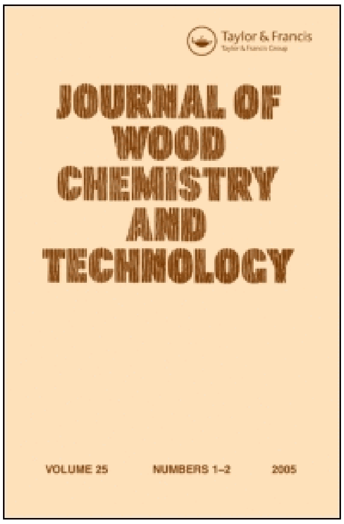

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# Lattice Conversion of Cellulose in Wood

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# LATTICE CONVERSION OF CELLULOSE IN WOOD

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## ABSTRACT

When peracetylated wood, prepared in an acetic anhydride-pyridine medium, was saponified and recrystallized, almost no conversion of cellulose I to cellulose II took place. Neither was conversion detected, when thirteen species of wood, differing in density from 0.17 to 0.71, as well as in lignin content from 18.1 to 38.8 %, were treated with 17.5 % aqueous NaOH, followed by recrystallization. The corresponding treatments for cellulose triacetate or cellulose resulted in complete conversion to cellulose II. Partial delignification of wood preceding the alkali-induced mercerization was found to cause partial lattice conversion to cellulose II, and the ratio of lattice conversion (L.C.R.) increased with the degree of delignification. The L.C.R. value reaches slightly more than 50 %, when one third of the lignin is removed, and the removal of about two third of the lignin from wood results in an almost complete conversion. The effect of lignin removal on lattice conversion was similar among the wood species, irrespective of their density and lignin content. Introduction of acyl groups larger than caproyl into wood, followed by saponification and mercerization resulted in a high conversion of cellulose in wood from cellulose I to cellulose II.

## INTRODUCTION

Since wood contains about 40 to 45 % of cellulose, which is a crystalline polymer, its decrystallization has significant effect on chemical reactivity of wood. This is quite understandable when we consider the results of various homogeneous reactions. For

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example, the rate of silylation[1)] or tritylation[2)] of cellulose in a non-aqueous cellulose solvent reaction medium is quite high. The reactions of wood in the presence of non-aqueous cellulose solvents have also been found to exhibit similar enhanced chemical reactivity[3,4)] and resulted in products with considerably altered properties. In these cases, for instance, improved thermoplastic properties were rendered even by a low degree of substitution.[5-7)] The important feature of the reactions in the presence of non-aqueous cellulose solvents was that reaction proceeded uniformly along the cellulose chain within wood from the earliest stage of reaction and, as a result, a permanent decrystallization occured in the cellulose within the wood structure even at an extremely low degree of substitution.[3,8)]

In connection with these findings, the transient decrystallization of cellulose within wood has been attained by treating with non-aqueous cellulose solvents, followed by washing with appropriate solvents (final washing should be with non-polar solvents) and drying. However, the washing with polar solvents resulted in some recrystallization of wood. Furthermore, at that time, it was observed that the recrystallized cellulose was the cellulose I form [8)]. This is in marked contrast to the general fact that regenerated cellulose, obtained after dissolving isolated cellulose into the non-aqueous cellulose solvents, followed by precipitating into water and drying, shows a cellulose II lattice structure. This difference in the behavior of cellulose present in wood and isolated cellulose towards the lattice conversion during the processes of decrystallization and recrystallization is interesting and worthy of systematic investigation.

In this sense, in the present article, we have studied the lattice conversion of cellulose present in wood after : (i) decrystallization by peracetylation and saponification followed by recrystallization, (ii) mercerization with aqueous sodium hydroxide solution, (iii) delignification followed by mercerization and (iv) loosening the lignin aggregate structures by introducing large substituent groups followed by saponification, where mercerization occurs simultaneously.

## EXPERIMENTAL

Thirteen species of wood meals (42-60 mesh, cold water and alcohol-benzene extracted), as shown in Table 1, were used for the study. Among them Makanba was chiefly used.

Mercerization : The oven dried samples (0.5 g) were treated with definite concentrations (1 to 25 %) of aqueous sodium hydroxide (40 ml) at room temperature for a definite period (1 hr). After the alkali treatment, the samples were washed with distilled water at room temperature, till the wash water was neutral in pH, filtered and dried in a vacuum oven.

