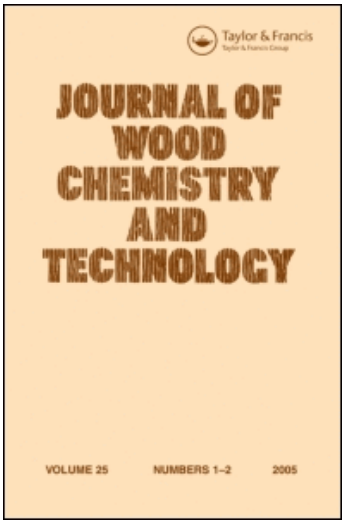

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Lignin Fragmentation and Condensation Reactions in Middle Lamella and Secondary Wall Regions during Kraft Pulping of Douglas-Fir

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To cite this Article Chiang, Vincent L. , Stokke, Douglas D. and Funaoka, Masamitsu(1989) 'Lignin Fragmentation and Condensation Reactions in Middle Lamella and Secondary Wall Regions during Kraft Pulping of Douglas-Fir', Journal of Wood Chemistry and Technology, 9: 1, 61 — 83
To link to this Article: DOI: 10.1080/02773818908050286
URL: http://dx.doi.org/10.1080/02773818908050286

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 9(1), 61-83 (1989)

LIGNIN FRAGMENTATION AND CONDENSATION REACTIONS IN MIDDLE LAMELLA AND SECONDARY WALL REGIONS DURING KRAFT PULPING OF DOUGLAS-FIR

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ABSTRACT

Kraft pulping of Douglas-fir (*Pseudotsuga menziesii*) was carried out from 90°C to a final temperature of 170°C at a heating rate of 1°C/min. At various stages of delignification, middle lamella and secondary wall enriched fractions were isolated from pulps and analyzed by nucleus exchange and alkaline nitrobenzene oxidation reactions to reveal the dissolution and condensation of lignin building units in these two morphological regions. For non-delignified Douglas-fir, the ratio of condensed/non-condensed phenyl nuclei varied significantly between middle lamella and secondary wall lignins. Values of 2.5/1 and 1/1 were found for middle lamella and secondary wall lignins, respectively. At early stages of pulping (below 110°C), the removal of phenyl nuclei in secondary wall lignin was due entirely to the dissolution of non-condensed phenyl nuclei. After the temperature reached 160°C, a rapid formation of diphenylmethane moieties in middle lamella was observed, whereas the formation of such moieties in secondary wall occurred after the peak pulping temperature (170°C) was reached.

INTRODUCTION

Microscopy studies on the topochemistry of kraft delignification indicated that secondary wall (SW) lignin is preferentially removed in the initial stages of delignification, followed by a rapid dissolution of lignin from the middle lamella (ML) region.[1,2] However, these studies could only demonstrate the dissolution patterns of total phenyl nuclei (non-

condensed and condensed types) in different morphological regions. Although it has never been demonstrated, it is conceivable that the proportions and types of non-condensed and condensed phenyl nuclei in SW and ML are different. Consequently, the dissolution of non-condensed and condensed phenyl nuclei and the formation of secondarily formed condensation subunits from non-condensed units should proceed differently in these two regions. Unfortunately, these cannot be demonstrated using current microscopy techniques. Alternatively, this can be done by characterizing the SW and ML enriched fractions isolated from pulps at various stages of pulping.

Fractionation of SW and ML tissues from softwood can be achieved based on the difference in densities between lignin and carbohydrate materials provided that the compression wood is relatively absent. This has been done and described in very great detail by both Whiting *et al.*[3] and Sorvari *et al.*[4] The current study modifies their procedures for preparation of starting material and the separation mechanism in order to obtain sufficient amounts of SW and ML fractions for chemical characterization. SW and ML lignins are characterized by a method combining nucleus exchange [5-16] and alkaline nitrobenzene oxidation. This method is able to determine the quantities of non-condensed (type A, in Figure 1), condensed (type B) and secondarily formed diphenylmethane type (types A' and B') phenyl nuclei in residual lignins[16-27]. This study uses this method to illustrate the different responses between SW and ML lignins of Douglas-fir towards the dissolution and condensation reactions in kraft pulping.

