ORIGINAL ARTICLE

Kazuya Minato · Rieka Shimizu · Shingo Kawaguchi

Contribution of lignin to the reactivity of wood in chemical modifications I: influence of delignification on acetylation

Abstract In order to examine the contribution of wood components to the acetylation of wood, we acetylated wood meal that had been partially delignified. The results were analyzed in terms of the reaction kinetics. The first-order rate equation was successfully adjusted to the weight gain data. The rate constant for acetylation initially increased with progress of lignin elimination and then turned to decrease; the apparent activation energy showed the reverse tendency and ranged from about 90 to 130 kJ/mol. These results suggest that lignin elimination brings not only separation of lignin but also drastic change of the chemical and/or physical structure in the residual lignin, and this affects the reactivity of wood meal as a whole. The ultimate weight gain estimated by the regression of the rate equation showed a minimum when lignin was moderately eliminated, which was explained in terms of enhanced reactivity of lignin and lower accessibility for holocellulose than predicted. The equilibrium moisture content had a maximum when lignin was moderately eliminated. This tendency is the opposite of that observed for the ultimate weight gain, and suggests that the sites for acetylation do not always correspond to those for moisture adsorption.

Key words Chemical modification · Acetylation · Lignin content · Reactivity · Reaction parameter

K. Minato (✉) · S. Kawaguchi
Graduate School of Agriculture, Kyoto Prefectural University, Shimogamo Hangi-cho, Sakyo-ku, Kyoto 606-8522, Japan
Tel. +81-75-703-5646; Fax +81-75-703-5646
e-mail: minato@kpu.ac.jp

R. Shimizu
Faculty of Agriculture, Kyoto Prefectural University, Kyoto 606-8522, Japan

Introduction

Acetylation is one of the most suitable methods for the enhancement of wood properties from the viewpoints of production cost, manufacturing facility, environmental considerations, and others. There have been many reports directly related to practical production, with descriptions of the performances achieved. Some of these results have been commercially applied to wooden products for use in humid surroundings. Nevertheless, it is important to go back to the basics and consider the particulars of the reaction, which should allow optimization of the reaction conditions, increased performance, development of novel reaction systems, and lowering of production costs.

Recently there have been many studies on the reaction mechanism of wood acetylation. Among them, many have dealt with acetylation from the perspective of reaction kinetics.[1–9] Meanwhile, Rowell[10] and Ohkoshi and Kato[11,12] referred to the priority among wood components to the acetylation. Via instrumental and chemical analyses, they found separately that lignin is much more reactive than cellulose. Furthermore, Rosenqvist[13] applied microautoradiography to the acetylated wood, and observed the even distribution of ^{14}C-labeled and ^{3}H-labeled acetyl groups in the wood cell wall.

In this study, we investigated the influence of lignin on the reactivity of wood to acetylation by applying reaction kinetics. The results offer information not only about the priority of components and regions taking part in the reaction, but also on the occurrences of each component in wood cell wall.

Materials and methods

Wood meal (150–355 μm) of spruce (*Picea sitchensis* Carr) was used after Soxhlet extraction with ethanol–benzene mixed solvent (v/v = 1:2) for 6 h. The elimination of lignin was carried out according to the sodium chlorite method

(so-called Wise's method). However, the original method is a means for determining the holocellulose content in wood and is designed to completely eliminate lignin using a small amount of wood meal. Therefore, the wood meal and reagents (sodium chlorite and glacial acetic acid) were proportionally scaled up to process 25 g of wood meal, while keeping the concentration of the solution the same as in the original protocol. For the gradual elimination of lignin, the addition of reagents at 1-h intervals was repeated one to four times.

A part of the partially delignified wood meal (ca. 1 g) was subjected to determination of lignin content by the sulfuric acid method. The lignin contents, which are based on the oven-dry weight of delignified wood meal, were 18.2%, 9.24%, 5.09%, and 1.81%, and corresponded to the times of addition of reagents. The degree of lignin elimination (E_L) was defined on the basis of the lignin content of untreated wood meal (27.0%) as follows:

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

The E_L ranged from 32.6% to 93.3%.

Another part of the wood meal (ca. 1 g) was subjected to a moisture adsorption test. The wood meal was kept over a saturated aqueous solution of $NaNO_2$ in a glass desiccator for 2 weeks at 20°C. The relative humidity inside the desic-

cator should be 66%. The equilibrium moisture content was calculated from the oven-dry and conditioned weights.

