

NOTE

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Contribution of lignin to the reactivity of wood in chemical modifications II: influence of delignification on reaction with vaporous formaldehyde

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Abstract Participation of lignin in the reaction between vapor-phase formaldehyde and wood was examined by using gradually delignified wood meal. A first-order rate equation was successfully applied to the weight gain data. From the estimated reaction parameters such as rate constant, k , and ultimate weight gain, a , the reactivity toward formaldehyde was discussed among wood components, and compared with that for acetylation. k decreased monotonously with progress of the elimination of lignin, suggesting that the reaction rate of lignin is dominant over that of whole wood, and the decrease in the ratio of lignin retarded the reaction of wood as a whole. On the other hand, a increased with decreasing lignin content. This may be attributable to the enhanced reactivity of the remaining lignin due to some structural changes and to the increase in the number of reactive sites in polysaccharides as a result of their exposure accompanying the elimination of lignin. The dependencies of k and a on the lignin content were not similar to the case for acetylation, probably because of the difference in the reaction phase. In vapor-phase formaldehyde treatment, the remaining lignin reacts as it is, whereas in liquid-phase acetylation it would undergo rearrangement or swelling of the structure in the reaction solution.

Key words Chemical modification · Formaldehyde treatment · Lignin content · Reactivity · Reaction parameter

Introduction

In part I of this study,¹ we considered the influence of lignin on the reaction parameters in the acetylation of wood. The

analysis by reaction kinetics suggested quantitative decrease in lignin and structural changes to the remaining lignin occur during the course of delignification, underlying the complicated effects on the reaction parameters of the acetylation, such as rate constant, activation energy, and ultimate value of the reaction.

In this part, we clarify the contribution of lignin to the reaction between wood and formaldehyde. With the reaction generally proceeding in the vapor phase, and involving cross-linking between two hydroxyl groups, the phase and the type of reaction differ significantly from those of acetylation. It is thus interesting to compare the participation of lignin in the two typical modifications of wood, namely acetylation and formaldehyde treatment.

Similar to the case for acetylation, lignin was gradually eliminated from the wood meal subjected to the reaction. Using the weight gain as a measure of the progress of reaction, we considered the reaction mechanism from kinetic aspects.

Material and methods

Wood meal (150–355 μm) of spruce (*Picea sitchensis* Carr) was used after Soxhlet extraction with ethanol–benzene (v/v = 1:2) for 6 h. Elimination of lignin was carried out according to the sodium chlorite method (so-called Wise's method), the detailed procedure of which is described in part I.¹ In order to prepare gradually delignified wood meal, we continued the elimination process for 0.5, 1, 2, 3, and 4 h at 75°C, while supplementing the reagents every hour. The remaining lignin content was determined by means of the sulfuric acid method using a part of delignified wood meal. The degree of lignin elimination (E_L) was defined by

$$E_L (\%) = \left(1 - \frac{\text{lignin content}}{27.0} \right) \times 100$$

with the lignin content of untreated wood meal set to 27.0%. Table 1 summarizes the lignin content for the partially del-

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Table 1. Lignin content and degree of lignin elimination, E_L , for partially delignified wood meals

Treatment time (h)	Lignin content (%)	E_L (%)
0	27.2	0
0.5	20.1	26.1
1	17.1	37.1
2	10.0	63.2
3	5.1	81.3
4	3.1	88.6

ignified wood samples and E_L along with the processing duration.

The reaction of wood meal with formaldehyde was conducted as follows. As a reaction vessel, a 4-l airtight glass vessel with a stopcock was used. About 1g of oven-dry wood meal and 3g of paraformaldehyde (reagent grade, Merck) were placed in separate small glass bottles and these were located in the preheated (120°C) vessel. After the vessel was evacuated, 400ml of SO_2 , which gave a concentration of approximately 2.23mM in the vessel, was introduced through a syringe. The whole vessel was then heated in an oven at 120°C for 0.5 to 36h. When the paraformaldehyde vaporized completely, the concentration of formaldehyde in the vapor phase was about 0.025 M.

