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Comparison of monopersulfuric acid and sulfuric acid as prehydrolysis reagents for high-purity cellulose production from Japanese cedar via soda–anthraquinone (soda–AQ) cooking and totally chlorine-free (TCF) bleaching

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Abstract

Prehydrolysis/soda–anthraquinone (AQ) cooking has emerged as a promising strategy for the production of high-purity cellulose; however, optimization of the prehydrolysis stage is still required. In this study, monopersulfuric acid (MPS) was evaluated as a prehydrolysis reagent for the production of cellulose from Japanese cedar (*Cryptomeria japonica*) via prehydrolysis/soda–AQ cooking and compared with sulfuric acid (H_2SO_4) under equivalent acid dosages. At high acid dosage, MPS-treated wood showed lower residue yield than H_2SO_4-treated wood, whereas H_2SO_4 treatment resulted in higher Klason lignin content after prehydrolysis. Nitrobenzene oxidation further confirmed lower vanillin yields in H_2SO_4-treated wood than in MPS-treated wood, indicating that lignin condensation was suppressed when MPS was used for prehydrolysis. Sugar analysis of the prehydrolysis liquor (PHL) showed that at low H_2SO_4 dosage (4.8%), MPS and H_2SO_4 treatments afforded comparable untreated total sugar contents. However, at high dosage (≥ 24%), the untreated total sugar content was lower in MPS-treated PHL, suggesting oxidative transformation or degradation of released carbohydrates. When soda–AQ cooking was conducted after MPS treatment, the resulting pulp showed lower kappa number, improved oxygen-bleaching response, and higher brightness of the final totally chlorine-free (TCF) bleached pulp (83.0% ISO) compared with soda–AQ cooking performed after H_2SO_4 treatment or without prehydrolysis. However, the brightness differences among the pulps became smaller after the subsequent TCF bleaching sequence, despite the higher brightness of MPS/soda–AQ pulp after oxygen bleaching. Although pulp viscosity did not reach dissolving-pulp grade specifications, the bleached pulp exhibited high glucan purity (≈96%) indicating applicability for high-purity cellulose applications. Overall, the results demonstrate that MPS/soda–AQ is a viable, sulfide-free and chlorine-free route for obtaining cellulose with high glucan content from Japanese cedar. These findings position MPS/soda–AQ cooking as a new biorefinery process for producing high-purity cellulose streams rather than conventional dissolving pulp for advanced material applications from domestic softwood resources in Japan.

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Keywords Monopersulfuric acid, Cellulose, Prehydrolysis/soda–AQ, Prehydrolysis liquor, Totally chlorine-free bleaching

Introduction

Planted forests account for about 40% of Japan's total forest area, many of which have now matured into well-developed stands with diverse values to society. The major species in these planted forests is Japanese cedar (*Cryptomeria japonica*), owing to its broad adaptability to various site conditions and its high growth rate [1]. Appropriate harvesting and utilization of these trees are essential for maintaining a sustainable forest cycle. However, in some regions of Japan, wood utilization risks stagnation due to population decline and other socio-economic factors. On the basis of cohort changes observed between 2010 and 2015, Tamura estimated that the number of forestry workers in Japan will decrease from 45,000 in 2015 to about 32,000 in 2030 (approximately a 30% decrease) and further to around 23,000 by 2050, representing nearly a 50% reduction compared with 2015 [2]. To revitalize forestry and promote regional resource circulation, developing high-value-added products from Japanese cedar grown in mountainous areas is becoming increasingly important.

Dissolving pulp refers to pulp with high cellulose content and a minimum amount of inorganic and non-cellulosic organic impurities [3]. As a representative form of high-purity cellulose, dissolving pulp is used as an essential raw material for cellulose rayon, cellulose esters, cellulose ethers, and other new cellulose-based products, including cellulose nanocrystals (CNCs) and cellulose filaments [4–6]. Traditionally, dissolving pulp used for such applications is produced via acid sulfite process or prehydrolysis followed by kraft cooking using sodium sulfide (Na_2S) [7–9]. However, the use of acid sulfite or Na_2S generates characteristic odors [10], potentially limiting the implementation of these processes in small-scale facilities, especially in regions subject to stringent environmental regulations. Therefore, an environmentally friendly and regionally adaptable high-purity cellulose production process is still required.

Prehydrolysis/soda–anthraquinone (soda–AQ) cooking has been investigated as an alternative delignification method to the prehydrolysis/kraft cooking for producing high-purity cellulose. In this process, prehydrolysis is conducted to remove hemicelluloses, followed by alkaline delignification with sodium hydroxide (NaOH) and a small amount of a catalyst (AQ in this case). To achieve this, diverse raw materials have been examined, including acacia [11, 12] and eucalyptus [12] as hardwoods, spruce and pine [13] as softwoods, and several nonwood materials, such as bamboo [14], sugarcane bagasse [15], *Metroxylon sagu* palm fronds [16], and oil palm empty fruit bunches [17]. Prehydrolysis methods include autohydrolysis under high-temperature hydrothermal conditions, as well as hydrolysis using mineral acids, such as nitric acid [17], sulfurous acid (H_2SO_2), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) [18]. Empirically, softwoods are more difficult to delignify than hardwoods under alkaline conditions [19]. Because soda–AQ cooking does not use Na_2S, its delignification behavior during cooking and the bleaching response of the pulp may differ from those of the kraft process. In addition, prehydrolysis conditions that promote lignin condensation or cellulose degradation may reduce delignification efficiency during subsequent soda–AQ cooking. Therefore, optimization of the prehydrolysis stage is essential for producing high-purity cellulose in prehydrolysis/soda–AQ cooking.

The prehydrolysis liquor (PHL) generated during high-purity cellulose production via prehydrolysis kraft or soda–AQ cooking contains various hemicellulose-derived sugars, acetic acid, and furfural as well as other organic compounds [20]. The chemical and biochemical conversion of these organic components into value-added compounds constitutes an active area of research. In particular, several studies have focused on the recovery and conversion of mono- and oligosaccharides (e.g., xylose and xylo-oligomers) into value-added products, such as furfural [21–23], xylitol [24, 25], acetic acid [23, 26], and bioethanol [27]. Such integrated utilization of hemicelluloses highlights the potential of combining cellulose production with biorefinery processes for enhancing the overall resource efficiency of woody biomass conversion. Thus, analyzing the sugar content in the PHL provides fundamental information for evaluating its possible valorization.

Peracids such as peracetic acid and monopersulfuric acid (MPS) are strong oxidants that react with lignin aromatic structures and induce reactions such as hydroxylation, demethylation, and cleavage of interunit aryl-ether linkages connecting lignin structural units, including β-*O*-4 bonds [28]. MPS, also known as Caro's acid, is synthesized from H_2SO_4 and hydrogen peroxide (H_2O_2) and has been applied in several kraft pulp bleaching processes owing to its strong oxidative potential [29]. During elementary chlorine-free (ECF) bleaching, the combined use of MPS and chlorine dioxide degrades

residual lignin while preserving carbohydrates more effectively than chlorine dioxide alone, thereby yielding bleached pulp with high brightness and minimal yield loss [30]. Moreover, Salaghi et al. reported that dissolving-grade hardwood pulp is successfully produced using prehydrolysis/kraft cooking followed by totally chlorine-free (TCF) bleaching with oxygen (O), MPS, and alkali extraction with H_2O_2 (E_p) in an O–MPS–E_p–MPS–E_p sequence [31]. Fiber bleaching achieves delignification via sequential acidic oxidation and alkaline extraction stages, through which lignin is progressively removed and fibers become nearly lignin-free. This efficiency can be attributed to the ready decomposition and dissolution in alkaline environments of oxidized lignin formed during the preceding acidic oxidation stage (i.e., the MPS stage) [32]. According to these insights, we hypothesized that using MPS in the prehydrolysis stage could facilitate delignification during the subsequent soda–AQ cooking step, similar to bleaching.

