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## KINETICS, CATALYSIS, AND REACTION ENGINEERING

## Kinetic Study of Hexenuronic and Methylglucuronic Acid Reactions in Pulp and in Dissolved Xylan during Kraft Pulping of Hardwood

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During kraft pulping, the side group in the xylan backbone, 4-*O*-methyl-D-glucuronic acid, is partly converted to hexenuronic acid. Simultaneously, degradation reactions of these side groups take place. The rates of these reactions were studied during the kraft pulping of hardwood and were shown to be strongly affected by the location of the xylan; dissolved xylan had markedly higher methylglucuronic acid and hexenuronic acid contents than pulp xylan did. The degree of substitution of methylglucuronic acid in dissolved xylan was found to be higher at reduced cooking temperatures; no such change was seen for pulp xylan. A kinetic model was developed that included the energies of activation for formation (129 kJ/mol) and degradation (143 kJ/mol) of hexenuronic acid and degradation (141 kJ/mol) of methylglucuronic acid and bulk delignification (118 kJ/mol, in accordance with earlier studies). Decreased cooking temperatures thus increase the number of acidic charged groups in the pulp and in dissolved xylan.

## Introduction

The delignification of wood during kraft cooking is accompanied by the simultaneous dissolution of carbohydrates, especially hemicelluloses. As early as the early 1950s, it was stated that under kraft pulping conditions, dissolved hexosans are largely degraded, whereas pentosans are more stable toward degradation reactions.<sup>1</sup> Later, the higher stability of glucuronoxylan than of other wood carbohydrates was related to its reduced end group (i.e., galacturonic acid together with the substituents methylglucuronic acid (MeGlcA)<sup>2</sup> and hexenuronic acid (HexA)).<sup>3</sup> HexA is formed from the native MeGlcA in xylan. Over the past decade, HexA has attracted great interest after new discoveries exposed its contribution to the kappa number,<sup>4</sup> reactivity to bleaching chemicals,<sup>5</sup> and strong involvement in the brightness reversion of pulp and paper.<sup>6</sup>

Because of its negative effects, it is crucial to minimize the amount of hexenuronic acid created in the kraft cook. Some studies have considered the kinetics of the formation and degradation of hexenuronic acids, together with the degradation of methylglucuronic acid. The recipe for minimizing the HexA content of pulp often involves high temperatures and high alkali levels.<sup>7,8</sup> Such cooking conditions, however, also minimize the xylan content of the produced pulp. For a pulp producer, high xylan content is essential, not only due to its contribution to pulp yield<sup>9,10</sup> but also to its ability to improve pulp strength.<sup>11–14</sup> The challenge is thus to produce a pulp with a high xylan content and a low hexenuronic acid content (i.e., minimizing the degree of substitution of the hexenuronic acid of xylan).

Later in the kraft cook, dissolved glucuronoxylans can be redeposited onto the fibers to a greater extent than the pulp glucuronoxylans are being dissolved,<sup>15</sup> causing a net increase in the xylan content of the pulp and also possibly in the MeGlcA

and HexA content. The amount of methylglucuronic acid in xylan affects the sorption of xylan onto the fibers.<sup>16</sup> It has been shown that introducing charged groups to the external parts of the fibers increases the strength of the fiber–fiber joints,<sup>17</sup> and the strength-enhancing effect of xylan can be fully explained by the xylan located on the surface.<sup>18</sup> Given this background, we hypothesize that a pulp containing xylan with a high carboxylic acid content located on the surface of the fibers might be stronger than a corresponding pulp with less carboxylic acid in the pulp xylan. Another possibility is that a higher xylan content on the surfaces may increase the strength independently of the surface charge.

