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## Differential behavior between acacia and Japanese larch woods in the formation and decomposition of hexenuronic acid during alkaline cooking

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**Abstract** The effects of anthraquinone (AQ) and polysulfide (PS) on the hexenuronic acid (HexA) content of pulp during kraft cooking were studied using *Acacia mearnsii* (acacia) and *Larix leptolepis* (Japanese larch) sapwood. In contrast to the results of cooking Japanese larch at an H-factor of 1200, the HexA contents of acacia pulp with a kappa number of 20 at an H-factor of 291 did not differ greatly between the kraft, kraft-AQ, and PS-AQ cooking methods, although the hydroxide ion concentration in the acacia cooking liquor decreased on the addition of AQ or sulfur. To explain this difference, we studied the behavior of the formation and degradation of HexA during alkaline cooking of glucuronoxylan from cotton linter, which was cooked with 1.0 and 2.0 mol/l NaOH. The relationship between HexA content and H-factor during alkaline cooking of glucuronoxylan was clarified. The amount of HexA and its rate of decomposition were higher in the 2.0 mol/l solution than in the 1.0 mol/l solution. At a low H-factor similar to that for hardwood cooking, HexA content increased to a maximum level and then started to decrease at high hydroxide ion concentrations such as 2.0 mol/l, whereas it slowly decreased at low hydroxide concentrations such as 1.0 mol/l. At an H-factor of around 450, the HexA formation/degradation curve for 1.0 mol/l of hydroxide crossed the decomposition curve for 2.0 mol/l of hydroxide. Therefore, it was shown that at a low H-factor, a decrease in hydroxide ion concentration during acacia wood cooking had little effect on the HexA content of pulp.

**Key words** Kraft · Anthraquinone · Polysulfide · Hexenuronic acid · Xylan

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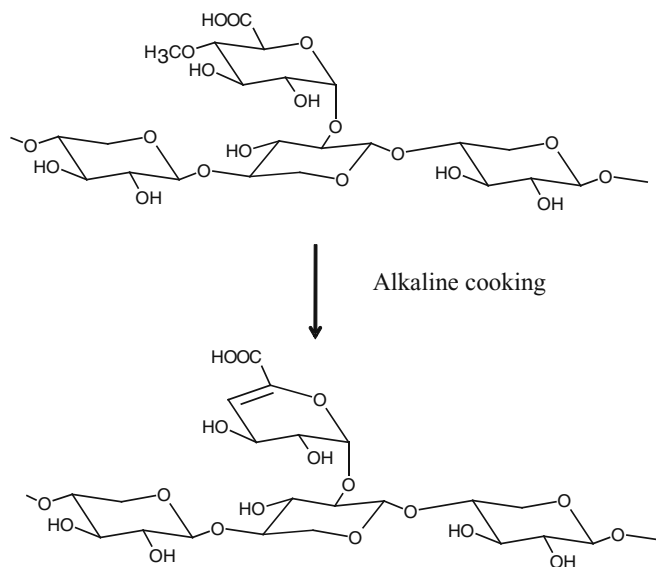
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### Introduction

The pulp yield of kraft cooking can be increased by the addition of anthraquinone (AQ) and polysulfide (PS). Several new methods have been studied to improve the pulp yields of hardwood kraft cooking.<sup>1–5</sup> Tanaka et al. reported that the best effect on pulp yield was obtained when a soluble AQ compound (SAQ) was added all at once during the initial phase of the cooking.<sup>1,2</sup> Watanabe et al. proposed a new cooking system using highly concentrated PS.<sup>3–5</sup> Although higher pulp yields at a given kappa number were obtained by these methods, the behavior of the hexenuronic acid (HexA) contents of these hardwood pulps is unclear.

