Reaction Optimization and Production of Value-added Products in Lignin Oxidation Reaction

by

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Abstract

When carbon resources are becoming limited there is a great interest to use renewable resources and replace biomass as a feed stock for different industries. It is necessary to investigate methods that isolate biomass resources and convert it into value added materials safely, efficiently, and effectively. Lignin is a natural polymer and valuable starting chemical with heterogeneous sources in nature. Different lignin pre-treatments methods in pulping and bleaching often provide different lignin streams with variable chemical characteristics. Among the different conversion strategies for lignin, oxidation has shown reliable results and valuable products. There are various methods to perform oxidation, and, in this study, free radical oxidation at mild condition was utilized. However, Lignin's complexity and structural diversity make it challenging to acquire high yield and conversion. The work developed in this thesis intends to study the production of vanillin and other value-added chemicals by oxidative depolymerization of lignin from lignin-rich side streams of pulp and paper industry. Characterization of lignin before and after oxidation shows physical and chemical changes in lignin. More oxygenates formed during the oxidation reaction, and addition of hydroxyl, methoxyl and carbonyl group can be determined in the product of oxidation.

Oxidation of lignin was performed in a batch reactor and compared with the microfluidic reactor regarding conversion and product achieved. Increased oxygen availability in the microfluidic reactor alongside enhanced mixing and mass transfer leads to fast conversion of lignin (within 1-minute residence time) and a high vanillin retention rate that is close to the vanillin formation in the batch experiment at 130C. In batch reactor degradation of long-chain aromatic hydrocarbon results into the formation of mono aromatics in primary oxidation and a significant amount of aliphatic compound including acids and other smaller compounds due to overoxidation. Low

oxygen availability in the batch reactor could potentially lead to increased formation of addition products since there is no sufficient oxygen to drive free radical oxidation to the final stage. In a continuous microfluidic experiment, oxidation of aromatics leads to the formation of new mono aromatics with a lower percentage of organic acids.

The results from this study can be employed in the pulping and bleaching section in paper making industry to substitute the oxidation process with chlorine-based strategies. Using greener oxidants like oxygen and hydrogen peroxide during oxidation will reduce the environmental impacts and toxic effects of bleached pulp mill effluent.

Dedication

To my beloved husband,
Kiarash, who is my best friend, my greatest support, and my truest smile

To my caring parents,
Shahla and Alireza, who made my success possible

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Table of Contents

1 Introduction 1
  1.1 Objectives 5
  1.2 Thesis outline 6
2 Literature review 7
  2.1 Introduction 7
  2.2 Lignin 7
  2.3 Structure of lignin 8
    2.3.1 Kraft lignin 11
    2.3.2 Sulfite lignin (lignosulfonate) 11
    2.3.3 LignoForce 12
  2.4 Lignin potential applications 12
  2.5 Products and chemicals from lignin 12
    2.5.1 Lignin to monoaromatics 14
    2.5.2 Aromatic aldehydes, ketons and acids 16
  2.6 Depolymerization of lignin 16
    2.6.1 Base-catalyzed degradation of lignin 17
    2.6.2 Acid-catalyzed Depolymerization 18
    2.6.3 Oxidative Depolymerization 19
  2.7 Oxidation Chemistry 19
    2.7.1 Oxidizing Agents 19
    2.7.2 Gas Phase and Liquid Phase Oxidation 20
  2.8 Lignin Oxidation 20
    2.8.1 Catalytic system 21
    2.8.2 Non-catalytic System 22
    2.8.3 Review on Oxidative Conversion 22
  2.9 The integrated process of oxidation and product purification 23
  2.10 Potential of Microfluidic Reactor in Oxidation 24
    2.10.1 Multiphase Oxidation in Microfluidic Reactors 25
3 Lignin oxidation experiments 27

3.1 Material and methods 27
  3.1.1 Batch reactor 28
  3.1.2 Continuous microfluidic reactor 29
  3.1.3 Sample preparation and analysis 32
3.2 Fourier transform infrared (FTIR) analysis 34
3.3 Fourier Transform Infrared Spectroscopy (FTIR) 34
3.4 Nuclear magnetic resonance (NMR) 34
3.5 Gas Chromatography-Mass Spectrometry (GC-MS) 35
3.6 Liquid Chromatography-Mass Spectrometry (LC-MS) 35
3.7 High-Performance Liquid Chromatography (HPLC) analysis 36
3.8 Thermogravimetric Analysis (TGA) 36
3.9 Density measurement 36
  3.9.1 Calculation formulas 36
4 Result and discussion 41
4.1 Identification of physical change after lignin oxidation 41
  4.1.1 Change in color 41
  4.1.2 Change in density, pH and surface charge 42
4.2 Identification of chemical change after lignin oxidation 42
  4.2.1 FT-IR results 42
  4.2.2 HPLC results 45
  4.2.3 NMR results 46
  4.2.4 Thermogravimetry results 47
  4.2.5 GC results 48
4.3 Oxidation mechanism 52
  4.3.1 Possible mechanism in lignin oxidation with hydrogen peroxide 54
4.4 Influence of Reaction Conditions on Lignin Oxidation 55
  4.4.1 Effect of NaOH concentration on lignin oxidation 55
  4.4.2 Effect of Temperature 57
  4.4.3 Effect of hydrogen peroxide and time 58
4.5 Microreactor hydrodynamics and flow characteristics 59
4.6 Comparing batch and microfluidic oxidation 64
  4.6.1 Vanillin degradation, effect of oxygen and reactor 66

5 Risk and hazard assessment of delignification in pulp bleaching 68
  5.1 Introduction 68
  5.2 Bleached Pulp Manufacturing Processes 70
    5.2.1 Pulping 70
    5.2.2 Bleaching 70
  5.3 Effluent Treatment 72
  5.4 Health hazards associated with pollutants 73
  5.5 Risk Assessment Criteria 74
  5.6 Risk Assessment Process 75
  5.7 Hazard Identification and Findings 76
  5.8 Case study (West Fraser Forestry effluent management) 78
    5.8.1 Effluent deposition 80
  5.9 Recommendations for Bleaching Substitution 82
  5.10 Summery 83
6 Conclusion and future work 85

List of Tables

Table 2.1. Types and occurrence of interlinkage bonds of lignin from different origins (Lin and Dence, 1992; Pinto et al., 2012; Santos R.B. et al., 2013) 10

Table 2.2. Potential lignin applications (Holladay et al. 2007) 13

Table 3.1. Lignin physical and elemental properties 27

Table 4.1. Chemical changes during lignin oxidation in batch reactor at three different temperature in alkaline media using O_2 and H_2O_2 after 1 hour. 42

Table 4.2. Infrared absorption frequencies of different functional groups (Peak et al., 1999; Maria et al., 2002; Xu et al., 2006; Williams and Fleming, 1989; Colthup et al., 1990; Silverstein et al., 2005). 43

Table 4.3. NMR analysis of lignin feed and oxidized lignin in batch (1hour) and microfluidic reactor at 100 °C 47

Table 4.4. The main components identified by GC-MS during alkaline oxidation of lignin from the volatile fraction in ethyl acetate. 49

Table 4.5A. Hydrodynamic properties, mass transfer coefficient during lignin oxidation in 130°C 61

Table 4.6. Dimensionless numbers for the oxidation of lignin in microfluidic rector with oxygen at 130C and 40 psi gauge pressure 63

Table 4.7. Comparison of the products retention rate obtained in batch reactor and continuous microfluidic reactor at 130 °C 65

Table 5.1. Proposed intensity factors for operating mills (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019) 77

Table 5.2. Current intensity factors for operating mills (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019). 77

Table 5.3. Water discharge by quality and destination (West Fraser annual report) 79

Table 5.4. Waste by type and disposal method (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com) 79

List of figures

2.1. Main structures present in alkali ultrafiltrated lignin fractions. H: p-coumaric acid; G: guaiacyl alcohol; S: syringyl alcohol. 9

Figure 2.2. Schematic representation of lignin by Lupoi et al., 2015. Reprinted permission automatically granted from John Wiley & Sons Inc. and its subsidiaries, including John Wiley & Sons Ltd 10

Figure 2.3. Taylor flow illustrating mixing within liquid slug 25

Figure 3.1. Batch experimental apparatus for lignin oxidation.......... 29

Figure 3.2. Microreactor channel layout 30

Figure 3.3. Experimental set up using microfluidic reactor for oxidation 30

Figure 3.4. (a) Illustration of gas-liquid slugs shows length of gas bubble (L_G), length of liquid slug (L_S), Unit length (L), liquid film and liquid cap and circulation within liquid slugs. (b) magnified gas-liquid slug in a microfluidic reactor. (c) microfluidic reactor used in this study.. 31

Figure 3.5. Liquid-liquid extraction of oxidation product with ethyl acetate 33

Figure 3.6. Derivatization of functional group in product with BSTFA and TMCS 34

Figure 4.1. Visual observation of lignin before and after oxidation in batch reactor with 10 bar O_2 pressure and H_2O_2 in alkaline solution at 130°C. a) Lignin solution before oxidation b) After 30 min oxidation. c) After 1h oxidation and d) After 2 hours oxidation 41

Figure 4.2. Infrared spectra of lignin and oxidized lignin in the 500-4000 cm^{-1} spectra region . 43

Figure 4.3. HPLC chromatogram of a) lignin and b) oxidized lignin at 130°C and identified products table 46

Figure 4.4. Thermogravimetric (TG) analysis of lignin.......... 47

Figure 4.5. Three possible oxidation mechanisms in aromatics (Sánchez and de Klerk, 2018). . 52

Figure 4.6. Oxidation reaction of lignin under alkaline condition (Kadla and Chang, 2001; Braun et al., 2005) 54

Figure 4.7. Lignin conversion and products retention rate in oxidation system under different NaOH concentration. 56

Figure 4.8. Lignin conversion and products retention rate in oxidation system under different temperature 57

Figure 4.9. Effect of time on lignin conversion and products retention rate in oxidation system 59

Figure 4.10. Graphical representation of oxidation in microfluidic reactor 60

Figure 4.11. (a) Flow pattern mapped by Triplett et al. and marked by Gupta et al. 2010; (b) Typical flow patterns in microchannels observed by Triplett et al., 1999. Reprinted permission automatically granted from SAGE Publications. 63

Figure 4.12. Product formation and lignin conversion during microfluidic oxidation of lignin . 64

Figure 5.1. Air and soil pollution due to pulp and paper industry waste (Mandeep et al., 2019). Reprinted permission granted from Elsevier. 69

Figure 5.2. Environmental impacts of pulp and paper industry and treatment techniques (Mandeep et al., 2019). Reprinted permission granted from Elsevier. 73

Figure 5.3. Biochemical Oxygen Demand (BOD) in Waste Fraser Western Canada locations (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com/responsibility/responsibility-report/ previous-reports/2017-responsibility-report/manufacturing/waste-man 80

Figure 5.4 Total Suspended Solids (TSS) in Waste Fraser Western Canada locations (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com/responsibility/responsibility-report/ previous-reports/2017-responsibility-report/manufacturing/waste-management). 81

Nomenclature

A	surface area of gas bubble
a	gas-liquid interfacial area, (m2/m3)
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
D_a	diffusivity of gas phase in liquid phase (m2/s)
d_H	hydraulic diameter, (m)
ECF	Elemental Chlorine Free
ECCC	Environment and Climate Change Canada
FID	flame ionization detector
FTIR	Fourier transform infrared
GC	gas chromatography
h	depth of the reactor, (m)
HPLC	high performance liquid chromatography
^1HNMR	proton nuclear magnetic resonance
J_A	mass transfer rate across the gas-liquid interface (mol/m3.s)
K_L	mass transfer coefficient (m/s)
k_La	overall mass transfer coefficient, (s^{-1})
L_G	length of gas bubble, (m)
L_S	length of liquid slug, (m)
LC	liquid chromatography
MS	mass spectrometry
m/z	mass-to-charge ratio
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance
SS	suspended solids
t	retention time
TGA	Thermogravimetric Analysis
TCF	Total Chlorine Free
TSS	Total Suspended Solids

U_G	superficial gas bubble velocity, (m/s)
U_L	superficial liquid slug velocity, (m/s)
U_T	two phase superficial velocity, (m/s)
V_G	volume of gas bubble, (m3)
V_L	volume of liquid slug, (m3)
w	width of the reactor, (m)
We	Weber number, $\mathrm{We}=\frac{\mathrm{D_h U_T^2 \rho_l}}{\sigma_l}$
δ	thickness of liquid film, (m)
$\emptyset_G$	volume fraction of gas bubble
ρ_G	density of gas, (kg/m3)
ρ_l	density of liquid, (kg/m3)
σ	surface tension, (N/m)

Chapter1

1 Introduction

Development in production from biobased resources has become a worldwide effort due to environmental concern and huge demand in alternative sources of chemicals and energy. Biorefinery products stand in competition with petroleum-based products concerning quality, economic efficiency, and product characteristics (Ragauskas et al., 2014). Lignocellulosic biomass offers many possibilities as feedstock for the energy sector but also for the chemical industry due to its chemical composition, abundant availability, and relatively low costs. They are available at large-scale from the side streams of pulp and paper industries, representing a valuable renewable resource (Pinto et al., 2011). The biobased economy is not only an implementation of innovative technologies using renewable resources but also it will be a real transition with a high impact on society at different levels (Langeveld and Sanders, 2010).

In 2010, the pulp and paper industry produced about 50 Mtons of low purity lignin. Only 2% was used commercially, and the remaining 98% was burned as fuel. Finding new ways for the utilization of excess lignin is important for enhancing the benefit of integrated lignocellulosic biorefineries. One reason for the low conversion of lignin is a complication in its structure and diversity between different plant sources of kraft, organosolv, and sulphite lignin. Therefore, introducing lignin to new markets will depend strongly on its structure and related properties (Strassberger et al., 2014). Converting lignin and lignocellulosic biomass to chemicals would substantially contribute to the economic viability of a biorefinery (Johannes, 2012).

Lignin deconstruction can be classified into different methods to generate valuable aromatic primary chemicals such as pyrolysis or thermolysis (Mohan et al., 2006) hydrolysis (Sun and Cheng., 2002), reduction or hydrogenolysis (Eachus and Dence, 2009), or oxidation (Crestini et al., 2010). Among the available processes for conversion of lignin, the oxidative process is a very promising way to yield highly functionalized monomers that can serve as starting materials for other processes in the chemical and pharmaceutical industries (Lange et al., 2013). De-polymerization of lignin by breaking the C-O-C bonds (β-O-4 ether linkage) proved to be a viable approach to increase its reactivity, miscibility, and compatibility with other chemicals (Roberts et al., 2011). Over the last decade, researchers are attempting to develop oxidation processes, which guarantee high selectivity under metal-free reaction conditions.

In this work, liquid phase oxidation of lignin to produce polyfunctional aromatics, aldehydes and acids performed. Among all the lignin-based products, vanillin was identified as the most important high added value compounds. Vanillin is used as flavouring and fragrance in food, cosmetic, and as intermediate for the synthesis of several second-generation fine chemicals and pharmaceuticals. Air is the most favourable oxidizing agent. This eliminates the bulk utilization of costly oxidizing agents. However, in some cases, the addition of small quantities of oxidants like hydrogen peroxide will increase carboxylate group (Dalimova, 2005) and reduce the time required for oxidation initiation.

Production of value-added chemical such a vanillin (flavoring and fragrance ingredient), ferulic acid, cinnamic acid, vanillic acid etc. is a big challenge due to complex and heterogeneous structure of lignin. Vanillin ($C_8H_8O_3$) is the major flavour component of vanilla. It has a wide range of applications in food industry as a flavour agent and in perfumery as an additive. Other applications include antioxidant additive, antifoaming agent, vulcanization inhibitor and chemical precursor for pharmaceutical and agrochemical industries (Cerrutti et al., 1997; Fitzgerald et al. 2003; Lopez-Malo et al., 1998; Villar et al., 1997). Currently 85% of vanillin is synthesized from guaiacol (a raw material from petrochemical industry) with the remaining 15% being produced from lignin (Triumph Venture Capital Ltd., 2004a). Since the yield of vanillin obtained from natural vanilla is limited by the production of vanilla beans, it is very expensive comparatively to the synthetic counterpart. In addition, its price is severely sensitive to several events (natural, economic or political) affecting its larger producer Madagascar (FAOSTAT, 2005). The unstable market of this natural product encouraged to develop chemical substitutions.

The controlled breaking of different linkage types in lignin needs detailed information on the stability of the bonds under different conditions and knowledge of the mechanisms of lignin decomposition. The most easily hydrolyzable bonds in lignin are the ester and ether bonds. Either a base, such as NaOH (with an extra nucleophile such as NaHS or anthraquinone), or acid-catalyzed oxidation (HCl or $AlCl_3$) can cleaves the β-O-4 ether linkage (Jia et al., 2011). Depolymerizing lignin is challenging because the resulting compounds can react to form even more stable species (Ragauskas et al. 2014). Acid and alkaline depolymerization of lignin will result in breaking of the ester bonds and some of the ether bonds, resulting in a rearrangement of bonds within lignin structure and even more condensed polymeric structure.

Overall, it is a challenge to obtain complete selectivity to aldehydes by oxidation depolymerization. Lignin has a complex aromatic structure, repolymerization of products could happen during oxidation (Li et al., 2007) and decomposition of target products under the experimental condition and over oxidation of aromatics (Lyu et al., 2018). There is a balance between aldehydes production, degradation, and competing reactions, which determines the maximum yield and selectivity. Because of the different reactivity of various types of lignin and particular structures, the oxidation conditions should be carefully adjusted to shift the balance for the aldehydes production (Pinto et al., 2011).

Furthermore, post treatment of reaction mixture is required following oxidation to recover lignin depolymerized product. Finding the optimum reaction condition for oxidation and product isolation is considered and addressed in this study. Oxidation reaction generally occurs at relatively low temperatures (below 250 °C) (Zakzeski et al., 210). However, the oxidation process cannot be easily controlled, and the alcohols, aldehydes and acids were usually formed simultaneously, which increased the cost of product separation in industry.

lignin oxidation has been widely studied and used in the pulp and paper industry in the bleaching process to remove lignin from wood pulp under relatively mild reaction conditions (Lange et al., 2013). Many oxidizing agents, such as oxygen, ozone, hydrogen peroxide, chlorine dioxide, and peroxy acids, have been used for oxidative depolymerization of lignin (Rahimi et al. 2014). Chlorine-containing oxidants (such as hypochlorite and chlorine dioxide) are efficient in lignin depolymerization, but they are environmentally hazardous due to the formation of chlorinated aromatics (Dence et al., 1996). Peroxide is an environmentally friendly oxidizing agent, but poor stability, weak oxidative power, and high cost are its drawbacks (Gellerstedt et al. 1982). Ozone and peroxy acids are highly efficient oxidants, but high cost limits their application at large scale (Ma et al. 2015). Molecular oxygen is the most attractive oxidant because of its abundance, low cost, nontoxicity, and environment-friendly nature (Rahimi et al. 2013). Since oxygen is a relatively weak oxidizing agent, strong base (such as NaOH) is usually required. Under alkaline condition, lignin is ionized and then oxidized and depolymerized by oxygen to aromatic aldehydes or acids (Gonçalves et al. 2001). NaOH solution is used to break down the non-condensed side-chain linkages within lignin fragments, transferring the S, G, and H units into syringaldehyde (S), syringic acid (SA), vanillin (V), vanillic acid (VA).

Using a batch reactor for lignin conversion has been extensively studied; however, there are some limitations when using a batch reactor for high temperature and pressure. For example, heating and cooling is time consuming and change the reaction behaviour, the interfacial area is low, safety concerns in aerobic oxidation process pose a challenge to develop a reliable process, and it is very important to work below flammability zone. These drawbacks can be overcome by performing the reaction in continuously operated in microreactors (Jensen et al., 2014). For fast screening of reaction conditions, continuously operated microfluidic devices open new possibilities compared to batch operation. Microfluidic reactors or microreactors refer to miniaturized reaction devices with sub–millimeter range dimension features (Liu et al., 2012). It has the potential to develop strategies to manipulate product selectivity independent of conversion by changing the hydrodynamics of reactor operation without changing operating temperature or pressure.

In order to enhance the process selectivity, many researches have employed continuous-flow microreactors for selective oxidation of petroleum-based hydrocarbon raw materials (Siddiquee et al., 2016; Leclerc et al., 2008; Fischer et al., 2010). The microfluidic reactor has been utilized to eliminate obstacles in batch reaction and study lignin oxidation in detail (Werhan et al., 2013). Oxidation study on hydrocarbons showed temperature, residence time and local oxygen present in close contact to liquid phase has great influence on the product selectivity as oxidation occurs mainly in the liquid phase. Also. increasing gas-liquid interfacial area and mass transfer coefficient can increase mass transfer at constant temperature and pressure (siddiquee et al., 2016). These researches can provide insight into the effect of oxygen availability during gas-liquid oxidation and how it is related to both oxidation rate and product selectivity.

Due to working in segmented flow condition and internal recirculation within the liquid segments, very short contact times of some seconds suffice to reach equilibrium. No preheating of the liquids was required as a large surface-to-volume ratio of the microchannels, provide rapid heat transfer and vanillin with purity higher than 96% was extracted (Assmann et al. 2011). In another work continuous flow microfluidic reactor was used by Assmann et al. (2013) for purification of vanillin and other oxidation products from the aqueous mixture using green solvent. Therefore, supercritical carbon dioxide was used to extract vanillin and methyldehydroabietate. Vanillin was hardly extracted by supercritical CO_2, but the products with higher molecular weight, like methyldehydroabietate, was extracted almost completely even at lower pressures (Werhan et al. 2013). Fries et al. (2008) discussed extraction of vanillin in aqueous phase with organic solvent using PDMS micro devices. Although further increase in the mass transfer was obtained using segmented flow, they found stratified flow more favorable due to the ease of phase separation in the chip (Fries et al. 2008).

1.1 Objectives

The main aim of this thesis is to study the potential of lignin to become the renewable aromatic resource for chemical industry in the future. Successful introduction of lignin and its derivatives into new market highly require knowledge about lignin and development of process to improve lignin reactivity. In-depth knowledge about these processes has been attained in this thesis for competition with fossil-based compounds and to produce value added green aromatic chemicals out of lignin.

Depolymerization of lignin by oxidative method, achieving the optimal process condition, and produce value added material. There is a great potential in oxidation of lignin since the native structure of lignin contain several functional groups that can be functionalised by oxidation. This thesis has the following objectives:

- Overcome the low reactivity of kraft lignin via oxidation.
- Efficient extraction of product mixture by organic solvent from aqueous solution by liquid-liquid extraction method.
- Determine the results of oxidation and production rate in microreactor and batch reactor to detect differences due to the different nature of the reactors.
- Influence of reaction hydrodynamic and partial pressure of O_2 in lignin oxidation reaction.
- Characterization of the product mixture to identify possible valuable products.
- Final objective is to develop a continuous process to produce aromatic green chemicals out of lignin. In this research emphasis is given to the production of a small group of interesting phenolic chemicals by a process performed under alkali condition.

1.2 Thesis outline

Chapter 1 presents an overview of lignin oxidation and the overall prospective of this MSc work.

Chapter 2 is a detailed literature review on the most important works published in literature about pulp and paper industries, lignin structure, oxidation method, including process conditions and principal results.

Chapter 3 presents the experimental procedure and materials used in oxidation reaction. It describes step by step using batch and microfluidic reactor with controlled temperature, oxygen pressure, and defined values of NaOH and lignin concentration for oxidative upgrading of lignin.

Chapter 4 discusses on the experimental data and characterization results from different batch and continuous reactor experiments. The characteristics of the products were investigated by means of FTIR, GC, HPLC as well as LC-MS.

Chapter 5 is about the risk assessment and hazard identification in pulping and bleaching process and a case study about water risk management for West Fraser company.

Chapter 6 includes the main conclusions of conducted research work developed in this thesis, as well as some key suggestions for future work.

Chapter 2

2 Literature review

2.1 Introduction

Global warming and shortage in fossil fuel resources have motivates the chemical industry to utilize renewable alternatives as a feedstock and replacing fossil-based products with biomass-based products (Hamaguchi et al., 2012). Sustainable feedstock needs to be cost-effective, available in large quantities, and be effectively converted to value-added products. Lignocellulosic biomass has become a great potential that provides a plentiful, inexpensive resource in the industry (Isikgor and Becer, 2015) for a variety of applications. This abundant availability is supported by the large numbers of world-wide annual lignocellulosic biomass production of about 200 billion tons (Zhang 2008). Forest biomass contains a rather complex mixture of carbohydrates, aromatics, lipids, proteins, and a wide range of smaller molecules such as vitamins, colourants, and odorants. (Argyropoulos, 2007). The key to the most efficient use of biomass is to design a sustainable process to separate biomass in its major compounds to generate the highest value added for all fractions. Various technologies are under development for lignocellulosic biorefineries. Mechanical and chemical processes are required to obtain pure compounds from this mixture to their utilization in downstream chemical transformations (Argyropoulos, 2007).

