Optimization of Alkaline Hydrogen Peroxide Treatment of Lignin Model Compound at High pH Levels for Producing Aromatic Aldehyde and Acid as Fine Chemicals

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Abstract

A non-phenolic β-*O*-4-type lignin model compound, veratrylglycerol-β-guaiacyl ether (VG), was treated with H_2O_2 at high pH levels in our previous study. Veratraldehyde (Vald) and veratric acid (Vacid), which are non-phenolic analogues of the most common lignin-based fine chemicals, vanillin and vanillic acid, respectively, were obtained with a high total yield of 77% based on the amount of degraded VG, although only 22% of VG was degraded and hence the total yield of Vald and Vacid was only 17% based on the initial amount of VG. This study optimized the alkaline H_2O_2 treatment to enhance the degradation of VG and yields of Vald and Vacid. The degradation of VG and total yield of Vald and Vacid were enhanced from 22% to 54% and from 17% to 39%, respectively, by optimizing the conditions as follows: 1.96 mmol of H_2O_2 were added stepwise 400 times with an interval of 15 s in a reaction solution containing 1.0 mmol/L VG, 3.0 mol/L NaOH, 1.08 mmol/L $FeCl_3$, and 3.24 mmol/L mannitol at 90℃. Doubling the reaction period and employing twice the amount of H_2O_2 (3.92 mmol) in the absence of mannitol further enhanced the degradation of VG to 61% and the total yield to 44%.

Keywords: Ferric ion; Ferrous ion; Hydrogen peroxide bleaching; Stepwise addition

INTRODUCTION

Practical utilization of all the components of woody biomass is important for reducing the environmental impact of industry. Because cellulose is already widely utilized and hemicelluloses have shown to be converted to potential high value-added products, the key in responding to this requirement is to establish a method for the practical utilization of lignin. A promising method is to produce fine chemicals from lignin. Fig. 1 shows the most common fine chemicals derived from lignin, vanillin (4-hydroxy-3-methoxybenzaldehyde), vanillic acid (4-hydroxy-3-methoxybenzoic acid), syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde), and syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid), the former and latter two of which originate from the guaiacyl- and syringyl-type, respectively. Many reports have examined the production of these compounds and their analogues from lignin or lignin model compounds [1-26]. The results can be summarized as follows: about 10% and 50% of these lignin-derived compounds were obtained from macromolecular lignin samples and lignin model compounds, respectively, as the maximum yields in systems containing rare metal catalysts, special solvents, special additives, *etc*., which are harmful to the environment.

In our previous study, a non-phenolic β-*O*-4-type lignin model compound, veratrylglycerol-β-guaiacyl ether (VG, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol, Fig. 1), was reacted with active oxygen species in treatments simulating alkaline oxygen (O_2) or hydrogen peroxide (H_2O_2) bleaching processes at high pHs [27,28]. The major exclusive reaction products were veratraldehyde (Vald, 3,4-dimethoxybenzaldehyde, Fig. 1) and veratric acid (Vacid, 3,4-dimethoxy-benzoic acid, Fig. 1), which are non-phenolic analogues of vanillin and vanillic acid, respectively, as well as guaiacol (2-methoxyphenol, Fig. 1). Vald and Vacid were quantified in our subsequent report [29]. The maximum total yield of these compounds in alkaline H_2O_2 bleaching processes at high pH levels

was 77% based on the amount of degraded VG (defined as the conversion ratio (CR) in the following text), which was highest among all the previous studies. However, an important issue remaining to be solved was that the oxidation power of H_2O_2 was wasted to generate water (H_2O) and O_2, *via* bimolecular self-decomposition, without the formation of active oxygen species that degrade VG to afford Vald and Vacid. Consequently, only 22% of VG was degraded (the percentage of degraded VG, defined as PD below), and hence, the total yield of these compounds based on the initial amount of VG (defined as TY below) was only 17%.

