THERMAL DEGRADATION OF WOOD AND ITS CONSTITUENTS ON SMOLDERING COMBUSTION IN OXYGEN ATMOSPHERE

Takashi HANDA, Yoshinori HASHIZUME,
Hidetoshi TSUSHIMA, and Shuji YOSHIZAWA

Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo,
1-3, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

(Received, July 18, 1985)

ABSTRACT

Thermal degradation of wood has been studied by the measurements of oxygen consumption (O.C.) and weight loss (W.L.) for wood and its constituents (cellulose, xylan, and lignin) under isothermal condition in pure oxygen atmosphere in the range 160-260°C. Lignin consumed a large amount of oxygen even at 160°C, nevertheless its W.L. value was extremely small. On the other hand, O.C. as well as W.L. of cellulose and xylan increased remarkably above 220°C and 180°C, respectively. The plots of W.L. vs. O.C. for wood components, which were evaluated on the basis of the component weight ratio of 2:1:1, gave a straight line up to 200°C. The plots for wood coincided fairly well with the evaluated plots up to 200°C. Above 220°C, however, the plots of W.L. vs. O.C. of wood increased largely as compared to those of 200°C and a breaking point occurred at an exposure time of 4h at 260°C. IR spectral measurements for these systems suggests that autoxidation of the amorphous region, due to the presence of peroxide and OH radicals, must occur until 200°C is reached, while above 220°C the oxidation and degradation prevail more definitively, where loosening and collapsing of the crystalline fibril region of wood occurs.

INTRODUCTION

The mechanism of wood oxidation is based on the theory of peroxidic oxidation⁽¹⁾. In general, it is believed that the free radical mechanism with degenerate branching is effective in the oxidation of macromolecular substances. The relatively slow noncombustive reactions of compounds with oxygen in the dark, have been called autoxidations. The autocatalytic character with degenerate chain branching of polymer substances is due to

free peroxidic radicals. The autoxidations of wood and cellulosic materials have been studied for the purpose of investigating the combustion and thermal destruction processes and the action of retarding agents^(1,2).

Chemical constituents of wood are mainly cellulose, hemicellulose (xylan) and lignin. The thermal behavior of wood reflects the sum of the thermal responses of these three major components⁽³⁾. The hemicellulose component is unstable and decomposes at 225-325

°C. Cellulose decomposes at higher temperatures within the narrow range of 325–375°C. Lignin, however, decomposes gradually within the temperature range of 250–500°C.

The cell wall polysaccharides provide most of the volatile pyrolysis products while lignin predominantly forms a charred residue.

Since the thermal reactions of the wood components are highly complex and additive, they have been studied individually.

In the thermal degradation in pure oxygen, it may be considered that the oxidative thermal decomposition of wood can be classified into the following three phases: (1) autoxidation due to the presence of radicals in low temperature regions, (2) thermal degradation due to a change in the structure at high temperature, (3) oxidation of fragments due to the presence of oxygen.

In this regard, we have made an extensive study on the stoichiometric correlation between oxygen consumption and the weight loss of wood and its constituents in a pure oxygen atmosphere at temperatures ranging from 160°C to 260°C.

EXPERIMENTALS

(1) Materials

The chemical constituents of wood are mainly cellulose, hemicellulose and lignin. Figure 1 shows the chemical structures of these major components. It should be noted that cellulose

has a single polysaccharide structure, whereas hemicellulose and lignin have various kinds of structures. Hemicellulose of hardwood (beech) contains 80–90% 4-O-methylglucuronoxylan in weight. Although a complete structure of natural lignin is yet unknown, it is known that hardwood lignin's major skeleton contains guaiacyl- and syringyl-propane units⁽⁴⁾. Therefore, the wood constituents used in the study were cellulose (Avicel SF and filter paper), xylan (4-O-methylglucuronoxylan), and lignin (al-

Cellulose

Xylan

Lignin (major skelton of C₃–C₆ structure)

Fig. 1 Chemical structures of three major components of beech wood.

kali lignin from birch wood).

The wood used in the study was of rotary-cut beech (*Fagus crenata* Blume), 2.5mm thick veneers. In addition, wood powder ground by a mortar was also used for comparison with wood constituents. All samples were oven-dried in a vacuo at 80°C for 30h, and then maintained in a desiccator with phosphorus pentoxide in vacuo to exclude the effects of water.