THEORY

DPM: Diphenylmethane

NEP: Nucleus Exchange Reaction Products

NOP: Nitrobenzene Oxidation Products

Phenyl nuclei in softwood protolignin are classified into non-condensed (type A) and condensed (type B) guaiacyl units (Figure 1). Guaiacyl nuclei in residual lignins are divided into non-condensed (type A), those (types A' and B') associated with DPM moieties[25-27,29-32] and other types of condensed (type B) units (Figure 1).

The quantities of phenyl nuclei having A, B, A', and B' types of structural units in residual softwood lignins can be obtained from the yields of their monomeric derivatives,[16-27] guaiacol + catechol (NEP), after direct degrading of pulps by nucleus exchange reaction, and, vanillin + vanillic acid (NOP), after nitrobenzene oxidation (Figure 2). The nucleus exchange

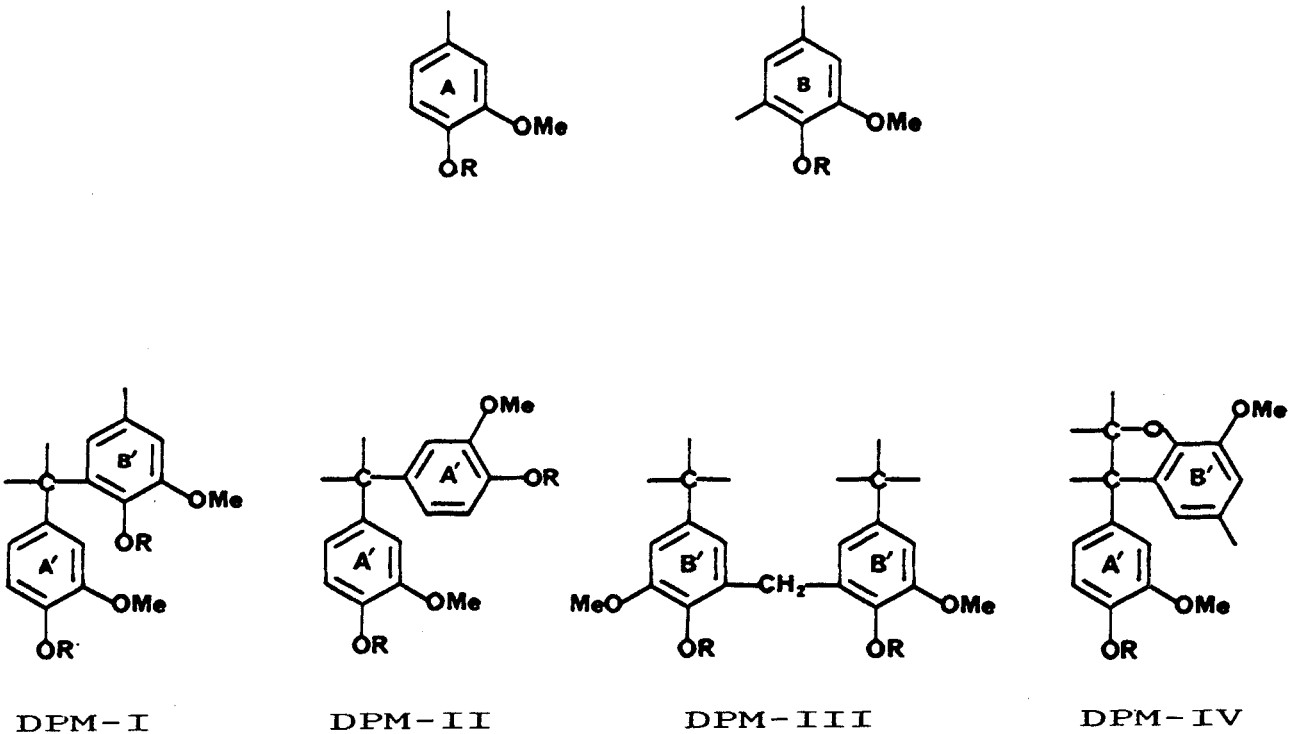

FIGURE 1. Types of phenyl nuclei in proto- and residual lignins.

