

Characterization of Chinese Kenaf Bark Fibers for Production of Bleached Chemical Pulp

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ABSTRACT:-- Due to the shortage of forestry resources, China is actively searching for new raw fibers with good paper-making properties. In this study, the potential of Chinese kenaf bark fibers was explored. The analyses of both chemical composition and dimensional characteristics indicate that the Chinese kenaf bark fibers are good paper making raw materials. The study on ultraviolet and infrared spectroscopic behaviours of the kenaf bark lignin shows that the kenaf bark lignin contains significant fraction of syringyl units and that the frequency of ester linkages in the native kenaf lignin is much less compared to that in the wheat straw lignin. Three pulping methods namely: Kraft, Soda-AQ and low temperature Soda-AQ, were tested, we concluded that the low temperature Soda-AQ process is most suitable to cook kenaf bark fibers. The characteristics of delignification and carbohydrate dissolution during the low temperature Soda-AQ pulping of kenaf bark fibers are included. Finally, it was found that a fully bleached kenaf bark pulps with good strength properties can be produced by the low temperature Soda-AQ cooking process and a C-E-H-P bleaching sequence.

INTRODUCTION

The recent rapid growth in the Chinese economy presents a strong challenge for the Chinese Pulp and Paper Industry. Due to the lack of the wood resources, extensive efforts are underway in China to develop a new class of no-wood species for production of strong chemical pulps. Kenaf has emerged as one of these potential fibrous raw materials.

Kenaf is an annual plant which has a growth cycle of about five months and a relatively higher growth yield. It contains two distinct fiber components: bark and core respectively. Usually, the bark fibers are quite long, comparable to those from softwoods; however, the core fibers are much shorter. Due to the great difference in the fiber

characteristics between the bark and core, it was suggested that these two fiber fractions should be pulped separately and methods for the separation of bark fibers from core fibers have been developed (Kaldor, 1989). The potential of kenaf as a fiber source for paper-making has been studied in the United States (Clark et al. 1971, Young. 1987) and

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in Australia (Kaldor, 1989). A good summary paper was given by Kaldor et al, (1991), which concludes that kenaf chemical pulps are of considerable potential as one of the alternatives to wood pulps in many areas of the world. In this paper, results obtained from Chinese kenaf bark fibers as the raw material for the production of chemical pulp are reported and the ultraviolet and infrared spectroscopic behaviour of kenaf bark lignin are given. Also described are the pulping trials with three different methods: kraft, conventional Soda-AQ, and low temperature Soda-AQ.

RESULTS AND DISCUSSION

Chemical Composition

Kenaf bark fibers, which are separated from the kenaf core fraction, were obtained from Anhui paper mill in the province of Anhui in China. Their chemical composition is given in Table 1. Like other non-wood fibers, the klason lignin content is much lower than that in wood species. This indicates that pulping of kenaf bark can be achieved more easily than pulping of wood chips. The holocellulose content in kenaf bark fibers is 81.34% which is higher than that found in pulp woods. Pentosans are roughly comparable to those of the hardwood, and about double those in softwoods. The extractive content, represented by the solubility in cold water, hot water, 1% NaOH solution and alcohol-benzene mixture is rather high. Therefore, it is

expected that more alkali could be required to remove the extractives during the pulping process.

Dimensional Characteristics

The dimensional characteristics of kenaf bark fibers, such as fiber length, fiber width, cell wall thickness, are determined and shown in Table 2. These results are in agreement with those from Illinois Kenaf by Clark and Wolff (1969). Included in Table 2 are also the dimensional parameters from other fibrous materials. We can observe that the average fiber length of kenaf bark fibers is about 2.43 mm, shorter than typical softwood fibers, but much longer than typical hardwood and non-wood fibers. Compared to wheat straw fibers which are important raw materials for the pulp production in China, the fibers from kenaf bark are much thinner. In general, one can find that the dimensional characteristics of kenaf bark fibers are very close to those of wood fibers. Therefore, we conclude that kenaf bark is a versatile raw material for the Chinese Pulp and Paper Industry.