Table 1

Wood Species used for the Study

| Wood Species | Specific Gravity | Lignin Content (%) |
|---|---|---|
| Balsa (Ochroma *lagopus* Sw.) | 0.17 | 26.5 |
| Kiri (Paulownia *tomentasa* Steud.) | 0.23 | 20.4 |
| Yamazakura (Prunus *sar gantii* Rehd.) | 0.46 | 22.2 |
| Kuri (Castanea *crenata* Sieb. et Zucc.) | 0.47 | 24.4 |
| Mizunara (Quercus *mongolica* Fisch var.) | 0.52 | 26.3 |
| Makanba (Betula *maximowicziana* Regel) | 0.59 | 22.9 |
| Akagashi (Quercus *acuta* Thunb) | 0.71 | 24.9 |
| Tsukubanegashi (Quercus *sessilifolia* Blume) | - | 18.1 |
| Todomatsu (Abies *sachalinesis* Mast.) | 0.33 | 28.5 |
| Hinoki (Chamaecyparis *obtusa* Endl.) | 0.34 | 32.9 |
| Sugi (Cryptomeria *japonica* D.Don) | 0.35 | 35.6 |
| Akamatsu (Pinus *densiflora* Sieb.) | 0.41 | 26.8 |
| Kusamaki (Podocarpus *macrophylla* D. Don) | 0.46 | 38.8 |

Decrystallization and Recrystallization of Wood and Cellulose : Wood meals and filter paper were acetylated in acetic anhydride/ pyridine medium at room temperature for 240 hr. Peracetylation of wood and cellulose was confirmed by IR spectroscopy and by determination of acetyl content.9,10) The decrystallized wood and cellulose were obtained by treating peracetylated wood and cellulose with 1% sodium methylate dissolved in anhydrous methanol or pure ethylenediamine. In both cases saponification was allowed to proceed for about 12 hr. The regenerated wood and cellulose were washed with various organic solvents, and vacuum dried to get decrystallized samples. For recrystallization of the samples, they were immersed in and washed with water and dried in a vacuum oven at 70 °C.

Partial Delignification of Wood and Determination of Lignin Contents : Partial delignification of wood was carried out by the conventional chlorite method11) as well as the peracetic acid method,12) for different reaction periods. The lignin contents of wood and partially delignified wood were also measured by the conventional method.11)

X-ray Diffraction : X-ray diffractograms were obtained with disks of 0.2 g in weight and 1.3 cm in diameter, pressed from wood meal or cellulose fiber samples at a pressure of 2.03 ton/cm$^2$. The diffractions were recorded with a Rigaku Denki Geiger Flex 2011B wide-angle X-ray diffractometer, by using an X-ray beam generated with a copper target at 35 kV and 20 mA. X-ray radial tracing were scanned between angular limit of $2\theta=5$ and $2\theta=35$.

Determination of Lattice Conversion Ratio (L.C.R.) : L.C.R. was determined by two methods. These were the Ellefsen method13) and the curve resolver method.14) In the former method, X-ray diffractograms of prepared mixtures of cellulose I and cellulose II sample were taken first. A calibration curve was obtained between the ratio X, shown below, and the known ratios of the prepared mixtures (Fig. 1). That is,

$$X=(I_x - I_2)/(I_1 - I_2)$$

where, $I_x$ is the measured intensity at $2\theta=16.2^\circ$ of a mixed sample. $I_1$ and $I_2$ are the corresponding intensities of the cellulose I and cellulose II sample, respectively. In this case, cellulose obtained by the complete delignification of alkali-treated wood was used as the cellulose I sample and the cellulose II sample was obtained by mercerization of the cellulose I sample.

On the other hand, the curve resolver method[14)] is based on the resolution of a X-ray diagram into the component curves. In Fig. 2, curve a is the experimental profile. Curve AA' is air scatter background. The region of amorphous scattering is assumed to be the area below BCD. The profile was resolved into six Gaussian curves, (101), ($10\bar{1}$), and (002) of celluose I, and (101), ($10\bar{1}$) and (002) of cellulose II, by means of a du Pont 310 curve resolver.

## RESULTS AND DISCUSSION

### Peculiarity of Lattice Conversion of Cellulose in Wood

Figure 3 shows the results of decrystallization of wood, in which peracetylated wood was saponified in 0.5 N anhydrous methanol solution of sodium methylate and subsequently washed with methanol, followed by washing with chlorine-containing organic solvents and drying. It is evident that wood meals with almost completely decrystallized cellulose can be obtained by this procedure when carbon tetrachloride, chloroform, trichloroethylene, etc. are used as final washing solvents. As the final washing solvent becomes more polar or contains polar bonds within the molecules, however, the resulting product tends to have a structure with slightly greater crystallinity. What is interesting, in this case, is the fact that when the decrystallized samples were recrystallized by washing with boiling water and dried, then the crystalline structure regenerated was cellulose I.[10)] That is, although the

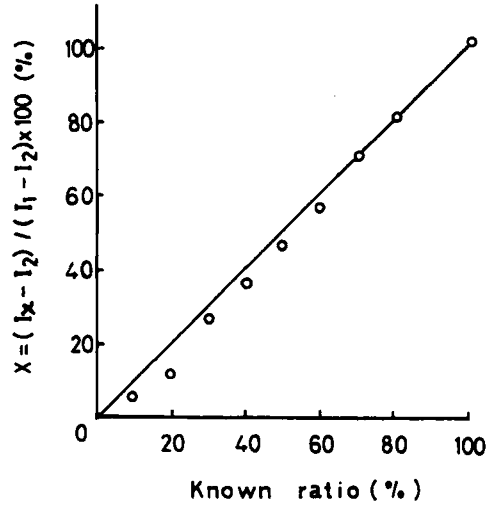

Fig. 1 Calculated ratio from X-ray data versus the known ratio of the prepared mixtures.

