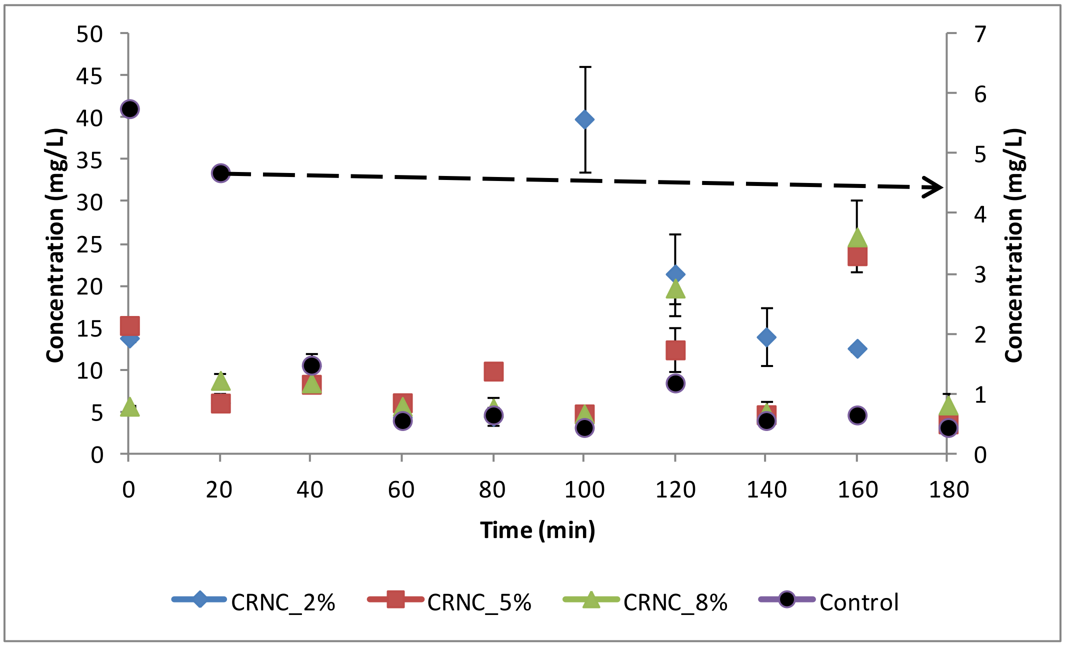

Figure 5.7: Acetovanillone Production using CRNC without H_2O_2 (Experimental conditions: Lignin - 8 g 100 mL^{-1}, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

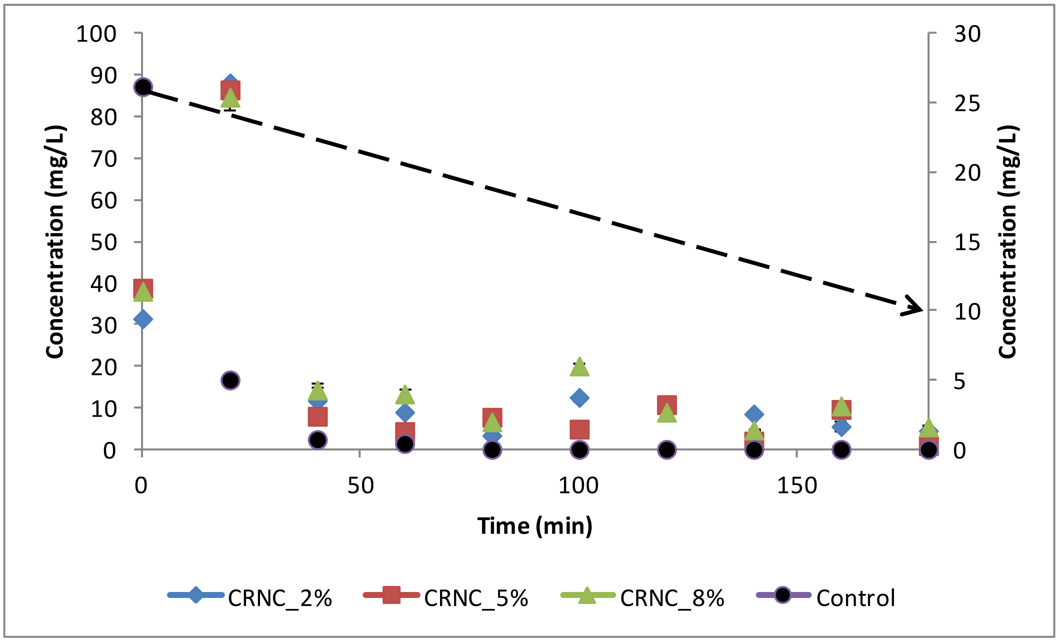

Figure 5.8: Vanillin Production using CRNC (Experimental conditions: Lignin - 8 g 100 mL^{-1}, H_2O_2 -0.5 mL, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