In this paper, we optimized the reaction conditions of the alkaline H_2O_2 bleaching treatments to degrade VG more completely (higher PD) and afford Vald and Vacid in larger amounts (higher TY), maintaining or further improving CR ($CR = TY/PD \times 100\%$) when compared with previous results [29]. The optimization parameters were the concentration of sodium hydroxide (NaOH), addition amounts of iron (as $FeCl_3$), magnesium (as $MgCl_2$), or copper (as $CuCl_2$), manner of H_2O_2 addition, and addition amount of D-mannitol.
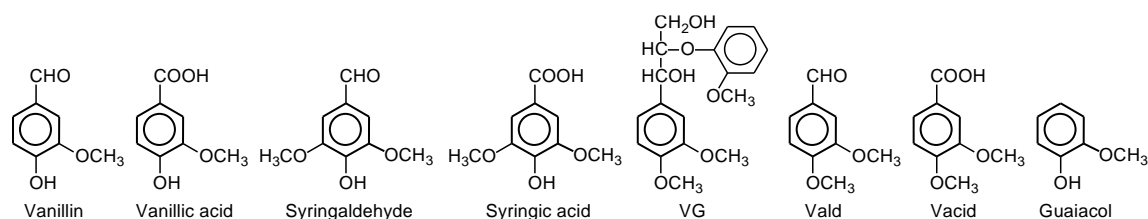

Fig. 1. Structures of the most common lignin-based fine chemicals (vanillin, vanillic acid, syringaldehyde, and syringic acid), VG (employed as the starting compound in this study), reaction products quantified in this study (Vald and Vacid), and a reaction product detected in this study (guaiacol).

EXPERIMENTAL

Materials

VG was synthesized as a mixture of the *erythro* and *threo* isomers according to Adler's method [30]. The structure and purity were confirmed by nuclear magnetic resonance spectroscopy (NMR, JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) using acetone-d_6 and an aliquot of deuterium oxide as the solvents. The spectral data were shown in our previous reports [27,31].

All other chemicals were purchased from Fujifilm Wako Pure Chemical Co. (Osaka, Japan), Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan), or Sigma-Aldrich Japan K. K. (Tokyo, Japan), and used without further purification. Ultrapure H_2O purified by a generator (Puric-Z, Organo Co., Tokyo, Japan) was used. The H_2O_2 solution used did not contain any stabilizer. Semiconductor grades of NaOH, $FeCl_3$, $MgCl_2$, and $CuCl_2$ were used.

Treatment of Alkaline Hydrogen Peroxide Bleaching

A reaction solution (30 mL) was prepared to contain 30 μmol (1.0 mmol/L) of VG and amounts of NaOH, $FeCl_3$, $MgCl_2$, $CuCl_2$, and D-mannitol as listed in Table 1 in a bottom-round Teflon flask (volume: 50 mL). The metal salts and D-mannitol were added before the addition of NaOH. The Teflon flask was heated to 90℃ with magnetic stirring in a water bath filled with a sodium chloride solution. A H_2O_2 solution of known concentration was added stepwise. The protocols are listed in Table 1. The reaction was initiated by the first addition of the H_2O_2 solution and continued until 30 or 20 min after the final addition. An apparatus for the stepwise addition was used when the addition interval was shorter than 1 min. Each reaction was repeated several times to confirm reproducibility.

In some runs, two internal standard compounds, 30 μmol (1.0 mmol/L) of 4-methoxybenzoic acid and 2.0 μmol (67 μmol/L) of 3,4,5-trimethoxybenzoic acid, were added together to the reaction solutions for quantifying VG and the reaction products (Vald and Vacid), respectively, with high reproducibility. Their high stabilities were confirmed under the employed conditions in advance.

Quantification

A portion of the reaction solution was withdrawn just after the reaction was terminated, poured into a glass tube, and immediately cooled in an ice water bath. Precisely 1.0 mL of the cooled solution was transferred to another glass tube. Then, an amount of acetic acid (CH_3COOH) sufficient for neutralization and 1.0 mL of methanol (CH_3OH) were added. When the internal standard compounds were not added to the reaction solutions in the previous section, this CH_3OH contained 1.0 µmol of 4-methoxybenzoic acid and 67 nmol of 3,4,5-trimethoxybenzoic acid for quantifying VG and the reaction products, respectively. After thorough shaking, a portion of this mixture was filtered with a membrane filter, and the filtrate was analyzed by high-performance liquid chromatography (HPLC) consisting of a system controller (CBM-20A, Shimadzu Co., Kyoto, Japan), online degasser (DGU-12A, Shimadzu Co.), solvent delivery unit (LC-10AD, Shimadzu Co.), column oven (CTO-10Avp, Shimadzu Co.), and photodiode array detector (SPD-M 10Avp, Shimadzu Co.). Quantification was based on calibration curves prepared in advance for VG, Vald, and Vacid with the internal standard compounds and their absorbances at 280 nm.

