

論文の内容の要旨

生物材料科学 専攻

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論文題目 : Studies on Introduction of MnO₂ into Prebleaching Stage and Mechanism of MnO₂ Oxidation of Lignin Model Compounds

(前漂白過程への MnO₂ の導入およびリグニンモデル化合物の MnO₂ 酸化機構に関する研究)

1. Introduction

Although MnO₂ is a recyclable chemical owing to its insolubility and oxidation-reduction interconversion with soluble Mn²⁺, which interests us to utilize MnO₂ in biomass conversion processes, the catalytic activity of MnO₂ in oxygen delignification and its potential as a delignification agent are still unclear.^[1] In this study, MnO₂ was added to oxygen delignification (prebleaching) stage or utilized in prebleaching stage as an oxidant to examine its catalytic activity or oxidation ability as a potential delignification agent, respectively. Besides, simple non-phenolic lignin model compounds were oxidized by MnO₂ to examine the oxidation mechanism in detail.

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

The serious problem in oxygen delignification is the severe degradation of carbohydrates, which is caused by active oxygen species (AOS) generated from decomposition of secondarily produced peroxides. Because MnO₂ catalyzes the self-decomposition of H₂O₂ to be H₂O and O₂ without formation of any AOS, MnO₂ is also expected to catalyze decomposition of peroxides without any formation of AOS when it is added to an oxygen delignification process. In this context, a carbohydrate model compound, methyl β-D-glucopyranoside (MGP), was treated under oxygen delignification conditions (1.0 MPa O₂, 0.5 mol/L NaOH, 95°C) together with a phenolic lignin model compound, vanilly alcohol (Valc, 4-hydroxy-3-methoxybenzyl alcohol), in the presence of MnO₂. In this system, Valc reacts with O₂ to consequently generate AOS which attack MGP. Because MGP was hardly degraded (**Figure 1**) in this system, it was suggested that MnO₂ is a potential protector of carbohydrates. When MGP was treated similarly in the presence of Fe species in a previous study, MGP was severely degraded.^[2]

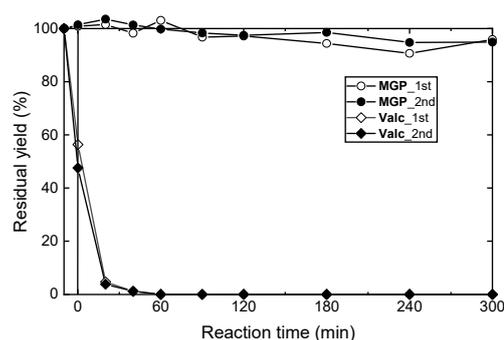


Figure 1 Time course of changes in the residual yields of MGP and Valc when treated together under conditions simulating oxygen delignification in the presence of MnO₂.

MnO₂ was added to an oxygen delignification process of hardwood unbleached kraft pulp (kappa number: 14.2, viscosity: 21.5 mPa•s) under an O₂ pressure of 0.5 MPa at an initial pH of 12.5 pulp consistency of 4.0%, and 95°C to examine whether or not the addition of MnO₂ protects carbohydrates from degradation. The addition of MnO₂ did not suppress the degradation of carbohydrates in the comparison with the reference oxygen delignification without the addition of MnO₂ (**Figure 2a**). Because MnO₂ must have existed at outside of pulp fibers in this case, hardwood pulp was then oxygen-delignified after MnO₂ was *in-situ* generated in pulp fibers. The pulp was immersed in an acidic MnSO₄ solution to penetrate Mn²⁺ into fibers, and then the Mn²⁺ was oxidized to MnO₂ by O₂ bubbling after alkalification. The addition of the *in-situ* generated MnO₂ had a deleterious effect on the degradation of carbohydrates (**Figure 2b**). The O₂ bubbling could not probably oxidize Mn²⁺ to MnO₂ completely to remain some active Mn³⁺-related species *etc.* Comprehensively, it was not successful to utilize MnO₂

as a protector of carbohydrates in the oxygen delignification process.

Because MnO_2 is a potential oxidant of lignin under acidic conditions, it is significant to introduce a MnO_2 oxidation process into prebleaching stage. A MnO_2 oxidation stage was thus introduced subsequently to an oxygen delignification process which was terminated at the middle stage, and the total bleachability was compared with that of the reference oxygen delignification. The MnO_2 oxidation stage was conducted at a pH of 2.0 (sulfate buffer solution) and 70°C . Switching the oxygen delignification to the MnO_2 oxidation in the middle stage had a beneficial effect after the whole process relatively to the reference oxygen delignification process (**Figure 2c**). It did not contrarily have any beneficial effect when the unbleached pulp was directly subjected to the MnO_2 oxidation without the first half oxygen delignification. Thus, the substitution of the MnO_2 oxidation stage with the latter half of the oxygen delignification can be a good bleaching sequence.

