

Utilization of Recyclable MnO₂ in Prebleaching Stage as a Catalyst for Oxygen Delignification or as a Delignifying Agent

Shirong Sun,^a Takuya Akiyama,^b Tomoya Yokoyama,^{a,*} and Yuji Matsumoto^a

^aLaboratory of Wood Chemistry, Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo 113-8657, Japan;

^bLaboratory of Wood Chemistry, Department of Forest Resource Chemistry, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba-shi, Ibaraki 305-8687, Japan;

*Corresponding author: yokoyama@woodchem.jp

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Abstract

MnO₂ can potentially suppress the degradation of carbohydrates in oxygen delignification, because MnO₂ catalyzes the decomposition of H₂O₂ to H₂O and O₂ and possibly that of organic peroxides to alcohols and O₂ without the formation of any active oxygen species, which degrade carbohydrates. The addition of MnO₂ actually suppressed the degradation of a carbohydrate model compound, methyl β -D-glucopyranoside, when reacted with active oxygen species generated from reactions between a phenolic lignin model compound, vanillyl alcohol, and O₂ under oxygen delignification conditions. However, the addition of MnO₂ did not have any meaningful effect when hardwood unbleached kraft pulp was oxygen-delignified. The addition surprisingly had a deleterious effect on pulp viscosity when MnO₂ was generated *in situ* in pulp fibers. This deleterious effect would result from a phenomenon whereby the oxidation of Mn²⁺ to MnO₂ was not complete in the *in situ* generation and Mn³⁺-related species, along others, were generated. In contrast, substitution of the latter half of oxygen delignification with a MnO₂ oxidation stage at a pH of 2 substantially suppressed the degradation of carbohydrates, compared to the common oxygen delignification without substitution.

Keywords: Kappa number; Manganese dioxide; Oxygen bleaching; Viscosity

INTRODUCTION

Oxygen delignification has widely been introduced into a prebleaching stage due to its environmental and economic benefits. However, severe degradation of carbohydrates has still been a serious drawback in oxygen delignification. The delignification is therefore terminated when the kappa number reaches about half that of the original unbleached pulp. Although the chemistry of oxygen delignification has extensively been studied to suppress the severe degradation of carbohydrates,¹⁻³⁸⁾ this goal has not yet been achieved.

The degradation of carbohydrates in oxygen delignification is caused by active oxygen species, whose formations accompany the decomposition of peroxides produced by reactions of phenolic substructure in lignin with O₂.^{1,16,17,23,27)} The decomposition of peroxides including H₂O₂ thus affects the degradation of carbohydrates in oxygen delignification. It is well known that some metal ions affect the stability of H₂O₂ and efficiency of radical formation accompanying the decomposition of H₂O₂ and consequently damage carbohydrates in hydrogen peroxide bleaching.³⁹⁻⁴¹⁾

MnO₂ catalyzes the decomposition of H₂O₂ to H₂O and O₂ without formation of any active oxygen species (radicals). If MnO₂ catalyzes the decomposition of not only H₂O₂ but also organic peroxides without any radical formation, addition of MnO₂ should suppress the degradation of carbohydrates in oxygen delignification. In fact, the addition of Mn²⁺, which was converted *in situ* to MnO₂ by the O₂ oxidation, to a treatment under oxygen delignification conditions reduced the degradation of a carbohydrate model compound, methyl β -D-glucopyranoside (MGP), when MGP was co-treated with a phenolic compound, 2,4,6-trimethylphenol, and active oxygen species were generated



by reactions of the phenolic compound with O_2 .²²⁾ The same addition suppressed the progress of oxidation of a dioxane-lignin isolated from an unbleached pulp.²⁴⁾ These results suggest that the *in situ* generated MnO_2 catalyzes the decomposition of organic peroxides as well as H_2O_2 produced in the system without formation of radicals, and has the potential to suppress the degradation of carbohydrates in oxygen delignification.