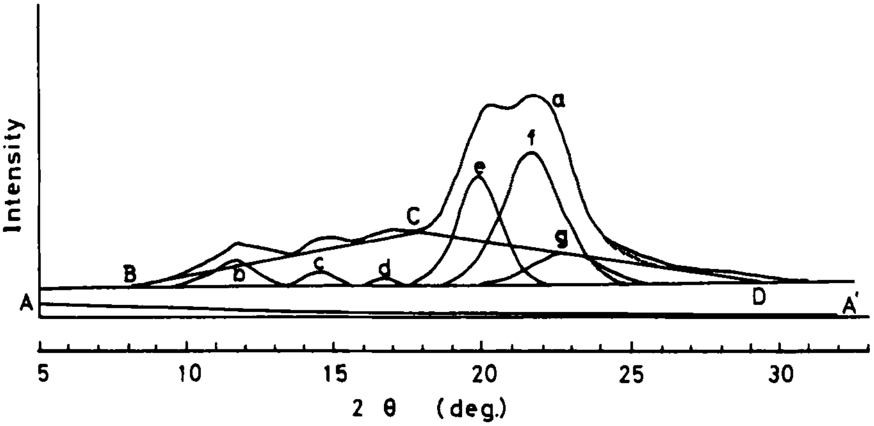

Fig. 2 Equatorial X-ray diffractograms for aqueous NaOH treated wood sample. curve a : experimental curve; curves b,c,d,e,f, and g : resolved components; dotted line : curve calculated by summation of component curves.

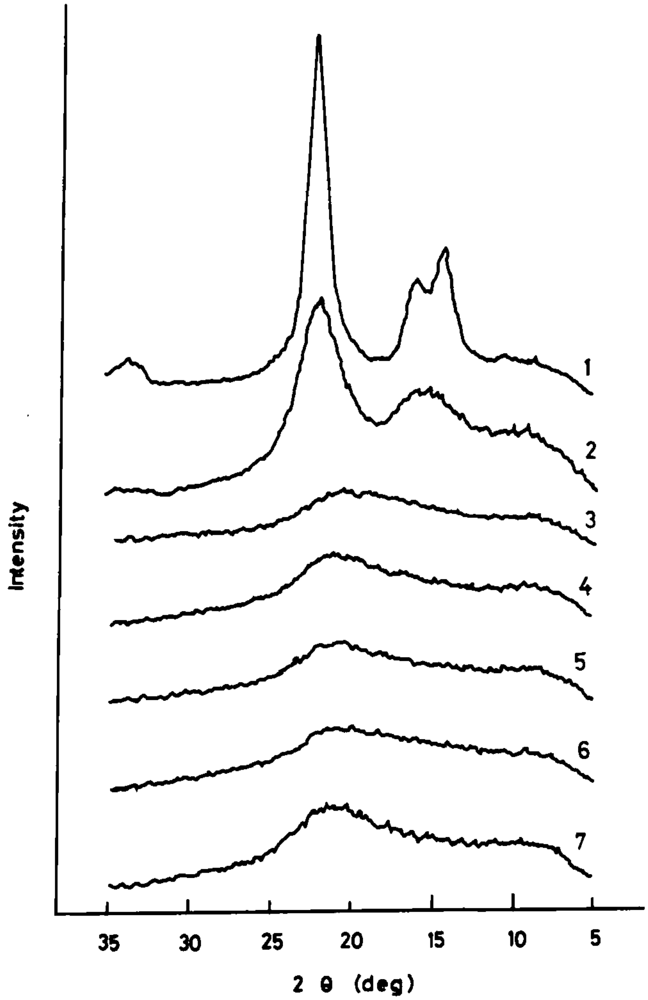

Fig. 3 Decrystallization of wood by peracetylation followed by saponification in an anhydrous medium followed by washing with methanol, exchanging solvents and drying. 1 : whatman cellulose powder CF-11, 2 : untreated wood, 3 : $NaOCH_3$-methanol treated, washed with methanol, solvent exchanged with $CCl_4$ and dried; final washing solvent : (4) $CHCl=CCl_2$ (5) $CHCl_3$ (6) $CCl_2=CCl_2$ (7) $ClCH_2-CH_2Cl$.