Herein, we propose a high-purity cellulose production process that combines MPS prehydrolysis with soda–AQ cooking (Fig. 1). Specifically, Japanese cedar chips are first treated with MPS, where reactive oxidative species generated from peroxides oxidize lignin aromatic structures and enhance delignification during the soda–AQ cooking stage without Na_2S. The unbleached pulp produced via MPS/soda–AQ cooking is then subjected to TCF bleaching by alternating MPS and E_p stages. This integrated MPS prehydrolysis and soda–AQ cooking process is expected not only to improve delignification efficiency but also to generate PHL containing sugars suitable for chemical or microbial conversion. In addition, the black liquor generated during soda–AQ cooking can be utilized for energy recovery as in conventional kraft mills, offering a potential pathway to establish a wood-based biorefinery system. The objectives of this study can be summarized as follows:

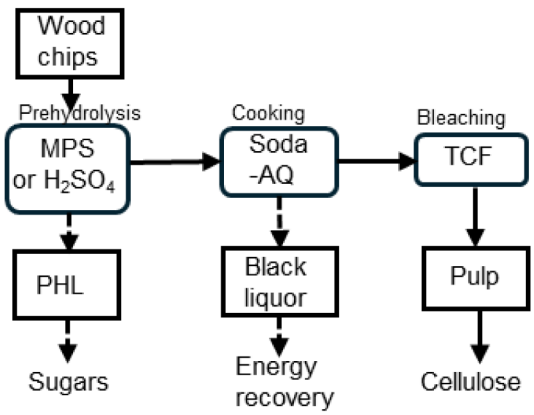


Fig. 1 Proposed scheme of prehydrolysis with MPS or H_2SO_4 followed by soda–AQ cooking for high-purity cellulose production and wood biorefinery process. Solid lines represent the flow of solid materials, and dashed lines represent the flow of liquid streams, including prehydrolysis liquor (PHL) and black liquor. Rectangular boxes with sharp corners indicate material streams, whereas those with rounded corners indicate process steps

To compare the yields and chemical compositions of Japanese cedar residues obtained after prehydrolyses between MPS and H_2SO_4 as the control.

To analyze the sugar compositions of PHLs obtained from MPS and H_2SO_4 prehydrolyses and to evaluate their potentials for chemical conversion and biorefinery applications.

To investigate the yields and kappa numbers of pulps obtained by MPS and H_2SO_4 prehydrolyses followed by soda–AQ cooking.

To evaluate the suitability of the resulting pulps for TCF bleaching for the chlorine-free production of high-purity cellulose.

Results and discussion

Comparison of yields between prehydrolysis of wood meal using MPS and H_2SO_4

To evaluate the role of oxidative species during prehydrolysis, Japanese cedar wood meals were treated with MPS or H_2SO_4 under identical conditions of temperature (120 °C) and time (1 h). In the initial experiments, wood meal was used to compare the effects of MPS and H_2SO_4 during prehydrolysis before conducting soda–AQ cooking experiments using wood chips. The yields of solid residues obtained after each treatment are shown in Fig. 2. For the MPS treatment, the H_2SO_4 dosage shown on the *x*-axis represents the amount of H_2SO_4 used for MPS synthesis. Therefore, the H_2SO_4 control treatment was conducted at the same H_2SO_4 dosage but without H_2O_2 (see "Materials and Methods" section). In both treatments, the solid yield decreased with increasing acid dosage. At lower H_2SO_4 dosages (< 15%), the yields were nearly identical between these two. For example, at a H_2SO_4 dosage of 14.4%, the yields were 81.2% after MPS treatment (3.0% MPS dosage) and 81.8% after H_2SO_4 treatment, indicating that the organic component removal proceeded to a similar extent. In contrast, when the H_2SO_4 dosage was increased to 72%, the yield was lower for the MPS-treated sample (73.1% at an MPS dosage of 15.0%) than for the H_2SO_4-treated one (75.9%), with the maximum difference reaching approximately 2.5 percentage points.

To clarify the origin of this difference, the chemical compositions of the treated residues were analyzed (Fig. 3). All lignin and carbohydrate contents and yields

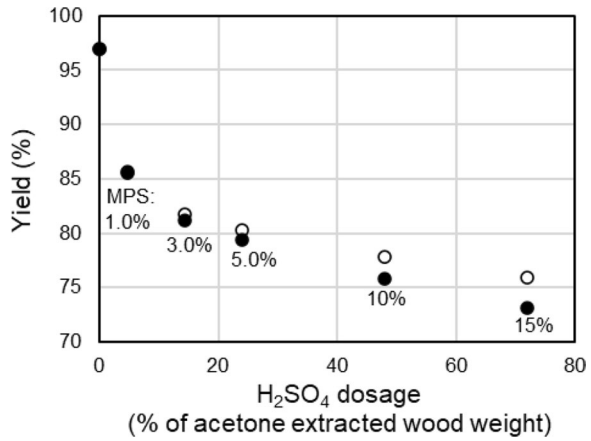


Fig. 2 Relationship between solid residue yield and H_2SO_4 dosage during prehydrolysis. The *x*-axis shows the H_2SO_4 dosage (% based on the acetone-extracted wood weight). For the MPS treatment, the amount of H_2SO_4 used for MPS synthesis are shown. In the MPS treatments, the dosages of MPS, residual H_2SO_4, and H_2O_2 were varied simultaneously by dilution of the same MPS stock solution (0.42 mol/L MPS, 2.02 mol/L H_2SO_4, and 0.52 mol/L H_2O_2). MPS (%) in the figure refers to its dosage (%) based on acetone-extracted wood weight. ● MPS and ○ H_2SO_4

described in this section are expressed on an oven-dry original acetone-extracted wood meal basis, consistent with Fig. 3. At 72% H_2SO_4 dosage, the glucan, mannan, and xylan contents after MPS treatment were 39.1%, 0.6%, and 1.2%, respectively—essentially identical to those obtained with H_2SO_4 treatment (39.3%, 0.6%, and 1.4%). This indicates that hemicellulose removal proceeded similarly regardless of the presence of oxidative species. In contrast, under the same conditions, the Klason lignin content after MPS treatment decreased to 31.0%, whereas H_2SO_4 treatment yielded 33.6%, even exceeding that of untreated wood (32.4%). The increase in Klason lignin content after H_2SO_4 treatment might be partially explained by the formation of carbohydrate-derived acid-insoluble compounds during prehydrolysis, which were quantified as Klason lignin. Overall, these results indicate that MPS prehydrolysis removes hemicellulose to a similar extent to H_2SO_4 prehydrolysis but results in a lower Klason lignin content, likely reflecting both enhanced lignin release and suppression of carbohydrate-derived acid-insoluble compound formation.