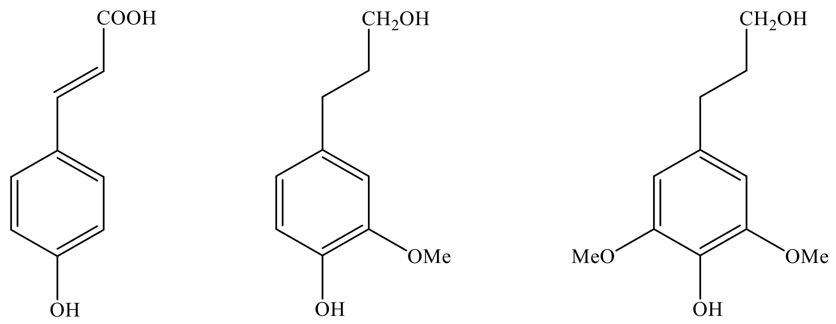
2.2 Lignin

Lignin plays a key role in structural components in the support tissues of vascular plants as a building material, giving it its strength and rigidity and resistance to environmental stresses (Ralph et al. 2007). It is one of the three main components in biomass and the second most available natural polymer after cellulose. It consists of three alcohol monomers (coniferyl alcohol, coumaryl alcohol, and sinapyl alcohol) linked by a variety of C-O and C-C bonds. It is worth mentioning that lignin is the only sustainable source of aromatic natural polymer (Sakakibari, 1980) and this characteristic brings very interesting future applications (Bozell et al., 2000). Lignin provides physical strength and protection from pathogens to plants. The pulping industry is the main significant producer of lignin, with sulfite and kraft processes being the two major techniques commercially used. It is separated from the black liquor of the Kraft pulping process (Sakakibari, 1980). Currently, lignin is mostly considered as a waste, and it is mostly burned in the recovery operation of kraft pulping process (Aresta et al., 2012).

Using lignin as a feedstock for producing value-added products has some favorable and unfavorable aspects. Lignin is not used as food by human, and it has an aromatic hydrophobic ring which is favorable. However, lignin is known for its non-uniform heterogeneous structure and large molecular weight which makes it low reactive and low in conversion (Satheesh Kumar et el al. 2009; Ragauskas et al. 2004). These complexities may hinder its conversion to other value-added products. For these reasons, lignin currently has a limited commercial production other than fuel source.

2.3 Structure of lignin

Lignin considers as a complex poly phenol composed of a three-dimensional network, lacking the regular and ordered repeating units of other biopolymers such as cellulose (Ralph et al, 2007). Lignin macromolecules has different structure and properties depending on its origin (i.e., hardwood, softwood, nonwood) and extraction process (i.e., enzymatic hydrolysis, kraft, sulfite treatment) in plant species (Toledano et al.,2010). lignin polymers exist in molecular composition and linkage types between the phenylpropane monomers. Lignin mostly contains functional groups such as carbonyl, benzyl alcohol, phenolic hydroxyl, and methoxyl, along with various types of linkages (Chen et al., 2014). Lignin is mainly derived from the polymerization of three alcohol monomers (also called monolignols), which are p-coumaryl, coniferyl, and sinapyl alcohols. These lignin monomer precursors build up the phydroxyphenyl (H), guaiacyl (G) and syringyl (S) lignin subunits Coniferyl (guaiacyl), sinapyl (synringyl), and p-coumaryl (phydroxyphenyl) alcohols are the main repeating units of lignin (Watkins et al. 2015; Helander et al. 2013). One example is depicted in figure 2.1.



H **G** **S**

2.1. Main structures present in alkali ultrafiltrated lignin fractions. H: p-coumaric acid; G: guaiacyl alcohol; S: syringyl alcohol.

In softwood lignin, coniferyl alcohol is the predominant building unit (over 95% guaiacyl structural elements), while in hardwoods the ratio coniferyl / synapyl shows considerable variation. In lignin of cereal straws and grasses the presence of coumaryl alcohol leading to p-hydroxyphenylpropane structures is typical. Lignin contents may vary in softwoods from 24-33%, in temperate zone hardwoods from 19- 28%, and in tropical hardwoods from 26-35% (Dence and Lin 1992). In non-wood fibre crops the lignin content is generally lower and ranges from below 3%, in cotton and in extracted flax or hemp bast fibres, to around 11-15% for sisal and jute (Van Dam et al. 1994).

Lignin structure is not exactly defined, but several researchers published representations of the prominent substructures of lignin (Figure 2.2). The most abundant bonds in lignin are C-O-C ether linkage type bond between phenylpropane units. The β-O-4 linkage accounts for more than half of the linkage structures and the easiest bond to cleave. It is responsive to pulping, bleaching and biological degradation reactions (Watkins et al, 2015). The C-C bonds between phenylpropane units, 4-O-5 and α-O-4 linkages are less than 10% of the total linkages. Furthermore, lignin includes branched and crosslinked structures. Table 2.1 shows the most occurring bond in different lignin structure.

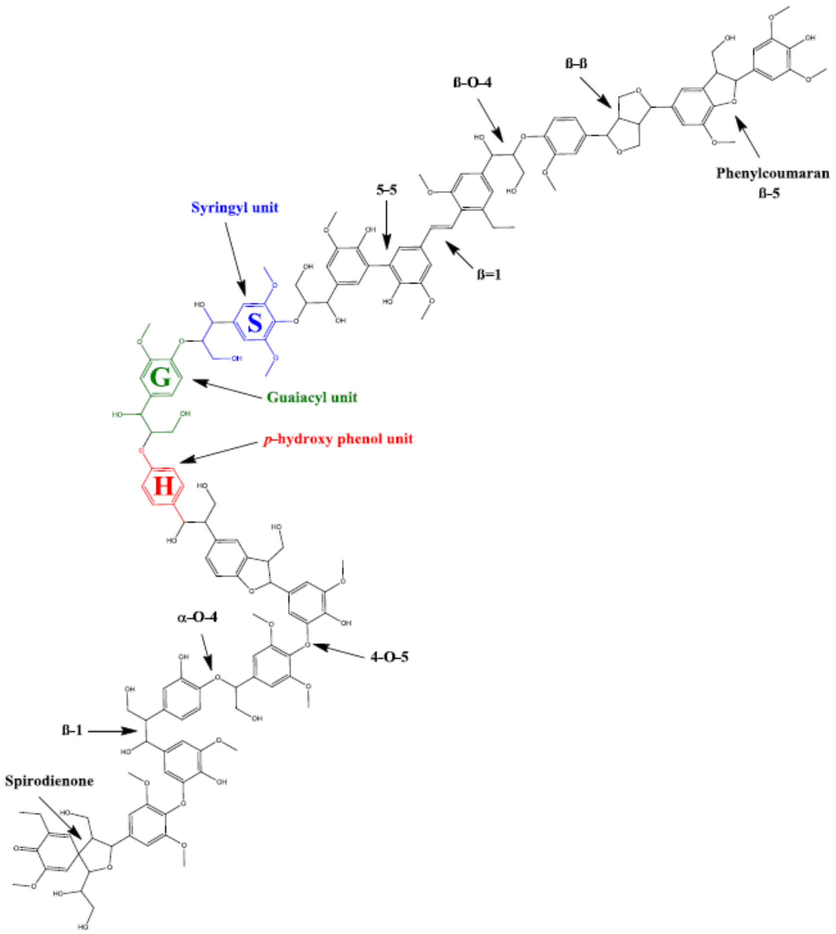


Figure 2.2. Schematic representation of lignin by Lupoi et al., 2015. Reprinted permission automatically granted from John Wiley & Sons Inc. and its subsidiaries, including John Wiley & Sons Ltd

Table 2.1. Types and occurrence of interlinkage bonds of lignin from different origins (Lin and Dence, 1992; Pinto et al., 2012; Santos R.B. et al., 2013)

Linkages	**softwood**	**Hardwood**
β-O-4	45-50	50-65
β-β	2-4	3-7
β-5	9-12	4-6
α-O-4	6-8	4-8
β-1	3-10	5-7
5-5	10-25	4-10
4-O-5	4-8	6-7

The total annual capacity of technical lignin production is around 785,000 tonnes/year of which approximately 60% corresponds to the production from Borregaard LignoTech and the remaining from other companies (as example, Tembfibre, Fraser Paper, Tolmozzo,Westvaco) Lignosulphonates (M.W. 20,000–50,000) have higher molecular weight and lower content in free phenolic hydroxyl groups than Kraft lignins (M.W. 2000–3000). The content in free phenolic hydroxyl groups of Kraft lignin is especially rich with values around 3.1meqg−1 (Saake and Lehnen, 2004).

The commercially used lignin is available in two categories: (1) the sulphur-free lignin, mainly obtained from biomass technologies that focused on biofuel production, organosolv pulping processes (Lebo et al., 2001), and soda pulping based on alternative resources like agricultural residues and non-wood fixbres (Lora and Glasser, 2002); and (2) the sulphur containing lignin, which result essentially from Kraft and sulphite pulping processes. This category almost provides the whole market of commercially available lignin.

2.3.1 **Kraft lignin**

Kraft lignin is readily available since it represents the residues of chemical pulping processes in paper production. This lignin is precipitated from the black liquor by pH-controlled precipitation. Kraft lignin is structurally highly modified, as approximately 70–75% of the hydroxyl groups become sulfonated during standard kraft pulping procedures. Degradation results in a low number average molecular weight (Mn) of about 1000–3000 Da, with an estimated average monomer molecular weight of 180 Da. Kraft lignin is soluble in alkali and in basic solution and in highly polar organic solvents (Lange 2013).

2.3.2 **Sulfite lignin (lignosulfonate)**

Lignin from sulfite pulping processes are indicated as lignosulfonates and are produced by using sulfurous acid and/ or a sulfite salt containing magnesium, calcium, sodium, or ammonium at varying pH levels (Meister, 2002). Hardwood lignosulfonate and softwood lignosulfonate are obtained from waste pulping liquor concentrate by the Howard process (Nunn et al., 1983) after recovery of the sulphur. Their monomer molecular weights are approximately 188 Da, and 215–154 Da, respectively. The number-average molecular weight (Mn) can vary from 1000 Da to

140,000 Da. Lignosulfonate is soluble in acidic and basic aqueous solutions, and highly polar organic solvents.

Neither kraft lignin nor lignosulfonate is suitable for studying the behaviours and the characteristics of natural lignin. However, their conversion to industrial by-product is important, and there is a lot of studies available on their degradation (Lange, 2013).

2.3.3 LignoForce

Another developing process is the LignoForce system. In this thesis, lignin is softwood Kraft from mixed species produced via Lignoforce process, where black liquor is oxidized by oxygen before CO_2 precipitation. Lignin from this process yields lower ash content and higher lignin purity without residual hydrogen sulfide (Kouisni et al., 2014). This lignin is studied to produce aromatic chemicals and carboxylic acids described in Chapter 4.

2.4 Lignin potential applications

Lignin production has been estimated to 50 million tons annually, however, only 2% of lignin is converted into value-added chemicals including dispersants, adhesives, and surfactants (Roberts et al., 2011) In addition to the high abundance, lignin has many desirable physiochemical characteristics including a large number of functional groups. As lignin has such a wide variety of reactive units arising from its monomeric structure, including phenol, ether, carboxylic acid, and O-H functional groups (Hatakeyama., 2010) it can be functionalized for desired applications, such as flocculants. (Fang et al., 2010) dispersants, (Konduri et al., 2015)] binders (Lumadue et al., 2012), adhesives (Zhao et al., 2016), hydrogels (Thakur et al., 2015) and composites (Mamun et al., 2016).

2.5 Products and chemicals from lignin

The opportunities and challenges for biorefinery lignin were studied in a detail by Holladay et al. (Holladay et al., 2007). This report demonstrates the versatility of lignin for multiple applications. Potential uses of lignin were classified in the three groups including:

1. power-fuel and syngas

2. macromolecules

3. aromatics

These groups can also be classified based on the time-to-market with group 1 as the most current or near-term applications, group 2 for medium term applications and group 3 for the longer term applications. In the first group, lignin is used as a carbon source for energy production, such as syngas. The second group makes use of lignin's macromolecular nature and will be used in wood adhesives (binders), carbon fibres, and polymers like polyurethane foams (Gandini and Belgacem, 2008; Abe et al., 2010). The third group uses technologies to break the lignin linkages mono aromatics without sacrificing the aromatic rings for the production of polymer building blocks, aromatic monomers such as benzene, toluene, and xylene (BTX), phenol, and vanillin. In this thesis potential value-added lignin applications from group 3 have been selected. Production of mono aromatics and carboxylic acids from oxidation is the main scope of this work.

Table 2.2. Potential lignin applications (Holladay et al. 2007)

Oxidized products	Aromatic chemicals Phenols	Hydrocarbons	Macromolecules	Syngas
lignin monomers • Syringaldehyde • Vanillin • Vanillic Acid Aromatic acids Aliphatic acids Aldehydes Quinones	Aromatic polyols • Cresols • Catechols • Resorsinols	Naphthenic and aromatic hydrocarbons	Dispersants, Emulsifiers, Surfactant Flocculant Binders Resins Adhesive Carbon fibers Polymer Modifiers	Methanol Ethanol Propanol Butanol Mixed alcohol Green fuels Olefins Reformulated Gasolines

Lignosulfonates has high adsorption affinity, dispersibility and wettability that provides attractive configuration to use in many industries. For example, they have been utilized as anionic surfactants in concrete admixtures, in pesticides as corrosion inhibitors, emulsifiers and as ion-exchange resins

(Elraies and Tan., 2012; Tejado et al, 2007; Flores and Dobado, 2010; Borchardt, 1998). Lignin has a great potential for use as a surfactant because its inherent hydrophobic aromatic structure (Shulga et al., 2011), however its purity and limited efficiency has hindered its application. In industry application there are several pathways alters the regular surfactant production like grafting hydrophilic groups or monomers into lignin to produce lignin-based surfactants (Alwadani and Fatehi, 2018). Recently, lignin has also been incorporated into the production of flocculants, dispersants, and hydrogels as it is biocompatible and biodegradable with low toxicity (Wang et al., 2018; Konduri and Fatehi, 2015; Brzonova et al., 2017) At a relatively low production cost.

Around 75% of commercial lignin is converted to dispersants, binders, emulsifiers, and sequestrants. These applications have low value and limited growth. The production of carbon fiber, adhesives, polymer modifiers, and resins benefits from the macromolecular structure of lignin (Holladay et al., 2007).

2.5.1 **Lignin to monoaromatics**

Lignin is the only renewable resource for industrial production of aromatics and its direct and efficient conversion into discrete molecules or defined classes of high-volume, low molecular weight aromatic compounds is a very attractive goal. The oxidative depolymerization of lignin involves the cleavage of aromatic rings, aryl ether linkages, and/or other linkages in the lignin structure. Lignin oxidation products range from aromatic aldehydes to carboxylic acids, depending on the lignin source and the harshness of the applied reaction conditions (Pinto et al., 2011; Pandey et al., 2011; Pinto et al., 2013).These days, significant interest is focused to develop eco-friendly processes to obtain vanillin and syringaldehyde, as well as other related phenolic compounds. Vanillin (V), vanillic acid (VA), acetovanillone (VO), syringaldehyde (Sy), syringic acid (SA), and acetosyringone (SO) are products obtained from lignin oxidation in an alkaline medium (Filipa et al., 2019).

2.5.1.1 Vanillin Production from lignin

Vanillin production from the oxidation of lignin obtained from side streams of pulp and paper industries and biorefineries is widely studied and reported in literature (Sandborn et al., 1936; Hocking, 1977; da Silva et al., 2009; Aarabi et al., 2017). Vanillin was first produced by Haarmann and Reimer in the late 1800s using guaiacol. The production of vanillin (3-methoxy-4-

hydroxybenzaldehyde) by oxidative depolymerization of lignin, mainly from black liquor of sulfite pulping, is well known and typically is performed at 160- 175°C under alkaline conditions with or without using a copper catalyst. Borregaard is the only industrial producer of lignin derived vanillin. Especially softwood lignin is yielding higher amounts of vanillin as compared to hardwood lignin (Evju 1979).

Between 1930s and 1980s, the major synthetic vanillin supply market share was generated by lignin-containing waste produced by the sulphite pulping process (Triumph Venture Capital Ltd., 2004a). Since the mid-1930s Tomlinson and Hibbert (Tomlinson and Hibbert, 1936) have reported the production of vanillin from waste sulfite liquor by using hydrolysis procedure. Mathias and Rodrigues reported the production of vanillin by oxidation of kraft lignin, as well as the effect of the operating conditions on the kinetics of lignin oxidation reaction (Fargues et al., 1996). Kinetics of vanillin production using oxygen in alkaline medium (NaOH) without the heterogeneous catalyst was investigated by Fargues and coworkers. They developed a kinetic model to evaluate the degradation of phenolic compound. They investigated effect of temperature, oxygen partial pressure and initial concentration of phenolic compound on the reaction rate using standard products (Fargues et al., 1996). The literature data showed a wide range of yields on vanillin and syringaldehyde obtained in alkaline oxidation using O_2 with or without catalyst. Villar and co-workers reported 4% of vanillin yield using softwood lignin (Villar et al., 2001). Tarabanko and co-workers (Tarabanko et al., 2004) claim as maximum yield as 6-8% (dry solids base) for sulfite liquor. The maximum yield obtained by Mathias and co-worker in a batch oxidation of Pinus lignin was about 10% (Mathias and Rodrigues, 1995). For batch oxidation of lignin from sugar cane bagasse, Sales and co-workers reported yields of 1.7% and 1.9% for vanillin and syringaldehyde, respectively (Sales et al., 2007). Wu and co-workers (Wu et al., 1994) reported 4.7% for vanillin and 9.5% for syringaldehyde in catalyzed oxidation of hardwood lignin.

Although production of vanillin from lignin is obtained in small amounts and low yield, it attracted great attention recently due to the low cost, high quality and unique aromatic structure of lignin as a bio-based sustainable compound (Pinto et al., 2012). Araújo et al. demonstrated a fast batch oxidation protocol for vanillin production from lignin with a yield of 3.5–7.6% depending on the lignin source (Araújo et al., 2010). Pacek et al. reported that catalytic oxidation of sodium lignosulfonate under strong alkaline condition produced vanillin, acetovanillone, vanillic acid, and other compounds (Pacek et al., 2013). Vanillic acid is the oxidized form of vanillin, it is mostly used as a preservative and as an acidity regulator in wine and vinegar. acetovanillone, also known as apocynin, is structurally related to vanillin and has been studied due to its important pharmacological properties (Hart et al., 1990; Stefanska et al., 2012)]. Considering its application as a flavouring and fragrance ingredient, the global demand for synthetic vanillin is currently around 16,000 tonnes/year (Triumph Venture Capital Ltd., 2004b). Rhodia SA dominates the vanillin market using the catechol-guaiacol process. Borregaard (Norway), the second largest vanillin producer, is one of the remaining producers of lignin-based vanillin.

2.5.1.2 Syringaldehyde

Syringaldehyde is an organic compound occurring widely in trace amounts in nature. This phenolic compound poses its antioxidant, anti-inflammatory, antimicrobial, and antifungal properties so it has applications pharmaceutical industries (Yancheva et al., 2016). Syringaldehyde has been patented for use as hair and fibre dye and as pharmaceutical precursor for obesity and breast cancer treatments and represents an even higher market value (Eckert et al. 2007). Syringic acid is extensively used as a therapeutic, antioxidant, antimicrobial, anti inflammatory, and anticancer agent (Karthik et al., 2014) while acetosyringone is a chemical compound related to acetophenone and is used as a plant hormone and insect attractor (Srinivasulu et al., 2018).

2.5.2 **Aromatic aldehydes, ketons and acids**

Selective oxidation under mild conditions can cleave inter-unit linkages, preserve aromatic rings, and transform lignin into phenolic aldehydes, ketones, and acids (Ma et al., 2018; Cheng et al., 2017). These are all value-added platform chemicals, and can be used as artificial flavors, pharmaceutical intermediates, organic synthetic precursors, and so on. In a study, oxidation of hardwood kraft lignin by oxygen resulted in phenolic derivatives and organic acids (Villar et al., 2001). In another study, Azarpira et al. investigated the oxidation of lignin model compounds to aromatic acids and aldehydes by molecular oxygen (Azarpira et al., 2014).

2.6 Depolymerization of lignin

Diverse technologies have been investigated for lignin degradation to produce value added primary feedstock chemicals, such as pyrolysis, hydrogenolysis, and oxidation. Pyrolysis with or without catalyst decomposes lignin at elevated temperature (400–600 °C) within short time (≤2 s) in the absence of oxygen (Mohan et al. 2006).However, pyrolysis showed low yield and poor selectivity of aromatic products due to the formation of significant amount of char (more than 40%) (Mante et al., 20150. Hydrogenolysis, is a catalytic reducing process in the presence of hydrogen and metal catalysts. This method extensively investigated to depolymerize lignin into aromatics. Despite high yield of phenolic compounds, the major issue of hydrogenolysis is high operational cost due to the use of expensive catalysts (H_2), organic solvents, and sever reaction high temperature and pressure condition (Parsell et al. 2013).

Oxidation is also an effective depolymerization method for lignin, which has been successfully applied to pulping and bleaching in paper industry (Lange et al., 2013). Among the available processes for conversion of lignin into value-added chemicals, oxidative processes is a very promising way, since it holds the possibilities to yield highly functionalised, monomeric or oligomeric products that can serve as starting materials for other valorisation processes in the chemical and pharmaceutical industries (Lange et al., 2013).

2.6.1 **Base-catalyzed degradation of lignin**

The inter-unit linkages in lignin can be selectively oxidized with the assistance of catalytic systems. Inexpensive and environmentally friendly inorganic bases such as the hydroxides of alkali metals, have been widely used as catalysts for the base catalyzed depolymerization of lignin. The reaction of alkaline metal hydroxides with lignin usually result in a formation of aromatics (phenolic aldehydes, ketones, and acids), benzoquinones, and aliphatic (di)carboxylic acids. Ether linkages (α- and β-aryl ether), being the weakest bonds in the lignin structure, are predominantly broken down during the depolymerization process (Dabral et al., 2018). Alkali metal cation forms adducts, which acts as catalyst over β-O-4 bonds (Robert et al., 2011). The concentration of base and lignin to solvent ratio is important in base-catalyzed lignin oxidation. In addition, thermodynamic parameters, such as temperature, pressure, and reaction time, also regulate the yield of aromatic compounds during lignin depolymerization (Mahmood et al., 2013).

Extensive research is available on base catalyzed depolymerization of lignin. This process originates from the pulp and paper industry where these processes are used to depolymerise (hydrolyse) and extract lignin from lignocellulosic matrix to produce so-called wood-free cellulose fibres. Long and co-workers conducted base-catalyzed depolymerization and the simultaneous hydrogenolysis of lignin with Ru/C. They reported a significant decrease in the solid and increase on aliphatic alcohol and phenolic monomer (Long et al., 2015).Certainly, NaOH prevented the hydrogenation of lignin aromatic ring, and indirectly promoted the lignin depolymerization was also contributed to the highest phenolic monomer yield with the synergic catalyst of NaOH and Ru/C.

Using base-catalyzed lignin depolymerization have shown couple of drawbacks in its process. The important issue to mention is repolymerization of degraded intermediates that result in the formation of solid residue. Capturing reactive radical species with the help of a suitable radical scavenger is the key controlling repolymerization. Several radical scavengers and proton donating solvents, such as boric acid, alcohols, formaldehyde, formic acid, phenol, p-cresol and 2- naphthol, have been used to avoid repolymerization by researchers (Toledano et al. 2014; Huang et l. 2015). In addition, The conventional route to isolate the reaction products during base-catalyzed lignin degradation is to acidify the reaction medium and extract the products with an organic solvent, thus requiring large amounts of acid and organic solvent, and producing significant amount of saline waste water and creates subsequent problems regarding products isolation (Zakzeski et al. 2010).