Johansson and Samuelson reported that 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylitol converts rapidly to 2-*O*-(4-*O*-deoxy- $\beta$ -L-threo-hex-4-enopyranosyluronic acid)-D-xylitol by  $\beta$  elimination of the C<sub>5</sub> proton and the methoxyl group in 1 M NaOH at 150°C and then levels decrease as a result of its decomposition into xylitol.<sup>6</sup> Teleman et al. identified a HexA group in xylans from both kraft pulp and black liquor.<sup>7</sup> The formation of HexA during alkaline cooking is shown in Fig. 1. Gustavsson and Al-Dajani proposed that the removal of HexA during alkaline cooking may be partly due to degradation and partly due to dissolution together with xylan.<sup>8</sup> Li and Gellerstedt<sup>9</sup> reported that HexA is oxidized by potassium permanganate under acidic conditions because of its double bond, and that 10  $\mu$ mol/g of HexA was determined as contributing 0.84–0.86 to the kappa number. Buchert et al.<sup>10</sup> reported that chlorine dioxide and ozone degrade HexA, but hydrogen peroxide and oxygen do not degrade HexA under alkaline conditions. In addition, they reported that the residual 4-*O*-methyl glucuronic acid group in unbleached pulp is stable against bleaching chemicals, whereas the 4-*O*-methyl glucuronic acid group is unstable under alkaline cooking.

When subjected to acid hydrolysis, HexA changes into 5-formyl-2-furancarboxylic acid (FF) and 2-furancarboxylic acid (FA).<sup>11</sup> Vuorinen et al.<sup>12</sup> reported that 95% of HexA in pulp is removed under mild acid treatment and that the brightness stability of totally chlorine-free (TCF) bleached



**Fig. 1.** Conversion of the 4-*O*-methylglucuronic acid group to a hexenuronic acid group during alkaline cooking

pulp subjected to the treatment is better than that of bleached pulp not subjected to the treatment. Furthermore, Kawae and Uchida<sup>13</sup> reported that FF, which is one of the degradation products of HexA, causes the yellowing of elementary chlorine-free (ECF) bleached pulp under aging conditions of 80°C and 65% RH.

Some studies have been conducted to investigate the relationship between cooking conditions and HexA contents of softwood pulp. For example, it has been reported that pulp containing a lower amount of HexA can be obtained under conditions with a higher active alkali (AA) charge of white liquor (kraft cooking liquor), which is based on the results of kraft cooking of pine woods at an H-factor of 1500 with 18% and 22% of AA charge.<sup>10</sup> Furthermore, the HexA content of pulp was lower under a higher hydroxide ion concentration of white liquor when Norwegian spruce wood was cooked with liquor containing 0.1–0.9 mol/l NaOH and 0.28 mol/l NaSH to yield pulp with a kappa number of 30.<sup>8</sup> In addition, the HexA content was high when the concentration of hydrosulfide and the ion intensity were high.<sup>8</sup> However, these results were obtained from softwood cooking.

Cooking additives such as AQ and PS have the effect of increasing pulp yield.<sup>14</sup> Chai et al.<sup>15</sup> reported that there was no difference in the HexA contents of pulp irrespective of the presence of AQ, observed in the case of loblolly pine wood soda-cooked with 18% AA or kraft-cooked with 15% AA. Thus, it is possible to control the HexA content by cooking, because various cooking factors affect the HexA content of unbleached pulp.

In a previous study,<sup>16</sup> it was shown that the HexA contents of kraft-AQ and PS-AQ pulp are higher than those of kraft pulp obtained from Japanese larch sapwood. This observation can be explained by the fact that the hydroxide concentration of kraft-AQ or PS-AQ cooking is lower than

that of kraft cooking for the same kappa number at a given H-factor.

Therefore, the first objective of this study was to elucidate the effects of AQ addition and alkali concentration on the HexA contents of pulp prepared from acacia, a hardwood, using the kraft, kraft-AQ, and PS-AQ methods. The second objective was to investigate HexA formation and decomposition behaviors during alkaline cooking of a glucuronoxylan model.

## Materials and methods

### Materials

Acacia (*Acacia mearnsii*) wood chips originally obtained from plantations in South Africa were cooked. These chips were kraft pulp mill-grade chips provided by Hokuetsu Kishu Paper. Japanese larch (*Larix leptolepis*) sapwood obtained from the Agricultural and Forestry Research center of University of Tsukuba was used for cooking, as was Japanese cedar (*Cryptomeria japonica*) and Japanese red pine (*Pinus densiflora*) woods obtained from Hachinohe Mill, Mitsubishi Paper Mills. 1,4-Dihydro-9,10-dihydroxyanthracene sodium salt (SAQ) obtained from Kawasaki Kasei Chemicals was used as a cooking additive. FF was purchased from Tokyo Chemical Industry and FA was purchased from Wako Pure Chemical Industries.