MnO_2 is an oxidant under acidic conditions, and can oxidize lignin model compounds.⁴²⁾ It is anticipated, therefore, that a MnO_2 delignification process under mildly acidic conditions where carbohydrates are not severely hydrolyzed can be achieved.

In this study, we examined and discussed the delignification efficiencies when MnO_2 was added to a common oxygen delignification process or when a MnO_2 delignification process was substituted for the latter half of this common process. The possibility of MnO_2 recycling is also discussed.

EXPERIMENTAL

Materials

MGP and a phenolic lignin model compound, 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, Valc), were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) and recrystallized from ethanol before use. Hardwood unbleached kraft pulp (kappa number: 14.2, viscosity: 21.5 mPa·s) was obtained from Oji Holdings Co. (Tokyo, Japan). All other chemicals used in this study were purchased from FUJIFILM Wako Pure Chemical Co. (Osaka, Japan), Tokyo Chemical Industry Co. Ltd., or Sigma-Aldrich Japan K. K. (Tokyo, Japan). Ultrapure H_2O purified by an ultrapure H_2O generator (Puric-Z, Organo Co., Tokyo, Japan) was used in all the experiments. Semiconductor grades of NaOH and $MnSO_4 \cdot 5 H_2O$ were used.

Reaction of Model Compound

A reaction solution (300 mL) was prepared to contain MGP (4.0 mmol/L), Valc (9.0 mmol/L), NaOH (0.50 mol/L), and $MnSO_4 \cdot 5 H_2O$ (0.36 mmol/L). The reaction solution was transferred into a Teflon-coated stainless steel autoclave (500 mL, Taiatsu Techno[®] Co., Tokyo, Japan). The vessel was introduced to a pressure of 1.1 MPa (1.0 MPa as gauge level) of O_2 , heated to 95°C for 10 min, and then stirred for 300 min. A portion of the reaction solution was withdrawn periodically to quantify residual MGP and Valc. The reaction was run twice to confirm its reproducibility.

Preparation of MnO_2 for Reaction

Aging of commercially available MnO_2 (commercial MnO_2)

Commercial MnO_2 (FUJIFILM Wako Pure Chemical Co.) was ground into powder in a mortar and aged in a solution of 1.0 mol/L H_2SO_4 for 120 min at room temperature followed by filtration under reduced pressure. The aged MnO_2 on the filter paper was washed with H_2O until washings were free from SO_4^{2-} . The washings were checked by mixing with a $Ba(OH)_2$ solution. The aged MnO_2 was air-dried for further use. Because the commercial MnO_2 did not consist only of MnO_2 , the oxidation power was measured by iodometric titration after grinding the aged MnO_2 into powder. The content was 90.2% of the theoretical value.

O_2 oxidation of Mn^{2+} to synthesize MnO_2 (synthetic MnO_2)

MnO_2 was synthesized from Mn^{2+} ($MnSO_4$) by O_2 oxidation under alkaline conditions. To a solution (700 mL) of $MnSO_4 \cdot H_2O$ (0.20 mol) was added drop-wise a solution (100 mL) of 4.0 mol/L NaOH. The resultant solution was subjected to O_2 bubbling for 60 min with stirring at room temperature. The suspension was neutralized with a solution (150 mL) of 1.0 mol/L H_2SO_4 with stirring for 30 min. The drop-wise addition of the NaOH solution and successive O_2 bubbling were then repeated to further advance the oxidation. The obtained precipitates (mostly MnO_2) were collected by filtration under reduced pressure, and washed with H_2O until the filtrate became neutral. The obtained precipitates were air-dried for further use. To examine the oxidation power, the precipitates were ground into powder in a mortar and iodometrically titrated. The content was 84.9% of the theoretical value, calculated on the basis of an assumption that all the applied Mn^{2+} was completely oxidized to MnO_2 .