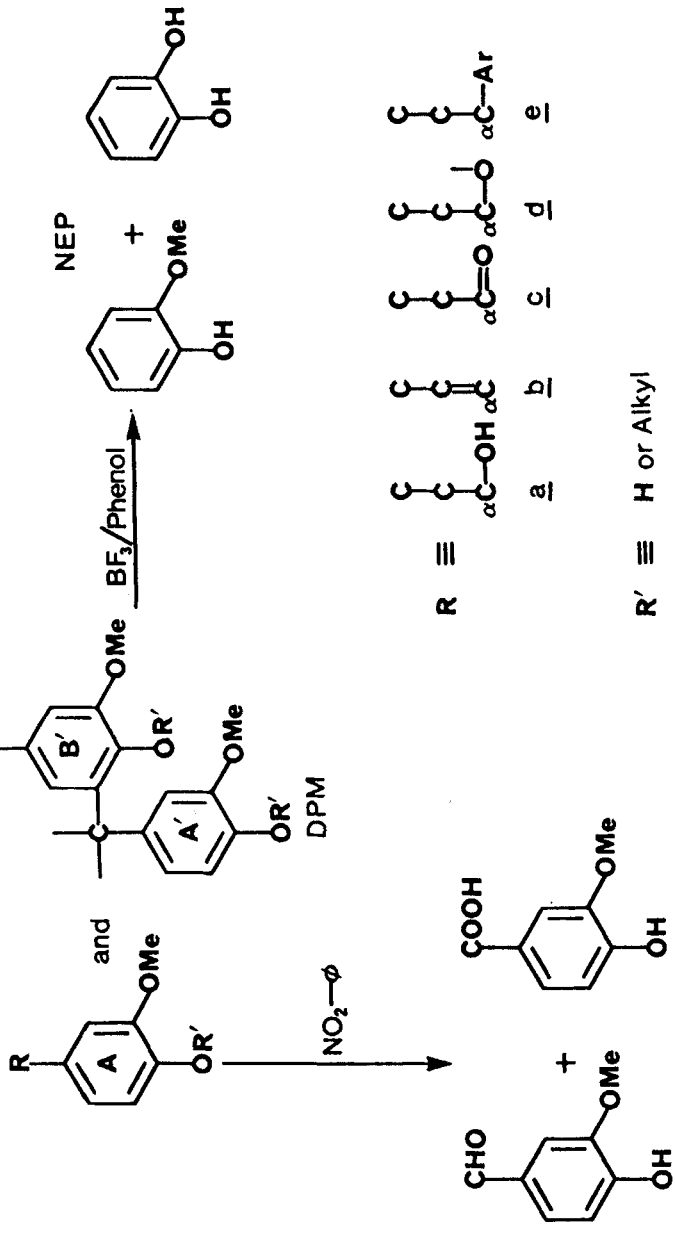

FIGURE 2. Reaction products from various lignin structural units after nucleus exchange (NEP) and nitrobenzene oxidation (NOP) reactions.

reaction is a combination of alkylation and dealkylation reactions in the presence of boron trifluoride and excess phenol. This reaction converts quantitatively the non-condensed phenyl nuclei (type A) with the side-chain structures of a, b, c, d, and e and the phenyl nuclei (types A'and B') that have the same side-chain structures and are associated with diphenylmethane moieties into guaiacol which is partially demethylated to catechol according to the reaction temperature (Figure 2). Thus the sum of guaiacol and catechol (NEP, mol%) represents the quantity of non-condensed phenyl nuclei in non-delignified wood or the quantities of non-condensed and diphenylmethane type condensed phenyl nuclei in delignified wood. Consequently, by subtracting the non-condensed phenyl nuclei in delignified wood sample from the yield of NEP, the quantity of diphenylmethane type condensed phenyl nuclei (types A' and B') can be obtained. The quantity of non-condensed phenyl nuclei (type A) in delignified wood can be calculated from the yield of vanillin+vanillic acid (NOP, mol%) after alkaline nitrobenzene oxidation of the delignified wood sample. The mechanism of this reaction was described by the original authors, Funaoka and Abe[16], in detail in a recent review article. The quantitation of each type of phenyl nuclei in residual pulp lignins was elucidated at length in three previous publications.[25-27]

EXPERIMENTAL

Kraft Delignification

Douglas-fir (*Pseudotsuga menziesii*) chips were delignified with a liquor-to-wood ratio of 5 and sulfidity and effective alkali of 25 and 17% (as Na_2O), respectively. The pulping schedule was the same as described by Chiang *et al.*[33]

Microscopy Examination of Douglas-fir Wood Sections

In order to assess for the presence or absence of compression wood, a random sample of chips was taken for observation with light microscopy. Chips were soaked in distilled water at 65°C and thin cross-sections were cut with a hand-held razor blade. Sections were placed in water on microscope slides and coverslipped. Sections were observed at 100 and 400X magnification using reflected light with a Nikon Optiphot microscope. Excitation at 495 or 365 nm was used to permit the visualization of helical cavities present in compression wood. Visual assessment of the tracheid morphology was used to categorize compression wood development as either absent or present. Further categorization into degrees of compression wood development were not deemed necessary for the purposes of this study. One area in

both earlywood and latewood was photographed for each section with Kodak Technical Pan 2415 black-and-white negative film. A total of forty chips were observed, photographed, and categorized.