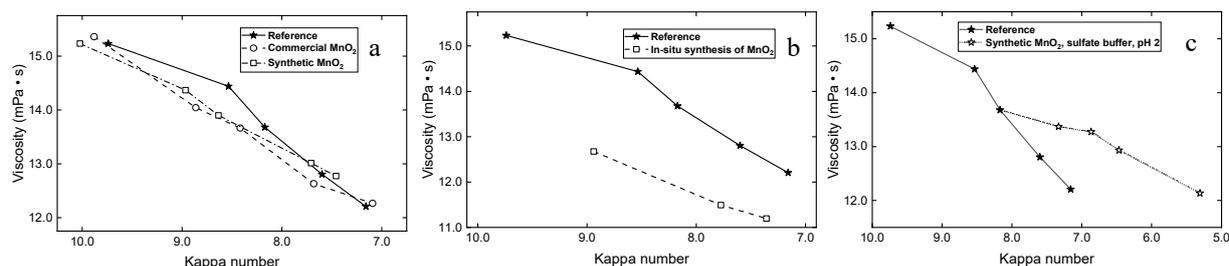


Figure 2 Correlations between pulp viscosity and kappa number during several bleaching processes and reference oxygen-alkali bleaching. a): Addition of MnO_2 , b): Addition of MnO_2 into pulp fibers by the *in-situ* generation, c): Successive treatment of the oxygen-alkali bleaching and MnO_2 oxidation.

3. Differences in the Mechanisms of MnO_2 Oxidation between $\text{C}_6\text{-C}_1$ -type Monomeric Lignin Model Compounds with the *p*-Hydroxyphenyl, Guaiacyl, and Syringyl Nuclei

It is generally known that MnO_2 oxidizes a benzyl hydroxy to the corresponding carbonyl group. In this chapter, $\text{C}_6\text{-C}_1$ -type monomeric lignin model compounds (**Figure 3**) were oxidized by MnO_2 at a pH of 1.5 and room temperature to examine the difference in the oxidation reactions between *p*-hydroxyphenyl (**H**), guaiacyl (**G**), and syringyl (**S**) types. The **E**-type compounds were employed in this chapter, because the total Hammett's substituent constants (σ values) of two methoxy groups of the **G**-type compounds is -0.153 ($= -0.268$ (*para*) + 0.115 (*meta*)), which is close to that of the ethyl group of the **E**-type compounds, -0.151 . Reactivity at the benzyl position of an aromatic compound with functional groups on the aromatic nucleus in a chemical reaction commonly correlates well with their σ values.

Although MnO_2 commonly oxidizes alcohol groups present at the benzyl position, it certainly oxidized the **G**- and **S**-nuclei of compounds **I_G** and **I_S**, respectively, which do not have the benzyl position and substructures corresponding to the side-chain portion of lignin, under the employed conditions. Based on the observation in this chapter, three possible reaction modes can be proposed for the MnO_2 oxidation of compounds **II** and **III**, as shown in **Figure 4**.

Mode **1** is direct oxidation of the benzyl position to afford the corresponding benzaldehyde-type products **A** or **A'**, respectively, which is the general mode of MnO_2 oxidation (red in **Figure 4**). Mode **2** begins with the oxidation of the aromatic nucleus, but finally results in the oxidation of the benzyl position to afford products **A** or **A'**, respectively (blue in **Figure 4**). In this mode, the aromatic cation radical must be the primary intermediate, which

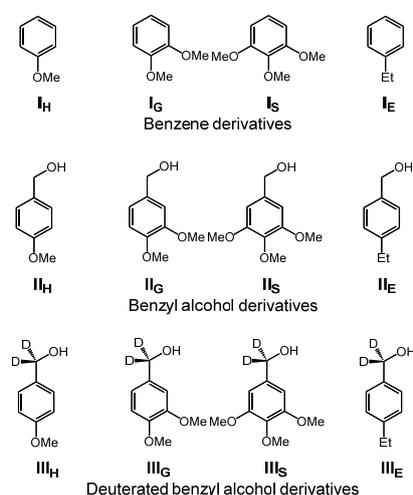


Figure 3 Non-phenolic lignin model compounds (the **H**-, **G**-, and **S**-types) and *p*-ethylphenyl type compounds (the **E**-types) employed in this chapter.

is generated by the one-electron oxidation of the aromatic nucleus by MnO₂. Mode 3 also begins with the oxidation of the aromatic nucleus, and finally results in the oxidative degradation of the aromatic nucleus to afford product **B** as well as other unidentified aliphatic reaction products (green in **Figure 4**).