(2) Oxygen consumption

Oxygen consumption was measured using an apparatus described in a previous publication⁽²⁾. The powder sample was first suspended on glass wool and then the sample was placed in a small test tube which was set in the measuring apparatus. During the oxidation of the sample, the measurement was carried out by the successive replacement of consumed oxygen stored in a gas burette while the atmospheric pressure was maintained at 760mm. A molecular sieve (5 A) was used for the absorption of volatile products.

(3) Infrared spectra

The infrared spectra was measured using a KBr disk method with a Hitachi EPI-G3 infrared spectrophotometer covering the range from 4000cm⁻¹ to 667cm⁻¹ at room temperature.

RESULTS AND DISCUSSION

(1) The effect of oxygen in the thermal decomposition of wood at 200°C

Figure 2 (a) shows the IR spectra of cellulose, xylan and lignin, and

Fig. 2(a) IR spectra of wood components.

1 : cellulose, 2 : xylan, 3 : lignin.

Fig. 2(b) IR spectra of a mixture of wood components and natural beech wood powder.

4 : the mixture of cellulose, xylan and lignin a weight ratio of 2 : 1 : 1,

5 : natural beech wood powder.

the assignments of the major absorptions are shown in Table 1. Figure 2 (b) shows the IR spectra of a mixture of cellulose, xylan and lignin in a weight ratio of 2 : 1 : 1, in order to compare them with those of natural beech wood powder. Both spectral patterns resemble each other except that the mixtures absorption bands at 1730 cm⁻¹ and around 1230-1275cm⁻¹ are considerably weaker as compared to those of the wood. As referred to Table 1, the absorptions at 1730cm⁻¹

Table 1 The assignments of the major absorption frequencies (cm^{-1}) of wood and its constituents.

cellulose	xylan	lignin	mixture	wood	assignment
892	890		890	890	β -linked glucose polymer
984	975		980	985	C-O stretching
1025	1037	1030	1024	1032	vibration of ring
1050			1046	1050	C-O stretching, $-\text{CH}_2\text{OH}$
	1110		1108	1110	$-\text{C}-\text{OH}$
		1125		1120	O-H in-plane bending
1155	1160	1155	1152	1150	anti-symmetric bridge of C-O-C
		1203		1224	syringyl-nucleus
	1242			1240	OH in-plane bending
		1260			guaiacyl-nucleus
1276			1270		CH bending
1311			1307	1320	CH_2 wagging
1365		1360	1360	1366	CH bending
1426	1412	1430	1420	1419	CH_3 scissoring motion
	1455	1450	1453	1454	CH_3 scissoring motion
		1495		1498	benzene ring
	1605	1592	1595	1591	C-C, COO
1630	1630		1630	1630	adsorbed water
		1700			C=O, ArCOR and ArCHO stretching
				1732	RCHO stretching
2880	2900	2920	2880	2890	CH stretching
3390	3390	3390	3340	3390	OH stretching

and 1242 cm^{-1} are results of the stretching of RCHO in lignin and the in-plane bending of OH of xylan, respectively.

Commercially available samples of xylan and lignin must differ from those of in-situ states, because amorphous materials oxidize or fuse during sample preparation. As for cellulose, the crystallinity of the commercially available sample was higher than that of in-situ one in wood. Therefore, the mode of the cellulosic absorptions in the IR spectrum of the mixture looks like that of the high crystallinity cellulose. In this regard, we first compared the IR spectra of untreated wood and its constituents

with those of heated wood in N_2 and O_2 atmospheres. As a preliminary study, it was examined how oxidation occurs competitively among the individual components, with the elevation of hot bath temperatures, regarding the oxidative thermal decomposition of wood in air.

Figure 3 shows the IR spectra of xylan (A), wood powder (B), and cellulose (C), which were heated to 200°C for 8 h. The spectrum of xylan heated in O_2 atmosphere differed remarkably from that in N_2 atmosphere. Thereby, the transmittances of O-H and C-H stretchings at 3400 cm^{-1} and 2900 cm^{-1} disappeared and a band at 1720 cm^{-1} appeared due to carbonyl

Fig. 3 IR spectra of xylan (A), beech wood (B) and cellulose (C) exposed in oxygen and nitrogen atmosphere at 200°C for 8h. The dotted curves represent the untreated samples.

group formation. The band near 1160 cm^{-1} was due to the presence of a anti-symmetric bridge of C—O—C. However, the spectrum of xylan heated in N_2 atmosphere was similar to that of untreated xylan. These results, the decrease in weight of xylan in O_2 atmosphere, indicate that the fission of the main chain and glucosidic ring due to oxidation, occur during the thermal degradation of xylan in an oxygen atmosphere at 200°C.