Ultraviolet and infrared spectroscopic behaviour of kenaf bark lignin

Ultraviolet absorption is a well-known method which has been widely used for lignin characterization. The UV spectra of the kenaf bark dioxane lignin was studied and comparison with other lignin samples was then made. The results are demonstrated in

Table-1

Chemical Composition of Kenaf Bark Fibers

Ash (%)	Extractives (%)				Klason lignin (%)	Pentosans (%)	Holocellulose (%)	Pectin (%)
	Alcohol benzene	Cold water	Hot water	1% NaOH				
4.13	3.23	13.31	13.36	29.7	9.34	20.33	81.34	2.60

Table-2

Dimensional Characteristics of Kenaf Bark Fibers As Compared to Other Fibrous Material

	Kenaf bark	Wheat straw	Reed	Poplar	Masson pine
Fiber Length (mm)	2.43	1.32	1.12	1.05	3.61
Fiber Width (μm)	21.2	12.9	9.7	25.3	50.0
Slenderness Ratio	115	102	115	42	72
Cell Wall Thickness (μm)	3.27	5.2	3.0	3.17	3.80
Lumen Width (μm)	10.5	2.5	3.4	12.5	33.1

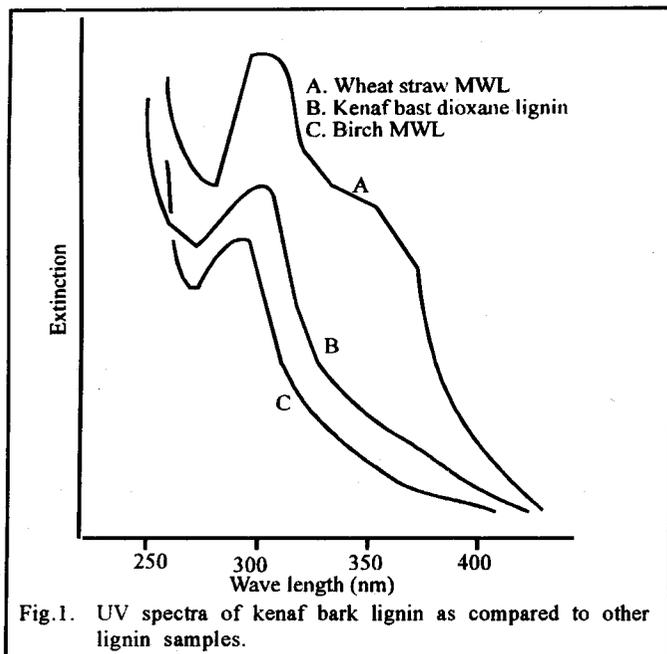


Fig.1. UV spectra of kenaf bark lignin as compared to other lignin samples.

Figure 1. The typical kenaf bark dioxane lignin comprises a maximum at a wave length of 277.4 nm, which is characteristic of hardwood lignin due to the presence of higher amounts of syringyl units. As a matter of fact, the UV spectra of kenaf bark dioxane lignin very much resembles that of Birch MWL. Comparison of UV spectra of wheat straw MWL with that of kenaf bark dioxane lignin reveals that only the former has a pronounced shoulder in the region of 315 nm, which is caused by p-coumaric and ferulic acid linked to lignin by ester bonds (Shimada et al., 1971).

Infrared spectra is another useful physical method of characterizing lignin samples. The assignments of the major absorption bands to the specific structural groups have been very well established (Fengel, Wegener, 1989). The IR spectra of kenaf bark dioxane lignin and wheat straw MWL are shown in Figure 2. The band at 1160 cm^{-1} is due to the C-O-C vibration of the ester functionality between p-coumaric acid and lignin structure. Apparently, the wheat straw MWL sample has