acetylation reaction was carried out by the "solution process", the saponified wood sample, after washing with water, and drying contained cellulose I polymorph. While on the other hand, when the cellulose triacetate prepared by solution process was saponified and washed with water and dried, then the crystalline structure obtained was cellulose II.15,16)

The above result is our second finding that even though the cellulose in wood is completely decrystallized, the conversion of cellulose I to cellulose II does not take place after the recrystallization treatment. The first finding was shown in our previous report,8) in which complete decrystallization of wood was achieved by treating wood with a non-aqueous cellulose solvent, a $SO_2$-diethylamine-DMSO solution, under appropriate condition, but, after the recrystallization treatment, the products were shown to exhibit the cellulose I structure. This specific lattice conversion behavior of cellulose in wood can be further confirmed by the data shown in Fig. 4. In this case, peracetylated filter paper and wood powder were saponified by treating with ethylenediamine (EDA). Recrystallization of the decrystallized wood powder resulted in reconversion to the cellulose I form, whereas the cellulose II lattice structure was obtained by recrystallization of the decrystallized filter paper sample. The X-ray pattern of the latter is shown to coincide with that of Fortisan, a typical cellulose II sample.

These above findings show us clearly that cellulose present in wood cell walls behaves quite differently from isolated cellulose with respect to the crystalline lattice conversion. Virtually no work has been reported in this respect, except that of Revol _et_. _al_ 17) and ours,18,19) as shown later. In that sense, it would be worthwhile to carry out a systematic investigation concerning this aspect. Generally, the crystalline lattice conversion of isolated cellulose is studied by mercerization with aqueous sodium hydroxide solution. The following sections deal with mercerization with aqueous sodium hydroxide solution of various wood species differing in density, wood structures and lignin contents, in addition to

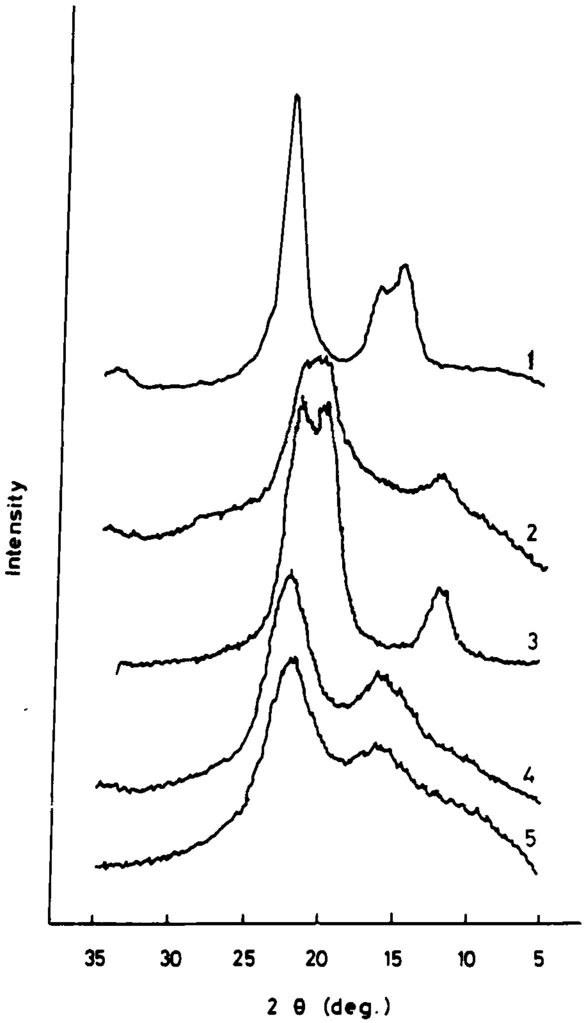

Fig. 4 Comparisons of X-ray diffractograms of samples obtained by recrystallization of decrystallized filter paper and wood with corresponding untreated filter paper, wood as well as Fortisan. The decrystallization was performed by peracetylation, followed by saponification with ethylene diamine and washing. curve (1) untreated filter paper (2) decrystallized-recrystallized filter paper (3) Fortisan (4) untreated wood (5) decrystallized-recrystallized wood.