Acetylation was carried out in a glass tube of 27 mm in diameter and 200 mm in length. Thirty-five milliliters of preheated acetic anhydride was added to about 1 g of oven-dry wood meal, and the whole vessel was kept under reflux at a given temperature (100° to 130°C) controlled by an oil bath. The reaction was terminated by pouring the reaction mixture into cooled methanol. The reaction mixture was filtered on a glass filter (G3), and then thoroughly rinsed with distilled water. The weight gain (WG) was calculated from the oven-dry weights before and after acetylation.

Results and discussion

Figure 1 shows the WG profiles with passage of reaction time for each reaction temperature. To the observed WG values, the first-order rate equation,

$$WG (\%) = a \times \left(1 - e^{-kt}\right) \tag{1}$$

was applied, where a is ultimate WG at an infinitely long reaction time, k is rate constant (h^{-1}), and t is reaction time (h).

a and k were estimated using a commercial computer program for nonlinear regression. The regression curves are

Fig. 1. Weight gain profiles with passage of reaction time for each reaction temperature and applied regression curves. Degrees of delignification (E_L) represented by *open circles*, 0%; *open triangles*, 32.6%; *squares*, 65.8%; *filled circles*, 81.1%; *filled triangles*, 93.3%
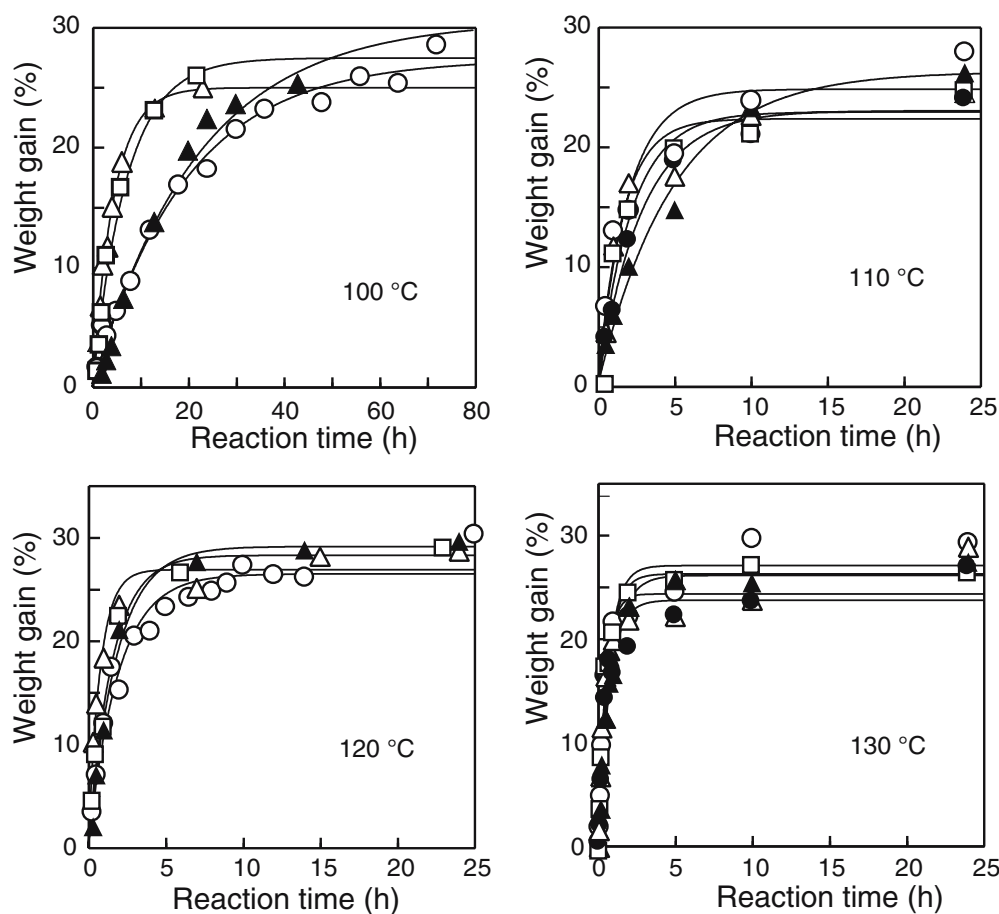
drawn in Fig. 1 along with the observed values. The ratios of contribution (r^2) summarized in Table 1 suggest that the first-order rate equations were fitted fairly well to every reaction condition.

In Fig. 2, the rate constants are plotted against E_L. The rate constant had a maximum at E_L values around 30%–40%, and was rather small for control samples and strongly delignified samples.

Figure 3 is an Arrhenius plot in which the natural logarithm of the rate constant is plotted against the reciprocal absolute temperature. When a straight line was applied for each E_L, fairly good correlation coefficients were obtained except for that of the control.