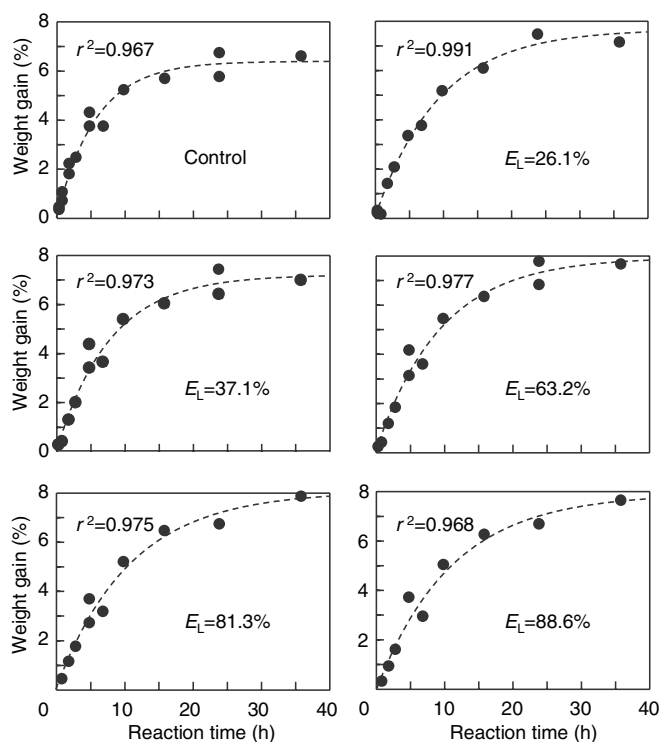
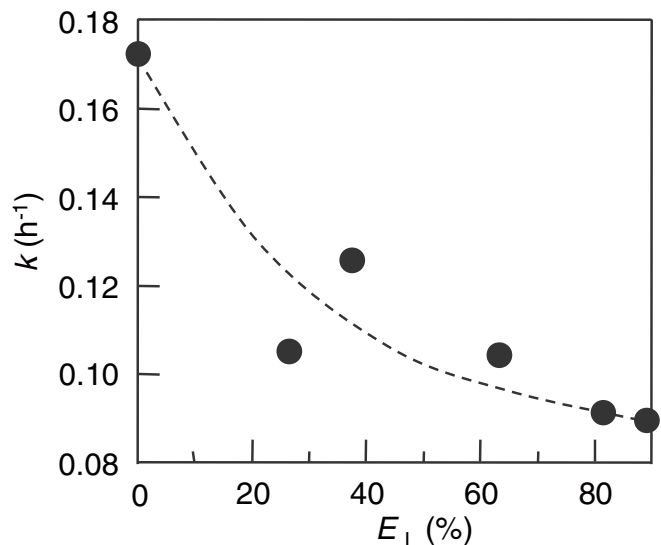
After the prescribed reaction duration, the bottle of wood meal was taken out of the vessel, and heated for a further 2h at 120°C to remove unreacted formaldehyde. The conditions of posttreatment were preliminarily confirmed to be sufficient. The weight percent gain (WG) calculated on the basis of oven-dry weight before reaction was regarded as a measure of the progress of the reaction for the following kinetic consideration.

Results and discussion

Figure 1 shows the reaction profiles for gradually delignified wood meal. In the range examined, the WG generally reached about 6.5% and leveled off between 6.5% and 8%. The reaction rate between formaldehyde molecules and hydroxyl groups in wood constituents is expressed by

$$\text{Reaction rate} = -d[\text{OH}]/dt = k' \times [\text{CH}_2\text{O}] \cdot [\text{OH}] \quad (1)$$

where k' is the second-order rate constant, $[\text{CH}_2\text{O}]$ and $[\text{OH}]$ are the concentrations of formaldehyde in vapor phase and accessible hydroxyl groups in wood components, respectively. In the reaction vessel, 3g of paraformaldehyde was supplied to 1g of wood meal. Even when the maximum WG is estimated to be 10%, the amount of required formaldehyde is 0.1g, which is around one thirtieth of the supplied formaldehyde, and hence if the paraformaldehyde vaporizes completely, as was the case, formaldehyde should be in vast excess at the reaction sites. Consequently, it is appropriate to regard the reaction as pseudo-first order. However, we followed the weight increase, namely WG, instead of the decrease of $[\text{OH}]$ and thus applied the first-order rate equation,

**Fig. 1.** Reaction profiles and applied regression curves for different degrees of lignin elimination**Fig. 2.** Dependence of rate constant on the degree of lignin elimination

$$\text{WG}(\%) = a(1 - e^{-kt}) \quad (2)$$

where, a is the ultimate WG (%), k is the rate constant (h^{-1}), and t is reaction time (h). The curves drawn in Fig. 1 are the optimal curves obtained by nonlinear regression using commercially available computer software. The ratios of contributions (r^2) were at least 0.967.

