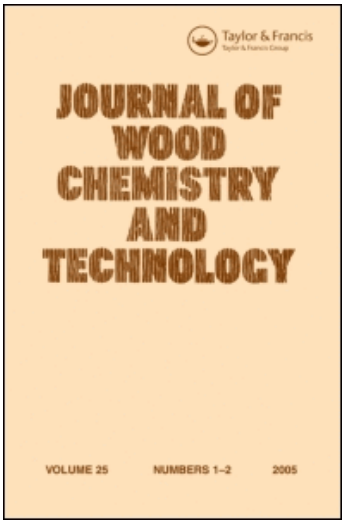

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Ultrastructure and Topochemistry of Delignification in Alkaline Pulping of Wheat Straw

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ULTRASTRUCTURE AND TOPOCHEMISTRY OF DELIGNIFICATION IN ALKALINE PULPING OF WHEAT STRAW

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ABSTRACT

This paper deals with the ultrastructure, lignin distribution and topochemistry in alkaline pulping of wheat straw. The ultrastructure of wheat straw fiber is similar to that of a wood tracheid. The lignin concentrations in various morphological regions of wheat straw are similar to the corresponding regions in birch wood fiber. But the lignin contents as a percentage of total lignin in ML and CC regions are much higher for wheat straw than for wood fibers. This study shows that there is hardly any topochemical effect during the delignification of wheat straw fiber in soda pulping process.

INTRODUCTION

Grass species are important pulping raw materials that are being used now and will be used for a long time in China. Thus, it is an important task for Chinese scientists to study and exploit grass fiber resources. Wheat straw occupies a main position in grass raw materials for papermaking in China. Previous investigations indicated that dissolution of wheat straw lignin in alkaline solutions can be obviously divided into three phases, which is different from that of wood, and that the degree of delignification required to reach the defibration point is higher for wheat straw as compared with wood[1]. In order to explain these differences, the ultrastructure, the morphological distribution and chemical structure of lignin, and the topochemistry of delignification were investigated.

EXPERIMENTAL

Purification of Wheat Straw Fibers

The wheat straw (Triticum aestivum C.V. Yang No. 4) was collected from Nanjing, Jiansu province. The wheat stems were cut into pieces of 25 mm length and ground in a Wiley mill. The fraction retained by a 40 mesh screen was softened in glycerin-alcohol. Small broken and non-fibrous cells were removed by rubbing followed by decantation. The specimen was thoroughly washed with distilled water and dried over P_2O_5 in vacuum to a constant weight.

Isolation of MWLs Rich in Secondary Wall Lignin and Middle Lamella Lignin

MWLs rich in secondary wall lignin and middle lamella lignin were isolated by grinding the wheat straw in a vibratory ball mill for different length of time according to the method of Lee et al[2] for hardwood. MWLs were purified according to Bjorkman's method.

Bromination

Brominations of wheat straw, pulps and cotton fibers were performed according to the method of Saka et al[3], but the extraction time with $CHCl_3$ was 7 days followed by extraction with absolute ethanol for 3 days. Bromination of MWLs rich in ML lignin and SW lignin was the same as that of wheat straw except that the quantity of bromine was doubled.

Preparation of the Tablet of the Brominated Samples and Analysis by SEM-EDXA

Spectroscopically pure carbon was quantitatively added to the brominated sample, ground in an agate mortar and then pressed into tablets in a hand press (Model SSP-10, Shimazu Corporation, Japan). The tablets were analyzed by the SEM-EDXA technique. Bromine L-layer (Br-L, 1.42-1.56 Kev) X-ray counts less background were measured by a 60-second surface analysis with an EDXA (Model

9100, Philips Company, Holland). The accelerating voltage was 25 KV with a SEM (Model 505, Philips Company, Holland). Other conditions were held constant throughout the entire measurement.

Analyses of the Distribution of Bromine in the Cross-section of the Cells

Digestion: Alkali charge: 29.8% on straw as NaOH;
Liquor:straw ratio 8:1;
Temperature 100°C.

Several cooks were made and the extent of lignin removal was controlled by different cooking times to achieve different degree of delignification ranging from 30-80%.