Isolation of Secondary Wall (SW) and Middle Lamella (ML) Enriched Fractions

The isolation procedure is schematically presented in Figure 3. Air-dried wood chips or pulps were ground to pass 80 mesh. The wood meal was extracted with ethanol-benzene (1:2) for 48 hours and dried over P_2O_5 for 5 days. About 5 g thus prepared wood meal was milled for 2 days in a porcelain jar (0.5 gal in volume) half-filled with two different sizes of stainless steel balls (1/4" and 1/16" dia., weight ratio = 1:1). The dry wood meal was screened with 20 μm stainless-steel sieve. The fraction that passed 20 μm was collected and the rejects were re-ground for one more day and screened using the same method described above. The fractions that passed 20 μm were combined and stored under vacuum until use. In this way, over 50% of the starting wood meal can be reduced to less than 20μm in particle size, whereas only about 30% yield was obtained by Whiting *et al.*[3] and Sorvari *et al.*[4]

About 1 g of the dry wood meal (< 20μm) was suspended in 50 ml of a mixture (A) of *p*-xylene and carbon tetrachloride in a 100 ml Erlenmeyer flask. The density of this mixture (A) ranged from 1.435 to 1.460 g/ml depending upon the pulp samples used. The suspension was well mixed in the capped flask with gentle stirring in an ultrasonic bath for 5 minutes. After the suspension was brought back to room temperature, the suspension was transferred into a glass centrifuge tube and centrifuged in a ultracentrifuge apparatus (Sorvall RC-2B) at room temperature for 10 min. at a speed of 10,000 rpm. The floating fraction, or the ML enriched fraction, was carefully collected, dried and stored under vacuum over P_2O_5 until use. The sinking fraction, still a mixture of ML and SW, was completely dried under vacuum over P_2O_5. This dry wood meal was re-suspended in 50 ml of a mixture (B) of *p*-xylene and carbon tetrachloride in a 100 ml Erlenmeyer flask. The density of the mixture (B) ranged from 1.455 to 1.472 g/ml. From here, the same procedures for mixing and centrifugation as mentioned above were used. After centrifugation, only the sinking fraction, or the SW enriched fraction, was collected by decantation and dried and stored under vacuum over P_2O_5 until use.

Acetyl Bromide Lignin Content

The lignin contents of SW and ML enriched fractions were determined as acetyl bromide lignin contents according to Chiang and Funaoka.[25]