2.6.2 **Acid-catalyzed Depolymerization**

Acid catalyzed depolymerization of lignin follows a similar mechanism to base-catalyzed depolymerization including dominantly cleavage of α- and β-aryl ether linkage. When running the reaction under acidic conditions with methanol methyl vanillate yields primarily as the main product while vanillin is the main product of the same reaction in alkaline oxidation. Furthermore, batch oxidation experiments have resulted in five more products including methyl dehydroabietate and carbomethoxy derivatives of vanillin and methyl vanillate. Apart from the monomeric products, significant amounts of dimers, trimers and oligomers were as well detected in the product mixture (Werhan et al. 2011). Rahimi and co workers conducted depolymerization of lignin under mild conditions (100 °C) using formic acid/sodium formate. Under acidic conditions greater than 60 wt% of the original oxidized lignin was converted to low molecular mass aromatic compounds (Rahimi et al. 2014).

2.6.3 Oxidative Depolymerization

In general, oxidative depolymerization of lignin is carried out to produce aromatics with increased oxygen groups, mostly aldehydes. Oxidation is a method to break selected bonds in lignin such as aryl ether bonds, carbon–carbon bonds or β-O-4 bonds in lignin. A significant amount of research has been carried out with a focus on lignin depolymerization targeting the β-O-4 bond cleavage. Generally, the hydroxyl group on the a-carbon in β-O-4 bond was oxidized to a ketone. This method involves using different oxidizing agents (e.g., oxygen gas, hydrogen peroxide and metal oxides). The products vary from aromatic aldehydes to carboxylic acids, for example, vanillin, vanillic acid, and syringaldehyde (Dai et al., 2016). Here, we wish to focus on methods and technologies aiming at the oxidative upgrade of lignin via radical pathways, since the native structure of lignin comprises several functional groups that can be selectively functionalised via oxidation.

2.7 Oxidation Chemistry

In organic chemistry, oxidation usually refers to either elimination of hydrogen (e.g. the sequential dehydrogenation of ethane) or the replacement of hydrogen atom bonded to a carbon with a more electronegative element such as oxygen (e.g. oxidative transformation of methane to CO_2) (Sheldon and Kochi, 1981). Oxidation is an important conversion process in pulp and paper industry to produce value-added products. Different oxidizing agents, catalysts and experimental conditions are employed in oxidation processes. These are discussed in brief to select an achievable oxidation process.

2.7.1 Oxidizing Agents

Oxidizing agents or oxidants are the compounds with a role as oxygen donors during the oxidation process. Chemicals such as permanganates or chromium salts are commonly used stoichiometric oxidants to produce fine chemicals (Centi et al., 2001). Other highly applicable oxidising agents are hydrogen peroxide, pure oxygen, air, and ozone. Centi et al. characterizes some commonly used oxidizing agents. Among all the oxidizing agents air is cheap and readily available. In the current research, hydrogen peroxide and oxygen were used as oxidants in oxidation reaction.

2.7.2 Gas Phase and Liquid Phase Oxidation

Gas phase and liquid phase oxidation of hydrocarbons are extensively studied in different research works (Bharadwaj and Schmidt, 1995; Emanuel et al., 1967). Gas phase oxidation is suitable for the lighter compounds such as C_4 hydrocarbons or compounds that would remain gaseous at oxidation conditions. The current study focused on liquid phase oxidation as lignin is not volatile and will be in the liquid phase at our experimental conditions. Lighter fractions produced during lignin oxidation could oxidize in the gas phase, but they have a negligible contribution to the overall oxidation process.

2.8 Lignin Oxidation

Basically, for oxygen used as an oxidant, radical and electrophilic mechanisms are involved in the lignin degradation, with vanillaldehyde/acid, syringaldehyde/ acid, and p hydrobenzaldehyde/acid as dominant products. In O_2-participant lignin degradation, the reactive species like O_2, $HOO^{\cdot}$, HOO^{-} and $HO^{\cdot}$ will co-exist with O_2. However, when using hydrogen peroxide, and subsequently chemically reactive species containing oxygen, the mechanisms usually follow radical and nucleophilic pathways, and the main products are aldehydes, acids, and quinines. Lignin oxidative conversion mainly contains three routes: side chain cleavage, ring opening, and condensation (He et al., 2017; Ma et al., 2015).

When aromatic products are desired, the oxidation is usually performed aerobically in aqueous alkaline media by using NaOH. Since alkaline media enables the selective production of aromatic aldehydes such as vanillin and syringaldehyde (Pinto et al. 2012). Additionally, some aromatic acids and acetophenone-like compounds are obtained. The reaction can be performed without a catalyst, although using catalysts such as CuSO4 have shown to enhance the product yields (Santos, 2010). Aerobic lignin oxidation into aromatics has also been demonstrated in acidic media, either in concentrated acetic acid with a Co–Mn–Zr–Br catalyst system (Partenheimer, 2009) or with diluted aqueous mineral acids such as HCl or $H_3PMo_{12}O$ (Werhan et al. 2011), yielding aromatic aldehydes and acids (or esters). Lignin oxidation can also be steered towards the generation of small carboxylic acids, such as formic, acetic and oxalic acid which can be further used as significant platform chemicals for chemical industries (Behling et al., 2016; Ma et al., 2015; Mota et al., 2016; Ma et al., 2014). This has been demonstrated under acidic, alkaline and neutral conditions, with oxygen or hydrogen peroxide as oxidant.

To avoid losses of vanillin by oxidation, two operational parameters should be controlled, oxygen partial pressure (pO_2) and reaction time. There is a conflicting effect on these two parameters, for example a high value of pO_2 can reduce reaction time but leads to vanillin degradation; on the contrary, a low pO_2 increases reaction time but it hinders vanillin oxidation. Moreover, during the Kraft lignin oxidation, formation of acid compounds can occur, lowering the pH of the medium. At lower pH values (<11–12) vanillin losses by oxidation become more significant (da Silva et al. 2009).

Suparno et al. reported using hydrogen peroxide for oxidative depolymerization of Kraft lignin, using hemin as a catalyst and hydrogen peroxide as an oxidising agent, which mimics the catalytic mechanism of lignin peroxidase. Relatively high yields of vanillin 19%, vanillic acid 9%, 2-methoxyphenol 2% and 4-hydroxybenzaldehyde 2% were obtained (Suparno et al. 2005). Xiang and Lee (2000) found that alkaline peroxide treatment of lignin at 80- 160°C yield mainly low molecular weight organic acids (up to 50%) with only traces of aromatics which are rapidly degraded by hydrogen peroxide. Zakzekski et al. (2010) reported catalytic process oxidation of lignin with low yield of aromatic aldehydes and acids which do not exceed 10% on lignin basis.

2.8.1 **Catalytic system**

Lignin catalytic oxidative depolymerization means converting lignin macromolecules to value-added platform chemicals catalyzed by selected catalysts under oxidative conditions. Activating heterogeneous macromolecules of lignin with high temperatures (as in pyrolysis), oxygen and/or water vapour produces phenolic compounds and bio-oils. Catalysts can improve the selectivity to target compounds and effectively decreases the required operating temperature. Pre-mixing the lignin with catalyst increases the cracking rate but it produces more coke, char and gas. Moreover, the catalyst deactivates more rapidly (Lotfi et al., 2016). With the effort of different catalysts or catalytic systems, functional groups, and chemical bonds such as side-chain linkages, phenolic hydroxyl groups and aromatic rings would be selectively oxidized. When the selective oxidative cleavage occurs in the sidechain linkages, the aromatics units would be retained, and lignin macromolecules can be transferred to phenolic platform chemicals (Liu at al. 2019). Some catalytic processes of lignin model compounds showed good conversions which are promising to further develop catalytic strategies for lignin depolymerization in a biorefinery concept.

2.8.2 **Non-catalytic System**

Although many metal-catalyzed methods are effective in oxidation, the reserves of metal catalysts are limited in the earth, and these catalysts generate harmful metal waste leading to increased costs and energy consumption in the post-treatment. Evidently, it is highly desirable to explore metal-free routes using O_2 or H_2O_2 as the oxidant in lignin depolymerization.

2.8.3 **Review on Oxidative Conversion**

Lyu et al. used molecular oxygen in alkaline media and sever condition than the typical condition for oxygen delignification in pulping and bleaching to crack lignin into monomeric aromatics and organic acids (Lyu et al. 2018). Lignin depolymerization yield was approximately 50–70% of the starting lignin, and p-coumarate (pCA) yield was 12.9. However, the yields of other mono aromatics such as vanillin, acetovanillone, 4-hydroxybenzaldehyde, and organic acids were negligible when oxygen was absent. These observations suggested that NaOH was able to directly extract pCA from the lignin without oxygen, but oxygen was necessary for the formation of other monoaromatics. Higher temperature and more oxygen resulted in fewer monoaromatics but more organic acids. For example, approximately 92% of the identified products at 160 °C for 1.5 h with 0.5 MPa initial oxygen pressure were the organic acids. Low temperature (up to 160 °C) and oxygen pressure were favorable to vanillin yield, but severe condition decreases the yield of vanillin due to excessive oxidation. Mathias and Rodrigues (1995) have reported that a 60 g/L solution of Kraft lignin from Pinus spp. can provide a maximum vanillin yield of 13% (w/w) value by using nitrobenzene in oxidation (7h of reaction, 147 ◦C, 2N NaOH and 0.84mL of nitrobenzene per gram of initial lignin). Villar et al. (1997), published a maximum yield for the total phenolic aldehydes (syringaldehyde + vanillin) of 14%, also based on nitrobenzene oxidation (40 min of reaction, 190 ◦C, 2N NaOH and 6mL of $C_6H_5NO_2$ per gram of initial lignin) using lignin precipitated from *Kraft* black liquor with the addition of a calcium salt dissolved in a water soluble alcohol. However, results from Araujo (2008) have shown a lower vanillin yield under identical operating conditions. Here, it is vital to notice that two different Kraft lignin was used as raw material. Seems to have a reduced capacity for vanillin production. The proper modification of lignin structure to make it favorable for the desired conversion is very crucial. In this aspect, the selective oxidation of CαH-OH in the β-O-4 linkages of lignin to Cα=O will obviously decrease the bond dissociation enthalpy of β-O-4 structures by 40–50 kJ·mol−1 (Kim et al., 2011), and then facilitate the conversion of lignin to high yields of products under mild conditions (Alireza et al., 2014). Moreover, the use of small organic compounds, e.g. formaldehyde (Shuai et al., 2016), alcohols (Lancefield et al., 2017), diols (Deuss et al., 2017; Deuss et al., 2015; Lahive et al., 2016) to react with lignin or its degraded intermediates, which could prevent undesired condensation reactions, results in an increase of value-added products. Overall, the successful conversion of lignin in biomass to valuable products should address multiple factors, from lignin itself to catalysts, solvents, and reaction conditions.

Fargues et al. stated during the lignin oxidation, a maximum amount of vanillin is formed when pH value begins to decrease, and consequently, the vanillin yield decreases. At higher alkali concentration ($pH > 12$) the rate of vanillin degradation is lower. At lower pH ($pH < 12$) the vanillin oxidation rate is second order with respect to the vanillin concentration (Fargues et al., 1996). Based on the results from different researches, it can be concluded that in addition to all the oxidation reaction conditions, oxidation time, can favor the production of aromatic acids because of the excessive oxidation of products. Therefore, the production of aromatic acids can be inhibited by reaction time controlling.

2.9 The integrated process of oxidation and product purification

Usually, lignin depolymerization processes generate a whole spectrum of mixed products so efficient and economic separation and purify the products stays a big challenge for practical lignin utilization (Zakzeski et al. 2010). For example, oxidation of lignin yields high-value monomeric chemicals including vanillin and methyl vanillate that must separate from the remaining mixture of high molecular weight reaction products (Silva et a., 2009). One of the applicable and well-established method for separating oxidation products is liquid-liquid extraction with an organic solvent. Liquid–liquid extraction with an organic solvent can recover the reaction products from the aqueous reaction mixture and a following organic solvent filtration step has been demonstrated to separate low molecular weight from high molecular weight products (Werhan et al.,2012).

Industrial companies as Monsanto (U.S.A.), Salvo Chemical Co. (U.S.A.), and Ontario Paper Co. (Canada) produce vanillin from the air oxidation of sulphite lignin and carry out the extraction of vanillin from the reactant medium by using liquid–liquid extraction with suitable solvents (benzene or toluene) after acidification of the medium. The acidification step is to precipitate the compounds of high molecular weight and a large amount of acidic solution is required. Furthermore, it is possible that vanillin is lost during this process, since vanillin may be co-precipitated during the acidification step of the lignin (Craig and Logan, 1962; Fargues et al., 1996; Zabkova et al., 2006). Accordingly, the traditional precipitation procedure, either by using chemicals or by the waste generation, is an option to be changed by more satisfactory solutions.

Other strategies like using ultrafiltration (da Silva et al. 2009) or using super critical carbon dioxide (Assmann et al., 2013) are also applied to separate oxidation products. Membrane processes has the requirement to act as separation units in biorefineries due their excellent fractionation capability, low chemical consumption, and low energy requisites. The cost of filtration processes can be reduced if optimal operating conditions are defined for this operation (Jonsson et al., 2008).

2.10 Potential of Microfluidic Reactor in Oxidation

Using continuous-flow liquid phase oxidation chemistry in microreactors has attracted so many researchers. It can assure high heat and mass transfer, safe use of hazardous oxidants, high interfacial areas as a result of large surface to volume ratios, and scale-up potential. Small characteristic dimensions of channels in microreactors provide a low liquid holdup, which is beneficial to avoid any safety risks associated with the use of hazardous oxidants.

By using microfluidic reactors, many parameters can be varied in short times and only small amounts of reagent are consumed. Elevated pressures and temperatures can be realized with limited risk due to the small volumes involved using continuous microreactor avoid transient phases where reactivity and selectivity can differ significantly (Jensen, 2001). The small-scale reactor assures safe operation even when working at high pressures (Marre et al. 2010). Furthermore, the small volumes processed in a microreactor are enough for chemical analysis.

2.10.1 **Multiphase Oxidation in Microfluidic Reactors**

Oxidation of lignin with oxygen is a multiphase (gas-liquid) reaction. Therefore, the reactants diffuse from one phase to the other phase for the reaction to take place. Gaseous component (here oxygen) is transferred from the gas phase to the liquid phase, where it can be consumed in the reaction to form products as in Equation (2.1). The driving force for the gas-liquid mass transfer of A is the concentration gradient, which is controlled by thermodynamic and chemical equilibria (Gemoets et al. 2016).

$$X(g) \xrightarrow{\text{mass transfer}} X(l) \xrightarrow{\text{oxidation}} \text{Product} \qquad \textbf{Equation (2.1)}$$

It is important to maximize the interfacial area between phases to promote mass transfer between phases. Consequently, the production rate can be maximized with using an appropriate reactor. Using microreactor is reasonable for liquid phase oxidation process (Hartman et al., 2011). Taylor flow is a uniform flow pattern which is characterized by gas bubbles, which are separated by liquid slugs and a liquid film on the channel walls. In the liquid and the gas bubble, internal circulations are arising from the interfacial friction and the slip velocity. This internal circulation facilitates mixing and fast transport of oxygen from the interface to bulk liquid (Su et al. 2009; Cubaud et al. 2012). For a Taylor flow (slug flow or segmented flow) regime in microreactors, the application of film theory for the calculation of the mass transfer coefficient (k_L) is highly applicable. Microreactor operating in the Taylor flow regime shows minimum axial dispersion and provides an excellent residence time distribution, allowing it to behave as an ideal plug flow reactor. (Leclerc et al. 2008; Waelchli et al. 2006; Yue et al. 2009). The mass transfer in multiphase oxidation processes is described using film theory model in Figure 2.3.

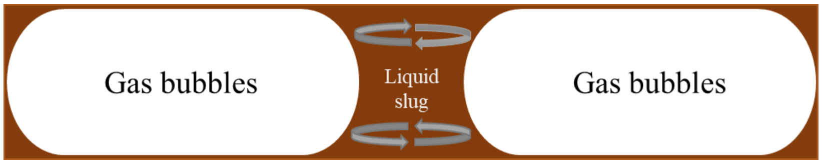


Figure 2.3. Taylor flow illustrating mixing within liquid slug

Based on film theory, mass transfer rate has been developed as:

$$J_A = K_L\ a\ (C_{Ai} - C_b) = \frac{D_A}{\delta}\ a\ (C_{Ai} - C_b)$$ **Equation (2.2)**

J_A is mass transfer rate across the gas-liquid interface (mol/m^3.s), K_L is the liquid side mass transfer coefficient (m/s), D_A is diffusivity of gas in liquid (m^2/s) , δ is the film thickness (m), a is gas-liquid interfacial area, (m^2/m^3), C_{Ai} is the concentration of gas at the interface, (mol/m^3), and C_b is the concentration of gas in bulk liquid (mol/m^3). δ and a are the two important parameters to enhance the gas-liquid mass transfer as change in the other parameters are limited. However, based on film theory δ is considered constant. Therefore, mass transfer in the oxidation reaction can be regulated with gas-liquid interfacial area. Microfluidic reactor platform assures increase the gas-liquid interfacial area (a) which would increase mass transfer coefficient (K_L). Moreover, the liquid film produced in microfluidic reactor is very thin which would also increase the mass transfer coefficient ($K_L = \frac{D_A}{\delta}$) and promote transport oxygen from gas phase into liquid phase (Danckwerts, 1970). The rate of gas-liquid reaction depends on the mass transfer through the film and on the reaction kinetics.

Werhan et al. compared batch reactor and microreactor for the formation of vanillin in acidic media, the final concentration of vanillin in each reactor was equally matched. However, the formation of vanillin in the microreactor was rapid and reaches to high concentrations within less than two minutes in residence time. They also studied the effect of temperature (150–250 °C), pressure (32–96 bar) and lignin concentration (2.5–10 g L^{-1}), on the monomeric products. Temperature had the most significant effect on reaction parameters, and elevated temperature resulted in a very fast reaction with an early maximum concentration of the products, especially for vanillin. Maximum concentration at 210 °C was more than seven times higher than at 170 °C and obtained within less than 1 minute of residence time (Werhan et al. 2013). Microfluidic reactor has also been used during the separation step in order to separate vanillin from the oxidized solution (da Silva et al. 2009). Significant enhancement in mass transfer from the aqueous phase to organic phase was reported for lignin extraction.

Chapter 3

3 Lignin oxidation experiments

With the purpose of determining the reactor performance for lignin oxidation the experiments of Kraft lignin oxidation were performed in different reactor configurations to compare oxidative conversion and productivity. In the first section we investigated the yield of chemical oxidation of kraft lignin and production to analyze the effect of operating process parameters. It was verified that operational parameters such as temperature, lignin concentration, oxygen partial pressure and sodium hydroxide concentration have significant effect on the produced vanillin amount. In this study, varying reaction temperatures (100–150 °C), reaction times (0, 0.5, 1, 2 hour), and initial O_2 pressures (0–20 bar) were investigated. The overall depolymerization yield of lignin during the alkaline oxidative cracking was calculated. To assure the oxidation is free radical conversion, a control experiment of lignin was performed with nitrogen and no products were identified via GC-MS analysis.

3.1 Material and methods

The lignin from West Fraser Hinton Pulp mill is softwood Kraft from mixed species produced via the Lignoforce process was selected for experiments. The properties of lignin are shown in table (3-1). Elemental analysis of CHNS-O was performed with Thermo Flash 2000 Elemental Analyzer.

Table 3.1. Lignin physical and elemental properties

Lignin Property	Units	Range
Solids	Dry solids, % of total	58 - 65
pH	15% slurry in DI water	9.0 – 10.0
Ash	% Dry solids	20 - 25
Sodium	% Dry solids	6 - 11
Sul3phur	% Dry solids	1.2 – 2.4
Carbohydrates	% Dry solids	1.2 – 2.4
Hydroxyl number	mg KOH/gm	225 - 245
Glass Transition Temperature	ºC	Not measurable
Molecular weight	Daltons, using GPC	5,000 – 8,000

Polydispersity		3.0 – 4.5
%N	% Dry solids	<0.1
%C	% Dry solids	32.74
%H	% Dry solids	3.68
%S	% Dry solids	1.38

Hydrogen peroxide (30%) and sodium hydroxide solution (50% in H_2O). Ethyl Acetate (99.5 %), Hydrochloric acid (1N) and Sodium Sulfate Anhydrous (99.0 %) used in liquid-liquid extraction process purchased from Fisher Scientific. Corning™ SFCA Syringe Filters (Fisher Scientific), Chloroform (98 %, HPLC grade, Fisher Scientific) used as a solvent in GC analysis, N,O-Bis (trimethylsilyl)trifluoroacetamide with (1% TMCS, Fisher scientific) for silylation process, extra dry oxygen (99.6 % molar purity) was used as an oxidizing agent and nitrogen (99.999 % molar purity) was used to control backpressure in the microfluidic reactor was supplied by Praxair Inc., Canada.

To facilitate identification of the oxidized products, several compounds were used as standards. Vanillin (99%), benzyl alcohol (99%), formic acid (99%), malic acid (99%), succinic acid (99%), lactic acid (85%), acetic acid (99.7%) were used for the identification of oxidation products by gas chromatography coupled with mass spectrometry (GC-MS). All chemicals were used without further purification. Standards for acetovanillone (98%), syringaldehyde (99%), hydroxybenzaldehyde (99%), p-hydroxyacetophenone (98%).

3.1.1 **Batch reactor**

The chemical oxidation of lignin with oxygen is a reaction that needs to be carried out on alkaline pH conditions (close to 14), temperatures near 100-150 ˚C and total pressure of 1000 Kpa. Batch oxidation of lignin performed under controlled operating conditions was used to compare the lignin conversion and product selectivity with a microfluidic reactor. Lignin, H_2O_2 and NaOH in different ratios were loaded into a 5 ml glass vial and placed in a ¾ inch stainless steel reactor. The reactor was purged three times and then pressurized with O_2 to the target initial pressure. Then the reactor was heated to the desired temperature. The temperatures inside the reactor and in a sand bath were measured using thermocouples, and a pressure gauge was installed to monitor the operating pressure. The reactor was then submerged into a preheated sand-bath (Model: FSB-3, Omega Engineering, Inc., USA) to control the oxidation temperature. The experimental apparatus is shown in figure 3.1. Reaction time was counted when the temperature in the reactor reached the target temperature. (usually took 8-15 minutes depending on target temperature). Once the temperature reached the target value, it was held for a specific desired time. When the reaction was completed, the reactor was cooled down to room temperature for 15 min using flowing air. The reactor was depressurized, and liquid oxidation products were collected for chromatographic analyses. A balance (Mettler-Toledo Model XP1203S, 1.2 kg weighing range, with 1 mg readability) was used to record the mass after each step of the experiment to ensure the mass balance.

The gas fraction was identified and measured on an Agilent 6890 gas chromatogram (GC) with a thermal conductivity detector (TCD) and a Flame Ionization Detector (FID). The results showed that the gaseous products from this process were less than 1 wt% of the feed lignin. Therefore, the yield of gas products was negligible and not taken into account in the mass balance.

