研 究 報 文

パルプ漂白中のアルカリ—過酸化水素の役割

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The Role of Alkali-Hydrogen Peroxide during Pulp Treatment

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Semi-quantitative method was developed for the determination of α -carbonyl structure in solid lignin. Deuteride reduction followed by nitrobenzene oxidation was applied to oxygen bleached softwood kraft pulp (NOKP) in order to evaluate the reactivity of hydrogen peroxide with α -carbonyl structures in lignin. We already showed that hydrogen peroxide attacked α -carbonyl structures in lignin very clearly during milled wood lignin treatment. However, when NOKP and hydrogen peroxide treated NOKP were analyzed by this method, the role of hydrogen peroxide was not clearly observed in terms of the content α -carbonyl structure. By the analysis of alkali treated NOKP without hydrogen peroxide, it was suggested that, at the hydrogen peroxide treatment, the effect of hydrogen peroxide on the α -carbonyl structure might be hidden by the generation of α -carbonyl structure and that actually hydrogen peroxide effectively degrades those newly produced structures. Hydrogen peroxide was found to play such a "hidden role" not only for newly produced α -carbonyl structures but also for the newly produced permanganate consuming substances during the treatment.

Keywords : kraft pulp, lignin, α -carbonyl structure, hydrogen peroxide, kappa number

分類 : K₈ 過酸化水素漂白, Y₈ リグニン化学

1. Introduction

The presence of various types of carbonyl groups in lignin has been well confirmed although carbonyl group is not present in lignin precursors, coniferyl alcohol and sinapyl alcohol. Fig. 1 shows examples of those carbonyl groups. Some carbonyl structures are present in side-chain part of phenylpropane units. Those are coniferylaldehyde structure (A), detached side-chain structures (B), and, α -carbonyl structures

(C). In technically processed lignins, some carbonyl groups may be present as quinone type structures (D).

Due to a large positive charge of carbonyl carbon, carbonyl groups are usually reactive towards various types of nucleophiles. Among many types of carbonyl groups possibly present in lignin, α -carbonyl structures are quite interesting from the point of lignin reaction during delignification processes. The presence of α -carbonyl group at side-chain makes the reactiv-

Fig. 1 Carbonyl groups possibly present in lignin

ity of aromatic nuclei of lignin towards electrophilic oxidants such as oxygen and ozone very low¹⁾²⁾. Therefore, formation and/or presence of α -carbonyl structure during oxygen and ozone bleaching are not beneficial for the delignification reaction³⁾. On the other hand, the great reactivity of carbonyl groups towards nucleophiles may bring about a big advantage for the reaction of α -carbonyl structures with hydrogen peroxide as were suggested by many model experiments⁴⁾⁵⁾. This reaction will result in the fragmentation of lignin⁴⁾⁶⁾⁷⁾.

The present research was conducted in order to confirm whether or not the reaction of hydrogen per-

oxide with α -carbonyl structures really takes place during the hydrogen peroxide treatment of pulp, and if it takes place, what condition is preferable for this reaction. For this purpose, the authors had developed a method to estimate the content of α -carbonyl structures in lignin that are applicable to solid lignin such as a residual lignin in pulp⁸⁾. The principle of this method is illustrated schematically in Fig. 2. This method consisted of two successive treatments, labeling of α -carbonyl structure with C-D linkage by reducing it to hydroxymethine structure (E) and subsequent nitrobenzene oxidation to D-vanillin (F) from the labeled structure. On the other hand, if side-chain

Fig. 2 Scheme for the estimation of α -carbonyl structures in lignin

α -position is not a carbonyl structure but a hydroxymethine structure with usual C-H linkage (G), nitrobenzene oxidation will give H-vanillin (H). Thus the proportion of D-vanillin/H-vanillin produced after two successive treatments will give a quantitative indication for the α -carbonyl structure. Hydrogen peroxide treatment of lignin is usually conducted under much milder alkaline condition than pulping. The effect of such mild alkaline condition on the kappa number of pulp and the role of hydrogen peroxide during the treatment will also be discussed.