Conditions for HPLC analysis were as follows: An HPLC column, Luna 5 u C18(2) 100 Å (length: 150 mm, inner diameter: 4.6 mm, particle size: 5.0 µm, Phenomenex, Inc., Torrance, CA, USA), was used at an oven temperature of 40℃ with a solvent flow rate of 1.0 mL/min. The solvent was a mixture of CH_3OH and 1.0vol% CH_3COOH, with the ratio adjusted from 15/85 to 19.5/80.5 for 40.5 min and from 19.5/80.5 to 44/56 for 2.5 min, and then maintained at 44/56 for 14.5 min (total 57.5 min).

Table 1. Reaction systems employed in this study.

System[a]	NaOH	H_2O_2 addition[b]	Total time	Fe/Mg/Cu[c]	D-Mannitol
1[d]	0.5 mol/L	10/10/196	120 min	0.36/—/—	—
2	0.5 mol/L	10/10/196	120 min	0.36/—/—	—
3	1.0 mol/L	10/10/196	120 min	0.36/—/—	—
4	2.0 mol/L	10/10/196	120 min	0.36/—/—	—
5	3.0 mol/L	10/10/196	120 min	0.36/—/—	—
6	5.0 mol/L	10/10/196	120 min	0.36/—/—	—
7	3.0 mol/L	10/10/196	120 min	0.12/—/—	—
8	3.0 mol/L	10/10/196	120 min	1.08/—/—	—
9	3.0 mol/L	10/10/196	120 min	3.24/—/—	—
10	3.0 mol/L	100/1/19.6	120 min	1.08/—/—	—
11	3.0 mol/L	200/0.25/9.8	170 min	1.08/—/—	—
12	3.0 mol/L	400/0.25/4.9	120 min	1.08/—/—	—
13	3.0 mol/L	800/0.25/2.45	220 min	1.08/—/—	—
14	3.0 mol/L	400/0.25/4.9	120 min	—/—/1.08	—
15	3.0 mol/L	400/0.25/4.9	120 min	1.08/2.16/—	—
16	3.0 mol/L	400/0.25/4.9	120 min	2.16/6.48/—	—
17	3.0 mol/L	400/0.25/4.9	120 min	2.16/4.32/—	—
18	3.0 mol/L	400/0.25/4.9	120 min	1.08/—/—	3.24 mmol/L
19	3.0 mol/L	400/0.25/4.9	120 min	3.24/—/—	3.24 mmol/L
20	3.0 mol/L	400/0.25/4.9	120 min	1.08/2.16/—	3.24 mmol/L
21	3.0 mol/L	800/0.25/2.45	220 min	1.08/—/—	3.24 mmol/L
22[e]	3.0 mol/L	800/0.25/4.9	220 min	1.08/—/—	—
23[e]	3.0 mol/L	800/0.25/4.9	220 min	1.08/—/—	3.24 mmol/L
24[e]	3.0 mol/L	800/0.25/4.9	220 min	3.24/—/—	—
25[e]	3.0 mol/L	800/0.25/4.9	220 min	3.24/—/—	9.72 mmol/L

[a] A temperature of 90℃ was employed in this study.
[b] Addition frequency (times) / interval (min) / amount of H_2O_2 added at each step (µmol).
[c] Added as $FeCl_3$ (mmol/L) / $MgCl_2$ (mmol/L) / $CuCl_2$ (mmol/L). These species precipitated and/or aggregated in systems **1~17**, **22**, and **24**.
[d] Conducted in our previous report in which a temperature of 95℃ was employed [29].
[e] Total amount of H_2O_2 added was 3.92 mmol, and different from all the other systems (1.96 mmol).