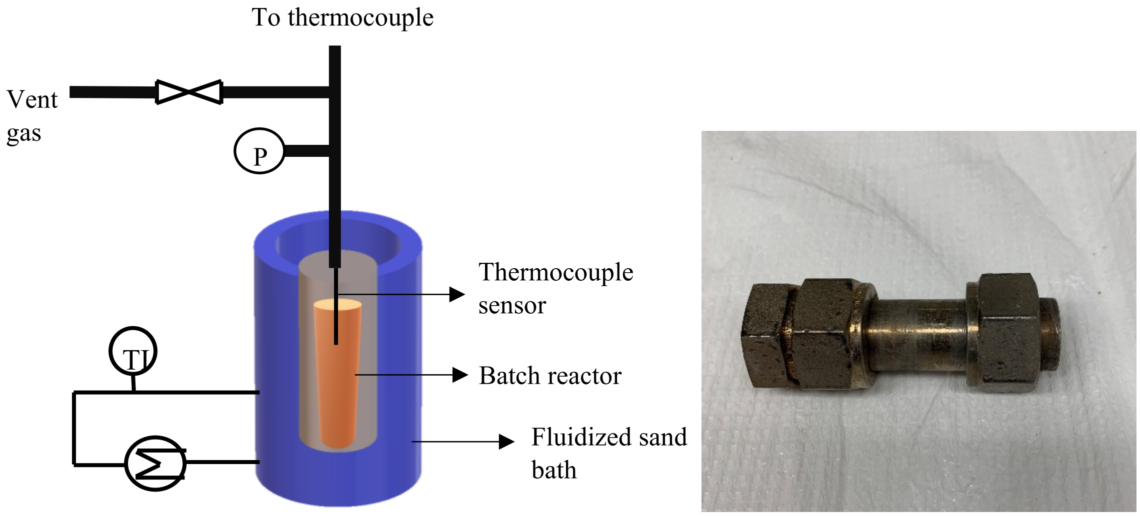


Figure 3.1. Batch experimental apparatus for lignin oxidation

3.1.2 Continuous microfluidic reactor

A 1000 µl glass microfluidic device (Figure 3.2) with a rectangular cross section for mixing and reaction of two or three liquid reagent streams was used for oxidation. The geometry information of the channels is described below.

mixing channel:

depth =1240 µm, width = 161 µm, length = 536 mm

reaction channel:

depth = 1240 µm, width = 391 µm, length = 1844 mm

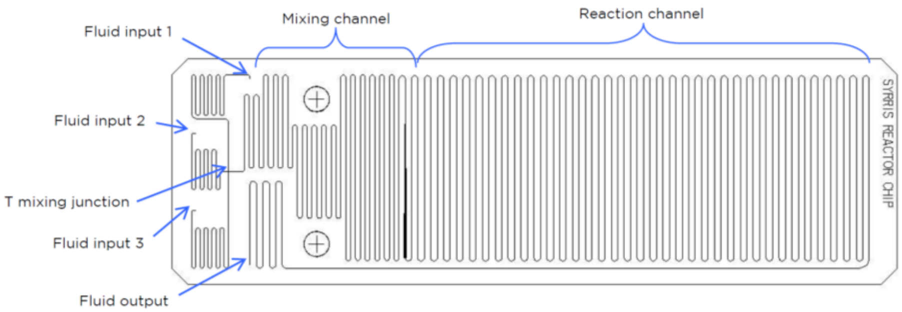


Figure 3.2. Microreactor channel layout

The reactor contains three inlets and one outlet port. The aqueous solution of lignin and other compounds was introduced through input 1 and oxygen injected through input 2 and input 3 was blocked. The gas and liquid phase brought to contact in the microfluidic device. The inlet design and back pressure regulator promoted slug flow, as the continuous liquid phase flowed through the main channel. The experimental setup employed for this investigation is shown in figure 3.3 image of the slug flow inside the microchannel is depicted in figure 3.4.

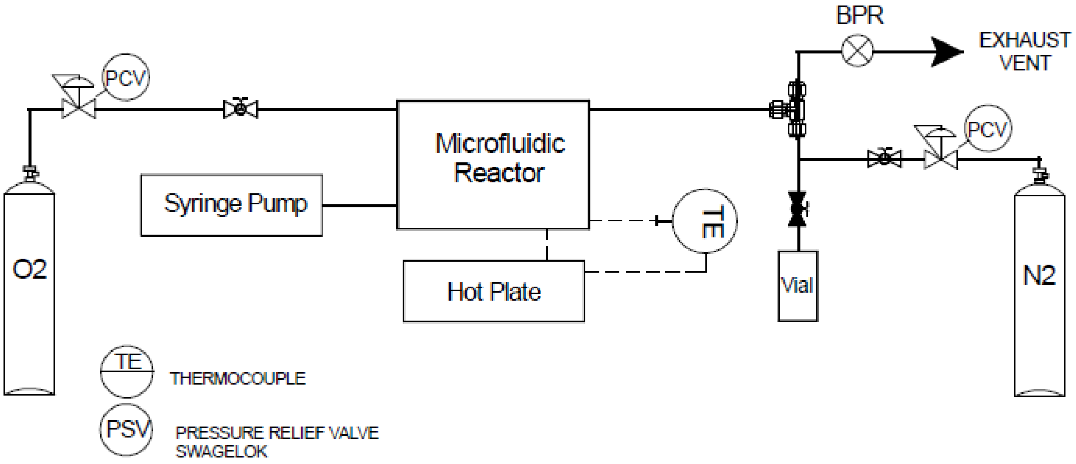
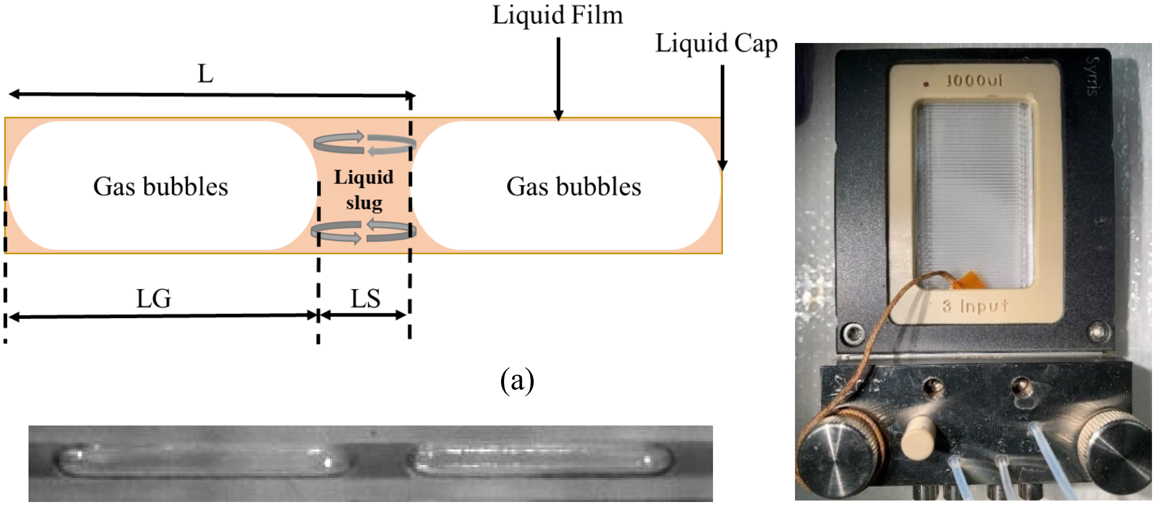


Figure 3.3. Experimental set up using microfluidic reactor for oxidation

The microfluidic experimental setup consisted of a microfluidic reactor (Dolomite Microfluidics, MA, USA), gas cylinder, gas flow meter (Swagelok, Canada), pressure bomb (Swagelok, Canada), and backpressure regulator (Swagelok, Canada). Syringe pump (HARWARD Apparatus) and syringes (1005TLL, Hamilton Co., USA) were used to inject the lignin solution into the reactor at the desired flow rate. A Heidolph MR Hei-Standard hot plate (Model: 505-20000-01-2, Heldolph Instruments, Germany) was used to provide the desired temperature of reaction in the microfluidic system. An aluminum block was used to limit the gap between the hotplate and the reactor. The reactor temperature was monitored using a surface mounted thermocouple (Model: CO 1, Cement-on Thermocouple, Omega Engineering, Inc., USA). A Flea3FL3-U3-13E4M camera (Point Grey Research Inc., Canada) was installed above the microreactor to capture the images of gas bubbles and liquid slugs. A Fiber–Lite lamp (Model: 3100, Dolan-Jenner Industries, Inc., USA) was improve lighting and the image quality. All the connections to and from the microreactor was made possible by using PTFE tubing, 1/16″ OD x 0.8 mm ID (Dolomite Microfluidics, MA, USA). Oxidation in microreactor was performed at 130 °C temperature and low pressure (2-3 bar). Tylor flow was maintained in the reactor to increase mass transfer between phases and oxygen bubbles were separated by liquid slugs to maximize interfacial area (Fig 3.4b)



(a)

(b)

(c)

Figure 3.4. (a) Illustration of gas-liquid slugs shows length of gas bubble (L_G), length of liquid slug (L_S), Unit length (L), liquid film and liquid cap and circulation within liquid slugs. (b) magnified gas-liquid slug in a microfluidic reactor. (c) microfluidic reactor used in this study.

In the experiment, 5 ml syringe was filled with aqueous solution of lignin. The system was pressurized to 40 psi using oxygen then lignin feedstock fed to the system by using syringe pump. Applied backpressure using a backpressure regulator and nitrogen gas was formed gas-liquid slugs in the system. The flow pattern was monitored during the experiment, and after the reaction was finished, the system was depressurized. Gas-liquid slugs were made at different size by changing injection rate of liquid feed. The oxidized product was collected from pressure vessel and analysed. The product mixture carried in vessel was washed with water then centrifuged. Solid fraction was washed three times with water. Then it was dried at 80 °C until constant weight. The supernatant was collected with water which was used for solid fraction washing for the qualitative and quantitative analysis. Hydrodynamic parameter, mass transfer characteristic and oxygen availability were calculated. Oxidation conversion and product selectivity were calculated from chromatographic analysis.

3.1.3 **Sample preparation and analysis**

The protocol used for sample preparation was similar to the one used by Mathias (1993). After oxidation, the mixture was transferred to beaker and acidified with HCl (drop-wise addition) to precipitate the lignin fraction that was not depolymerized during the oxidation. The supernatant was separated from the solid residue by centrifugation (20min, 4000 rpm). For batch samples Eppendorf centrifuge 5430 and for microreactor samples Eppendorf Microcentrifuge 5418 R was used. The solid fraction was washed three times with deionized water, dried at 80 °C until a constant weight and quantified by weighing. The supernatant was subjected to liquid-liquid extractions in a separating funnel for three times with ethyl acetate to recover lignin depolymerization products (figure 3.5). The three extracts were combined and dried over anhydrous sodium sulfate to assure removing traces of water from organic solution. The organic phase then filtered through syringe filter (0.2 µm) and identified using gas chromatography-mass spectrometry (GC-MS) and LC-MS. The aqueous phase was analysed using high performance liquid chromatography (HPLC) and Fourier transform infrared (FTIR) analysis, as described below. Liquid-liquid extraction process was necessary prior to analyses to transfer products from aqueous phase to the organic phase for analysis with GC-MS and LC-MS.

Figure 3.5. Liquid-liquid extraction of oxidation product with ethyl acetate

Derivatization of lignin depolymerization products

Alcohols, carboxylic acids, amines, thiols, and phosphates can be silylated. The process involves the replacement of a proton with a trialkylsilyl group, typically trimethylsilyl ($-SiMe_3$). Generally the substrate is deprotonated with a suitable strong base followed by treatment with a silyl chloride (e.g. trimethylsilyl chloride). The introduction of a silyl group(s) gives derivatives of enhanced volatility, making the derivatives suitable for analysis by gas chromatography. It is applicable using in structure investigations, or characteristic ions of use in trace analyses employing selected ion monitoring and related techniques (Blau and Halket, 1993).

The ethyl acetate extractable products were silylated by N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) in ratio 99:1 prior to GC-MS analysis. The ethyl acetate extract of 200–500 µl loaded in a 1 ml vial and dried with nitrogen. BSTFA (100 mm3) was added to the dried products in the vial and mixed by vortexing. The silylation was conducted at 60 °C for 30 min. Then the silylated samples were analyzed with GC-MS, as described below. Figure 3.6 shows how the functional groups react with the derivatization reagents.

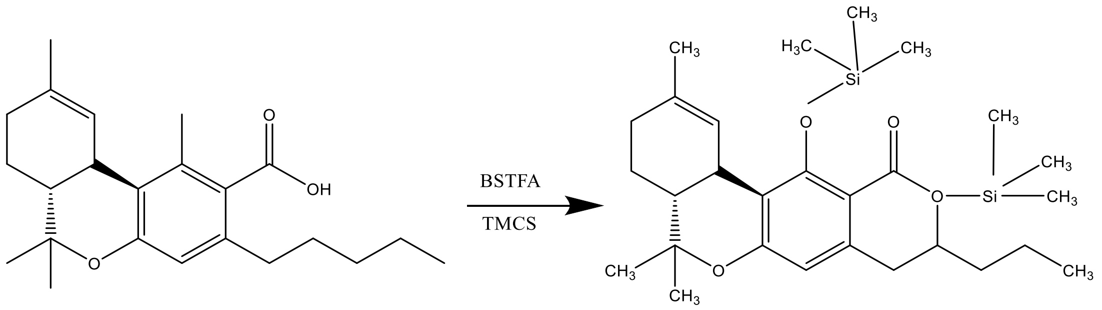


Figure 3.6. Derivatization of functional group in product with BSTFA and TMCS

3.2 Fourier transform infrared (FTIR) analysis

FTIR analysis of kraft lignin and oxidized lignin was also carried out at room temperature for both organic and aqueous phase using an ABB MB 3000 Fourier Transform Infrared (FTIR) spectrometer. A small amount of sample was placed on a potassium bromide (KBr) disc and the spectrum was collected over the wave number range 4000 to 500 cm^{-1} as the average of 120 scans per sample. The spectral resolution was 2 cm^{-1}, signal strength was 70 %, the acquisition mode was absorbance and detector gain was 243.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of the solid fraction were characterized by FTIR. Dried solid residues were blended with KBr (30% solid residue and 70% KBr) and pressed into thin pellets. The FTIR spectra were obtained using an ABB MB 3000 Fourier transform infrared (FTIR) Spectrometer. Spectrum was collected over the with 120 scans in the range of 4000 to 500 cm^{-1} at a resolution of 4 cm-1signal strength was 70 % and the acquisition mode was absorbance and detector gain was 729.

3.4 Nuclear magnetic resonance (NMR)

The proton nuclear magnetic resonance ($_1$H NMR) spectra of bitumen and oxidized bitumen samples were measured by a NMReady 60 spectrometer (Nanalysis Corp., Calgary, Canada). $CDCl_3$ and deuterium oxide (D_2O) (99.96 %, Fisher Scientific) was used as solvent and sample preparation. Samples were analyzed using standard 5 mm NMR tubes (NORELL, Landisville, USA). Experimental conditions was: frequency = 60 MHz, spectral range = 14 ppm, number of scans = 32. Peak assignments were annotated based on the different report in publications.

3.5 Gas Chromatography-Mass Spectrometry (GC-MS)

Identification of main monophenolic products and organic acids was performed by GC-MS using an Agilent 7820A GC system (Agilent Technologies Canada Inc., Mississauga, ON) and an Agilent 5977E MSD (Agilent Technologies Canada Inc., Mississauga, ON) mass spectrometer (MS). The products were separated on an HP-PONA 50 m × 0.2 mm × 0.5 μm column. Detected compounds were identified by the use of the National Institute of Standards and Technology (NIST) library of electron ionization mass spectra.

3.6 Liquid Chromatography-Mass Spectrometry (LC-MS)

Detection of analytes from lignin oxidation reaction and relative quantification was performed using reverse phase high performance liquid chromatography followed by detection using mass spectrometry (RP-HPLC-MS). An Agilent 1200 SL HPLC system with a Phenomenex Luna Omega Polar C18, 1.6um, 100Å, 2.1x50mm column (Phenomenex, Torrance, USA) with guard thermostated at 50°C was used. A buffer gradient system composed 0.1% formic acid in water as mobile phase A and 0.1% formic acid in acetonitrile (ACN) as mobile phase B was used. An aliquot of 1 µL of sample was loaded onto the column at a flow rate of 0.5 mLmin^{-1} and an initial buffer composition of 99% mobile phase A and 1% mobile phase B. After injection, the column was washed using the initial loading conditions for 1 minute to remove salts effectively. Elution of the analytes was done by using a linear gradient from 1% to 95% mobile phase B over a period of 6.0 minutes and kept at 95% mobile phase B over a period of 2 minutes. Mass spectra were acquired using an Agilent 6220 Accurate-Mass TOF HPLC/MS system (Santa Clara, CA, USA) equipped with a dual sprayer electrospray ionization source with the second sprayer providing a reference mass solution. Mass correction was performed for every individual spectrum using peaks at m/z 121.0509 and 922.0098 from the reference solution. Mass spectrometric conditions were drying gas 10 L/min at 325°C, nebulizer 30 psi, mass range 100-1100 Da, acquisition rate of ~1.03 spectra/sec, fragmentor 200V, skimmer 65V, capillary 3300V, instrument state 4GHz High Resolution. Data analysis was performed using the Agilent MassHunter Qualitative Analysis software package version B.07.00 SP2.

3.7 High-Performance Liquid Chromatography (HPLC) analysis

HPLC having Waters e 2695 Separation Module, Waters 2998 Photodiode Array Detector, and Waters 2414 Refractive Index Detector was used for the analyses of lignin and oxidized lignin. In this column chromatography sample mixture or analyte is pumped in a solvent (known as the mobile phase) at high pressure through a column with chromatographic packing material (stationary phase). The sample was carried by a moving carrier gas stream of nitrogen. The mixture of water and acetonitrile was used as the mobile phase (1:9 (v/v)) with a flow rate of 0.5 ml/min.

3.8 Thermogravimetric Analysis (TGA)

The lignin was characterized by using a TGA analyzer (TGA/DSC 1, Mettler-Toledo), for characterizing the decomposition temperature of the samples. The temperature was increased from room temperature to 700 °C at a 10 °C/min heating flow rate with a 100 mL/min nitrogen flow rate. TGA can provide information about the thermal decomposition/stability of kraft lignin.

3.9 Density measurement

A density meter (Anton Paar, DMA 4500M) was employed to measure the density of lignin solution feed and oxidized lignin at various temperatures.

3.9.1 Calculation formulas

The Dietz-method (Dietz, 1967) was used to calculate the response factor for model compound.

Depolymerization rate of lignin (%):

$$\frac{\text{Initial lignin weight (g)-Residual lignin weight (g)}}{\text{Initial lignin weight (g)}}\times 100 \qquad \textbf{(Equation 3.1)}$$

Yield of specific product (wt.%):

$$\frac{\text{Weight of specific product (g)}}{\text{Weight of lignin}}\times 100 \qquad \textbf{(Equation 3.2)}$$

Selectivity of a specific product:

$$\frac{\text{Relative peak area of specific product}}{\text{Sum of relative peak area of all the product}}$$ **(Equation 3.3)**

Hydrodynamic parameters and mass transfer coefficients were calculated using equations below and image analysis of gas bubbles and liquid slugs in the microfluidic reactor.

(1) Gas liquid interfacial area per unit liquid slug volume (a)

$$a=\frac{A}{V_L}$$ **(Equation 3.4)**

A is the surface area of gas bubble,

$$A = 2\left(wL_{G,actual} + hL_{G,actual}\right) + 4\pi\left(\frac{w+h}{4}\right)^2$$ **(Equation 3.5)**

$$L_{G,\ actual}=L_G-(w+h)/2$$ **(Equation 3.6)**

w and h are the width and depth of the reactor channel, respectively. L_G is the lengths of the gas bubble and w and h are the width and depth of the reactor channel, respectively.

(2) Radius of the cap of liquid slug can be approximated since the geometry formed by the two liquid cap is not a complete sphere.

$$r_{cap}=\frac{(w+h)}{4}$$ **(Equation 3.7)**

And hydraulic diameter of the reaction channel

$$D_h=2[\,wh/(w+h)]$$ **(Equation 3.8)**

(3) Volume of liquid slug

$$V_L = whL_S + wh\left[\frac{w+h}{2}\right] - \left(\frac{4}{3}\right)\pi\left[\frac{w+h}{4}\right]^3$$ **(Equation 3.9)**

L_s is the lengths of liquid slug.

(4) volume of gas bubble

$$V_G = whL_{G,\,actual} + \frac{4}{3}\pi\left(\frac{w+h}{4}\right)^3$$ **(Equation 3.10)**

Approximated radius of the cap of liquid slug:

$$r_{cap} = \frac{d_H}{2}$$ **(Equation 3.11)**

(5) Two-phase superficial velocity can be calculated from liquid slug velocity and gas bubble velocity.

$$U_T = \emptyset_G U_G + (1-\emptyset_G)U_L$$ **(Equation 3.12)**

U_G is the gas bubble velocity and U_L is the liquid slug velocity and were calculated from the distance gas and liquid phase traveled in the channel. Distance over time traveled were measured in the channel by using images captured from the flow in the microfluidic reactor. $\emptyset_G$ is the volume fraction of gas in the channel.

$$\emptyset_G = V_G/(V_G+V_L)$$ **(Equation 3.13)**

(6) Residence time was calculated using the two-phase superficial velocity divided by reactor length.

$$t = U_T/L$$ **(Equation 3.14)**

(7) The mass transfer coefficient (m s^{-1}) using film theory,

$$K_L=\frac{D_A}{\delta_{int}}$$ **(Equation 3.15)**

Mass transfer is frequently represented by a liquid side volumetric mass transfer coefficient, k_La (s^{-1}) which is a product of the mass transfer coefficient (k_L) and the effective interfacial area (a) with the known liquid side volumetric mass transfer coefficient and the gas-liquid interfacial area, liquid mass transfer coefficient can be calculated ($k_L = (k_La)/a$). where D_A is the molecular diffusivity of the gas phase in liquid phase (m^2s^{-1}). δ_{int} is the interfacial film thickness (m) and considered to be equal to the thickness of liquid film around the gas bubbles.

(8) Interfacial film thickness for rectangular microchannel is calculated using the equation provided by Yun et al. δ_{max} and δ_{min} are the maximum and minimum thicknesses of the liquid film (m), respectively (Yun et al., 2010).

$$\frac{\delta_{max}}{D_h}=0.39\ We^{0.09}$$ **(Equation 3.16)**

$$\frac{\delta_{min}}{D_h}=0.02\ We^{0.62}$$ **(Equation 3.17)**

(9) Weber number

$$We=\frac{D_hU_T^2\rho_l}{\sigma_l}$$ **(Equation 3.18)**

D_h is hydraulic diameter of channel; U_T is the two phase velocity (ms^{-1}); ρ_l is the density of liquid (kg m^{-3}); w and h are the width and depth of the reactor channel respectively, and σ_l is the surface tension of a liquid (N. m^{-1}).

(10) Capillary number

$$Ca=\frac{U_G\mu}{\sigma}$$ **(Equation 3.19)**

where U_G is the superficial bubble velocity, μ is the viscosity of liquid, and σ is the surface tension.

(11) Reynolds number

$$Re=\frac{d_H U \rho}{\mu_l} \qquad \textbf{(Equation 3.20)}$$

Where ρ is the fluid density and μ is the dynamic viscosity of fluid.

Chapter 4

4 Result and discussion

The identification of the intermediate products is an essential prerequisite in an investigation of any reaction mechanism. Thus, intermediate products after reaction were identified in detail by GC/MS, HPLC, FTIR and NMR. Besides, lignin oxidation results in physical changes like change in color, and chemical changes like change in functional groups, product formation and change in charge density. These are discussed in the following sections.

4.1 Identification of physical change after lignin oxidation

4.1.1 Change in color

During oxidation of lignin in batch reactor change in the color of feed solution observed. Lignin, dark brown in color (Figure a), was turned to light brown due to oxidation at 130 °C for 30 minutes in alkaline media (Figure b), very light brown after 1 hour (figure c), and turned colorless because of oxidation at 130 °C for 2 h (figure d). Oxidation performed in alkaline media using 1000 Kpa pressure of O_2. H_2O_2 was also used as oxidant. This change in color might be due to the formation of products having different functional groups, break in chromogenic bonds or production of smaller products.

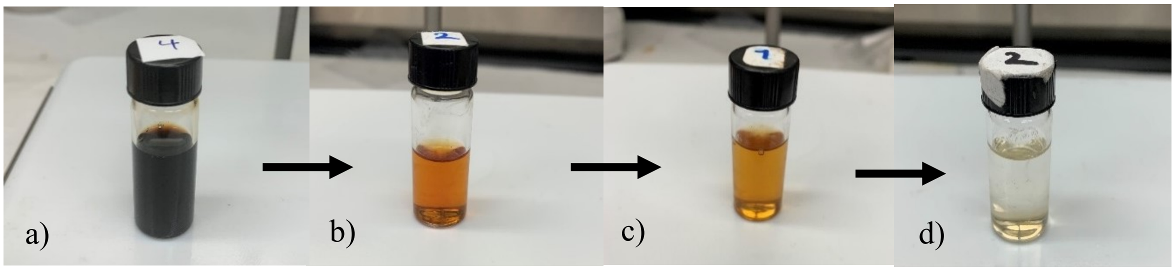


Figure 4.1. Visual observation of lignin before and after oxidation in batch reactor with 10 bar O_2 pressure and H_2O_2 in alkaline solution at 130°C. a) Lignin solution before oxidation b) After 30 min oxidation. c) After 1h oxidation and d) After 2 hours oxidation

4.1.2 **Change in density, pH and surface charge**

As shown in Table 4.1 density of lignin decrease due to the oxidation. Density of lignin solution was 1067.68 kg/m^3 (measured at 25 °C). After oxidation of lignin at different temperature for 1 hour with oxygen and hydrogen peroxide density decrease due to formation of smaller molecules with lower molecular weight and breaking lignin structure. The zeta potential of solution increased from -41.6 to -0.28. The increase in zeta potential is due to the decrease in ions on the surface of particles and shows the overall zeta potential is less negative. Therefore, particles repel each other less strongly when oxidation happens at higher temperature and form stable suspension. Conductivity is increased, and pH decreased when oxidation happens due to formation of organic acids.