The apparent activation energies (E_a) estimated from the slopes of the Arrhenius plot are plotted against E_L in
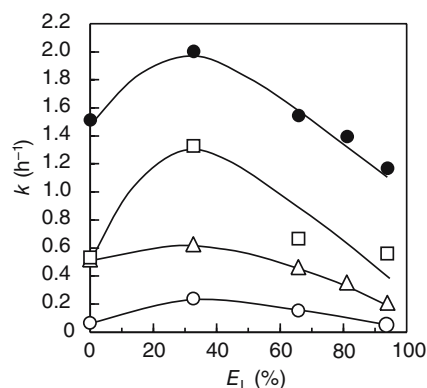
Fig. 4. The E_a for the control (127 kJ/mol) may be less reliable owing to the rather low correlation, but this may not necessarily be the case because we obtained equivalent values (120 and 130 kJ/mol) in separate studies as cited in the figure.[7,8] The E_a of the acetylation decreased with increasing E_L, had a minimum at about 90 kJ/mol, and then increased.

The increase of k and decrease of E_a for the moderately delignified wood meal suggest a qualitative change in the remaining lignin moiety. That is to say, during the delignification process the remaining lignin may change to some complicated state in chemical and/or physical structure. In Table 2, the activation entropies ($\Delta S^{\ddagger}$) estimated at 373 K using the intercept of the Arrhenius plot are summarized for variously delignified wood meals. The negative values of $\Delta S^{\ddagger}$ for the moderately delignified wood meal support complication of the nature of the lignin moiety. However, the lowered reactivity of the lignin inferred from the negative $\Delta S^{\ddagger}$ may be behind the increased reactivity shown by the low E_a. Consequently, the enhanced reactivity of the remaining lignin seems to dominate that of wood meal as a whole.

When the delignification advances further, the values of k and E_a approach those for lignin-free wood meal because of the disappearance of lignin. In the complementary test, we observed a much lower rate constant (2.7×10^{-3} h^{-1} at 120°C) for the uncatalyzed heterogeneous acetylation of pure cotton cellulose than that for wood meal. Therefore, it is likely that the reactivity of lignin-free wood meal is also low as analogized with cotton cellulose.

Fig. 2. Relationship between degree of lignin elimination and rate constant. *Open circles*, 100°C; *triangles*, 110°C; *squares*, 120°C; *filled circles*, 130°C
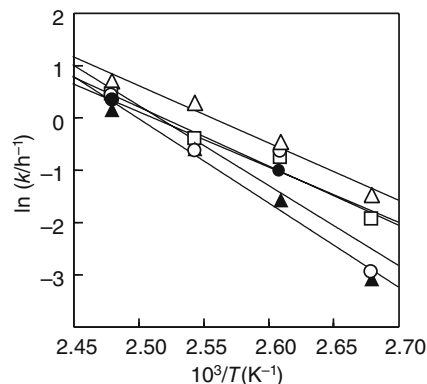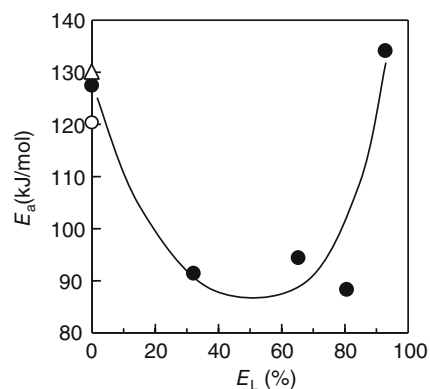

Fig. 3. Arrhenius plot for acetylation of partially delignified wood. Symbols are the same as in Fig. 1

Fig. 4. Dependence of apparent activation energy on the elimination of lignin. *Open circle*, data from Minato;[8] *triangle*, data from Minato and Ogura[7]

Table 1. Ratio of contribution (r^2) in the regression of the first-order rate equation

E_L (%)	100°C	110°C	120°C	130°C
0 (control)	0.988	0.896	0.953	0.950
32.6	0.991	0.910	0.957	0.929
65.8	0.982	0.916	0.980	0.971
81.1	–	0.990	–	0.939
93.3	0.986	0.985	0.989	0.989

Table 2. Activation entropy at 373 K for the acetylation of partially delignified wood meal

E_L (%)	$\Delta S^{\ddagger}$ (J·K^{-1}·mol^{-1})
0	64.8
32.6	−22.3
65.8	−18.1
81.1	−34.3
93.3	79.5

Table 3. Molecular parameters for each wood component proposed by Norimoto[14] and simplified weight fraction adopted in this study