Both the ground straw specimen and the pulp specimen (1 mm * 0.5 mm * 5 mm) were brominated in chloroform inbedded in epoxy resin, and then sectioned with a glass knife mounted on a LKB Model V ultramicrotome. The transverse sections (1.0 um) were placed on a handmade carbon grid and studied by the SEM-EDXA technique after coating with carbon in a vacuum evaporator. The analytical conditions were the same as above. Br-L (1.42-1.56 Kev) X-ray counts less background were measured from different morphological regions by 120-second point analyses.

Study of Ultrastructure of Wheat Straw

Analysis of ultrastructure of wheat straw was performed according to Cote, et al[4].

RESULTS AND DISCUSSION

Ultrastructure of Wheat Straw

Just like wood tracheid, the wheat straw fiber consists of the middle lamella (ML), the primary wall (P), the outer (S_1), the middle (S_2), and the inner (S_3) layers of the secondary wall as shown in Figure 1.

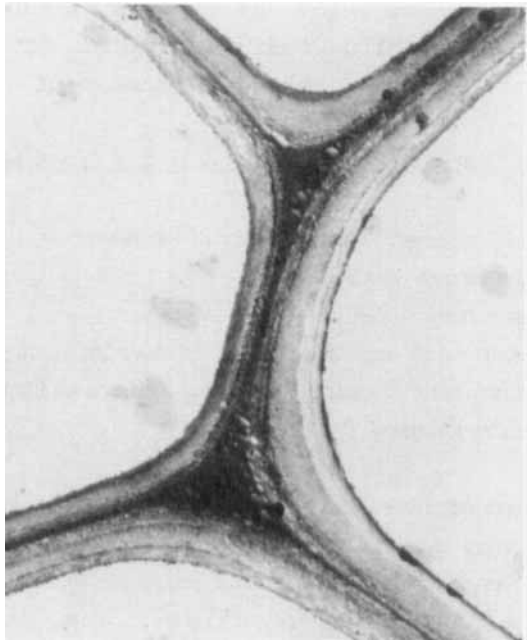

FIGURE 1 Transverse Section of Fiber
TEM x6000

TABLE 1

The Thickness and Percentage Volume Fraction (PVF) of Various Morphological layers in Wheat Straw Fiber and Spruce Cell Walls

	Wheat Straw				Spruce	
	Thick Fiber		Thin Fiber		Tracheid	
	Thickness (um)	PVF (%)	Thickness (um)	PVF (%)	Thickness (um)	PVF (%)
ML+P	0.1 -0.2	9.3	0.06-0.12	12.3	0.05-0.1	10.2*
S_1	0.1 -0.3		0.2-0.3		0.15-0.2	9.9
S_2	1.8 -2.5	83.5	0.5-0.8	80.7	0.7 -2.0	75.9
S_3	0.15-0.3		0.1-0.2		0.1	4.0
CC	---	5.4	---	7.0	---	---

* Containing the CC region

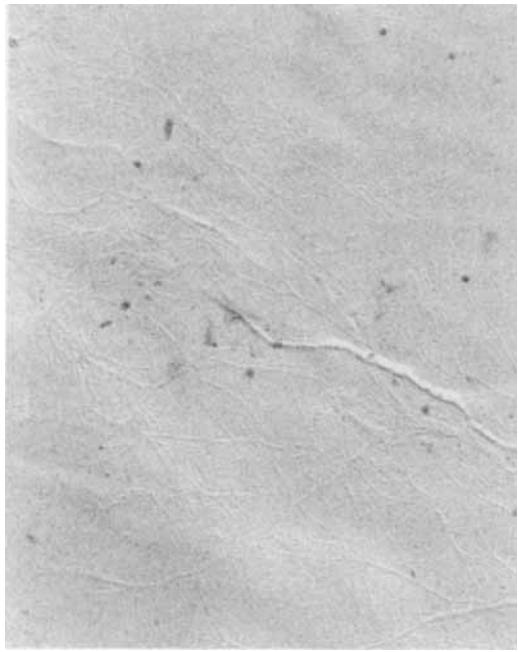

FIGURE 2 Fibrils of P Layer of Fiber Replica x10000

The thickness of various morphological layers in the wheat straw cell wall was measured under TEM at a magnification of 6000-8000 times. The results together with those obtained for spruce are given in Table 1. It is clear that the S_1 layer of the wheat straw fiber is thicker than that of the spruce tracheid and the percentage volume fraction (PVF) of the middle lamella and the cell corner in wheat straw fiber is greater than that of spruce tracheid.