RESULTS AND DISCUSSION

Mechanism Resulting in High CR in Alkaline H_2O_2 Treatments at High pH Levels

Vald and Vacid were yielded from VG with high CRs in alkaline H_2O_2 bleaching treatments at high pH levels in our previous study [29]. These high CRs can be explained with respect to self-decomposition of H_2O_2 and reactivity of active oxygen species generated by the self-decomposition clarified in our previous reports [27-29,32-36]. H_2O_2 (pK_a=11.6 [37]) and its conjugate base (hydroperoxide anion, HO_2^-) do not directly attack VG at any pH, because VG does not have any active site for their attack. Hydroxyl radical ($HO\bullet$, pK_a=11.9 [38]), its conjugate base (oxyl anion radical, $O\overset{\bullet}{}^-$), hydroperoxyl radical ($HO_2\bullet$, pK_a=4.8 [39]), and its conjugate base (superoxide anion radical, $O_2\overset{\bullet}{}^-$) form as the exclusive active oxygen species accompanying self-decomposition of H_2O_2 in the co-presence of metal ion, precipitates, and/or aggregates. $HO\bullet$ and $O\overset{\bullet}{}^-$ attack VG to degrade it, while $O_2\overset{\bullet}{}^-$ does not attack VG due to its low ability as an oxidant. Although $HO_2\bullet$ may be able to degrade VG, the acidic conditions required for its formation are not appropriate in this study, as discussed for the reactivity of $HO\bullet$ below.

Concerning $HO\bullet$ and $O\overset{\bullet}{}^-$, $HO\bullet$ is the major species that degrades VG in alkaline H_2O_2 bleaching treatments at pH equal to or lower than 11.5 due to its pK_a value, 11.9, while $O\overset{\bullet}{}^-$ substitutes for $HO\bullet$ at pH equal to or higher than 12.5. A remarkable difference in reactivity is seen between $HO\bullet$ and $O\overset{\bullet}{}^-$. $HO\bullet$ preferably attacks the aromatic nucleus of VG rather than the aliphatic side-chain despite the general knowledge that its reaction rate is diffusion control in most cases, while $O\overset{\bullet}{}^-$ shows the reverse reactivity owing to its negative charge generating the consequent electronically repulsive force to the π-electron system of the aromatic nucleus [32,34]. This preferable attack of $O\overset{\bullet}{}^-$ on the aliphatic side-chain preserves the aromatic nucleus, and consequently affords Vald and Vacid in the alkaline H_2O_2 bleaching treatments in the high pH range. However, most HO_2^- molecules (as all H_2O_2 mostly dissociates at high pH) self-decompose to O_2 and hydroxide anions (HO^-) in the high pH range without forming $O\overset{\bullet}{}^-$ ($2\,HO_2^- \rightarrow O_2 + 2\,HO^-$) probably due to the catalytic activity of surface of metal precipitates and/or aggregates. This phenomenon results in wasted HO_2^- from the viewpoint of producing Vald and Vacid from VG, and thus relatively small amounts of degraded VG and afforded Vald and Vacid. This wasted HO_2^- was noted in our previous study [29] and should be solved by this study.

General Description of Alkaline H_2O_2 Treatment at High pH

Three major peaks appearing on chromatograms of the HPLC analyses corresponded to Vald, Vacid, and guaiacol. Guaiacol originated from the aromatic nucleus constituting the *β-O*-4 bond of VG. Its formation accompanies the *β-O*-4 bond cleavage. However, guaiacol was also degraded in the alkaline H_2O_2 treatments owing to its phenolic nature and hence the detected yield was lower than the amount of guaiacol actually produced during the reaction. Guiaicol was therefore not quantified.

When Vald was treated as the starting compound under conditions identical to those in this study except for employing a temperature of 95℃, Vacid quantitatively formed [29]. Vacid was stable when treated as the starting compound [29]. Vacid did not appear as soon as the reaction was initiated but after the initial stage, and then increased monotonically in the reactions of VG performed in this study. All of these results comprehensively indicate that Vacid did not originate directly from VG but from Vald. Thus, not the individual yields of Vald and Vacid but mainly TY is discussed below.

We did not confirm whether H_2O_2 remained after completing the reaction. However, we can rationally presume that most H_2O_2 added at each addition completely decomposed during the interval between any two consecutive additions.

Because the catalytic activity of Fe species was not stable when a stock solution of $FeCl_3$ was prepared in advance at a neutral pH, an acidic stock solution was used. After mixing a specific amount of the acidic stock solution with NaOH solution, brown to black precipitates and aggregates of Fe species formed. Despite using concentration as the unit of added $FeCl_3$ in Table 1, most Fe species precipitated and/or aggregated, so the system was heterogeneous with respect to Fe species.

Table 2 lists the PDs ((amount of degraded VG)/(initial amount of VG)×100%), yields of Vald

and Vacid based on the initial amount of VG, TYs ((yield of Vald)+(yield of Vacid)), and CRs (TY/PD×100%) observed in this study.