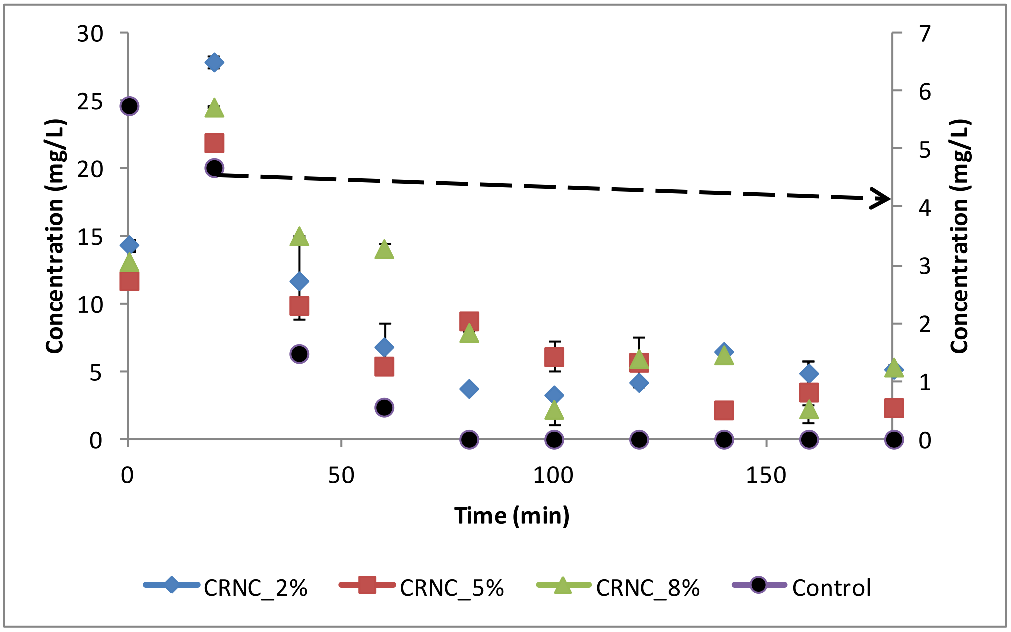

Figure 5.9: Vanillin Production using CRNC (Experimental conditions: Lignin - 8 g 100 mL^{-1}, H_2O_2 -0.5 mL, Catalyst - 1 g 100 mL^{-1}, and temperature 95 ºC)

4. Conclusion

- As hypothesized, both oyster shell supported niobium catalyst (OSNC) and carbon rod supported niobium catalyst (CRNC) successfully degraded lignin into vanillin, acetovanillone and homovanillic acid.
- From batch experiments for OSNC, concentration of vanillin at 2%, 5% and 8% loading were 40.08 mg L^{-1}, 86.25 mg L^{-1}, and 39.01 mg L^{-1} respectively.
- When hydrogen peroxide was introduced to the system along with OSNC the concentrations of vanillin decreased to 37.63 mg L^{-1}, 34.53 mg L^{-1}, and 36.77 mg L^{-1} at 2%, 5% and 8% respectively.
- For OSNC, lattice oxygen was the dominant oxidizing agent. Decrease in vanillin concentration due to addition of H_2O_2 was may be due to reaction of OH^- with H_2O_2 to form HOO^- which may have caused over oxidation.
- Similarly, for CRNC concentration of vanillin at 2%, 5% and 8% loading were 139.40 mg L^{-1}, 95.97 mg L^{-1}, and 75.16 mg L^{-1} respectively.
- With inclusion of hydrogen peroxide as an addition oxidizing agent concentration of vanillin at 2%, 5% and 8% loading were 88.18 mg L^{-1}, 86.78 mg L^{-1}, and 84.75 mg L^{-1} respectively.