The orientation of fibrils in various layers in wheat straw fiber is different. The fibrils of the primary wall (p), as shown in Figure 2, display a netlike texture. on the other hand, the

FIGURE 3 Fibrils of S_1 Layer in Fiber Replica x10000

fiber in Figure 3 shows that the fibrils are oriented helically and almost perpendicular to the fiber axis which is considered to be the S_1 layer. The fibrils with a slope of about 20-30° can be seen on the S_2 layer in Figure 4.

Since the wheat straw fiber has a thick S_1 layer in which the fibrils are oriented laterally in cross helix[1], it makes defibration of wheat straw pulp more difficult. The increase in beating degree of wheat straw pulp during beating is due mainly to the crushing of its parenchymas.

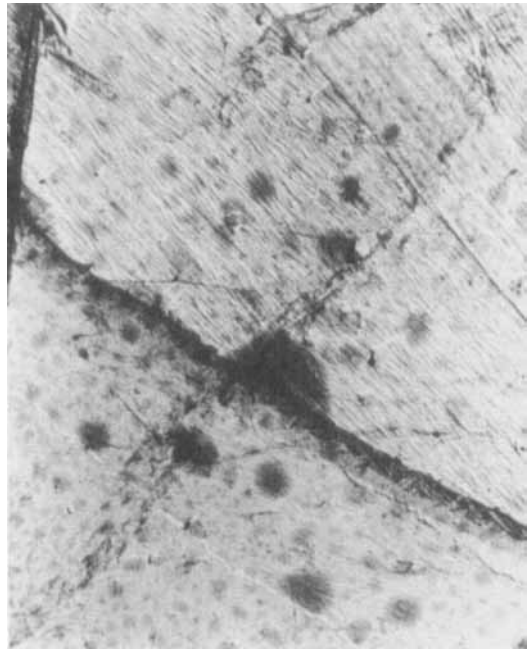

FIGURE 4 Fibrils of S_2 Layer in Fiber Replica x10000

The pits in wheat straw fiber are irregular conical chambers (Figure 5). A warty layer can be observed in Figure 5. This is the first discovery of a warty layer in non-wood raw materials.

The walls of vessels (on upper left corner of Figure 6) and parenchyma (Figure 7) also have layered structures. It is also noted that the parenchyma cell corner is empty where liquor penetrates easily. The epidermis has thicker walls and its cell wall has a layered structure (Figure 8). The pits in parenchyma are simply circular or elliptical (Figure 9). However, the pits in vessels are conical chambers (Figure 10).

FIGURE 5 Pit of Fiber Replica x30000

Microscopic Distribution of Lignin in Wheat Straw Fiber

Distribution of lignin in wheat straw fiber was studied with SEM-EDXA technique. For this purpose, two MWL fractions, one rich in compound middle lamella lignin (CML lignin) and one rich in secondary wall lignin (SW lignin) were isolated from the wheat straw fiber sample relatively free from non-fibrous cells. Previous study indicated that in hardwood, MWL initially originated mainly from the compound middle lamella whereas the contribution from secondary wall increased with increasing milling time[2]. On the other hand, Whiting and Goring[5] reported that with spruce wood, MWL was extracted mainly from the secondary wall, in contradiction to the above results for hardwood. The effects of milling time on

