

FORMATION OF VANILLIN AND SYRINGALDEHYDE IN AN OXYGEN DELIGNIFICATION PROCESS

Zhaojiang Wong, Kefu Chen, and Jun Li *

The formation of vanillin and syringaldehyde during an oxygen delignification process was evaluated. The cleavage of conjugated C_α-C_β bonds in phenolic lignin caused by the attack of oxygen leads to the formation of aromatic aldehydes and ketones. The formation mechanism was confirmed by the organic compounds identified in the spent liquor by GC/MS. Additionally, the formation of aromatic aldehydes and ketones of hardwood, softwood, and grass was investigated. The results showed that the formed aromatic aldehydes and ketones were related to the units of lignin structure. Among the aromatic aldehydes and ketones present in the spent liquor from oxygen delignification, vanillin and syringaldehyde are of high content, making the spent liquor a potential resource for vanillin and syringaldehyde production.

Key words: Formation; Oxygen delignification; Syringaldehyde; Vanillin

*Contact information: State Key Laboratory of Pulp & Paper Engineering South China University of Technology, Tianhe District, Guangzhou City, China. Post code: 510640. *Corresponding author: June_Lee@yea.net*

INTRODUCTION

Vanillin and syringaldehyde are widely used aromatic molecules in the food, pharmaceutical, and cosmetic industries. At present, there are two commercial ways to carry out synthetic vanillin and syringaldehyde production, i.e. synthesis based on either petroleum-derived compounds or biomass. It is reported that up to 85% of the production is highly dependent on petroleum-derived compounds (Sales *et al.* 2004; Cortez and Roberto 2010; Xiang and Lee 2001). Stimulated by an awareness of energy and resources shortages, the concept of a biorefinery has attracted much attention and gained great popularity. Statistics show that about 15% of the vanillin and syringaldehyde is synthesized from biomass, mainly from lignin oxidation (Sinha *et al.* 2008). The oxidation of lignin is carried out under the conditions of high pH values, high temperatures, and high oxygen pressure (Hocking, 1997). Hence, the lignin route requires great energy and consumption of chemicals. Furthermore, under these oxidation conditions, cleavage of large complex lignin molecules occurs, thus creating a complex medium containing not only the desired vanillin and syringaldehyde but also some other oxidation products such as acetovanillone, dehydrodivanillin, guaiacol, p-hydroxybenzaldehyde, and aromatic acids (Marthias 1995).

Oxygen delignification is an environmentally benign bleaching technology (Zhan *et al.* 2008; Yin and Lin 2008; Puitel *et al.* 2007). The process involves an oxidation reaction between the residual lignin in unbleached pulp and oxygen under alkaline

conditions. The reactions between oxygen and the residual lignin involve initial electrophilic attack by oxygen-containing radical species ($O_2\cdot$, $HOO\cdot$, $HO\cdot$, O_2), in which these oxygen-containing radical species open rings and cleave side-chains of lignin, giving a complex mixture of small oxygenated molecules. Therefore, the functional groups of these oxygenated molecules often include aldehyde, ketone, and phenol (Gierer 1986). Realizing that the mechanisms of oxygen delignification are exactly the same as those used in vanillin and syringaldehyde production from wood, an attempt was made, based on determination of components from oxygen delignification spent liquor, to find an alternative resource for vanillin and syringaldehyde production.

Fundamental studies on oxygen delignification have been carried out systematically, in particular by Gellerstedt et al. (1999) and Gierer (1997). However, investigations on the formation of vanillin and syringaldehyde during the oxygen delignification process are still limited, especially with respect to information about byproduct formation. Therefore, in the present work, the mechanism of vanillin and syringaldehyde formation in oxygen delignification process is introduced. Based on the mechanism, vanillin and syringaldehyde were identified from the spent liquor from oxygen delignification.

EXPERIMENTAL

Materials and Chemicals

Pine, eucalyptus, and wheat straw pulps were used as the raw material for oxygen delignification. The characteristics of the pulp before and after oxygen delignification are listed in Table 1. After the oxygen delignification, the spent liquor was squeezed out of the pulp, filtered to remove all small particles, diluted five times, and then cooled down before the GC/MS analysis.

Table 1. Conditions for Oxygen Delignification and Characteristics of the Pulps

	Before oxygen delignification		Conditions of oxygen delignification				After oxygen delignification	
	Kappa	Klason Lignin %	Alkali Charge (%)	Oxygen Pressure (MPa)	Temperature (°C)	Time (min)	Kappa	Klason Lignin %
pine	34.9	3.99	6	0.7	100	60	11.5	0.22
eucalyptus	23.7	1.98	4	0.7	100	60	12.3	0.16
wheat straw	17.5	2.08	4	0.6	100	60	6.9	0.22

Chromatographically pure guaiacol, p-hydroxybenzaldehyde, vanillin, and syringaldehyde were commercially prepared and used as standard references for quantitative analysis. They were all purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd.