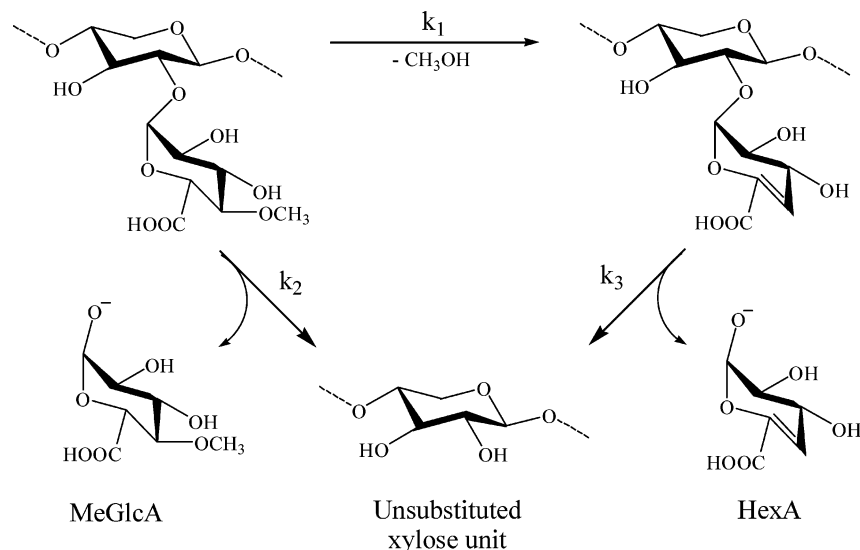
The change of methylglucuronic acid content during kraft pulping is due to four separate processes: (1) the formation of hexenuronic acid, (2) the dissolution and redeposition of xylan, (3) the degradation of xylan through primary peeling, secondary peeling, and alkaline hydrolysis, and (4) the cleavage of the glycosidic bond connecting methylglucuronic acids to the xylan backbone. The same reactions are responsible for changes in the hexenuronic acid content of pulp. In the study presented here, the methylglucuronic and hexenuronic acid contents of pulp xylan and of dissolved xylan were studied after different cooking times. The MeGlcA and HexA lost due to the dissolution of polymeric xylan were not considered to be degraded but as still present in the cook.

This paper proposes a kinetic model that simultaneously considers the decrease in the methylglucuronic acid content of pulp and liquor due to the cleavage of methylglucuronic acids from the xylan backbone and to the degradation of the xylan itself and the formation of hexenuronic acid together with its degradation reactions.

## Materials and Methods

Hardwood (*Betula pubescens/pendula*) industrial chips from the Skärblacka Mill, Billerud AB, were air-dried. All chips were

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**Figure 1.** Rate constant of the formation of hexenuronic acids through the elimination of methanol from methylglucuronic acids is referred to as  $k_1$ . The degradation of MeGlcA and HexA is controlled by rate constants  $k_2$  and  $k_3$ , respectively.

laboratory screened, and the 2–8 mm fraction was used. Chips with knots and bark were removed by hand. Screened birch chips were placed in steel autoclaves (25 g in each) and evacuated for 30 min. The cooking liquor was then sucked into the autoclaves. To keep the concentrations constant and to vary only one parameter at a time, a high liquor-to-wood ratio of 75:1 L/kg was employed with the following initial concentrations:  $[\text{OH}^-] = 0.4 \text{ mol/L}$  and  $[\text{HS}^-] = 0.2 \text{ mol/L}$ . Sodium chloride was added to achieve a sodium ion concentration of 1.0 mol/L to simulate the ionic strength in an industrial cook. The autoclaves were placed in a poly(ethylene glycol) bath. The temperature was increased by 1 °C/min from 120 °C to the final temperature and then held constant at this temperature for particular lengths of time (see Table 1). The cooking time includes the heating period but is calculated using the energy of activation (117 kJ/mol) for the bulk delignification of birch<sup>19</sup> at the final temperature for all cooks.

After cooking, all pulps were washed for 12 h in deionized water and defibrated in a water jet NAF defibrator (Nordiska Armatur Fabriken, Sweden). The total amounts of oxidizable structures in all pulps were determined as the kappa number (SCAN C 1:00). The residual hydroxide ion (SCAN N 33:94) and hydrogen sulfide ion concentrations (SCAN N 31:94) of all spent black liquors were determined.

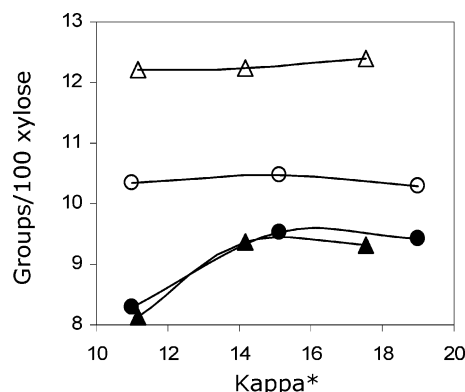
Xylan was isolated from the black liquors produced in the cooks outlined in Table 1 using a method described in Axelsson et al.,<sup>20</sup> but with one modification: in the last washing step, acetone was used instead of ethyl ether. The amounts of Klason lignin in the wood, pulps, and precipitated black liquor xylan were determined using TAPPI method T222 om-83, and the

carbohydrate composition was determined after acid hydrolysis according to Theander and Westerlund.<sup>21</sup>

The hexenuronic acid content of the pulps and precipitated xylan were determined using the method described by Gellerstedt and Li.<sup>22</sup> In this method, HexA is selectively hydrolyzed by mercury acetate, followed by oxidation. The oxidation product,  $\beta$ -formyl pyruvic acid, is then condensed with thiobarbituric acid to the colored structure suitable for HPLC separation and UV detection. The total uronic acid contents of the pulps and precipitated xylan were determined using the colorimetric method described in Filisetti-Cozzi and Carpita.<sup>23</sup> The samples were prepared to always contain 200–300 nmol of uronic acid. The MeGlcA contents were subsequently calculated by subtracting the HexA content from the total uronic acid content.

