Influence of lignin origin on the efficiency of the catalytic oxidation of lignin into vanillin and syringaldehyde

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The oxidation of a number of lignin species by molecular oxygen was studied. The selectivity of the process was found to be close to that of the oxidation with nitrobenzene. The influence of lignin origin on the yields of vanillin and syringaldehyde as well as the correlation between the rates of wood delignification and the aldehydes formation are discussed.

Key words: vanillin; syringaldehyde; lignin, lignosulfonates, oxidation, catalysts.

Oxidation of wood lignin provides a means for producting considerable amounts of aromatic aldehydes. Vanillin is formed from coniferous lignins, whereas foliate lignins afford vanillin together with syringaldehyde.

The aldehyde ratio is determined mainly by the composition of the raw material. The yield of aldehydes depends on lignin origin, as well as on the conditions of the production or pretreatment and oxidation of lignin (Tables 1 and 2).[1—11]

Nitrobenzene is commonly known as the most selective oxidant for lignin (alkaline medium, 160—170 °C).

Table 1. Oxidation of lignins of different origin into vanillin (V) and syringaldehyde (SA) by nitrobenzene

Lignin sample	Yield (wt. % of lignin used)		Ref.
	V	SA	
Abies wood	24.3	—	1
Abies Alba			
Norwegian fir-tree wood	27.5	0.06	3
Picea abies			
White fir-tree wood	20.1	—	4
Picea glauca voss			
Asp wood	12.9	30.7	4
Populus tremuloides Mishk			
Birch wood	12	35	5
Betula verrucosa			
Maple wood	3.5	32	6
Acer platanoides	13	37	7
Ethanol-lignin*	6.7	17.0	8
Sulfate lignin	13.1	0.6	8
from conifers			
Sulfate lignin	5.3	7.9	8
of foliates			
Sulfite lignin	16.5	C	8
of conifers	19.7	—	1
Sulfite lignin	6.1	10.1	8
of foliates			
Caramel from	8.00**	—	9
prehydrolysis			
Lignin from fir brown rot	13.9	—	10
Klason lignin	1.5	—	11

* Obtained by treatment of wood with 0.012 *M* HCl in 50 % aqueous ethanol at 156 °C [8].
** Based on substrate being oxidized.

Table 2. Yield of vanillin (V) in the oxidation of lignins of different origin by molecular oxygen

Lignin sample	Oxidant, catalyst (notes)	Yield of V (% of lignin used)	Ref.
Fir-tree wood (28 % lignin)	Air, without catalyst	11.4	13
Fir-tree wood	Air, 10% Cu(OH)$_2$ based on wood used	18.9	13
Fir-tree wood	Air, 10 % MnO$_2$ based on wood used	18.2	13
Asp wood	Oxygen, CuO, flow-type apparatus	36*	14
Lignosulfonates	Air, without catalyst (Sjas' paper and pulp mill)	5—7	2,15
Lignosulfonates	Air, Cu catalyst (Monsanto)	10	16
Lignosulfonates	Oxygen, Co(OH)$_3$, Mn$_3$O$_4$	12.5	1
Lignosulfonates	Oxygen, Cu(SO$_4$)$_2$	15.5	1,15

* The total yield of vanillin and syringaldehyde.

Native lignins of foliates provide higher total yields of aldehydes (42—50 %) than do lignins of conifers (20—27 %). This fact can be connected with the known tendency of the guaiacyl fragments of coniferous lignins to undergo condensation at the unsubstituted position 5 of the aromatic ring.[3,12] The condensation processes in the pretreatment stage can, apparently, also be the cause of the lower yield of aldehydes from technical lignins.

Among the other selective oxidants for lignins the oxides and hydroxides of the transition metals, Co^{III}, Ag^{I}, Mn^{IV}, Hg^{II}, and especially Cu^{II}, should be noted. In the latter case the selectivity is close to that of oxidation with nitrobenzene.[1,4] But the difficulties in Cu^{II} recovery prevent the wide use of this reagent.[13]

Although the most preferable technologically, oxidation with molecular oxygen is, in general, less selective. The selectivity of the process and the yield of the aldehydes can be made 1.5—2 times greater by use of a catalyst (see Table 2, Refs. 1,2 and 13—16). In general, in the case of catalytic oxidation with oxygen the yield of aldehydes is somewhat lower than that of oxidation with nitrobenzene. Even when a catalyst is used, the contribution of low-selective non-catalytic radical autooxidation by oxygen is fairly high. The variations in the yields of vanillin can partly be explained by this fact.