Table 4.1. Chemical changes during lignin oxidation in batch reactor at three different temperature in alkaline media using O_2 and H_2O_2 after 1 hour.

Sample	**Density at 30 °C [kg/m^3]**	**Zeta potential**	**Conductivity**	**pH**
Lignin solution	1067.68±0.5	-41.6±6.26	1.49±0.3	13.78±3.2
Oxidized lignin at 100 °C	1063.72±1	-6.32±1.32	137±2.8	13.31±1.5
Oxidized lignin at 130 °C	1059.78±1	-2.56±3.35	130±4.1	13.34±2.1
Oxidized lignin 150 °C	1052.24±0.5	-0.28±0.03	135±3.58	12.87±0.3

4.2 Identification of chemical change after lignin oxidation

During lignin oxidation different functional groups has been changed. Characterization analysis performed to confirm the presence of these groups and additional products. the products of oxidation from batch and continuous microfluidic experiments were analyzed off-line using different techniques and instruments.

4.2.1 **FT-IR results**

The change in functional group was confirmed by using FTIR. The FTIR spectra of lignin and oxidized lignin are shown in Figure 4.2 revealed some slight differences between the 3 spectra in the peak intensity and shape. Oxidized lignin includes more oxygenate functional groups than lignin. It was complex to identify exact functional groups due to the overlapping of some absorption frequencies. For example, the fingerprint region (1800–800 cm−1) was composed of a group of complicated IR absorbance, which in spectral intensity and distribution of peak position.

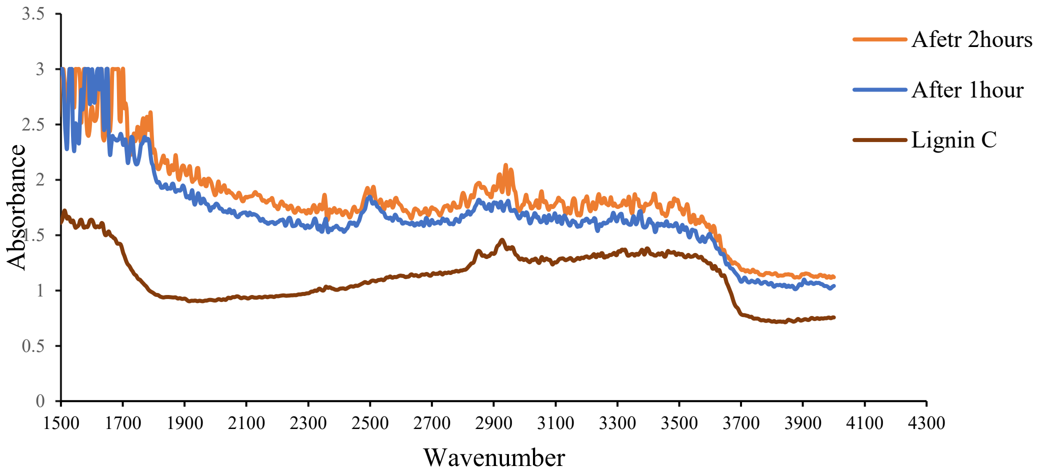


Figure 4.2. Infrared spectra of lignin and oxidized lignin in the 500-4000 cm^{-1} spectra region

The absorbance bands of functional groups in lignin include hydroxyl (OH), methoxyl, carbonyl group (C=O), and aromatic rings. The various lignin units (i.e., p-hydroxyphenyl, guaiacyl and syringyl units) and functional groups can be determined. Lignin shows diagnostic aromatic skeletal absorbance at 1500–1560 cm^{-1}.

Table 4.2. Infrared absorption frequencies of different functional groups (Peak et al., 1999; Maria et al., 2002; Xu et al., 2006; Williams and Fleming, 1989; Colthup et al., 1990; Silverstein et al., 2005).

Wave number	**Functional group**
3000-2500, stretching	OH carboxylic acid
3710 for water in solution 3600-3200 (b) stretch; for H-bonded O H	OH alcohol
1750-1735 (s) for saturated ester 1730-1715 for aryl and αβ-unsaturated ester	C = O ester
1725-1700 for saturated acid	C = O carboxylic acid

1715-1690 for αβ-unsaturated acid	
1725-1705 for saturated ketone 1685-1665 for αβ-unsaturated ketone 1750-1740 for five-ring ketone 1760 and 1730 for 1,2-diketones s-cis, six ring 1775 and 1760 for 1,2-diketones s-cis, five ring	$C = O$ keton
1740-1720 (s) for aliphatic aldehyde 1710-1685 for aromatic aldehyde 1705-1680 for αβ-unsaturated aldehyde	$C = O$ aldehyde
1510-1600	$C = C$ aromatic skeleton vibration
1606,1507,1434	Aromatic skeleton vibration
1460	Aromatic methyl group vibration
1374	Aliphatic C-H stretch in methyl
1043	Aromatic C-H in plane deformation

The strong and broad band at around 3670 cm^{-1} is a characteristic of OH groups of lignin. Peaks at 2500-3000 shows the stretching vibration of the aromatic OH group is larger in product spectrum. Oxidized product shows more alcohol/carboxylic acid production during oxidation reaction. The absorption bands at around 3400-3700 cm^{-1} (weaker hydrogen bonds) decreased in product, whereas those at 2300-3300 cm^{-1} (stronger hydrogen bonds) increased. This result indicates that oxidative degradation of lignin formed rather strong hydrogen bonds of OH groups, such as carboxyl OH, regardless of the total amount of OH.

Sharp peak at 2500 shows carboxylic acid production during oxidation. Peaks at 1750-1735 is C=O stretching in ester and peaks at 1740-1720 in product shows aliphatic aldehyde. Absorption at 1710 cm^{-1} belongs to formation of aromatic aldehydes in product. Peak at 1760 in product shows 6-ring ketone in product.

Considerable increase in the formation of carbonyl group in the spectrum of product than in the lignin indicates of diversity of C=O bond in the functional group after oxidation. There is also remarkable increase in C-H stretching (2600 3000 cm^{-1}). Absorption peak at 2350 cm-1 in product shows C=N=O asymmetric stretch vibration. Absorption in 3000 cm^{-1} and above shows aromatic C-H stretching which overlaps O-H bond.

There was an increase in the oxygenate functionality in the oxidized lignin. An increase in both C–O and C=O bonds were apparent from infrared spectroscopy.

4.2.2 **HPLC results**

To identify the organic acids formed during the oxidative degradation in this study, the aqueous phase behind the ethyl acetate extraction (Fig. 3.6) from different experiments of batch operation was analyzed using HPLC. The formation of acids is either from the oxidation of lignin side chains or the further degradation of the monoaromatics. The top three organic acids were acetic, propanoic and formic acids. HPLC trace of the liquid had only a few small peaks. HPLC chromatograms of lignin and oxidized lignin after reaction at 130◦C and for 1hour are shown in Figure 4.3. There are more peaks in the chromatogram of oxidized lignin (Figure 4.3b-d) compared to lignin (Figure 4.3a) and it is an indication of formation of oxidative products. Also, there is a small peak at the retention time of approximately 41.5 minute (Figure 4.3b) that might be due to the formation of heavier molecules.

Among these compounds, peaks labeled 0–5 represent compounds identified as shown in Figure 4.3. These compounds were mainly a variety of low molecular weight carboxylic acids with 1–4 carbon atom(s), including unsaturated dicarboxylic acid like fumaric acid and saturated monocarboxylic acids like acetic acid and formic acid. Formic and acetic acid is formed due to the cleavage of methyl and ethyl constituents followed by oxidation (Lotfi et al., 2016).

Products	Retention time
0-Propanoic acid	3.51
1-Formic acid	4.23
2-Acetic acid	5.89
3-Fumaric acid	9.23
4-Malic acid	15.68
5-Butyric acid	18.46

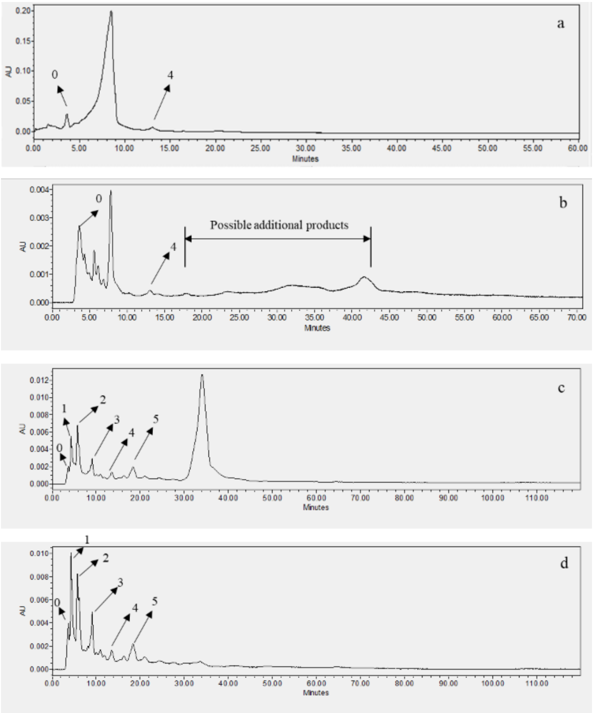


Figure 4.3. HPLC chromatogram of a) lignin and b) oxidized lignin at 130°C and identified products table

4.2.3 **NMR results**

In the ^{1}H NMR spectra the proton shift-values of $\delta = 0$ to 4.5 ppm was assigned to aliphatic hydrogen and the proton shift-values of $\delta = 6.3$ to 8.5 ppm was assigned to aromatic hydrogen. Table 4.4 compare this aliphatic and aromatic ratio in lignin before and after oxidation. Lignin oxidation resulted in the increase in aliphatic to aromatic hydrogen ratio. As indicated in table 4.3 relative aliphatic to aromatic hydrogen ratio was changed from to 0.1 to 0.98 during oxidation at 130 °C in batch reactor and to 0.25 in continuous microfluidic rector. Increase in the ratio of aliphatic to aromatic in batch experiment shows formation of aliphatic hydrogen from loss of aromatic hydrogen. However, in continuous reactor the loss of aromatic hydrogen selectively formed another aromatic hydrogen.

Table 4.3. NMR analysis of lignin feed and oxidized lignin in batch (1hour) and microfluidic reactor at 100 °C

Sample	**NMR analysis percentage**	
	Aromatic hydrogen (wt%)	**Aliphatic hydrogen (wt%)**
Lignin solution before oxidation	90.31	9.69
After batch oxidation	50.26	49.74
Continuous microreactor oxidation	79.88	20.12

4.2.4 **Thermogravimetry results**

Thermogravimetry analysis shows a typical thermogram of lignin TG analysis. Given its heterogeneous structure, lignin covers a broad temperature range, mainly from 150 °C to 800 °C, with the highest degradation rate between 360 °C and 400 °C. Kraft lignin loses 40% of its mass in thermogravimetric analyzer heated to 475 °C regardless of heating rate (figure 4.4). The first weight loss range 200–330 °C is from breaking monomers and release ammonia, acids and small quantities of CO. The second weight loss in range of 400–500 °C with breaking phenolic structures. Lignin loses weight, up to 650 °C and thereafter loses weight almost linearly with increasing temperature. Accordingly, at a maximum operating temperature (800 K), some of the lignin remains as a solid.

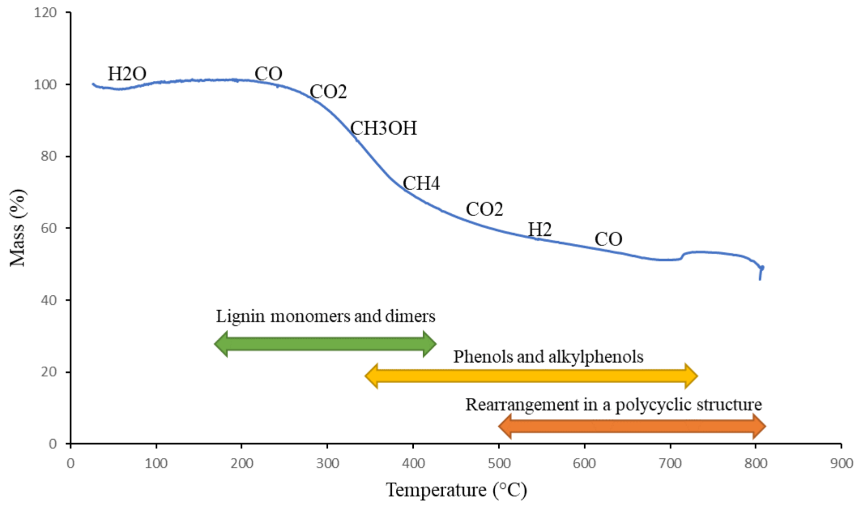


Figure 4.4. Thermogravimetric (TG) analysis of lignin

4.2.5 **GC results**

With the purpose of determining the reactor performance for lignin oxidation in terms of product formation, the experiments of kraft lignin oxidation were performed in two different reactors. Batch and continuously working microreactor has been utilized. According to the GC–MS spectrum (table 4.4), oxidation products involve monophenols, carboxylic acids, alcohols, and hydroxyl acid, while small molecules such as formic acid, acetic acid, methanol, and ethanol were removed by the L-L extraction and detected by HPLC. Monophenols include vanillin, *p* hydroxybenzaldehyde, acetovanillone, benzyl alcohol.

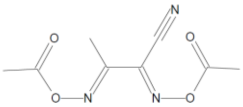
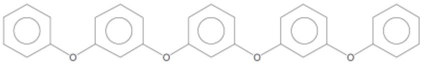
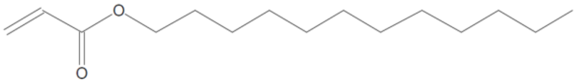
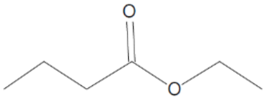
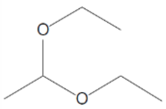
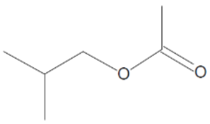
GC-MS analyses confirmed the presence of alcohol, ketones, and addition products. Depending on the oxidation stages, various carboxylic acids having aromatic and non-aromatic structures with mono- or di-carboxyl functional groups were characterized. One potential limitation of the selectivity determination based on GC-FID analysis is that the heaviest addition products will not elute and will not be detected.

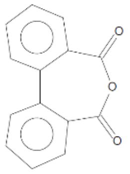
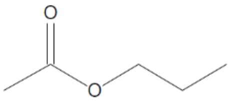
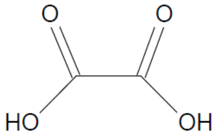
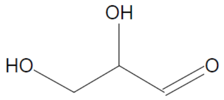
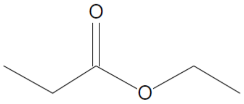
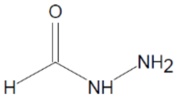
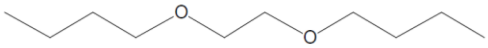
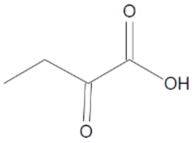
In this study, we observed very low amounts of aldehydes produced as compared to other studies, which may be due either to over-oxidation of aldehydes by hydrogen peroxide, leading to formation of carbon dioxide and water, or to the strong degree of condensation (C-C linkages) of lignin, which probably suppressed production of monomers. Various lignin structures that have different ratios of hydroxyphenyl, syringyl and guaiacyl units can lead to different oxidation products. Consequently, lignin produced higher amounts of vanillin than syringaldehyde; As Tarabanko and coworkers mentioned in their work, this was expected as source of the lignin used in this study was softwood and overall lower yields of aldehydes implied that the lignin was from conifers (Tarabanko et al., 1995). The yield of phenolics produced from lignin is dependent on the lignin's structure, which is dependant strongly on the source of biomass, part of the plant, pulping, and recovery processes (Villar et al., 2001; Robert et al., 1984).

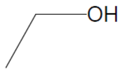
There is a maximum obtainable vanillin yield from a specific type of lignin. The formation of phenolic compounds like vanillin is strictly dependant to the available percentage of its precursor in the lignin structure. Most of the oxidation products had an aromatic ring in their structures, however; some non-aromatic mono- and di-carboxylic acids products were also detected in low percentages.

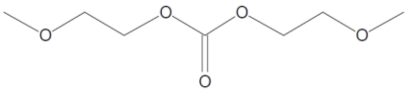
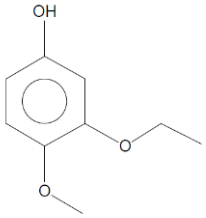
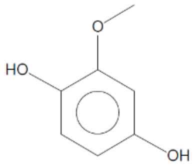
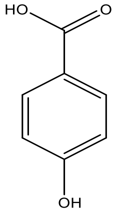
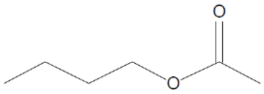
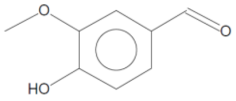
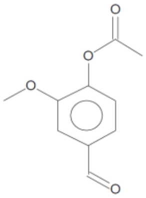
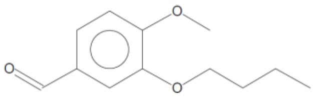
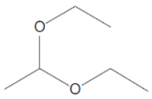
The significant oxidation products of lignin observed were vanillin. Other products formed by conversion of the aldehyde group to carboxylic acid like 4-hydroxy benzoic acid. After hydroxyl group added to the aromatic ring, the structure was unstable and further degrade into non-aromatic oxidation products. The absence of compound having three hydroxyl groups addition to carboxylic acid group in the aromatic ring indicates that these products are unstable and react very fast with the next hydroxyl group then result in breaking down the aromatic ring. This has been confirmed by Kang and coworkers (Kang et al., 2019).

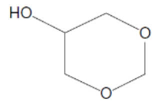
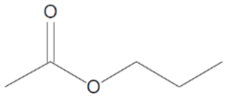
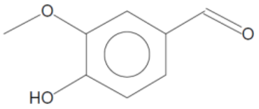
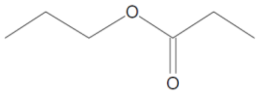
Table 4.4. The main components identified by GC-MS during alkaline oxidation of lignin from the volatile fraction in ethyl acetate.

Retention time (min)	**Compound**	**Structure**	**Mw**
6.04	Butanenitrile, 2,3-dioxo-, dioxime, O,O'-diacetyl-		211
3.69	Benzene, 1,3-bis(3-phenoxyphenoxy)- Polyphenyl ether		446
20.9	Dodecyl acrylate		240
7.54	Butanoic acid, ethyl ester		116
6.47	Ethane, 1,1-diethoxy- Acetaldehyde, diethyl acetal		118
7.08	Isobutyl acetate		116

25.07	Diphenic anhydride		224
6.12	n-Propyl acetate/ Acetic acid n-propyl ester		102
3.19	Oxalic acid		89.9
6.87	Propanal, 2,3-dihydroxy		90
6.087	Propanoic acid, ethyl ester/ Propionic ester		102
6.96	Formic acid hydrazide		60
	1,2-Dibutoxyethane		174
6.75	Butanoic acid, 2-oxo-		102

3.56	ethanol		46

	Ethanol, 2-methoxy-, carbonate (2:1)		178
16.83	3-Ethoxy-4-methoxyphenol		168
17.82	1,4-Benzenediol, 2-methoxy-		140
18.07	4-Hydroxybenzoic acid		138.03
7.74	Acetic acid, butyl ester		116
17.05	Vanillin		152
22.34	Vanillin, acetate		194
23.07	Benzaldehyde, 3-butoxy-4-methoxy-		208
6.46	Ethane, 1,1-diethoxy		118

6.5	1,3-Dioxan-5-ol		104
6.1	Propanoic acid, ethyl ester		102
17.07	Vanillin		152
7.75	Propanoic acid, propyl ester		116

4.3 Oxidation mechanism

Oxidation conversion mechanism in lignin usually starts with breaking of β-O-4 bond that is the easiest bond to break. Phenol radical formed as a result of this breaking. Redistribution of charge over the phenol ring in the presence of molecular oxygen, degrade side alkyl chain into formic acid and acetic acid passing through alcohols and aldehyde as intermediates. When the side chain is methyl and ethyl chains it can be oxidized to formic acid and acetic acid, respectively. Side alkyl chains containing double bonds can hydrate and then crack to form acetic acid (Hasegawa et al, 2011).

Oxidation of aromatics generally follows three routes- (i) preserving aromatic ring (phenol or benzoquinone formation), (ii) cleavage of aromatic ring to form oxygenates (benzene oxidation to produce maleic anhydride), (iii) H-abstraction from side chain at aromatic ring to form oxygenates (oxidation of toluene to produce benzaldehyde or benzoic acid) (Sánchez and de Klerk, 2018). These three routes are illustrated in Figure 4.5.

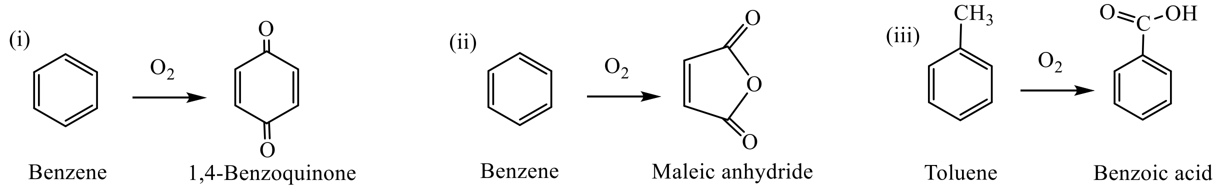


Figure 4.5. Three possible oxidation mechanisms in aromatics (Sánchez and de Klerk, 2018).

Catalytic routes usually follow the first two routes. Free radical oxidation mechanism follow route type (iii) and degradation mechanism is also shown in equation 4.1 to 4.7. As the C-H bond is relatively weak and requires lower level of energy in comparison to aromatic ring, in free radical oxidation the hydrogen transfer is easier. Further degradation of aromatic acids happens to form small molecules such as oxalic acid, acetic acid, formic acid, ethanol, methanol, and other undetected fragments.

Initiation starts with the reaction between hydrocarbons and molecular oxygen and free radicals are formed. Hydrogen atom transfer from hydrocarbon to molecular oxygen to form alkyl radical and perhydroxyl radical species. Free radicals that are formed in reaction 4.1 react with hydrocarbons and oxygen to produce new free radicals in reaction (4.2) and (4.3). (Emanuel et al., 1967; De Klerk, 2003).

Chain propagation by alkyl perhydroxyl can take place as shown in Reactions (4.4). In termination the free radicals like alkoxy radicals ($RO^{\cdot}$) play an important role in changing the product selectivity. They can form alcohol via hydrogen abstraction from the aromatic ring form alcohol and rapidly disappear as equation (4.6) and (4.7).

$RH+O_2 \rightarrow \dot{R}+HO\dot{O}$ **(Equation 4.1)**

$\dot{R} + O_2 \rightarrow +RO\dot{O}$ **(Equation 4.2)**

$RO\dot{O}+RH \rightarrow \dot{R}+ROOH$ **(Equation 4.3)**

$ROOH \rightarrow R\dot{O}+H\dot{O}$ **(Equation 4.4)**

$H\dot{O}+R \rightarrow \dot{R}+HOH$ **(Equation 4.5)**

$R'\dot{O}+R\dot{O} \rightarrow R=O+R'OH$ **(Equation 4.6)**

$ROOH \rightarrow R=O+HOH$ **(Equation 4.7)**

Auto oxidation leads to a series of highly reactive oxygen-based radical, which in further oxidize the lignin structure. In the presence of air, auto-oxidation introduces carbonyl and carboxyl groups to the lignin structure.

