Review

Ajinkya More, Thomas Elder and Zhihua Jiang*

A review of lignin hydrogen peroxide oxidation chemistry with emphasis on aromatic aldehydes and acids

https://doi.org/10.1515/hf-2020-0165
Received June 26, 2020; accepted January 27, 2021;
published online March 17, 2021

Abstract: This review discusses the main factors that govern the oxidation processes of lignins into aromatic aldehydes and acids using hydrogen peroxide. Aromatic aldehydes and acids are produced in the oxidative degradation of lignin whereas mono and dicarboxylic acids are the main products. The stability of hydrogen peroxide under the reaction conditions is an important factor that needs to be addressed for selectively improving the yield of aromatic aldehydes. Hydrogen peroxide in the presence of heavy metal ions readily decomposes, leading to minor degradation of lignin. This degradation results in quinones which are highly reactive towards peroxide. Under these reaction conditions, the pH of the reaction medium defines the reaction mechanism and the product distribution. Under acidic conditions, hydrogen peroxide reacts electrophilically with electron rich aromatic and olefinic structures at comparatively higher temperatures. In contrast, under alkaline conditions it reacts nucleophilically with electron deficient carbonyl and conjugated carbonyl structures in lignin. The reaction pattern in the oxidation of lignin usually involves cleavage of the aromatic ring, the aliphatic side chain or other linkages which will be discussed in this review.

Keywords: hydrogen peroxide; lignin; oxidation; vanillic acid; vanillin; wood.

***Corresponding author: Zhihua Jiang**, Department of Chemical Engineering, Alabama Center for Paper and Bioresource Engineering, Auburn University, Auburn, AL 36849, USA,
E-mail: zhihuajiang@auburn.edu
Ajinkya More, Department of Chemical Engineering, Alabama Center for Paper and Bioresource Engineering, Auburn University, Auburn, AL 36849, USA
Thomas Elder, United States Department of Agriculture – Forest Service, Southern Research Station, Auburn, AL 36849, USA

1 Introduction

Practically viable and economic conversion of lignocellulosic biomass to value added products is an important challenge that requires integrated processing and effective utilization of lignin (Werpy and Petersen 2004). Lignin is nature's second most abundant polymer after cellulose and it contributes as much as 30% of the organic carbon content in the biosphere (Ludmila et al. 2015; Wettstein et al. 2012). Lignin obtained from paper and biofuel production is currently being used as energy, however it can be further converted to value added chemicals (Sakakibara 1980; Smith et al. 2000). Several studies have reported on the conversion of lignin to value added chemicals including aromatic fine chemicals, carboxylic acids and monomers for polymer production (Bozell et al. 1995; Lange et al. 2013; Zakzeski et al. 2010; Zhang et al. 2011). The controlled breaking of carbon-carbon and carbon-oxygen bonds in lignin represents a very selective de-polymerization that could produce a whole series of monomeric, aromatic species (Bozell et al. 1998; Ma et al. 2014).

Oxidation is one of the most widely studied lignin valorization processes. Over the years different routes have been followed to study lignin oxidation (Cole et al. 1990; Crestini et al. 1999; Genin et al. 1995; Herrmann and Fischer 1995; Moodley et al. 2012; Ni et al. 1993; Ouyang et al. 2014; Solomon and Lowery 1993). Oxidative degradation of lignin produces low molecular weight phenolic compounds which are value-added chemicals. Vanillin is one of the main value-added chemicals produced from this process. It is the major flavor constituent of vanilla and has a wide range of applications in food and perfume industry. It is sold as a crystalline solid in two grades, technical and Food Chemicals Codex (FCC) grade. The FCC grade requires a minimum assay of 97.0% on dried basis. The technical grade is applied where there are no standards for quality and impurity levels and generally sells for about $2.00/kg less than FCC grade (Araújo 2008).

The commercial route for vanillin synthesis is being carried out by Solvay which is the world's leading producer

of synthetic vanillin under the brand name Rhovanil®. It is followed by Borregaard, the second largest producer of vanillin which also has ethyl vanillin production capacity and is the main supplier of vanillin to Europe (Araújo 2008). The Borregaard process uses lignosulfonate as the starting lignin source which is catalytically oxidized at high pH with a transition metal catalyst at elevated temperature and pressure resulting in vanillin yields ranging from 5–7% with respect to lignosulfonate using oxygen as the oxidizing agent (Pacek et al. 2013). Over the recent years the demand for natural vanilla flavors from flavor manufacturers and from the food industry in general has been increasing. To answer the budding demand for natural vanillin, Solvay and Borregaard have developed Rhovanil® Natural and EuroVanillin respectively as an alternative to synthetic vanillin. However, the raw material costs for natural vanillin are more expensive than the synthetic counterpart which makes synthetic vanillin more competitive and widely used (Pinto et al. 2012).

From an industrial point of view, only sulfite lignin is currently used to prepare vanillin, despite the fact that it accounts for less than 10% of the total lignins extracted (Pinto et al. 2012). Kraft lignin which represents majority of lignins separated is mainly used as a low grade fuel in the pulping operation (Hu 2002). Therefore, there is a tremendous opportunity and economic incentive to use kraft lignin as a source to produce high added value aromatic aldehydes. It is key to note that nitrobenzene is the oxidant that gives the highest yields of aromatic aldehydes and acids from kraft lignin. Nitrobenzene, however, is an expensive oxidant and its reduction products are harmful and difficult to separate, limiting its industrial application (Fache et al. 2016). Oxygen is the preferred choice for producing value added products such as vanillin from kraft lignin, mainly because of its environmental friendliness, high atom economy and low price. However, catalysts in combination with oxygen are required to improve the yield of aromatic aldehydes by a factor of 1.5–2 (Tarabanko and Tarabanko 2017). In the kraft pulping process, it is imperative to avoid the use of catalysts so that downstream processing of kraft liquor is easily handled in evaporators and recovery boilers. Also, the oxidation of lignin with oxygen and nitrobenzene usually requires high temperatures and pressures and may result in many undesirable byproducts (He et al. 2017).

Hydrogen peroxide is an industrially attractive and environmentally benign chemical which is commonly used in pulp and paper industry (He et al. 2017). It is easy to use and doesn't require any special equipment. Higher reactivity of hydrogen peroxide also enables it to cause significant degradation of non-phenolic lignin structures unlike oxygen (Kadla and Chang 2001). The reduction potential of H_2O_2/H_2O pair is +1.763 V, compared to only +1.229 V for the O_2/H_2O pair in acidic medium whereas, in alkaline medium the reduction potential of H_2O_2/H_2O pair is +0.994 V, compared to only +0.401 V for the O_2/H_2O (Ma et al. 2015; Tarabanko and Tarabanko 2017). In contrast, nitrobenzene has a reduction potential (nitrobenzene to phenyl hydroxylamine) of –1.1 V in aqueous alkaline medium and –0.37 V in acidic medium. A significant amount of experimental data in the field of lignin oxidation using oxygen and nitrobenzene has been accumulated and there are a number of modern reviews available based on these reagents. However, the recently published reviews only briefly discuss the use of hydrogen peroxide as an oxidizing agent for lignin (Fache et al. 2016; Guadix-Montero and Sankar 2018; Tarabanko and Tarabanko 2017). The purpose of this review is to highlight the basic

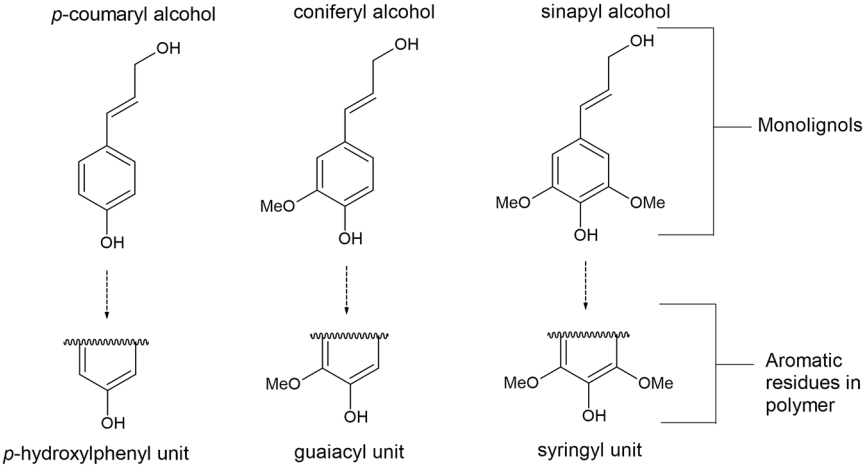


Figure 1: Monolignols present in the lignin (Calvo-Flores et al. 2015) (reproduced with permission from John Wiley & Sons).

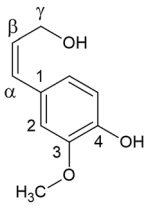


Figure 2: Nomenclature followed in lignin model compounds.

patterns, mechanisms and optimal conditions for utilizing hydrogen peroxide for oxidation of lignin.

2 Lignin structure

Lignin is an amorphous high molecular mass biopolymer with a chemical structure distinct from the other constituents of wood. The chemical structure of the lignin is made up of phenyl-propane units that are not linked to each other in any systematic order. In general, lignins are categorized into three major groups: softwood, hardwood, and grass lignins. They arise from radical coupling of three main precursors: *p*-coumaryl, coniferyl, and sinapyl alcohols (Figure 1) (Calvo-Flores et al. 2015).

Peroxidase and laccase enzymes in the plant cell wall oxidize the phenolic OH groups of the monolignols, generating free radicals. Subsequently the complex lignin polymer is formed by homo-coupling or cross-coupling the monolignol radicals. Its composition is generally characterized by the relative abundance of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units (derived from each of the three major precursors) and by the distribution of interunit linkages in the polymer. The nomenclature followed in lignin model compounds is highlighted in Figure 2. Softwood, hardwood and grasses differ in major interunit linkages, abundance, methoxyl content, and bond dissociation energies which are represented in (Table 1 and Figure 3).