Table 2. Percentage of degraded VG (PD), yields of Vald and Vacid based on the initial amount of VG, their total yield (TY), and conversion ratio of VG to Vald and Vacid (CR) at the end of the reaction (30 or 20 min after the final addition of H_2O_2).

System	NT[a]	PD[b]	Yield[b]			CR[d]
			Vald	Vacid	TY[c]	
1[e]		22%	5%	12%	17%	77%
2	3	11% (±0.8)	3% (±0.1)	5% (±0.4)	8%	78%
3	3	19% (±0.7)	4% (±0.5)	8% (±0.3)	11%	59%
4	3	21% (±0.5)	4% (±0.1)	9% (±0.3)	13%	64%
5	3	24% (±0.0)	5% (±0.1)	12% (±0.3)	17%	69%
6	3	38% (±0.1)	3% (±0.1)	20% (±0.2)	22%	59%
7	3	22% (±0.6)	4% (±0.0)	10% (±0.2)	14%	63%
8	3	26% (±0.4)	4% (±0.0)	12% (±0.3)	16%	61%
9	3	23% (±0.2)	4% (±0.2)	10% (±0.5)	14%	62%
10	3	50% (±0.4)	8% (±0.2)	29% (±0.2)	36%	73%
11	3	44% (±3.4)	3% (±0.3)	19% (±1.9)	22%	50%
12	3	46% (±1.8)	8% (±0.3)	26% (±1.0)	34%	75%
13	3	51% (±2.7)	9% (±0.3)	29% (±2.1)	38%	74%
14	3	10% (±1.9)	3% (±1.7)	5% (±1.3)	8%	82%
15	4	49% (±3.5)	6% (±0.4)	31% (±1.5)	37%	75%
16	5	22% (±4.6)	2% (±0.2)	10% (±2.3)	12%	55%
17	4	47% (±1.5)	4% (±1.6)	27% (±4.2)	32%	67%
18	4	54% (±3.8)	7% (±0.2)	33% (±1.6)	39%	73%
19	2	53% (±1.0)	7% (±0.1)	30% (±0.4)	37%	69%
20	3	36% (±1.8)	5% (±0.2)	26% (±1.6)	30%	83%
21	2	52% (±5.1)	6% (±1.0)	29% (±3.4)	35%	67%
22[f]	4	61% (±2.1)	9% (±1.2)	35% (±4.3)	44%	73%
23[f]	3	57% (±7.3)	9% (±1.1)	30% (±2.9)	39%	68%
24[f]	2	49% (±0.2)	8% (±0.3)	34% (±0.3)	42%	86%
25[f]	3	41% (±1.6)	6% (±0.3)	21% (±1.0)	27%	66%

[a] Number of trials.
[b] Values are rounded to whole numbers. Numerals in the parentheses are standard deviations.
[c] Yields of Vald and Vacid before rounding were used for the calculation.
[d] Equation: TY/PD×100%. Values of TY and PD before rounding were used for the calculation.
[e] Data obtained in our previous study where a temperature of 95℃ was employed [29].
[f] Total amount of added H_2O_2 was 3.92 mmol in these systems, and different from all the others (1.96 mmol).

Effects of Temperature and Concentration of NaOH

System **1** was conducted in our previous study [29], employing a temperature of 95℃. System **2** was conducted in this study under the identical conditions except for the temperature of 90℃. PD and TY were clearly lower in system **2** than in system **1**, although the CRs were similar in both systems. System **1** was thus better than system **2** for obtaining high PD and TY as well as CR. $O_2^{\cdot-}$ may be produced more efficiently at higher temperature. However, a temperature of 90℃ was employed in all the systems in this study due to limitations of the apparatus.

Because PD and TY had increased with increasing pH from 11.5 to 13.3 (0.5 mol/L) while maintaining a rather high CR in our previous study [29], we expected that high TYs and PDs would be obtained by applying concentrations of NaOH higher than 0.5 mol/L. When pHs lower than 11.5 had been employed in our previous study [29], the PDs and TYs had been very high and very low, respectively, resulting from the fact that the major active oxygen species exclusively generated from the self-decomposition of H_2O_2 at these relatively low pHs was not $O_2^{\cdot-}$ but HO· that preferably attacks and degrades the aromatic nucleus of VG as described above. Systems **3**−**6** were prepared using the different