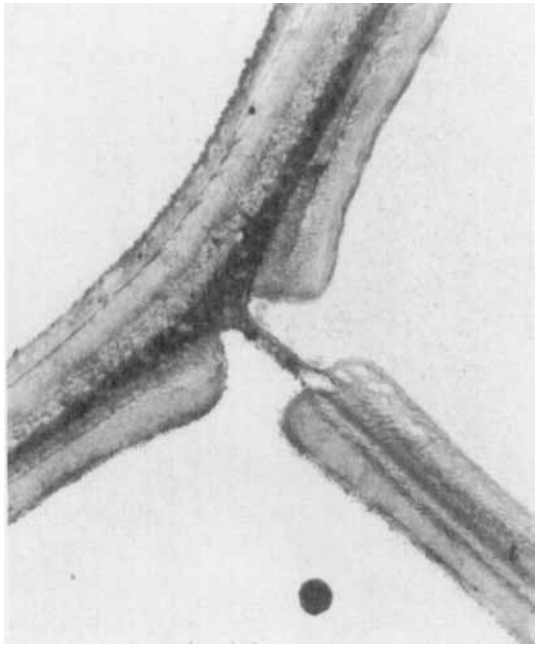

FIGURE 6 Transverse Section of Vessel
TEM x10000

lignin yield and sugar content of MWL from the wheat straw fiber are given in Table 2. As can be seen, the Klason lignin contents decreased and the total sugar contents increased with increasing milling time, suggesting that wheat straw lignin behaves similarly to hardwood lignin. Thus, MWL rich in CML lignin and MWL rich in SW lignin can be isolated by different milling times. In this study, CML lignin fraction was isolated after 18 hrs of milling whereas SW lignin fraction was isolated after 141 hrs of milling.

In order to determine the different reactivity of the two lignin fractions towards bromine, chemical analysis and SEM-EDXA technique were adopted to measure the bromine contents in the brominated products. The results are shown in Table 3.

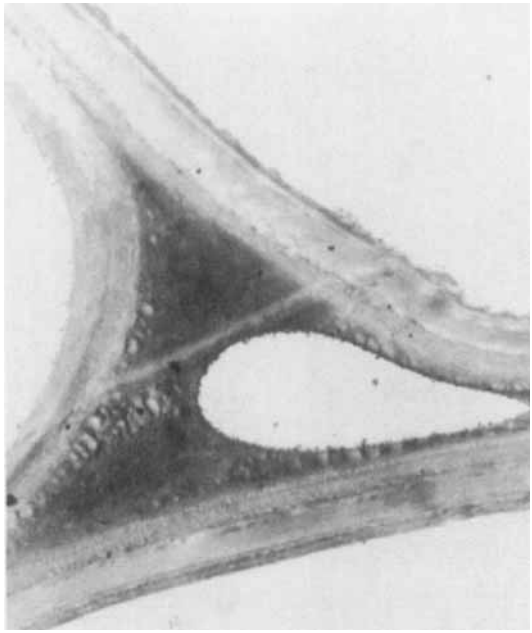

FIGURE 7 Transverse Section of Parenchyma
TEM x15000

The ratio between reactivities of the secondary wall lignin and the middle lamella lignin towards bromination was 1.84 and 2.08 using chemical analysis and the SEM-EDXA technique, respectively. These results are consistent with those of Saka et al[6] and Donaldson and Ryan[7] but are not consistent with those of Westermark[8]. Disregard the latter, the results indicated that in both wheat straw and wood, the middle lamella lignin differs from the secondary wall lignin in their reactivities towards bromination and that the method used for the separation of the two lignin fractions is appropriate.

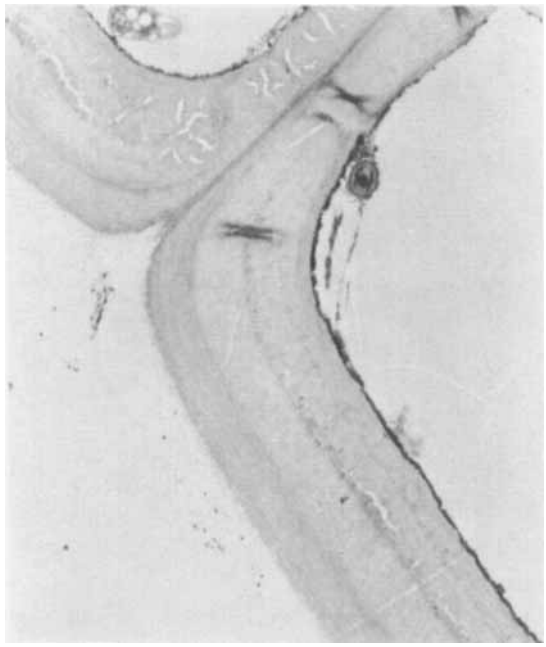

FIGURE 8 Transverse Section of Epidermis
TEM x6000

The Br-L X-ray counts of the different brominated cell determined by the SEM-EDXA technique are shown in Table 4. The following two conclusions can be drawn:

1. Just as in the case of wood, in both fiber and non-fiber cells the lignin concentration is the highest in the cell corner and the lowest in the secondary wall.
2. In the morphological regions of all cells, the lignin concentration is the highest in parenchyma cells, followed by fibers, and is the lowest in epidermis cells. The latter is probably due to the higher content of silicon in epidermis cells.