On the other hand, the IR spectral pattern of cellulose heated at 200°C for 8 h in O_2 atmosphere approximately coincided with that of cellulose heated at 200°C for 8 h in N_2 atmosphere except for the formation of the small band near 1720 cm^{-1} (carbonyl) for O_2 atmosphere. This indicates that cellulose is oxidized in an oxygen atmosphere, and the thermal degradation of cellulose is not promoted even

Fig. 4 Time dependent change in IR spectra of beech veneer heated at 200°C in oxygen atmosphere.

Fig. 5 Oxygen consumption of wood and its three major constituents.
 ○: beech veneer, ○: beech powder, ●: beech fine powder,
 ▽: cellulose (Avicel SF), ▲: cellulose (filter paper),
 □: xylan, △: lignin, and x: calculated wood.

in an oxygen atmosphere at 200°C.

The IR spectrum of wood powder heated at 200°C for 8 h in N₂ atmosphere is similar to that of unheated wood powder. However, the broadening of spectral pattern and the decrease in the transmittances at 1160 cm⁻¹ and 1242 cm⁻¹ were observed in the IR spectrum of wood powder heated at 200°C for 8 h in oxygen atmosphere.

Figure 4 shows the time-dependent change of the IR spectra for wood pulverized from thin veneer heated at 200°C in O₂ atmosphere. It can be seen that the transmittance peaks at 3400, 2880 and 893 cm⁻¹ decreased with

time whereas those at 1600 and 1700 cm⁻¹ increased. This indicates that dehydration and oxidation proceed with heating time. Instead of the disappearance of the absorption peak at 1242 cm⁻¹ due to the OH group of xylan, within less than 4 h new peaks appeared prominently, at 1210 and 1270 cm⁻¹ in the spectrum. The 1210 and 1270 cm⁻¹ bands can be assigned to syringyl- and guaiacyl-nucleus of lignin as shown in Table 1. This means that the primary structure of lignin did not decompose thermally even at 200°C. The results in Figures 3 and 4 suggest that the thermal degradation of wood in oxygen atmosphere at 200°C can primarily be attributed to the oxidative thermal decomposition of xylan.

In the oxygen atmosphere, a different mechanism prevails which does not involve the formation of levoglucosan in nitrogen^(5,6). Rogers and Ohlemiller⁽⁷⁾ proposed a oxidatively-assisted depolymerization mechanism for cellulose component materials, presuming that first, a OH radical be produced from a C-1 radical of glycoside linkage and secondarily cyclization by oxygen must be achieved, and finally carbonyl segments are produced as a result of the cleaving of molecular chains and the OH radical is driven off. This radical reaction leads to the formation of aldehyde and carboxyl groups in the initial stage of cellulose oxidation, which agrees with the results of IR spectra in Figure 3. Further, this

process also occurs in a similar polysaccharide xylan which is oxidized easily and tends to be gasified upon exposure to oxygen.

Figure 5 shows the time-dependent changes in the oxygen consumptions (O. Cs) of wood and its three major constituents at a hot-bath temperature of 200°C. Cellulose has extremely low O. C, when compared to lignin and xylan. Therefore, it can be said that the oxygen consumption of wood below 200°C is due to the oxidation of lignin and xylan.

On the other hand, lignin showed a very small weight loss at 200°C for 8 h even in O₂ atmosphere whereas xylan showed a remarkable weight loss under these same conditions. Therefore, the weight loss of wood at 200°C is mainly due to the oxidative thermal decomposition of xylan.

The total amount of O.C of wood either in the form of a thin veneer or pulverized powder seems to correspond to the combination of the O.Cs of its three major constituents. The theoretical O.C values of beech wood was calculated using the obtained O. Cs on the basis of the weight ratio of 2 : 1 : 1 for cellulose, xylan and lignin, respectively. At 200°C, the time-dependent change of the calculated O.C values with that of the beech veneer were similar in a first approximation.

In addition, the obtained O.C values of wood powder were found to stay somewhat higher than those of

wood veneer in the later stage of oxidation after 1 h. This is presumably due to the increased surface area of the wood powder, which was prepared by pulverizing the wood veneer, since the deformation and peeling off of the cell walls must occur at the cross-section. Thereby, the exposure of the new lignin layer occurs more frequently for the powder wood. In other words, the obtained lower O.C values of wood veneer means that most of xylan and lignin are still tightly enclosed in the wood structure which prevent oxygen from penetrating into the lamellar fibril in the cell in the cell wall.