In this paper, we report a study of the use of molecular oxygen for the alkaline oxidation of pine wood that has been deeply affected by brown mold[17] under natural conditions. This method of wood oxidation is not only of theoretical but also of practical interest. First, an analogous substrate, *i.e.*, lignin from enzymatic wood hydrolysis, is a by-product of a promising method of wood processing.[18] Second, the supply of putrescent wood is fairly rich. And finally, the lignins from enzymatic wood conversion are quite close to the native ones in their structure and, therefore, their oxidation may afford vanillin and syringaldehyde in high yields. The oxidation of molds fir wood affected by brown mold using nitrobenzene has been studied earlier,[10] but oxidation of the analogous substrates with oxygen has not yet been reported.

In order to make a correct comparison of the efficiency of the oxidation of lignins of different origin, the oxidation of pine and asp wood, as well that of the lignosulfonates from some Russian paper and pulp mills (PPMs) were studied in the present work along with the oxidation of pine rot.

Experimental

Brown pine trunks, that had rottet under natural conditions, had retained a visible structure of the initial wood, and could easily have been kneaded into dust, were used. The lignin content of the dry rot was equal to 66 wt. % (determined by the sulfuric acid method).

Solid substrates, *i.e.*, rot and asp and pine wood, were crushed prior to loading, and the $d < 0.1$ mm fraction was used. The distillery grain concentrate (the fermented sulfite liquor) was used without any further treatment. The distillery grain concentrate from the Svetlogorsk paper and pulp mill

was treated with an alkali solution with heating to remove the ammonia.

In order to prepare the reaction mixture (60 mL), a reactor was successively loaded (with stirring) with a concentrate of lignosulfonates (or with wood dust), the catalyst ($Cu(OH)_2$, $CuSO_4 \times 5H_2O$ or the Monsanto Cu catalyst), water, and 50 % aqueous alkali solution. The oxidation of the substrate was carried out in a rocking steel 12×18H10T reactor with a volume of 80 mL.

Samples of the oxidized reaction mixture (3—4 g) were acidified with 30 % aqueous H_2SO_4 to pH 3. The resultant specimens were extracted three times with equal portions of chloroform (20 mL). The combined extract was evaporated to dryness on a rotary vaporizer, and the residue was dissolved in chloroform (1 mL) containing 1 mg mL^{-1} of naphthalene as the internal standard. The vanillin and syringaldehyde contents of the samples were determined by GLC on a Biokhrom-2 chromatograph (20 m×0.25 mm SE-30 column, isotherm at 120 °C for 2 min, temperature programming at the rate of 8 deg/min from 120 to 160 °C and again isotherm at 160 °C for 4 min; FID).

Results and Discussion

The method used enabled us to obtain the kinetic curves of aldehyde accumulation and oxygen absorption during the oxidation of a substrate. As can be seen from Fig. 1, the kinetic curve of vanillin accumulation during the oxidation of pine rot has a shoulder and a maximum. The shape of the curve can be explained by the existence of two forms of lignin with different reactivities toward oxidation. The presence of the shoulder is apparently connected with the consumption of a "quick lignin" followed by the kinetic manifestation of a "slow lignin". Such an approach has been successfully used earlier for
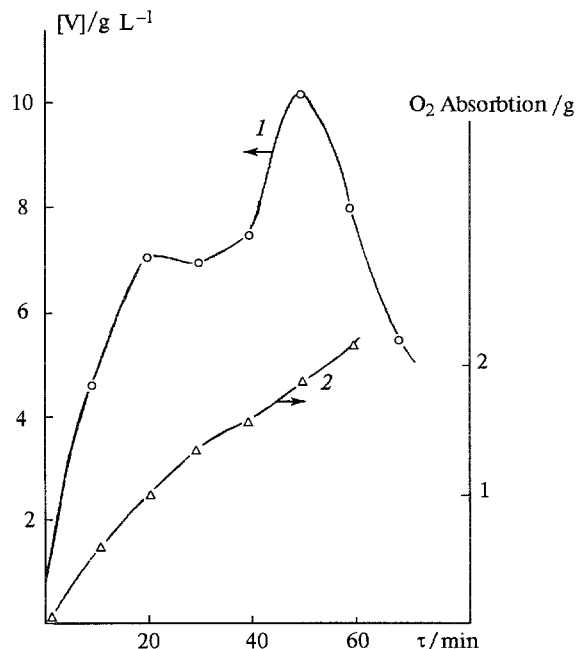

Fig. 1. Time dependence of the vanillin concentration ([V]) (*1*) and the volume of oxygen consumed (*2*) during the catalytic oxidation of pine rot.