Oxygen Delignification in the Presence of MnO₂

To a suspension of hardwood unbleached kraft pulp (12.0 g, OD basis) was added the commercial or synthetic MnO₂ (300 mg, OD basis). A NaOH solution and H₂O were added to the pulp suspension to adjust the pH to 12.5 or 11.5 and the pulp consistency to 4.0%. A carbonate buffer solution was added to the suspension when a lower initial pH (10.5 or 9.2) was applied. After the pulp slurry was transferred into the Teflon-coated stainless steel vessel, O₂ was introduced to the reactor at a pressure of 0.60 MPa (0.50 MPa as gauge level), and then the vessel was heated to 95°C. After the reaction, the vessel was cooled with ice water. The obtained pulp slurry was washed thoroughly with H₂O and air-dried for further use.

For the preparation of a reference pulp, oxygen delignification without adding any MnO₂ was also carried out under the same conditions.

Oxygen Delignification in the Presence of MnO₂ Generated *in situ* in Pulp Fibers

MnSO₄ • H₂O (6.0 mmol) was added to a suspension of the hardwood unbleached kraft pulp (12.0 g, OD basis). A H₂SO₄ solution was added to adjust the pH to 2.0, and then stirred at 50°C for 120 min. A NaOH solution and H₂O were used to adjust the pH and pulp consistency to 12.5 and 4.0%, respectively. After the pulp slurry was transferred into the Teflon-coated stainless steel vessel, O₂ bubbling was performed at room temperature for 120 min to generate MnO₂ in the pulp fibers *in situ*. The procedure of this *in-situ* generation of MnO₂ was exactly the same as described above. Oxygen delignification was then carried out under the same conditions as described above.

Successive Stages of Oxygen Delignification and MnO₂ Oxidation

The hardwood unbleached kraft pulp was primarily oxygen-delignified without addition of MnO₂ at a pH of 12.5 for 120 min, following the procedure described above for the reference pulp. The synthetic MnO₂ (300 mg, OD basis) was added to a suspension of the oxygen delignified pulp (12.0 g, OD basis), and then a H₂SO₄ or sulfate buffer solution and H₂O were added to adjust the pH and consistency of the suspension to specific values and 4.0%, respectively. The prepared pulp slurry was transferred into the Teflon-coated stainless steel vessel, and the vessel was heated to 70°C. After the reaction, the vessel was cooled with ice water. The obtained pulp slurry was washed thoroughly with H₂O and air-dried for further use.

Quantification of Model Compound

For quantification of MGP and Valc, a portion of the reaction solution was withdrawn (2.0 mL) at prescribed reaction times and neutralized with acetic acid. A solution of an internal standard compound (*myo*-inositol) was added and the resulting mixture was dried under a vacuum. The dried sample was acetylated with pyridine (2.0 mL) and acetic anhydride (3.0 mL) at 100°C for 60 min and then injected into a gas-chromatograph (GC-2010plus, Shimadzu Co., Ltd., Kyoto, Japan) equipped with a flame ionization detector and a capillary column (TC-17, 0.25 mm × 30 m, GL Science Inc., Tokyo, Japan). Conditions of GC were as follows; carrier gas: He, split ratio: 15, flow rate: 1.55 mL/min, injection temperature: 220°C, detector temperature: 230°C. The oven temperature was increased from 195°C to 200°C at 1°C/min and then from 200°C to 220°C at 4°C/min, holding for 10 min. The total running time was 20 min.

Determination of Kappa Number and Viscosity of Obtained Pulp

Kappa numbers and viscosities of obtained pulps were determined according to TAPPI Methods T236 and T230, respectively. The amount of MnO₂ remaining in the obtained pulps was separately determined iodometrically, and was taken into consideration in the calculation of the kappa numbers.