The extremely small O.C values of cellulose must be due to its crystalline structure which does not collapse at 200°C and prevents the penetration of oxygen into the tightly hydrogen-bonded structure. Since the crystallinity index (Cr. I) of cellulose fibrils in wood was found to be lower than that of isolated cellulose, it is expected that microcrystalline cellulose fibrils in wood to begin to oxidize at a temperature of ca. 230°C, which corresponds to the indicated temperature of the viscoelastic loss modulus (E'') peak⁽⁷⁾. From the above results, it can be said that thermal decomposition of wood in an oxygen atmosphere at 200°C is proceeded by the consumption of oxygen, which is presumably due to the initiation of the disintegration and loosening of wood structure by the

Fig. 6 Time dependent changes in oxygen consumption of beech wood powder (a), cellulose (b), xylan (c), and lignin (d).
 ∇ : 160°C, $\circ$: 180°C, $\triangle$: 200°C, $\square$: 220°C, $\bullet$: 240°C, $\blacktriangle$: 260°C.

peeling and oxidative depolymerization of amorphous part of wood fibrils consisting of cellulose, xylan and lignin.

(2) Oxygen consumption of wood constituents

To obtain the effect of wood constituents on the thermal degradation in an oxygen atmosphere, the measurement of oxygen consumption of wood constituents was performed over the temperature range 160°C to 260°C. Wood powder was used for the comparison to the powder of the wood constituents, although thermal degradation of powder samples was accelerated more than solid mass samples.

Fig. 7 Temperature dependent changes in oxygen consumption (a) and residual weight (b) heated for 8h.
○ : beech wood powder, ▲ : cellulose, □ : xylan, and △ : lignin.

Figure 6 shows the time dependence of O.C values of wood powder (a), cellulose (b), xylan (c) and lignin (d) at given temperatures. The O.C of wood powder was initiated at 180°C, whereupon the induction period was observed. The O.C, at 260°C of the wood powder was similar to that at 240°C. Wood powder, cellulose and xylan showed similar modes of O.C which were initiated at 180°C, 220°C and 180°C, respectively. On the other hand, lignin showed a large amount of oxygen consumption which increased with the elevation of temperature.

Figure 7 shows the oxygen consumption (a) and weight loss (b) for wood and its constituents heated at given temperatures for 8 h. It is obvious that lignin possesses a highest affinity for oxygen among the three major constituents of wood due to the high reactivity of its unstable components. Handa et al. elucidated that the unstable components of lignin on the inner surface vessel extensively terminate the propagation of radicals from forming polymer chains by electron-beam irradiated radicals. A heat-cure process is used to produce wood-polymer composites (8). This suggests that the active sites in lignin will act to trap triplet oxygen molecules as a peroxide bridge ($-O-O-$) or short-live radicals ($OH\cdot$, and $CH\cdot$) from oxidative thermal decomposition. Then to release trapped oxygen or radicals as active singlet oxygen, O_2 , $O\cdot$, $OH\cdot$, etc. a re-

Fig. 8 Relations between oxygen consumption and weight loss for cellulose (▲), xylan (□), lignin (△), beech wood powder (○) and calculated wood powder (●).
a : 160°C, b : 180°C, c : 200°C,
d : 220°C, e : 240°C, f : 260°C.

combination process with ascending hot-bath temperature is necessary.

However, lignin itself shows a small weight loss which could hardly reach 30% even at 260°C in an oxygen atmosphere. Thereby, oxygen which functions in the decomposition of lignin is responsible for the thermal softening and structural change of lignin to produce the precursors of char.

Xylan scarcely showed oxygen consumption at 160°C but it showed a recognizable weight loss which reached ca. 15% after 8 h at 160°C indicating that xylan is subject to decomposition with gasification. Xylan showed a considerable oxygen consumption as well as weight loss at 180°C.

Cellulose itself rejects the penetration of oxygen into its highly crystalline structure up to 220°C.

Figure 8 shows the relationship

of weight loss to oxygen consumption for wood powder and its constituents. It can be said that xylan reacts with oxygen approximately in a molar ratio 1 : 1 in taking the average molecular weight of xylan as ca. 144 for the pyranose ring structure in Figure 1. Cellulose reacts with oxygen approximately in a molar ratio of 1 : 2 up to a not bath temperature of 220°C, and in a molar ratio 2 : 3 in the temperature range of 220°C to 260°C. Lignin reacts with oxygen approximately in a weight ratio of 1 : 1.4.