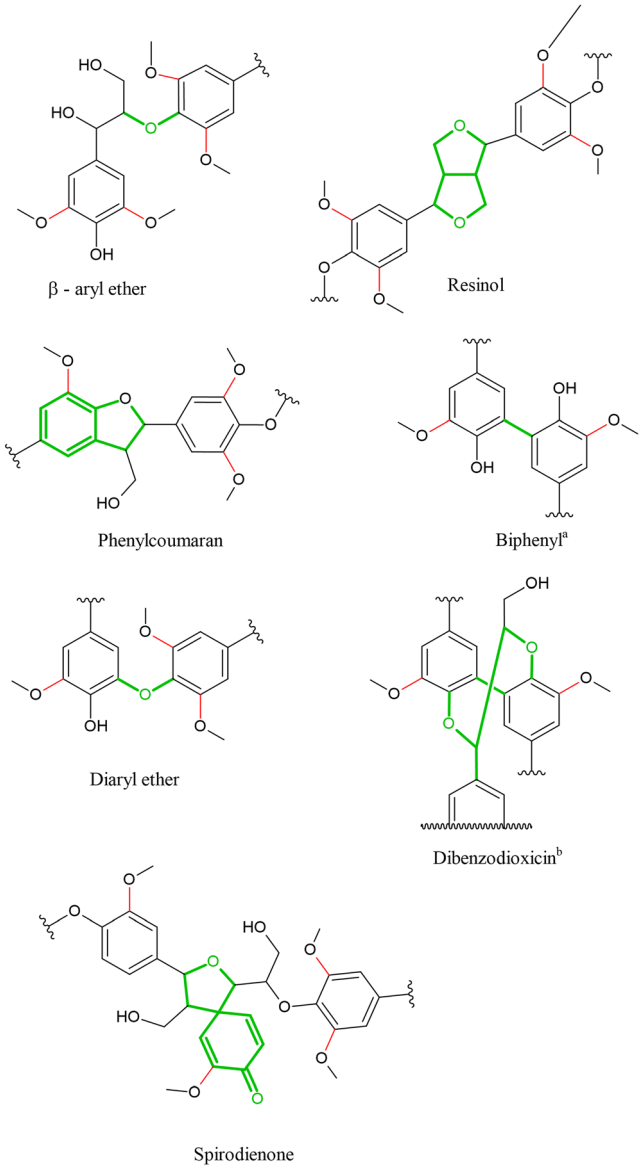


Figure 3: Major interunit linkages found in lignin (Rinaldi et al. 2016) (reproduced with permission from John Wiley & Sons).

Table 1: Different interunit linkages, their structure, abundance and bond dissociation energies found in softwood, hardwoods and grasses (Rinaldi et al. 2016).

Major interunit linkages found in lignin	β–aryl ether	Resinol	Phenyl-coumaran	Biphenyl[a] + dibenzodioxicin[b]	Spirodienone	Diaryl ether
Interunit linkage	β–O–4	(β–β) + (γ–O–α)	(β–5) + (α–O–4)	5–5[a] (5–5) + (α–O–4) + (β–O–4)[b]	β–1 + (α–O–α)	4–O–5
Softwood (%)	45–50	2–6	9–12	5–7[b]	1–9	2
Hardwood (%)	60–62	3–16	3–11	<1[b]	1–7	2
Grasses (%)	74–84	1–7	5–11	n.d	n.d	n.d
Bond dissociation energy (kcal/mol)	$C_β$–O–C_4, 54–72 $C_α$–$C_β$ 75–80	$C_α$–O 68 $C_α$–$C_β$ 67 $C_γ$–O 79 $C_β$–$C_β$ 81	$C_α$–O–C_4, 50–56 $C_α$–$C_β$ 54–63	C_5–C_5, 115–118	$C_β$–C_1, 65–69 (for open structure)	C_4–O–C_5 78–83

3 Sources of lignin

Lignins obtained from raw plant biomass are termed native lignins. The extraction of native lignins from lignocellulosic biomass may be future targets. The byproduct lignin obtained from conventional pulping routes such as kraft and sulphite processes are often called as technical lignins (Guadix-Montero and Sankar 2018). The largest source of lignin comes wood pulping processes, most of which is derived from the kraft and sulphite processes (Pinto et al. 2013). In some mills, part of the liquor/lignin produced is diverted to increase the pulp production capacity. Since kraft technology is evolving, the utilization of kraft lignin to make value added products seem a viable approach.

3.1 Kraft lignin

Kraft lignin accounts for 85% of all the lignin produced in the world which is industrially produced from the kraft pulping process, and approximately 45 million metric tons/year of kraft lignin is produced worldwide. The aim of the kraft process is conversion of wood into pulp which is the main raw material for paper. Kraft lignin is commonly found in black liquor, the byproduct stream of pulp and paper mills. β-aryl ether bonds are broken via sulfidolytic cleavage in phenolic phenyl propane units and via alkaline cleavage in non-phenolic phenyl propane units to result in a highly modified structure of kraft lignin (Figure 4). It has low average molecular weight (M_n) of about 1000–3000 Da with a polydispersity between two and four and an estimated average monomer molecular weight of 180 Da. It is soluble in alkali and highly polar organic solvents (Lange et al. 2013).

3.2 Lignosulfonates

Sulfite lignins or lignosulfonates (Figure 5) are obtained from sulfite pulping of wood. The annual global production of lignosulfonates is two million metric tons/year (Hu 2002). In this process the wood is made soluble by sulfonation mainly at benzyl alcohol, benzyl aryl ether and benzyl alkyl ether linkages on the side chain of phenyl propane units (Kirk-Othmer 2005). Hardwood lignosulfonates and softwood lignosulfonates are obtained from waste pulping liquor concentrated by the Howard process after stripping and recovery of sulfur (Nunn et al. 1985). They have an average monomer molecular weights in the range of 188 and 215–154 Da, for softwood and hardwood lignosulfonates respectively. They exhibit number-average molecular weight (M_n) from 1000 to 140,000 Da, with the majority lying between 5000 and 20,000 Da (Lange et al. 2013). Lignosulfonate is soluble in acidic and basic aqueous solutions, and in highly polar organic solvents but hydrolysis reactions, and eventually excessive sulfonations can occur.

3.3 Biorefinery lignin

Biorefinery lignin refers to lignin that is isolated from both woody biomass and agricultural residues by different pretreatment methods. The structural characteristics of

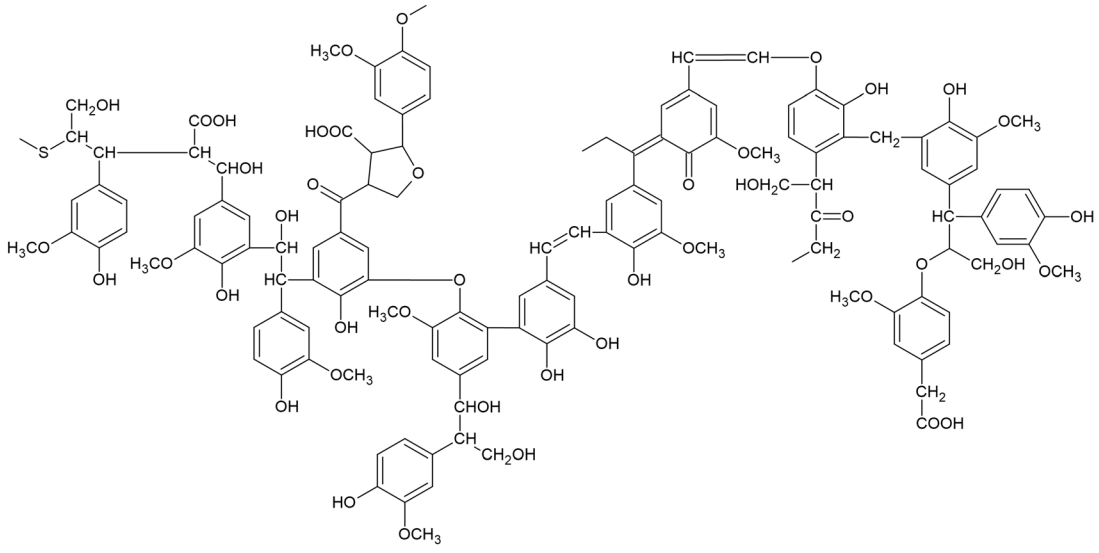


Figure 4: Structure of kraft lignin (Huang et al. 2019) (reproduced with permission from Elsevier).

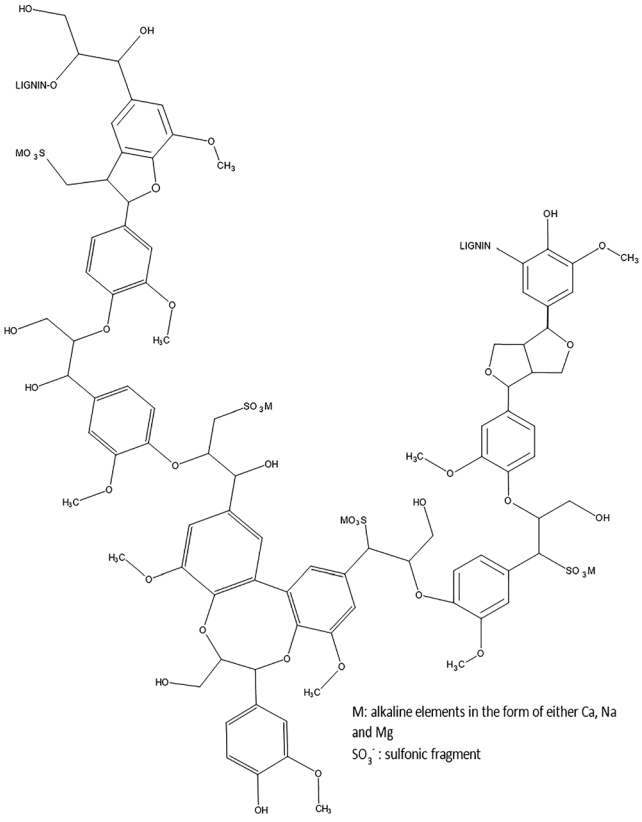


Figure 5: Structure of lignosulfonate (Lange et al. 2013) (reproduced with permission from Elsevier).

biorefinery lignin vary depending upon the pretreatment methods (Ma et al. 2018). As the biomass refinery is emerging over the recent years, tremendous amounts of biorefinery lignin are becoming available in addition to kraft and sulfite lignin (Ma et al. 2014). The main features of biorefinery lignin are represented in Table 2.

4 Mechanism of lignin oxidation by oxygen and peroxide

It is well documented that there are clear commonalities between the oxidative chemistries of lignin by oxygen and peroxide (Gierer 1997; Ma et al. 2015; Tarabanko and Tarabanko 2017). Both oxygen and peroxide are present and involved in the oxidation of lignin by oxygen and peroxide because hydrogen peroxide is formed during oxygen oxidation while oxygen is generated during peroxide oxidation (Agnemo and Gellerstedt 1979; Gierer 1997; Kadla and Chang 2001; Ma et al. 2015). The chemistry of oxygen oxidation is also linked to hydrogen peroxide within the oxidation cycle via superoxide anion radicals as shown in Figure 6 (Gierer 1997).