Table 3. Effect of the conditions of pine rot oxidation on the formation of vanillin (V)

Substrate concentration /g L^{-1}	Catalyst concentration /g L^{-1}	Shoulder appearance time /min	Time /min	Parameters of maximum		
				[B] /g L^{-1}	O_2 consumption /g L^{-1}	Yield of V (wt. % on lignin)
9.1	—	10	30	5.3	0.34	8.8
9.1	3.8	10	20	11.8	0.22	19.8
9.1	1.9	10	35	6.6	0.45	11.4
9.1	5.7	10	30	6.3	0.53	11.0
11.8	3.9	15	50	8.8	0.65	11.5
14.3	3.6	20	50	10.3	0.39	10.8
16.7	3.7	30	>60*	14.9	0.44	13.0

Note. Oxidation conditions: 160 °C, 0.9 MPa, O_2 as the oxidant, 20 % NaOH, 75 % filling of a reactor, $Cu(OH)_2$ as the catalyst. *Maximum is not achieved.

Table 4. Effect of substrate origin on the yield of vanillin (V) and syringaldehyde (SA) in the oxidation of lignins

Entry	Substrate	Substrate concentration /g L^{-1}	Catalyst concentration /g L^{-1}	Parameters of maximum		
				$Time_{max}$ /min	[B] /g L^{-1}	Yield of V (wt.% on lignin)
1	Pine wood	70	—	15	2.5	12.8
2	Pine wood	70	4.1	20	4.5	23.1
3	Asp wood	91	0.25*	30	1.3	21.0**
4	Asp wood	91	—	30	0.95	12.5**
5	Lye from Sjas' PPM	173	6.2	15	16.2	14.4
6	Lye from Sveto-gorsk PPM	173	9.1	40	10.5	9.3
7	Lye from Sveto-gorsk PPM	260	—	30	5.8	3.4
8	Birch brown rot	70	—	3	2.3	14.9**

Note. Oxidation conditions: 0.9 MPa, 160 °C, O_2 as the oxidant, NaOH concentration of 200 and 120 g L^{-1} for the entries 1—4 and 5—8, respectively. Lignin content of the lyes was assumed t be 65 wt. %; lignin content of birch brown rot was equal to 75 wt. % (determined by the sulfuric acid method).

* Anthraquinone as the catalyst. ** Overall yield of V and SA.

the description of the kinetics of wood delignification.[19—21] In the process of lignosulfonate oxidaion, the shoulder on the kinetic curve is slightly expressed. In the oxidation of asp wood, the shoulder was not detected at all due to the high reaction rates.

The time of the appearance of the shoulder and the maximum on the kinetic curve increases with the concentration of pine rot (Table 3). This must be connected with the diffusional limitations on the rate of oxidation. The uptake of oxygen during the oxidation of pine rot is equal to 22—50 wt. % based on the substrate used.

Similar results of oxygen consumption during the oxidation of lignosulfonates into vanillin have been obtained earlier.[22]

The relationship between the vanillin yield and the loading of a copper catalyst has an extreme character, reaching its maximum at $Cu(OH)_2$ contents of 4 g L^{-1}. In the presence of $Cu(OH)_2$, the vanillin yield is twice that obtained without a catalyst (20 vs. 9 wt. %) (see Table 3).

In order to compare the efficiency of pine rot oxidation, we also studied the oxidation of other substrates (Table 4). The yields of vanillin from intact or rotten wood match closely, differing by 15—20 %. The closeness of the yields points to the fact that the lignins from sound wood and from brown rot are similar in structure and are equally usable for vanillin production.