RESULTS AND DISCUSSION

Reaction of Model Compound

As described in the Introduction section, addition of MnO₂ can potentially suppress the

degradation of carbohydrates during oxygen delignification. A model experiment was conducted to confirm this suppression using not 2,4,6-trimethylphenol but a phenolic ‘lignin’ model compound, Valc. MGP and Valc were co-treated under conditions simulating oxygen delignification, where active oxygen species were generated by reactions between Valc and O_2 and degraded MGP. Hydroxyl radical ($HO\cdot$, $pK_a=11.9$) and its conjugate base, oxyl anion radical ($O\cdot^-$), are believed to be the active oxygen species most responsible for the degradation of carbohydrates.^{2,17,27} In our previous study, this model experiment was conducted in the presence or absence of $FeCl_3$ under similar conditions to those employed in this study.¹⁶ MGP was degraded significantly to be a residual yield of 57% at a reaction time of 300 min under the same conditions as those employed in this study, although a different reactor was used and it took a longer period (30 min) to raise the temperature to the target degree ($95^\circ C$). The recovery yield of MGP was 82% at a reaction time of 300 min when no metal ion was intentionally added at an oxygen pressure of 0.4 MPa (0.3 MPa as a gauge level) using this different reactor. At the lower oxygen pressure, Valc disappeared completely from the reaction solution just before a reaction time of 300 min.

Fig. 1 shows the time course of the changes in the residual yields of MGP and Valc when these compounds were treated together under conditions simulating oxygen delignification in the presence of MnO_2 . Although Mn^{2+} was primarily applied, its oxidation to MnO_2 probably completed in the early stage of the reaction. The degradation of MGP was not great. The residual yield was more than 95% at a reaction time of 300 min, which suggests that the addition of MnO_2 suppresses the degradation of carbohydrates. This result also suggests that the amount of active oxygen species generated by decomposition of peroxides controls the degree of the degradation of carbohydrates in an oxygen delignification system.

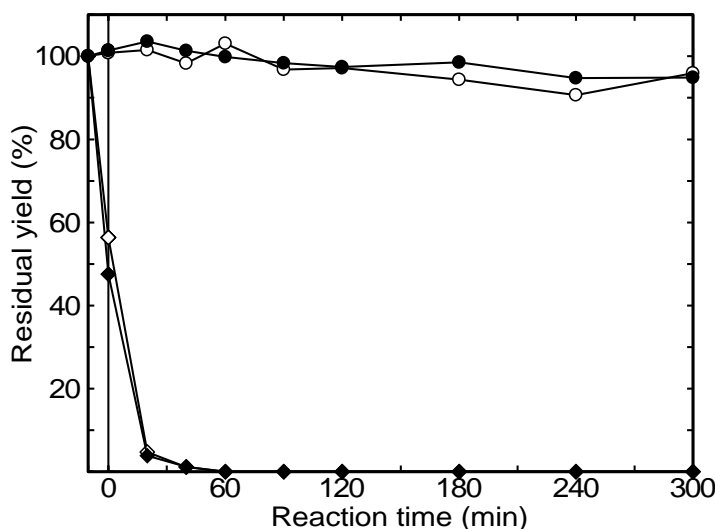


Fig. 1. Time course of changes in the residual yields of MGP (white and black circles) and Valc (white and black diamonds) when treated together under conditions simulating oxygen delignification in the presence of MnO_2 . (white marks: 1st trial, black marks: 2nd trial).

Oxygen Delignification in the Presence of MnO_2

On the basis of the results of the model experiment, hardwood unbleached kraft pulp was oxygen-delignified in the presence of the commercial or synthetic MnO_2 . The kappa numbers and viscosities of delignified pulps were compared with those of the reference pulp prepared by oxygen delignification without the addition of MnO_2 . Fig. 2 shows the correlations between the viscosities and kappa numbers for the pulps obtained when the hardwood unbleached pulp was oxygen-delignified in the absence of MnO_2 (reference) or in the presence of the commercial or synthetic MnO_2 . This correlation is defined as the ‘reaction selectivity’. The reaction selectivity of a delignification process conducted here is desirably high when it prepares pulps with high viscosities at a constant kappa number.