Analytical Methods

Identification of organic compounds in oxygen delignification spent liquor was conducted with an Agilent 7890 GC gas chromatography device equipped with an Agilent 5975C inert MSD. The organics extracted from the oxygen delignification spent liquor using dichloromethane as solvent at pH 2.0 were carefully concentrated, filtered through a 0.42 μ m membrane, and then injected into the GC. A capillary column DB-5 was used. The temperature program used in GC/MS analysis was as follows: 40 °C for 4 min, 5 °C \cdot min⁻¹ to 280 °C for 10min. The MS analysis was carried out with ionization of electronic impact (70eV), and the spectrum was recorded within an interval of 35 to 200amu. Compounds were identified by comparing their spectrum with those available in the NIST 2.0 libraries. Commercially prepared guaiacol, p-hydroxybenzaldehyde, vanillin, and syring- aldehyde were used as standard references for quantitative analysis.

RESULTS AND DISCUSSION

Oxygen Delignification and Aromatic Aldehyde/ketone Formation

As we know, lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 Da. It is incorporated structurally in the form of the phenyl propane units, i.e. p-hydroxyphenyl (H), guaiacyl (G), and syringal (S) (Fig.1). It has been shown that the monocotyledonous lignin is a mixture of these three lignin units, while many grasses have mostly G and S (Boerjan *et al.* 2003). In the pulp and paper industry, oxygen delignification is a chemical process resulting in partial or total removal of the residual lignin from unbleached pulps by the action of oxygen under alkaline conditions at high temperature. It is generally believed that the main reaction of oxygen-alkali bleaching is oxidation, with the residual lignin being degraded to become hydrophilic and transferred into spent liquor by solubilization.

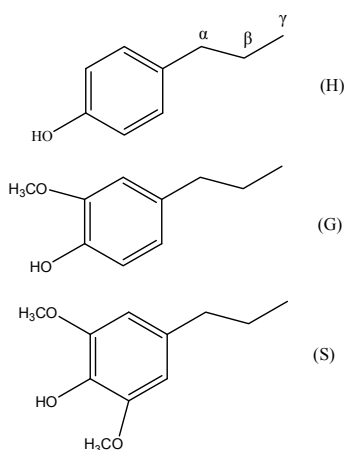


Fig. 1. Common units of lignin: p-hydroxyphenyl (H), guaiacyl (G), and syringal (S)

According to the studies of Gierer (1986) and Kratzl *et al.* (1974), the steps of oxygen delignification begin with the autoxidation of the ring-conjugated structure of

phenolic lignin unit, i.e. conversion into a phenoxy radical and addition of the oxidant to the mesomeric form of the radical (Fig. 2, Scheme I). The immediate addition product is a peroxy radical, which abstracts a further electron from phenolate ions and becomes converted into a peroxide anion. The peroxide anion attacks a vinylogous carbon in the quinone methide intermediates in an intramolecular nucleophilic reaction, giving rise to four-membered cyclic peroxides (1,2-dioxetanes) (Fig. 2, Scheme II). The final rearrangement results in fragmentation by cleavage of the C_{α} - C_{β} bond, forming the chemical structures of aromatic aldehyde and ketone (Eckerk 1973). Given the variety of $-R_1$, $-R_2$, and $-R_3$ substituents on the phenolic lignin unit, there are six kinds of possible aromatic aldehydes/ketenes to be formed, i.e. p-hydroxybenzaldehyde, vanillin, syringaldehyde, p-hydroxyacetophenone, aceto- vanillone, and acetosyringone.