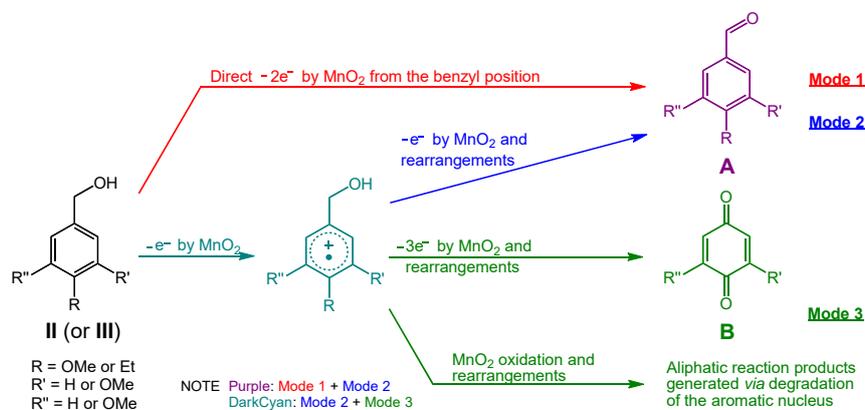


Figure 4 Three possible reaction modes in the MnO₂ oxidations of the benzyl alcohol analogues, compounds **II** and **III**.

The oxidation rates of the benzyl alcohol derivatives were in the order of **G**- > **S**- >> **H**- > **E**-type, which suggests that the rates are determined by the electronic effects of their methoxy and ethyl functional groups on not only their benzyl positions but also their aromatic π -electron systems. The kinetic isotope effect was observed in the MnO₂ oxidations of the same derivatives deuterated at their benzyl hydroxymethyl groups. The observed magnitudes, which are estimated from the ratio of the rate constant of each compound **II** to the corresponding compound **III**, were in the order of **E**- (8.6) >> **H**- (4.7) > **G**- (4.0) >> **S**-type (2.7). These magnitudes suggest that the contribution of oxidation of their aromatic nuclei (modes 2 and 3), in which the kinetic isotope effect must not be observed, increases in the reverse order with increasing the electron density of the aromatic nuclei.

4. Further Investigation of the Mechanisms of MnO₂ Oxidation using C₆-C₂-type Monomeric Lignin Model Compounds with the *p*-Hydroxyphenyl, Guaiacyl, and Syringyl Nuclei

It should be noted that hydroxyl groups at the benzyl position in lignin samples commonly exist as secondary alcohols rather than primary alcohols like the C₆-C₁-type monomeric lignin model compounds used in Chapter 3. In this chapter, representative C₆-C₂-type monomeric lignin model compounds (**Figure 5**), in which benzyl hydroxyl groups exist as secondary alcohols, were reacted under the same conditions as those in Chapter 3 to compare differences in the MnO₂ oxidation between C₆-C₂-type monomeric lignin model compounds.

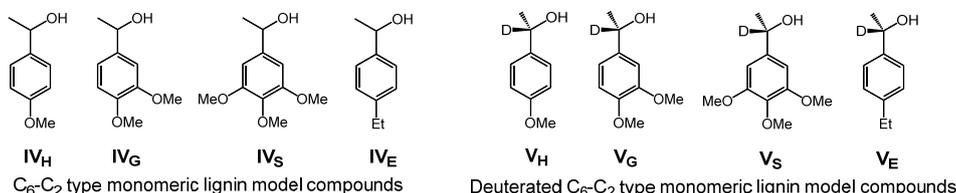


Figure 5 Non-phenolic C₆-C₂-type monomeric lignin model compounds (the **H**-, **G**-, and **S**-types) and *p*-ethylphenyl type compounds (the **E**-types) employed in this chapter.

MnO₂ oxidized compounds **IV** with the rates in the order **G**- > **S**- >> **H**- > **E**-type. This order is the same as that of the C₆-C₁-type compounds **II**. The magnitudes of the observed kinetic isotope effects in the MnO₂ oxidations (ratio of the rate constant of compound **IV** to the corresponding compound **V**) were in the order of **E**- (7.6) >> **H**- (4.2) > **G**- (3.3) >> **S**-type (1.9). The order is also the same as that observed in the reactions of the C₆-C₁-type compounds. However, the magnitude of each compound was smaller than that observed in the reactions between compounds **II** and **III**. These smaller magnitudes indicate that the MnO₂ oxidation of the aromatic nuclei

as the initial step (modes 2 and 3 in Figure 4) is more contributable among the three reaction modes 1, 2, and 3 in the MnO₂ oxidations of the C₆-C₂-type compounds IV and V than in those of the C₆-C₁-type compounds II and III. This must be owing to their larger steric factors at the benzyl carbon, interfering with the attack of MnO₂ on the carbons.