### Cooking method

Alkaline cooking of acacia wood was carried out on the basis of the kraft, kraft-AQ, and PS-AQ methods with 23–33% AA charge and 25% sulfidity at 148°C for 2.5 h. The SAQ charge was 0.1% on the basis of the oven-dried wood weight. For the PS-AQ method, the PS cooking liquor was prepared from kraft cooking liquor by adding sulfur at a dosage of 1.0% of the oven-dried wood weight. The ratio of liquor to wood was 5.5 l/kg. The alkaline cooking conditions of Japanese larch sapwood, Japanese red pine, and cedar were described in a previous article.<sup>16</sup> After cooking, the pulp yields and kappa numbers were determined according to methods described in a previous study.<sup>16</sup>

### Determination of HexA contents

The pulp samples were acid hydrolyzed with formic acid (pH 2.5) at 120°C for 3 h according to the method of a previous study.<sup>16</sup> After acid hydrolysis, the hydrolysate was analyzed using high-performance liquid chromatography (HPLC) and the UV method.

### HPLC method

The HPLC system consisted of a PU-614 pump (GL Sciences, Tokyo, Japan), a UV-620 UV-Vis detector (GL Sciences), and a CTO-2A column oven (Shimadzu, Kyoto,

Japan). Separations were carried out with 10  $\mu$ l of solution on a Zorbax ODS column (4.6  $\times$  250 mm) (GL Sciences) using a UV detector and a mobile phase water–acetonitrile mixture (4:1, v/v) which was adjusted to pH 2.5 with formic acid at a flow rate of 0.5 ml/min. The column temperature was 40°C. UV detection at 265 nm was used to detect FF and FA. Calibration was performed using FF and FA as standards. The total amount of FF and FA was used to determine the amount of HexA.

Moreover, after acid hydrolysis with formic acid (pH 2.5) at 120°C for 3 h, the pulp samples were washed with distilled water. The washed pulp was treated again by a second round of hydrolysis, and HexA contents were determined after the first and second rounds of hydrolysis.

Using a photodiode array (PDA) detector (Hewlett Packard Series 1100), the peaks on the chromatograms of the hydrolysate obtained from formic acid hydrolysis were compared with the spectra of authentic compounds (FF and FA).

#### UV method

In the UV method, after acid hydrolysis, the absorbance of hydrolysate samples at 245 nm was determined using a UV–Vis spectrophotometer (UV-1700 Shimadzu). The calibration line was performed using the FA solution as a standard.

#### Determination of H-factor

The H-factor combines cooking time and cooking temperature as a single variable and is defined as follows:

$$H = \int_0^t \exp\left(43.2 - \frac{16113}{T}\right) dt$$

where  $H$  is the H-factor,  $t$  is the cooking time (h), and  $T$  is the cooking temperature (K).

#### Behavior of HexA formation during alkaline cooking of acacia and Japanese larch sapwood

We determined the HexA contents of acacia pulp resulting from kraft, kraft-AQ, and PS-AQ cooking methods at a kappa number of 20 using the HPLC method described above. The hydroxide ion concentrations were calculated from the AA charge.

In a previous article,<sup>16</sup> alkaline cooking of Japanese larch sapwood was carried out using the kraft, kraft-AQ, and PS-AQ methods, and the following experimental equation for Japanese larch sapwood pulp was obtained by conducting multiple classification analysis of the correlation between HexA content and cooking conditions:

$$\ln [\text{HexA}] = 8.28 - 3.14[\text{OH}^-] + 0.247AQ + 0.16S - 0.44t$$

where [HexA] is the HexA content ( $\mu$ mol/g), [OH<sup>-</sup>] is the hydroxide ion concentration of the cooking liquor, AQ is the AQ charge (% based on oven-dried wood),  $S$  is the

sulfur charge (% based on oven-dried wood), and  $t$  is the cooking time. Using this equation, we determined the HexA content in pulp at a kappa number of 25 given by the kraft, kraft-AQ, and PS-AQ methods.