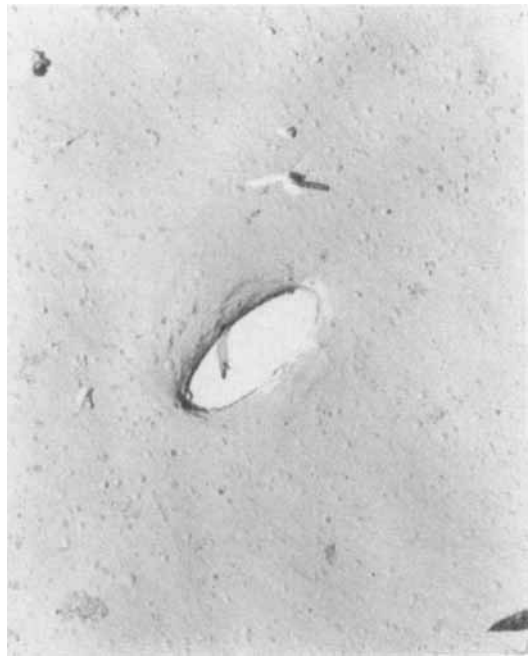

FIGURE 9 Pit of Parenchyma Replica x10000

The lignin concentrations in various morphological regions of wheat straw fibers were calculated based on the Br-L X-ray counts, the volume fractions of various regions, the total lignin content of the straw fibers and the relative reactivity of the middle lamella lignin and the secondary wall lignin towards bromination.

The results are shown in Table 5. As can be seen, lignin concentrations in various morphological regions of wheat straw are similar to those in the corresponding regions of birch fiber.

The distribution of lignin in various morphological regions of straw fiber is listed in Table 6. Because the volume fraction of

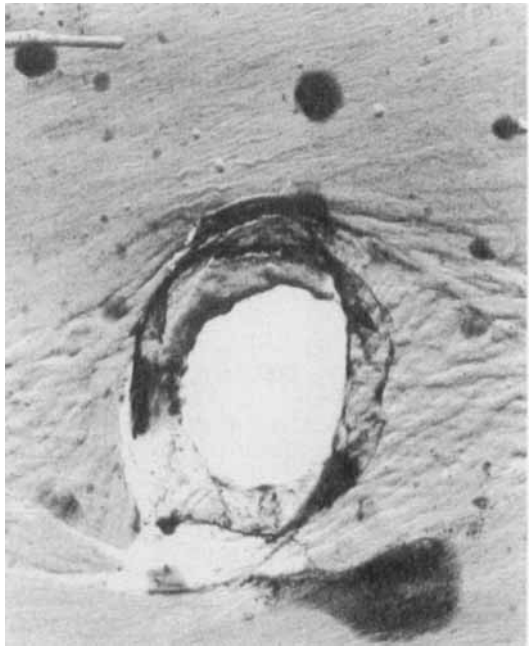

FIGURE 10 Pit of Vessel Replica x10000

TABLE 2

The Effects of Milling Time on Yield, Purity, and the Total Sugar Content of MWLs

Milling Time (hr)	18	21	56	72	141	Residue
Yield (%)*	5.7	7.0	9.3	11.6	16.3	--
Klason lignin(%)**	92.9	92.8	92.1	91.5	90.3	13.6
Total sugar(%)**	1.1	1.4	2.3	2.5	4.2	--

* On the basis of Klason lignin content in wheat straw
** On the basis of MWL

TABLE 3

Relative Reactivity of the Middle Lamella Lignin and the Secondary Wall Lignin towards Bromine

	Chemical method (gm Br/gm lignin)	SEM-EDAX (X-ray counts/gm lignin)
Straw fiber	0.394	--
SW lignin fraction	0.424	$1.62*10^6$
ML lignin fraction	0.230	$7.80*10^5$
Ratio SW/ML	1.84	2.08

