Histochemical Consideration of Delignification by Solvolysis*

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ソルボリシスによる脱リグニンの組織化学的考察*

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Abstract

The manner of delignification of beech (*Fagus crenata*) and fir (*Abies sachalinensis*) woods by solvolysis pulping has been investigated histochemically by use of the ultraviolet (UV) microscopy.

Beech wood was effectively delignified by cooking with various cresol (C) and water (W) systems. The UV absorbances of the secondary walls (SW) of fibres, the vessel walls and the ray cell walls disappeared by cooking for 40 min of the reaction time although the absorbance of the cell corner still could be measured at that time. The absorbances of the SW markedly decreased up to 30%-40% of delignification and then slowly reduced with further delignification. On the other hand, a significant decrease of the optical density of the cell corner areas was shown up to 20% of delignification and a slow reduction of them was indicated during 20%-50% of delignification. Consequently, it is clear that the selective delignification takes place in the SW of fibres at the early stage of cooking.

Delignification of fir wood by the solvolysis pulping was more difficult than that of beech wood. During the solvolysis pulping, the absorbances of the SW of tracheids and the

Key words: Delignification, solvolysis, UV microscopy, beech, fir.

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cell corner in early wood gradually reduced with the reaction time. Their absorbances with various cooking conditions were decreased nearly linear manner. It suggests that no selective delignification of the SW of tracheids take place during the solvolysis pulping.

Contents

1. Introduction

Hardwoods were more easely delignified by solvolysis pulping with the solvent system of cresol(C) and water(W) (8:2) at 180°C for 90 min than softwoods were under the same condition. The solvolysis pulps from birch wood were obtained in high yields, and had the comparable strength properties as those of sulphate pulp from the same wood except tear strength[1]. The delignification of softwood by solvolysis pulping was more difficult than that of hardwoods, and however it could be improved by an elevation of the reaction temperature or by an addition of acetic acid as a catalyst[2]. This suggests that the manner of delignification differs between hard- and softwoods.

Goring *et al* had observed by the UV microscopy that pulps from spruce wood with sulphate and acidic sulphite pulping were selectively delignified from the cell walls of fibres at early stage of cooking, and then delignification took place in the middel lamellae when the rate of delignfication went up to over 50%[3]. Also, they had pointed out that no selective delignification was observed in spruce pulp prepared by neutral sulphite process. On the other hand, Fergus *et al* had mentioned that the lignin located in the fibres and the vessel walls of birch wood was more easely removed by sulphate cooking than that in the middel lamellae[4].

In this paper, the solvolysis pulps from beech and fir woods have been observed by the UV microscopy to know the manner of delignification by solvolysis pulping.

2. Experimental

Beech chips used were consisted of pale and intense coloured woods and then were divided into two parts according to the colour. The later seemed to be the false heartwood and was tentatively regarded as heartwood in this experiment. Small size chips (3x3x10 mm) of beech (*Fagus crenata* Blume) and fir (*Abies sachalinensis* Masters) were prepared and were pre-extracted with the mixture of ethanol-benzene (1 : 2) for 48 hrs. Taking off

the solvent, the chips (1.5 g, od) in 20 ml micro-autoclave were cooked by three solvent systems of cresol (C) and water (W) (2 : 8, 5 : 5 and 8 : 2) at 180°C for 0-100 min. The liquor-to-wood ratio was 7 : 1. The prescribed temperature could be attained after 90 min. After cooking, the pulps obtained were washed with acetone-water (9 : 1). Furthermore, these pulps and uncooked woods (control) were entirely dehydrated with acetone and then were embedded by epoxy-resin. The thin sections (1 μm thick) were prepared from the epoxy-embedded samples. After de-embedded, these sections were mounted with quartz cover glass on quartz slide glass with glycerin.

The manner of delignification in solvolysis pulping was observed with an UV microscope photometer, Carl Zeiss, Model MPM 01 and the absorbances of various morphological regions of beech and fir pulps were measured.

3. Result and discussions

3.1. Delignification by solvolysis pulping.

The pulp yields, the residual lignin (Klason lignin KL) in pulps and the rate of delignification of beech woods by solvolysis pulping with three sovent systems are shown in Table 1 and 2. Delignification of each pulp obtained was apparently progressed with the reaction time, and however it considerably depended on the differences of the solvent systems. The residual KL content in the pulp from the pale coloured beech wood with

Table 1. Yield and lignin content of beech (pale coloured) pulps by solvolysis

Time (min)	Control	0	20	40	60	80	100
C : W=5 : 5							
Yield(%)	100	93.0	73.3	59.4	54.3	50.1	47.7
K L(%)	22.3	19.8	16.0	11.6	9.3	6.2	4.9
Delignification (%)	0	17.3	47.5	69.2	77.4	86.1	89.5
C : W=8 : 2							
Yield(%)	100	98.0	89.9	74.1	69.9	62.7	63.5
K L(%)	22.3	19.9	19.3	15.8	13.3	10.0	7.9
Delignificaton (%)	0	12.8	22.2	47.6	58.4	72.0	77.6
C : =2 : 8							
Yield(%)	100	90.2	70.6	60.1	-	-	-
K L(%)	22.3	20.2	16.4	13.3	-	-	-
Delignification (%)	0	18.3	42.7	64.2	-	-	-