## Results and Discussion

**Methylglucuronic Acids in Xylan.** The amounts of methylglucuronic acids in pulp xylan and dissolved xylan are shown in Figure 2 for two different cooking temperatures.



**Figure 2.** Methylglucuronic acid contents of dissolved (unfilled markers) and of pulp xylan (filled markers) presented as the number of groups per 100 xylose units at different degrees of delignification. Kappa\* indicates the corrected kappa number to exclude the contribution of hexenuronic acid, which was calculated from the HexA content according to Li and Gellerstedt.<sup>4</sup> Triangles indicate 140 °C as the cooking temperature, and circles indicate 160 °C.

**Table 1. Cooking Parameters**

temperature (°C)	cooking time <sup>a</sup> (min)	H factors	kappa number	pulp yield (%)
140	384	418	20.5	49.6
	421	460	17.4	48.2
	501	555	14.5	48.3
150	148	400	23.7	48.7
	180	488	17.8	49.3
	205	555	15.0	48.0
160	76	488	21.7	49.2
	86	555	18.1	48.3
	101	655	14.2	47.8

<sup>a</sup> At final cooking temperature.

As seen, the degree of substitution of methylglucuronic acids on xylan is higher for the dissolved substance than for pulp

xylan. It is also seen that the influence of cooking temperature is high in the dissolved phase, whereas the amount of methylglucuronic acid in pulp xylan is not markedly affected by increased temperature. To be able to calculate the rate of methylglucuronic acid degradation, we assumed that the change with time of the methylglucuronic acid content can be expressed as follows:

$$\frac{d[\text{MeGlcA}]}{dt} = k_{\text{MeGlcA}}[\text{MeGlcA}] \quad (1)$$

where  $k_{\text{MeGlcA}}$  is the rate constant of all methylglucuronic acid-consuming reactions. The solution to eq 1 is shown in eq 2, where  $[\text{MeGlcA}]_0$  is the MeGlcA content of wood.

$$[\text{MeGlcA}] = [\text{MeGlcA}]_0 e^{-k_{\text{MeGlcA}} t} \quad (2)$$

The rate constant,  $k_{\text{MeGlcA}}$ , was estimated from the least-squares fit of eq 2 to the amounts of MeGlcA shown in Figure 2 at different cooking times. The energy of activation for the consumption of methylglucuronic acids in both pulp and dissolved xylan can be estimated from the temperature dependency of the rate constant  $k_{\text{MeGlcA}}$ , using Arrhenius' law of kinetics shown in eq 3.

$$k = A e^{-E_a/RT} \quad (3)$$

Here,  $k$  is the rate constant,  $A$  is the Arrhenius' preexponential factor,  $E_a$  is the energy of activation,  $R$  is the general gas constant, and  $T$  is the absolute temperature. The same type of equation was used to describe the rate of delignification at the different studied temperatures, as shown in eq 4.

$$\frac{d(\text{kappa}^*)}{dt} = k_{\text{delignification}} \text{kappa}^* \quad (4)$$

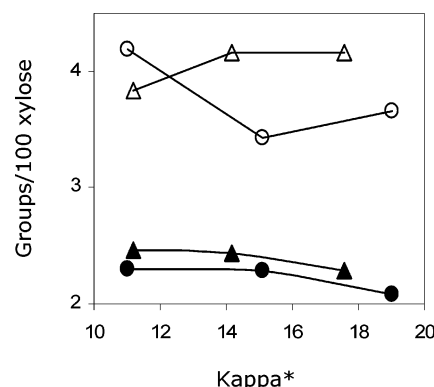
The observed  $k$  values are presented in Table 2.