4.1 Oxygen oxidation

The mechanism of lignin oxidation using oxygen has been proposed by various authors (Araújo 2008; Fache et al. 2016; Tarabanko and Petukhov 2003; Tarabanko and Tarabanko 2017). The reaction mechanism of oxygen proceeds via formation of following species (Ma et al. 2015):

$$\cdot O - O \cdot + e^- \rightleftharpoons O_2^{\cdot -}$$

$$O_2^{\cdot -} + HOO^{\cdot} \rightarrow \cdot O - O \cdot + HOO^-$$

$$HOOH + HOO^- \rightarrow O_2^{\cdot -} + H_2O + HO^{\cdot}$$

$$HO^{\cdot} + O_2^{\cdot -} \rightarrow \cdot O - O \cdot + HO^-$$

The mechanism of lignin oxidation using oxygen typically involves radicals. In the absence of catalysts, the

Table 2: Main features of biorefinery lignin (Ma et al. 2018).

Spectral region	Number of moieties per aromatic ring				
	Milled wood lignin	Deep eutectic solvent based lignin	Dilute acid-pretreated corn-stover lignin	Steam-exploded spruce lignin	Soda-pretreated wheat-straw lignin
Methoxy content	0.97	0.90	1.19	0.97	1.25
C_{Ar}–H	2.75	3.09	2.45	2.46	2.67
C_{Ar}–C	1.66	1.69	1.93	2.12	1.80
C_{Ar}–O	1.59	1.22	1.62	1.42	1.53
Phenolic hydroxyl	0.05	0.49	0.22	0.30	0.01
Aliphatic hydroxyl	1.62	1.54	0.95	1.03	1.30
Saturated CH_2 or CH_3 on aliphatic side chain	1.83	1.97	2.33	2.41	1.93
C_γ in β–5 and β–O–4 with C=O	0.65	ND	0.26	0.29	0.36
C_α in β–O–4	0.57	ND	0.21	0.28	0.51
C_β in β–O–4	0.42	0.16	0.36	0.20	0.21

ND, not determined.

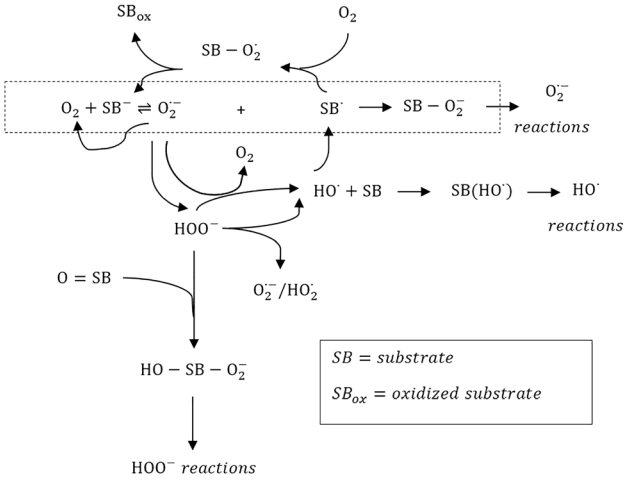
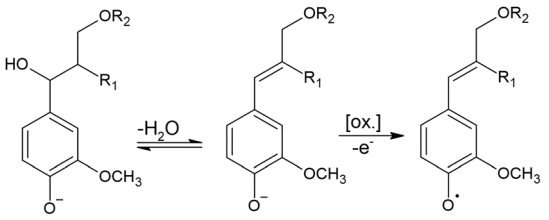
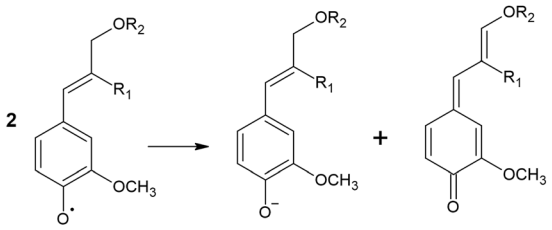


Figure 6: Course of oxygen and hydrogen peroxide oxidation cycle (Gierer 1997) (reproduced with permission from De Gruyter).

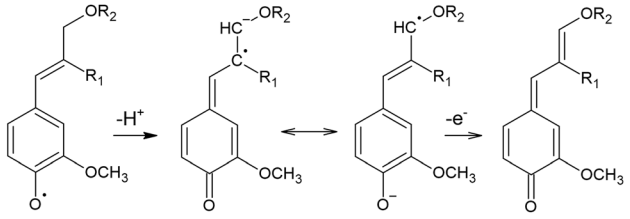
oxidation proceeds via chain reactions involving alkoxyl, hydroxyl and peroxyl radicals that are too active to achieve process selectivity (Tarabanko and Tarabanko 2017). In alkaline conditions, the reaction begins with dehydration of C_α–C_β bond followed by electron abstraction from the phenoxyl anion (**Step 1**). The oxygen oxidation is initiated by single electron transfer from activated phenoxyl anion species with the formation of a superoxide anion radical $O_2^{\cdot-}$ and phenoxyl radical. This step happens at elevated temperatures or in the presence of traces of heavy metals which act as redox catalysts. This may further yield a substrate linked peroxide anion. The formation of quinone methide intermediate can take place by the disproportionation of the phenoxyl radical (Ralph et al. 2009) (**Step 2a**) or by the oxidation of this radical preceded by proton detachment (**Step 2b**). Under thermodynamic control, the addition of nucleophilic agents to quinone methides (**Step 3**) occurs mainly at the γ-position whereas under kinetic control the addition occurs at the α-position (Tarabanko and Petukhov 2003). The formation of vanillin from retroaldol cleavage of an α – unsaturated aldehyde (**Step 5a**) requires strong alkalinity and if the conditions are not maintained, byproducts are formed by the oxidation of unsaturated aldehydes. The retro-aldol cleavage is a reversible reaction and the probability of the reaction favoring vanillin formation is dependent on the pH, thermodynamic and kinetic control of the reaction conditions. The final step proceeds through dissociation of C–H bond of the phenoxyl anion (Tarabanko and Tarabanko 2017). Hence, from the mechanism proposed below, vanillin formation from lignin requires proper control of desired conditions. The following is the step by step explanation of the proposed mechanism.



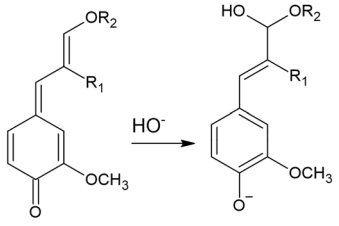
Step 1: Initiation with electron detachment of phenoxyl anion to form phenoxyl radical.



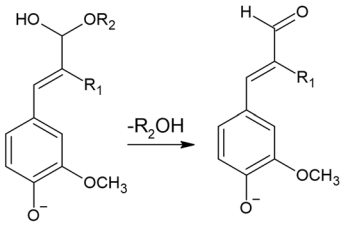
Step 2a: Disproportionation of phenoxyl radical to form quinone methide.



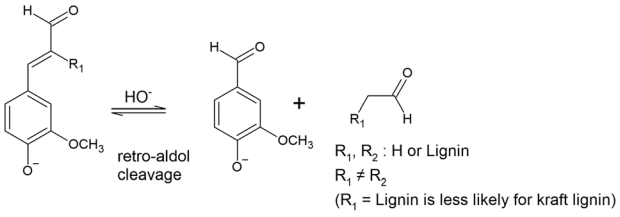
Step 2b: Oxidation of phenoxyl radical preceded by proton detachment.



Step 3: Nucleophilic addition of hydroxide ion to form coniferyl alcohol structure from quinone methide.

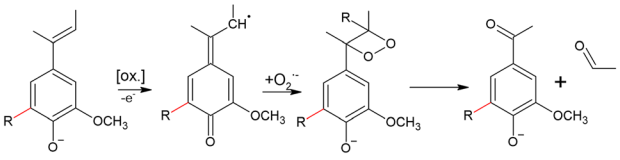


Step 4: Oxidation of coniferyl alcohol structure to γ-carbonyl group.



Step 5a: Retroaldol reaction of α-unsaturated aldehyde to form vanillin.

The formation of substrate linked peroxide anion from superoxide anion radicals may also further yield aromatic aldehydes such as vanillin (**Step 5b**) (Gierer 1997; Ma et al. 2015). This proceeds through cleavage of conjugated double bonds. The drawback of this pathway is that it cannot be extrapolated towards selective oxidants such as nitrobenzene or copper oxide (Tarabanko and Tarabanko 2017).



Step 5b: Formation of aromatic aldehydes via attack of superoxide anion radical $O_2^{\cdot-}$. Figures in **Steps 1** to **5b** are reproduced from open access article published by MDPI; Tarabanko and Tarabanko 2017).

Besides C–C cleavage, superoxide anion radicals may also undergo proton and heavy metal catalyzed dismutation under alkaline conditions (pH > 6) to form oxygen and hydrogen peroxide as shown in Figure 6. In presence of alkali promoted, heavy metal-catalyzed reactions, hydrogen peroxide may disproportionate to form hydroxyl and re-form superoxide anion radicals (Gierer 1997). The hydroxyl radical is the most reactive among all the reactive oxygen species. The formation of hydroxyl radical is accelerated in the presence of transition metal catalysts required in the oxygen oxidation of lignin (Ma et al. 2014; Santos et al. 2011; Tarabanko and Tarabanko 2017). In this oxidation cycle in the presence of metal catalysts, the Haber-Weiss reaction generates hydroxyl radicals from hydrogen peroxide and superoxide anion radical (Sharma et al. 2012). The following reactions occur:

a) Fe(III) reduction by $O_2^{\cdot-}$
b) Fe(II) oxidation by hydrogen peroxide (Fenton reaction)

$$Fe^{3+} + O_2^{\cdot-} \rightarrow Fe^{2+} + O_2 \quad \text{(a)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \quad \text{(b)}$$

$$O_2^{\cdot-} + H_2O_2 \rightarrow OH^{\cdot} + OH^- + O_2 \quad \text{(net reaction)}$$

The presence of transition metal catalysts is crucial for the Haber-Weiss reaction since the rate of reaction in the absence of catalysts is negligible. The effect of hydroxyl radical in the oxidation processes can be explained through the redox potential. In alkaline media, the redox potential of hydroxyl radical is +1.89 V, whereas the superoxide anion radical is close to the redox potential of molecular oxygen +0.40 V (Gierer 1997; Tarabanko and Tarabanko 2017). The hydroxyl radical is too active for vanillin preservation. Therefore, it is evident that to enhance the yield of vanillin, it is important to decrease the impact of oxygen and its reactive radical forms such as hydroxyl radicals. This may be addressed by using hydrogen peroxide which is relatively stable compared to other reactive oxygen species. Also, non-phenolic lignin structures are not attacked by oxygen to any noticeable extent since the initial step of electron transfer (Figure 6) from the non-phenolic substrate to oxygen does not take place (Gierer 1997). Hydrogen peroxide is moderately active and does not have unpaired electrons unlike oxygen radicals. Another major advantage of using hydrogen peroxide is that non-phenolic lignin structures are also reactive during oxidation reaction unlike oxygen (Kadla and Chang 2001). An effort to address the developments in oxidation of lignin using hydrogen peroxide is made in following sections to further develop the understanding.