TABLE 4

Br-L X-ray Counts of Different Kinds of Brominated Cells in Wheat Straw

	SW	CML	CC
Thick Wall Fiber	1620	2156	2992
Thin Wall Fiber	1340	2004	3336
Parenchyma Cell	2005	2599	--
Epidermis Cell	1022	1690	1743

TABLE 5

Lignin Concentrations in Various Morphological Regions of Straw and Wood Fibers

	Lignin Concentrations (gm lignin/gm tissue)		
	SW	ML	CC
Wheat Straw			
Thick Wall Fiber	0.168	0.412	0.571
Thin Wall Fiber	0.154	0.339	0.664
Birch Fiber[9]	0.16-0.19	0.34-0.40	0.72-0.85
Spruce Tracheid[10]			
Earlywood	0.225	0.497	0.848
Latewood	0.222	0.60	1.00

TABLE 6

Distribution of Lignin in Different Morphological Regions

		% Lignin Distribution in SW	ML	CC
Wheat Straw	Thick Wall Fiber	67.5	18.0	14.5
	Thin Wall Fiber	57.5	20.3	22.2
Birch Fiber[9]		77.5	11.3	11.2
Spruce Tracheid[10]	Earlywood	72.1	15.8	12.1
	Latewood	81.7	9.7	8.6

TABLE 7

Distribution of the Lignin during Soda Pulping of the Thick Wall Fiber

Samples	Cooking Time (min)	Lignin Concentration				Delignification (%)			
		Pulp	C_S	C_{ML}	C_{CC}	Pulp	S	ML	CC
Uncooked	0	0.218	0.168	0.412	0.571	0	0	0	0
S-1	6	0.171	0.133	0.331	0.453	31.0	30.2	29.1	30.1
S-2	15	0.124	0.096	0.227	0.326	64.3	63.9	65.3	62.3
S-3	45	0.098	0.072	0.204	0.274	72.9	74.3	70.2	71.2
S-4	110	0.073	0.059	0.131	0.165	81.3	80.6	82.2	83.8

the middle lamella and the cell corner in wheat straw fiber is larger than that in wood fiber, the percentage of total lignin in the middle lamella and the cell corner is greater for wheat straw fiber than for wood fiber. This is a characteristic of lignin distribution in wheat straw fiber.

Topochemistry of Delignification of Wheat Straw

At 100°C, the variations of lignin concentration in various morphological regions of the thick fiber with cooking time are shown in Table 7 and Figure 11.

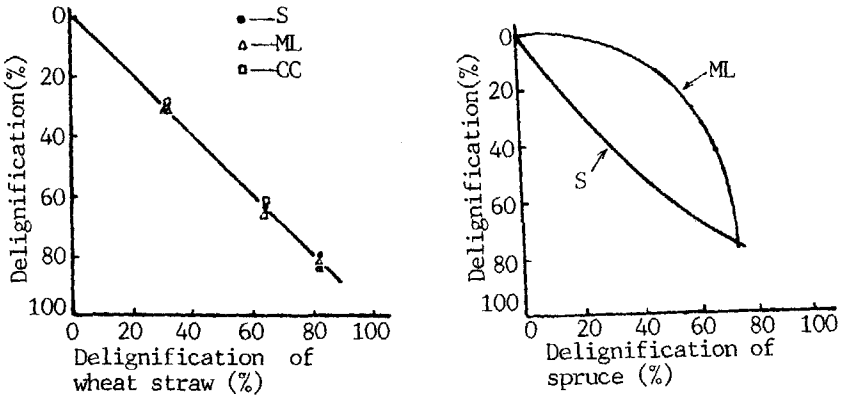

FIGURE 11 Plot of Percent Lignin Removed from the S, ML and CC of the Wheat straw or Spruce vs Percent Lignin Removed from the Wheat straw or Spruce

It is of interest to note that percent delignification values of the different morphological regions in the fiber and the whole are almost the same as shown in Table 7 and Figure 11. This indicates that there is hardly any topochemical effect in soda pulping of straw fiber. This is further demonstrated by the delignification kinetics characteristic of straw fiber as discussed below.