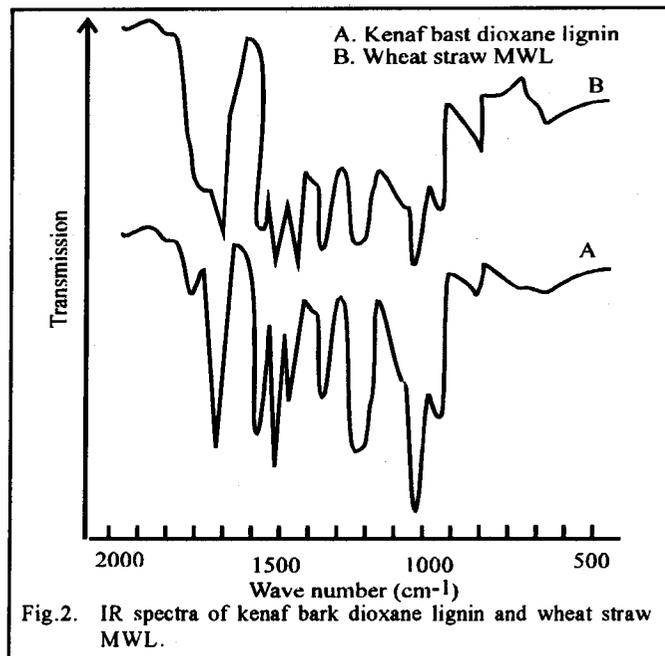


Fig.2. IR spectra of kenaf bark dioxane lignin and wheat straw MWL.

a strong absorption at 1160 cm^{-1} while the band at 1160 cm^{-1} for the kenaf bark dioxane lignin is relatively weaker, indicating that more ester linkages are present in the wheat straw lignin than in the kenaf bark lignin. This is consistent with the interpretation of the results obtained from UV spectra analysis.

The typical guaiacyl band is located at about 1275 cm^{-1} while the absorption at about 1330 cm^{-1} is due to the syringyl lignin structure. Compared to the IR spectra of the wheat straw lignin, the kenaf bark dioxane lignin has a stronger absorption at 1330 cm^{-1} , but a weaker absorption at 1275 cm^{-1} . Therefore, it can be concluded that there are more syringyl units in the kenaf bark lignin than in the wheat straw lignin.

Pulping of Kenaf Bark Fibers

Three processes; Kraft, Soda-AQ and low temperature Soda-AQ were tested. The cooking conditions are shown in Table 3. The liquor-to-wood ratio was 5 in all the runs.

Table-3

Conditions of Pulping Kenaf Bark Fibers

	Kraft Process	Soda-AQ	LT Soda-AQ
Active Alkali ^a (%)	14, 16, 18	14, 16, 18	14, 16, 18
Sulfidity ^a (%)	20	---	---
Temperature. (°C)	165	165	150
Time at Temperature. (hr)	1,2	1,2	2,3
AQ (%)	---	0.1	0.1

^a calculated as Na_2O , on oven dried material

Table-4

Pulping Characteristics of Kenaf Bark Fibers

	Active Alkali (% Na ₂ O)	Time at Temperature (hr)	Residual Alkali (g/l)	Pulp Yield (%)	Kappa Number
Kraft	14	1	1.22	53.8	---
	14	2	0.73	51.5	---
	16	1	2.43	51.2	33.5
	16	2	1.82	50.3	31.4
	18	1	3.89	50.1	22.7
	18	2	3.40	49.0	23.9
Soda-AQ	14	1	2.19	52.9	28.6
	14	2	1.46	51.4	29.7
	16	1	4.50	50.3	18.9
	16	2	3.46	49.7	19.0
	18	1	7.17	49.5	18.6
	18	2	5.65	48.7	17.9
LT Soda-AQ	14	2	3.11	57.4	---
	14	3	2.85	56.9	---
	16	2	5.18	56.3	27.2
	16	3	5.54	5.55	24.5
	18	2	9.02	53.9	23.4
	18	3	8.75	52.4	22.2

The pulping results are summarized in Table 4. One can find that kenaf bark fibers were well pulped by all the three processes tested, as indicated by the kappa number of the pulps. However, at the same active alkali charge, the delignification degree in kraft process is less than that in Soda-AQ process. In addition, since kraft process results in the formation of malodorous volatile compounds, we prefer Soda-AQ process to kraft process for cooking kenaf bark fibers. Comparison of the Soda-AQ method with the low temperature Soda-AQ method shows that at the same alkali charge the latter process leads to a higher residual alkali. This might be due to the fact that less carbohydrates are dissolved at a lower temperature, so that less alkali is consumed to neutralize the carboxylic acids from hemicellulose. This argument is supported by the higher pulp yields obtained from the low temperature Soda-AQ process as compared to those from the Soda-AQ. The kappa number after low temperature Soda-AQ process is about 4-5 units higher at the same active alkali charge, equivalent to about 0.7 to 0.8% higher in pulp yield due to the higher lignin content when a factor of 0.15 was considered to convert the kappa number to lignin content. However, the pulp yield of the low temperature Soda-AQ process is 3.7 to 5.5% higher than that of the Soda-AQ process. Therefore, we can conclude that the higher pulp yield in the low temperature Soda-AQ process is mainly due to the fact that more carbohydrates remain compared to the Soda-AQ process.