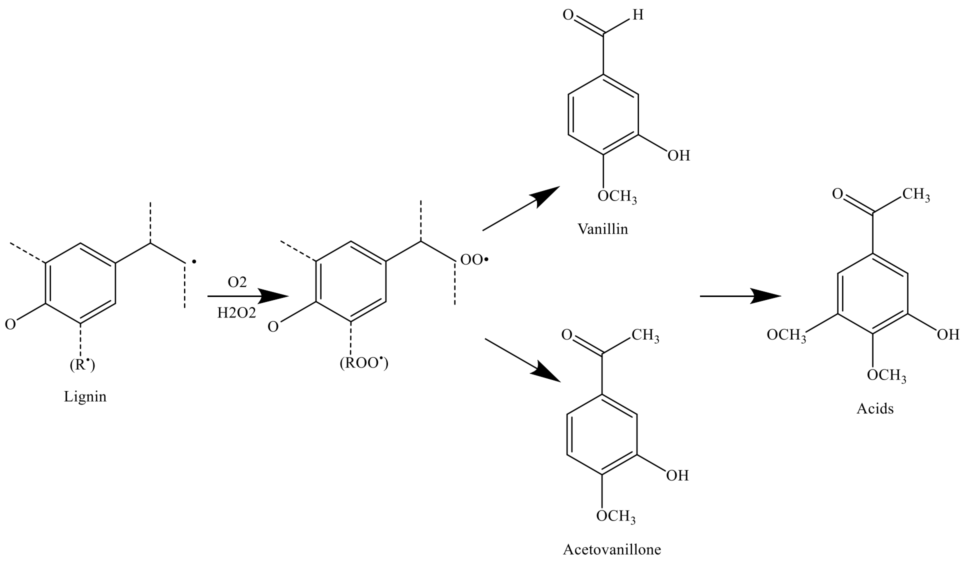


Figure 4.6. Oxidation reaction of lignin under alkaline condition (Kadla and Chang, 2001; Braun et al., 2005)

Using initiators like hydrogen peroxide increase rate of free radical formation and enhance initiation process. Using catalyst and organic salts of metals promote propagation (Emanuel et al., 1967). Selectivity of the products formed during termination depends on the experimental conditions like temperature, pressure, mixing, time, oxygen availability and use of catalyst.

4.3.1 **Possible mechanism in lignin oxidation with hydrogen peroxide**

Based on the results on reactions between hydrogen peroxide with lignin, a possible reaction mechanism has been proposed in Equation 4.8 and 4.9. Under alkaline condition hydrogen peroxide dissociates into hydroxyl radicals and superoxide ions. These compounds may react with each other or with hydrogen peroxide, resulting in oxygen and water as final products (Agnemo et al., 1979). Decomposition of hydrogen peroxide occurs through a disproportionation reaction that attains its maximum rate at the pH of its pKa (11.6) (Agnemo and Gellerstedt, 1979).

$H_2O_2+HO_2^-\rightarrow OH^-+O_2^-+H_2O$ **(Equation 4.8)**

$H_2O_2+OH^-\rightarrow H_2O+HOO^-$ **(Equation 4.9)**

Hydrogen peroxide by itself does not react with lignin, but the decomposed products from hydrogen peroxide react with lignin. As shown in Equation 4.9 perhydroxyl anion (HOO^-), being a strong nucleophile and the most active agent in alkaline hydrogen peroxide, breaks the α and β-aryl ether bonds of lignin to produce corresponding benzaldehydes, which are susceptible to subsequent oxidation (Kadla and Chang, 2001). A higher pH generates more perhydroxyl anions, which promotes the oxidation efficiency of hydrogen peroxide (Süss et al., 1998).

In addition, hydrogen peroxide oxidation of lignin is an endothermic reaction, so the higher temperature increases the reactivity of lignin, accelerated the oxidation, and increase the rate of lignin depolymerization. At temperature higher than 90 °C, the decomposition of hydrogen peroxide into hydroxyl radicals and other side reactions becomes more likely (Süss et al., 1998).

In the catalytic reaction of hydrogen peroxide with kraft lignin under alkaline conditions, the perhydroxyl anion cleaves the side chains of lignin, opens benzene ring, and produces new compounds. Under severe conditions, these groups may undergo ring cleavage reaction and further degrade to form a variety of low molecular weight compounds, such as oxalic acid, formic acid, and malonic acid.

4.4 Influence of Reaction Conditions on Lignin Oxidation

It was clear from the results that temperature, oxygen pressure, oxidants, alkaline media, reaction time and reactor hydrodynamics would affect oxidation products and selectivity. The following discussion compare the results from LC-MS relative quantification of products and show the effect of different parameters on oxidation.

4.4.1 **Effect of NaOH concentration on lignin oxidation**

Aliphatic alcohol is more stable than phenolic compound due to its saturated structure. In lignin depolymerization the ether bond, such as β-O-4 and $AOCH_3$, can degraded to produce phenolic monomer and unstable oligomer. Lavoie and co workers reported that the ether bond of lignin can be efficiently break with the base catalyst, resulting in more complete depolymerization of the lignin (Lavoie et al., 2011). In this study effect of NaOH concentration, ranging from 0 to 10 wt%, on vanillin, acid production and lignin depolymerization investigated. The Reaction for these experiments includes 20 mg lignin, 6.6 wt% H_2O_2 solution and NaOH aqueous solution (0-10 wt%), oxygen pressure was 1MPa and reaction performed at 130 °C for 1hour. The results in Figure 4.7 is a relative quantification of products in samples that prepared in the exact same condition. It shows that almost no product detected after oxidation without NaOH, and the small amount of vanillin present in the lignin as it was analysed at time zero may be in the process of preparation and purification of lignin. This is indication of the crucial role of NaOH. The exact function of NaOH is under investigation but covers assistance in C−O−C bond cleavage, phenolics solubility, and pH-dependent reactions (Ouyang et al., 2016; Tarabanko et al., 2004).

Retention rate is a relative amount for each product that measured based on area under the curve from LC-MS analysis. Figure 4.7 shows increasing the alkali concentration from 6 to 10 wt%, decrease vanillin retention rate 56.41% and 30.5% increase organic acid production (from 15.4 to 20.1%), mainly due to the fact that high alkali concentrations accelerate the oxidation of vanillin to acids. This is also reported by Mathias et al., 1955 and Silva et al., 2009. After adding the base at 5% the concentration had mall impact on lignin decomposition. Therefore, high base concentration leads to the condensation reaction more than lignin conversion.

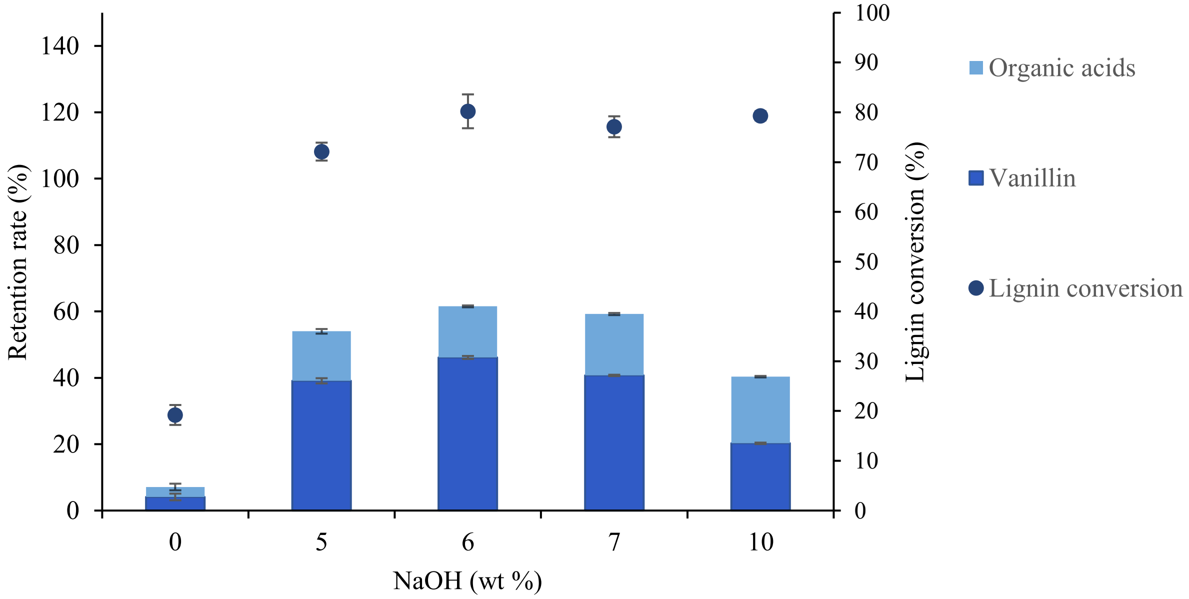


Figure 4.7. Lignin conversion and products retention rate in oxidation system under different NaOH concentration.

4.4.2 Effect of Temperature

Temperature have substantial impact on oxidation of lignin. Although vanillin formed at 130°C and 140°C, which indicated higher activity of hydroxyl radicals and superoxide ions at this temperature, percentage of produced small molecule compounds (organic acids) increased from 100 to 150 °C (figure 4.8).

In high temperature lignin depolymerization rate is promoted. At the same time secondary oxidation of products happens. Data shows that favorite condition to achieve efficient lignin conversion with high vanillin production are sufficiently high temperature and short reaction time. Impact of temperature on the kraft lignin including 20 mg lignin, 6 wt% NaOH aqueous solution, 1MPa oxygen pressure, 6.6 wt% H_2O_2 aqueous solution and 1hour reaction time in the temperature range of 100−150 °C was investigated (Figure 4.8). Lignin conversion reaches 83.4 % at 130 °C. Vanillin ratio increase to 46.5% for reactions at 130 °C and then decreased to 32.74 % at 150 °C. This can be explained by high activity of hydroxyl radicals and oxygen starvation at these temperatures. Besides vanillin and acetovanillone, other smaller compounds such as carboxylic acids, and alcohols present in the nonaqueous fraction.

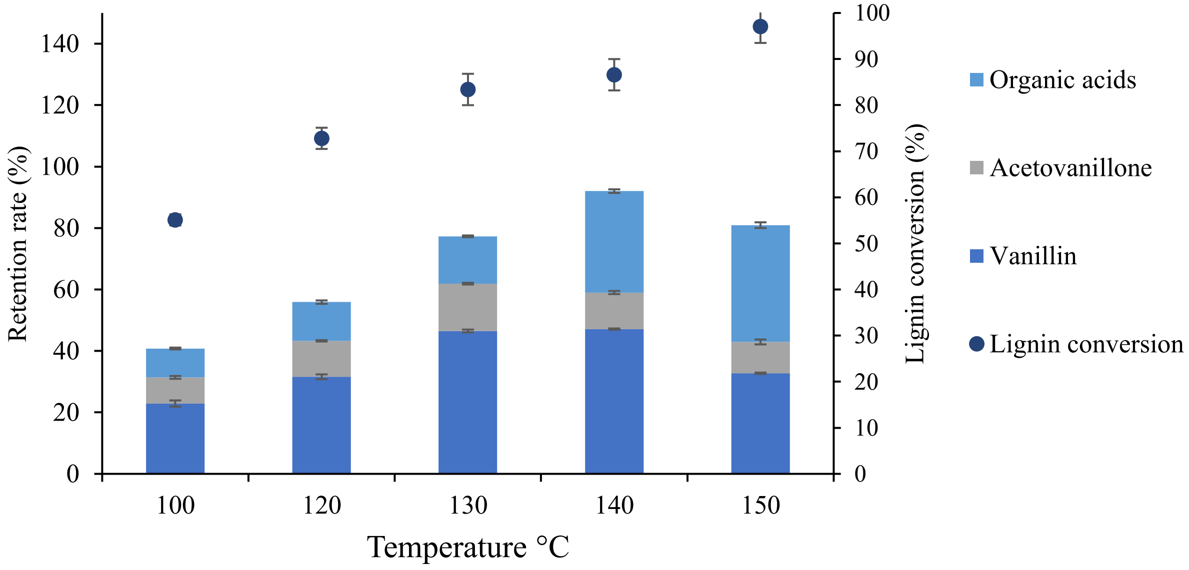


Figure 4.8. Lignin conversion and products retention rate in oxidation system under different temperature

4.4.3 **Effect of hydrogen peroxide and time**

Overall, 97.1% of lignin was consumed during the batch oxidation after 1 hour at higher temperature (150 °C) with addition of 6.6 % hydrogen peroxide in reaction media. and formations of dicarboxylic acids were significantly increased. With increasing hydrogen peroxide to 8% in reaction media, 100% lignin conversion obtained and increase in small components like acids observed. Time has the same effect on products when extending reaction time to 2 or 3 hours. Significant portion of the products determined in the sample were aliphatic mono (eCOOH) or dicarboxylic acids (HOOC—COOH). This is also confirmed by analyzing the aqueous phase from the reaction with HPLC. There were also some minor peaks that were not identified in those samples. These non-aromatic carboxylic acids are key building blocks that can be further converted into numerous chemicals, including plastic, polymer and resin products like paint and coatings.

The effect of reaction time was studied for the optimal reaction conditions, that is 6 wt % NaOH, 1.0 MPa O_2, and 130 °C. Vanillin production at 130 °C reached maximum in 60 minutes reaction time and then reduced afterwards. At the same time, the increase of reaction time led to an increase in the yield of small molecules and acetovanillone due to cascade reactions happen at long reaction time. In addition, products are oxidized more than once and usually consist of short chain aromatic acids and alcohols. Long reaction time in this study enabled high lignin conversion up to 87.3 % but reduced vanillin retention rate.

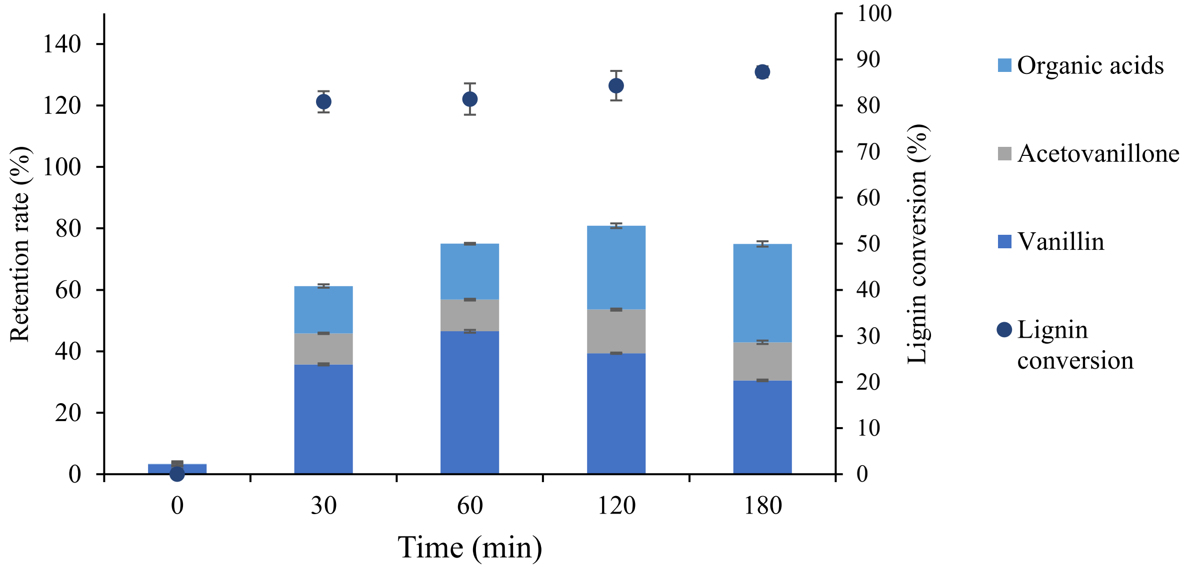


Figure 4.9. Effect of time on lignin conversion and products retention rate in oxidation system

4.5 Microreactor hydrodynamics and flow characteristics

The optimum operating condition in batch reactor was obtained, so it is easier to operate the microfluidic reactor using these conditions. In the initial phase of experiment in microfluidic reactor, the flow pattern in the microreactor was investigated to ensure that all experiments were performed in the slug flow regime. This regime, characterized by slugs of liquid alternated with gas bubbles, is known to benefit from high mass and heat transfer rates. All the experiments were performed under 40 psi oxygen, using lignin as feedstocks in 1000 µl rectangular cross section microfluidic reactor at different feed flow rate to obtain different slug sizes. The images were captured during the experiments to calculate the hydrodynamic parameters in microfluidic reactor. The length of liquid slugs L_S and gas bubble L_G were calculated from captured images. For calibration, a ruler was placed between the camera and the microfluidic reactor. The frequency of camera is 60 HZ. Figure 4.10 shows an example of photos taken during experiments with lignin.

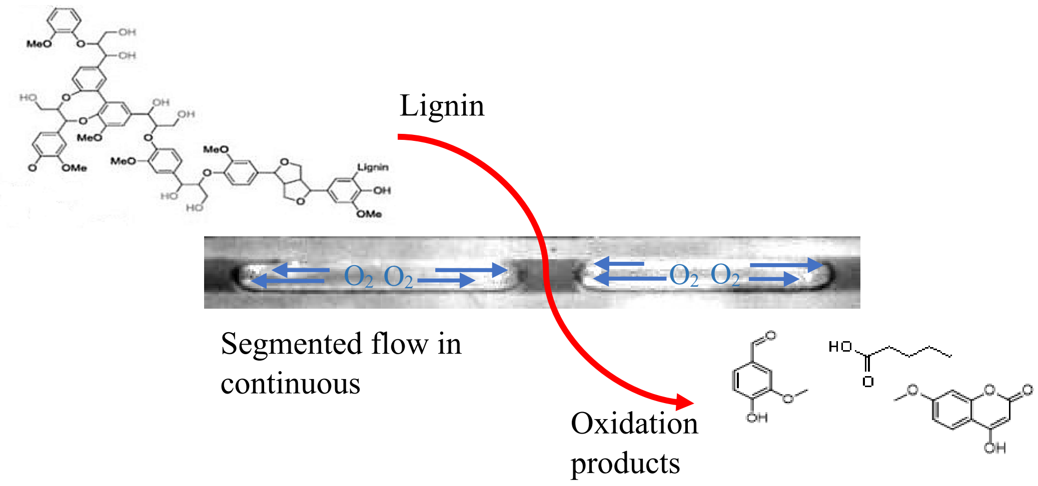


Figure 4.10. Graphical representation of oxidation in microfluidic reactor

The effect of the size of gas bubble and liquid slug on the flow pattern was determined by using a constant liquid flow rate and varying the oxygen inlet flow to achieve a range of gas–liquid interfacial areas (a), film thickness gas-liquid transfer area and mass transfer coefficient. Oxidation performed in 1000 µL microreactor showed liquid slugs (2×10^{-3} m to 3.8×10^{-3} m) and gas bubble (approximately 2.8×10^{-3} m to 7.2×10^{-3} m) resulting in maximum gas-liquid interfacial area (a) of approximately 1.31×10^{4} ($m^2\ m^{-3}$). Table 4.5 shows hydrodynamic parameters for the oxidation performed at 130 °C and 275 kPa gauge by using pure oxygen and hydrogen peroxide as the oxidizing agent. The two-phase superficial velocity (U_T) changes with sizes of the slugs and gas bubble. The highest two-phase superficial velocity was 8.04×10^{-3} m s^{-1}, that obtained in the case of smaller liquid slugs (series 1). Residence time decreased with increasing two-phase superficial velocity. The max and minimum estimation of film thicknesses of liquid film surrounding the gas bubble were calculated, respectively, based on equation (3.16) and (3.17).

Liquid side volumetric mass transfer coefficient was calculated using equation (3.15). The maximum liquid side volumetric mass transfer coefficient was 1.3×10^{-2} and was obtained in series 3 when we have obtained maximum interfacial area between liquid and gas phase. Hydraulic diameter of the reaction channel is $d_H = 6.0 \times 10^{-4}$ m and Diffusion coefficient was recorded from Garver and Callaghan, 1991.

Table 4.5A. Hydrodynamic properties, mass transfer coefficient during lignin oxidation in 130°C

series	Length of liquid slug $\times 10^3$(m)	Length of gas slug $\times 10^3$(m)	Gas slug surface area $\times 10^5$ (m^2)	Volume of liquid slug $\times 10^9$ (m^3)	Volume of gas bubble $\times 10^9$ (m^3)	Two phase superficial velocity $\times 10^3$ (m/s)	Interfacial area $\times 10^{-4}$ ($m^2\ m^{-3}$)	Total residence time (min)
Slug 1	2	4	1.25	0.97	1.94	8.04	1.13	4.28
Slug 2	3.3	2.8	0.856	1.6	1.36	3.22	0.497	10.7
Slug 3	2.1	4.8	1.51	1.02	2.33	4.03	1.31	8.54
Slug 4	3.8	7.2	2.29	1.84	3.49	3.36	1.15	10.2

Table 4.5B. Hydrodynamic properties, mass transfer coefficient during lignin oxidation in 130°C

series	Based on maximum film Thickness δ_{max} Based on Eq. 3.17			Based on minimum film thickness δ_{min} Based on Eq. 3.18		
	Film thickness δ_{max} $\times 10^4$	Mass transfer coefficient, k_L $\times 10^8$ (m/s)[a]	Liquid side volumetric mass transfer coefficient, K_La $\times 10^4$ (s^{-1})	Film thickness δ_{min} $\times 10^6$	Mass transfer coefficient, k_L $\times 10^6$ (m/s) [a]	Liquid side volumetric mass transfer coefficient, K_La 10^2 (s^{-1})
Slug1	1.29	4.16	4.7	5.31	1.01	1.1
Slug2	1.1	4.9	2.4	5.23	1.03	0.5
Slug3	1.14	4.71	6.1	5.25	1.027	1.3
Slug4	1.11	4.86	5.5	5.23	1.03	1.1

Reactor hydrodynamics along with temperature would affect oxidation of lignin. Film thickness as shown in equation (3.16) and (3.17) ensures a radial diffusion path and would increase the mass transfer. Liquid film thickness depends on reactor geometry, liquid agitation, interfacial properties of the channel, etc. (Danckwerts, 1970). For a rectangular microchannel, liquid film thickness (δ) surrounding a gas bubble is expected to be different. This can be explained by the Capillary number (Ca), equation (3.19), as increase in capillary number result in increases in film thickness (Hessel et al., 2005).

For Ca values less than 10^{-3}, the film thickness surrounding the gas bubble would be very thin in the corners. For values of Ca greater than 10^{-3}, the liquid film occupies a significant portion of the microchannel (Hazel et al., 2002). Ca is dependant on bubble velocity and increase in velocity would increase the film thickness. In this study, the calculated Ca value of $4.0 \times 10^{-5} - 9.9 \times 10^{-5}$ (Table 4.5) suggest a very thin film thickness in microchannel pattern. Yun et al. studied the film thickness for a rectangular microchannel and suggested correlations equation (3.16 and 3.17) to calculate the maximum and minimum film thickness (Yun et al., 2010). Since the maximum and minimum film thickness of the liquid film calculated are almost constant for all flow patterns (Table 4.7b) and the diffusivity of oxygen in lignin solution was expected to be constant at 130 °C, a change in the liquid side volumetric mass transfer coefficient (k_La) was mostly due to the increase in interfacial area. Therefore, the gas–liquid interfacial area was the most important parameter to assess the role of oxygen availability during the oxidation of lignin.

Different dimensionless numbers may be useful to approximate the gas–liquid two phase flow characterization in microchannel reactors. Depending upon the interaction among the gravitational, interfacial, inertial, and viscous forces, the flow in microchannels can take different forms such as bubbly, slug or annular flow. The importance of these forces can be understood using the characteristic dimensionless numbers (Table 4.5). A Reynolds number (Re) indicates laminar flow throughout the microchannel, as a characteristic of Taylor flow in microchannels (Günther et al., 2004). A small Reynolds number indicated that viscous forces dominated over inertial forces. Weber numbers (We) indicated inertial forces over surface tension forces that is essential to break down the slug between two phases. The Capillary number (Ca) characterizes the relative importance of viscous forces relative to surface tension forces. A smaller Ca indicated that surface tension had a larger effect than viscous force. Both the Ca and We indicated that surface tension is dominant, and slug formation is expected.