#### Behavior of HexA formation during alkaline cooking of glucuronoxylan

Following the method of Teleman et al. (Fig. 2),<sup>11</sup> 0.25 g (oven-dried weight) of glucuronoxylan prepared from cotton linter was soaked in a 10-ml autoclave with 5 ml of NaOH aqueous solution (liquor ratio 20 ml/g) under a nitrogen atmosphere at room temperature for one night. Then, the glucuronoxylan samples were cooked at 100°–160°C for 1–4.5 h. The concentrations of the NaOH aqueous solution were 1.0 and 2.0 mol/l. After cooking, 0.25 ml of glycerin was added to the sample, after which the sample was neutralized to pH 7 with formic acid, mixed with 5 ml of methanol, and centrifuged at 3600 g for 40 min. The precipitate was separated, sufficiently mixed with a water–methanol mixture (1:1), and centrifuged again for 40 min. This procedure was carried out three times. Finally, the precipitate was suspended in 10 ml of methanol and then dried under vacuum with a rotary evaporator. The obtained precipitate contained HexA and is hereafter referred to as hexenuronoxylan.

## Results and discussion

#### Comparison of HexA analysis methods

There are three major methods of HexA analysis: the Technical Research Centre of Finland (VTT),<sup>17</sup> Royal Institute of Technology (KTH),<sup>18</sup> and Helsinki University of Technology (HUT)<sup>12</sup> methods. In the VTT method, HexA combined with xylobiose and xylotriose is separated and determined with anion exchange chromatography after hydrolysis of the pulp sample with enzymes (cellulase and hemicellulase). In the KTH method, the hydrolysis compounds are determined using a color meter after selective hydrolysis of the pulp with mercuric acetate. In the HUT method, the HexA in pulp is hydrolyzed selectively with formic acid, and then UV detection of the total hydrolysate mixture is carried out in order to determine FA derived from HexA. According to the HUT method, the molar absorption coefficient of FA (the maximum UV absorption at 245 nm), FF (the maximum UV absorption at 285 nm), and others is 8700 l/(mol·cm) at 245 nm.

In this study, the HexA content was determined by both the UV method and the HPLC method. In the UV method, the HexA content of pulp was determined by the UV absorbance of the hydrolysate sample at 245 nm with calibration performed using an FA solution as a standard. The HexA content of the pulp sample is then based on the amount of FA in the hydrolysate sample. In the HPLC method, the HexA content of pulp was determined by UV absorbance of the FF and FA at 265 nm. Calibration was performed using FF and FA as standards. The total amount of FF and

**Table 1.** Comparison of hexenuronic acid (HexA) content measured by the UV method and the high-performance liquid chromatography (HPLC) method

Sample	UV (245 nm)	HPLC (265 nm)			Ratio of HexA content UV/HPLC (%)
	HexA content ( $\mu\text{mol/g}$ )	FF content ( $\mu\text{mol/g}$ )	FA content ( $\mu\text{mol/g}$ )	HexA content (FF+FA $\mu\text{mol/g}$ )	
Soda-AQ pulp (Japanese larch sapwood)	4.9	0.2	0.6	0.7	692
PS-AQ pulp (Japanese larch sapwood)	11.9	2.3	8.3	10.6	112
PS-AQ pulp (acacia)	21.6	4.2	15.9	20.1	108

Soda-AQ, soda-anthraquinone; PS-AQ, polysulfide-anthraquinone; FF, 5-formyl-2-furancarboxylic acid; FA, 2-furancarboxylic acid

**Table 2.** HexA content after the first and second hydrolysis processes

Sample	HexA content after first hydrolysis ( $\mu\text{mol/g}$ )	HexA content after second hydrolysis ( $\mu\text{mol/g}$ )	Total HexA content ( $\mu\text{mol/g}$ )
Acacia kraft pulp	30.4 (99.3%)	0.2 (0.7%)	30.6
Japanese cedar kraft pulp	15.6 (99.0%)	0.2 (1.0%)	15.8
Japanese red pine kraft pulp	4.2 (98.3%)	0.1 (1.7%)	4.3

Numbers in parentheses show the percentage of HexA content after the first or second hydrolysis to that for total hydrolysis

FA was used to determine to the amount of HexA. As shown in Table 1, compared to the HPLC method, the UV method yielded higher amounts of HexA for all pulp samples. In particular, the value for soda-AQ pulp by the UV method was 4.9  $\mu\text{mol/g}$ , which was seven times that found by the HPLC method (0.7  $\mu\text{mol/g}$ ). This implies that the UV method clearly overestimates the HexA content of pulp samples containing small amounts of HexA. Tenkanen et al.<sup>17</sup> reported that the HUT method (in which the UV method is employed) can be affected by acid hydrolysis compounds from pulp other than FA and that the detection limit of the method is 1  $\mu\text{mol/g}$ .