This is consistent with the result that a higher alkali residue is observed in the low temperature Soda-AQ process. The time at temperature of the low temperature Soda-AQ process is about 1 hour longer in order to achieve the same delignification degree. However, the obvious advantage of the low temperature Soda-AQ process over the Soda-AQ process is that the pulp yield is significantly increased.

Another observation from Table 4. is that a 16% charge of active alkali is suitable for the low temperature Soda-AQ process. Further increase in alkali charge is insignificant.

The dissolution of carbohydrates and lignin during the low temperature Soda-AQ cooking is further studied. Figure 3 shows the total lignin and

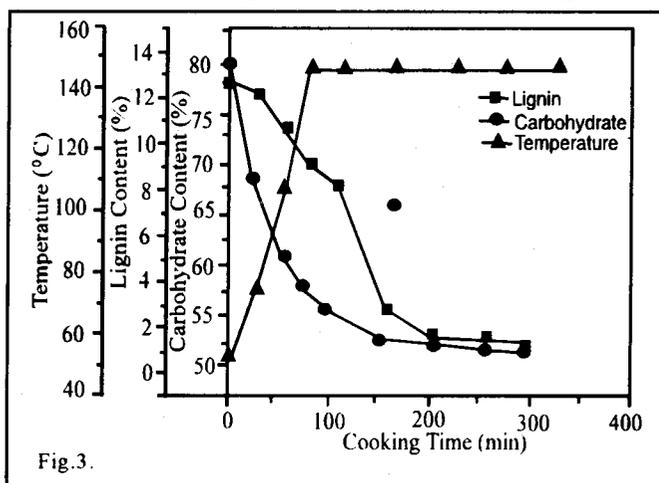


Fig.3.

carbohydrate contents of the kenaf bark pulp versus cooking time. The carbohydrates are dissolved already at a relatively lower temperature. This may be explained by the higher hemicellulose content in kenaf bark fibers as illustrated in Table 1. After 2 hours of cooking, the carbohydrate dissolution slows down significantly.

The profile of lignin dissolution is very typical, which can usually be divided into three phases: initial delignification, bulk delignification and residual delignification. The initial phase of delignification takes place already during the heating-up period. Further increase in temperature leads an acceleration in delignification rate. The rate of lignin dissolution remains high during this "bulk delignification" phase, until about 85% of the total lignin has been removed. Subsequently, the delignification rate decreases significantly and enters the so-called "residual delignification" phase.

The relative rate of delignification to carbohydrate dissolution can be estimated from the slopes of the delignification curve and carbohydrate dissolution curve shown in Figure 3. In the initial phase, the rate of carbohydrate dissolution is faster than that of delignification. At 105°C, 20.33% of carbohydrate had already been dissolved while only 2.31% of the total lignin was removed. In the "bulk delignification phase, delignification rate surpasses that of the carbohydrate dissolution. The majority of the delignification is achieved during this period of the reaction. In the third phase, the delignification rate is almost the same as that of carbohydrate dissolution, suggesting that the pulping process is not selective anymore. Therefore, we suggest that cooking should be terminated after about 3 hours when kenaf bark fibers are pulped in a low temperature Soda-AQ process.

The development of the ratio of guaiacyl unit to syringyl unit (G/S) of the lignin structures during the course of cooking was estimated from ¹H-NMR in accordance with the method developed by Lenz (1968), and was shown in Figure 4. The initial G/S ratio of the native lignin present in the kenaf bark fibers is 0.41. At a delignification degree of 26.8%, the G/S ratio of the residual lignin was decreased to 0.29. This indicates that the guaiacyl units are more easily removed than their syringyl counterparts during this period of the reaction. The above conclusion is supported by the much higher G/S ratio