2. Experiment

2.1 Materials

Oxygen bleached kraft pulp (NOKP 1) was prepared in the laboratory by oxygen bleaching of softwood unbleached kraft pulp (Nippon Paper Industries, kappa number 11.5). Oxygen bleaching condition was pulp concentration 3 % in 0.03 N aqueous sodium hydroxide, reaction temperature 90°C, reaction time 3 hours, oxygen pressure 0.6 Mpa. NOKP 1 was used to study the behavior of α -carbonyl structure in lignin during hydrogen peroxide bleaching. Oxygen pre-bleached pulp (NOKP 2, kappa number 9.197 after washing) was made by Nippon Paper Industries, and was used to examine the hidden role of hydrogen peroxide.

Other reagents were commercially available.

2.2 Removal of α -carbonyl structure from pulp by hydrogen peroxide treatment

1) Hydrogen peroxide treatment

NOKP 1 (0.5 g dry weight) was treated with 5 mmol hydrogen peroxide in 50 ml aqueous sodium hydroxide at pH 10 and pH 13, reaction temperature 70°C, reaction time 10, 30, 60 min. EDTA was added to the reaction system to suppress the metal-catalyzed decomposition of hydrogen peroxide. As control run of hydrogen peroxide treatment, pulp was treated under the same reaction condition without the addition of hydrogen peroxide and subjected to the same analysis.

2) Estimation of α -carbonyl structure

After hydrogen peroxide treatment, pulps were separated from the reaction liquor by filtration and washed by deionized water, and then subjected to the estimation of α -carbonyl structures according to our new method⁹⁾ shown in Fig. 2. Whole hydrogen perox-

ide-treated pulp was placed in about 15 ml of diluted NaOD in D₂O solution and mixed with excess amount of NaBD₄ (100 mg or above) and kept at room temperature for 12 hours. The pulp was separated from the reducing liquor and washed thoroughly by water. The whole recovered pulp was put in 10 ml of 0.5 mol/L LiOH aqueous solution in a stainless autoclave and mixed with 0.15 ml of nitrobenzene. The autoclave was kept in a oil bath under 170°C for 60 min.

After nitrobenzene oxidation, oxidation products (vanillin and others) were extracted from the acidified reaction mixture. Vanillin was dissolved in acetone and subjected to GC-MS analysis without derivatization. The proportion of D-vanillin and H-vanillin, and the absolute amount of H-vanillin and D-vanillin were calculated based on the peak height of two fragmentation ion at m/z 152 and 153 according to a method described in our previous paper⁹⁾.

2.3 The hidden role of hydrogen peroxide to reduce kappa number of pulp

NOKP 2 (1 g dry weight) was treated with 10 mmol hydrogen peroxide in 100 ml aqueous sodium hydroxide at pH 10 and pH 13, reaction temperature 70°C or 90°C, reaction time 10, 30, 60 min. After hydrogen peroxide treatment, pulp was filtrated and washed by water. Filtrate and washing were combined and was added small amount of manganese dioxide to destroy residual hydrogen peroxide. After the destruction of hydrogen peroxide, manganese dioxide in the combined filtrate was removed by filtration very carefully. Permanganate consumption of pulp was measured according to micro kappa number method (TAPPI Useful Method 246). Permanganate consumption of dissolved lignin was also measured in a similar way as the micro kappa number method. Namely, aliquot of combined filtrate was mixed with 10 ml of 4 N H₂SO₄ and the total volume was adjusted to 100 ml. Permanganate solution (0.02 mmol/L, 10 ml) was poured into the mixture and kept at 25°C for 10 minutes. Procedure after this was exactly the same as micro kappa number method.

As control run of hydrogen peroxide treatment, pulps were treated under the same reaction condition without the addition of hydrogen peroxide and subjected to the analysis of permanganate consumption of both pulp and liquor as described above.

3. Results and Discussion

3.1 Removal of α -carbonyl structure from pulp by hydrogen peroxide treatment

The reaction of α -carbonyl structure with hydrogen peroxide has been expected to occur on lignin by many researchers. One typical reaction is Dakin-like reaction, which is illustrated in Fig. 3. By this type of reaction or similar Baeyer-Villiger reaction, or by related reactions, lignin structures having α -carbonyl structure can be degraded. It is a big advantage of hydrogen peroxide treatment, because, as was discussed in the introductory part, α -carbonyl structure is hardly oxidized by other oxygen related reagents such as molecular oxygen and ozone.