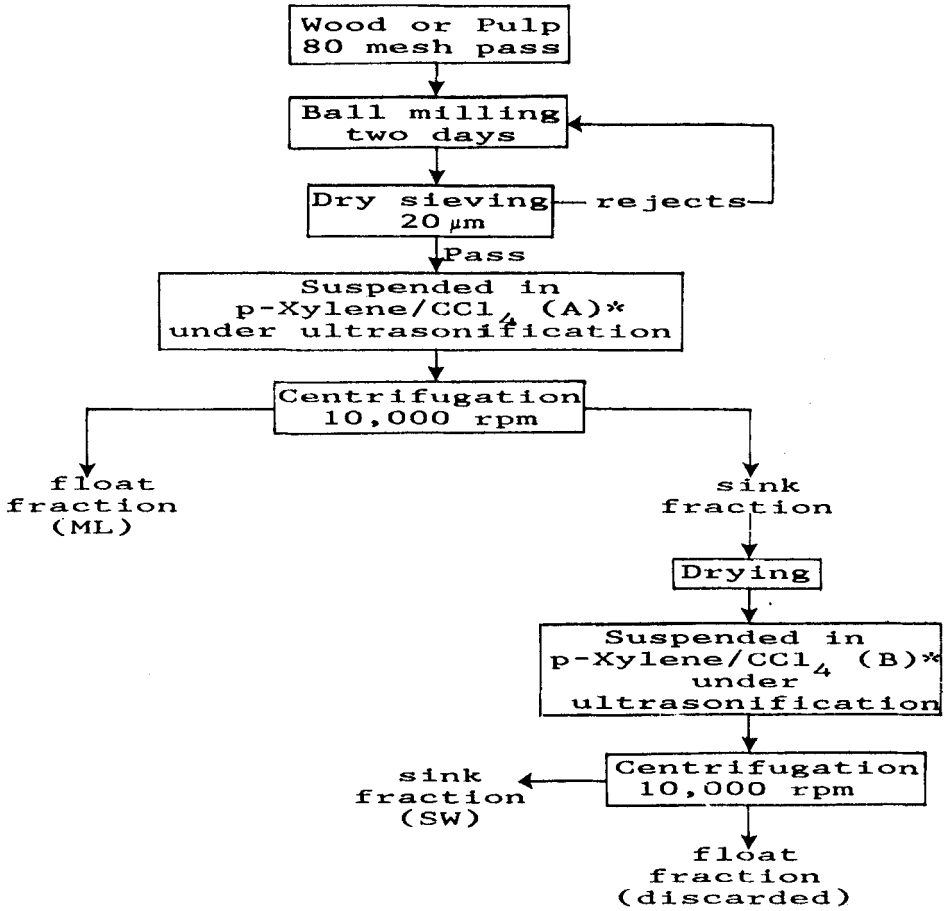

FIGURE 3. Scheme for fractionation of SW and ML.

Nucleus Exchange and Alkaline Nitrobenzene Oxidation Reactions

These were done according to the procedures described in a previous publication.[25]

Microscopy of Isolated Fractions

Samples of the isolated cell wall fractions were examined microscopically. Dry samples were observed with both bright field transmitted light and polarized transmitted light with a Nikon Optiphot microscope. Photographs were taken with the Technical Pan film. For scanning electron microscopy, air-dried particles were placed on a piece of double-stick adhesive tape which was mounted on an aluminium sample stub. The samples were then coated with carbon in a vacuum evaporator and observed with a JEOL JSM-35C scanning electron microscope at 15 KV accelerating voltage. Images were recorded on Polaroid Type 55 positive/negative black-and-white film.

RESULTS AND DISCUSSION

Chemical and Microscopic Characterization of SW and ML from Wood and Pulps

Pulping of Douglas-fir was carried out from a temperature of 90°C to a final temperature of 170°C at a heating rate of 1°C/min. Pulp samples obtained at various stages of delignification were selected for fractionating into ML and SW enriched fractions. Since the extent of delignification and carbohydrate removal varied at various stages of pulping, it was expected that the optimal density of the solution (*p*-xylene+carbon tetrachloride) for fractionation should also vary and increase with increasing extent of delignification. Table 1 shows the proper densities of the fractionation solutions and the lignin contents of SW and ML enriched fractions from selected pulp samples and the fractionation yields. The fractionation of SW and ML from pulps with low lignin content failed to provide enough material for analysis.

When the non-delignified Douglas-fir and its SW and ML enriched fractions were analyzed for their lignin contents and degree of condensation using acetyl bromide method and nucleus exchange reaction, respectively, it was found that the lignin content and the nature of the linkages in lignin of whole wood represented closely those of SW lignin but differed significantly from ML lignin (Table 2). The ratio of condensed guaiacyl units/non-condensed guaiacyl units was about 1:1 for both whole wood and SW, whereas a ratio of 2.45:1 was found for ML lignin. This suggests that the frequencies of β-5, 5-5, and 4-O-5 types of linkages are

TABLE 1

Data on Fractionation of SW and ML from Douglas-fir Wood and Pulps

	Middle Lamella			Secondary Wall			Whole Wood
Sample	Density of p-xylene/CCl_4	AcBr lignin %	Yield %	Density of p-xylene/CCl_4	AcBr lignin %	Yield %	Lignin %
Original	1.435 float	46.2	0.76	1.455 sink	25.9	9.54	29.8
110 C	1.446 float	39.4	0.68	1.458 sink	26.9	12.63	30.6
140 C	1.448 float	39.1	0.85	1.460 sink	27.1	13.81	30.3
150 C	1.449 float	38.8	0.56	1.462 sink	26.8	10.47	29.7
160 C	1.450 float	36.8	0.50	1.466 sink	24.7	15.01	27.1
170 C	1.456 float	28.9	0.17	1.471 sink	19.9	18.85	22.8
170 C 30 min.	1.460 float	15.0	0.13	1.472 sink	11.1	20.09	12.2