concentrations of NaOH but otherwise the same conditions as those in system **2** to examine the effect of NaOH concentration on PD, TY, and CR. PD and TY increased with increasing NaOH concentration from system **2** to **6**, while CR did not show a clear trend. These increases in PD and TY suggest that the amount of $O\overline{\cdot}$ generated by the self-decomposition of a specific amount of HO_2^- increases with increasing concentration in this high alkalinity range, probably accompanying the change in the catalytic activity of Fe species as well as direct effect of the high concentrations on the self-decomposition. The NaOH concentration of 3.0 mol/L employed in system **5** was applied to the subsequent systems (**7**−**25**), although the highest PD and TY were obtained in system **6** (5.0 mol/L). It was problematic to stir and withdraw the reaction solution in system **6** due to the high viscosity and low reliability of the system homogeneity.

Effect of Addition Amount of FeCl₃

Fe is the most common metal contaminant in chemical pulp for paper making. The presence of Fe generally causes the degradation of carbohydrates in an alkaline O_2 or H_2O_2 bleaching process. The degradation of carbohydrates is caused by active oxygen species including $HO\cdot$ and $O\overline{\cdot}$ generated by the decomposition of organic peroxides and H_2O_2 (and/or HO_2^-) catalyzed by Fe species. On this basis, Fe was added to many systems in this study to efficiently generate $O\overline{\cdot}$, consequently degrade VG (attain high PD), and increase TY. Fe is a common contaminant in chemical pulp in amounts of around 20 ppm [40], which corresponds to 0.36 mmol/L in this study.

In the self-decomposition of HO_2^- at a high pH catalyzed by Fe species, $O\overline{\cdot}$ is generated following the formula: $HO_2^- + Fe^{2+} \rightarrow O\overline{\cdot} + HO^- + Fe^{3+}$. The generated Fe^{3+} is reconverted to Fe^{2+}, following the formula: $HO_2^- + HO^- + Fe^{3+} \rightarrow O_2\overline{\cdot} + H_2O + Fe^{2+}$. These Fe^{2+} and Fe^{3+} include Fe species in the precipitates and/or aggregates that can behave as the free cations, because the free cations dissolving in the solutions must be tiny amounts. $O_2\overline{\cdot}$ does not attack VG, as described above, but reduces something to convert to O_2, or combines with another radical. The pseudo as well as real free Fe cations thus catalyze the formation of $O\overline{\cdot}$ as well as $O_2\overline{\cdot}$. However, because Fe species mostly precipitated and/or aggregated in the high pH range and catalyzed the bimolecular self-decomposition of HO_2^-, $2\,HO_2^- \rightarrow O_2 + 2\,HO^-$, on their surface without the formation of active oxygen species, the amount of generated $O\overline{\cdot}$ was small. This resulted in the low PDs and consequent low TYs observed in our previous study [29]. The addition amount of Fe was therefore varied (systems **5**, **7**, **8**, and **9**) to attain high PD and TY while maintaining or further increasing CR.

PD, TY, and CR were not largely different between systems **5**, **7**, **8**, and **9**. This result may suggest that the amounts of the pseudo and real free Fe cations were not largely different between these systems, although these systems contained different amounts of Fe species. The consumption of HO_2^- may have become faster with the increased amount of Fe species from systems **5** to **9**, because the amounts of the precipitates and/or aggregates increased with it. The addition amount of 1.08 mmol/L in system **8** was applied to many of the subsequent systems.

Effect of Addition Manner of H₂O₂

The manner of H_2O_2 addition has decisive effects on the amounts of $O\overline{\cdot}$ generated by the self-decomposition of a specific amount of HO_2^- [33], and hence, on PD, TY, and CR. The generation amount of $O\overline{\cdot}$ is large when the concentration of HO_2^- remains low. This is because maintaining a low concentration decreases the bimolecular self-decomposition of HO_2^- without the formation of $O\overline{\cdot}$ relatively to the unimolecular self-decomposition and chain-type decomposition of HO_2^-. The chain-type decomposition is propagated by $O\overline{\cdot}$ and $O_2\overline{\cdot}$ ($HO_2^- + O\overline{\cdot} \rightarrow O_2\overline{\cdot} + HO^-$, $HO_2^- + O_2\overline{\cdot} \rightarrow O\overline{\cdot} + HO^- + O_2$) to consequently increase the attack of $O\overline{\cdot}$ on VG. Therefore, stepwise addition of H_2O_2 was employed in all the systems in this and our previous studies [29] to enhance the generation of $O\overline{\cdot}$ and its attack on VG [33]. Several different stepwise addition protocols were examined in systems **8** and **10**−**13**. The total amount of H_2O_2 added was 1.96 mmol in these systems. The interval between any consecutive two H_2O_2 additions was fixed at 15 s in systems with intervals shorter than 1 min, owing to limitations of the apparatus.