4.2 Hydrogen peroxide oxidation

Phenolic cinnamaldehyde structures of coniferaldehyde type are readily cleaved by alkaline hydrogen peroxide giving rise to corresponding aromatic aldehyde such as vanillin which can be further converted to aromatic acids such as vanillic acid (Gellerstedt and Agnemo 1980; Ma

et al. 2015). The reaction proceeds with nucleophilic attack of hydrogen peroxide at C_α position forming an intermediate epoxide. The α-carbonyl structures in phenolic units are quantitatively cleaved to form the corresponding methoxy-hydroquinone derivatives (Kadla and Chang 2001; Ma et al. 2015). In the presence of phenolic units, the reaction proceeds via a Dakin-reaction and the intermediate formation of an epoxide which under alkaline conditions is rapidly hydrolyzed accompanied by cleavage of the C_α–C_1 forming the corresponding methoxy hydroquinone derivatives. The mechanism representing this cleavage reactions is shown in Figure 7, Scheme A.

For α-carbinol structures, the reaction proceeds via formation of a quinone methide intermediate followed by the Daikin-like reaction as represented in Figure 7, Scheme B. The corresponding hydro peroxide is formed when the quinone methide rapidly reacts with superoxide ions (Agnemo and Gellerstedt 1979). The hydroperoxide derivative then forms *p*-quinone type structures. In the case where reactive moieties are absent in the α-position, nucleophilic attack by the hydroperoxide takes place at ortho-position, where the methyl group is eliminated. Subsequently, *o*-quinone type structures are then formed. Multiple reaction sites present in the *o*- and *p*-quinone rings are feasible for

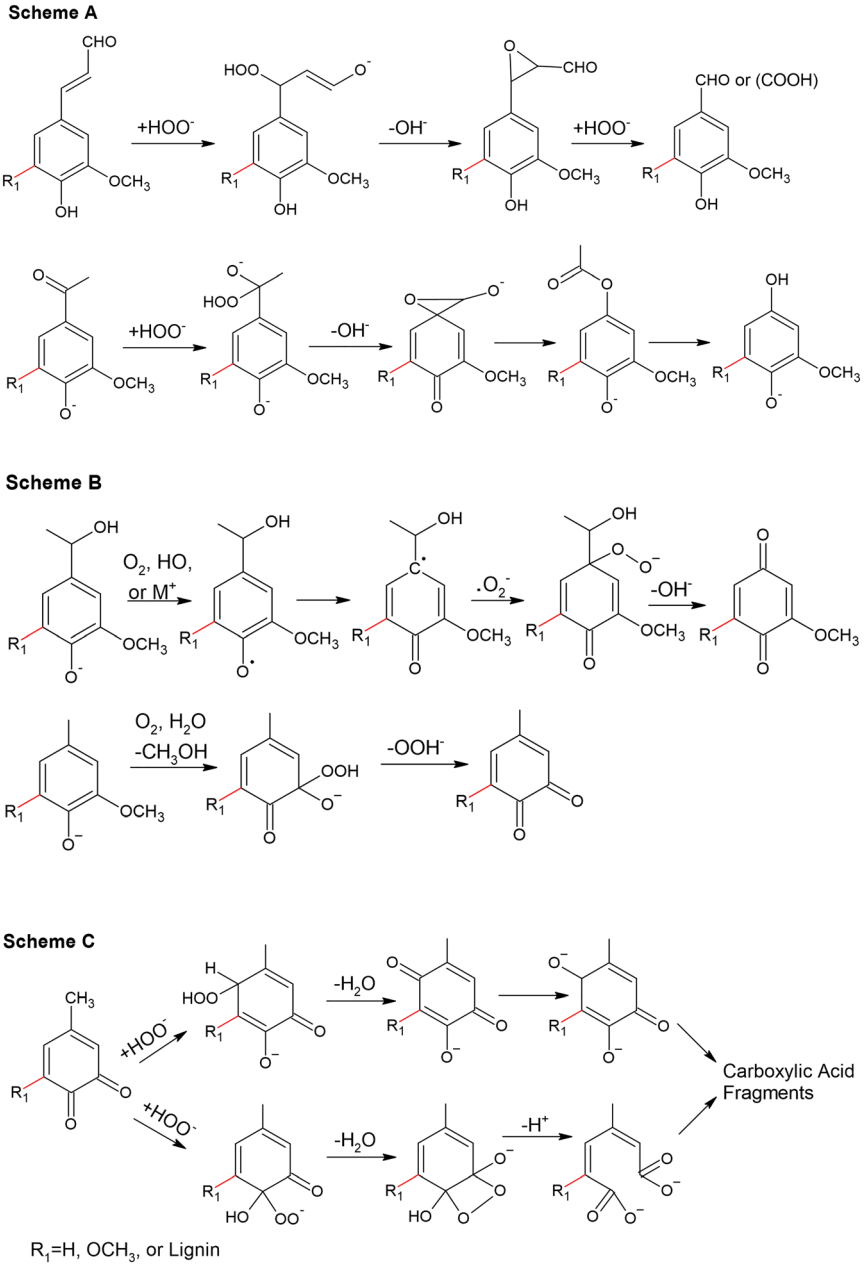


Figure 7: Hydrogen peroxide oxidation of phenolic-lignin mechanisms: (Scheme A) conjugated side-chain oxidation, (Scheme B) aromatic ring oxidation to benzoquinone structures, (Scheme C) aromatic ring cleavage (Ma et al. 2015) (reproduced with permission from John Wiley & Sons).

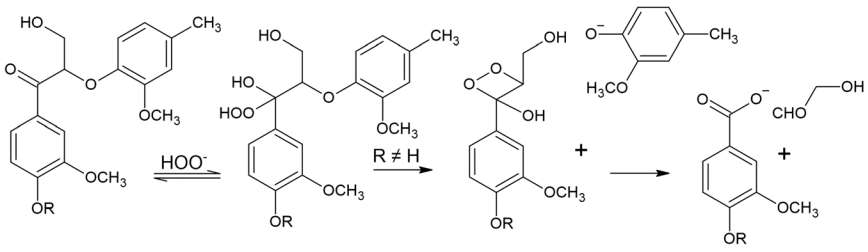


Figure 8: Hydrogen peroxide oxidation of non-phenolic lignin with aryl-α-carbonyl conjugated structures (Kadla and Chang 2001) (reproduced with permission from American Chemical Society).

attack by hydroperoxide anions leading to ring opening products as shown in Figure 7, Scheme C.

Unlike oxygen oxidation of lignin, hydrogen peroxide can react with non-phenolic lignin structures. In the case of non-phenolic units with aryl-α-carbonyl conjugated structures, intramolecular nucleophilic attack leads to formation of a new phenolic hydroxyl group and a dioxetane intermediate which decomposes to the corresponding benzaldehyde which can further oxidize (Kadla and Chang 2001). The Dakin reaction is precluded in this case due to absence of a free-phenolic hydroxyl group as shown in Figure 8.

In non-phenolic cinnamaldehyde type structures, the hydroperoxide anion nucleophilically attacks α-carbon. An intermediate epoxide is formed after elimination of hydroxide ion, which subsequently forms veratraldehyde type structures as shown in Figure 9. The side chain of these compounds is simultaneously oxidized to form an intermediate glyoxal which further results into the formation of formic acid (Gellerstedt and Agnemo 1980). In the case of α-carbinol structures like veratryl alcohols, the reaction proceeds via formation of veratric acid as shown in Figure 10, Scheme A. The reaction proceeds by way of an S_N2 mechanism due to the presence of an etherified phenolic hydroxyl group. An intermediate formation of veratraldehyde takes place due to deprotonation-oxidation of hydroperoxide formed from veratryl alcohol. Veratraldehyde is further nucleophilically attacked by the hydrogen peroxide anion to form hydroperoxyacetal which is a highly unstable tetrahedral intermediate. This intermediate finally results in veratric acid via deprotonation followed by oxidation (Kadla et al. 1997). Due to the low pK_a of the perhydroxy anion, competition between oxidation and dimerization takes place between veratryl alcohol and its corresponding hydroperoxide intermediate as shown in Figure 10, Scheme B.

4.2.1 Effect of pH

Hydrogen peroxide is a powerful oxidizing agent reacting both as an electrophile and nucleophile depending upon the pH of the medium. Under acidic conditions, it acts as an electrophile by forming OH^+ species (Xiang and Lee 2000). The reaction is summarized as follows:

$$H_2O_2 + H^+ \leftrightarrow H_2^+OOH \leftrightarrow H_2O + OH^+$$

Whereas, under alkaline conditions it mainly works by forming the perhydroxyl ion OOH^- as shown in the following reactions (Johnson et al. 2002; Zeronian and Inglesby 1995)

1) $H_2O_2 + OH^- \leftrightarrow OOH^- + H_2O$
2) OOH^- + chromophore → bleaching (chromophore destroyed)

In nucleophilic reactions, it is commonly accepted that the conjugate base perhydroxyl anion HOO^- is the active species. This improved nucleophilicity is due to unshared pair of electrons on the atom adjacent or the alpha to the nucleophilic atom and is termed as 'the alpha effect' (Kadla and Chang 2001). At 30 °C, the rate of decomposition of hydrogen peroxide is maximized at pH 11.5. In a study of reaction of hydrogen peroxide with α-methyl syringyl alcohol, it was found that the rate of decomposition of peroxide was directly related to the rate of degradation of

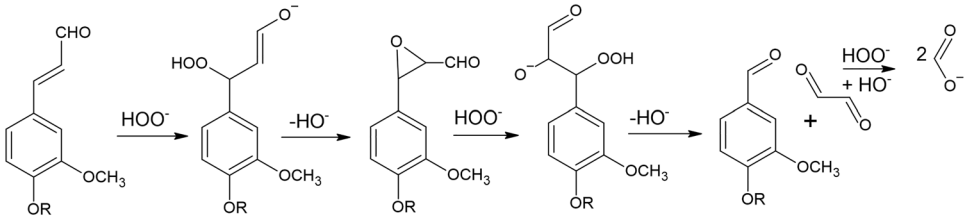


Figure 9: Hydrogen peroxide oxidation of non-phenolic lignin with cinnamaldehyde conjugated structures (Gellerstedt and Agnemo 1980) (reproduced with permission from John Wiley & Sons).