The figure also shows the theoretical plots which are calculated from the observed weight loss and O.C values for wood composed of cellulose, xylan and lignin in a weight ratio of 2 : 1 : 1. These plots are linear and the plots of wood powder fall on the same line up to 220°C. However, in the temperature range of 220°C to 260°C, there appears a break for the observed values of wood powder. This suggests that the oxidative thermal decomposition of wood proceeds up to 220°C by a single scheme which is the algebraic sum of three major constituents of wood. There is the structural change of cellulose fibrils of wood above 220°C as mentioned previously. This indicates that both reactions of gasification and charring must be proceeded competitively in wood due to the collapse of its crystalline structure.

Therefore it is expected that the oxidative thermal decomposition of

Fig. 9 Time dependent changes in oxygen consumption (a) and residual weight (b) for wood veneer.

▽ : 160°C, ○ : 180°C, △ : 200°C,
□ : 220°C, ● : 240°C, ▲ : 260°C.

Fig. 10 Relation between oxygen consumption and weight loss for beech veneer.

▽ : 160°C, ○ : 180°C, △ : 200°C,
□ : 220°C, ● : 240°C, ▲ : 260°C.
a : 15min, b : 1h, c : 4h, d : 8h,
e : 30h, f : 72h.

wood above 220°C is strongly influenced by the ability of the three

major constituents in cell wall to penetration oxygen as well as the specific surface area of wood.

(3) Oxidative thermal decomposition of wood

Figure 9 (a) shows how the oxygen consumption of wood increased with increasing temperature (160°C to 260°C) and Figure 9 (b) shows the weight loss with time at the same temperatures due to oxidative thermal decomposition of wood veneer.

Figure 10 shows the relationship between oxygen consumption and weight loss. The plots in the temperature range from 160°C to 200°C fall on the same straight line (I) which agrees very closely with the plot obtained for the wood constituents in Figure 8. Elongation of the reaction time merely leads to the increase of oxygen consumption and weight loss on the straight line (I), confirmed by the data collected at 200°C for 30 h. On the other hand, the data collected at the temperature of 220°C or above formed another straight line (II), and the plots at 260°C over 4 h gives straight line (III). Two different straight lines (I and II) in the initial stage suggest that the oxidative thermal decomposition of wood proceeds through dual schemes with temperature dependent ratios of weight to oxygen consumption.

As for straight line (I), we analyzed the wt % of H, C and O in the wood samples which were heated at 180°C for 4 h and 12 h in an oxygen

Table 2 Results of elementary analysis of wood samples

sample	O.C (Wt %)	R.W (Wt %)	H (Wt %)	C (Wt %)	O (Wt %)
untreated	0	100	5.4	47.8	46.8
180°C for 4h	2.0	94	5.0	49.2	45.9
180°C for 12h	5.6	86	4.4	50.2	45.4

Table 3 Relative intensities of around 3400, 2900, 1700, 1600 and 1040 cm^{-1} band / 1500 cm^{-1} band in infrared spectra of wood heated to different temperature for 8 h in oxygen atmosphere.

sample	Wave number (cm^{-1})					
	3400	2900	1700	1600	1500	1040
untreated	252	49	130	94	100	286
180°C	353	51	209	131	100	398
200°C	250	54	340	182	100	347
220°C	327	24	323	217	100	347
240°C	68	20	196	184	100	115
260°C	59	19	150	161	100	101

Fig. 11 IR spectra of beech veneer heated in oxygen atmosphere for 8 h

a : untreated, b : 180°C, c : 200°C,
d : 220°C, e : 240°C, f : 260°C.

atmosphere. The results are shown in Table 2. The content of carbon in the residue increased gradually with time whereas recognizable decreases were observed for the content of hy-

drogen and oxygen. Accounting for the atomic ratios of C and H to O in the gasified fraction on the basis of the lost weight of H, C and O as a sum of the weight of each atom in the lost-fraction and consumed oxygen, it was found that the atomic composition ratio in the gasified fraction were about $\text{H}_{12}\text{C}_2\text{O}_6$ for 4 h and $\text{H}_{12}\text{C}_3\text{O}_6$ for 12h. Further, the atomic composition ratio in lost-fraction of wood per one molecule of consumed oxygen were about $\text{H}_{11}\text{C}_2\text{O}_4$ for 4 h and $\text{H}_9\text{C}_2\text{O}_3$ for 12h.