The yield of aldehydes in the oxidation of asp wood in the presence of anthraquinone is almost twice as high as that in the non-catalyzed process. The aldehyde yield from a flow-type process in the presence of the copper catalyst approximates that obtained by oxidation with nitrobenzene.[4,14] The oxidation of birch brown rot afforded syringaldehyde as the main product (the vanillin to syringaldehyde ratio was 1 : 3). An analogous make-up of the product mixture was obtained in the oxidation of birch wood with nitrobenzene[5] and in the oxidation of birch ethanol-lignin with oxygen with no catalyst (see Table 4).

The catalyzed oxidation of lignosulfonates from the Syas' paper and pulp mill afforded vanillin in 14.4 wt. % yield (based on lignin used). This value is slightly lower than those obtained both in the oxidation of lyes with nitrobenzene and in the oxidation of pine wood or pine rot with oxygen (see Tables 3 and 4). The lower vanillin yield obtained by the oxidation of the lyes from the Svetogorsk paper and pulp mill can be caused by the removal of a base during cellulose production.

The results reported here and the literature data on the oxidation of different lignins make it possible to consider the whole problem of the reactivity of native and isolated lignins of foliates and conifers. Thus, the results of lignin oxidation with nitrobenzene were used (with some restrictions) to analyze the structures of the substrates.[3] These restrictions could be possibly caused by the fact that not the real structure of the initial lignin is revealed by its oxidation with nitrobenzene but one that is intermediately formed during the process. The oxidation with nitrobenzene proceeds under rather severe conditions, which do not rule out by-processes, including condensation. Therefore, the changes in the structure of lignin, that occur under mild conditions, *e.g.*, by heating to 120 °C in an alkaline medium,[3] cannot be detected by this method. On the other hand, technical lignins, which were obtained under severe conditions and whose structure was already altered and condensed, are less liable to condensation during oxidation with nitrobenzene. In other words, the more stable the lignins either by their nature or owing to the conditions of their production, the more adequately their structure can be characterized by the results of their oxidation with nitrobenzene.

It is well known that the wood of foliates is easier to delignify than that of conifers. This fact can be quantitatively interpreted by the above concept of the higher stability of the syringyl fragments, compared to the guaiacyl fragments, due to the inability of the former to undergo condensation at position 5 of substituted phenylpropanes:[12]
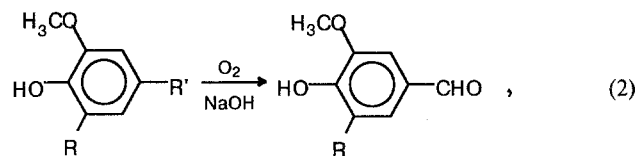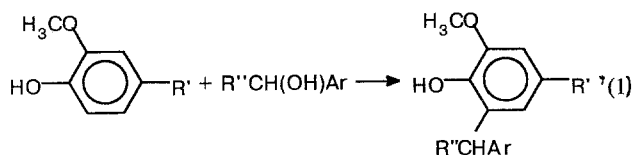
$R = CH_3O$ or H .

The results obtained can be explained by competition between condensation (1) and oxidation into aldehydes (2). The portion of the guaiacyl fragments that is stable toward oxidation by nitrobenzene, is also sufficiently stable in the other processes. As a result, the vanillin yield decreases slightly in the following order: native (23 %) > fermentative (20 %) > sulfite (17 %) lignin. This decrease in the yield also occurs when nitrobenzene is replaced with another oxidant, *i.e.*, oxygen. The stability of foliate lignins toward condensation with nitrobenzene makes it possible to observe a decrease in the yield of aldehydes when the conditions of substrate isolation are more severe: the aldehyde yields from ethanol-lignin and from lignosulfonates are smaller than that from native lignin by factors of 2 and 3, respectively.

The contents of the fragments stable during boiling (in the course of production) are similar for foliates and conifers and are in accordance with the formation of 16—18 % aldehydes either by oxidation with nitrobenzene or by catalytic oxidation with oxygen. This value is about 1/3 of the total guaiacyl and syringyl content in native lignins. It is noteworthy that the same quantity of lignin, unlike the rest, is dissolved very quickly during the delignification process.[19] Thus, ~30 % of the uncondensed phenylpropane structures of native lignins are stable toward condensation during both the delignification process and the oxidation into aldehydes. About 40 % of the guaiacyl fragments of coniferous species are condensed much faster than the syringyl fragments of foliates, and they cannot be oxidized into vanillin by the known methods. This part of the lignin is the cause of the known difficulties of the delignification of coniferous wood compared to that of foliate wood.[12]