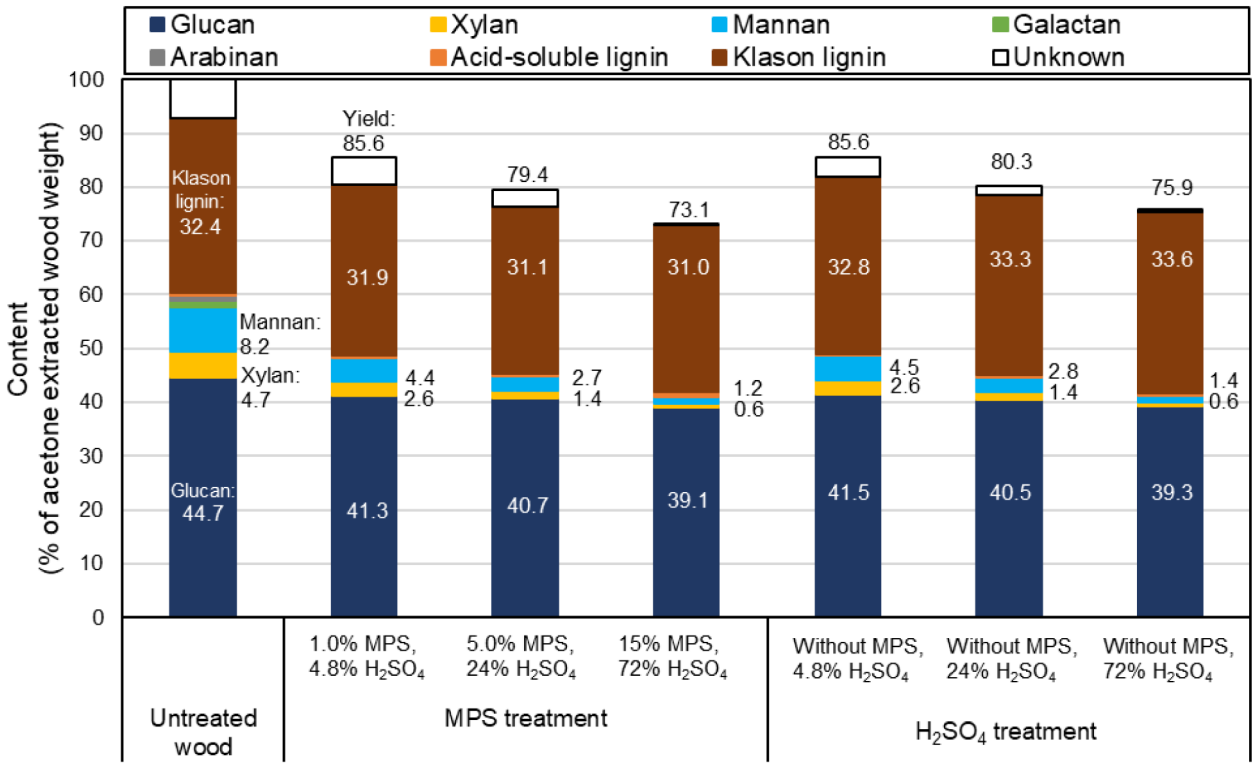


Fig. 3 Chemical composition of wood meal after prehydrolysis with MPS or H_2SO_4. The *x*-axis shows the H_2SO_4 dosage (% based on the acetone-extracted wood weight). For the MPS treatment, the MPS dosage and the H_2SO_4 amount used for its synthesis are shown. The numeric values within each stacked bar represent, from top to bottom, yield, Klason lignin, mannan, xylan, and glucan

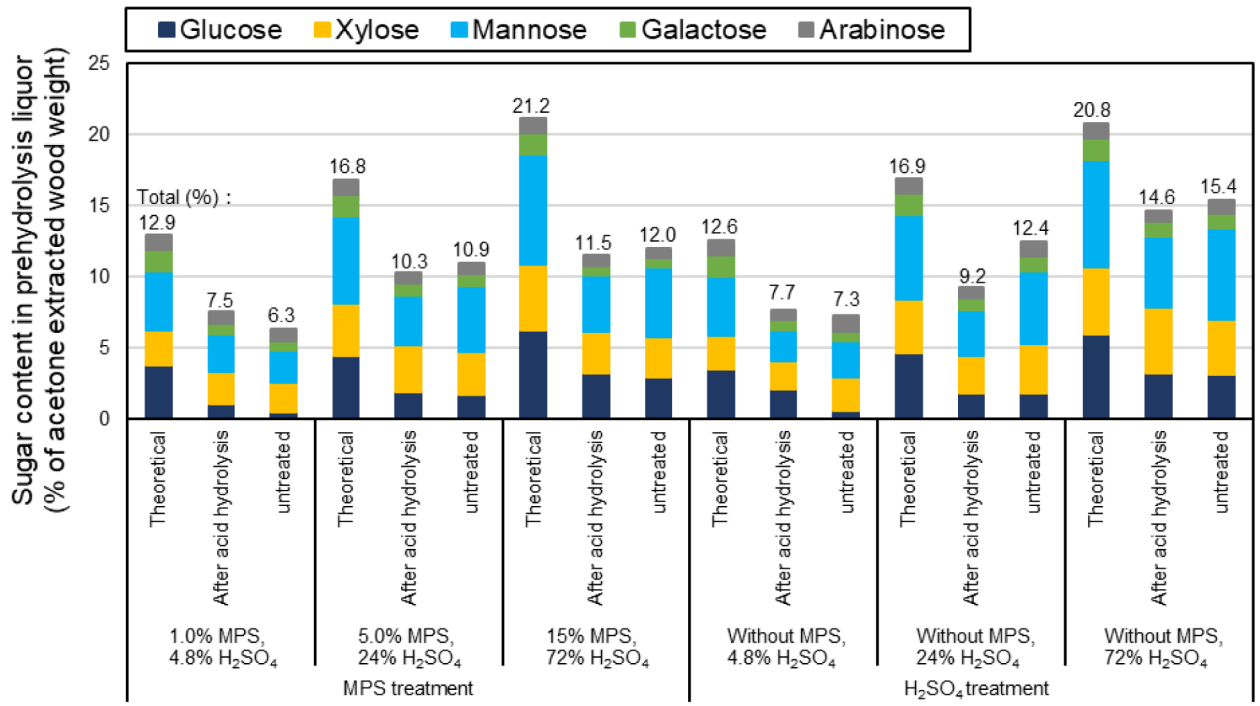


Fig. 4 Total sugar content in PHL obtained after MPS or H_2SO_4 prehydrolysis. The *x*-axis shows the H_2SO_4 dosage (% based on the acetone-extracted wood weight). For the MPS treatment, the MPS dosage and the H_2SO_4 amount used for its synthesis are shown. Total (%) values shown above each bar represent the sum of detected monosaccharides. Theoretical = calculated maximum sugar liberation (monoequivalent). After acid hydrolysis = monosugar content in PHL after 4% H_2SO_4 hydrolysis (mono + oligo). Untreated = monosugar directly detected in PHL by GC without hydrolysis

Sugar composition in PHL derived from MPS and H_2SO_4 prehydrolyses

Figure 4 shows the sugar content in the PHL, where *theoretical* indicates the calculated maximum total sugar release (monomer equivalent), *untreated* represents total sugars detected directly as monosaccharides in the PHL, and *after acid hydrolysis* represents total sugars quantified as monosaccharides after the post-hydrolysis for the conversion of oligosaccharides to monosaccharides. The theoretical sugar content in the PHL was calculated from the decrease in polysaccharide contents of the solid residues shown in Fig. 3, based on the original acetone-extracted wood weight. The difference between untreated wood and treated residues was converted to monosaccharide equivalents by dividing by 0.90 for C6 sugars and by 0.88 for C5 sugars to account for the anhydro-to-monomer mass conversion.

At the lowest dosage (4.8%), the total sugar content increased after acid hydrolysis, from 6.3 to 7.5% in the MPS-treated PHL and from 7.3 to 7.7% in the H_2SO_4-treated PHL, indicating the presence of oligosaccharides in the PHL under these mild conditions. However, at dosages ≥ 24%, the values after acid hydrolysis were similar to or lower than those of untreated total sugars, suggesting that oligosaccharides were largely absent and that monosaccharides were partially degraded under these conditions. Thus, oligosaccharides were likely released only under the mildest prehydrolysis condition (4.8%).

The untreated total sugars at 72% dosage were 12.0% in the MPS-treated PHL and 15.4% in the H_2SO_4-treated PHL, both lower than the theoretical values (21.2% and 20.8%, respectively), suggesting partial degradation of released sugars during prehydrolysis. The untreated total sugar content was lower in the MPS-treated PHL than in the H_2SO_4-treated PHL at this dosage, although the theoretical values were similar. These results suggest that oxidative species may have promoted sugar degradation during prehydrolysis.

With increasing dosages of MPS or H_2SO_4, the xylan content in the solid residues decreased, and the glucan content also decreased (Fig. 3). At the 72% dosage, the theoretical xylose contents in the PHLs were 4.6% for MPS and 4.6% for H_2SO_4, while the corresponding theoretical glucose contents were 6.2% and 6.0%, respectively, which were higher than the xylose contents in both PHLs. In contrast, in the untreated PHLs, the xylose contents (MPS: 2.9%, H_2SO_4: 3.9%) were similar

to or slightly higher than the glucose contents (MPS: 2.9%, H_2SO_4: 3.1%). Xylan that has uronic acid residues in its side chains is known to be relatively resistant to acid hydrolysis, and consequently, xylan oligomers that retain these side chains may remain in the PHLs even at higher dosages. Therefore, the smaller decrease in xylose content from the theoretical values compared with glucose and mannose may reflect the higher resistance of xylan to acid hydrolysis, which may result in the persistence of xylan oligomers in the PHLs.

Compared with the untreated PHL, mannose in the PHL decreased during post-acid hydrolysis, whereas glucose tended to increase. For example, at the 72% dosage, the mannose content decreased from 4.9 to 4.0% in the MPS-treated PHL and from 6.4 to 4.9% in the H_2SO_4-treated PHL, whereas the glucose content increased from 2.9 to 3.2% and from 3.1 to 3.2%, respectively. The increase in glucose during post-acid hydrolysis suggests the presence of glucose-containing oligomers in the PHL. Although glucomannan, a major hemicellulose component, contains both mannose and glucose units, the present results suggest that mannose may exist mainly as monosaccharides, whereas glucose may partly remain as oligomers. This behavior suggests that glucose-containing oligomers in the PHL may originate from glucomannan and may also include carbohydrates more resistant to acid hydrolysis than glucomannan, for example, cellulose.