On the basis of the above observations, pulp samples, particularly those such as bleached pulp containing a small amount of HexA, need to be analyzed by the HPLC method, which can separate and determine the hydrolysis compounds after formic acid hydrolysis. Therefore, HexA content was determined by the HPLC method as described in the following section. In addition, the optimum conditions for determination were investigated to improve the accuracy of the method.

#### Conditions for hydrolysis with formic acid for HexA determination

Table 2 lists the values of HexA content of the pulp after the first and second hydrolysis processes. The HexA contents were determined for pulp samples that contained 4.2–30.4  $\mu\text{mol/g}$  of HexA. In all samples, the values of HexA content given by the second hydrolysis were below 1  $\mu\text{mol/g}$ . The percentage of HexA content after the first hydrolysis to that after the total hydrolysis was greater than 98%. This implies that hydrolysis of pulp with formic acid is carried out effectively at 120°C for 3 h.

Figure 3a shows an HPLC chromatogram for the solution obtained by the hydrolysis of pulp with formic acid at 265 nm. Peaks 1 and 2 in the chromatogram were derived

from FF and FA, respectively. As shown in Figs. 3b,c, spectra of peaks in a wide range of UV lights were obtained with a PDA detector to confirm the purity of the peaks. At the retention time of the FF peak (Fig. 3b), some other peaks were also detected. This observation indicates that the peak determined at 265 nm as FF is not a single FF peak. However, it is clearly shown by the PDA spectrum that the peak at the retention time of FA does not contain compounds other than FA.

On the basis of the above observations, the amount of FF might be overestimated because the peak at the retention time of FF also contains compounds other than FF. However, as shown in Fig. 3a, the peak area for FF and other compounds is small and only about 10%–20% that of FA. Therefore, it appears that overestimation due to some other peaks can be ignored.

#### Behavior of HexA formation during alkaline cooking of acacia and Japanese larch sapwood

In a previous study,<sup>16</sup> it was shown that the PS-AQ method yields the highest HexA contents among the kraft, kraft-AQ, and PS-AQ methods for Japanese larch pulp with a kappa number of 25. The H-factor and sulfidity were constant, and the AA charge of white liquor was varied across the three methods. That the PS-AQ method yields the highest HexA content may be explained by the fact that compared to other methods, it requires a smaller concentration of hydroxide ions for a kappa number of 25.

To confirm this, kraft cooking and PS-AQ cooking of Japanese larch sapwood were carried out to obtain pulps with the same kappa number. The cooking conditions were determined by using the predictive equation obtained in a previous study. As shown in Table 3, for Japanese larch sapwood, the PS-AQ pulp had a higher HexA content than the kraft pulp did. However, the behavior of HexA formation during acacia cooking was quite different from that

during softwood cooking. Table 3 lists the results for acacia pulp with various kappa numbers.

Figure 4 summarizes the hydroxide ion concentration required for a kappa number of 20 in acacia pulp on the basis of the results in Table 3. By adding either AQ or sulfur, the hydroxide ion concentration can be decreased. Figure 4 also summarizes the HexA contents of the acacia pulp with a kappa number of 20, as obtained by the kraft, kraft-AQ, and PS-AQ methods. Observations similar to those in the case of Japanese larch pulp might be expected due to differences in hydroxide ion concentrations. However, there were no large differences in the HexA