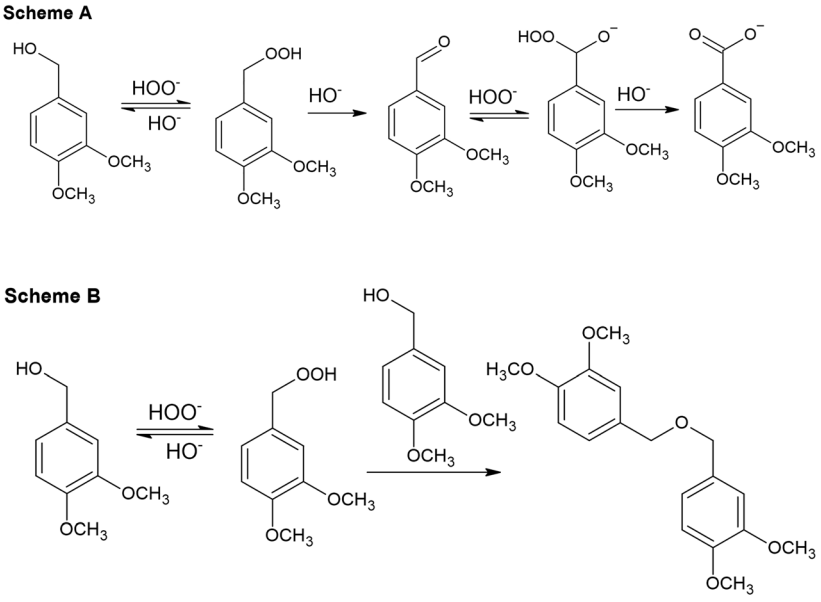


Figure 10: (Scheme A) hydrogen peroxide oxidation of non-phenolic lignin with α-carbinol structures. (Scheme B) Dimer formation in the reaction of α-carbinols (Kadla et al. 1997) (reproduced with permission from De Gruyter).

Table 3: First order reaction rate constants k_1(obs) for the decomposition of hydrogen peroxide (Agnemo and Gellerstedt 1979).

pH	Temperature (°C)	k_1(obs)/10^{-3} min^{-1}
10.0	30	3.09
10.5	25	3.24
10.5	30	5.50
10.5	40	12.08
11.0	30	10.38
11.5	30	11.72
12	30	3.36
12.5	30	0.68

phenol. Hence, the maximum degradation of phenol was obtained at pH of 11.5 (Agnemo and Gellerstedt 1979). The rate constants for the decomposition of hydrogen peroxide as a function of pH is shown in Table 3. Another study showed that reactivity of *p*-hydroxybenzyl alcohols is yet another factor dependent on the pH of the system (Kadla et al. 1997). It also affects the formation of quinone methide and the reactivity of hydroperoxy intermediate Figure 11 [Ia]. As the pH is increased, the amount of quinone methide is decreased resulting in a decrease in reaction rate as shown in Figure 12. Also, the pK_a of the hydroperoxy intermediate is likely to be 12–12.5, thereby contributing to the decrease in reactivity of apocynol at higher alkalinity (Kadla et al. 1997). Hence, pH control is an important parameter and should be maintained at pH 11.5 to prevent ionization of the hydroperoxy intermediates that are formed and maximize lignin oxidation.

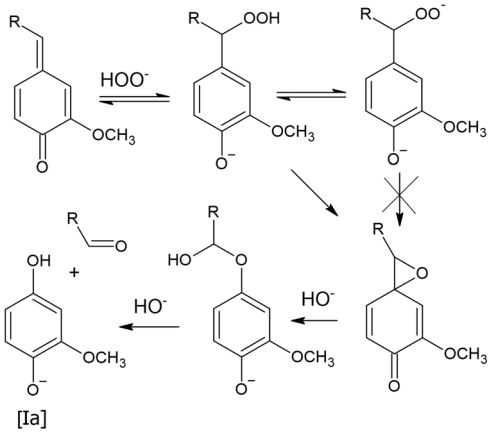


Figure 11: The effect of pH on the reaction mechanism of apocynol (Kadla et al. 1997) (reproduced with permission from De Gruyter).

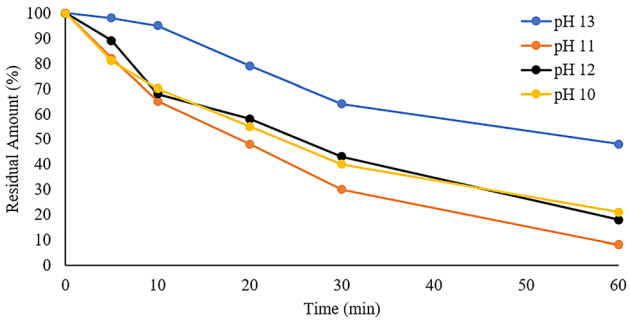


Figure 12: The effect of pH on the reactivity of apocynol at 90 °C (Kadla et al. 1997) (reproduced with permission from De Gruyter).

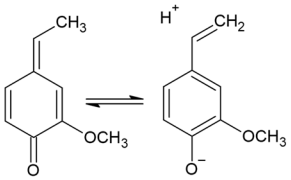


Figure 13: Stabilization of quinone methide from apocynol through hyperconjugation (Kadla et al. 1997) (reproduced with permission from De Gruyter).

In the mechanism of *p*-hydroxyacetophenone oxidation, the reaction rate was profoundly dependent on the base type and concentration (Hocking and Crow 1994). The reaction rate proceeds at a maximum when the base concentration is about 0.3 M. It was also found that hydroquinone monoacetate – HMA (reaction intermediate) can be hydrolyzed to hydroquinone and acetate if hydroxide ions are present in excess of the amount required to produce hydroperoxide anion. Hence, hydroxide ions can compete with the hydroperoxide anion for the available HMA causing a lower steady state concentration of both HMA and peracetate, and a slower reaction. Therefore, aqueous sodium carbonate can provide enough alkalinity in this case with a lower concentration of hydroxide ions compared to sodium hydroxide solution. At higher pH, *o*-hydroxyacetophenone reacted by the same mechanism whereas *m*-hydroxyacetophenone does not react with hydrogen peroxide under these conditions due to electronic reasons (Hocking and Crow 1994).

The degradation of precipitated hardwood lignin (PHL) using hydrogen peroxide was investigated at moderate to high temperatures (Xiang and Lee 2000). It was found that under alkaline conditions, the reaction proceeds even at low temperatures (80–90 °C) compared to higher temperatures of (130–160 °C) required under acidic conditions. Mono- and di-carboxylic acids were obtained as the major products. Under alkaline conditions, the main mono- and di-carboxylic acids detected were oxalic acid and formic acid with maximum yields of 17.4% (w/w) and 15.8% (w/w) respectively at 90 °C for short reaction time of 10 min. Aldehydes and aromatic acids which are the intermediate products were detected only in trace amounts (Xiang and Lee 2000). The yield of vanillin and vanillic acid was 0.12% (w/w) and 0.15% (w/w) under alkaline hydrogen peroxide oxidation of PHL. On the other hand, these compounds were not detected by GC-MS in acidic condition of oxidation. This was due to acid insoluble nature of PHL and aromatic structure instability of phenolic aldehydes in acidic conditions. The yields of mono- and di-carboxylic acids were lower compared to similar operating conditions in basic conditions. The maximum yields of formic and acetic acid were 26.6% (w/w) and 10.1% (w/w) respectively obtained at 140 °C for the reaction period of 30 min.

4.2.2 Effect of temperature

The dissociation constants for various phenols depends on the temperature of the system. As the temperature is increased, the dissociation constants for various phenols decrease. This in turn increases the amount of quinone methide intermediate because it depends on the ionization of the phenol and the tendency of α-hydroxide elimination (Kadla et al. 1997). Also at higher temperatures, the stabilization effects due to hyperconjugation (Figure 13) can be eliminated due to the thermal energy of the system.

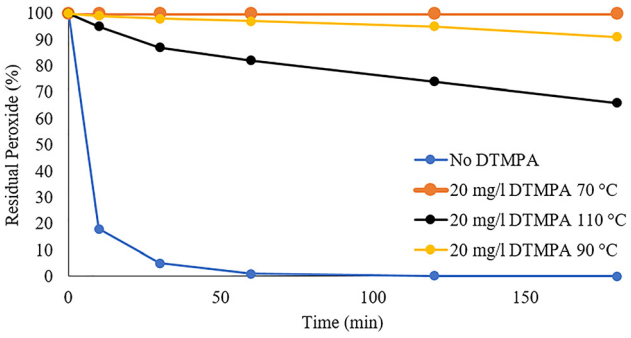


Figure 14: Effect of DTMPA and temperature on hydrogen peroxide stability pH 11.5 (Kadla et al. 1999) (reproduced with permission from De Gruyter).

Higher temperatures also enable ionization of hydrogen peroxide. The effect of stabilization on hydrogen peroxide at higher temperatures by using DTMPA (diethylenetriaminepentamethylene phosphonic acid) is shown in Figure 14. In this study of the oxidation of lignin model compounds using hydrogen peroxide at 90 °C, phenolic compounds such as apocynol and *p*-hydroxybenzyl alcohol reacted completely in the presence of DTMPA at a pH of 11.2 (Kadla et al. 1997). At lower temperatures of around 50 °C, the formation of the quinone methide is the rate determining step and is under thermodynamic control. Whereas at higher temperatures of around 90 °C, oxidation of the hydroperoxy intermediate determines the rate and extent of reaction. Hydrogen peroxide decomposition at 90 °C and 110 °C is bimolecular with second order rate constants of 1.67×10^{-4} and $3.98 \times 10^{-4} \mathrm{lmol^{-1}s^{-1}}$ ($R^2 = 0.99$) respectively (Kadla et al. 1999).

In a study of oxidation of pine kraft lignin (Indulin AT), the highest percentage reduction of phenolic hydroxyl group/methoxyl group as a function of hydrogen peroxide consumed (g/l) was observed at 90 °C in the presence of DTMPA (Kadla et al. 1999). The compounds that were identified as the products of hydrogen peroxide oxidation of kraft lignin are shown in Figure 15.