To further examine the carbohydrate degradation behavior, a comparison was made with acid sulfite cooking. A previous study reported that short-time cooking (1–2 h) of Japanese larch under acid sulfite conditions (140 °C) produced both monomeric and oligomeric sugars in spent sulfite liquor (SSL, pH 1.4–2.0) [33]. In contrast, the PHL in the present study contained mainly monomers owing to the more acidic environment (pH < 1). This suggests that proton concentration and reaction conditions (time and temperature) govern the balance between oligomer release from carbohydrates and their hydrolysis to monomers. Peracetic acid treatment of cellulose has been reported to generate uronic acids via C6-oxidation [34], indicating that carbohydrates can undergo oxidative transformation in the presence of peroxides. Therefore, the lower total sugar in the MPS-treated PHL at higher acid dosage likely reflects rapid hemicellulose hydrolysis to monomers followed by further oxidative degradation. Accordingly, when MPS is used for prehydrolysis, a lower dosage is preferable, because it suppresses sugar degradation and enhances the utilization potential of PHL.

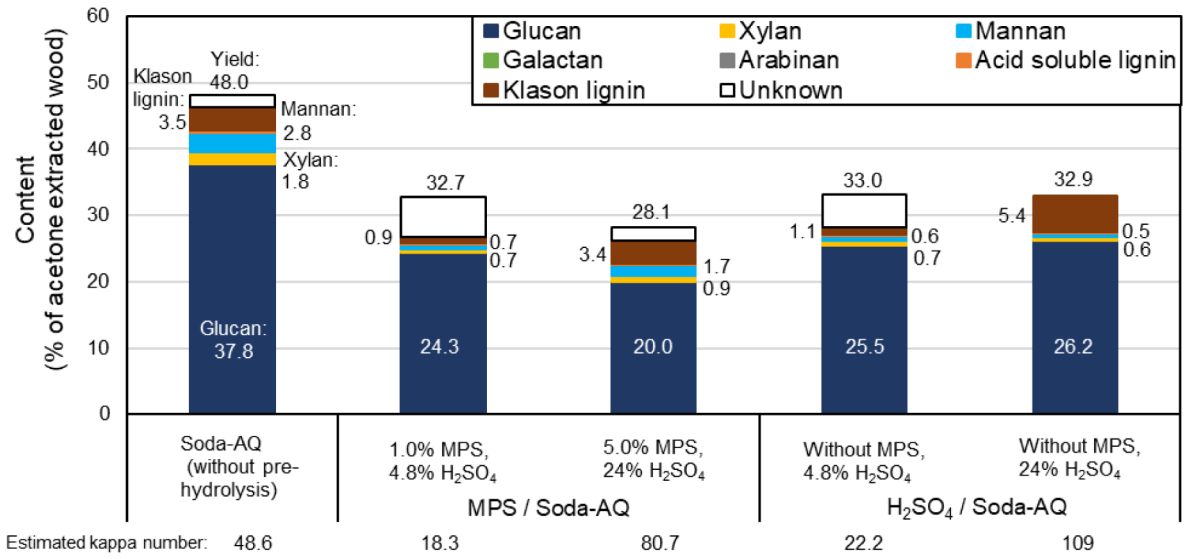


Fig. 5 Chemical composition of wood meal after MPS/soda–AQ or H_2SO_4/soda–AQ treatment. The *x*-axis shows the H_2SO_4 dosage (% based on the acetone-extracted wood weight). For the MPS treatment, the MPS dosage and the H_2SO_4 amount used for its synthesis are shown. The numeric values within each stacked bar represent, from top to bottom, yield, Klason lignin, mannan, xylan, and glucan. The values shown below the bars are estimated kappa numbers calculated from Klason lignin contents on a treated-residue basis using a conventional conversion factor (Klason lignin/0.15)

Soda–AQ treatment of wood meal after MPS or H_2SO_4 prehydrolysis

Figure 5 shows the results of the soda–AQ treatment of wood meal after prehydrolysis. Soda–AQ treatment without prehydrolysis resulted in a solid residue yield of 48.0%, with a Klason lignin content of 3.5% (based on acetone-extracted wood). The residue also contained 1.8% xylan and 2.8% mannan, indicating that some hemicellulose remained. When wood meal was prehydrolyzed with MPS at 4.8% H_2SO_4 dosage (1.0% MPS dosage) followed by soda–AQ treatment (MPS/soda–AQ) under the same conditions, the residue yield decreased to 32.7% and the Klason lignin content was markedly reduced to 0.9%. The xylan and mannan contents decreased to 0.7% in both cases, confirming the removal of most hemicellulose. These results were comparable to those obtained via prehydrolysis with H_2SO_4 followed by soda–AQ treatment (H_2SO_4/soda–AQ) at the same acid dosage, which produced a residue yield of 33.0% and a Klason lignin content of 1.1%, slightly higher than that in the residue after MPS/soda–AQ treatment. However, when the H_2SO_4 dosage was increased to 24%, the yield after MPS/soda–AQ treatment decreased further to 28.1% and the Klason lignin content increased to 3.4%. In contrast, H_2SO_4/soda–AQ treatment at the same dosage resulted in a higher residue yield of 32.9%, a glucan content of 26.2% and a Klason lignin content of 5.4% compared with the MPS-based treatment at an equivalent acid dosage.

To further clarify the delignification behavior shown in Fig. 5, kappa numbers were estimated from Klason lignin content by converting that content to a treated-residue basis after prehydrolysis/soda–AQ treatment and applying the conventional conversion factor (Klason lignin content/0.15) [35] while recognizing that this relationship is approximate for oxidatively treated samples. The estimated kappa numbers after soda–AQ treatments were 48.6 for the residue without prehydrolysis, 18.3 for MPS prehydrolysis at 4.8% dosage, 80.7 for MPS prehydrolysis at 24% dosage, 22.2 for H_2SO_4 prehydrolysis at 4.8% dosage, and 109 for H_2SO_4 prehydrolysis at 24% dosage. These values indicate that prehydrolysis at the lower dosage decreased the kappa number, whereas prehydrolysis at the higher dosage markedly increased it compared with the soda–AQ treatment without prehydrolysis, regardless of the presence of MPS. At both the low and high dosage conditions, the estimated kappa numbers of the MPS/soda–AQ residues were lower than those of the corresponding H_2SO_4/soda–AQ residues at the same dosage. These results suggested that MPS prehydrolysis had no negative impact on delignification during soda–AQ cooking and may even slightly enhance delignification relative to H_2SO_4 prehydrolysis.

However, when the H_2SO_4 dosage was increased to 24%, MPS treatment resulted in higher content of xylan and mannan (0.9% and 1.7%, respectively), while the glucan content decreased to 20.0% in the residue, compared with the lower H_2SO_4 dosage (4.8%). Notably, under the 24% H_2SO_4 condition, despite the higher hemicellulose content, glucan (likely cellulose-derived) decreased, suggesting that carbohydrate degradation was not limited to hemicellulose removal but also involved partial loss of cellulose.

Moreover, the contents estimated as unknown decreased with increasing acid dosage during both MPS and H_2SO_4 prehydrolyses (Fig. 3) and the subsequent soda–AQ treatments (Fig. 5). The unknown fraction generally includes chemical components not quantified in lignin determination and neutral sugar analyses. In softwood hemicellulose, arabinoglucuronoxylan contains side chains, such as 4-*O*-methylglucuronic acid and acetyl groups. Therefore, compounds derived from arabinoglucuronoxylan, including 4-*O*-methylglucuronic acid, xylose containing oligomers with uronic acid residues, and acetic acid released from acetyl groups, may contribute to the unknown fraction. Such uronic acid containing oligomers are not always completely hydrolyzed during the conventional two step sulfuric acid hydrolysis (72–4%) used for carbohydrate analysis, and, therefore, may not be fully detected in the subsequent monosaccharide analysis [36]. Previous studies have reported that MPS treatment decreases the hexenuronic acid content in pulp during MPS bleaching [37]. However, whether MPS directly reacts with glucuronic acid residues, which are precursors of hexenuronic acid under alkaline conditions, remains unclear. Therefore, although uronic-acid-derived structures may also be affected during MPS prehydrolysis, their quantitative contribution to the unknown fraction observed in the present study cannot be determined. In Fig. 5, the lignin contents of residues after MPS/soda–AQ or H_2SO_4/soda–AQ treatments were higher at higher dosage (24%) than at lower dosage (4.8%), whereas the unknown fraction was lower at higher dosage. The increase in lignin content at higher dosage may be attributed to lignin condensation or may have been influenced by denatured substances derived

Table 1 Yield of vanillin obtained via NBO from Japanese cedar wood treated with MPS and H_2SO_4

	Vanillin (mmol/g-lignin)
Untreated	1.78
MPS-treated	1.51
H_2SO_4-treated	1.17

from hemicellulose and other origins during prehydrolysis, which can be accounted for as lignin in the Klason analysis.