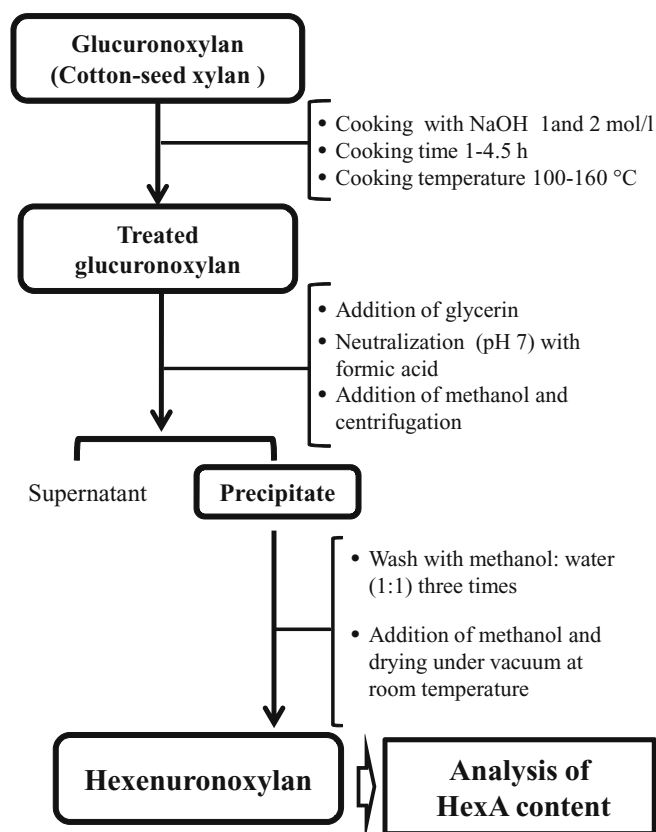


Fig. 2. The preparation of hexenuronoxylan

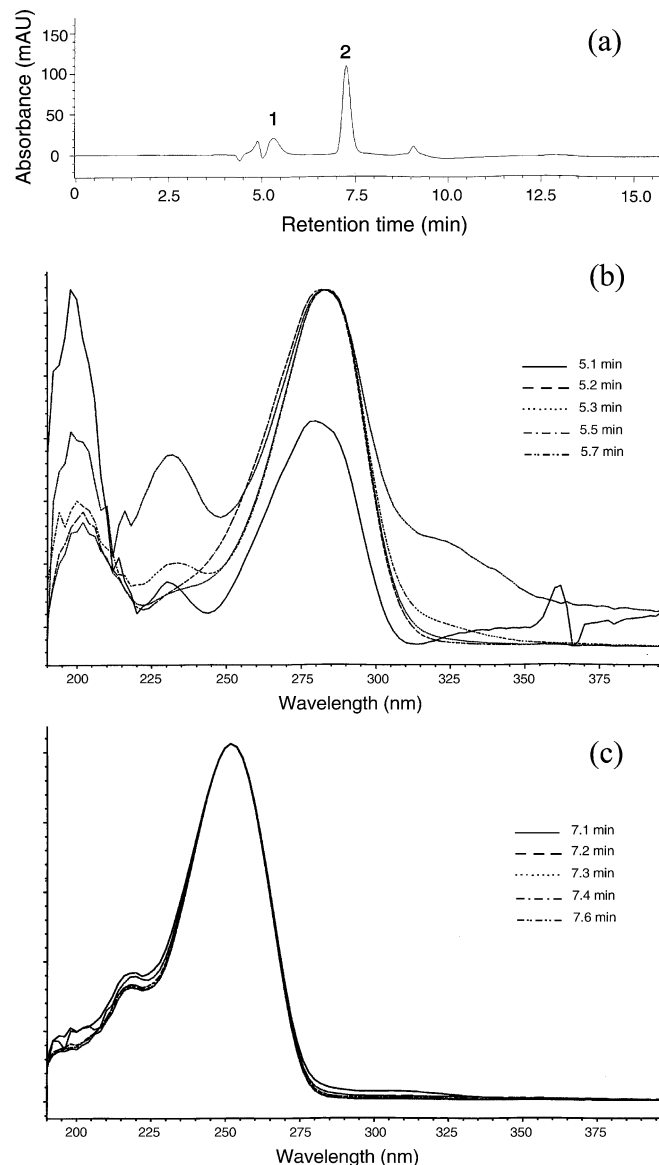
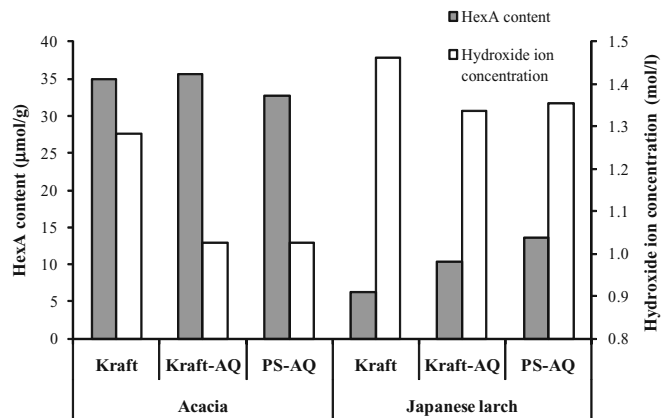