From these results, it can be said that the dehydration process proceeds the oxidative fission of glucose linkages.

On the other hand, straight line (II) indicates that oxygen effectively promotes the gasification of wood veneer above 220°C. The straight line

(Ⅲ) which appears after 4 h at 260 °C and belongs to another category, resulting from the continuance of oxygen consumption by tar and charred material, the latter of which was presumably produced by the thermal decomposition of lignin. As mentioned above, a certain synergistic effect of cellulose and other constituents in the cell wall, on the oxidative thermal decomposition of wood, must occur above 220°C.

In order to obtain information as to how oxidation proceeds on a molecular level at given temperature, IR spectra were measured on the charred material from the wood veneer exposed in oxygen atmosphere for 8 h, as shown in Figure 11. The absorption band at 1125 cm⁻¹, resulting from O-H bending of xylan disappeared at 200°C. This suggests that the threshold temperature for the decomposition of xylan is 200 °C in an oxygen atmosphere. In temperatures above 220 °C, we observed a significant decrease in absorbance for absorption around 2900 cm⁻¹(OH), 3400 cm⁻¹ (CH) and 1040 cm⁻¹ (CO and -CH₂OH). The relative intensities of those absorption bands are shown in Table 3. The relative intensities of the IR absorption bands (D_v/D_{1500}) × 100⁽¹⁰⁾ are characteristic of IR spectral curves. The absorption band at 1500 cm⁻¹ is assigned to the benzene ring of lignin, and the thermal stability of the benzene ring is relatively high. The absorption band around 1700 cm⁻¹

(C=O) also showed a significant decrease of absorbance above 220°C, while the decrease of absorbance around 1600 cm⁻¹ (C=C) was slow above 220°C. These results suggest that the decomposition and carbonization of wood proceeded to the overall region of the wood above 220°C.

CONCLUSION

Three temperature ranges for the oxidative thermal decomposition of wood were selected and assigned.

(1) In the temperature range ca. 160°C to 200°C, thermal degradation occurs in the amorphous region as a result of oxygen consumption of lignin and xylan. Then xylan decomposes with weight loss, whereas lignin depolymerized with no weight loss. And the calculated relationship between oxygen consumption and weight loss for wood assumed the weight ratio of 2 : 1 : 1 for cellulose, xylan and lignin.

(2) At a temperature of ca. 220°C, thermal degradation comes from the decomposition of cellulose and xylan due to oxidative pyrolysis accompanied with weight loss. The results for wood powder were similar to those for calculated wood.

(3) At a temperature of ca. 260°C, thermal degradation comes from the carbonization of cellulose fibril. The ratio of weight loss to oxygen consumption increased greater for wood powder, therefore thermal degradation of wood must be a result of a certain synergistic effect of cellulose and

other constituents in the cell wall.

ACKNOWLEDGMENT

The authors wish to thank Mr. Takayuki UNO and Mr. Motoyuki TAKAHASHI for helping with this experiment.

REFERENCES

- (1) M. Kosik, V. Lužaková, and V. Blazej : Fire and Materials, 23, p19 (1976)
- (2) T. Handa, Y. Hashizume, and S. Yoshizawa : Fire Science and Technology, 3, p 35 (1983)
- (3) F. Shafizadeh, and P. P. S. Chin : In Wood Technology, Chemical Aspects (Edited by I. S. Goldstein), p57, ACS Symposium Series 43 (1977)
- (4) H. L. Hergert, "Lignins", ed. by K. V. Sarkanen and C. H. Lundwig, Wiley-Interscience, p 272 (1971)
- (5) M. J. Antal, H. L. Friedam and F. E. Rogers : Combust. Sci. Tech., (1979)
- (6) M. Miura, H. Kaga and H. Nishizaki : Mokuzai Gakkaishi, 29, p 756 (1983)
- (7) F. E. Rogers and T. J. Ohlemiller : Combust. Sci Tech. Vol. 24 (1980)
- (8) T. Handa, S. Yoshizawa, M. Suzuki, and M. Fukuoka : Proc. 22nd. Japan Congr. Mat. Res., p 223 (1979)
- (9) T. Handa, S. Yoshizawa and K. Hatakeyama : J. Appl. Polym. Sci., 23, p 1527 (1979)
- (10) I. Kawamura and D. E. Bland : Holzforschung, 21, p 65 (1967)