Table 1 shows the aldehyde yields obtained via the nitrobenzene oxidation (NBO) of wood chips prehydrolyzed at 5.6% H_2SO_4 dosage using either MPS (1.0% MPS dosage) or H_2SO_4. It should be noted that the H_2SO_4-equivalent dosage corresponding to the nominal MPS dosage of 1.0% slightly differed between the wood meal experiments and the wood chips (not the wood meal used above) experiments. This is because MPS was synthesized in a separate batch for the wood chips prehydrolysis, and the titrated sulfuric-acid-equivalent acidity of the resulting MPS solution was slightly different, leading to a small shift in the calculated H_2SO_4-equivalent dosage (4.8% vs 5.6%). Untreated wood yielded 1.78 mmol vanillin/g-lignin, whereas MPS-treated wood produced a slightly lower yield of 1.51 mmol/g-lignin. The lowest vanillin yield was observed for H_2SO_4-treated wood (1.17 mmol/g-lignin), indicating that acid-catalyzed condensation proceeded even at moderate acidity (~5%), reducing the number of cleavable lignin structures available for NBO. Collectively, these results indicated that the presence of MPS suppressed lignin condensation relative to the case without MPS; therefore, delignification during soda–AQ treatment was facilitated.

Unbleached pulp quality and oxygen-bleaching response of prehydrolysis/soda–AQ cooking

In contrast to the above experiments conducted using wood meal, the following experiments were carried out using wood chips. The experimental conditions differed slightly from those used in the wood meal experiments and are described in the Materials and Methods section. Figure 6 shows the result of soda–AQ cooking of wood chips after prehydrolysis. When MPS prehydrolysis was conducted at a 5.6% H_2SO_4 (1.0% MPS) dosage and the subsequent soda–AQ cooking was performed at an active alkali (AA) charge of 35%, the pulp yield (28.1%) and kappa number (30.1) were lower than those obtained upon H_2SO_4/soda–AQ cooking under the same H_2SO_4 dosage and AA charge (32.4% yield, kappa number 32.1). This indicates that MPS prehydrolysis promoted lignin removal more effectively than H_2SO_4 prehydrolysis during subsequent soda–AQ cooking. It should be noted that the Klason lignin contents of the wood chips after MPS and H_2SO_4 prehydrolyses were comparable (37.6% and 37.8%, respectively, based on the wood-chip weight after prehydrolysis; data not shown), suggesting that the enhanced delignification observed during the MPS/soda–AQ treatment was not primarily due to lignin removal during prehydrolysis, but was likely related to structural changes in lignin induced by MPS, which facilitated subsequent delignification during soda–AQ cooking. In contrast, soda–AQ cooking of untreated chips at an AA charge of 35% produced pulp with a kappa number of 26.2, lower than that of both prehydrolyzed pulps, suggesting that lignin denatured during MPS and H_2SO_4 prehydrolyses became more resistant to delignification during soda–AQ cooking, thereby limiting kappa number reduction. In the wood chip experiments, soda–AQ cooking of chips prehydrolyzed with MPS or H_2SO_4 resulted in higher kappa numbers and lower pulp yields than soda–AQ cooking without prehydrolysis at the same AA charge (35%), whereas in the wood meal experiments the estimated kappa number of both MPS/soda–AQ and H_2SO_4/soda–AQ pulps was lower than that obtained by soda–AQ cooking without prehydrolysis. The reason for this difference between the wood chips and wood meal experiments is not clear, but it may be related to differences in the experimental conditions. First, different liquor-to-wood (L/W) ratios were used (5 mL/g for wood chips and 10 mL/g for wood meal), which resulted in different NaOH concentrations in the cooking liquor. Second, in the wood chip experiments an impregnation step at 80 °C for 4 h was applied before the prehydrolysis reaction to ensure chemical penetration into the chips, whereas such a step was unnecessary for wood meal. Third, the H_2SO_4 dosage used in the prehydrolysis differed slightly between the two experiments (5.6% for wood chips and 4.8% for wood meal; see "Materials and methods" section). When soda–AQ cooking of untreated chips was performed under reduced AA charge (30%), pulp with a comparable kappa number (31.1) was obtained while maintaining a higher pulp yield (44.3%). Table 2 summarizes the chemical composition of pulps

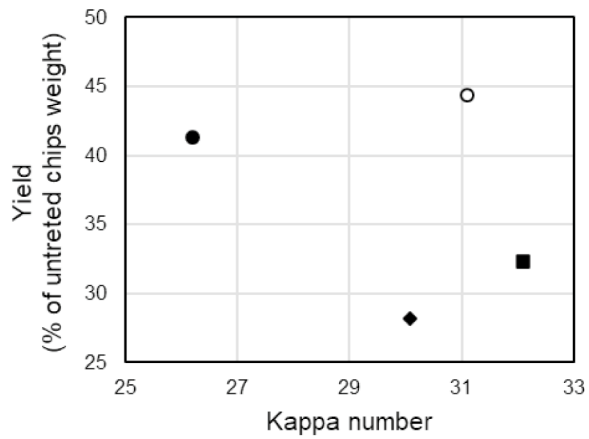


Fig. 6 Relationships between kappa number and pulp yield obtained by soda–AQ cooking with or without prehydrolysis of wood chips. ●, ○ without prehydrolysis, ◆ MPS prehydrolysis, ■ H_2SO_4 prehydrolysis, ● AA charge 35%, and ○ AA charge 30%

Table 2 Chemical composition of pulps prepared by MPS/soda–AQ, H_2SO_4/soda–AQ, and soda–AQ cooking

	MPS/soda–AQ	H_2SO_4/soda–AQ	Soda–AQ
	(% of unbleached pulp weight)		
Klason lignin	4.2	4.8	5.7
Acid-soluble lignin	0.6	0.6	0.8
Arabinan	–*	–*	0.2
Galactan	–*	–*	0.2
Mannan	1.4	1.6	5.4
Xylan	1.4	1.5	2.6
Glucan	80.1	80.8	73.2
Unknown	12.3	10.7	11.9

* Not detected

Table 3 Kappa number and brightness of pulps after O_1–O_2 bleaching of soda–AQ pulps with or without prehydrolysis

	MPS/soda–AQ	H_2SO_4/soda–AQ	Soda–AQ
Kappa number	7.6	11.2	14.3
Brightness (%-ISO)	54.0	50.1	51.1

Unbleached brightness (ISO) before O_1–O_2 bleaching: MPS/soda–AQ, 47.3%; H_2SO_4/soda–AQ, 45.6%; soda–AQ without prehydrolysis, 46.6%

with a kappa number of around 31. Soda–AQ pulp without prehydrolysis retained higher amounts of xylan and mannan (2.6% and 5.4%, respectively, on unbleached pulp weight basis) than MPS/soda–AQ pulp (1.4% and 1.4%) and H_2SO_4/soda–AQ pulp (1.5% and 1.6%). Conversely, the glucan content of MPS/soda–AQ (80.1%) and H_2SO_4/soda–AQ (80.8%) pulps was higher than that of soda–AQ pulp without prehydrolysis (73.2%), confirming that both MPS and H_2SO_4 prehydrolyses effectively removed hemicellulose before cooking.