TABLE 2

Characteristics of Douglas-fir Lignin

	Whole Wood	Secondary Wall	Middle lamella
Lignin content	29.8 (% on wood)	25.9 (% on SW)	46.2 (% on ML)
Condensed / Non-condensed	50/50	48/52	71/29

significantly higher in ML lignin than in SW lignin. This would also indicate that the polymerization of lignin in ML region is mainly of "bulk type" polymerization, generating highly condensed lignin macromolecule. Qualitatively, this has also been demonstrated by Meshitsuka and Nakano[34]. As expected, the lignin concentration of ML fraction was much higher than that of SW fraction. Values of ML lignin content ranging from 55~60% have been reported for spruce wood by Whiting *et al.*[3] These high values were believed to be caused by the involvement of compression wood.[35] In the present study, in addition to the lower value of 46.2% (Table 1) for Douglas-fir ML fraction as compared to the values of 55~60%, the relative absence of compression wood in our case was demonstrated by optical microscopy. Of the chips microscopically examined for compression wood characteristics, over 85% were free of compression wood. Normal wood structure (i.e., wood categorized as "compression wood free") is shown in Figures 4a and 4b. Fifteen percent of the chips examined contained compression wood; an example of the most severe case encountered is shown in Figure 4c. Although there exists the possibility that small amounts of compression wood could have been present in the fractionated wall samples in the present study, examination of the lignin content values does not reveal abnormally high results, as would be expected for compression wood.

Micrographs of the isolated middle lamella and secondary wall fractions from non-delignified wood are shown in Figures 5 and 6. The scanning electron micrographs (Figure 5) reveal that the size and morphology of the particles is similar for both fractions, with particles ranging from approximately 3 X 3 μm to 15 X 15 μm. Fibrillar striations are not apparent on

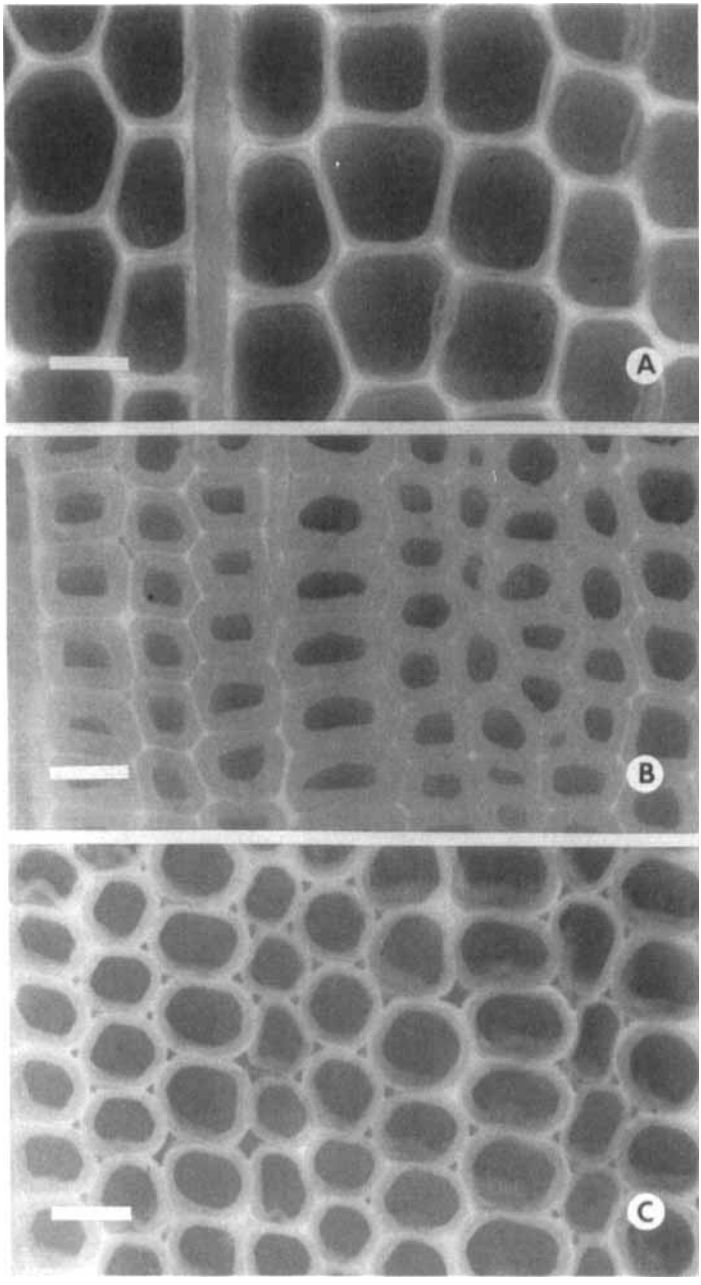

FIGURE 4. (a) Normal earlywood structure, (b) normal latewood structure, and (c) compression wood structure in latewood zone of growth ring. Reflected light at 495 ηm excitation; bars = 25 μm.