In our previous report⁹⁾, milled wood lignin that had been enriched with α -carbonyl structure by DDQ oxidation (DDQ-MWL) was treated with hydrogen peroxide under different pH conditions. The reaction products were subjected to the scheme shown in Fig. 2 for the estimation of α -carbonyl structure. It was proven that treatment under pH 13 was more

preferable than pH 10 for the reaction of α -carbonyl structure with hydrogen peroxide.

In the present report, softwood oxygen prebleached kraft pulp (NOKP 1) was treated by hydrogen peroxide under different reaction conditions, and resultant pulps were subjected to the estimation of α -carbonyl content by the scheme shown in Fig. 2. By the scheme, the decrease of α -carbonyl structure should be shown as the lower D-vanillin/H-vanillin ratio of nitrobenzene oxidation products.

Fig. 4 A shows the D-vanillin/(D-vanillin + H-vanillin) ratio obtained for NOKP 1 after hydrogen peroxide treatments. Results for α -carbonyl enriched MWL⁹⁾ are also shown in Figure 4 B for a comparison purpose. Contrary to the case of MWL, the effect of hydrogen peroxide on the α -carbonyl structure was not clearly observed for NOKP 1 when the proportion of D-vanillin to total vanillin was evaluated. The proportion was almost constant throughout the reaction. From the data shown in this figure, it seems as if hydrogen peroxide did not effectively react with α -carbonyl structure in pulp residual lignin in spite of its

Fig. 3 Degradation of lignin by reaction of α -carbonyl structure with hydrogen peroxide

Fig. 4 Ratio of D-vanillin to total vanillin produced by nitrobenzene oxidation treated with hydrogen peroxide.

Graph A : NOKP 1, Graph B : DDQ-MWL

Reaction condition a : pH 13 without H_2O_2 , b : pH 10 with H_2O_2 , c : pH 13 with H_2O_2

Fig. 5 Yield of D-vanillin and H-vanillin by nitrobenzene oxidation of NOKP 1 treaded with hydrogen peroxide. Data point is 0, 10, 30, 60 min
 A : pH 10 H₂O₂ treatment, B : pH 13 H₂O₂ treatment, C : pH 13 alkali treatment
 Kappa number

positive effect on DDQ-MWL.

However, when the absolute yields of D-vanillin and H-vanillin from NOKP 1 before and after hydrogen peroxide treatments were evaluated (Fig. 5 A to 5 C), the effect of hydrogen peroxide treatment at pH 13 was clearly observed. As is shown in Fig. 5 B, both the yields of D-vanillin and H-vanillin decreased effectively under pH 13, which is in a clear contrast with the data under pH 10 (Fig. 5 A). In the experiment of DDQ-MWL, hydrogen peroxide treatment resulted in the decrease of only D-vanillin but not H-vanillin (data not shown). The difference between MWL experiment and pulp experiment should be able to explain the removal of lignin from the pulp with hydrogen peroxide. When lignin removal, not only α -carbonyl structure (origin of D-vanillin) but also non- α -carbonyl structures (origin of H-vanillin) must be removed, even though hydrogen peroxide reacts almost exclusively with α -carbonyl structure. Under pH 10, hydrogen peroxide treatment did not cause any change in the yield of both D- and H-vanillins (Fig. 5 A).

What is interesting was the yield of D- and H-vanillins from the pulp treated under alkali at pH 13 without hydrogen peroxide (Fig. 5 C). The yields increased tremendously by alkali treatment. When the differences between the data of Fig. 5 B and 5 C are taken into consideration, the actual effect of hydrogen peroxide on removing α -carbonyl structure must be

more significant, indicating that hydrogen peroxide played a "hidden role" during the treatment of NOKP under pH 13.

At the moment, the reason why yields of vanillin increased only by mild alkali treatment is not clear. Although the pulp had already experienced several alkali treatments such as cooking and oxygen bleaching, it must be assumed that lignin and/or carbohydrates still can change by mild alkali treatment even after strong alkali treatments. The importance of "mild alkali chemistry" of wood components seems to be suggested.