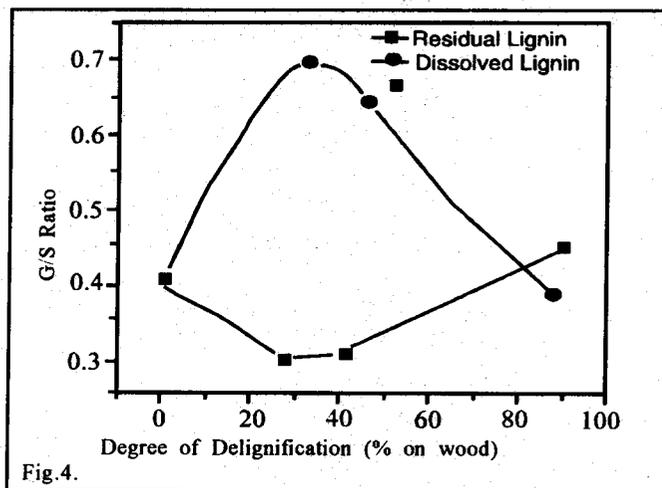


Fig.4.

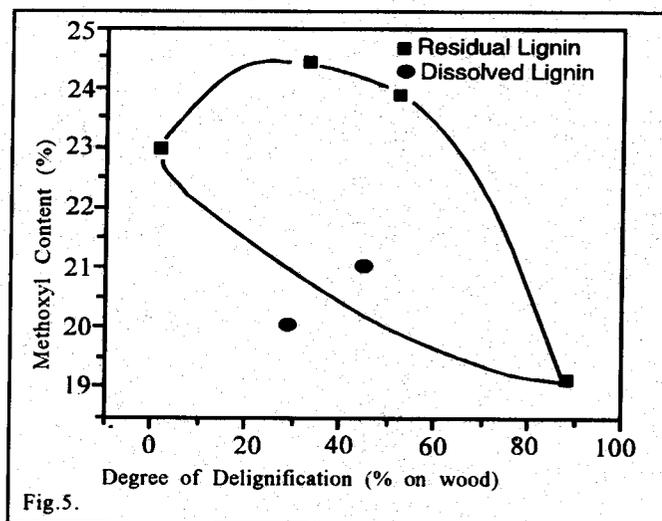


Fig.5.

in the dissolved lignin obtained at the same time, as shown in Figure 4. Further increase in the delignification degree to 37.9% leads to a G/S ratio in the residual lignin of 0.30. However, towards the end of the cooking at a delignification degree of 90.3%, the G/S ratio in the residual lignin of the kenaf pulp was found to increase to 0.44 while the G/S ratio of the dissolved lignin was decreased to 0.39. This suggests that the dissolution rate of syringyl structures is faster than that of guaiacyl structures during this period. Therefore, the characteristics of delignification during low temperature Soda-AQ pulping of kenaf bark fibers can be described by an initial period where the dissolution of guaiacyl lignin structures is faster than that of their syringyl counterparts and a second phase where the opposite is true. The G/S ratio of the residual lignin in the kenaf bark pulp at an approximately 90% delignification degree is almost the same as that of the original kenaf lignin.

The change in lignin structure during low temperature Soda-AQ cooking of kenaf bark fibers is further investigated by the methoxyl content analysis. Included in Figure 5 are the methoxyl contents in the residual lignin as well as in the dissolved lignin as a function of the degree of delignification. The results show that methoxyl content of the residual lignin is increased compared to that in the native kenaf lignin during the initial phase of the delignification. This is consistent with the conclusion that in this period the delignification rate of guaiacyl structures is faster than that of syringyl structures.

Towards the end of the low temperature Soda-AQ cooking when the degree of delignification reaches 90.3%, the methoxyl content of the residual lignin was decreased to 19.20%. This is in agreement with the earlier results that as the cooking enters the final stage. Dissolution of syringyl lignin units become faster than that of guaiacyl lignin units.

Taking into account the bleaching technology presently available in China, we bleached a 27.2 kappa number kenaf bark pulp by a C-E-H-P sequence with a total active chlorine charge of 3.8% and a hydrogen peroxide charge of 0.5%. The final brightness of the bleached pulp is 85.2%. The related strength properties are listed in Table 5. One can observe that the tensile breaking length and the burst index of the bleached kenaf bark pulps are very much similar to those of typical bleached hardwood kraft pulps. The tear index of the kenaf bark pulps is very high due to the long kenaf bark fibers, as shown in Table 2. Therefore, it can be concluded that kenaf bark fibers are good raw materials for the production of chemical pulps with strength properties similar to those of hardwood kraft pulps.