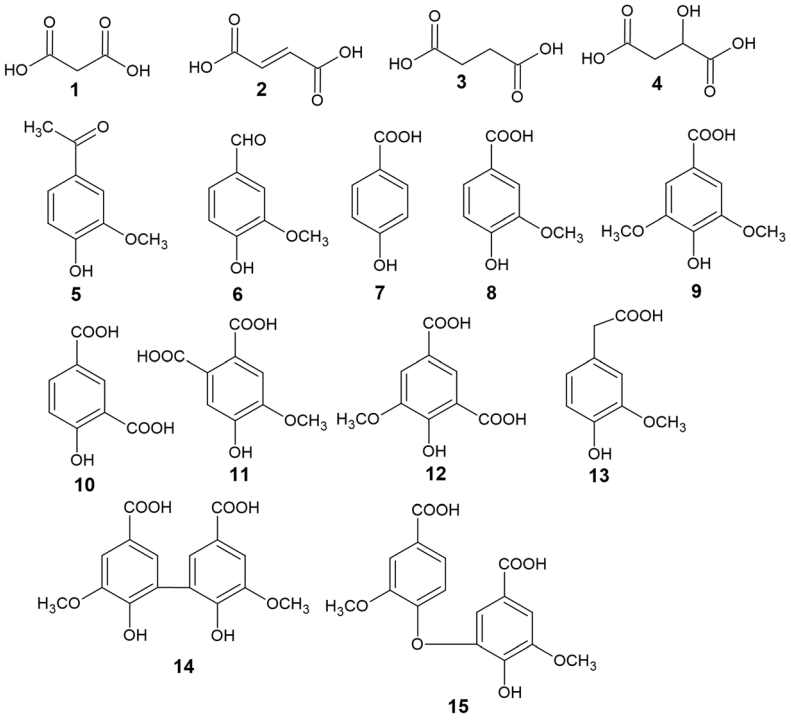


Figure 15: Low molecular weight products obtained from the oxidation of kraft lignin by hydrogen peroxide (Kadla et al. 1999) (reproduced with permission from De Gruyter).

A significant amount of the lignin (around 80%) was degraded at 110 °C which was the highest degradation based on yield and it accounted for 90% hydrogen peroxide consumption under stabilized conditions. Since the presence of radical species limits the extent of lignin degradation by consuming oxidizing agents, the extensive degradation of the lignin along with low residual hydrogen peroxide implies radicals may not be involved under these operating conditions. Significant amounts of isophthalic acid and aliphatic dicarboxylic acids were generated at these conditions. Isophthalic derivatives such as compound **10** and **12** are a result of oxidation of phenolic phenylcoumaran structures. Compound **12** comprised over 60% of the isolated compounds at 110 °C. In non-stabilized systems the amount of compound **12** was extremely low at 90 °C. The reduced yield at 90 °C in the absence of DTMPA is due to the consumption of available oxidant by radical species limiting lignin degradation. On the contrary, the higher yield obtained at 110 °C under stabilized conditions suggests that the use of extreme conditions facilitate the degradation of condensed lignin structures and enhance the formation of new phenolic hydroxyl groups (Kadla et al. 1999). Therefore, the percentage reduction of phenolic group/methoxy group at 90 °C was higher compared to 110 °C under stabilized conditions. The effect of temperature was also observed in case of aliphatic dicarboxylic acids. Trace levels of aliphatic acids were obtained at 70 °C with and 90 °C without DTMPA. Substantial amounts of malonic acid **1**, maleic/fumaric acid **2**, and succinic acid **3** from ring opening reactions of transient quinone intermediates were formed from lignins at 90 °C and 110 °C with DTMPA. Vanillin (compound **6**) and acetoguaiacone (compound **5**) were only detected in the non-stabilized system at 90 °C. It is suggested that rapid decomposition of H_2O_2 avoids the further degradation of these compounds. The amount of vanillin formed in this study is unclear (Kadla et al. 1999), but it can be concluded that the amount of vanillin formed in non-stabilized conditions will be significantly lower compared to stabilized conditions due to enhanced degradation of condensed lignin structures and formation of new phenolic hydroxyl groups.

4.2.3 Effect of metal ions

Transition metal catalysts in their highest oxidation state enhance the process of electron abstraction as shown in Figure 16 (Ma et al. 2014; Santos et al. 2011). The phenoxyl radical is formed by abstraction of an electron from phenolate anion (PhO^-). It is evident that presence of catalytic amounts of copper (II), iron (III) or manganese (IV) increases the rate of reaction of phenolic lignin model compounds (Agnemo and Gellerstedt 1979; Gellerstedt and Agnemo 1980; Ma et al. 2014).

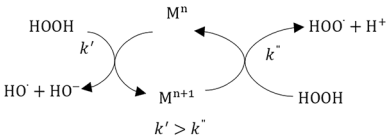


Figure 16: Transition metal induced decomposition of hydrogen peroxide (Kadla et al. 1997) (reproduced with permission from De Gruyter).

Hydrogen peroxide is also susceptible to thermal and transition metal induced homolytic fragmentation reactions in which hydroxyl ($HO^{\cdot}$) and superoxide anion ($O_2^{\cdot-}$) radicals are generated (Kadla and Chang 2001). Peroxides in alkaline conditions decompose via a disproportionation reaction with a maximum rate at the pH of its pK_a of 11.6 at 25 °C (Xiang and Lee 2000)

$$HOOH + HOO^- \rightarrow HO^{\cdot} + HOO^{\cdot} + HO^- \quad (1)$$

$$HOOH + HOO^- \rightarrow HO^- + O_2 + H_2O \quad (2)$$

Disproportionation leads to autocatalytic decomposition of hydrogen peroxide. The following reactions occur in aqueous media which provide the base induced decomposition of hydrogen peroxide into oxygen and water (Kadla and Chang 2001).

$$HOO^- + HO^{\cdot} \rightarrow O_2^{\cdot-} + H_2O \quad (3)$$

$$HOOH + HO^{\cdot} \rightarrow HOO^{\cdot} + H_2O \quad (4)$$

$$HOO^{\cdot} \leftrightarrow O_2^{\cdot-} + H^+ \quad (5)$$

$$HO^{\cdot} + O_2^{\cdot-} \rightarrow HO^- + O_2 \quad (6)$$

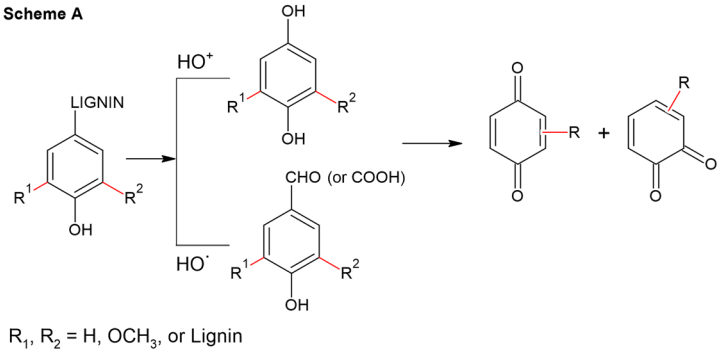
$$HOOH + O_2^{\cdot-} \rightarrow HO^{\cdot} + HO^- + O_2 \quad (7)$$

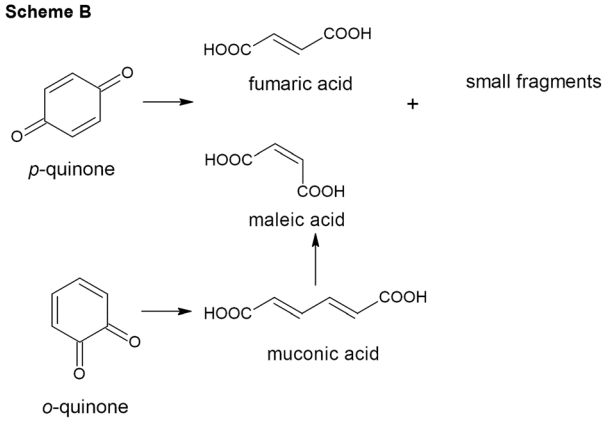
As discussed in earlier sections, hydrogen peroxide decomposes in aqueous media to form hydroxyl and superoxide radicals. The $HO^{\cdot}$ radical is one of the strongest thermodynamically stable one-electron oxidants in aqueous media. The reduction potential in acidic solution E_0 ($HO^{\cdot}$, H^+/H_2O) = +2.72 V and in neutral and alkaline solution E_0 ($HO^{\cdot}/HO^-$) = 1.89 V (Klaning et al. 1985; Schwarz and Dodson 1984). It exhibits strongly electrophilic properties and selectively attacks electron-rich aromatic and olefinic moieties in lignins. It can also react with the aliphatic side chains at a comparatively lower rate. In strongly alkaline conditions (pH > 12), the hydroxyl radical $HO^{\cdot}$ is converted into its conjugate base $O^{\cdot-}$, the oxyl anion radical. The oxyl anion can only react with aliphatic side chains in lignins. In contrast to $HO^{\cdot}$, the superoxide anion radical ($O_2^{\cdot-}$, H^+/HO_2^-) = +0.2 V; ($O_2^{\cdot-}$, $2H^+/H_2O_2$) = +0.87 V, does not oxidize lignin to a substantial extent (Gierer 1997). Kraft lignin and phenolic model compounds were not degraded when reacted with potassium superoxide at room temperature (Barkhau et al. 1985). The decomposition products of hydrogen peroxide such as hydroxyl radicals, superoxide ions and oxygen can attack phenols present in lignin (Agnemo and Gellerstedt 1979). The phenoxyl radicals also have the tendency to react with superoxide ions that are formed due to decomposition giving rise to hydroperoxide which is subsequently degraded to low molecular weight compounds.

The formation of aliphatic acids such as malonic, succinic, malic acid from aromatic ring opening of lignin and its model compounds have been reported in the literature (Kadla et al. 1999; Ma et al. 2014; Xiang and Lee 2000). It has been hypothesized that initial ring hydroxylation is responsible for the formation of dicarboxylic acids. This reaction takes place due to the reactive species such as $HO^{\cdot}$ and HO^+. $HO^{\cdot}$ radicals react with aromatic and aliphatic structures generating initially radical sites but are unable to result in direct degradation by opening aromatic rings or fission of conjugated structures (Gierer 1997). The depolymerization of lignin by side chain substitution and/or oxidative side chain cleavage using HO^+ is the initial step to form low molecular weight aromatic compounds. They are further oxidized to *p*- and *o*-quinone derivatives. Quinones further convert to maleic/fumaric acid and muconic acid derivatives by aromatic ring cleavage. It is probable that quick conversion of muconic acid takes place to form maleic/fumaric acid. This acid then forms malonic/succinic acid by hydrolysis. The reaction scheme is shown in Figure 17. Radical formation can be inhibited by addition radical scavenging agents. Hence, the ring opening reactions can be minimized, and aromatic ring stability can be improved (Ma et al. 2014).

4.2.4 Effect of lignin feedstock

The origin of lignin is yet another important parameter affecting the aldehydes yield (Tarabanko and Tarabanko 2017). The use of low molecular weight lignin provides better yields whereas the presence of impurities such as sugars can negatively impact the yield. The isolation processes also modify lignin structure. Hence, chemically treated lignins such as technical lignins show reduced yields compared to native lignins. This is due to the condensation reactions happening at C–5 position as a result of acid preparation of lignin (Fache et al. 2016). The low yields obtained from various lignin sources are shown below in Table 4. The effect of lignin feedstock on yield of aromatic aldehydes using hydrogen peroxide as an oxidizing agent is still a matter of study (Agnemo and Gellerstedt 1979; Gellerstedt and Agnemo 1980; Kadla et al. 1997). Hence, this section highlights the available literature to show the effects lignin feedstock on yield of aromatic aldehydes.