**Table 2. Apparent Rate Constants for MeGlcA Degradation in Pulp and Dissolved Xylan**

temperature (°C)	$k_{\text{MeGlcA}}(\text{pulp})$ (min <sup>-1</sup> )	$k_{\text{MeGlcA}}(\text{solution})$ (min <sup>-1</sup> )	$k_{\text{delignification}}$ (min <sup>-1</sup> )
140	0.0013	0.0003	0.0042
150	0.0031	0.0013	0.0090
160	0.0050	0.0022	0.0159
$E_a$ (kJ/mol)	120	180	118

The energy of activation was found to be 120 and 180 kJ/mol in pulp and in black liquor, respectively. This should be compared to the energy of activation for the bulk delignification of birch, which was previously reported to be 117 kJ/mol<sup>19</sup> and was here found to be 118 kJ/mol. The decrease in the methylglucuronic acid content of pulp xylan displays a temperature dependency very close to that of delignification, which implies that it is hard to control the MeGlcA content of pulp xylan by temperature. For dissolved xylan, the situation is different, and the temperature dependency of the methylglucuronic acid-consuming reactions is higher than the comparable value for delignification. It seems as though part of the methylglucuronic acid content of pulp xylan is stable during the kraft cook independent of temperature, whereas another part dissolves together with the xylan, degrading to a certain extent depending on temperature.

**Hexenuronic Acid.** The hexenuronic acid content of the same set of pulp and black liquor xylan samples as shown in Figure 2 is shown in Figure 3. The temperature did not affect the



**Figure 3.** Hexenuronic acid content of dissolved (unfilled markers) and of pulp xylan (filled markers) presented as the number of groups per 100 xylose units at different degrees of delignification. Triangles indicate 140 °C as the cooking temperature, and circles indicate 160 °C.

hexenuronic acid content of pulp xylan very much within the studied kappa number interval. Also, in this case, the dissolved xylan displays greater substitution, especially at the lower temperature. A common recipe for minimizing the hexenuronic acid content of pulp is to use high temperature and high alkalinity during cooking; this method, however, also minimizes the amount of xylan in pulp, which rarely is a desired effect. Figure 3 shows the parameter one should try to minimize, namely, the amount of hexenuronic acid in pulp xylan. Although the cooking temperature was varied within the range of values found in industrial processing, the amount of hexenuronic acids in pulp xylan was only slightly lower with the higher cooking temperature.

Studying the degree of side group substitution in the xylan that goes into solution and to some extent also readsorbs onto the fibers is troublesome. The change in methylglucuronic acid content with cooking time might well be related to either the selective dissolution of high-substituted xyans and/or the readsorption of low-substituted xyans. To get around this problem, the total amounts of methylglucuronic and hexenuronic acids (in both dissolved and pulp xylan) were determined for different cooking times and temperatures. To obtain addable data for pulp and dissolved xylan, the amounts of hexenuronic acids and methylglucuronic acids will from now on be expressed in  $\mu\text{mol/g}$  of wood cooked. This means that when xylan is degraded, a decrease in methylglucuronic acid and to some extent in hexenuronic acid content is observed.

**Estimation of the Rate Constants  $k_1$ ,  $k_2$ , and  $k_3$ .** As seen in Figure 1, the change of the hexenuronic acid content of xylan is determined by both the methylglucuronic and the hexenuronic acid contents, as expressed in eq 5.

$$\frac{d[\text{HexA}]}{dt} = k_1[\text{MeGlcA}] - k_3[\text{HexA}] \quad (5)$$

The initial condition is  $[\text{HexA}] = 0$  at  $t = 0$ .

This differential equation can be solved using eq 2, and the solution is shown in eq 6.

$$[\text{HexA}] = \frac{k_1[\text{MeGlcA}]_0}{k_1 + k_2 - k_3} (e^{-k_3 t} - e^{-(k_1 + k_2)t}) \quad (6)$$

In Table 2,  $k_{\text{MeGlcA}}$  is shown; it can be seen in Figure 1 that the reactions consuming MeGlcA are  $k_1$  and  $k_2$ , which give eq 7.

$$k_{\text{MeGlcA}} = k_1 + k_2 \quad (7)$$

From eq 6, together with obtained data, the constants could be

estimated as follows. For each temperature, the equation was written as a ratio between two points.

$$\frac{[\text{HexA}](t_1)}{[\text{HexA}](t_2)} = \frac{e^{-k_3 t_1} - e^{-(k_1+k_2)t_1}}{e^{-k_3 t_2} - e^{-(k_1+k_2)t_2}} \quad (8)$$

where  $t_1$  is one cooking time and  $t_2$  is another. The ratio can be created for any two points in a series; in this study, the first and last points were used.