When the pulp compositions listed in Table 2 were converted to contents relative to the original wood chip by multiplying the pulp compositions by the corresponding pulp yields, the glucan contents (on the original wood chip weight basis) of the MPS/soda–AQ (22.5%) and H_2SO_4/soda–AQ (26.2%) pulps were lower than that of the soda–AQ pulp without prehydrolysis (32.4%). Similarly, the mannan contents of the MPS/soda–AQ (0.4%) and H_2SO_4/soda–AQ (0.5%) pulps were lower than that of the soda–AQ pulp without prehydrolysis (2.4%). In comparison with the untreated wood shown in Fig. 3, the decrease in glucan was larger than that in mannan, although the carbohydrate contents in Fig. 3 are expressed on an acetone-extracted wood basis (the acetone extractives content of the wood was 2.9%). Glucomannan, consisting of both mannose and glucose units, was largely removed during the prehydrolysis. However, the decrease in glucan content was greater than that expected from glucomannan removal alone, suggesting that a portion of cellulose was also degraded during the prehydrolysis and/or subsequent soda–AQ cooking.

The three pulps (MPS/soda–AQ, H_2SO_4/soda–AQ, and soda–AQ) with a similar initial kappa number of ~ 31 were subjected to two-stage oxygen bleaching (O_1–O_2), and the results are presented in Table 3. The MPS/soda–AQ pulp exhibited the lowest kappa number (7.6) and the highest brightness (54.0), meaning that lignin was most efficiently removed from this pulp during oxygen bleaching. As shown in Table 2, the unbleached pulps obtained after MPS and H_2SO_4 prehydrolyses had similar chemical compositions, except for a slightly lower kappa number in the MPS/soda–AQ pulp. Despite this similarity, their responses to oxygen bleaching differed markedly. The bleaching response during O_1–O_2 of H_2SO_4/soda–AQ pulp was less effective, likely due to greater lignin condensation during prehydrolysis. The lignin content of the unbleached soda–AQ pulp without prehydrolysis was higher (5.7%, Table 2) than those of the MPS/soda–AQ and H_2SO_4/soda–AQ pulps, and the kappa number after O_1–O_2 bleaching was also higher for the soda–AQ pulp (Table 3). This higher lignin content might have contributed to the higher kappa number observed after oxygen bleaching. Thus, MPS/soda–AQ pulp demonstrated markedly superior oxygen-bleaching response compared with H_2SO_4/soda–AQ and soda–AQ without prehydrolysis, achieving better delignification and higher brightness, although the characteristics of the unbleached pulps did not differ significantly between the MPS and H_2SO_4 prehydrolyses. This observation indicates that the enhanced oxygen-bleaching response of the MPS/soda–AQ pulp was associated with structural changes in residual lignin induced by MPS during the prehydrolysis stage.

TCF bleaching response and final pulp property

Figure 7 shows the evolution of brightness during the bleaching sequence. The final brightness of MPS/soda–AQ pulp after the O_1–O_2–MPS–E_p–MPS–E_p–MPS*–E_p* sequence reached 83.0% ISO, which was slightly higher than that of H_2SO_4/soda–AQ pulp (82.3% ISO) and soda–AQ pulp without prehydrolysis (81.7% ISO). However, none of the pulps obtained in this study reached the target brightness of 88% ISO established in Indonesia for dissolving pulp production [38]. Although the MPS/soda–AQ pulp showed a higher brightness than the other pulps after O_1–O_2 (Table 3), the brightness differences among the pulps became smaller after the subsequent TCF bleaching sequence. Because chlorine dioxide was not employed in this study, unlike in conventional ECF bleaching, the brightness increase achieved by repeated MPS–E_p treatments was limited, even when the final MPS and E_p stages were conducted at elevated

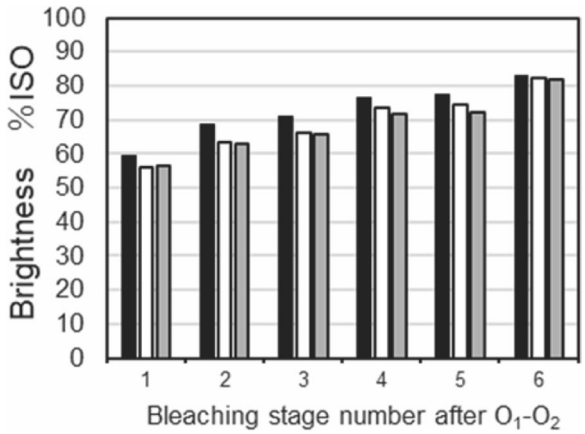


Fig. 7 Brightness change of pulps across bleaching stages after O_1–O_2 sequence. black bars: MPS/soda–AQ, white bars: H_2SO_4/soda–AQ, and gray bars: soda–AQ. Stage numbers represent the bleaching progression after O_1–O_2 treatment:

1 = O_1–O_2–MPS,

2 = O_1–O_2–MPS–E_p,

3 = O_1–O_2–MPS–E_p–MPS,

4 = O_1–O_2–MPS–E_p–MPS–E_p,

5 = O_1–O_2–MPS–E_p–MPS–E_p–MPS*,

6 = O_1–O_2–MPS–E_p–MPS–E_p–MPS*–E_p*,

E_p: alkaline extraction with H_2O_2; E_p*: hot E_p stage; MPS*: hot MPS stage; O_1, O_2: first and second oxygen-bleaching stages

Table 4 Viscosity change during bleaching of MPS/soda–AQ, H_2SO_4/soda–AQ, and soda–AQ pulps

	MPS/soda–AQ	H_2SO_4/soda–AQ	Soda–AQ
	Viscosity (cP)		
Unbleached	4.7	5.3	7.5
After O_1–O_2	4.0	3.9	5.7
TCF final	2.4	2.4	2.8

temperatures. This convergence in final brightness suggests that the repeated MPS–E_p stages had limited effectiveness in further improving brightness by acting on residual chromophoric structures, mainly derived from residual lignin. The viscosity of TCF-bleached MPS/soda–AQ and H_2SO_4/soda–AQ pulps was 2.4 cP (Table 4), notably lower than the industrial requirement (6.2 cP) [38]. In particular, the viscosity of unbleached MPS/soda–AQ pulp was below this standard (4.7 cP), and even that of soda–AQ pulp without prehydrolysis was similarly low (7.5 cP). These results indicate that soda–AQ cooking inevitably reduces cellulose degree

Table 5 Carbohydrate composition of TCF-bleached pulps prepared by MPS/soda–AQ, H_2SO_4/soda–AQ, and soda–AQ cooking

	MPS/soda–AQ	H_2SO_4/soda–AQ	Soda–AQ
	(% of unbleached pulp weight)		
Arabinan	–*	–*	–*
Galactan	–*	–*	–*
Mannan	1.8	1.9	6.4
Xylan	1.6	1.5	2.2
Glucan	95.7	96.6	89.2
Unknown	0.9	0.0	2.2

* Not detected

of polymerization, limiting its applicability to high-viscosity dissolving-pulp grades. Rizaluddin proposed an O–MPS–E_p–MPS–E_p bleaching sequence for chlorine-free bleaching of hardwood prehydrolysis/kraft pulp, reporting that pulps produced from an *Eucalyptus* hybrid achieved a final brightness of 87.3–88.3% ISO with viscosities of 5.1–6.0 cP. Although these values were slightly below the industrial dissolving-pulp standard in Indonesia, the achieved brightness was higher than that obtained using an O–MPS–Z–E_p sequence (83.1% ISO) incorporating ozone (Z) as a bleaching agent [39]. Salaghi et al. successfully produced high-quality dissolving pulp from *E. globulus* prehydrolysis/kraft pulp using an O–MPS–E_p–MPS–E_p bleaching sequence, achieving a brightness of 90.1% ISO and a viscosity of 7.0 cP [31]. Evelyn et al. also demonstrated that the same O–MPS–E_p–MPS–E_p sequence successfully produced dissolving pulp (89.9% ISO, 9.1 cP) from nonwood *Metroxylon sagu* palm fronds processed by prehydrolysis/soda–2-methyl-AQ cooking [16]. Because the Japanese cedar used in this study is a softwood, cooking required a higher AA charge (35%) and more severe conditions (170 °C and 2 h) than those reported for *E. globulus* (an AA charge of 15%, 150 °C, and 3 h) and *M. sagu* palm fronds (an AA charge of 23%, 160 °C, and 1.5 h). As a result, degradation of cellulose under alkaline conditions could not be sufficiently suppressed, leading to reduced pulp viscosity after cooking. Therefore, for softwood, the use of appropriate additives under alkaline cooking conditions may be desirable to enhance delignification while preserving cellulose polymerization. In addition to the conditions used in previous reports, this study applied high-temperature MPS and high-temperature E_p stages for pulp bleaching; however, the final brightness remained lower than that reported for *E. globulus* and *M. sagu* palm fronds. This indicates that the bleaching response of MPS/soda–AQ pulp from Japanese cedar was inferior to that of these hardwood- or nonwood-derived pulps. Notably, even

when high-temperature MPS bleaching was introduced (Stage 5 in Fig. 6), the brightness increased by only one point relative to the previous stage (Stage 4), suggesting that the effect of MPS bleaching in Japanese cedar pulp is most pronounced during earlier bleaching stages. Thus, optimization of the TCF bleaching sequence for softwood-derived MPS/soda–AQ pulp remains to be addressed.