PDs and TYs as well as CRs in systems **10**−**13** were clearly higher than in system **8**, which

confirms that maintaining a low concentration of HO_2^- is desirable for attaining high PD, TY, and CR. TY and CR were clearly lower in system **11** than in systems **10**, **12**, and **13**, although PDs were not largely different. This result suggests that the degradation of VG was not accompanied by the formation of Vald and Vacid in system **11** relatively to those in the other systems and that other degradation modes of VG existed in system **11**. System **13** showed the highest PD and TY with rather high CR among these systems, which indicates that frequent stepwise addition of a small amount at each step is desirable to attain high PD and TY as well as CR. The reaction period was very long in system **13**, despite it affording the highest PD and TY. Therefore, H_2O_2 was added 400 times with an amount of 4.9 μmol at each addition and interval of 15 s in many of the subsequent systems, as performed in system **12**.

Effect of Metal Profile

It is well known that the metal profile significantly affects the degradation mechanism of H_2O_2 (and HO_2^-) as well as organic peroxides during alkaline O_2 bleaching, and consequently the amount of active oxygen species including $O \cdot^-$ generated in the system [41-48]. Cupper (Cu) is another metal commonly contaminating chemical pulp. The presence of Cu is also considered to cause the degradation of carbohydrates in alkaline O_2 bleaching, similarly to Fe. The effect of Cu addition was examined in system **14**. Cu also precipitated and/or aggregated under the employed conditions. PD and TY were quite low despite a rather high CR in system **14**. This result suggests that Cu species mainly catalyzed the bimolecular decomposition of HO_2^- without formation of $O \cdot^-$.

Mg is known to coprecipitate and/or coaggregate with various metals, varying their catalytic activity in the self-decomposition of H_2O_2 and organic peroxides [42,45,47]. In an alkaline O_2 bleaching process, Mg is known to be a protector of carbohydrates, which are degraded by active oxygen species generated by the decomposition of organic peroxides and H_2O_2 [46]. Mg was thus added in systems **15−17** to vary the catalytic activity of the added metals. The obtained results should be compared with those in system **12**. The color of the precipitates and aggregates varied from dark brown to white with increasing amount of Mg added in these systems. PD, TY, and CR in system **16** were clearly lower than those in system **12**. Those in systems **15** and **17** were similar to those in system **12**. It was shown in our previous report that the addition of a large amount of Mg relative to Fe suppresses the degradation of a carbohydrate model compound under alkaline O_2 bleaching conditions while the addition of a small amount of Mg contrarily enhances the degradation [48]. These suppressing and enhancing effects of the Mg addition result from a phenomenon whereby the catalytic activity of the precipitates and/or aggregates is varied by the coprecipitation and/or coaggregation of Mg to produce active oxygen species including $O \cdot^-$ more or less efficiently depending on the addition amount of Mg. The result in system **16**, in which a large amount of Mg was added and the coprecipitates and/or coaggregates had less catalytic activity to produce $O \cdot^-$, is thus in good agreement with our previous report [48]. Because PD and CR were not clearly higher in systems **15−17** than in system **12**, Mg was not added in most of the subsequent systems.

Effect of D-Mannitol Addition

D-Mannitol was reported to form a complex with Fe cations [49]. Indeed in this study, the precipitates and/or aggregates of Fe species did not form when $FeCl_3$ and D-mannitol were added before the addition of NaOH, indicating complex formation. This complex formation may possibly result in a phenomenon whereby the Fe^{3+} constructing the complex with D-mannitol catalyzes the self-decomposition of HO_2^- as a free cation to generate $O \cdot^-$ with high efficiency. It was thus expected that the addition of D-mannitol possibly increased PD and TY as well as CR. However, because D-mannitol is also known to be a radical scavenging agent [49,50], we considered that its addition may have reversely consumed $O \cdot^-$ to consequently decrease PD and TY as well as CR. On this basis, D-mannitol was added in systems **18−21** to examine the effect of the addition.