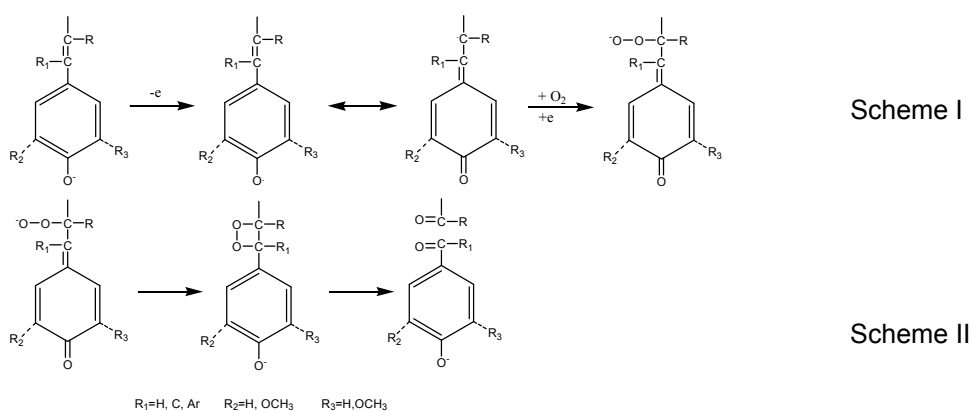


Fig. 2. Pathway of aldehyde/ketone formation, adopted from Gierer (1986). Scheme I: alkaline autoxidation of phenolic unit to give hydroperoxide intermediate; Scheme II: intramolecular nucleophilic attack by peroxide anions to give aromatic aldehyde/ketene, via dioxetane intermediate

Chemical Composition of Oxygen Delignification Spent Liquor

To confirm the mechanism of aromatic aldehyde/ketene formation mentioned above, the organics in the oxygen delignification spent liquor were extracted using dichloromethane as solvent, and then the contents were determined by GC/MS analysis. The total ion chromatogram of GC/MS and the identified organics are shown in Fig. 3 and Table 2, respectively.

As the results in Table 2 show, besides the six kinds of the aromatic aldehyde/ketene oxidation products, some undesired byproducts were also found in the spent liquor. These byproducts can be divided into three categories according to the reaction pathway of their formation. First, lactone and cyclopentenone derivatives (i.e. butyrolactone; 2-cyclopenten-1-one, 2-hydroxy-3-methyl-; 2,5-furandione, 3,4-dimethyl-; and 3-ethyl-2-hydroxy-2-cyclopentenone) are the oxidation products formed when the oxygen attacks the reactive centre of aromatic nuclei of the lignin unit (Gierer 1986). Second, guaiacol and syringol are the degraded products of the nucleophilic attack to C_{α} which is bonded in the form of an ether linkage in the propane side chain of the phenolic

lignin unit. Third, isovanillic acid and syringic acid may be further oxidation products of vanillin and syringaldehyde, respectively, or may be produced from different routes.

Based on the results described above, it appears that spent liquor from oxygen delignification is quite suitable for vanillin and syringaldehyde production. Otherwise, taking ozone delignification and chlorine dioxide delignification as examples, the majority of the desired vanillin and syringaldehyde would be oxidized further into isovanillic acid and syringic acid due to the relatively higher oxidation capacity of the oxidants (Kreetachat *et al.* 2007). In addition, the contents of p-hydroxybenzaldehyde and p-hydroxyacetophenone were really low in the oxygen delignification spent liquor, which indicates that the raw material (i.e. wheat straw) contained mostly G and S lignin units. In other words, the spent liquor from oxygen delignification of wheat straw pulp is very well suited for vanillin and syringaldehyde production. Calculated from the area percent of chromatography by assuming the response of all the identified organics are identical, the undesired lactone, cyclopentenone derivatives, and aromatic ketones, as well as other impurities, were all of low content compared with the two desired aromatic aldehydes, which accounted for up to 56% of the entire extracted organics.

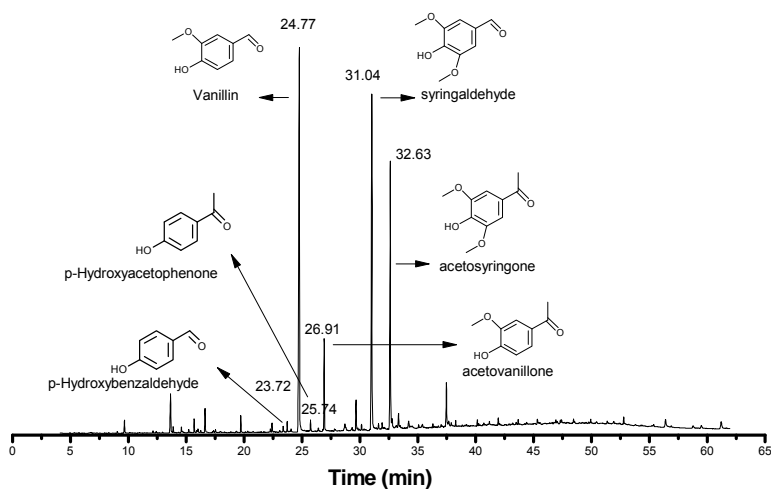


Fig. 3. Total ion chromatogram of organic compounds in oxygen delignification spent liquor