C : W ; Cresol : Water, K L ; Klason lignin

Table 2. Yield and lignin content of beech heartwood pulps by solvolysis

Time (min)	Control	0	20	40	60	80
C: =5 : 5						
Yield(%)	100	93.3	73.8	66.8	-	51.7
K L(%)	23.8	22.3	19.9	16.6	-	8.6
Delignification (%)	0	12.6	38.3	53.5	-	81.2
C: W=8 : 2						
Yield(%)	100	97.4	83.9	78.4	68.2	65.8
K L(%)	23.8	22.7	18.4	16.7	15.7	11.7
Delignification (%)	0	6.0	35.0	45.2	54.9	67.7
C: W=2 : 8						
Yield(%)	100	90.4	63.5	55.3	50.0	50.2
K L(%)	23.8	25.1	18.4	14.0	9.2	7.5
Delignification (%)	0	4.7	50.9	67.5	80.7	84.2

C: W; Cresol: Water, K L; Klason lignin

solvent system of C : W (8 : 2) at 180°C for 40 min was 15.8% and the elongation of the reaction time up to 100 min could be reduce it to 7.9%. With the solvent system of C : W (5 : 5), the pale coloured beech wood yielded 59.4% of pulp which contained 11.6% of the residual KL. Also, the elongation of the reaction time for 100 min delignified up to 4.9% of the residual KL. The mixture consisting of the equal portion of cresol and water seemed to be a favorable solvent system for delignification. A similar tendecy was found in the case of the beech heartwood. The residual KL in the pulp from the beech heartwood with solvent system of C : W (8 : 2) at 180°C for 80 min was 11.7% although that of the pulp with C : W(5 : 5) was 8.6%. However, the heartwood was more difficult to delignify than the pale colourd one was. It suggested that the different feature of delignification between the pale and highly discoloured woods may be attributed to the existence of polyphenols other than lignin in the later.

Fir wood also was delignified by solvolysis pulping with various solvent systems and these results are shown in Table 3. Fir wood was suspectible to delignify with the reaction time. The residual KL in the pulp with the solvent system of C : W (5 : 5) at 180°C for 100 min was 11.9%, whereas that of the pulp from the pale coloured beech wood was 4.9%. The results indicated that fir wood was more difficult to be delignified than beech wood was. At that time, the rate of delignification in the pulp from the fir wood was estimated 78.0% on the original lignin basis and also the pulp yield was 58.3% on the wood basis.

Table 3. Yield and lignin content of fir wood pulps solvolysis

Time (min)	Control	0	20	40	60	80	100
C : W=5 : 5							
Yield(%)	100	93.1	81.0	73.6	66.6	64.3	58.3
K L(%)	30.1	27.9	25.7	22.9	19.1	17.2	11.9
Delignification (%)	0	13.7	30.8	44.0	57.7	63.3	78.0
C : W=8 : 2							
Yield(%)	100	98.1	91.8	87.9	85.9	82.9	79.3
K L(%)	30.1	28.7	27.5	26.6	25.3	23.4	22.1
Delignification (%)	0	6.7	16.1	22.3	27.8	35.6	41.8
C : W=2 : 8							
Yield(%)	100	92.5	80.1	71.7	66.4	63.3†	58.3
K L(%)	30.1	28.7	27.1	26.2	23.5	20.3†	17.2
Delignification (%)	0	11.8	27.9	37.6	48.2	58.3†	66.7

C : W ; Cresol : Water, K L ; Klason lignin, † ; Cooking time : 70min

With the solvent system of C : W (2 : 8) at 180°C for 100 min, fir wood yielded 58.3% of pulp which contained 17.2% of the residual KL. Under the later cooking condition, a part of polysaccharide was considerably dissolved into the reaction liquor. On the other hand, fir wood with the solvent system of C : W (8 : 2) at 180°C for 100 min was more difficult to be delignified than in the former systems. The pulp yield was 79.1% and the residual KL in the pulp was 22.1%. Consequently, the mixture of the equal portion of cresol and water seemed to be a favorable solvent system for delignification such as the case of beech wood.

3.2. Observation of solvolysis pulps by UV microscopy.

The UV photomicrographs taken at 280 nm of untreated wood (contral) and some solvolysis pulps are shown in Photos 1-4. The samples for observation of delignification were prepared with the solvent system of C : W (5 : 5) at 180°C for 0-40 min. In Photo 1, the most intense absorption of the UV light at 280 nm was observed at the cell corner region of the fibers and the next was the vessel walls. However, the secondary walls (SW) of fibres has the weaker absorption than have the formers. Goring *et al* have suggested that the lignin located in the fibre walls of birch wood consisted mainely of syringyl residues while the vessel wall lignin consisted chiefly of guaiacyl residues. In addition, the guaiacyl residues absorb four times as much light as the syringyl residues at 280 nm[5,6]. The result observed in the SW of fibres of the control seems to be comparable to those of white birch wood. Microphotographs of the pulps delignified up to 17.3%, 47.5% and

EXPLANATION OF PHOTOGRAPHS

All photographs are ultrviolet microphotographs at 280 nm and shows the cross sections of the samples. Photographs indicate those of the control (untreated) and various pulps by solvolysis pulping with cresol : water (5 : 5) at 180°C for 0-80 min.

Photographs 1-5 are the samples of beech wood (untreated) and various pulps.

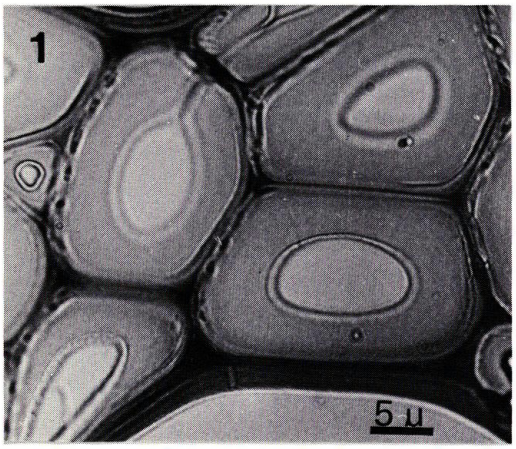
Photo. 1. shows the control (untreated) of beech wood (pale coloured)
Photo. 2. shows the pulp delignified up to 17.3%.
Photo. 3. shows the pulp delignified up to 47.5%.
Photo. 4. shows the pulp delignified up to 69.2%.
Photo. 5. shows the pulp delignified up to 81.2%. (heartwood)

Absorbance of fibres from beech wood decreased markedly at the early stage of cooking and that of the middle lamella disappeared at the later stage of solvolysis. The polyphenols other than lignin was observed in the ray cell.