The addition of D-mannitol in an amount three times that of Fe was confirmed to slightly increase PD and TY with no large effect on CR in the comparison between systems **18** and **12**. This slight increase can probably be attributed to the complex formation between Fe^{3+} and D-mannitol, increasing the efficiency of the $O \cdot^-$ generation. An equimolar addition of D-mannitol accompanying the

increase in the amount of added Fe did not affect PD and TY in the comparison between systems **18** and **19**. The addition of D-mannitol in the presence of Mg rather decreased PD and TY in the comparison between systems **18** and **20**, although it increased CR. The efficiency of the O$\overline{\cdot}$ generation was thus lower in the presence of Mg than in its absence when D-mannitol was added. In system **21**, H_2O_2 was added step-wise with an addition frequency twice that of system **18** and an addition amount at each step half that of system **18**. PD, TY, and CR were slightly lower in system **21** than in system **18**. Thus, the addition of D-mannitol had an increasing effect on PD and TY as well as CR in the absence of Mg, which can result from the complex formation to vary the catalytic activity.

Effect of Further Addition of H_2O_2

Among systems **1−21**, in which the total amount of added H_2O_2 was 1.96 mmol, TY was equal to or more than 35% in systems **10**, **13**, **15**, **18**, **19**, and **21**. The highest PD (54%) and TY (39%) were obtained in system **18**. It can roughly be stated that high TY was obtained when $FeCl_3$ as well as D-mannitol was added with frequent stepwise H_2O_2 addition. Systems **22−25** were thus conducted to examine whether PD and TY as well as CR further increased when the total amount of H_2O_2 added was increased to twice those in systems **1−21** (3.92 mmol) by extending the reaction period from 120 to 220 min and increasing the addition frequencies from 400 to 800 times in the presence of Fe species with or without D-mannitol. Because the reaction was extended by adding twice amount of H_2O_2, PD and TY were naturally expected to increase.

The effect of the extended reaction in the presence of Fe species without D-mannitol was examined by comparing systems **12** and **22**. Both PD and TY were higher in system **22** than in system **12** with almost the same CR. Thus, the extended reaction was desirable, as expected. The effect of the extended reaction in the presence of Fe species with D-mannitol was examined by comparing systems **18** and **23**. Both systems showed the same TY and similar PDs and CRs. Thus, the extended reaction was meaningless in this case. Because PD, TY, and CR were lower in system **23** than in system **22**, the D-mannitol addition decreased PD, TY, and CR in the extended reaction. This undesirable effect of D-mannitol addition in the extended reaction can be attributed to D-mannitol strongly expressing its character as a radical scavenger in the extended reaction [49,50].

The addition amount of Fe was increased in systems **24** and **25** in the extended reaction. The results should be compared with those of systems **22** and **23**, respectively. The addition amount of D-mannitol was also increased in system **25**, accompanying the increase in the addition amount of Fe. This increase of the addition amount of Fe did not largely affect TY in the comparison between systems **22** and **24**. The addition of Fe with an amount of 1.08 mmol/L was thus large enough to attain high TY in the extended reaction. PD and TY were clearly smaller in system **25** than in system **23** with similar CRs. This decreasing effect of the presence of D-mannitol on PD and TY was thus great when the absolute amounts of added Fe and D-mannitol were large. D-Mannitol can express its character as a radical scavenger more strongly when increased amounts are added.

CONCLUSIONS

1. PD and TY were desirably high with high CR when the concentration of NaOH or employed temperature were high.

2. The increase in the addition amount of $FeCl_3$ did not largely affect PD, TY, and CR.

3. PD and TY as well as CR were clearly high for stepwise addition of H_2O_2 with many addition steps even when the total amount of added H_2O_2 was the same.

4. PD and TY as well as CR did not increase when $CuCl_2$ was added instead of $FeCl_3$ or when $MgCl_2$ was added together with $FeCl_3$.

5. PD and TY as well as CR increased in the presence of $FeCl_3$ but decreased in the presence of both $FeCl_3$ and $MgCl_2$ when D-mannitol was added.

6. PD and TY increased with extension of the reaction by doubling the stepwise addition of H_2O_2 in the presence of $FeCl_3$. However, PD and TY clearly decreased when extending the reaction in the same manner when $MgCl_2$ was also added.

7. System **22** was the most desirable, showing the highest PD (61%) and TY (44%).

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