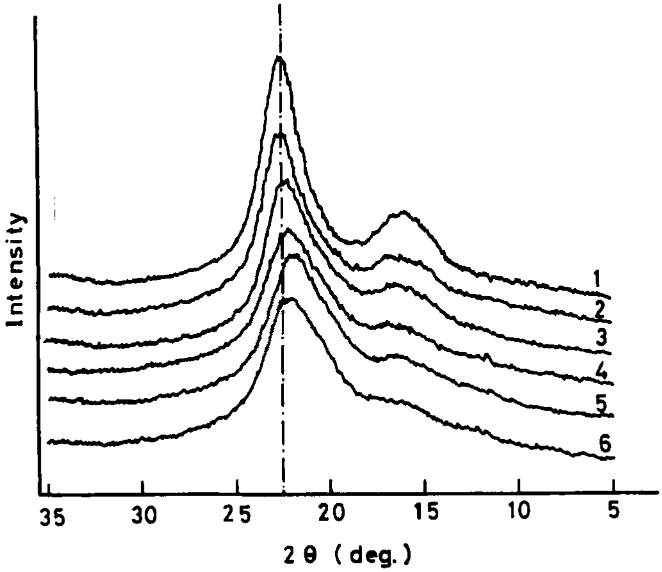

Fig. 5 Equatorial X-ray diffractograms of Makanba wood meals after treating with 1-25 % aqueous NaOH solution (20 °C, 1 hr) and subsequently washed with water and dried. concentration of NaOH sol. (1) : 1 %, (2) : 12 %, (3) : 15 %, (4) : 18 %, (5) : 20 %, (6) : 25 %.

some pretreatments which would faciliate swelling of cellulose in alkali to different degrees.

## Mercerization of Wood with Aqueous Sodium Hydroxide

### a) Effect of the Concentration of Aqueous Sodium hydroxide on Lattice Conversion of Cellulose in Wood

Figure 5 shows the equatorial X-ray diffractograms of Makanba wood meals after treating with 1 to 25 % aqueous sodium hydroxide solution at 20 °C for 1 hr, and subsequently washed thoroughly with water and dried. The wood samples treated with the aqueous sodium hydroxide solutions with concentrations below 15 % do not show any change in the crystallinity index[8] obtained from the X-ray diagrams, when compared with that of untreated wood powder. On the other hand, wood treated under mercerization conditions, that is, with the sodium hydroxide concentration of 15 to 25 %, shows fairly decrystallized X-ray diagrams. In these cases, the soda-cellulose intermediate formed in wood was observed by X-ray diffractometry, showing that the wood has been penetrated by the sodium hydroxide. This has also been confirmed by Revol et. al.17) Thus, it can be said that diffractograms shown in Fig. 5 for the samples treated under mercerization conditions, are regenerated by recrystallization. Another finding here is that the recrystallized cellulose samples reveal cellulose I structure. Though the curves show broadening and slight shifting of 002 peak, due to the reminiscences of amorphous state, almost no trace of cellulose II polymorph is detected. This can be further confirmed by comparing Fig. 5 with Fig. 7 or Fig. 8. This is in contrast to Revol's conclusion.17) They stated that a mixture of cellulose I and cellulose II resulted after mercerization of wood, and the ratio of cellulose II to cellulose I was estimated to be between 40 and 60 %. However, the mercerization conditions could be different in their case. Under prolonged duration of mercerization, there is a possibility that hemicelluloses might be leached out resulting in increased swelling of cellulose in alkali. A detailed investigation, with emphasis on the wood form and mercerization conditions is underway in this laboratory and will be reported in the near future.

On the other hand, on the basis of the above data, we adopted the mercerization conditions of treating wood meals with 17.5 % aqueous sodium hydroxide solution for 1 hr at 20 °C, followed by washing with water and drying, as the standard conditions for the subsequent experiments, except when otherwise specified.

### b) Mercerization of a Series of Wood Species

Mercerization was carried out under the conditions described above with 13 wood species, among which the density varies from

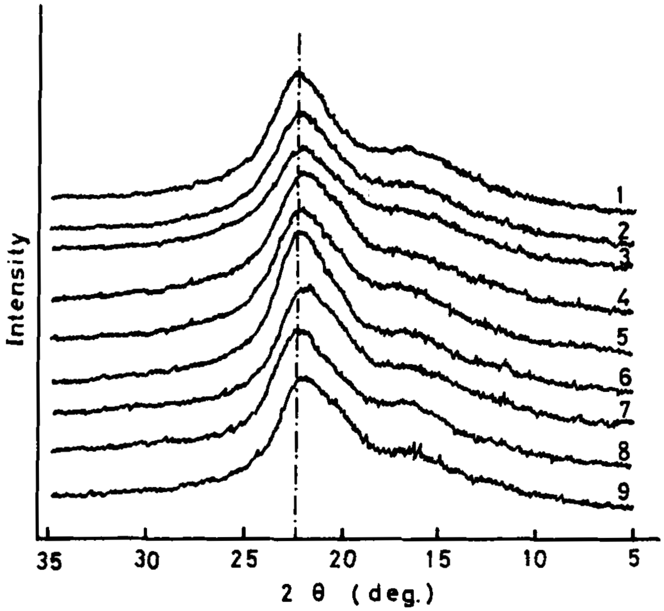

Fig. 6 Equatorial X-ray diffractograms of a series of mercerized woods with different lignin contents. (1) Kusamaki (38.8 %), (2) Sugi (35.6 %), (3) Hinoki (32.9 %), (4) Todomatsu (28.5 %), (5) Akamatsu (26.8 %), (6) Makanba (19.4 %), (7) Kuri (24.4 %), (8) Yamazakura (22.2 %), (9) Tsukubanegashi (18.8 %). The numerical numbers in the parentheses represent the lignin content.