Photographs 6-10 are the samples of fir early wood (untreated) and various pulps under the same solvolysis condition such as beech wood.

Photo. 6. shows the control (untreated) of fir early wood.
Photo. 7. shows the pulp delgnified up to 13.3%.
Photo. 8. shows the pulp delignified up to 30.8%.
Photo. 9. shows the pulp delignified up to 44.0%.
Photo. 10. shows the pulp delignified up to 63.3%.

Lignins located in tracheids and middle lamella were delignified with the reaction time, and however the topochemical effect by solvolysis was not observed.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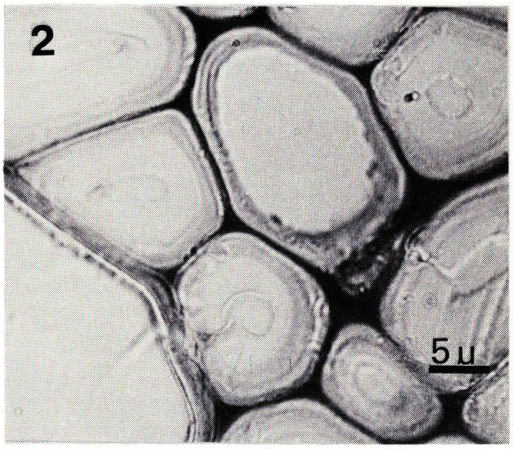
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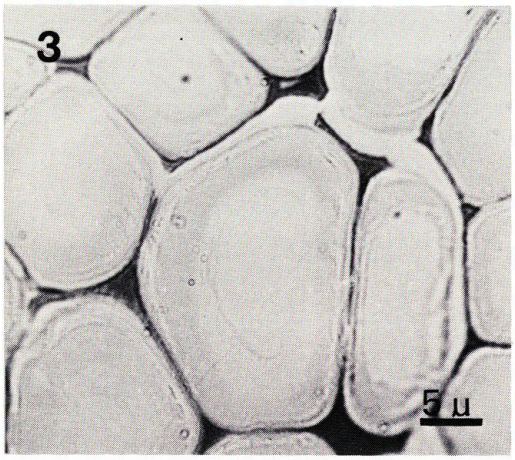
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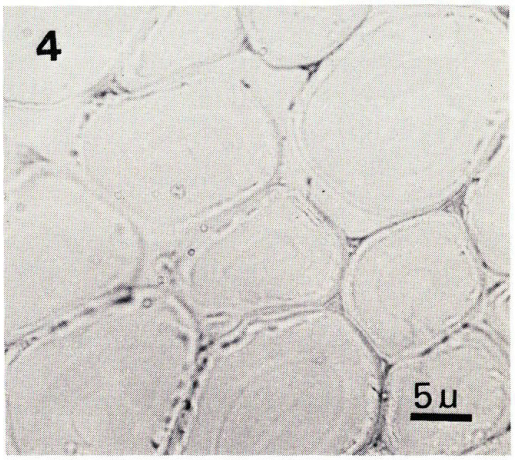
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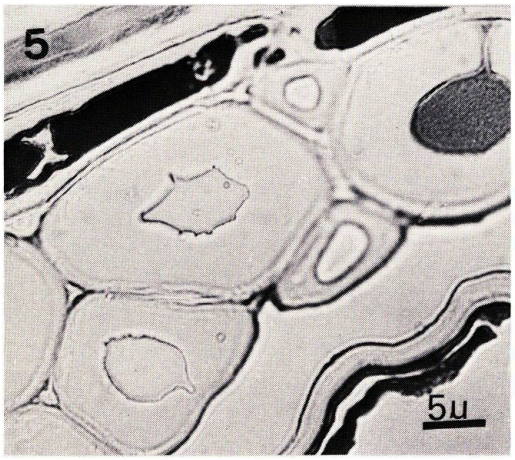
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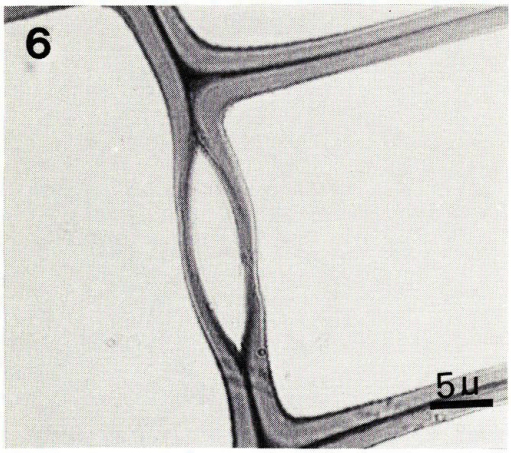
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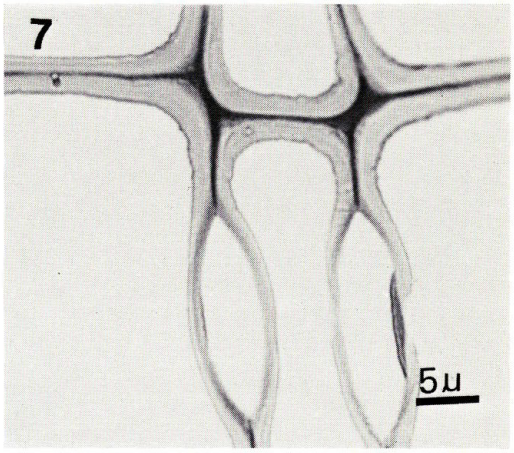
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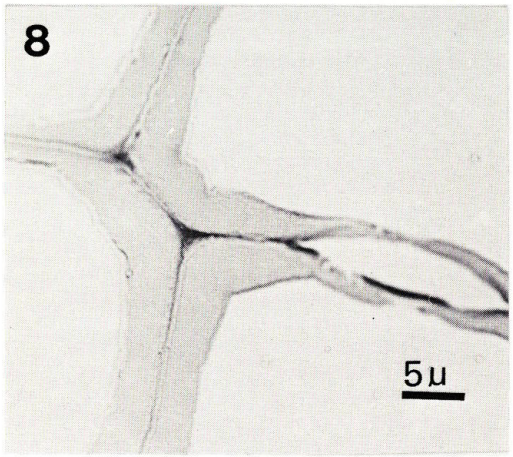
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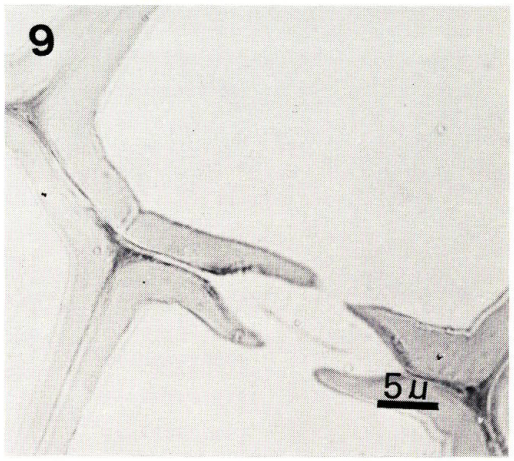
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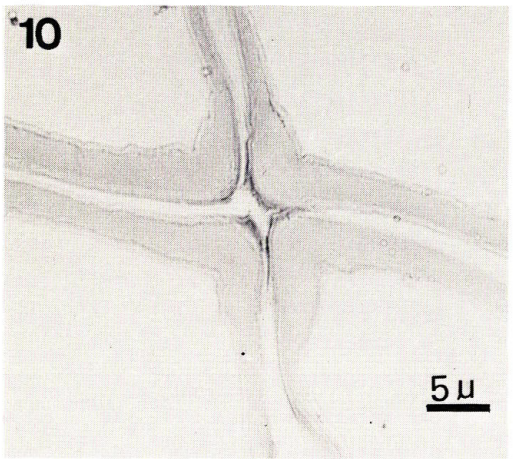
10
5μ