Aromatic Aldehyde/ketone Formation of Softwood, Hardwood and Grasses Pulp

As discussed above, lignin is comprised of phenyl propane units, i.e. p-hydroxyphenyl (H), guaiacyl (G), and syringal (S). Gymnosperms have a lignin comprised almost entirely of G units with small quantities of H units. That of dicotyledonous angiosperms is more often than not a mixture of G and S (with very little H), and monocotyledonous lignin is a mixture of all three. To provide a general idea of the aromatic aldehyde/ketones in oxygen delignification spent liquor of softwood, hardwood, and grass, pine, eucalyptus and wheat straw pulps were used as raw materials for oxygen delignification. The aromatic aldehyde/ketones in oxygen delignification spent liquor were identified by GC/MS, and the results are listed in Table 3. Among the six formed aromatic aldehyde/ketones listed in Table 3, the concentrations of vanillin and

acetovanillone of pine were much higher than the other four, which is consistent with our expectation that the guaiacyl (G) was the major unit of pine lignin structure. For eucalyptus and wheat straw, the concentrations of vanillin, acetovanillone, syringaldehyde, and acetosyringone were close to each other, but the concentrations of p-hydroxyacetophenone and p-hydroxybenzaldehyde are much lower, consistent with the fact that the lignin of softwood and grass is a mixture of guaiacyl (G) and syringal (S) with little of p-hydroxyphenyl (H).

Table 2. Organic Components in Oxygen Delignification Spent Liquor Determined by GC/MS

Time (min)	Area percent (%)	Name	Conc.(mg/L)
9.66	0.70	Butyrolactone	*
13.65	2.46	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	*
13.87	0.28	2,5-Furandione, 3,4-dimethyl-	*
15.69	0.65	Guaiacol	0.09
16.64	1.18	3-ethyl-2-hydroxy-2-cyclopentenone	*
22.42	0.47	Vinylguaiacol	0.10
23.38	0.32	Syringol	0.04
23.72	0.51	p-Hydroxybenzaldehyde	0.30
24.77	30.64	Vanillin	21.49
25.74	0.56	p-Hydroxyacetophenone	3.90
26.95	4.67	Acetovanillone	2.77
28.72	0.18	Isovanillic acid	*
31.04	26.05	Syringaldehyde	19.85
32.63	17.60	Acetosyringone	13.41
34.21	0.56	Syringic acid	*

* Not measured

The yields listed in Table 3 were low, less than 10%, which indicates that the formation of the aromatic aldehyde/ketones was due to minor reactions during oxygen oxidation of lignin. The low yield can be explained by the following fact that we described earlier: The aldehyde/ketones are certainly produced by oxygen oxidation of phenolic lignin units with ring conjugated double bonds at the side chains. But these origins are not involving the major substructures in residual lignin of the pulp, and furthermore, the aromatic ring opening reaction is competitive with the production of aldehydes even in these origins, making the yield of aromatic aldehyde/ketones lower.

Table 3. Formation and Yields of Aldehyde/Ketones in Oxygen Delignification

	Pine		Eucalyptus pulp		Wheat straw pulp	
	Conc.(mg/L)	Yield (%)	Conc.(mg/L)	Yield (%)	Conc.(mg/L)	Yield (%)
p-Hydroxy-acetophenone	7.41	0.96%	0.03	0.01%	3.90	1.03%
p-Hydroxybenz-aldehyde	2.49	0.32%	2.43	0.65%	0.30	0.08%
Vanillin	67.68	8.80%	17.16	4.62%	21.49	5.66%
Acetovanillone	49.14	6.39%	9.72	2.62%	2.77	0.73%
Syringaldehyde	5.55	0.72%	29.17	7.85%	19.85	5.23%
Acetosyringone	3.47	0.45%	15.58	4.20%	13.41	3.53%

CONCLUSIONS

In the present work, the formation of aromatic aldehyde and ketone during an oxygen delignification process was studied. It was observed that the cleavage of the conjugated C α -C β bond in phenolic lignin caused by the attack of oxygen in alkaline condition would result in the formation of aromatic aldehydes and ketones.

GC/MS was applied to determine the organic components in spent liquor from oxygen delignification. Six kinds of aromatic aldehydes or ketones (vanillin, p-hydroxybenzaldehyde, syringaldehyde, p-hydroxyacetophenone, acetovanillone, and acetosyringone) were identified in the oxygen delignification spent liquor. The high content of vanillin and syringaldehyde makes oxygen delignification spent liquor a possible resource for vanillin and syringaldehyde production.

The formation of aromatic aldehyde and ketone in oxygen delignification process varies depending on the raw materials. The pulps of pine, eucalyptus, and wheat straw were used as raw materials, and the results were consistent with expectations that the lignin of pine mainly consists of guaiacyl (G) units, while the lignin of eucalyptus and wheat straw was a mixture of guaiacyl (G) and syringyl (S) units with little of p-hydroxyphenyl (H).

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