References

1. K. Kyurshner, *Zh. Prikl. Khim.*, 1955, **28**, 956 [*J. Appl. Chem. USSR*, 1955, **28** (Engl. Transl.)]
2. M. I. Chudakov, *Promyshlennoe ispol'zovanie lignina* [*Industrial Use of Lignin*], Lesn. Prom., Moscow, 1983, 42 (in Russian).
3. O. P. Grushnikov and V. V. Jolkin, *Dostizheniya i problemy khimii lignina* [*Progress and Problems of the Chemistry of Lignin*], Nauka, Moscow, 1973, 189 (in Russian).
4. J. M. Pepper and B. W. Casselman, *Can. J. Chem*, 1967, **45**, 3009.
5. B. Leopold and I. L. Malmstrom, *Acta Chem. Scand.*, 1952, **6**, 49.
6. H. Hibbert, *J. Am. Chem. Soc.*, 1941, **63**, 3049.

7. W. G. Simson and E. Sondhimer, *TAPPI Journal*, 1960, **43**, 1025.

8. J. Wozniak and D. R. Dimmel, *J. Wood Chem. and Techn.*, 1989, **9**, 491.

9. N. G. Moskovtsev and S. A. Strel'skaya, *Khimiya drevesiny* [*Wood Chemistry*], 1986, N 1, 63 (in Russian).

10. B. Leopold, *Svensk Kem. Tidskr.*, 1951, **63**, 260.

11. Z. N. Kreitsberg, *Tr. In-ta lesokhosjaistvennykh problem AN Latv. SSR* [*Proceedings of the Institute of Forestry Problems of the Academy of Sciences of Latv. SSR*], 1955, **8**, 55 (in Russian).

12. G. A. Chirkin and D. V. Tishchenko, *Zh. Prikl. Khim.*, 1962, **1**, 153 [*J. Appl. Chem. USSR*], 1962, **1** (Engl. Transl.)].

13. R. B. Epshtein, *Tr. Ukr. NII pishchevoi promyshlennosti* [*Proceedings of the Ukrainian Institute of the Food Industry*], 1959, **2**, 201 (in Russian).

14. V. E. Taraban'ko, A. V. Kudrjashev, G. R. Gul'bis, and N. V. Koropachinskaya, in *Problemy okislit'el'no-vosstanovitel'nykh prevrashchenii komponentov drevesiny. Tez. dokl. mezhdunar. konf.* [*Problems of Oxidative-Reductive Transformations of Components of Wood, Abstr. of Papers of Int. Conf.*], Arkhangel'sk, 1992, 85 (in Russian).

15. O. D. Kamaldina and Ya. A. Massov, *Poluchenie vanilina iz lignosulfonatov* [*Production of Vanillin from Lignosulfonates*], TsBTI TsINIS, Moscow, 1959 (in Russian).

16. F. E. Brauns and D. A. Brauns, *Khimiya lignina* [*Chemistry of Lignin*], Lesn. Prom., Moscow, 1964 (in Russian).

17. V. Ripachek, *Biologiya derevorazrushayushchikh gribov* [*Biology of Wood-destroying Fungi*], Lesn. Prom., Moscow, 1967 (in Russian).

18. K. A. Kalun'yants, E. F. Shanenko, and L. V. Zaitseva, *Itogy nauki i tekhniki, Ser. khimiya i tekhnologiya pishchevykh produktov* [*Results of Sciense and Industry, Div. of Chemistry and Technology of Foods*], Moscow, 1988, **1**, 3 (in Russian).

19. T. N. Kleinert, *TAPPI Journal*, 1966, **49**, 53.

20. K. Forss, R. Kokkonen, and P. E. Sagfors, in *Int. Symp. Wood and Pulp Chem*, Raleigh, N. C., Atlanta, 1989, 411.

21. V. E. Taraban'ko, A. V. Kudrjashev, G. R. Gul'bis, and N. V. Koropachinskaya, in *Problemy okislit'el'no-vosstanovitel'nykh prevrashchenii komponentov drevesiny. Tez. dokl. mezhdunar. konf.* [*Problems of Oxidative-Reductive Transformations of Components of Wood, Abstr. of Papers of Int. Conf.*], Arkhangel'sk, 1992, 64 (in Russian).

22. Pat. USA 2434626, 1948; *Chem. Abstr.*, 2403h, **42**, 1948.