69.3% are shown in Photos 2, 3 and 4, respectively. The overall absorption became not clear with the progress of delignification. The SW of fibres with 47.5% of delignification showed very weak absorption (Photo 3). In the case of 69.2% of delignification, the shape of lumen disappeared (Photo 4). Also, the UV absorption of the middel lamella (ML)-intercellular layer- was to be reduced with delignification, while that of the cell corner middel lamella (ccML)[7] could be detected even when the delignification was reached up to 69.2% (Photo 4). This feature suggested that lignin located in the ccML is more resistant to delignification than those in the vessel walls and ML. Consequently, it is considered topochemically that the selective delignification initiated from the fibre walls at early stage of solvolysis pulping.

In the beech heartwood, the absorption of the SW and ML in fibres disappeared effectively at the stage of 81.2% of delignification, but still the strong absorption remained in a part of the vessel walls and the contents of the ray cells (Photo 5). The intense absorption in the ray cells appears to be the polyphenols and it seems to be a factor of difficulty in solvolysis pulping of the beech heartwood.

The UV microphotographs of untreated wood (control) and some solvolysis pulps from fir wood are shown in Photos 6-10. These photographs were taken from the tracheids of early wood and the cooking condition was the same as the case of beech woods. Photo 6 shows a photograph of untreated one (control). A distinct absorption of the UV light at 280 nm was observed at the cell corner, the ML and the inner layer in the SW. Also, a clear absorption was recognized at the SW of tracheids compared with the absorption of the SW of fibres from beech woods. Photo 7, 8, 9 and 10 show the pulps delignified up to 13.7%, 30.8%, 44.0% and 63.3%, respectively. The absorption due to lignin is gradually decreased with the reaction time or a progress of delignification during solvolysis pulping. A part of lignin located in the ML disappeared by delignification up to 30.8%. At that time, the absorptions at the SW of tracheids and the cell corner reduced considerably. The pulp obtained by solvolysis pulping at 180°C for 80 min was delignified up to 63.3% on the original lignin and a bundle of thracheids markedly released (Photo 10). In this case, the UV absorption at 280 nm almost disappeared in most morphological regions, although a part of the cell corner regions indicated a still appreciable absorption. This suggested that lignin located in tracheids was more difficult to be dissolved by solvolysis pulping compared with those in fibres of beech woods.