Table 4.6. Dimensionless numbers for the oxidation of lignin in microfluidic rector with oxygen at 130C and 40 psi gauge pressure

series	Re(L) $Re=\frac{d_H U_L \rho_l}{\mu_l}$	Re(G) $Re=\frac{d_H U_G \rho_G}{\mu_G}$	Weber number $\times 10^{-3}$ $We=\frac{D_h U_T^2 \rho_L}{\sigma_L}$	Capillary number $\times 10^5$ $\frac{U_G \mu_L}{\sigma_L}$
Slug 1	15.82	0.33	1.58	9.99
Slug 2	6.34	0.13	0.25	4.0
Slug 3	7.93	0.17	0.40	5.0
Slug 4	6.62	0.14	0.30	4.17

Determining the flow regime map for the channel is generally the first step in characterising two-phase flow behaviour. The various flow configurations that occur are dependent on the relative gas and liquid properties, flow rates and channel geometry. Two-phase flow regimes in microchannels have been experimentally investigated in many researchers (Fukano et al. 1993; Bao et al., 1994 Triplett et al., 1999). Figure 4.11a shows the flow regime map of Triplett et al. 1999 which was developed for air-water two-phase flow behaviour in a horizontal circular channel of 1.45 mm inner diameter in gas superficial velocity (UG) versus liquid superficial velocity (UL) coordinates. Five main flow regimes were identified: bubbly, slug, churn, slug-annular and annular. Figure 4.11b shows the morphology of the representative flow regimes

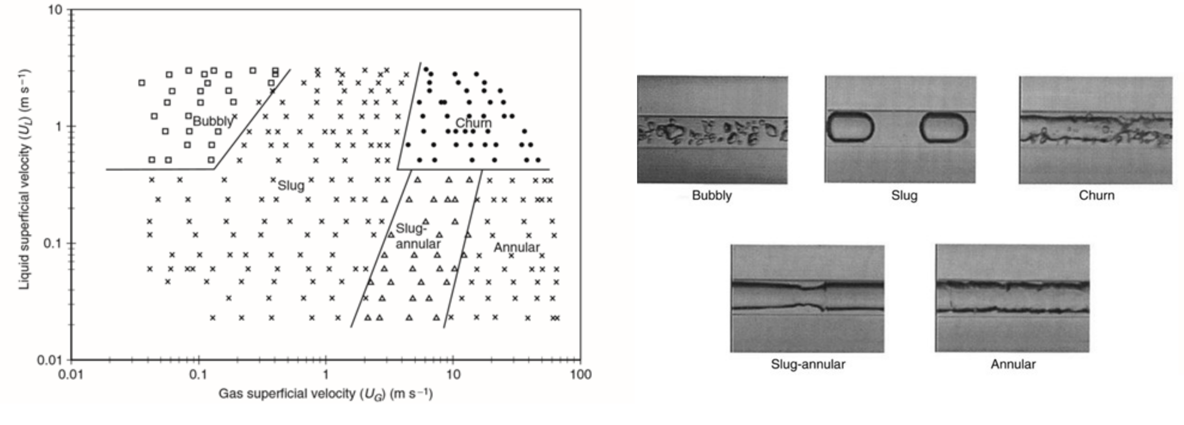


Figure 4.11. (a) Flow pattern mapped by Triplett et al. and marked by Gupta et al. 2010; (b) Typical flow patterns in microchannels observed by Triplett et al., 1999. Reprinted permission automatically granted from SAGE Publications.

The results from lignin oxidation in batch reactor were used to obtain good set of reaction condition in microfluidic reactor. Based on the flow characterization that obtained in table 4.5A and 4.5B, the effect of residence time and interfacial area on the amount of monomers after oxidation that can be detected by LC-MS analysis is presented in figure 4.11. In different slugs conversion almost remains constant with changing residence time and interfacial area. Probably because of the reason that the thicknesses of a liquid film surrounding the gas bubble was almost identical for all experimental conditions. This is not expected as increasing interfacial area leads to larger gas bubbles resulting in higher oxygen mass transfer that is essential in oxidation when reaction is happening in liquid phase. Organic acids formed at a very low degree due to the fast reaction. Oxidation in microfluidic reactor dominantly result in formation of vanillin compared to acids.

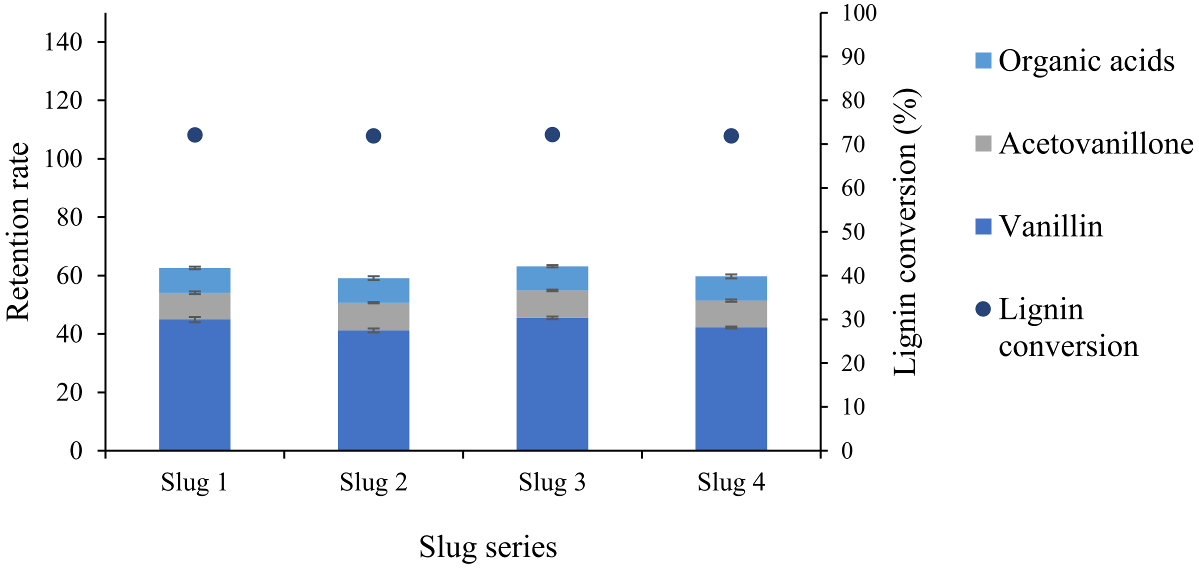


Figure 4.12. Product formation and lignin conversion during microfluidic oxidation of lignin

4.6 Comparing batch and microfluidic oxidation

Oxidation of Kraft lignin in alkaline medium has been carried out in a batch reactor and the optimum operational conditions for vanillin production obtained. The feasibility of a continuous process for vanillin production has been analyzed using a microfluidic reactor. It is obvious that it is easy to depolymerize lignin into low-molecular-weight compounds, but very challenging to do it with high selectivity and yield.

To compare previous research in batch setup, microfluidic setup shows better results for the latter most likely due to enhanced mass transfer of oxygen to liquid phase in microreactor. Batch studies achieved the same conversion level while utilizing higher oxygen pressure (1MPa) and longer reaction time (1 hour) under the conditions applied. By comparing the two systems, the microreactor is clearly advantageous, by more effectively consuming the oxygen present at (much) lower residence times. In spite of illustration of relative quantification data that shows how much more/less analyte is present when comparing the different samples, it can be imposed that the selectivity of vanillin increased due to an enhanced mass transfer of oxygen from gas phase to liquid phase. The lower residence time in the microreactor setup suppresses the formation of secondary reaction products like small acids, like oxalic and acetic acid and formic acid (Table 4.8).

Table 4.7. Comparison of the products retention rate obtained in batch reactor and continuous microfluidic reactor at 130 °C

Reactor	Residence time (min)	O_2 Pressure (MPa)	Vanillin retention rate (%)	Acetovanillone retention rate (%)	Organic acids (%)	Depolymerization rate of lignin (%)
Batch[1]	30	1	35.75	10.1	15.4	80.8
	60	1	46.5	10.3	18.2	81.4
Continuous microfluidic[1]	8.54	0.27	45.5	9.4	8.3	72.2
	10.2	0.27	42.2	9.2	8.3	71.9

[1]Experimental Condition: 20 mg lignin, 6% NaOH aqueous solution, 6.6 wt% H_2O_2, 130 °C.

One of the factors that enhance microreactor overall results is mixing. In microfluidic reactor mixing is usually occurred by diffusion because of smaller dimensions and operating at small Reynolds numbers and laminar flow (Jensen, 2001). Moreover, microreactors take advantage of mixing within a single phase. It is resulted from the Marangoni effect due to no-slip boundary conditions (Günther et al., 2004). Recirculation zones formed in liquid slug mix the liquid within itself as illustrated in figure 3.5a and lead to mixing improvement in the plug. Marangoni effect is limited to the liquid slug and not global to the total liquid. Mixing at this level is very dependant to the reactor dimensions, length of the liquid slug, two-phase superficial velocity, and on the physical properties of the liquid such as viscosity, density, and surface tension. In free radical oxidation, usually oxidative products are surface active and more reactive than the feed (Siddiquee et al., 2016). mixing within the liquid is very important, as it would prevent the overoxidation and would facilitate the conversion and product selectivity.

Although there are challenges using a microfluidic reactor. One reason that can disrupt mass transfer characteristics would be the presence of minimum and maximum film thickness surrounding the gas bubbles. The liquid present at the edge of microchannel would make differences in mass transport. In reactors with higher dimensions amount of fluid present in the edge would increase and affect the mass transport and differences in local oxygen availability. Sometimes clogging might happen in the channel caused by small coagulates or particle in the media, besides limitation in operational condition depending on the channel materials are challenges that we can point out.

4.6.1 **Vanillin degradation, effect of oxygen and reactor**

From the batch reactor, it was possible to achieve the same vanillin level obtained in the microfluidic reactor, in a longer reaction time and higher oxygen pressure. Continuous processes are easier to control and to attain constant product characteristics as well as their overall investments and operating costs are usually lower (Lebo et al., 2001; Rase, 1977).

The low level of vanillin yield obtained in batch experiments with kraft lignin seem to be limited by the used raw material and by the low rates of oxygen transfer to the liquid in the reaction chamber. These two points are crucial for improving the vanillin formation from Kraft lignin.

Since the oxygen mass transfer was the limiting step to vanillin production, in microfluidic reactor the liquid residence time should be decreased, as the oxygen mass transfer rate increases in order to avoid excessive oxidation of vanillin. Acetovanillone can be the product of reaction between vanillin and small acids or alcohols. It can also be generated in the alkaline oxidation of lignin, which shows the production of these chemicals in lignin oxidation may come from lignin itself or vanillin secondary oxidation. The formation of these monophenols leads to vanillin low selectivity.

Possible mechanism of vanillin degradation was proposed by Zhu el al. They reported three different ways vanillin can degrade into smaller molecules. All routes start from condensation and end by ring opening. Route 1 is to form vanillic acid after direct oxidation and vanillic acid further degraded via ring-opening to produce small molecules such as oxalic acid, acetic acid, formic acid, ethanol, methanol, and other fragments. In Route 2, small molecule fragments re-condensed with vanillin to produce other monophenols with side chain. In Route 3, vanillin molecules and/or other monophenols condense into dimers. Afterwards, dimers decomposed to complex monophenols. Then, all monophenols obtained by three routes will further degrade to long-chain acids (Zhu et al., 2018).

Chapter 5

5 Risk and hazard assessment of delignification in pulp bleaching

5.1 Introduction

Pulp bleaching is the process by which pulped wood particles are brightened or whitened. Bleaching is important to produce not only white but also colored paper since a bleached surface is needed for dyeing. The process also contributes to the chemical balance of the finished paper product and removes dirt and foreign particles. The bleaching operation of a kraft pulping process generates a large amount of effluents with high organic loads. Disposal of the toxic components in pulp and paper mill effluents such as resin acids and fatty acids naturally occurring in the wood pulped, and in effluents from bleaching processes toxic chlorinated compounds causes severe harm to the aquatic ecosystem, disturbs the food chain, and causes eutrophication of lakes, ponds and other hydric bodies. In soils, some undesirable elements, e.g. heavy metals, can harm the nutrient dynamics (Hutchins, 2004; Simão, et al., 2018). Effluents from Canadian pulp and paper mills using bleaching are discharged in wastewater. These effluents are generated in different mill processes such as cooling, pulping, papermaking, chemical recovery, and power generation that also involve chlorine or chlorine dioxide pulp bleaching. They are not generated at all pulp and paper facilities in Canada, but only those utilizing a chlorine or chlorine dioxide process. These discharges are treated prior to being deposited into the receiving waters (Canadian Environmental Protection Act. 1991)

The toxic effects of bleached pulp mill effluents on human health have not been widely studied. The acute lethality of pulp mill effluents has been documented extensively in the scientific literature, but there has been less emphasis on chronic toxicity or fate. Between 1985 and 2017, the quality of pulp and paper effluent released directly to the environment has improved. The toxicity of dioxins and furans, as well as their potential to harm human health, has been well established and they were the first substances on the Priority Substances List (PSL) to be declared "toxic" under CEPA. Insufficient data were found about bleached pulp mill effluents to be able to judge their effects on the quality of fish for human consumption or on drinking water. In this chapter we are going to investigate the maximum loadings of effluent that is being considered for operating mills and introducing substitution processes for bleaching process.

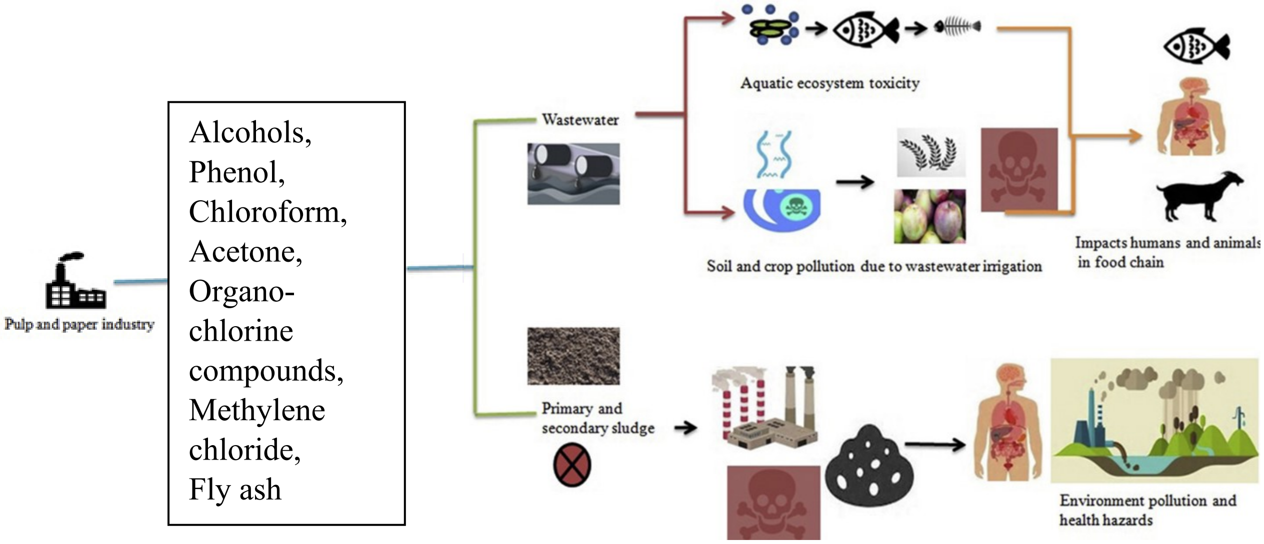


Figure 5.1. Air and soil pollution due to pulp and paper industry waste (Mandeep et al., 2019). Reprinted permission granted from Elsevier.

The use of molecular chlorine or chlorine-based chemicals compounds as bleaching agents by the pulp and paper sector react with materials released from wood during the pulping process, resulting in the formation of chlorinated organic compounds which are finally released into the aquatic environment via effluents Many of these chlorinated organic compounds are persistent and have been detected in water, sediments and biota up to 1400 km from bleached pulp mills outfalls. Compounds with low chlorine substitution degrade within hours to days, whereas highly chlorinated organic compounds may persist from days to weeks or longer. Persistence may be longer in winter, especially under ice (Canadian Environmental Protection Act. 1991).

Seventy percent of Canadian freshwater bleached pulp mills discharge whole effluent. This effluent is at levels which cause chronic effects even upon dilution by the receiving waters. Chronic disorders, such as reproductive anomalies, biochemical changes, and behavioural alterations in aquatic organisms, and mutagenic and reproductive damages in aquatic life as well as terrestrial organisms including humans have been observed in Canadian field studies at 0.5 to 5 % whole effluent (Dwivedi, et al., 2010).

Laboratory studies using individual chlorinated organic compounds that are commonly discharged from bleached pulp mills have demonstrated such chronic effects as deformities, and embryo and larval mortalities in fish. These chronic effects include significant irreversible factors which jeopardize the continuance of the species and the integrity of the ecosystem. The effect of pollutants on the environment is assessed many times, but their mitigation still poses a great challenge.

In Canada, the Pulp and Paper Effluent Regulations is a responsible authority which controls the limits set on amounts of total dissolved solids and biological oxygen demand and mitigates the discharge of wastewater from the pulp and paper mills into the water, which are responsible for the acute lethality to aquatic life (Hubbe, M. A. 2016).

5.2 Bleached Pulp Manufacturing Processes

5.2.1 **Pulping**

Pulping process separates cellulose fibre from lignin and prepares the fibres for papermaking. Mechanical and chemical are the main types of pulping processes. Mechanical process utilizes heat and mechanical forces to break down the lignin which light-coloured produced pulp requires a bleaching step. Kraft and sulphite pulping are two major chemical processes. The first one is conducted in an alkaline medium that fibre is released by dissolving lignin in a caustic solution (i.e. sodium hydroxide and sodium sulfide). In the second process, sulphite process is conducted under acidic environment and solubilizes lignin through sulphonation (Duan et al., 2014). Produced pulp through chemical processes has a dark color and requires bleaching. It is worth mentioning that oxygen delignification, can be applied as an additional step in chemical processes to break down the lignin further and reduce the amount of bleaching agent, subsequently (Requejo et al., 2012).

5.2.2 **Bleaching**

The bleaching of cellulose fibres is an extension of the delignification in the pulping stage. Mechanical pulping process usually brightens using hydrogen peroxide. Therefore, no chlorinated organic compounds are generated during the process due to absence of chlorine-based chemicals. The wastewaters from mechanical pulping, secondary fiber pulping, and condensates from semichemical pulping are nontoxic to methanogenic degradation and contain degradable organic compounds (Rintala, J. A., & Puhakka, J. A.,1994).

On the contrary, bleaching of chemical pulps is normally a complicated multi-stage process with the presence of chlorine-based chemicals. Produced pulp is contacted with a chlorine-water solution. Chlorinated-water solution could be replaced by a chlorine gas such as chlorine dioxide to reduce the formation of chlorinated organic compounds. Chlorine-based chemicals are mostly effective in breaking down lignin with almost no effect on color removal at this stage. Next step of bleaching is caustic extraction that caustic solution (i.e. sodium hydroxide) dissolves modified lignin. After caustic extraction, chlorine dioxide or hypochlorite is added to the pulp. Depends on the desired brightness, color, and the quality of the product, extra bleaching stages and chemicals can used during the process (Claeys, R.R., L.E. LaFleur and D.L. Borton., 1979). For instance, 80% to 90% of the lignin is removed during the chemical pulping process of wood. However, the residual lignin is highly coloured and extra bleaching stages are required to remove the extra remaining lignin (Reeve, Douglas W, 1996). Wastewater effluents of a kraft pulping process includes various sources like debarking, washing and screening, evaporation, and bleaching. Bleaching contains 50% to 60% of the total organic load of effluents (Rintala, J. A., & Puhakka, J. A., 1994).

While mechanical pulps are brightened with a lignin-retaining chemical such as sodium hydrosulphite, chemical pulps are bleached using a lignin-degrading chemical, such as chlorine dioxide and ozone. Depending on the conditions, hydrogen peroxide is used as a lignin-preserving or a lignin-degrading chemical (Ellis, Michael E.,1996). Some of the bleaching chemicals are narrowed to lignin removal while many others are more general and cause appreciable carbohydrate degradation and diminished yield. Although oxygen and chlorine are inexpensive, they are not selective for lignin removal. As a result, they are used in the early stages of bleaching to remove most of the lignin. Residual lignin requires more expensive and selective bleaching agents such as chlorine dioxide, hypochlorite, and hydrogen peroxide which is removed in the later stages (Pratima Bajpai, 2018).

5.3 Effluent Treatment

Wastewater effluents of pulping and bleaching processes require treatment prior to discharge. There are a primary and secondary treatment stages which the primary treatment reduces the biological oxygen demand (BOD) of the wastewater on the aquatic environment by removing emulsified solids through settling process. In secondary treatment, the effluents contact with bacteria that decompose organic substances. The second treatment process removes components that consume oxygen as well as substances toxic to fish. *"In Canada, 49% of bleached pulp mills employ secondary treatment, 43% employ only primary treatment, and 9% of the mills employ no effluent treatment"* (Effluents from Pulp Mills Using Bleaching, Canadian Environmental Protection Act, Priority Substances List Assessment Report No. 2, ISBN 0-662-18734-2).

Environmental impacts of the pulping and bleaching process reduce using wastewater treatment methods. Figure 5.2 shows pulp and paper industry impacts on environment as well as treatment techniques. There are chemical and biological wastewater treatment methods. Biological treatment removes lignocelluloses from effluents. The success of this process depends on the low biodegradability of dissolved lignocelluloses in the effluents because of their complex structures and the presence of inhibitory substances (Rintala, J. A., & Puhakka, J. A. 1994). While pre-treatment processes such as photo catalysis, ultrafiltration, precipitation, coagulation, and flocculation can potentially improve the biological treatment, they are limited to a high capital investment and energy consumption (Garg et al., 2005).

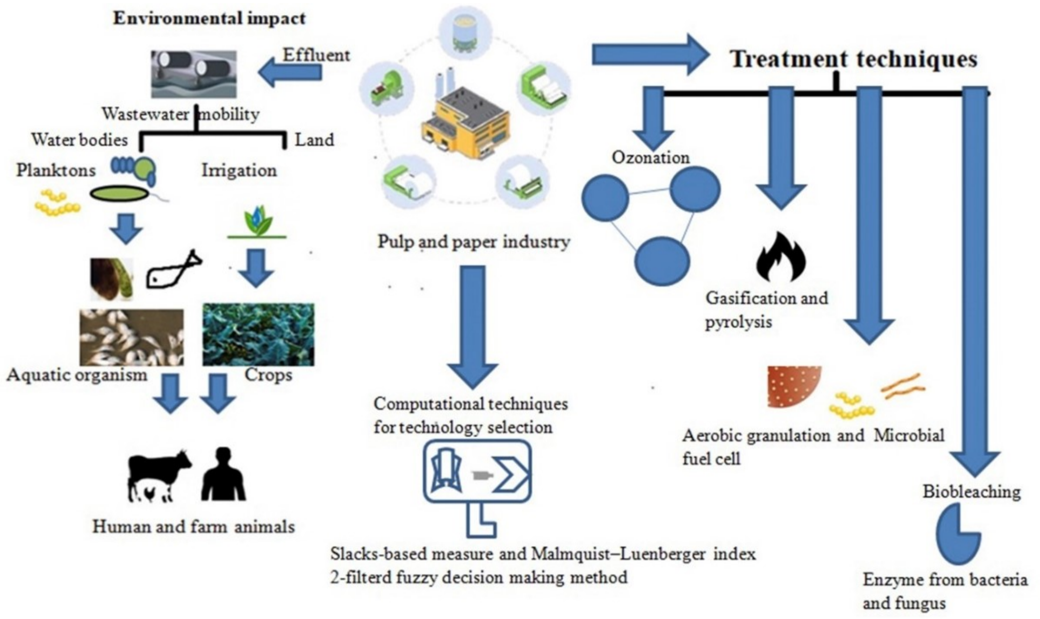


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Figure 5.2. Environmental impacts of pulp and paper industry and treatment techniques (Mandeep et al., 2019). Reprinted permission granted from Elsevier.

5.4 Health hazards associated with pollutants

As mentioned by Kamali et. al (Kamali. M., 2016) the main waste of the pulp and paper industries is generated during the pulping, bleaching, and deinking process. Different countries assess and reuse the effluent in a safe and ecological condition. For example, Spain, Netherland, and Germany have restricted prohibitory rules of effluent discharge at landfill sites. Moreover, legislation and augmented taxes have led to research on new methods for the supervision or use of pulp and paper industry wastes (EPA Washington., 2002). The straight disposal of effluents without following the safety protocols threatens the wildlife such as aquatic organisms and shows a potential mutagenic outcome.

In addition to wildlife, effluent's compounds are challenging for biodegradation and can accumulate in the food chain. Effluents comprise bits of bark, stray wood chips, cellulose filaments, disintegrated ligneous substance (30–45%), acetic acid, formic acid (10%), saccharinic acid (25–35%), and extractives (3–5%). The United States Environmental Protection Agency (USEPA 2006) has reported pentachlorophenol as one of the most toxic agents at the concentration of 1.0 mg.l^{-1} (Lindholm-Lehto, P. C. et al., 2015). As mentioned by Yadav et. al (Yadav, S., &

Chandra, R. 2018) the effluent of wastewater from pulp and paper mill causes phytotoxicity and chromosomal aberration in *Allium cepa*.