Component	Molecular weight of monomer	OH/monomer	Weight fraction in wood	Simplified weight fraction
Amorphous cellulose	162.14	3	0.216[a]	0.442[b]
Hexosan	162.14	3	0.099	
Pentosan	132.11	2	0.090	
Lignin	194.18	1.16	0.330	0.270
Accessible fraction			0.735	0.712

[a] Calculated assuming the degree of crystallinity to be 55%
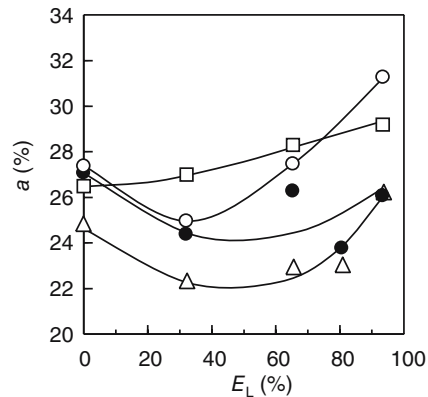[b] Combined value for amorphous cellulose, hexosan, and pentosan

Fig. 5. Dependence of a on the elimination of lignin. Symbols are the same as in Fig. 2

Figure 5 shows the dependence of the a value (ultimate WG) on the E_L for each reaction temperature. Generally, a was a minimum in the moderate E_L region.

Norimoto[14] estimated the WG when all of the accessible hydroxyl groups in wood participate in the acetylation. According to his proposal, the ultimate WG (a') can be calculated by:

$$a'(\%) = 42 \times \sum_{i=1}^{4} \frac{n_i \delta_i}{m_i} \times 100 \quad (2)$$

where m_i is the molecular weight of the monomer for each wood component, n_i is the number of hydroxyl groups per monomer, δ_i is the weight fraction of each component in the wood, and $i = 1, 2, 3, 4$ are amorphous cellulose, hexosan, pentosan, and lignin, respectively. The real values used by Norimoto[14] are cited in Table 3.

For simplification, we dealt with cellulose and hemicellulose together as holocellulose. The reduced values of molecular weight for holocellulose monomer and those of hydroxyl groups per monomer were calculated by the proportional allocation based on the weight fractions of amorphous cellulose and hemicellulose in wood shown in Table 3: they were 155.5 and 2.78, respectively.

In the following consideration, we used 0.270 (obtained here) for the weight fraction of lignin in place of 0.330 as used by Norimoto,[14] and proportionally shared the remaining portion (0.730) to inaccessible (crystalline fraction in cellulose) and accessible fractions (amorphous fraction in cellulose plus hemicelluloses) according to Norimoto's es-

timation, where the amorphous fraction in cellulose is supposed to be 0.45. As a result, the fraction of accessible region in whole wood meal becomes 0.712 (Table 3). Under these assumptions, the a' is given by:

$$a'(\%) = 42 \times \left\{ \frac{n_H \times (0.712 - f_L)}{155.5} + \frac{n_L \times f_L}{194.2} \right\} \times 100 \quad (3)$$

where n_H and n_L ($= n_4$) are the numbers of hydroxyl group per monomer for holocellulose and lignin, respectively, and f_L is the weight fraction of lignin in wood.

According to Eq. 3, a' for untreated wood is estimated as 40.0%, using 0.27, 2.78, and 1.16 for f_L, n_H, and n_L, respectively, for untreated wood. Because the a value and observed ultimate WG are both around 30%, three quarters of the accessible hydroxyl groups should take part in the acetylation at the maximum.

As shown in Fig. 5, the a value initially decreased with progress of the lignin elimination. This situation can be realized only when $n_H/155.5$ is smaller than $n_L/194.2$, namely when n_H/n_L is smaller than 1.25. Because n_H and n_L are 2.78 and 1.16, respectively, n_H/n_L is 2.40. To make n_H/n_L less than 1.25, smaller n_H and/or larger n_L than the estimated values are required. Hiller[15] reported that large fractions of hydroxyl groups could not participate in the heterogeneous acetylation of fibrous cellulose, hence a much smaller value of n_H than 2.78 is likely. Moreover, the increase of n_L can be explained by justifying the activation of lignin referred to above. In other words, the decrease of a in the early stage of the delignification seems to reflect that the real n_H was much smaller than 2.78 and that n_L increased at that stage.

When lignin is eliminated further, a' should increase monotonously because the contribution of the second term in Eq. 3 diminishes. Actually, the a value turned to increase with increasing E_L. According to Eq. 3, a' is about 53% if the lignin content becomes zero. On the other hand, the WG observed for almost lignin-free wood meal was 29.7% at the maximum (Hiller[15] reported around 10% for cotton cellulose). Also from this large gap, it is supposed that the real n_H is rather smaller than 2.78.