3.3. UV absorbances at some morphological regions.

The absorbances at 280 nm in some morphological regions of the pale coloured beech wood (control) were observed most intensely at the cell corner of the fibres, and gradually decreased in that order of the vesell walls, the ray cells and the SW of fiber. The absorbances of the cell corner, vessel walls and SW of fibres were 0.60, 0.51 and 0.20, respectively (Table 4). The facts above mentioned supported the observation presented by Goring *et al*[5,6]. Also, these absorbances were reduced with the reaction time. Consequently, the optical densities of the SW of fibres, the vessel walls and the ray cell walls of solvolysis pulps from the pale coloured beech wood with solvent system of C : W (5 : 5) could not be determined at 40 min of the reaction time. However, that of the cell corner regions of fibers was still measured (Table 4). These results were similarly observed from the findings of the absorption at 280 nm (Photo 4). At the solvent system of C : W (8 : 2), the various morphological regions of the pulps can be determined even when the delignifi-

Table 4. Absorbance of some morphological regions (pale coloured beech wood : 280 nm)

Time (min)	Control	0	20	40	60	80
C : W=5 : 5						
S. wall	0.20	0.07	0.01	0.00	-	-
Cell corner	0.60	0.28	0.27	0.07	-	-
Vessel	0.51	0.23	0.10	0.00	-	-
Ray cells	0.33	0.21	0.02	0.00	-	-
C : W=8 : 2						
S. wall	0.20	0.12	0.06	0.04	0.03	0.02
Cell corner	0.60	0.34	0.36	0.17	0.15	0.03
Vessel	0.51	0.27	0.19	0.14	0.12	0.05
Ray cells	0.33	0.19	0.14	0.08	0.09	0.04
C : W=2 : 8						
S. wall	0.20	0.12	0.02	0.02	-	-
Cell corner	0.60	0.28	0.20	0.07	-	-
Vessel	0.51	0.28	0.07	0.03	-	-
Ray cells	0.33	0.17	0.03	0.05	-	-

S. wall ; Secondary wall, C : W ; Cresol : Water

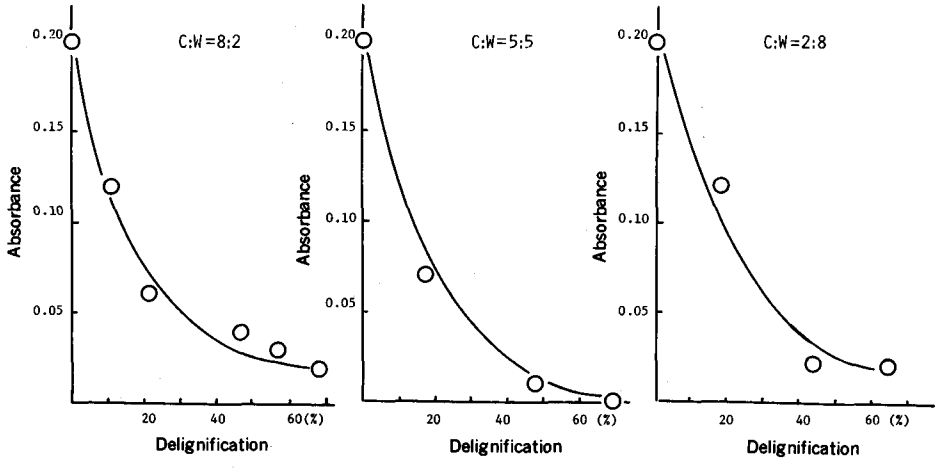

Fig. 1. Relationship between absorbance and delignification rate of secondary wall (pale coloured beech wood).

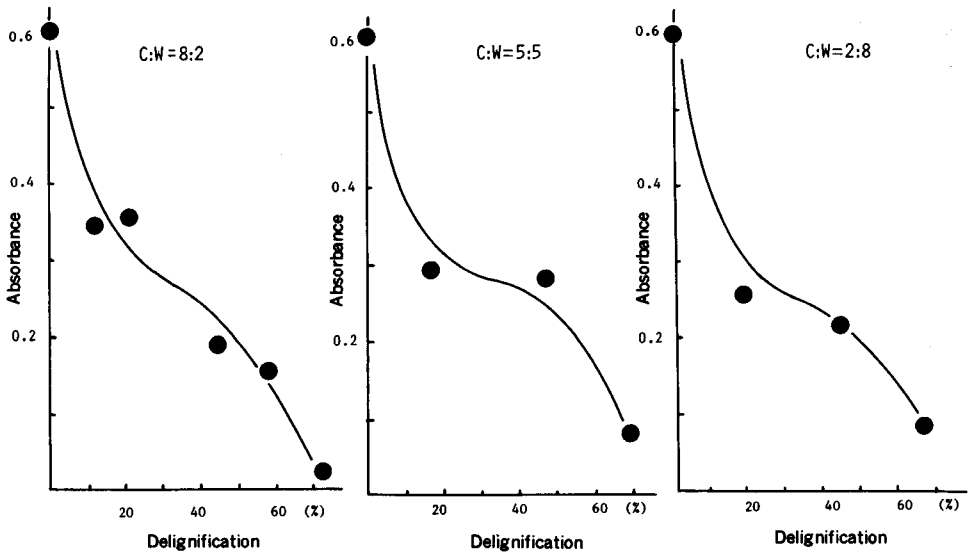

Fig. 2. Relationship between absorbance and delignification rate of cell corner (pale coloured beech wood)

cation up to 77.6% or for 100 min of the reaction. A relationship between the UV absorbances of the SW of fibres and the delignification of pulps are shown in Fig. 1. The absorbances markedly decreased up to 30%-40% of delignification and then slowly reduced with delignification. On the other hand, a significant decrease of the optical densities of the cell corner areas was shown up to 20% of delignification and a slow reduction of them