0.17 to 0.71 and the lignin content from 18.1 to 38.8 %, as shown in Table 1. The equatorial X-ray diffractograms for 9 species of mercerized wood are shown in Fig. 6, in which the lignin content decreases from the top to the bottom. It is evident that reconversion to cellulose I takes place irrespective of the lignin content. The same conclusion was also obtained with respect to the effect of the density of wood. Even the wood with lowest density (Balsa) exhibits almost complete cellulose I structure after mercerization, and its X-ray diagram is comparable to or similar to that of mercerized wood with the highest density examined (Akagashi).

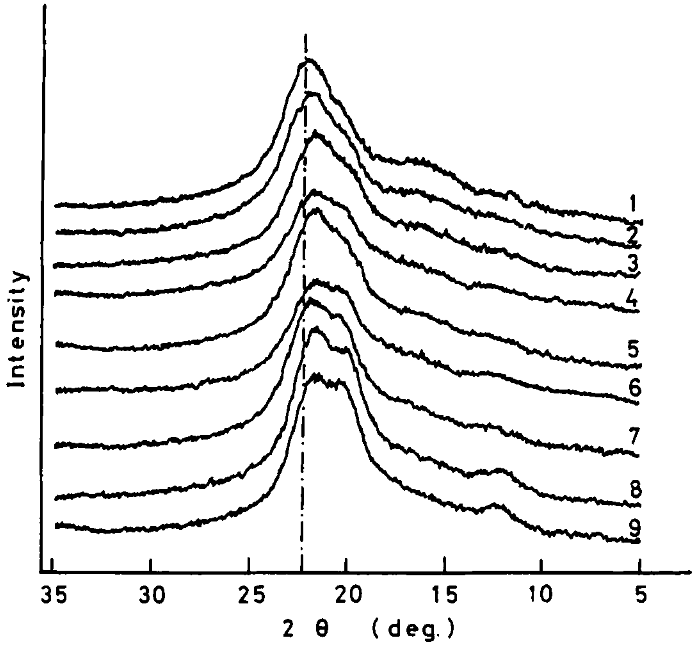

Fig. 7 Equatorial X-ray diffractograms of mercerized wood (Makanba) previously delignified with the sodium chlorite method for different reaction periods. (1) 0 min (2) 15 min (3) 30 min (4) 45 min (5) 60 min (6) 75 min (7) 90 min (8) 120 min (9) completely delignified.

### c) Mercerization of a Series of Delignified Wood Samples

Mercerization was undertaken with wood meals previously delignified to varying extents, in order to find a role of lignin for the hindered lattice conversion of cellulose in wood during the mercerization process. Figure 7 shows a series of equatorial X-ray diffractograms of mercerized wood previously delignified with the sodium chlorite method for different reaction periods. It is evident that partial lattice conversion to cellulose II can be recognized in X-ray diagrams after each delignification, and the ratio of the lattice conversion increases with the degree of delignification.

In connection with these results, delignification with the peracetic acid method was also examined, but mercerization of the wood sample previously delignified by this method was found to give almost the same results as described above.

In order to get some quantitative information from Fig. 7, the lattice conversion ratio (L.C.R.), the ratio of lattice conversion of cellulose I to cellulose II, was obtained by two methods, that is, the Ellefsen method[13)] and the curve resolver method.[14)]

Since the former method should adopt a calibration curve based on mixtures of isolated cellulose I and cellulose II with various known ratios, for comparison's sake, all the mercerized samples included in Fig. 7 should completely be delignified again before the measurement of L.C.R. Thus, it was necessary to examine whether some change in X-ray diffractograms took place or not during this complete delignification process for the sample once partially delignified and mercerized. In this sense, X-ray diffractograms of the mercerized samples of Fig, 7 were taken again after their complete delignification without additional mercerization and shown in Fig. 8. Comparison of Figs. 7 and 8 reveals that almost no change in X-ray diffractograms took place during the final complete delignification process. This can be further confirmed by the fact that both the plots of the delignification time vs. L.C.R. based on this Ellefsen method and the curve resolver method agree well, as will be described later (Fig. 9). At any rate, these results imply that, although the mercerized crystalline structure of cellulose present within wood cell wall is directly affected by the presence of lignin, it is not influenced by the subsequent delignification.

In Fig. 9, plots of L.C.R. and the lignin content against the delignification period are shown. L.C.R. obtained by the Ellefsen method is shown with the open circle mark and that obtained by the curve resolver method with the open triangular mark. The lignin content is expressed as a percentage part remaining after each delignification period.