Figure 6 shows the equilibrium moisture content at 20°C and 66% relative humidity for nonacetylated wood meal with various E_L. The equilibrium moisture content increased initially, and then decreased with increasing E_L. The increase of equilibrium moisture content may be due to the exposure of holocellulose from matrix substance accompanied with the elimination of lignin, and the subsequent de-
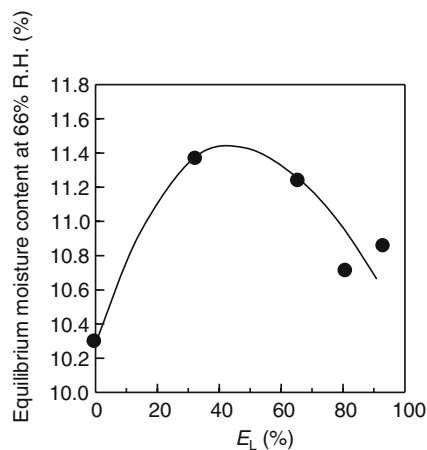
Fig. 6. Dependence of moisture adsorption on the elimination of lignin

crease is likely due to the degradation and removal of amorphous cellulose in the process of lignin elimination.[16] The dependencies of equilibrium moisture content and a on the E_L showed opposite trends, which suggests that the sites for reaction do not always entirely correspond with those for moisture adsorption.

Conclusions

By controlling the lignin content and by using reaction parameters, we examined the effect of lignin on the heterogeneous acetylation of wood. The following points are suggested:

1. The elimination of lignin from wood meal causes not only the separation of lignin but also some activated state in the remaining lignin moiety, which enhances the reactivity of wood meal as a whole.
2. In the lignin-free wood meal, the proportion of hydroxyl groups taking part in heterogeneous acetylation is somewhat lower than the estimation.

3. The number of hydroxyl groups available to moisture adsorption does not always coincide with the number affected by acetylation.

References

1. Hill CAS, Jones D (1996) The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. The effect of chain length. Holzforschung 50:457–462
2. Hill CAS, Jones D, Strickland G, Cetin NS (1999) Kinetic and mechanistic aspects of the acetylation of wood with acetic anhydride. Holzforschung 52:623–629
3. Hill CAS, Jones D (1999) Dimensional changes in Corsican pine sapwood due to chemical modification with linear chain anhydrides. Holzforschung 53:267–271
4. Hill CAS, Cetin NS, Ozmen N (2000) Potential catalysts for the acetylation of wood. Holzforschung 54:269–272
5. Hill CAS, Papadopoulos AN (2002) The pyridine-catalysed acylation of pine sapwood and phenolic model compounds with carboxylic acid anhydrides. Determination of activation energies and entropy of activation. Holzforschung 56:150–156
6. Ramsden MJ, Blake FSR (1997) A kinetic study of the acetylation of cellulose, hemicellulose and lignin compounds in wood. Wood Sci Technol 31:45–50
7. Minato K, Ogura K (2003) Dependence of reaction kinetics and physical and mechanical properties on the reaction systems of acetylation I. Reaction kinetic aspects. J Wood Sci 49:418–422
8. Minato K (2004) Application of a modified rate equation to the acetylation of wood. J Wood Sci 50:455–458
9. Minato K, Ito Y (2004) Analysis of the factors influencing the acetylation rate of wood. J Wood Sci 50:519–523
10. Rowell RM (1982) Distribution of acetyl groups in southern pine reacted with acetic anhydride. Wood Sci 15:172–182
11. Ohkoshi M, Kato A (1997) ^{13}C-NMR analysis of acetyl groups in acetylated wood I. Acetyl groups in cellulose and hemicellulose. Mokuzai Gakkaishi 43:327–336
12. Ohkoshi M, Kato A (1997) ^{13}C-NMR analysis of acetyl groups in acetylated wood II. Acetyl groups in lignin. Mokuzai Gakkaishi 43:364–369
13. Rosenqvist M (2001) Acetyl group distribution in acetylated wood investigated by microautoradiography. Holzforschung 55:270–275
14. Norimoto M (1988) Acetylated wood (in Japanese). Wood Res Tech Not Wood Res Inst Kyoto Univ 24:13–30
15. Hiller LA Jr (1954) The reaction of cellulose with acetic acid. J Polym Sci 14:555–577
16. Yasuda S (1985) Analysis of wood components (in Japanese). In: Nihon Mokuzai Gakkai (ed) Mokuzaikagaku Jikkensho, II. Kagaku-hen. Chugaisangyo Chosakai, Tokyo, p 155