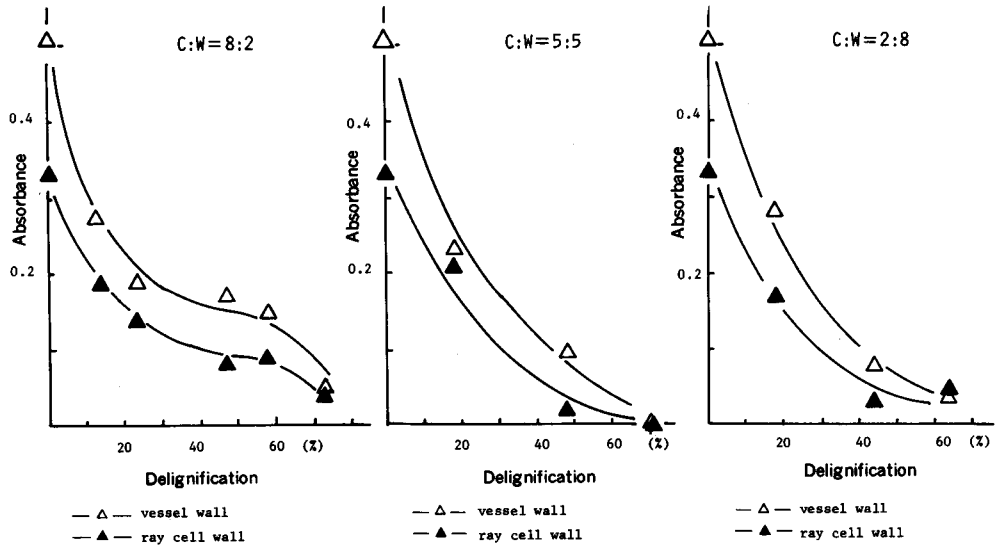

Fig. 3. Relationship between absorbance and delignification rate of vessel and ray cell walls (pale colored beech wood).

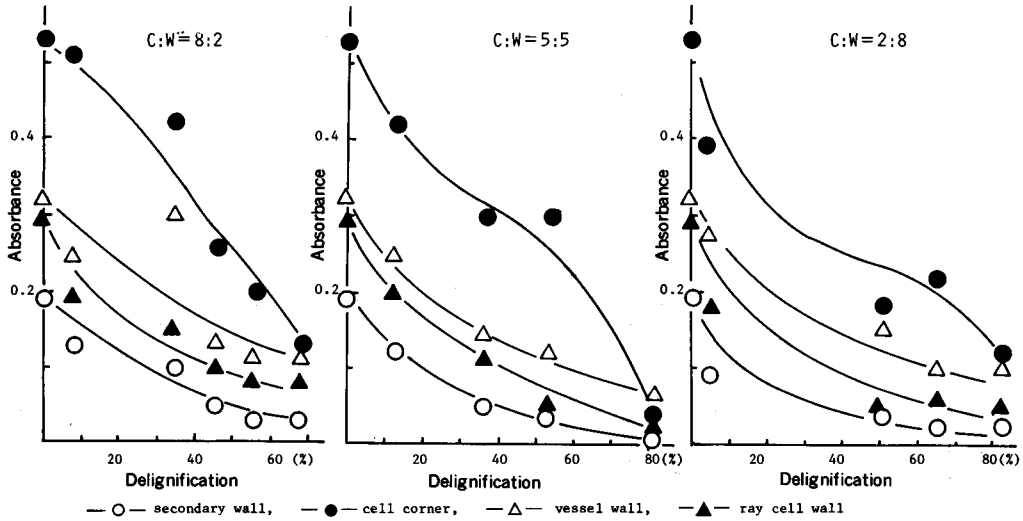

Fig. 4. Relationship between absorbance and delignification rate of some morphological regions (beech heartwood)

was indicated during 20%-50% of delignification (Fig.2). Then, the absorbances reduced again over 50% of delignification. It is therefore presumed that the selective delignification from the SW of fibres takes place during a slow delignification of the cell corner regions, which was delignified about 20%-50% at that time. The optical densities of the vessel walls and the ray cell walls with a progress of delignification varied with the manner of those on the SW of fibres (Fig.3).

In beech heartwood, the absorbances of some morphological regions decreased with the reaction time and also changed with solvent systems (Fig.4). The absorbance in the SW of fibres has still measured after solvolysis pulping for 80 min (Table 5), whereas that

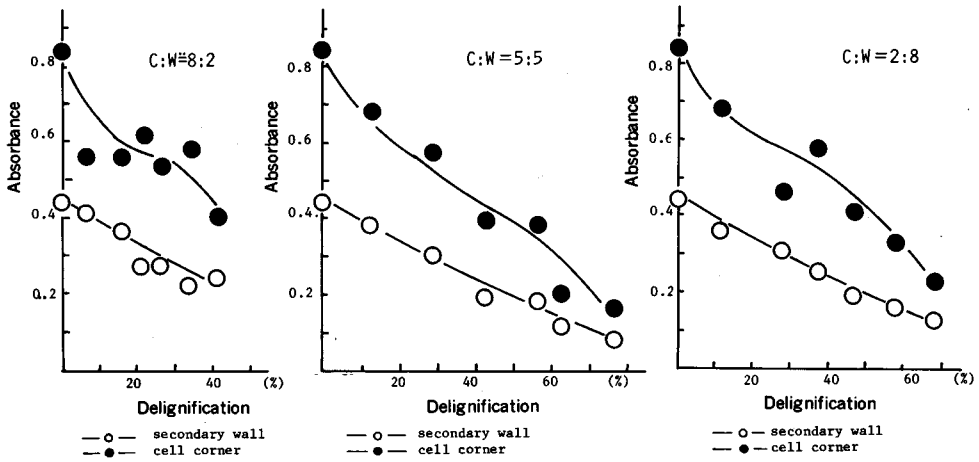

Fig. 5. Relationship between absorbance and delignification rate of secondary wall and cell corner (fir wood : early wood).