Table-5

The Strength Properties of Bleached Kenaf Bark Soda-AQ pulp at 500 ml CSF

Degree of polymerization	1930
Tensile breaking length (km)	6.8
Burst index (kPa.m ² /g)	4.14
Tear index (mN.m ² /g)	33.9

CONCLUSION

Analysis of the chemical composition of the

Chinese kenaf bark fibers shows that the klason lignin content is 9.34%, which is substantially lower than that of typical wood fibers. The extractive content, represented by the solubility in cold water, hot water, 1% NaOH solution and alcohol-benzene mixture, however, is higher than that in wood fibers. Study on the dimensional characteristics indicated that the Chinese kenaf bark fibers are very close to the typical wood fibers. The ultraviolet and infrared spectra reveals that the kenaf bark lignin contains significant fraction of syringyl units and that the frequency of ester linkages in the native kenaf lignin is much less compared to the wheat straw lignin.

Among the three pulping methods tested; Kraft, Soda-AQ, and low temperature Sold-AQ, we concluded that the low temperature Soda-AQ process is most suitable to cook kenaf bark fibers. The delignification characteristics during low temperature Soda-AQ cooking of kenaf bark fibers was further studied. The results showed that the relative removal rate of the syringyl and guaiacyl lignin structures is different at different cooking stages. During the initial period, the dissolution rate of guaiacyl units is faster than that of syringyl units, which leads to a decreased G/S ratio in the pulp residual lignin and an increased G/S ratio of the dissolved lignin compared to the G/S ratio of the native lignin in the raw material. In the late stage of delignification, on the other hand, the lignin removal rate of syringyl structures is higher than that of guaiacyl counterparts. As a result, the G/S ratio of the residual lignin in the kenaf bark pulp (at approximately 85% delignification degree) is almost the same as that of the original lignin in the kenaf bark fibers.

Finally, a 27.2 kappa number kenaf bark pulp obtained from a low temperature Soda-AQ process with an active alkali charge of 16%, temperature of 150°C and time at temperature of 2 hours was bleached by a C-E-H-P sequence with a total active chlorine charge of 3.8% and a hydrogen peroxide charge of 0.5%, a fully bleached pulp was produced, its strength properties are at least comparable to those of hardwood kraft pulps.

EXPERIMENTAL

The Kenaf bark used in this study were supplied by the Anhui Paper Mill in Anhui province,

China. Procedures for chemical analyses were followed according to Tappi standard methods, and to other recognized sources as indicated. All Compositional data were calculated to an oven-dry basis.

Pulping of kenaf bark fibers was performed in a rotating digester which is heated electrically under specified conditions. The crude pulp thus obtained was washed with water in a screen-bottomed basket. The washed pulp was then dewatered in a laundry-type centrifuge and stored in a refrigerator for further processing.

Bleaching experiments were conducted by the C-E-H-D sequence. The conditions are detailed in Table 6. The pulp sample was thoroughly washed after each stage with distilled water. Prior to the handsheet making, the bleached kenaf pulp was processed in a valley heater. The brightness and the strength properties were determined in accordance with the Tappi standard methods.

Table-6

Conditions for Bleaching Kenaf Pulps

Treatment	Chemical Charge (%)	Time (min)	Temperature (°C)	Consistency (%)
Chlorination	3.0	45	45	2
Extraction	1.5	90	70	10
Hypochlorite	0.8	90	38	5
Hydrogen Peroxide	0.5	120	70	10

The kenaf dioxane lignin sample was obtained following the method of Browning (1967). The kenaf bark sample was first extracted with ethanol-benzene and thoroughly dried in a desiccator. The extracted sample was then heated with acidic dioxane-water mixture under the specified conditions. Subsequently the acidic extract was concentrated, and the lignin was separated by centrifugation and decantation, washed thoroughly and dried in a

vacuum desiccator over phosphoric anhydride.

For the determination of UV spectra, the lignin sample was dissolved in methyl cellulose and diluted with 95% ethanol. The IR spectra were analyzed using Shimadzu IR-440 spectrophotometer.

The ¹H NMR study was performed in a JEOL FX90 NMR spectrometer. The lignin samples were analyzed in deuteriochloroform (DCCl₃). Tetramethylsilane (TMS) was used as internal standard.

The methoxy group contents in the pulp samples were measured according to Tappi T209.

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