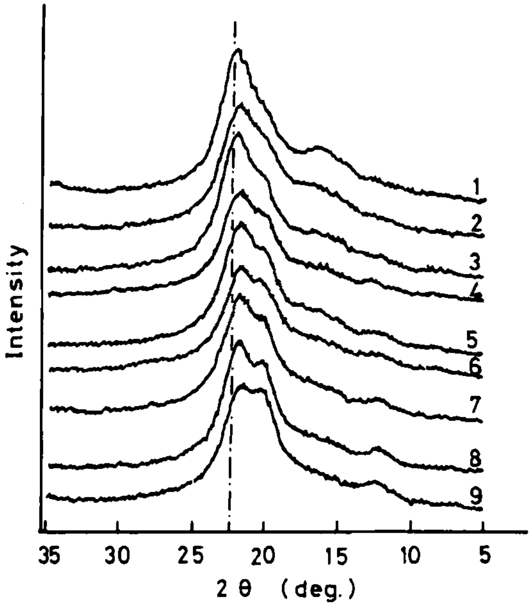

Fig. 8 X-ray diffractograms of the samples taken after complete delignification of the mercerized samples of Fig, 7; numbering of curve is similar to that of Fig. 7.

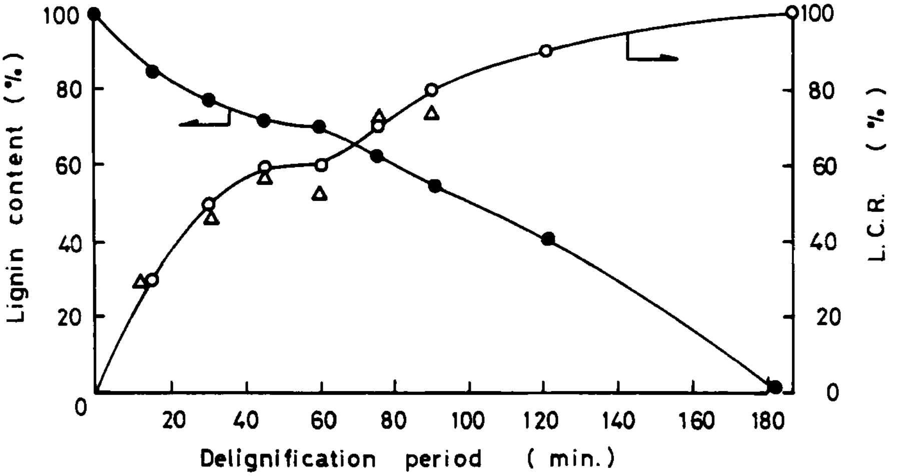

Fig. 9 Plots of L.C.R. and the lignin content against the delignification period. (Makanba) ○ : L.C.R. obtained by the Ellefsen method, △ : L.C.R. obtained by the curve resolver method, ● : the lignin content.

As described above, the values of L.C.R. obtained by two different methods are found to coincide well in Fig. 9 confirming reasonable reliability of both methods.

From Fig. 9, it is also found that the L.C.R. value reaches slightly more than 50 %, when about one third of the lignin is removed from wood. The removal of about two thirds of the lignin from wood results in an almost complete conversion of cellulose I to cellulose II in mercerization.

Makanba was used in the above experiments. Makanba is a hardwood, and it's lignin content is intermediate among the wood species. Thus, it was of interest to examine, further, the effect of lignin removal on the lattice conversion, with wood having a higher as well as a lower lignin content. Among the wood species used in these experiments, Kusamaki has the highest lignin content of 38.8 %, and Tsukubanegashi has the lowest content of 18.1 %.

The results of this examination for Kusamaki and Tsukubanegashi are given in Fig. 10. Although it is known from the figure (a) that the delignification of Tsukubanegashi proceeds much faster than that of Kusamaki, the dependence of L.C.R. on the lignin removal is found to be almost the same for both the wood species, as shown in the figure (b). From the latter figure, it is also known that the initial removal of lignin from the wood cell wall, up to 40 %, increases steeply the value of L.C.R. The increased extent of L.C.R. in the initial stage of lignin removal is almost six times larger than that in the final stage. These findings agree well with that found previously for Makanba, which has an intermediate lignin content.

The facts so far adduced indicate that the existence of lignin within the wood cell wall plays a part in depressed conversion of cellulose I to cellulose II in mercerization.