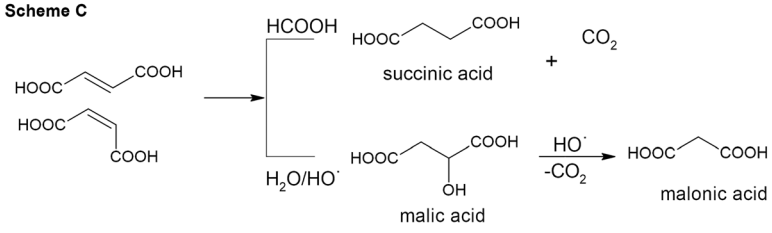


Figure 17: Proposed mechanisms for (Scheme A) lignin depolymerization and aromatic nuclei oxidation, (Scheme B) aromatic ring cleavage, and (Scheme C) formation of final products (Ma et al. 2014) (reproduced with permission from John Wiley & Sons).

Table 4: Effect of lignin feedstock on aromatic aldehyde yield.

Sr. no.	Lignin source	References	Oxidizing agent	Yield (%)
1	*Pinus* spp. kraft	Mathias and Rodrigues (1995)	Nitrobenzene	V: 13
2	Calcium salt in alcohol precipitated kraft	Villar et al. (1997)	Nitrobenzene	V+S: 14
3	Indulin AT kraft	Araújo (2008)	Oxygen	V: 3.7
4	Lignoboost softwood kraft	Rodrigues Pinto et al. (2011)	Oxygen	V: 3.1
5	Hardwood kraft	Villar et al. (2001)	Oxygen, CuO	V: 1.1, S: 3.5 SA: 1.5
6	Lignosulfonates	Tarabanko et al. (1995)	Oxygen, $Cu(OH)_2$	V: 12[a]
7	Lignosulfonates	Bjørsvik and Minisci (1999); Pacek et al. (2013)	Oxygen, $CuSO_4$	V: 5–7[b]
8	Precipitated hardwood kraft	Xiang and Lee (2000)	Hydrogen peroxide	V: 0.12 VA: 0.15 OA: 17.4 FA: 15.8

[a]65 wt.% of lignosulfonates assumed. [b]Ash content of lignosulfonate is unclear. V, vanillin; S, syringaldehyde; VA, vanillic acid; SA, syringic acid; OA, oxalic acid; FA, formic acid.

5 Conclusion

Alkaline hydrogen peroxide can be used at high temperatures for the peroxide degradation of kraft lignin using stabilization agents. It not only increases the amount of lignin oxidation but also improves peroxide utilization more efficiently (Kadla et al. 1999). pH control is crucial and should be maintained at pH 11.5 to prevent ionization of the hydroperoxy intermediates and maximize lignin oxidation (Kadla et al. 1997). Under these conditions, chromophoric groups are generated through Dakin and Dakin-like reaction pathways. In contrast, under acidic conditions aromatic compounds are not well preserved due to attack by HO^+ and other radicals (Xiang and Lee 2000).

Among the oxidizing agents used for degradation of lignin into aromatic aldehydes, nitrobenzene is the oxidant that gives the highest yields, followed by oxygen (Araújo 2008). However, nitrobenzene is expensive and its reduction products are harmful and difficult to separate (Wu et al. 1993). This makes industrial scale up of this process more complex. Another unresolved problems in oxidation of lignins into aromatic aldehydes in high consumption of oxygen – over 10 mol per mol of obtained vanillin (Tarabanko and Petukhov 2003). These challenges with oxygen and nitrobenzene remain to be addressed and hence, hydrogen peroxide can be an important oxidant to tackle these challenges.

The differences in oxidative chemistries between oxidizing agents such as hydrogen peroxide, oxygen and nitrobenzene do not allow for a straightforward comparison as represented by the yields. The extent of oxidation for each of these mechanisms can be weighed based on the amount of carboxylic acids produced in this process. Peroxide treatment also improves the carboxylic acid groups on lignin thereby enhancing its hydrophilicity and facilitating its dissolution. Since carboxylic acids are formed as the end products of aromatic ring degradation, the extent of oxidation can be evaluated based on their yields (Ma et al. 2014; Xiang and Lee 2000).

Transition metals catalyze the decomposition of hydrogen peroxide into highly reactive radical species. Therefore, in order to utilize hydrogen peroxide and its corresponding anion on lignin and its model compound oxidation a sequestering agent is necessary. By using chelating agents, it is possible to use hydrogen peroxide at higher temperatures (Gellerstedt and Agnemo 1980). These conditions are also favorable for the reactions of non-phenolic lignin structures which are predominant in all different sources of lignin discussed above (Kadla and Chang 2001; Villar et al. 2001; Xiang and Lee 2000) and otherwise unreactive at conventional oxidation conditions.

6 Scope for future work

Vanillin, which is a high value-added product from oxidation of lignin is formed as a reaction intermediate, however, there is a scope to improve the yield of this product. A recent study showed that vanillin and vanillic acid were produced by hydrolysis in the absence of oxygen which started at 100 °C (Pacek et al. 2013). Vanillic acid was formed in this process without the presence of oxygen, suggesting that vanillic acid was not the oxidation product of vanillin. The yield of vanillin by hydrolysis in the absence of oxygen did not increase upon the addition of catalyst (Pacek et al. 2013). Based on this study, there is a scope to utilize hydrogen peroxide at lower temperatures to further develop the understanding of hydrolysis. The inclusion of molecular oxygen in combination with hydrogen peroxide has shown to improve the extent of lignin degradation (Kadla et al. 1999). The optimum combination of both these oxidizing agents for degradation of lignin is still under investigation.

Another factor that can impact vanillin yield is the characteristics of lignin molecule that is used as a feedstock for oxidation treatment. The understanding of lignin molecule should not be limited to mean molecular weight or ratio of lignin precursors but also details at the level of chemical structure which includes types and amounts of functional groups that deviate the purpose of oxidation of lignin molecule (Araújo 2008). Technical lignins are obtained as byproducts from various conventional pulping routes such as kraft and sulphite processes (Guadix-Montero and Sankar 2018). The differences in these processes causes technical lignins to have different structures and impurities. Compared to native lignins, technical lignins have more condensed structures resulting in higher C–C linkages. Native lignins, on the other hand, have a higher proportion of C–O inter-unit linkages. This undesired condensation reactions occur during delignification process and efforts are being made by researchers to minimize condensations. Successful methods to address condensation reactions are split into two main categories: (1) strategies that are focused on in situ trapping of the reactive intermediates to convert them into stable molecules and (2) strategies that are focused on directly stabilizing the β–O–4 ether linkages (either physically or chemically) (Lan and Luterbacher 2019). The use of phenolic compounds as additives during kraft pulping is also a promising approach to minimize condensation reactions. Addition of phenolic compounds such as 2, 4–xylenol during kraft pulping can reduce Kappa number by 13.9% (Jiang and Aksoy 2019). There are other factors such as molecular weight, polydispersity, moisture, ash content, homogeneity, certain functional groups that

should also be taken into account for valorization of technical lignins (Matsushita 2015; Vishtal and Kraslawski 2011). Biorefinery lignin which mainly consists of native lignin structures is an important feedstock to selectively utilize the uncondensed unit linkages for oxidation reactions. Lignosulfonates can produce higher yields phenolic aldehydes and acids due to the elimination of sulfonic group at C-α position under alkaline oxidative conditions. Due to the more severe conditions carried out in kraft pulping, the availability of reactive structures in non-condensed fraction is comparatively lower in kraft lignins (Pinto et al. 2013). Hence, selective sulfonation of kraft lignin at the C–α position is a critical parameter to evaluate for improving vanillin yield from kraft lignins. Also, the treatment of lignosulfonates with hydrogen peroxide has not been reported in various literatures and there is a scope for investigation (Agnemo and Gellerstedt 1979; Kadla et al. 1997; Kadla et al. 1999; Ma et al. 2014; Xiang and Lee 2000). The results and mechanisms discussed provide details on developing processes for production of the aromatic aldehydes from hydrogen peroxide oxidation of lignin. Under optimized process conditions, there is a scope to develop value-added products using hydrogen peroxide as an oxidant.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: The authors gratefully acknowledge the financial support provided by the Alabama Center for Paper and Bioresource Engineering.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

Agnemo, R. and Gellerstedt, G. (1979) The reactions of lignin with alkaline hydrogen peroxide. Part II. Factors influencing the decomposition of phenolic structures. Acta Chem. Scand. B33: 337–342.

Araujo, J.D.P. (2008). *Production of vanillin from lignin present in the Kraft black liquor of the pulp and paper industry*, Ph.D. thesis. Porto, Portugal, University of Porto.

Barkhau, R., Bastian, J., and Thompson, N. (1985). The reaction of model lignins with oxygen radicals. Tappi J. 68: 110.

Bjørsvik, H.R. and Minisci, F. (1999). Fine chemicals from lignosulfonates. 1. Synthesis of vanillin by oxidation of lignosulfonates. Org. Process Res. Dev. 3: 330–340.

Bozell, J.J., Hames, B.R., and Dimmel, D.R. (1995). Cobalt-Schiff base complex catalyzed oxidation of para-substituted phenolics. Preparation of benzoquinones. J. Org. Chem. 60: 2398–2404.

Bozell, J.J., Hoberg, J.O., and Dimmel, D.R. (1998). Catalytic oxidation of para-substituted phenols with nitrogen dioxide and oxygen. Tetrahedron Lett. 39: 2261–2264.

Calvo-Flores, F.G., Dobado, J.A., Isac-García, J., and Martín-Martínez, F.J. (2015). *Lignin and lignans as renewable raw materials: chemistry, technology and applications*. John Wiley & Sons, New York, United States.

Cole, J.L., Clark, P.A., and Solomon, E.I. (1990). Spectroscopic and chemical studies of the laccase trinuclear copper active site: geometric and electronic structure. J. Am. Chem. Soc. 112: 9534–9548.

Crestini, C., Saladino, R., Tagliatesta, P., and Boschi, T. (1999). Biomimetic degradation of lignin and lignin model compounds by synthetic anionic and cationic water soluble manganese and iron porphyrins. Bioorg. Med. Chem. 7: 1897–1905.

Fache, M., Boutevin, B., and Caillol, S. (2016). Vanillin production from lignin and its use as a renewable chemical. ACS Sustain. Chem. Eng. 4: 35–46.

Gellerstedt, G. and Agnemo, R. (1980). The reactions of lignin with alkaline hydrogen peroxide. Part III. The oxidation of conjugated carbonyl structures. Acta Chem. Scand. B34: 275–280.