Fig. 3. **a** The high-performance liquid chromatography chromatogram of hydrolysate of Japanese red pine kraft pulp with formic acid detected by UV at 265 nm. Peaks 1 and 2 represent 5-formyl-2-furancarboxylic acid and 2-furancarboxylic acid, respectively. **b** UV spectrum of peak 1 at around 5.3 min detected by photodiode array (PDA). **c** UV spectrum of peak 2 at around 7.3 min detected by PDA

Table 3. HexA contents of acacia and Japanese larch pulps given by various alkaline cooking methods

Wood species	Cooking method	H-factor	AA charge (%)	AQ charge (%)	Sulfur charge (%)	Pulp yield (%)	Kappa number	HexA content ( $\mu\text{mol/g}$ )
Acacia	Kraft	291	20	–	–	55.6	28.9	35.5
	Kraft		23	–	–	55.1	23.2	35.6
	Kraft		25	–	–	53.6	19.5	34.9
	Kraft-AQ	291	20	0.10	–	56.0	20.9	35.7
	Kraft-AQ		18	0.20	–	58.7	23.7	32.4
	Kraft-AQ		19	0.20	–	56.3	22.1	34.5
	PS	291	20	–	1	57.0	26.3	34.1
	PS		20	–	2	57.0	24.5	32.0
	PS		23	–	1	53.7	19.7	36.3
	PS-AQ	291	20	0.10	1	56.3	21.4	32.8
Japanese larch	Kraft	1239	32.2	–	–	45.0	23.6	5.2
	PS-AQ	1549	24.5	0.21	2	48.5	23.6	13.7

AA, active alkaline; AQ, anthraquinone; PS, polysulfide



**Fig. 4.** Hexenuronic acid (*HexA*) content and hydroxide ion concentration required for acacia and Japanese larch pulp given by the kraft, kraft-anthraquinone (*kraft-AQ*), and polysulfide-anthraquinone (*PS-AQ*) methods. Acacia pulps had a kappa number of 20 at H-factor 291 and Japanese larch pulps had a kappa number of 25 at H-factor 1200

contents of the acacia pulp between the three methods. It is clear that the behavior of the HexA contents on the addition of AQ and sulfur for acacia pulp was quite different from that for Japanese larch pulp.

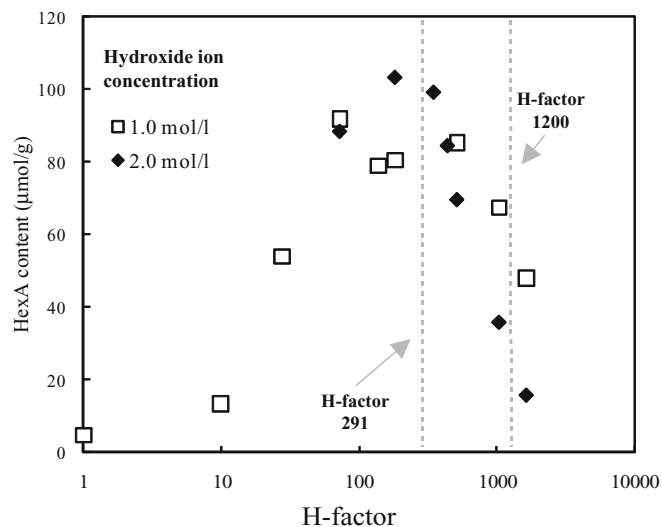
Next, we used a glucuronoxylan model under alkaline cooking conditions to further elucidate the differential behaviors of HexA formation between hardwood and softwood for the various cooking methods.