Figure 2 shows the dependence of k on E_L , where k monotonously decreased with the elimination of lignin. This

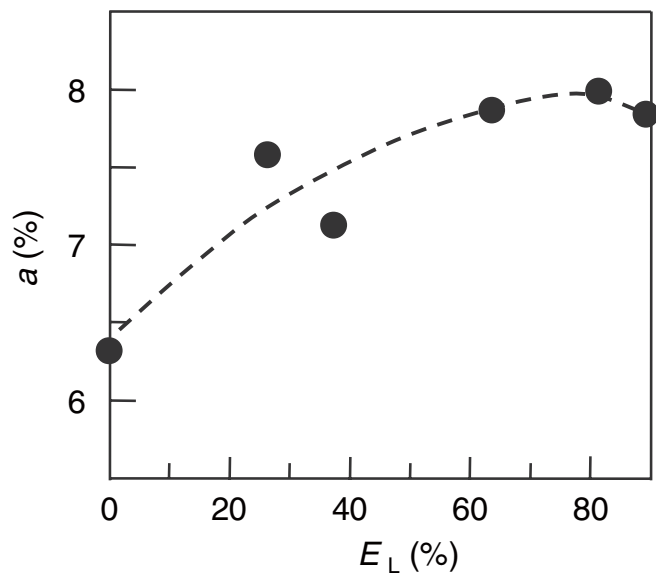


Fig. 3. Dependence of ultimate weight gain on the degree of lignin elimination

result suggests the priority of the reaction of formaldehyde with lignin over other wood components, such as cellulose and hemicellulose. If this is not the case, the decrease of lignin content should not cause a large decrease of rate constant of wood as a whole. In the acetylation, the overall reaction rate had a maximum with increasing E_L , and it was speculated that chemical and/or physical changes in structure as well as separation of lignin occur during the process of delignification. Rearrangement or swelling of the once-changed structure, which may increase the reaction rate, would appear when the delignified wood meal was soaked in the reaction solution, but this was not the case for formaldehyde treatment in which the reaction occurs in the vapor phase and the meal thus remains in a dry state throughout the process.

The ultimate WG, namely a , calculated by regression increased with the advance of lignin elimination (Fig. 3). This result also differs from acetylation, in which a decreased, showed a minimum, and then increased. The ultimate WG for the heterogeneous vapor phase reaction of cotton cellulose with formaldehyde may be 2% at most,^{2,3} although there is not sufficient data to estimate it precisely. Thus, the reactivity of cellulose in wood may be somewhat lower than wood as a whole. The large a value for highly delignified wood meal thus cannot be explained without knowledge of the qualitative changes in remaining lignin and enhanced accessibility of polysaccharides, which is probably due to their exposure accompanying the elimination of lignin. The increases of equilibrium moisture content observed for delignified wood meal in part I¹ suggest the enhanced accessibility of polysaccharides. Nevertheless, the increased reactivity in the remaining lignin also has to be taken into account, because the slight change in equilibrium moisture content cannot fully explain the high WG.

When cross-linkage of one molecule of formaldehyde ($-\text{CH}_2\text{O}-$) is formed between two hydroxyl groups and one water molecule is removed, the ultimate WG of wood can be calculated as 5.5% on the basis of the estimation by Norimoto;⁴ the detailed prerequisite conditions and procedure of the calculation are similar to the case for acetylation referred to in part I.¹ On the other hand, the observed value was about 6.6% when native wood meal was treated with formaldehyde for 36 h. The observed value being higher than the calculated value is attributable to the error in the estimation of the amount of accessible hydroxyl groups, incomplete removal of unreacted formaldehyde, and the existence of polymeric cross-linkages, namely $(-\text{CH}_2\text{O}-)_n$ in which $n \geq 2$.

Conclusions

The participation of lignin in the reaction between formaldehyde and wood meal was examined by means of reaction kinetics. The conclusions are as follows:

1. Rate constant, k , decreased monotonously with progress of the elimination of lignin. From this result, it is considered that the reaction rate of lignin dominates the overall reaction rate, and the decrease in the ratio of lignin retarded the reaction of wood as a whole.
2. The ultimate WG, a , increased in accordance with the extent of delignification. This may be explained by the enhanced reactivity of the remaining lignin due to some changes in the chemical and/or physical structure and by the increase in the number of reactive sites in polysaccharides accompanying the elimination of lignin.
3. The effects of k and a on the lignin content did not coincide with the case for acetylation, and this is attributed to the difference of the reaction phase for the different reactions. That is to say, in the vapor-phase formaldehyde treatment, the remaining lignin reacts as it is, whereas in the liquid-phase acetylation it undergoes rearrangement or swelling of the structure in the reaction solution. Similar tendencies for k and a to the acetylation found in the region of extremely low lignin content may reflect the decreasing contribution of lignin.

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