3.2 The hidden role of hydrogen peroxide to reduce kappa number of pulp

In this section, the ability of hydrogen peroxide to oxidize lignin and/or to remove lignin from pulp was evaluated. It is a well-accepted idea that hydrogen peroxide is not a very good oxidizing reagent for lignin. But it is also well recognized that active oxygen species produced from hydrogen peroxide are not always harmful but could contribute to the delignification reaction. The ability of hydrogen peroxide to oxidize lignin could be evaluated by measuring the permanganate consumption of both pulp and bleaching waste liquor. If total permanganate consumption decreases after certain treatment, it suggests that lignin was oxidized. The similar analysis was already applied successfully for the measurement of oxidation reaction during oxygen bleaching process¹⁰⁾.

Because the kappa number of NOKP 1 after the hydrogen peroxide treatment was too low to evaluate, a series of experiments in this section was conducted by the use of different pulp, NOKP 2. In the previous section, it was shown that the role of hydrogen peroxide on the α -carbonyl structure became visible by the comparison with the blank alkali run. Therefore the results obtained here were always evaluated by the comparison with blank alkali run.

In Fig. 6, the permanganate consumption of both hydrogen peroxide-treated pulp and reaction liquor obtained under various reaction conditions are systematically compared. Permanganate consumption was simply expressed as kappa number. Kappa number of reaction liquor was calculated from its permanganate consumption measured under the similar condition as kappa number of pulp. Hydrogen peroxide treatment under pH 10 (C and G) seems quite interesting because total permanganate consumption decreased only in these two cases. Because the decrease of total permanganate consumption suggests the occurrence of lignin oxidation during hydrogen peroxide, it has to be explained why lignin oxidation pro-

ceeded effectively under pH 10. Two explanations are possible at this moment. One explanation is that active oxygen species reacts with lignin more preferably at lower pH than higher pH. This is already shown by Yokoyama et al for oxygen bleaching process¹¹⁾. Another is that the production of active oxygen species from hydrogen peroxide beneficial for lignin oxidation is more efficient under lower pH. Considering the pKa value of hydrogen peroxide (10.8), this is also highly presumable.

Although the total permanganate consumption decreased under only pH 10, the decrease of pulp kappa number was more significant under pH 13 (compare pulp kappa numbers A and C, or, E and G). In other words, delignification proceeded more significantly under higher pH. It is well recognized that under pH 13 hydrogen peroxide decreased the pulp kappa number by a way other than oxidative degradation of lignin.

When high (pH 13 : Fig. 6 A, B, E, F) and low (pH 10 : Fig. 6 C, D, G, H) alkalinities concentrations were compared, more lignin (or permanganate consuming substances) dissolved into liquor under the higher al-

Fig. 6 Increase and decrease of kappa number of NOKP 2 and reaction liquor treated with hydrogen peroxide. Data points are 0, 10, 30, 60 min.

A : pH 13 90°C H₂O₂ treatment, B : pH 13 90°C alkali treatment, C : pH 10 90°C H₂O₂ treatment, D : pH 10 90°C alkali treatment, E : pH 13 70°C H₂O₂ treatment, F : pH 13 70°C alkali treatment, G : pH 10 70°C H₂O₂ treatment, H : pH 10 70°C alkali treatment

kalinity concentration. In alkali treatment without hydrogen peroxide, total kappa number increased (Fig. 6 B, D, F, H). These results showed that alkali treatment produced permanganate-consuming substances from NOKP. Those two results demonstrates that alkali has two roles—positive and negative. Negative role of alkali is to produce those permanganate-consuming substances and positive role is to remove those substances partly from pulp.

However, when hydrogen peroxide is present results become quite different. Presence of hydrogen peroxide inhibited the increase in permanganate consumption of pulp against the creation of those substances by the action of alkali (Fig. 6 A, C, E, G). Under high alkali condition in the presence of hydrogen peroxide (A, E), total permanganate consumption was almost constant during the treatment. As stated above, in all experiments in the presence hydrogen peroxide, pulp kappa number decreased. Under the same temperature, the decrease of pulp kappa number was almost same regardless of the alkalinity (A and C, or, E and G). These results suggest that the removal of permanganate consuming substances in the pulp is not affected by the ionization of hydrogen peroxide. The main role of ionized hydrogen peroxide seems to be the inhibition of re-attachment of dissolved permanganate consuming substances to the pulp or the inhibition of production of permanganate consuming substances (A and B, or, E and F).

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