Although the reaction selectivity was slightly different between three oxygen delignification

processes and lower in the presence of either commercial or synthetic MnO_2 than in the reference treatment before their late stages, these delignification processes showed similar degrees of the reaction selectivity in the late stage. This confirmed that the presence of MnO_2 does not increase the reaction selectivity, although this was contrary to our expectation based on the results of the model experiment. These small effects of the MnO_2 addition can be explained if we assume that the added MnO_2 was present only on the outside of the pulp fibers, and thus its catalytic activity to decompose peroxides without formation of any active oxygen species was not available within the fibers.

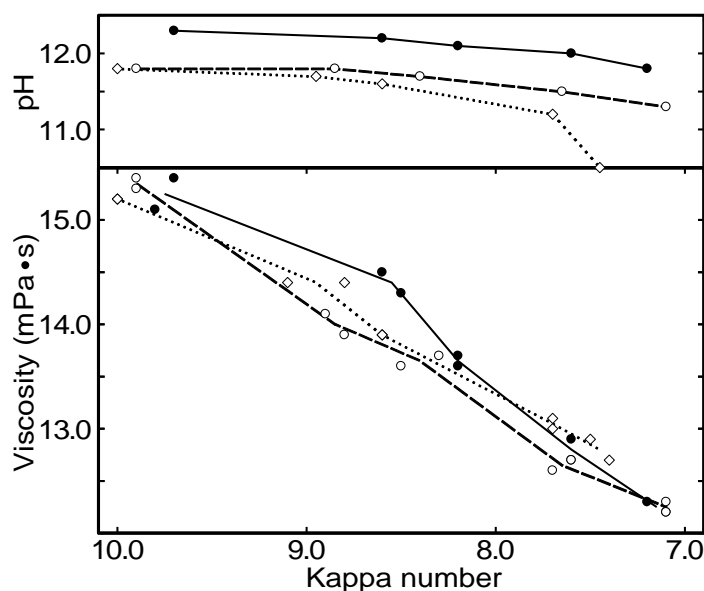


Fig. 2. Reaction selectivity (lower) and variation of pH (upper) when the hardwood unbleached kraft pulp was oxygen-delignified in the absence of MnO_2 (reference, black circles, solid line) or in the presence of commercial MnO_2 (white circles, long broken line) or synthetic MnO_2 (white diamonds, dotted line) at an oxygen pressure of 0.6 MPa, initial pH of 12.5, pulp consistency of 4.0%, and 95°C for 40, 80, 120, 240, or 360 min. Each oxygen delignification was conducted twice. Three lines showing the reaction selectivities are drawn by connecting the average values observed at these reaction times in the duplicated oxygen delignifications.

Table 1. Kappa number and viscosity of the pulps obtained by the oxygen delignification at pHs lower than 12.5 with the initial and final pH.

Initial pH ^a	MnO_2^b	Reaction period	Kappa number			Viscosity ^c			Final pH ^d
			1st	2nd	Mean	1st	2nd	Mean	
11.5	×	80 min	10.7	10.8	10.8	18.1	18.4	18.3	8.8
	○		10.7	10.6	10.7	17.9	18.0	18.0	8.4
10.5	×	80 min	9.3	9.4	9.4	14.8	15.0	14.9	—
	○		9.3	9.3	9.3	14.1	14.1	14.1	—
9.2	×	40 min	11.7	11.7	11.7	17.9	17.8	17.9	—
	○		11.7	11.7	11.7	17.1	17.4	17.3	—
	×	80 min	10.7	10.8	10.8	16.9	16.9	16.9	—
	○		10.4	10.5	10.5	16.7	16.8	16.8	—
	×	180 min	10.1	10.1	10.1	16.2	16.3	16.3	—
	○		9.9	10.0	10.0	15.9	15.9	15.9	—

^a Alkaline source was NaOH for pH 11.5 or carbonate buffer for the others.