It has been proved that lignin has, by nature, a spongy structure, in the cell wall of wood.[20)] Cellulose is interwoven in the form of fibril bundles through the meshes of lignin aggregates and the spaces are filled with hemicellulose. Thus, it can be said that swelling of cellulose in whole wood in the mercerizing alkali

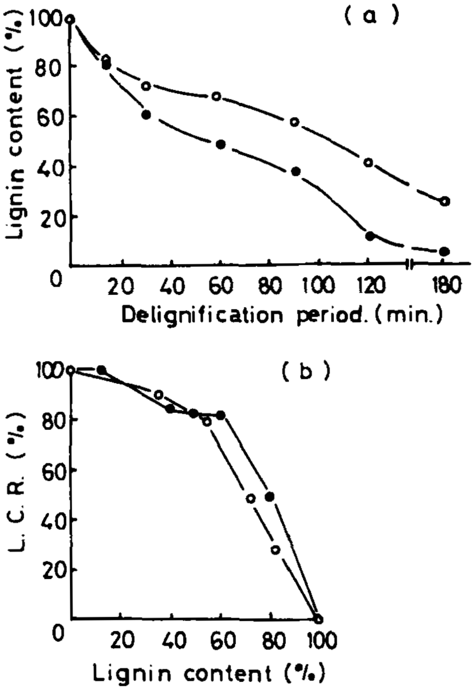

Fig. 10 Lignin content and L.C.R. as a function of the delignification period. (a) lignin content versus delignification period (b) L.C.R. versus deignification period. ○ : Kusamaki, ● : Tsukubanegashi.

is partially restricted by the existence of lignin aggregates, when compared with the swelling of isolated cellulose. Since the alkali-induced conversion of cellulose from cellulose I to cellulose II is known to be governed by the swelling of the fiber 21), the restriction of the swelling causes depressed lattice conversion. It should be emphasized here, again, that another requirement of mercerization, that is, complete penetration of alkali to crystalline fibril, was satisfied.

### d) Effect of Loosening Lignin Aggregates Prior to Mercerization

In the preceding section we have shown that removal of lignin results in the lattice conversion of cellulose within wood owing to

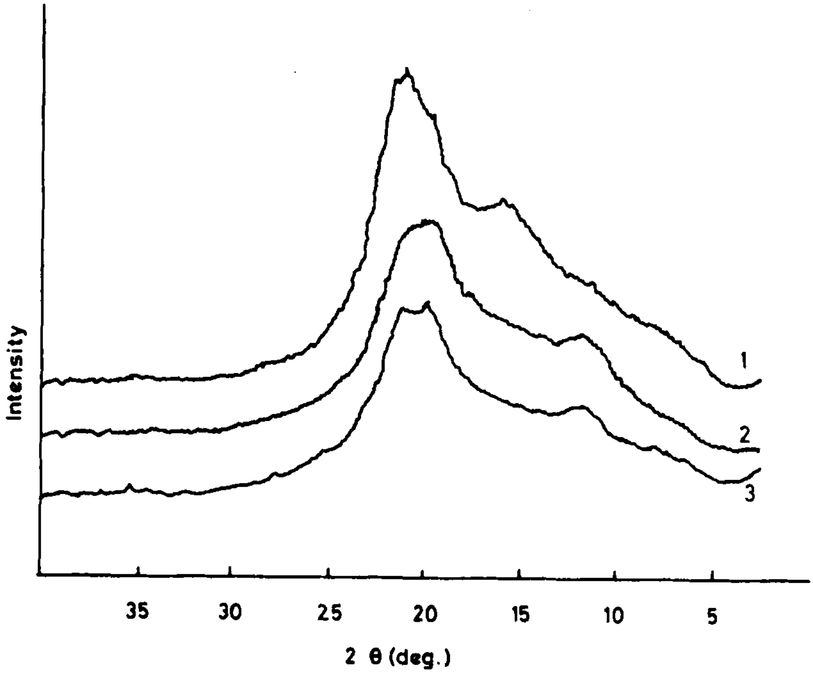

Fig. 11 Equatorial X-ray diffractograms of the acylated-mercerized wood meal. Acylation was carried out by DMF/pyridine/acid chloride method. (1) acetylated wood (2) caproylated wood (3) lauroylated wood.

the enhanced swelling in mercerizing alkali. Swelling of cellulose within wood in mercerizing alkali can be faciliated, without removing any wood component, by loosening the lignin aggregates. This could be achieved by introducing large substituent groups in wood. In the present case, substituent groups introduced were acetyl, caproyl and lauroyl. The acylation was carried out at 100°C using DMF as a solvent by the pyridine-acid chloride procedure reported by Malm and coworkers.22) The degree of substitution in all three cases was identical as was determined by IR spectroscopy. The acylated wood meals were simultaneously saponified and mercerized with 23 % solution of sodium hydroxide in water/methanol mixture at room temperature for 24 hr. After mercerization/saponification, they were washed thoroughly with water and dried.

As shown in Fig. 11, the acetylated sample showed no change, the caproylated sample revealed a partial but significant lattice conversion, while the cellulose I was completely changed to cellulose II in the case of lauroylated wood meals. These results mean that the acetyl group is too small to loosen the lignin aggregates, and that acyl groups larger than caproyl are large enough to loosen the lignin structures in wood, allowing the cellulose to swell sufficiently and resulting in the high lattice conversion.

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