Table 5. Absorbance of some morphological regions (beech heartwood : 280 nm)

Time (min)	Control	0	20	40	60	80
C : W=5 : 5						
S. wall	0.19	0.12	0.05	0.03	-	0.01
Cell corner	0.53	0.42	0.30	0.30	-	0.04
Vessel	0.32	0.25	0.14	0.12	-	0.07
Ray cell	0.29	0.20	0.11	0.05	-	0.03
C : W=8 : 2						
S. wall	0.19	0.13	0.10	0.05	0.03	0.03
Cell corner	0.53	0.51	0.42	0.26	0.20	0.13
Vessel	0.32	0.24	0.30	0.13	0.11	0.11
Ray cell	0.29	0.19	0.15	0.10	0.08	0.07
C : W=2 : 8						
S. wall	0.19	0.09	0.03	0.02	0.02	
Cell corner	0.53	0.39	0.18	0.22	0.12	
Vessel	0.32	0.27	0.15	0.10	0.10	
Ray cell	0.29	0.18	0.05	0.06	0.05	

S. wall ; Secondary wall, C : W ; Cresol : Water

of the pale coloured beech wood diminished at cooking for 40 min (Table 4). However, the manner of delignification of the heartwood by solvolysis pulping could be considered nearly the same as those of the pale coloured wood.

In fir wood, the optical densities on the SW of tracheids and the cell corner regions of the control wood and various solvolysis pulps were measured and these results are listed in Table 6. A relationship between the UV absorbances and the rate of delignification on the early wood is indicated in Fig. 5. The absorbances of some morphological regions were reduced with the reaction time using the various solvent systems. The UV absorbance of the SW of tracheids was reduced slowly by solvolysis pulping with C : W (5 : 5) system and that at 100 min of the reaction time was 0.08 (Table 6). On the other hand, the cell corner under the same condition was difficult to be delignified than the SW of tracheids and its optical density (0.16) was two times of that of the SW of tracheids. The change of absorbances at the SW and the cell corner under the condition with C : W (2 : 8) showed a similar tendecy such as that of C : W (5 : 5). By solvolysis pulping with the solvent system of C : W (8 : 2), delignification proceeded slowly compared with those of the formers. The absorption of lignin located at the cell corner in tracheids (control) was 0.84. With delignification up to 6.7%, the absorption of the cell corner was 0.56. This delignification was obtained upon 0 min of the reaction time at 180°C and it indicated that delignification proceeded somewhat up to the prescribed temperature. The absorbances barely changed during 16.1%-36.6% of delignification, and then a decrease of absorbances

Table 6. Absorbance of some morphological regions (fir wood : 280 nm)

Time (min)	Control	0	20	40	60	80	100
C : W=5 : 5							
S. wall(e)	0.44	0.38	0.30	0.19	0.18	0.11	0.08
(l)	0.38	0.37	0.24	-	-	0.08	0.09
Cell corner(e)	0.84	0.68	0.57	0.39	0.38	0.20	0.16
(l)	0.77	0.58	0.55	-	-	0.26	0.16
C : W=8 : 2							
S. wall(e)	0.44	0.41	0.36	0.28	0.28	0.22	0.24
(l)	0.38	0.32	0.33	0.25	0.19	0.22	-
Cell corner(e)	0.84	0.56	0.56	0.62	0.53	0.58	0.40
(l)	0.77	0.64	0.49	0.56	0.58	0.47	-
C : W=2 : 8							
S. wall(e)	0.44	0.36	0.31	0.25	0.19	0.16†	0.13
(l)	0.38	0.36	0.31	0.25	0.17	-	0.10
Cell corner(e)	0.84	0.68	0.46	0.58	0.41	0.33†	0.23
(l)	0.77	0.67	0.57	0.62	0.50	-	0.10

S. wall ; Secondary wall (e) ; early wood (l) ; late wood
C : W ; Cresol : Water
† ; Cooking time : 70min

was again observed at the stage over 41.8% of delignification. The Absorbances on the SW of tracheids and the cell corner with various solvolysis pulping conditions decreased nearly linear manner, except that of the cell corner under the condition of C : W (8 : 2). This suggested that no selective delignification was taken place in the SW of tracheids by solvolysis pulping with three solvent systems.

Lignin located in the SW of fibres of beech woods was more subjectd to delignify at the early stage of solvolysis pulping than those of the vessel walls and the ray cell walls and this fact supported the results on white birch with sulphate pulping obtained by Fergus *et al*[4]. In fir wood, no selective delignification was observed in the SW of tracheids by solvolysis pulping and this finding was not agreed with the result on spruce wood with sulphate and acidic sulphite pulping by Goring *et al*[3]. Yamashita *et al* had reported that no selective delignification was taken place in sapwood of spruce (*Picea jezoensis* Carr.) with chlorite procedure[8]. Fergus and Goring had reported that a distinct distortion of the cell corner regions and a marked deformation of the compound middel lamella due to swelling of fibres observed at the later stage of sulphate cooking, but such phenomenone not arose in spruc wood[3,4]. By solvolysis pulping, a remarkable deformation of the fibres of beech woods could not be found with the cooking time for 40 min, but in the case of fir wood a clear change of the cell corner and the compound middle lamella was taken place during solvolysis pulping for 100 min.