^b ×: No addition of MnO_2 (reference), ○: Addition of synthetic MnO_2 .

^c Unit: $\text{mPa}\cdot\text{s}$

^d Final pH values are not shown when carbonate buffer was used as the alkaline source.

Table 1 lists the kappa numbers and viscosities of the pulps that were oxygen-delignified at an initial pH of 11.5, 10.5, or 9.2 under otherwise the same conditions described in the caption of Fig. 2 with the final pH values. The alkaline source was NaOH at an initial pH of 11.5 or a carbonate buffer solution at a pH of 10.5 or 9.2. The effect of the addition of the synthetic MnO_2 was also small at these lower pH values, which can also be attributed to the added MnO_2 existing only outside of the pulp fibers.

Oxygen Delignification in the Presence of MnO_2 Generated *in situ* in Pulp Fibers

To confirm whether or not the presence of MnO_2 in pulp fibers increases the reaction selectivity, the *in situ* generation of MnO_2 in pulp fibers was carried out before the oxygen delignification. Mn^{2+} was primarily infused into pulp fibers under mildly acidic conditions, and then oxidized to MnO_2 by O_2 bubbling under alkaline conditions. Both the kappa number and viscosity slightly decreased from 14.2 to 13.2 and from 21.5 to 20.4 $\text{mPa}\cdot\text{s}$, respectively, during the Mn^{2+} infusion under mildly acidic conditions. Both also further decreased slightly from 13.2 to 12.7 and from 20.4 to 18.8 $\text{mPa}\cdot\text{s}$, respectively, during the O_2 bubbling under alkaline conditions. Fig. 3 shows the reaction selectivities of the oxygen delignification processes in the reference treatment and with the *in situ* generated MnO_2 .

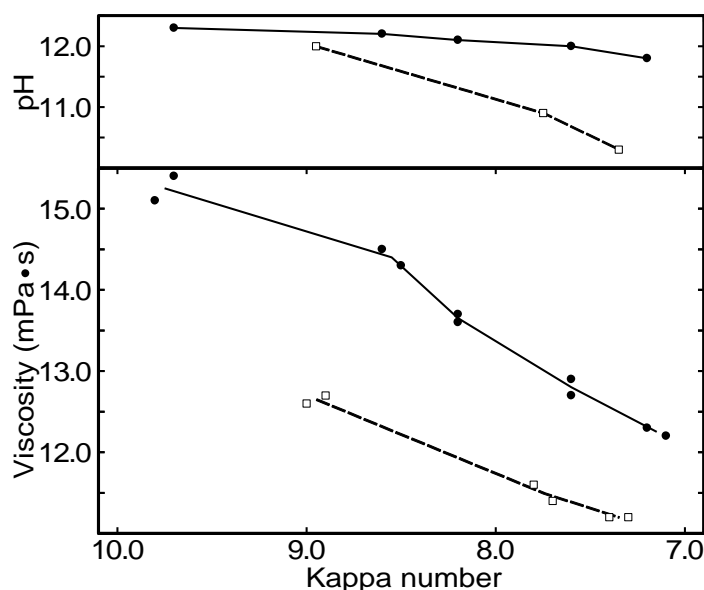


Fig. 3. Reaction selectivity and variation of pH when the hardwood unbleached kraft pulp was oxygen-delignified in the presence of MnO_2 generated *in situ* in pulp fibers at an oxygen pressure of 0.6 MPa, initial pH of 12.5, pulp consistency of 4.0%, and 95°C for 40, 80, or 120 min (white squares, long broken line). Black circles and solid line show the reference, and are the same as those shown in Fig. 2. Each oxygen delignification was conducted twice. Two lines showing the reaction selectivities are drawn by connecting the average values observed at these reaction times in the duplicated oxygen delignifications.