By using eq 7, the only unknown left in eq 8 is  $k_3$ , leading to a unique solution. When  $k_3$  has been determined, eqs 6 and 7 can be used again.

$$[\text{HexA}](t) = \frac{k_1[\text{MeGlcA}]_0}{k_{\text{MeGlcA}} - k_3} (e^{-k_3 t} - e^{-k_{\text{MeGlcA}} t}) \quad (9)$$

Here, the only unknown is  $k_1$ , so it would be possible to calculate  $k_1$  for all values of  $[\text{HexA}]$  at different cooking times. However, these values should all produce the same results, so the average value was used in this study.

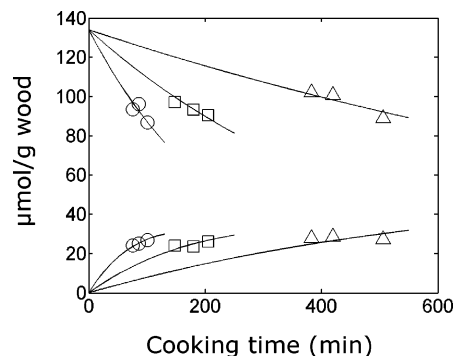
Once  $k_1$  has been determined,  $k_2$  can also be determined from eq 7. The values of the rate constants are shown in Table 3 together with the energies of activation that were calculated in the same way as stated previously.

**Table 3. Rate Constants at Different Cooking Temperatures**

temperature (°C)	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )	$k_3$ (min <sup>-1</sup> )
140	0.0006	0.0001	0.0011
150	0.0016	0.0004	0.0028
160	0.0036	0.0007	0.0071
$E_a$ (kJ/mol)	129	143	141

It can be seen in the table that the degrees of temperature dependency of the degradation reactions of MeGlcA and HexA are very similar. These degradation reactions are not only due to the cleavage of the side groups but also to the degradation of xylan itself. The energy of activation for HexA formation is slightly lower; as the energy of activation for delignification is even lower still, it is possible to control these reactions by adjusting the cooking temperature. This means that cooking at low temperatures produces a xylan richer in MeGlcA than when xylan is cooked at a higher temperature. As seen in Figure 2, this highly charged xylan stays in solution, and the MeGlcA content of pulp xylan is only slightly affected by a change in cooking temperature. The situation is different for the hexenuronic acids since the reaction rates of both formation and degradation are more temperature sensitive than the delignification rate is. The effect of temperature will not be as pronounced as in the case of MeGlcA. However, the HexA content is higher for xylan cooked at lower rather than higher temperatures since the energy of activation is higher for the degradation than for the formation of HexA. All HexA and MeGlcA contents are shown in Figure 4; the solid lines represent the models expressed in eqs 2 and 6 with the  $k$  values shown in Table 3.

The energies of activation shown in Table 3 are all considerably higher than was recently reported by Simao et al. for *Eucalyptus globulus*.<sup>7</sup> Their approach was somewhat different, and no analyses were made of the dissolved xylan. As well, they divided the methylglucuronic acid content into different portions in terms of their reactivity. These differences in method make it very difficult to compare the different studies. However, both these studies of hardwood pulps found that the methylglucuronic acids are not totally degraded early in the cook, as



**Figure 4.** Upper curves show the methylglucuronic acid content, and the lower curves show the hexenuronic acid content of the sum of the pulp xylan and the dissolved xylan manufactured at different cooking temperatures; triangles indicate 140 °C, squares 150 °C, and circles 160 °C.

has been reported in the case of softwood xylan.<sup>5,24</sup> Approximately half of the methylglucuronic acid content of pulp xylan seems to remain at the end of the cook, while even more remains in the dissolved xylan.

## Conclusions

(1) Dissolved xylans are richer in methylglucuronic acids and hexenuronic acids than is the xylan located in the pulp. (2) The change in temperature primarily affected the methylglucuronic acid content of the dissolved xylan, whereas the methylglucuronic acid content of pulp xylan was not affected at a given corrected kappa number. The hexenuronic acid content of pulp xylan was only slightly affected by a change in temperature. (3) The energies of activation for the formation of hexenuronic acids, the degradation of methylglucuronic acids, and the degradation of hexenuronic acids in the kraft cooking of birch were found to be 129, 143, and 141 kJ/mol, respectively. The energy of activation for the delignification of birch was found to be 118 kJ/mol. (4) The differences in activation energies imply that xylan cooked at lower temperatures contains more acidic charged groups than does xylan cooked at higher temperatures. This study demonstrated that this is indeed the case for the dissolved xylan, whereas pulp xylan is not markedly affected by a change in cooking temperature.

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