In Figure 12, the logarithms of lignin concentration during soda pulping are plotted versus cooking time for the three morphological regions of the straw fiber. It is obvious that all three morphological regions follow two distinct pseudo-first-order delignification phases, a rapid bulk delignification phase followed by a slower supplementary phase. The third residual phase can not be observed under the conditions used in this study. The rate constants of these two pseudo-first-order delignification phases were computed for all three regions and the results are shown in Table 8. In all three regions, there is little difference in the

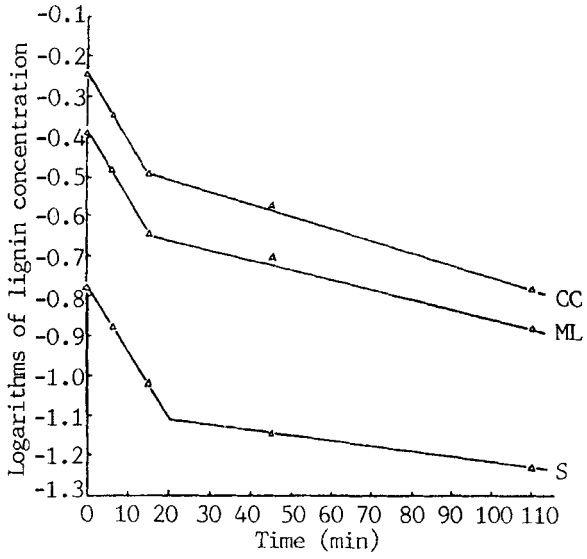

FIGURE 12 Comparison of Delignification Kinetics for Different Morphological Regions by Soda Pulping

TABLE 8

The Rate Constants (k) of the S, CML and CC Regions in Different Delignification Phases ($min.^{-1}$)

	Bulk Phase ($k*10^2$)	Supplementary Phase ($k*10^3$)
S	3.8	2.2
CML	3.8	4.7
CC	3.9	6.5

TABLE 9

The Degree of Delignification of various Fibrous Raw Materials at the Point of Fiber Liberation

Raw Materials	Pulping Methods	Delignification(%)	References
Larch	Kraft	86	13
Rice Straw	Kraft	91	13
Amur Silver Grass	Kraft	96	13
Wheat Straw	Soda-AQ	92-94	1

rate constants of bulk delignification, indicating lack of topochemical effect. The rate constants of the supplementary phase did show some differences but this should not affect the overall kinetics since the bulk delignification accounted for nearly 70% of delignification and the rate constants of the supplementary phase are much smaller than those of the bulk phase.

However, a previous study on topochemistry of delignification of spruce wood during kraft pulping showed that the secondary wall lignin is preferentially removed in the initial stage of delignification, followed by a rapid dissolution of lignin from the middle lamella regions[11]. These results were supported by a later study on kraft pulping of Douglas fir[3]. A topochemical effect was also observed in the kraft pulping of birch wood[12], but the effect is smaller than with spruce. Thus, the topochemistry of the wheat straw during soda pulping is quite different from that of softwood during kraft pulping and is more nearly like that of birch wood. The lack of topochemical effect in soda pulping of wheat straw is probably caused by three factors: (1) the structure of lignin in the middle lamella of wheat straw differs from that of softwood, (2) the tissue structure of the wheat straw is looser than that of softwood such that the penetration of liquor and

diffusion of dissolved lignin are easier, and (3) the average pore size in the secondary wall increases because of the dissolution of a large amount of hemicelluloses during the initial phase of delignification[1].

Defibration Point of Grass Fibrous Raw Materials

Previous investigations demonstrated that the delignification at the liberation point of grass fiber is higher than that of wood fiber in alkaline pulping as shown in Table 9.

Two factors may contribute to the higher degree of delignification required to reach fiber liberation point for the grass fibrous raw materials: (1) the higher percentage of lignin in the middle lamella and cell corner, and (2) the lack of topochemical effect. Therefore, the lignin concentration of ML and CC regions always maintains a level 2.2 to 3.8 times higher than that of the S region. Thus, a higher degree of delignification must be achieved before the lignin concentration in the ML and CC is low enough to reach the fiber liberation point. In order to increase the strength and the yield of pulp from grass fibrous raw materials, it is important to find new chemical pulping methods that selectively dissolve lignin in the ML and CC regions or to combine mechanical measures after chemical pulping to some extent.

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