The reaction selectivity in the presence of the MnO_2 generated *in situ* in pulp fibers was surprisingly much lower than that in its absence (reference). This result suggests that active oxygen species were efficiently generated in pulp fibers and mainly degraded carbohydrates as well as lignin. A possible explanation for this result is that the oxidation of Mn^{2+} within the pulp fibers was not sufficient for complete conversion to MnO_2 , and hence, not only MnO_2 but also trivalent Mn species, among others, were generated *in situ*. This incomplete oxidation may have resulted from some interactions between Mn^{2+} and hydroxy groups in the pulp components. These incompletely oxidized Mn species must have been able to generate active oxygen species efficiently, which is quite different from the catalytic activity of MnO_2 . Because the result did not change when the O_2 bubbling was prolonged, the oxidation of Mn^{2+} must have reached a maximum by the method employed in this study.

We thus confirmed, contrary to our expectation based on the result of the model experiment, that the addition of any type of MnO_2 does not improve the reaction selectivity in oxygen delignification.

Successive Stages of Oxygen Delignification and MnO₂ Oxidation

Because MnO₂ can degrade lignin as an oxidant under acidic conditions,⁴²⁾ we tried to substitute a later stage of oxygen delignification with a MnO₂ oxidation stage under acidic conditions to examine the reaction selectivity of this strategy and compare it with that of the reference oxygen delignification.

Fig. 4 shows the reaction selectivity of the reference oxygen delignification (black circles) and successive stages of the oxygen delignification for 120 min, which was terminated at the third data point, and oxidation by synthetic MnO₂ at a pH of 2 (white triangles) or 1 (white inverted triangles) prepared by a H₂SO₄ solution for 60 or 180 min, respectively. The reaction selectivity of the successive stages was higher than that of the reference oxygen delignification when the synthetic MnO₂ oxidation was conducted at a pH of 2. However, the amount of acid was not sufficient to continue the reaction at this pH, because at a reaction time of 60 min the pH increased to 3.7, where MnO₂ does not sufficiently oxidize organic substances. Although the kappa number greatly decreased when the synthetic MnO₂ oxidation was conducted at a pH of 1, the reaction selectivity was not high. This lower reaction selectivity must have resulted from the extensive hydrolysis of carbohydrates at this pH.

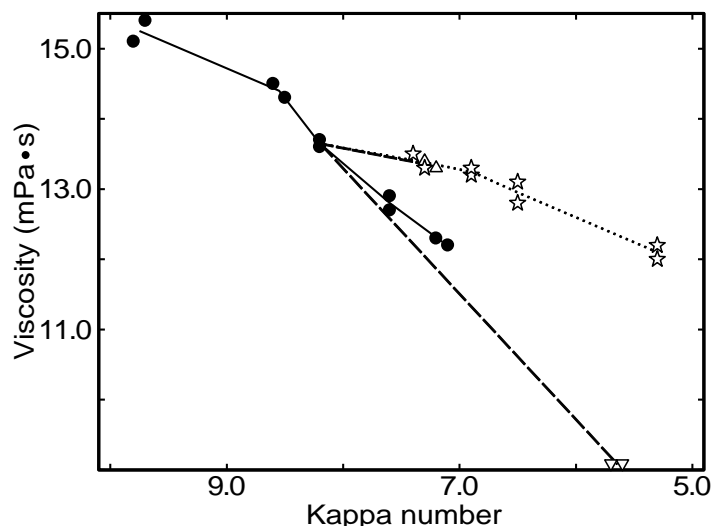


Fig. 4. Reaction selectivity in the reference oxygen delignification for 40, 80, 120, 240, or 360 min (black circles, solid line) and in the successive stages of the reference oxygen delignification for 120 min and the synthetic MnO₂ oxidation. The synthetic MnO₂ oxidation stage was conducted at a pH of 2 (white triangles, long broken line) or 1 (white inverted triangles, long broken line) prepared by H₂SO₄, or at a pH of 2 prepared by sulfate buffer (white stars, dotted line). Each oxygen delignification was conducted twice. All the lines showing the reaction selectivities are drawn by connecting the average values observed at the specific reaction times in the duplicated oxygen delignifications.