5. MnO₂ Oxidation of β -O-4-type Lignin Model Compounds with Syringyl or Guaiacyl Nucleus Focusing on the Difference in the Reactivities between the *erythro* and *threo* Diastereomers

It is well known that lignin is not simple monomeric structures, but a highly complex aromatic polymer. Among all the linkage-types between lignin monomeric units, β -O-4 bonds occupy with the highest content. In this chapter, six dimeric non-phenolic β -O-4-type lignin model compounds consisting of guaiacyl (G) and/or syringyl (S) nuclei with or without the *erythro* or *threo* side-chains (Figure 6) were oxidized by MnO₂ to examine the dependence of the reactivity on these differences.

Interestingly, major reaction products were not only the corresponding α -ketone derivatives, which are derived from the oxidation of the α -hydroxyl groups and common as products of the MnO₂ oxidation, but also benzaldehyde-type products derived from the cleavage of the C _{α} -C _{β} bond of each compound. In the reaction of SG or S'G carrying the S-nucleus as A-ring (Figure 6), 2,6-dimethoxybenzoquinone formed as a major reaction product derived from the oxidation of the S-nucleus followed by the cleavage of the C_{aryl}-C _{α} bond. In the reaction of GG or G'G, 2-methoxybenzoquinone was obtained. Because the MnO₂ oxidation of compound II_G, III_G, IV_G, or V_G afforded the corresponding benzaldehyde derivatives as the exclusive only major reaction product, 2-methoxybenzoquinone obtained in the reaction of GG or G'G must have originated from the oxidation of the B-ring of GG or G'G. Acetophenone-type compounds were obtained from the reaction of C₆-C₂-type of G'G or S'G, which is different from C₆-C₃-type of GG or SG.

The reaction rates of these model compounds depended on their structures. When the effect of the different aromatic A-rings, G- and S-nuclei, is focused, the reaction rates were in the order of: GG_{*erythro*} > SG_{*erythro*}, GG_{*threo*} > SG_{*threo*}, and G'G > S'G, respectively. These results indicate that the presence of the additional methoxy group on the S-nucleus of the A-ring relative to the G-nucleus decelerates the reaction. For the C₆-C₃-type of GG or SG, the MnO₂ oxidation of the *threo* isomers was faster than the corresponding *erythro* isomers, namely, the order of these rates was GG_{*threo*} > GG_{*erythro*}, or SG_{*threo*} > SG_{*erythro*}, respectively. It is presumed that MnO₂ aggregates can approach the *threo* compounds more readily than the *erythro* compounds due to the stereostructures of the side-chain. When the side-chain structure is focused, the reaction rates were in the order of: GG_{*threo*} > GG_{*erythro*} > G'G and SG_{*threo*} > S'G > SG_{*erythro*}. These results indicate that the presence of the γ -hydroxymethyl group accelerates the reactions of the compounds carrying the G-nucleus as the A-ring while it accelerates or decelerates those carrying the S-nucleus as the A-ring depending on the side-chain structure. Therefore, the effect of the presence of the γ -hydroxymethyl group originates not only simply from the steric factor but also from some interactions with the type of the aromatic A-ring.

References

- [1] Johansson, E., Ljunggren, S., *J. Wood Chem. Technol.*, **14** (4), 507-525 (1994)
 [2] Yokoyama, T., Nakagawa, A., Konishi, F., Matsumoto, Y., *J. Wood Sci.*, **57** (6), 512-519 (2011)

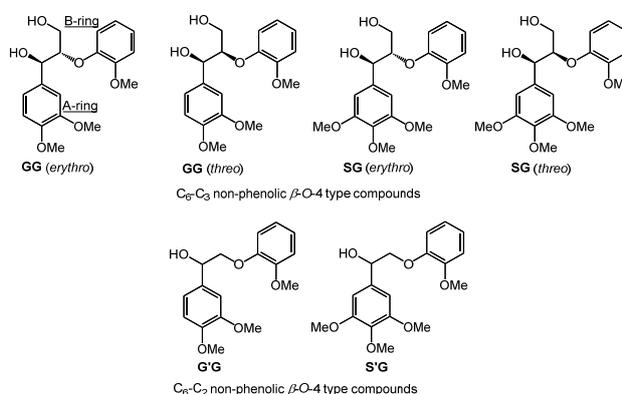


Figure 6 Chemical structures of the dimeric non-phenolic β -O-4 type lignin model compounds employed in this chapter.