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CHAPTER 6

SUMMARY AND FUTURE DIRECTION

The goal of this research was to investigate selective catalytic oxidation of lignin into value-added aromatics. In this study, niobium-based catalysts were investigated for depolymerization of commercial kraft lignin. The objectives were to: (1) investigate niobium-based catalysts for oxidation of lignin (2) test the activity of the catalysts during oxidization of lignin into aromatic chemicals (3) optimize the process parameters, and (4) investigate mechanism involved in the breakdown of lignin.

The objectives of this study were accomplished in three phases. The major conclusions are listed below.

Phase One

- In the first phase, a homogenous catalyst (Niobium Oxalate) in presence of hydrogen peroxide was used for studying lignin oxidation. The purpose of using this catalyst was to investigate oxidation mechanism and effect of different process parameters, and to obtain information that would help in synthesizing a solid supported niobium catalyst.
- This phase started with the hypothesis that in presence of an oxidant, niobium oxalate a selective catalyst can facilitate partial degradation of lignin to lower molecular weight compounds.

- The main focus of this study was to determine the combined effect of catalyst loading, lignin concentration and hydrogen peroxide concentration. Batch experiments revealed the production of vanillin and syringaldehyde as the two major products.
- A central composite design was implemented which revealed that product formation was independent of H_2O_2 concentration. Catalyst had significant effect on vanillin production ($p=0.0404$) whereas lignin ($p=0.0036$) and catalyst ($p=0.0053$) had significant effect on syringaldehyde formation.
- A maximum concentration of vanillin (65.58 mg g^{-1} of lignin) and syringaldehyde (23.12 mg g^{-1} of lignin) were obtained at experimental condition of 3 mL H_2O_2, 0.5 g catalyst loading, and 7.26 g/100 mL lignin.
- Concentration of products increased with increase in temperature, with maximum product concentrations were produced at 100 ºC. This dependency on temperature indicated greater activity of hydroxyl radicals and superoxide ions at higher temperature.

Phase Two

- Results obtained from the first phase were used to continue exploring niobium catalyst in the second phase. In this study, a heterogeneous catalyst (Niobium oxide) was investigated for lignin oxidation.

- A 3^2 factorial design was used to study the effect of temperature and catalyst loading on lignin oxidation and subsequent product formation. Testing of the catalyst resulted in production of vanillin, acetovanillone, syringaldehyde and homovanillic acid.
- Catalyst loading had a significant (p=0.0288) effect on production of vanillin whereas temperature was independent (p=0.507) of vanillin production.
- Both catalyst loading and temperature were independent (p=0.158, p=0.641) of acetovanillone production.
- A maximum concentration of 137.194 mg L^{-1} of vanillin and 30.290 mg L^{-1} of acetovanillone were obtained a temperature of 90 °C, and catalyst loading of 0.5 g.
- Production of vanillin with no oxidant was significantly (p=0.0046) different form H_2O_2 but is not significantly (p=0.1527) different form $KMnO_4$ whereas production of acetovanillone was independent of oxidants. Lattice oxygen present in the catalyst was believed to be responsible for the deconstruction of lignin.
- Effect of mixing on product formation reveled that both vanillin and acetovanillone were independent of mixing.

Phase Three

- Conclusions from the above two phase were taken into consideration for synthesis of solid catalyst in the third phase.
- Niobium oxalate (2%, 5% and 8%) was deposited onto oyster shell and carbon rods to synthesize solid heterogeneous catalyst for breakdown of lignin.

- Oyster shell supported niobium (5%) catalyst produced maximum of 86.25 mg L^{-1} of vanillin whereas carbon rod supported niobium (2%) produced maximum of 139.39 mg L^{-1} of vanillin.
- Overall lignin oxidation mechanism was believed to have occurred via breaking of α and β-aryl ether bonds of lignin.

Catalytic oxidation of lignin using metal oxides proved to be effective in depolymerizing lignin to aromatic aldehydes and acids. However, further studies are required to improve the yield to make it economically feasible for commercialization. Some of the proposed future directions are discussed below:

1. In this study, batch experiments were conducted in aqueous solution which raises the question of lignin solubility. To improve the solubility of lignin different solvents such as ionic liquid, ethanol, pyridine, benzene etc. may be investigated.
2. Effect of oxidants demonstrated that products formation is not dependent on H_2O_2, so other oxidants like ozone and molecular oxygen could be explored.
3. Characterization lignin using NMR and wet chemistry is expected to give an insight on the presence of functional groups and break down of particular bonds and may help in better understanding of lignin mechanism
4. More inexpensive and efficient catalysts along with extensive economic analysis of the complete process would enable better decision regarding scalability of the system.