Table 5 presents the sugar composition of bleached pulps. The glucan content of MPS/soda–AQ pulp was 95.7%, comparable to that of H_2SO_4/soda–AQ (96.6%) and clearly higher than that of soda–AQ cooking without prehydrolysis (89.2%). The combined sum of mannose and xylose content was 3.4% in both MPS/soda–AQ and H_2SO_4/soda–AQ pulps, whereas that in soda–AQ was 8.6%, confirming that MPS prehydrolysis enables cellulose recovery with a purity equivalent to that obtained via H_2SO_4 prehydrolysis. As shown in Table 4, the viscosities of MPS/soda–AQ and H_2SO_4/soda–AQ pulps were consistently lower than that of soda–AQ pulp without prehydrolysis at all stages, including the unbleached, O_1–O_2, and final TCF-bleached stages. The lower viscosity values indicate a reduction in the average degree of polymerization of cellulose, implying that depolymerization occurred during prehydrolysis and/or soda–AQ cooking. Despite maintaining high glucan content after TCF bleaching (Table 5), the reduction in pulp viscosity likely resulted from random cleavage of glycosidic bonds along the cellulose chains rather than sequential degradation from reducing ends. Although the pulp produced by MPS/soda–AQ did not satisfy dissolving-pulp quality in terms of brightness and viscosity, MPS prehydrolysis provided cellulose purity equivalent to H_2SO_4 prehydrolysis using a chlorine-free TCF bleaching sequence, achieving higher brightness compared with H_2SO_4 prehydrolysis. Moreover, although the reduced viscosity of the pulp is not suitable for applications requiring high-molecular-weight cellulose, such as viscose or rayon, its high glucan purity makes it a promising material for emerging applications, including CNCs, cellulose powder, and other functional cellulose-based products. These findings highlight MPS/soda–AQ cooking as a new domestic-wood-based biorefining process not only for traditional dissolving pulp but also for high-purity cellulose streams for advanced material applications.

Conclusions

This study evaluated MPS as a prehydrolysis reagent for Japanese cedar and compared it with H_2SO_4 under equivalent acid dosages. Under mild conditions (4.8% H_2SO_4 dosage), hemicellulose was removed at comparable levels via MPS and H_2SO_4 prehydrolyses. However, the residue yield (32.7%) and Klason lignin content (0.9%) after MPS treatment were lower than those obtained via H_2SO_4 prehydrolysis (33.0% and 1.1%), indicating enhanced delignification selectivity. The NBO results supported this trend, showing higher vanillin yield for MPS-treated wood (1.51 mmol/g-lignin) than for H_2SO_4-treated wood (1.17 mmol/g-lignin), suggesting that lignin condensation was more suppressed under MPS treatment.

The sugar analysis of the PHL showed that at low H_2SO_4 dosage (4.8%), the untreated total sugar contents were similar for MPS treatment (6.3%) and H_2SO_4 treatment (7.3%). Conversely, at high dosage (72%), the untreated total sugar content was lower in MPS-treated PHL (12.0%) than in H_2SO_4-treated PHL (15.4%), indicating oxidative monosaccharide degradation. These results identify low-dosage MPS prehydrolysis (4.8% H_2SO_4-equivalent) as the optimal treatment for preserving sugars in PHL.

MPS/soda–AQ cooking yielded pulp with a lower kappa number (30.1) than H_2SO_4/soda–AQ (32.1), confirming improved delignification efficiency. In TCF bleaching (O_1–O_2–MPS–E_p–MPS–E_p–MPS*–E_p^*), MPS/soda–AQ pulp achieved the highest final brightness (83.0% ISO) among the three pulps tested in this study. However, the brightness differences among the pulps became small after the subsequent TCF bleaching sequence, despite the higher brightness of MPS/soda–AQ pulp after O_1–O_2. Although viscosity remained below dissolving-grade standards (2.4 cP), the bleached pulp exhibited high glucan purity (95.7%), indicating applicability for CNCs, cellulose powder, and other functional cellulose products rather than viscose-grade materials.

Overall, the results demonstrate that MPS/soda–AQ is a viable, sulfide-free and chlorine-free route for obtaining cellulose with high glucan content from domestic softwood, particularly when using a low H_2SO_4 dosage during prehydrolysis. These findings position MPS/soda–AQ cooking as a new Japanese cedar-based biorefinery process for producing high-purity cellulose streams rather than conventional dissolving pulp for advanced material applications.

Experiment

Materials

Japanese cedar (*Cryptomeria japonica*) wood chips were obtained from the commercial market in Japan. MPS (H_2SO_5) was prepared by adding 95% H_2SO_4 (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) dropwise into 40% aqueous H_2O_2 (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) at 70 °C. The total oxidant concentration (H_2O_2 + MPS) was determined by iodometric titration with potassium iodide and sodium thiosulfate, and the H_2O_2 concentration was determined separately by cerium sulfate titration; the

MPS concentration was calculated by subtracting the H_2O_2 concentration from the total oxidant concentration [37]. A 0.42 ± 0.01 mol/L MPS solution was prepared by reacting 2.45 mol/L H_2SO_4 with 0.93 ± 0.15 mol/L H_2O_2 at 70 °C, followed by cooling to room temperature prior to titration. Based on the quantified concentrations after cooling, the concentrations of residual H_2SO_4 and H_2O_2 in the final solution were estimated to be 2.02 ± 0.02 mol/L and 0.52 ± 0.12 mol/L, respectively. NaOH (2 mol/L and 4 mol/L solutions) and nitrobenzene were purchased from FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan.

MPS or H_2SO_4 treatment of wood meals

Wood chips were milled using a cutting mill (MF 10 basic, IKA-Werke GmbH & Co. KG, Staufen, Germany) with a cutter head (screen size: 1.0 mm), and the resulting wood meals were sieved to obtain a 40–80 mesh fraction. The samples were Soxhlet-extracted with acetone at 70 °C for 6 h prior to all experiments. One gram (oven-dry basis) of the acetone-extracted wood meal was placed in a 100-mL Erlenmeyer flask and mixed with 10 mL of either MPS or H_2SO_4 solution. The flask was then placed in a sterilization autoclave and heated at 120 °C for 1 h. The MPS dosage was set at 1.0–15.0% based on the oven-dried wood meal weight after acetone extraction. The desired MPS dosage was adjusted by diluting the stock MPS solution with distilled water, while the total liquid volume was fixed at 10 mL. Because MPS was synthesized from H_2SO_4 and H_2O_2, an H_2SO_4 control treatment was conducted using the same H_2SO_4 dosage as that used for MPS synthesis, but without H_2O_2.

After treatment, the reaction mixture was filtered through a 1GP16 glass filter (SHIBATA Scientific Technology Ltd., Saitama, Japan, 16 μm pore size), and the solid residue was washed with water until the filtrate showed a neutral pH range, as confirmed using pH test paper. The solid residue was oven-dried at 105 °C, and the yield was determined gravimetrically. The filtrate and washings were combined and diluted to 100 mL. The solid residue and filtrate were subjected to further experiments.

Soda–AQ treatment of treated wood meals

Three types of wood meals were subjected to soda–AQ treatment: (i) wood meal without pre-hydrolysis, (ii) wood meal after MPS pre-hydrolysis, and (iii) wood meal after sulfuric acid pre-hydrolysis. Each sample was placed into a 10-mL stainless steel autoclave and treated at 170 °C for 4 h. The cooking liquor was prepared using a 4 mol/L NaOH solution, with a L/W ratio of 10 mL/g, an AA charge of 35% (as Na_2O), and an AQ charge of 0.1% based on the oven-dried wood weight after acetone extraction. The resulting pulp residue was filtered through a 1GP16 glass filter, and the yield was determined. The recovered residue was used for further analysis.