To continue the reaction and confirm the high selectivity at a pH of 2, the synthetic MnO₂ oxidation stage was carried out in a sulfate buffer solution. This solution contained sufficient acid to continue the reaction. Fig. 4 also shows the reaction selectivity of the successive stages of the reference oxygen delignification terminated at a reaction time of 120 min and synthetic MnO₂ oxidation at a pH of 2 using sulfate buffer. The data points of the synthetic MnO₂ oxidation stage were obtained at reaction times of 30, 90, 180, and 360 min. The reaction selectivity of the successive stages was much higher than the reference oxygen delignification when the pH of the synthetic MnO₂ oxidation stage was made to be 2 by sulfate buffer. The kappa number decreased from about 5 to 3 with almost the same viscosity by the substitution of the later stage of the common oxygen delignification with the synthetic MnO₂ oxidation at a pH of 2 using sulfate buffer. The degree of this improvement is rather surprising.

Because the successive stages showed much higher reaction selectivity than the reference oxygen delignification, the latter synthetic MnO₂ oxidation stage seems to be very effective for increasing the reaction selectivity. In this context, the hardwood unbleached kraft pulp was directly treated with the synthetic MnO₂ oxidation at a pH of 2 in the sulfate buffer solution without the common

oxygen delignification. Contrarily to the expectation, however, the delignification did not proceed in this synthetic MnO_2 oxidation, despite a slight viscosity drop. The synthetic MnO_2 may not have penetrated into pulp fibers when the unbleached pulp was directly treated with the synthetic MnO_2 .

Possibility on the Recycle of MnO_2

Because MnO_2 is reduced to Mn^{2+} in the synthetic MnO_2 stage, almost all the MnO_2 can be converted to soluble Mn^{2+} when MnO_2 is applied in an appropriate amount. After filtration and washing of the pulp, all the Mn^{2+} is present in the filtrate (effluent) with organic matter. The Mn^{2+} can be reconverted to precipitates of MnO_2 by O_2 bubbling under alkaline conditions, and the MnO_2 can be isolated by filtration. Most co-present organic matter in the effluent would not precipitate even under alkaline conditions.

MnO_2 can be added before the initial oxygen delignification process because, as shown in Fig. 2, the addition of MnO_2 does not have a large effect on the reaction selectivity. In this context, it is possible to filter the reconverted MnO_2 not with filter paper but by using unbleached pulp, which can then be subjected to the successive stages.

CONCLUSIONS

1. The addition of MnO_2 suppressed the degradation of a carbohydrate model compound, MGP, when it was treated under oxygen delignification conditions together with a phenolic lignin model compound, Valc. This result is attributed to the catalytic action of MnO_2 to decompose peroxides without the formation of any active oxygen species.
2. The addition of MnO_2 did not have any meaningful effect on the reaction selectivity in oxygen delignification of hardwood unbleached pulp. This is because the MnO_2 was present not within but only outside of the pulp fibers.
3. When MnO_2 was generated *in situ* in pulp fibers and the fibers were subjected to oxygen delignification, the reaction selectivity was much worse than the oxygen delignification without the addition of MnO_2 . This is because the *in situ* generation of MnO_2 was not complete, and not only MnO_2 but also trivalent Mn species, among others, were generated in the pulp fibers, catalyzing the decomposition of peroxides to generate active oxygen species.
4. The successive stages of common oxygen delignification for 120 min followed by synthetic MnO_2 oxidation at a pH of 2.0 using a sulfate buffer solution showed a much higher reaction selectivity than that of the common oxygen delignification.

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