4. Conclusion

The behaviours of delignification by solvolysis pulping have considered from the results by the UV microphotographs and by the absorbances at 280 nm. The mixture of cresol and water (5 : 5) on solvolysis pulping is markedly effective to delignification than those of other solvent systems. On the UV microscopic observation of some morphological regions in the pale coloured beech wood, the SW of fibres is selectively delignified than the cell corner, the vessel walls and the ray cell walls are. On the other hand, the vessel walls and the ray cell lumens of the beech heartwood still show a distinct absorption at 280 nm after solvolysis pulping for 80 min. The contents in the ray cell lumen appear to be the polyphenols other than lignin. The difficulty of pulping of beech heartwood by solvolysis cooking can be partly explained by the existence of these polyphenols.

Delignification of fir wood by solvolysis pulping is more difficult than that of beech wood. Furthermore, the manner of delignification on the SW of tracheids and the cell corner regions appears not to be explicit with each other. It suggests that the selective delignification on the SW of tracheids is not caused by solvolysis cooking.

Since an observation with the UV microphotograohs and a determination of absorbances at 280 nm result in the ambiguous evidence at the stage over 50% of delignification, a further search on the residual lignin in the pulps seems to be required to know the detail of the manner of delignification on beech wood by solvolysis pulping.

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要　　約

ブナ材およびトドマツ材のソルボリシスによる脱リグニンの挙動を知る為，パルプおよび未処理材の紫外線（UV）顕微鏡による観察ならびに吸光度の測定の結果を基に，組織化学的な考察を行った。

1)　ソルボリシスによる脱リグニン

クレゾール（C）—水（W）の混合溶媒，180°C，0～100 minのパルプ化を行った。時間経過による脱リグニンの挙動はパルプ残存リグニン（KL）量により考察した。C：W（5：5）の溶媒，80 minの反応でブナ材は50.1%のパルプを生じ，残存KLは6.2%であった。100 minまでの蒸解時間は残存KLを4.9%まで減少させる（Table 1）。ブナ心材は上記条件80 minで，51.7%のパルプ収率，残存KL 8.6%を示し，若干脱リグニンし難い（Table 2）。これはUV顕微鏡写真に見られるように，心材放射細胞ray cellの内容物が未だ除去されない為と推察される（Photo 5）。一方，トドマツ材は同一条件下，100 minのソルボリシスパルプ化で得られたパルプ収率は58.3%，残存KLは11.9%とブナ材に比べ，かなり脱リグニンされ難い（Table 3）。しかしながら，ブナ材およびトドマツ材に対し，C：W（5：5）の混合系が脱リグニンに効果的といえる。

2)　UV顕微鏡法によるソルボリシスパルプの観察

UV顕微鏡法による観察はC：W（5：5）の混合溶媒，反応温度180°C，反応時間0～100 minによって得られたパルプおよび未処理材について行った。

ブナ未処理材（コントロール）中，最も強い吸収を示すのはコーナー部の細胞間層部であり，ついで道管壁であった。木繊維二次壁（SW）は前二者に比べかなり弱い吸収を示す（Photo 1）。これは広葉樹繊維のSWのリグニンは主としてシリンギルタイプから構成されており，このタイプは270～280 nm領域でグアイアシルタイプの約¼の吸収強度しか有せず，Photo 1はこの結果をよく反映している。反応時間の経過と共に各構成要素の吸収は減少し（Photo 2→4），反応時間20 min後ではほとんど観察し難く，40 min後ではコーナー部の細胞間層の一部を除きほとんど消失した（Table 4，Photo 4）。これは脱リグニンが反応の初期段階でSWで開始している事を示す。ブナ心材では80 min反応後，パルプの吸収は未処理材に比べ著しい減少が認められるが，とくに放射柔細胞内容物による吸収が顕著であり，これが蒸解困難に関与しているものと考えられる（Table 5，Photo 5）。

トドマツ未処理材（早材）では，細胞間層（ML），二次壁内層に強い吸収が認められる（Photo 6）。100 min反応経過後すなわち78.0%の脱リグニン率段階でも未だ吸収が認められ，ブナ材

と大きく異なる (Table 6)。また，細胞壁の変形，繊維間の弛緩も認められる (Photo 10)。しかしブナ材で観察されたようにSWからの優先的な吸収の減少は認められない。

3) 各部位の吸光度 (280 nm) の変化

ブナ材およびソルボリシスパルプの各構成要素の吸光度と脱リグニン率との関係を考察した。SWは脱リグニン率30～40%の段階で急速なリグニンによる吸光度が減少し，以後緩やかに減少する (Fig. 1)。しかし，コーナー部では脱リグニン率20%の段階までは幾分減少し，脱リグニン率20—50%の間では非常に緩慢に変化し，その後急速に減少する (Fig. 2)。仮管壁および放射柔細胞壁もほぼSWと似た挙動を示す(Fig. 3)。これらの脱リグニンの挙動はソルボリシスパルプ化で，選択的脱リグニンが蒸解初期の段階でSWから開始されている事を意味する。一方，ブナ心材の吸光度の変化は前者と類似しているが，脱リグニン率80%に達してもかなりの吸光度が測定され，心材のリグニン除去がやや困難である事を示唆する (Fig. 4)。

トドマツ未処理材 (早材) およびパルプの吸光度と脱リグニン率との関係はFig. 5に見られるごとく，仮道管SWの吸光度の変化はブナ材に比べ非常に緩慢であり，78.0%の脱リグニン率のパルプにおいてもかなり高い吸光度を示す。またその減少の傾向はほぼ直線的である。コーナー部もまた，反応時間の経過と共に吸光度の減少は認められるが，ブナ材に比べソルボリシス反応中，ソグニンの溶出が困難である。C：W (8 ： 2) の例を除き，ほぼ直線的な減少の傾向を示す。これらの結果はブナ材とは異なり，仮道管SWからの選択的脱リグニンが認められない事を示唆した。