Prehydrolysis and soda–AQ cooking of wood chips

Oven-dried wood chips (50 g) were placed into a 500-mL DURAN glass bottle and mixed with MPS or H_2SO_4 solution at an L/W ratio of 5.5 mL/g, corresponding to an acid dosage of 5.6% as H_2SO_4 (equivalent to 1.0% MPS) based on the oven-dried wood weight. The mixture was subjected to prehydrolysis by autoclaving at 120 °C for 1 h. After the reaction, the PHL and the treated chips were separated by decantation. The chips were then immersed in water at 50 °C for more than 30 min, followed by repeated decantation and reimmersion (≥ 5 cycles) until the pH of the wash liquor reached neutrality. The washed chips were air-dried, and their moisture content and yield were determined.

After prehydrolysis, 45 g of the treated chips were placed into a 350-mL stainless steel autoclave and subjected to soda–AQ cooking at 170 °C for 2 h at an L/W ratio of 5.5 mL/g, with an AA charge of 35% and an AQ charge of 0.1% based on the oven-dried wood weight. For comparison, untreated chips were also cooked under the same conditions at AA charges of 30% and 35%. The resulting pulp was disintegrated using a mixer and filtered through a Büchner funnel. This operation was repeated four times. For the fifth disintegration, the pulp was dispersed in 3.2 L of water, and 0.8 L of the suspension was taken and filtered through a Büchner funnel to form pulp sheets (four sheets in total). The sheets were air-dried, and their moisture content and pulp yield were determined.

TCF bleaching

The TCF bleaching sequence employed was O_1–O_2–MPS–E_p–MPS–E_p–MPS^*–E_p^*, where O_1–O_2 is a two-step oxygen-bleaching stage, MPS^* is an MPS stage at higher temperature (80 °C), and E_p^* is an E_p stage at higher temperature (80 °C). At each stage, the treated pulp was disintegrated with a mixer, filtered through a Büchner funnel, and formed into pulp sheets for subsequent bleaching.

Two-stage oxygen bleaching (O_1–O_2)

Two consecutive oxygen-bleaching stages were applied to decrease the kappa number. Unbleached prehydrolysis/soda–AQ pulp (12 g oven-dried) was treated with 1.0% NaOH at 10% pulp consistency (PC) in a Teflon-lined stainless steel autoclave, which was initially pressurized with O_2 to 0.5 MPa at room temperature and then sealed during the reaction. The reaction was conducted

in a closed system without continuous oxygen supply. The autoclave was placed in an oil bath and heated for 60 min, with time zero defined as the time at which the internal temperature first exceeded 95 °C. After 60 min, the final temperature reached 110 °C ± 5 °C (O_1 stage). The obtained pulp (10 g oven-dried) was washed, and pulp sheets were formed. A part of the sheets was then subjected to the O_2 stage under identical conditions to those of O_1, except that the NaOH charge was reduced to 0.5%.

MPS stage (MPS)

Pulp was treated at 70 °C for 70 min with 1.5% MPS (on an oven-dried pulp basis) at 10% PC and pH 3, which was adjusted using small amounts of NaOH and H_2SO_4.

Alkali extraction with H_2O_2 (E_p)

Pulp was treated at 70 °C for 60 min with 2.0% H_2O_2 and 1.4% NaOH (on an oven-dried pulp basis) at 10% PC.

Hot MPS stage (MPS.)*

MPS* treatment was conducted under the same conditions as in the MPS treatment, except that the MPS dosage and the treatment temperature were increased to 2.5% and 80 °C, respectively.

Hot E_p stage (E_p.)*

E_p* treatment was conducted under the same conditions as E_p, except that the H_2O_2 dosage was increased to 5.0% and other conditions were modified to 80 °C for 120 min.

Chemical composition analysis

Following a previous report [40], the samples were first hydrolyzed in 72% H_2SO_4 at room temperature for 2.5 h. Subsequently, water was added to adjust the H_2SO_4 concentration to 4%, and the mixture was then subjected to a second hydrolysis in an autoclave at 121 °C for 1 h. The hydrolyzed suspension was filtered, and the Klason lignin content was determined gravimetrically from the acid-insoluble residue. The filtrate was diluted to 500 mL, and the acid-soluble lignin content was determined by measuring the absorbance at 205 nm.

The monosaccharide content in the filtrate of the second hydrolysis was analyzed according to a modified method reported by Blakeney et al. [41]. The filtrate (600 µL) was placed in a screw-cap test tube and mixed with 20 µL of myo-inositol (5 mg/mL) as an internal standard. Approximately 30 µL of saturated aqueous ammonia was added to neutralize the solution, and completion was confirmed using pH test paper. Then, 1 mL of 20 mg/mL sodium borohydride in dimethyl sulfoxide was added, and the mixture was allowed to react at room temperature for at least 2 h. Excess reagent was decomposed by adding 100 µL of acetic acid, followed by adding 200 µL of 1-methylimidazole and 2 mL of acetic anhydride for acetylation at room temperature for 40 min. The heat generated during the addition of 1-methylimidazole and acetic anhydride promoted the conversion of alditols in the solution to alditol acetates. After the reaction, 5 mL of water was added to terminate acetylation, followed by 2 mL of dichloromethane, and the mixture was vortexed. The aqueous upper phase was discarded, and the organic phase was dried over anhydrous sodium sulfate for at least 1 h. A 1 µL aliquot of the dichloromethane layer was injected into a gas chromatograph (GC-2010, Shimadzu Corporation, Kyoto, Japan; column: Supelco SP-2380, Supelco/Sigma-Aldrich, Bellefonte, PA, USA) to quantify the resulting alditol acetate derivatives.

Sugar analysis in PHL

Using the same analytical method as described above, the monosaccharides in the PHL were quantified by mixing 600 µL of PHL with 20 µL of 5 mg/mL myo-inositol as an internal standard, derivatizing, and analyzing. To determine the oligosaccharide content, 540 µL of PHL was mixed with 60 µL of 40% H_2SO_4 and hydrolyzed at 121 °C for 1 h to convert the oligosaccharides into monosaccharides. After cooling, the internal standard was added, and quantification was performed using the same derivatization and analytical procedures.

NBO of wood after prehydrolysis

Following a modified version of a previously reported method [42], approximately 200 mg (oven-dried basis) of wood meal (untreated, MPS-prehydrolyzed, or H_2SO_4-prehydrolyzed), 7.0 mL of 2 mol/L NaOH, and 0.4 mL of nitrobenzene were placed in a 10-mL stainless steel reactor and heated at 170 °C for 2 h. After the reaction, the reactor was cooled to room temperature, and 2 mL of isovanillin solution (1 mg/mL in ethyl ether) was added to the reaction mixture as an internal standard. The liquid phase was separated from the solid residue by filtration. The remaining nitrobenzene was removed via diethyl ether extraction under alkaline conditions (before neutralization), after which the pH was adjusted to 2–3 using 1 mol/L HCl. The vanillin produced during oxidation was then extracted with diethyl ether and analyzed by gas chromatography using an InertCap 1 column (GL Sciences Inc., Tokyo, Japan).

Analysis of pulp quality

The kappa number, viscosity, and brightness of the pulp were determined according to TAPPI Test Methods T236 om-13 [43], T230 om-94 [44], and T452 om-92 [45], respectively. The brightness was measured using an

Elrepho 2000 spectrophotometer (Datacolor, Lawrenceville, NJ, USA).

Abbreviations

AA	Active alkali
AQ	Anthraquinone
CNC	Cellulose nanocrystal
E_P	Alkaline extraction with H_2O_2
E_P^*	Hot E_p stage
ECF	Elemental chlorine-free
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
MPS (H_2SO_5)	Monopersulfuric acid
MPS*	Hot MPS stage
NaOH	Sodium hydroxide
Na_2S	Sodium sulfide
NBO	Nitrobenzene oxidation
O	Oxygen
O_1, O_2	First and second oxygen-bleaching stages
PHL	Prehydrolysis liquor
PC	Pulp consistency
SSL	Spent sulfite liquor
TCF	Totally chlorine-free
L/W ratio	Liquor-to-wood ratio

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Author contributions
KT had the major role in implementing the overall work, including the experimental design, performing the required experiments and writing the manuscript. ST was a major contributor in overall work by giving conceptual advice during the research. ST also provide soda–AQ pulps without prehydrolysis during this research.

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Declarations

Competing interests
The authors declare that they have no competing interest.

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