A study of 4247 personnel in a Norwegian pulp and paper mill reported 380 case of cancer which 322 cases showed ovarian cancer (Soskolne, C. L., & Sieswerd, L. E. 2010). Another case-study in Spain confirmed high risk for lung cancer along with tumors of the ovary, stomach, prostate, breast, and nervous system for the workers in pulp and paper industry (Monge-Corella, S., et al,2008). Organochlorine compounds are released in water due to consumption of chlorine-based chemicals for the pulping and bleaching processes. Organochlorine compounds are measured as Adsorbable Organic Halides (AOX). These components are the main reason of respiratory disease, chronic disorder, skin irritation disease, and genetic and reproductive damage (Singh, A. K., & Chandra, R. 2019).

5.5 Risk Assessment Criteria

A qualitative and quantitative evaluation of reported data from various bleaching pulp mill wastewater studies is conducted in this study. Risk level estimation is highly affected by the released effluent to the environment, level of exposure, direct field observations, and harmful effects level. As reported by the Canadian Environmental Protection Act (CEPA), there are four approaches to risk assessment including (Effluents from Pulp Mills Using Bleaching, Canadian Environmental Protection Act, Priority Substances List Assessment Report No. 2, ISBN 0-662-18734-2):

1. Effects on biota caused by exposure to bleached pulp mill wastewater can be considered as a high level of risk.
2. Recorded aquatic exposure data can be correlated in accordance with laboratory environmental effects data.
3. Indication of a threat to any wildlife considered in the "*vulnerable, threatened or endangered categories*".
4. Evidence of any "*residues or metabolites in biota exposed to bleached pulp mill effluents corresponding to or exceeding known threshold levels*" is an indication of harmful effects.

5.6 Risk Assessment Process

The risk assessment starts with parametric study of chemical components, biological indications, and environmental literature. The next step is to add field tests, experimental observations, and lab studies on the literature. Important information such as harmful effects on environment and human activity and its short, mid, and long-term exposures are also included in the study (Effluents from Pulp Mills Using Bleaching, Canadian Environmental Protection Act, Priority Substances List Assessment Report No. 2, ISBN 0-662-18734-2). According to previous studies (Effluents from Pulp Mills Using Bleaching, Canadian Environmental Protection Act, Priority Substances List Assessment Report No. 2, ISBN 0-662-18734-2), risk assessment process in pulp and paper industry along with bleaching technique could be studied into the following categories:

- Review of physical and chemical properties of organic components in bleaching.
- Track of bleaching effluent that releases to the aquatic environment.
- Analytical measurement of organochlorine concentrations in bleached pulp mill effluents.
- Review and study of related regulations, rules, guidelines, and legislations to the organochlorine pollution of the environment.
- Comparison between the detected bleaching effluent components of various reports to determine the severity level.
- *"The acute and chronic toxicities to aquatic organisms associated with whole bleached"*.
- Review and comparison between bleaching effluents components (i.e. organochlorine concentration) of field and laboratory conditions (CEPA, 1991).

The current improvements on assessment process account for the following reasons (Proposed Modernization of the Pulp and Paper Effluent Regulations: Consultation document, Environment and Climate Change Canada, September 2017):

- Environmental effects monitoring (EEM) studies required by the Pulp and Paper Effluent Regulations (PPER) have shown that the effluents from 70% of pulp and paper mills are impacting fish and/or fish habitat, and that the impacts at 55% of these mills pose a high risk to the environment (Proposed Modernization of the Pulp and Paper Effluent

Regulations: Consultation document, Environment and Climate Change Canada, September 2017).

- Improvement of wood industry with new products such as cellulose nanocrystalline (CNC) and lignin.
- According to statistics, Canadian mills, discharge higher effluents including solid particles and harmful components as requires higher chemical oxygen compared with Europe and United States.
- There is a considerable improvement in control of wastewater treatment since new regulations were put in place and related technologies were documented by PPER since 1992.

5.7 Hazard Identification and Findings

Environment and Climate Change Canada (ECCC) recommends several activities related to identification of hazards such as (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019):

- Review intensity effluent factors for biochemical oxygen demand (BOD), suspended solids (SS).
- Consider an intensity factor for chemical oxygen demand (COD).
- Consider nitrogen and phosphorus concentration, temperature, and pH limit in effluent streams.

Table 5.1 shows the proposed intensity factors for operating mills in the three process categories of chemical, mechanical, and paper recycling papermaking and table 5.2 are the intensity factors applied for operating mills until May 2019 (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019).

Table 5.1. Proposed intensity factors for operating mills (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019)

Mill category	BOD kg/t		SS kg/t		COD kg/t	
	Daily	Monthly	Daily	Monthly	Daily	Monthly
Chemical	4.25	2.6	6.25	3.75	75	45
Mechanical	1.25	0.75	2.5	1.5	50	30
Paper Recycling Papermaking	1.25	0.75	2.5	1.5	12.5	7.5

Table 5.2. Current intensity factors for operating mills (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019).

Mill category	BOD kg/t		SS kg/t		COD kg/t	
	Daily	Monthly	Daily	Monthly	Daily	Monthly
All mills	12.5	7.5	18.75	11.25	None	None
Dissolving Grade Sulphite (maximum allowances)	45	27	62.5	37.5	None	None

Loading limits are calculated according to the above intensity factors and reference production rate (RPR) defined by PPER:

$$\text{Daily maximum loading (kg)} = (\text{daily intensity factor}) \times \text{ RPR.} \qquad \text{(equation 5.1)}$$

$$\text{Monthly maximum loading (kg)} = (\text{monthly intensity factor}) \times (\text{calendar days in the month}) \times \text{ RPR} \qquad \text{(equation 5.2)}$$

Total loading limits of a complex including different facilities discharge into the same wastewater treatment is calculated based on the sum of facilities as:

$$\text{Daily Maximum Loading (kg)} = \sum_{1}^{\text{N facilities}} (\text{F} \times \text{RPR})\text{facility 1} + (\text{F} \times \text{RPR})\text{facility 2} + \cdots + (\text{F} \times \text{RPR})\text{facility N} \qquad \text{(equation 5.3)}$$

$$\text{Monthly Maximum Loading (kg)} = \sum_{1}^{\text{N facilities}} (\text{F} \times \text{d} \times \text{RPR})\text{facility 1} + (\text{F} \times \text{d} \times \text{RPR})\text{ facility 2} + \cdots + (\text{F} \times \text{d} \times \text{RPR})\text{facility N} \qquad \text{(equation 5.4)}$$

Where F is the intensity factor of each facility, RPR is the reference production rate of each facility, d is the number of calendar days in each month, and N is the number of facilities (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019).

As proposed by the Environment and Climate Change Canada (Modernization of the Pulp and Paper Effluent Regulations – Detailed Proposal, Environment and Climate Change Canada, May 2019), recognized solutions to the environmental effects of effluent require a three years study period to identify and verify the solution. Three-year timeframe study falls into the following steps:

- Assessment and confirmation of the effects: if confirmed effects are equal to or greater than Critical Effect Size (CES) or has no CES, go to the next step.
- Investigation Study: three-year timeframe to evaluate and identify the causes and solutions.
- Implementation of the solutions: three years to implement solutions and reassessment of the effects.

5.8 Case study (West Fraser Forestry effluent management)

The case study of this work is West Fraser, a wood products company producing lumber, LVL, MDF, plywood, pulp, newsprint, wood chips and energy. West Fraser enters $150 Million Committed Revolving Credit Facility and adopts Shareholder Rights Plan. (Retrieved from https://www.westfraser.com). West Fraser facilities in Western Canada utilize recycling programs to track and recycle consumable landfill waste. Recycling programs including re-use materials, supplier take back programs, and incorporate new employees training to increase the participation level in the programs. Table 5.3 shows West Fraser's waste by type and disposal method in 2016 and 2017 (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com).

In Canada, effluent treatment is highly regulated at provincial and federal governmental levels. Water treatment regulations such as the degree of the chemical's removal, levels of suspended solids, and oxygen level in the returned water to river to thrive organisms. Returned water of West Fraser's Bleached Chemi-Thermo Mechanical Pulp (BCTMP) and Northern Bleached Softwood Kraft (NBSK) pulp operations is represented in table 5.4 (West Fraser annual report).

Table 5.3. Water discharge by quality and destination (West Fraser annual report)

Total (m^3/year)	**2016**	**2017**	**2018**
Total water diverted	87.5 million	88 million	90.4 million
Total water returned	81.8 million	83.7 million	85 million

Table 5.4. Waste by type and disposal method (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com)

(m^3/year)	2016	2017	% Change
Recovered Residuals used for energy (hog fuel, black liquor, turpenes); used onsite or sold as hog fuel			
Recovered (beneficial) residuals	2,696,441	2,672,039	-0.9%
Reuse			
Reused tall oil in NBSK kraft Pulp mills	6,149	6,149	0%
Land application program, road base, agriculture, oil field absorbent	99,625	90,790	
Landfill Residuals sent to onsite or offsite landfills			
Ash	14,170.5	15,472	+9.2%
Wood	24,428	21,906	-10.3%
Pulp Mill	55,063.5	53,099	-3.6%

5.8.1 **Effluent deposition**

According to Waste Fraser's reports, deposits of effluent into water is in accordance with PPER. Environment Canada set regulations to support aquatic wildlife that requires oxygen (biochemical oxygen dissolved in water) and monitor solid particle deposited into aquatic environment from pulp and paper mills. PPER prevent the deposit of any effluent that is harmful to aquatic wildlife. As reported in figure 5.3 and figure 5.4, Waste Fraser facilities in Cariboo Pulp & paper, Hinton Pulp, Quesnel River Pulp, and Slave Lake pulp follows the regulations (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com/responsibility/responsibility-report/previous- reports/2017-responsibility-report/manufacturing/waste-management).

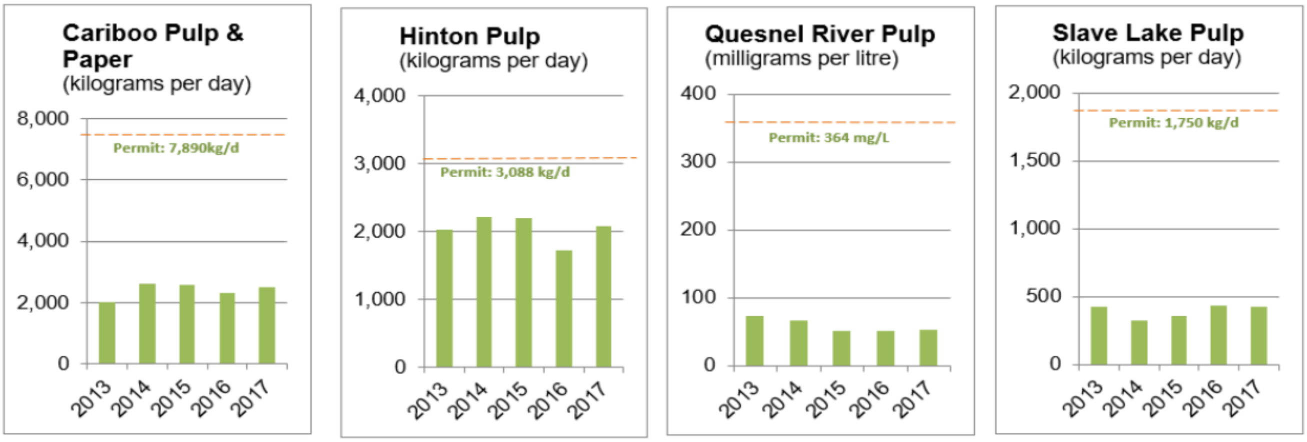

Figure 5.3. Biochemical Oxygen Demand (BOD) in Waste Fraser Western Canada locations (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com/responsibility/responsibility-report/ previous-reports/2017-responsibility-report/manufacturing/waste-man

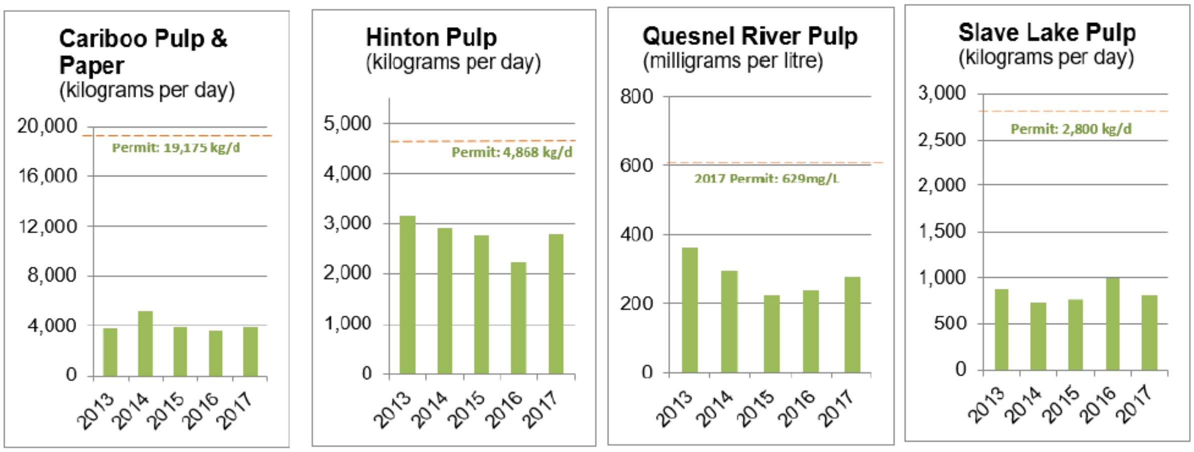

Figure 5.4 Total Suspended Solids (TSS) in Waste Fraser Western Canada locations (Waste Fraser Waste Management, Retrieved from https://www.westfraser.com/responsibility/responsibility-report/ previous-reports/2017-responsibility-report/manufacturing/waste-management).

Calculations for daily exposure in Cariboo pulp and paper industry in 2017:

daily maximum BOD loading for chemical operating mill:

$2050 \times 4.25 = 8712$ kg/day

daily maximum BOD loading for mechanical operating mill:

$2050 \times 1.25 = 2562$ kg/day

daily maximum suspended solids loading for chemical operating mill:

$3900 \times 6.25 = 24375$

daily maximum suspended solids loading for mechanical operating mill:

$3900 \times 2.5 = 9750$

From above calculations the company is operating in a safe range for effluent discharge. Water bodies were significantly affected by water discharges or runoff from operations in 2018, 2017 or 2016. All of the pulp and paper facilities participated in the Canada's federal Environmental Effects

Monitoring program. Science-based effluent measurement program monitoring fish, fish habitats and the usability of fisheries resource.

5.9 Recommendations for Bleaching Substitution

Traditional bleaching techniques along with regulations contributed to reduce pollutants from the pulp and paper industries, however effluent contaminations require more advancement in traditional methods or alternative technologies. There are some environmentally friendly alternatives to traditional bleaching process such as hydrogen peroxide, ozonation, and extended cooking. Enzymes give an easier and efficient manner to diminish the use of chemical agents (ClO_2) and other bleach agents (Raj, A. et al., 2018). Pre bleaching enzyme like xylanase have been used in laboratory and commercial scales in Europe, USA, Canada, and Asian (Bajpai, P. 2012). Widely applied techniques are microbial fuel cells, anaerobic digestion, bleaching technologies, cleaner production, and transformation pathways (Mandeep, 2019).

In addition to aforementioned techniques, adsorption is the most promising and simplest techniques for removing organic pollutants, including biologically recalcitrant substances, from wastewater effluents (Kurniawan, T. A., et al., 2006; Vandenbusch, M. B., & Sell, N. J. 1992; Yuliani, G.et al., 2012). Recently, coal-based fly ash is considered as a toxic metal removing method (Wang, S. et al., 2008) and dyes, organic and inorganic pollutants removing from wastewaters (Ahmaruzzaman, M., 2010; Yildiz, E., 2004). Srivastava et. al. (Srivastava V. C. 2005) reported Bagasse fly ash as an effective adsorbent for treating the effluent of the pulp and paper industry with 50% COD and 55% color removals, using 2 g/L fly ash in the system at pH 4.

In is worth mentioning that some researchers believe best option is bleaching without chlorinated compounds or not to use bleaching in any processes. For example, white papers are bleached using hydrogen peroxide (or other oxygen-based methods). In other cases, non-chlorin processes such as Total Chlorine Free (TCF) was introduced which there is no chlorine or chlorine derivatives used to make the paper (Dence. D. W., 1996). This resulted in the development of TCF bleaching technologies by applying oxygen, hydrogen peroxide, ozone, and peracetic acid in bleaching sequence. Although Sjostrom et al. (Sjostrom., 1981) reported a worldwide increase in TCF bleaching technology demand, only 5% of total pulp production in the world was using this technology until 2010. Disadvantages of this technology are high cost of bleaching, lower product strength, and higher brightness reversion compared with Elemental Chlorine Free (ECF) method.

Unlike the TCF technology, ECF which is widely applied in recycled papers and tissue products, uses chlorine derivatives. Other works (Miri et al., 2015) recommended application of Oxon bleaching as an eco-friendly alternative to TCF and ECF bleaching technologies. In ECF bleaching Cl_2 is not used, but instead hypochlorite (ClO^-) or chloride dioxide (ClO_2) is used as the bleaching reagent. Hypochlorite is a nucleophilic reagent, it mainly oxidizes the chromogenic groups of lignin, like quinone structure and side-chain conjugated structure result in pulp whiteness improvement and form final products of dicarboxylic acids. (Yang, 2001). TCF bleaching uses greener H_2O_2, O_2, and O_3 as bleaching reagents. H_2O_2 bleaching is usually carried out in alkaline conditions. Alkaline condition eases the reaction between H_2O_2 and OH− to produce hydroperoxide anions (HOO−). HOO− is a strong nucleophile reagent, and its nucleophilic reactions with residual lignin are the main reactions during H_2O_2 bleaching.

O_2 bleaching is also performed under alkaline conditions using MgCO3 or MgSO4 as catalyst. This process is known as oxygen-caustic bleaching. This process is very similar to those in H_2O_2 bleaching. In addition, molecular oxygen can generate (HO−, HOO−, O2−·) anions and (HO· and HOO·) radicals, increasing the complexity of oxygen-caustic bleaching reactions (Ma et al., 2015).

5.10 Summery

- Pulp bleaching is one form of lignin oxidation. In the bleaching process chlorine (Cl_2) is a highly efficient lignin oxidant used for pulp bleaching. During lignin chlorination link cleavage of aliphatic side chains on lignin happens and makes the residual lignin fragmented and dissolved. On the other route it can attack the methoxy group, result in ring opening reaction, as the mechanisms illustrated by Ma et al (Ma et al., 2015). During chlorine bleaching, large amounts of organohalogens (AOX) are generated. They dissolve in the bleaching effluent with low concentrations and this is a serious threat to the environment. Therefore, elemental chlorine free (ECF) and total chlorine free (TCF) bleaching, as discussed in this research, have been developed to replace chlorine bleaching.
- The pulp and paper industry have been able to manage water in the context of a regulatory environment. Industry participants are committed to better understanding of impacts and have identified the evaluation of water foot printing tools and water disclosure as a key initiative. Intensity factors for biochemical oxygen demand (BOD), suspended solids (SS)

was proposed by ECCC Canada and mills need to consider effluent treatment by regulations for their operations in Canada.

- Information of importance includes environmental effects and human toxicity data, as well as data dealing with the routes, levels and effects of short and long term exposure. A major goal is to decrease damage to environment by waste minimization, reuse and recycle.
- Besides the regulation proposed by ECCC to control the intensity factor of effluents from pulp and paper industry, application of environmentally friendly alternatives to traditional bleaching process is desirable.

Chapter 6

6 Conclusion and future work

- The aim of the research described in this thesis was to review the potential of oxidative upgrading of lignin as a renewable aromatic resource for the chemical industry. With the floating price of oil and environmental concern it is crucial to develop applications for sustainable biodegradable materials. Sustainable procedures involve using biodegradable resources for the industrial production of material. In this regard, lignin is available in a large amount as a by-product of pulping industry. Lignin is a very attractive raw material to produce vanillin, biopolymers, and organic acids as value added material.
- Lignin is a huge macromolecule and because of non-uniform heterogeneous structure, and the unique chemical reactivity its commercially usage is very limited. Hence, breaking it down to smaller molecule with oxidation is one of the ways to produce phenolic compounds. Various kinds of C–O and C–C linkages with numerous bond dissociation energy between aromatic rings cause difficulties in selective lignin depolymerization.
- Usage of liquid phase oxidation in this research has advantages such as mild reaction conditions, up to 150 °C and up to 1 MPa O_2 pressure. Products, such as vanillin, have high commercial value today. The disadvantage of oxidation is selectivity control of products and overoxidation to compounds with lower value. Some products of oxidation are usually prone to oxidation even more than the starting substrate and make it difficult to produce desired product in high yield. All lignin degradation result in the production of small amount of several monomeric, oligomeric, and polymeric compounds.
- Depending on the oxidation stages, formation and concentration of mono aromatics and acid compounds varied. The products from alkaline reaction media were concentrated in non-aromatic carboxylic acids at the longer reaction time and higher temperature in batch reaction due to secondary oxidation products.

- Temperature was the most influential parameter in oxidation in batch reactor and elevated temperature resulted in a very fast reaction with maximum concentration of the products, especially for vanillin. Vanillin retention rate at 130 °C was 29% higher than at 150 °C at 1hour reaction time.
- The findings from this study indicated that the aldehydes produced are over-oxidized, due to an abundance of perhydroxyl anion in the reaction solution that leads to formation of carbon dioxide and water, or strong degree of condensation (C-C linkages) of lignin. Perhydroxyl anion group cleaves the side chains of lignin, opens benzene ring, and form new compounds. Under severe conditions, ring opening reactions may happen degrade lignin into variety of low molecular weight compounds, such as oxalic acid and formic acid.
- There is a great interest on continuous process of lignin oxidation as large volume of kraft lignin generated in pulp and paper industry. Microfluidic reactor is very favorable for study lignin oxidation behavior in miniaturized scale. The platform has already been adopted by many pharmaceutical companies and the success story of processes in employing continuous flow chemistry can be adopted to fit the needs of biomass industry.
- Oxygen availability in microfluidic reactor ensure creating gas-liquid flow pattern (Taylor flow). Furthermore, Tylor flow pattern combined with improved heat and mass transfer, result in a more advanced reaction in terms of short residence time, uniform reaction temperature, good mixing, and high oxygen transport. This will increase selectivity to the desired product.
- Although the result of vanillin and other aromatic compounds yield and selectivity was not included in this work, these experiments allow understanding the involved phenomena, performances and expected problems related to this operation.
- Although burning lignin to fulfil the energy requirements of pulp and paper industry contributes in less consumption of fossil resources, processing lignin into added-value applications in different industry is a key factor for creating economically feasible biorefinery processes. In this regards, traditional pulp and paper mills can be upgrade into integrated forest biorefineries that will produce not only pulp and paper but also building blocks like phenolic compounds and carboxylic acids that is environmentally friendly building blocks for pharmaceutical applications.

- Due to the importance of environmental regulations, it is crucial to study the feasibility of replacement of traditional bleaching process for lignin isolation and purification with green technology like oxidation. Study on the microfluidic reactor is a powerful pre-screening process for future investigation on mixing and mass transfer improvement for utilizing oxidation in a large scale.

- In fact, this research contributes to forest sustainability and reprocessing of pulp and paper industry by-products which is crucial for Canada, not only to balance competing forest uses in the short term, but to ensure we appreciate forest's benefits for future generations.

Future work

- Results showed that degradation of vanillin is a major reason that limits vanillin high yield in lignin alkaline oxidation. Therefore, to increase vanillin yield, mild reaction conditions and intensive purification like in situ extraction of vanillin and other valuable monophenols can be helpful to avoid unnecessary condensation.
- Due to selectivity problems various products/by-products can be formed and oxidation has no application in industry. Consequently, the design of new catalysts and oxidants to increase the selectivity of oxidation reactions is essential for developing oxidation process requires further research.
- Feasibility analysis of using results from microfluidic reactor to substitute traditional bleaching process with oxidation process in continuous flow at large scale is a great potential for future study.
- The pharmaceutical and biotech industry has made major advances in drug production at full length with the help of continuous flow operations scheme and this can benefit biomass industry as well. These terms need to be discussed by an introduction of lignin as a biopolymer with its versatile and intriguing properties.

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