#### Behaviors of HexA formation during alkaline cooking of glucuronoxylan

In this study, glucuronoxylan prepared from cotton linter was used as a model. It contains mainly residue of 4-*O*-methyglucuronic acid and some residue of glucuronic acid with xylan.<sup>19</sup> Figure 5 shows HexA formation and decomposition behaviors during cooking of the model in 1.0 or 2.0 mol/l hydroxide. The HexA content of the hexenuronoxylan model reached a maximum of 92.0 μmol/g for an H-factor of 72 (at 140°C for 1 h) with 1.0 mol/l of hydroxide. It reached a higher maximum of 103.5 μmol/g for an H-factor of 182 (at 150°C for 1 h) with 2.0 mol/l of hydroxide. In addition, the HexA contents of the model with 2.0 mol/l of hydroxide were smaller than those with 1.0 mol/l of hydroxide for H-factors greater than 438.

On the basis of these model experiments, it was shown that cooking with 2.0 mol/l of hydroxide yields a higher maximum value of HexA formation and a higher HexA decomposition rate than cooking with 1.0 mol/l of hydroxide does. Magara et al.<sup>20</sup> prepared hexenuronoxylan from beech xylan and studied HexA formation under alkaline conditions. They found that at a given H-factor, the formation rate was higher when the alkaline concentration was higher.

The differential behavior of HexA contents between Japanese larch pulp (kappa number of 25) and acacia pulp



**Fig. 5.** Behaviors of HexA formation and degradation during the cooking of glucuronoxylan with various hydroxide ion concentrations

(kappa number of 20) can be explained using the results of the model experiment, i.e., the H-factor of 1200, under which the cooking of Japanese larch wood was carried out, was in a higher range than that for the cooking of acacia wood. Clearly, HexA decomposition has already started at an H-factor around this value (1200). The rate of decomposition was obviously accelerated by the increase in hydroxide ion concentration in the cooking liquor. Thus, it was thought that HexA in the pulp decomposes more slowly because the addition of cooking additives such as AQ was accompanied by a decrease in the required hydroxide ions in the liquor. In contrast, the cooking of acacia wood was carried out at an H-factor of 291, which was lower than that for cooking Japanese larch. In this H-factor range, HexA content increases to a maximum level and then starts decreasing at high hydroxide ion concentrations such as 2.0 mol/l, whereas it slowly decreases at low hydroxide concentrations such as 1.0 mol/l. Two curves – the HexA formation/decomposition curve with 1.0 mol/l of hydroxide and the decomposition curve with 2.0 mol/l of hydroxide – cross at an H-factor of around 450. This could explain why the hydroxide ion concentration hardly affected the HexA content of acacia pulp with a given kappa number for the kraft, kraft-AQ, and PS-AQ methods.

## Conclusions

We investigated methods for determining the HexA content of pulp by formic acid hydrolysis. The UV method was found to overestimate HexA contents as compared to the HPLC method. In particular, overestimation was greater for pulp containing a small amount of HexA. It is thus necessary to separate FA and FF from the hydrolysate and to determine the HexA of the pulp by HPLC.

We investigated HexA formation and decomposition behaviors during the kraft, kraft-AQ, and PS-AQ cooking of acacia wood. Although the addition of AQ and sulfur to the kraft cooking liquor caused a decrease in the hydroxide ion concentration for obtaining a given kappa number, it did not affect the HexA content of acacia pulp. This observation is quite different from that for Japanese larch pulp.

To elucidate the reason for this difference, we used glucuronoxylan from cotton linter as a model and cooked it with 1.0 and 2.0 mol/l NaOH. The amount of HexA formed and its decomposition rate were higher in the 2.0 mol/l solution than in the 1.0 mol/l solution. At a low H-factor similar to that for hardwood cooking, the HexA content first increased to its maximum level and then decreased. This decrease was slower at low hydroxide ion concentrations than at high concentrations. The HexA formation/decomposition curve with 1.0 mol/l of hydroxide crossed the decomposition curve with 2.0 mol/l hydroxide at an H-factor of around 450. This could explain why the hydroxide ion concentration hardly affected the HexA content of acacia pulp with a given kappa number for the kraft, kraft-AQ, and PS-AQ methods.

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