Genin, H.S., Lawler, K.A., Hoffmann, R., Herrmann, W.A., Fischer, R.W., and Scherer, W. (1995). Multiple bonds between main-group elements and transition metals. 138. Polymeric methyltrioxorhenium: some models for its electronic structure. J. Am. Chem. Soc. 117: 3244–3252.

Gierer, J. (1997). Formation and involvement of superoxide (O2·/HO2·) and hydroxyl (OH·) radicals in TCF bleaching processes: a review. Holzforschung 51: 34–46.

Guadix-Montero, S. and Sankar, M. (2018). Review on catalytic cleavage of C–C inter-unit linkages in lignin model compounds: towards lignin depolymerisation. Top. Catal. 61: 183–198.

He, W., Gao, W., and Fatehi, P. (2017). Oxidation of kraft lignin with hydrogen peroxide and its application as a dispersant for kaolin suspensions. ACS Sustain. Chem. Eng. 5: 10597–10605.

Herrmann, W.A. and Fischer, R.W. (1995). Multiple bonds between main-group elements and transition metals. 136. "Polymerization" of an organometal oxide: the unusual behavior of methyltrioxorhenium (VII) in water. J. Am. Chem. Soc. 117: 3223–3230.

Hocking, M.B. and Crow, J.P. (1994). On the mechanism of alkaline hydrogen peroxide oxidation of the lignin model *p*-hydroxyacetophenone. Can. J. Chem. 72: 1137–1142.

Hu, T.Q. (2002). *Chemical modification, properties, and usage of lignin*. Kluwer Academic/Plenum Publisher, New York.

Huang, J., Fu, S., and Gan, L. (2019). Structure and characteristics of lignin. In: *Lignin chemistry and applications*. Elsevier, Cambridge, MA, USA, pp. 25–50.

Jiang, Z. and Aksoy, B. (2019). Phenols as additives in kraft pulping, US patent application no. 20190112757A1, pp. 2–7.

Johnson, D., Park, S., Genco, J., Gibson, A., Wajer, M., and Branch, B. (2002). Hydrogen peroxide bleaching of TMP pulps using $Mg(OH)_2$. In: *TAPPI pulping conference proceedings*, TAPPI fall conference and trade fair. TAPPI, Atlanta, GA, USA.

Kadla, J., Chang, H., and Jameel, H. (1999). The reactions of lignins with hydrogen peroxide at high temperature. Part 2. The oxidation of kraft lignin. Holzforschung 53: 277–284.

Kadla, J.F. and Chang, H. (2001). *The reactions of peroxides with lignin and lignin model compounds*. ACS Publications, Columbia, DC, USA.

Kadla, J.F., Chang, H.-M., and Jameel, H. (1997). The reactions of lignins with hydrogen peroxide at high temperature. Part I. The

oxidation of lignin model compounds. Holzforschung 51: 428–434.

Kirk-Othmer. (2005). *Encyclopedia of chemical technology*. John Wiley & Sons, New York.

Kläning, U.K., Sehested, K., and Holcman, J. (1985). Standard Gibbs energy of formation of the hydroxyl radical in aqueous solution. Rate constants for the reaction $ClO_2^- + O_3 \rightleftharpoons O_3^- + ClO_2$. J. Phys. Chem. 89: 760–763.

Lan, W. and Luterbacher, J.S. (2019). Preventing lignin condensation to facilitate aromatic monomer production. CHIMIA Int. J. Chem. 73: 591–598.

Lange, H., Decina, S., and Crestini, C. (2013). Oxidative upgrade of lignin – recent routes reviewed. Eur. Polym. J. 49: 1151–1173.

Ludmila, H., Michal, J., Andrea, S., and Ales, H. (2015). Lignin, potential products and their market value. Wood Res. 60: 973–986.

Ma, R., Guo, M., and Zhang, X. (2014). Selective conversion of biorefinery lignin into dicarboxylic acids. ChemSusChem 7: 412–415.

Ma, R., Xu, Y., and Zhang, X. (2015). Catalytic oxidation of biorefinery lignin to value-added chemicals to support sustainable biofuel production. ChemSusChem 8: 24–51.

Ma, R., Zhang, X., Wang, Y., and Zhang, X. (2018). New insights toward quantitative relationships between lignin reactivity to monomers and their structural characteristics. ChemSusChem 11: 2146–2155.

Mathias, A. and Rodrigues, A. (1995). Production of vanillin by oxidation of pine kraft lignins with oxygen. Holzforschung 49: 273–278.

Matsushita, Y. (2015). Conversion of technical lignins to functional materials with retained polymeric properties. J. Wood Sci. 61: 230–250.

Moodley, B., Mulholland, D., and Brookes, H. (2012). The chemical oxidation of lignin found in Sappi Saiccor dissolving pulp mill effluent. Water SA 38: 1–8.

Ni, Y., Van Heiningen, A., and Kubes, G. (1993). Mechanism of formation of chloro-organics during chlorine dioxide prebleaching of kraft pulp. Nord. Pulp. Pap. Res. J. 8: 350–351.

Nunn, T.R., Howard, J.B., Longwell, J.P., and Peters, W.A. (1985). Product compositions and kinetics in the rapid pyrolysis of milled wood lignin. Ind. Eng. Chem. Process Des. Dev. 24: 844–852.

Ouyang, X.-P., Tan, Y.-D., and Qiu, X.-Q. (2014). Oxidative degradation of lignin for producing monophenolic compounds. J. Fuel Chem. Technol. 42: 677–682.

Pacek, A.W., Ding, P., Garrett, M., Sheldrake, G., and Nienow, A.W. (2013). Catalytic conversion of sodium lignosulfonate to vanillin: engineering aspects. Part 1. Effects of processing conditions on vanillin yield and selectivity. Ind. Eng. Chem. Res. 52: 8361–8372.

Pinto, P.C.R., da Silva, E.A.B., and Rodrigues, A.E. (2012). Lignin as source of fine chemicals: vanillin and syringaldehyde. In: Baskar, C., Baskar, S., and Dhillon, R.D. (Eds.). *Biomass conversion*. Springer, London, pp. 381–420.

Pinto, P.C.R., Costa, C.E., and Rodrigues, A.E. (2013). Oxidation of lignin from Eucalyptus globulus pulping liquors to produce syringaldehyde and vanillin. Ind. Eng. Chem. Res. 52: 4421–4428.

Ralph, J., Schatz, P.F., Lu, F., Kim, H., Akiyama, T., and Nelsen, S.F. (2009). Quinone methides in lignification. In: Rokita, S. (Ed.). *Quinone methides*. Wiley-Blackwell, Hoboken, NJ, pp. 385–420.

Rinaldi, R., Jastrzebski, R., Clough, M.T., Ralph, J., Kennema, M., Bruijnincx, P.C., and Weckhuysen, B.M. (2016). Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis. Angew. Chem. Int. Ed. 55: 8164–8215.

Rodrigues Pinto, P.C., Borges da Silva, E.A., and Rodrigues, A.E. (2011). Insights into oxidative conversion of lignin to high-added-value phenolic aldehydes. Ind. Eng. Chem. Res. 50: 741–748.

Sakakibara, A. (1980). A structural model of softwood lignin. Wood Sci. Technol. 14: 89–100.

Santos, S.G., Marques, A.P., Lima, D.L., Evtuguin, D.V., and Esteves, V.I. (2011). Kinetics of eucalypt lignosulfonate oxidation to aromatic aldehydes by oxygen in alkaline medium. Ind. Eng. Chem. Res. 50: 291–298.

Schwarz, H. and Dodson, R. (1984). Equilibrium between hydroxyl radicals and thallium (II) and the oxidation potential of hydroxyl (aq). J. Phys. Chem. 88: 3643–3647.

Sharma, P., Jha, A.B., Dubey, R.S., and Pessarakli, M. (2012). Reactive oxygen species, oxidative damage, and anti-oxidative defense mechanism in plants under stressful conditions. J. Bot. 2012: 1–26.

Smith, B., Rice, R., and Ince, P. (2000). Pulp capacity in the United States. General technical report FPL-GTR-139, USDA Forest Service.

Solomon, E.I. and Lowery, M.D. (1993). Electronic structure contributions to function in bioinorganic chemistry. Science 259: 1575–1581.

Tarabanko, V.E. and Petukhov, D. (2003). Study of mechanism and improvement of the process of oxidative cleavage of lignins into the aromatic aldehydes. Chem. Sustain. Dev. 11: 655–667.

Tarabanko, V.E. and Tarabanko, N. (2017). Catalytic oxidation of lignins into the aromatic aldehydes: general process trends and development prospects. Int. J. Mol. Sci. 18: 2421.

Tarabanko, V.E., Koropatchinskaya, N.V., Kudryashev, A.V., and Kuznetsov, B.N. (1995). Influence of lignin origin on the efficiency of the catalytic oxidation of lignin into vanillin and syringaldehyde. Russ. Chem. Bull. 44: 367–371.

Villar, J., Caperos, A., and García-Ochoa, F. (1997). Oxidation of hardwood kraft-lignin to phenolic derivatives. Nitrobenzene and copper oxide as oxidants. J. Wood Chem. Technol. 17: 259–285.

Villar, J., Caperos, A., and García-Ochoa, F. (2001). Oxidation of hardwood kraft-lignin to phenolic derivatives with oxygen as oxidant. Wood Sci. Technol. 35: 245–255.

Vishtal, A.G. and Kraslawski, A. (2011). Challenges in industrial applications of technical lignins. BioResources. 6: 3547–3568.

Werpy, T. and Petersen, G. (2004). *Top value added chemicals from biomass: volume I-results of screening for potential candidates from sugars and synthesis gas*. National Renewable Energy Lab, Golden, CO, USA.

Wettstein, S.G., Alonso, D.M., Gürbüz, E.I., and Dumesic, J.A. (2012). A roadmap for conversion of lignocellulosic biomass to chemicals and fuels. Curr. Opin. Chem. Eng. 1: 218–224.

Wu, G., Heitz, M., and Chornet, E. (1993). The depolymerization of lignin via aqueous alkaline oxidation. In: Bridgewater, A.V. (Ed.).

Advances in thermochemical biomass conversion. Springer, Cham, Switzerland, pp. 1558–1571.

Xiang, Q. and Lee, Y. (2000). Oxidative cracking of precipitated hardwood lignin by hydrogen peroxide. Appl. Biochem. Biotechnol. 84: 153–162.

Zakzeski, J., Bruijnincx, P.C., Jongerius, A.L., and Weckhuysen, B.M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. Chem. Rev. 110: 3552–3599.

Zeronian, S. and Inglesby, M.K. (1995). Bleaching of cellulose by hydrogen peroxide. Cellulose 2: 265–272.

Zhang, X., Tu, M., and Paice, M.G. (2011). Routes to potential bioproducts from lignocellulosic biomass lignin and hemicelluloses. Bioenerg. Res. 4: 246–257.