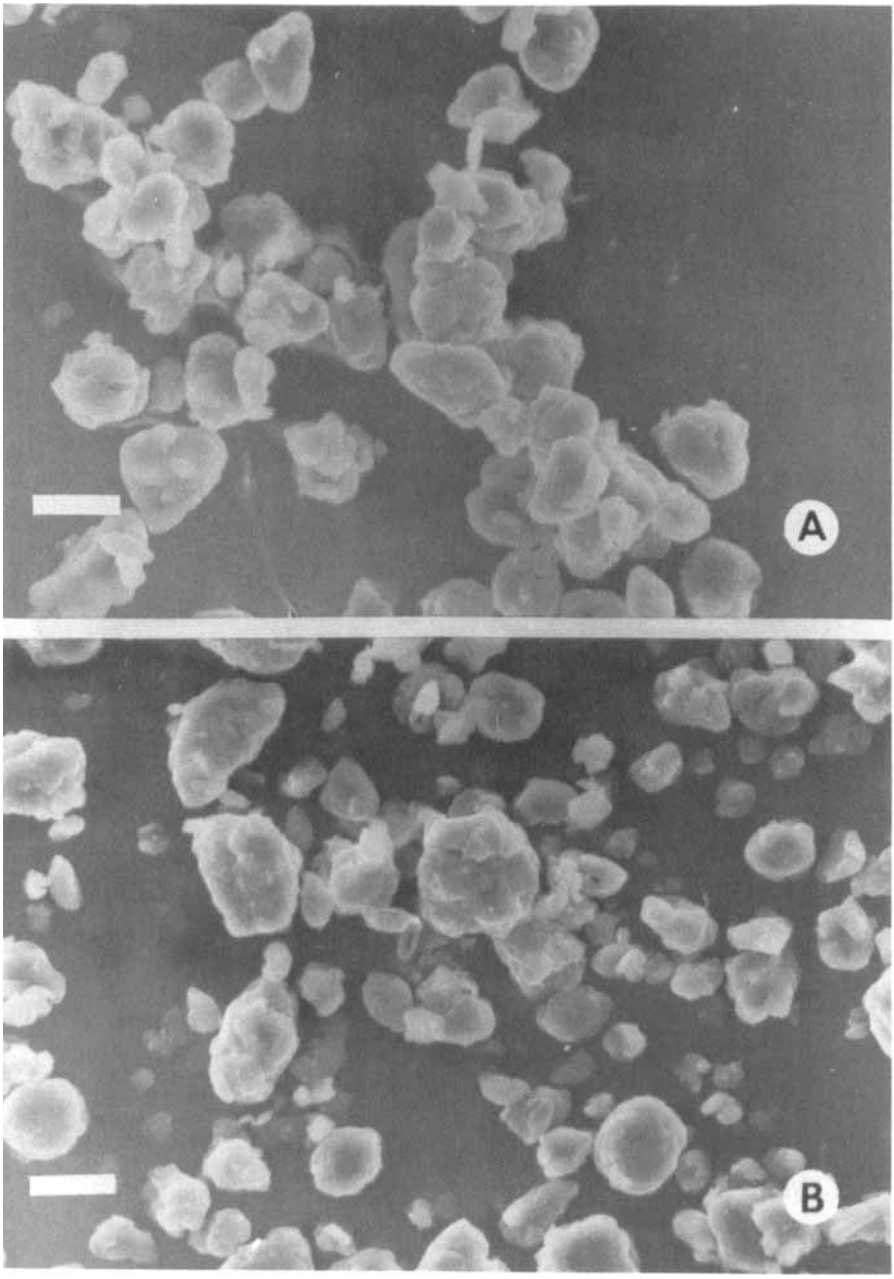

FIGURE 5. Scanning electron micrographs of (a) ML and (b) SW particles; bars= 10 μm.

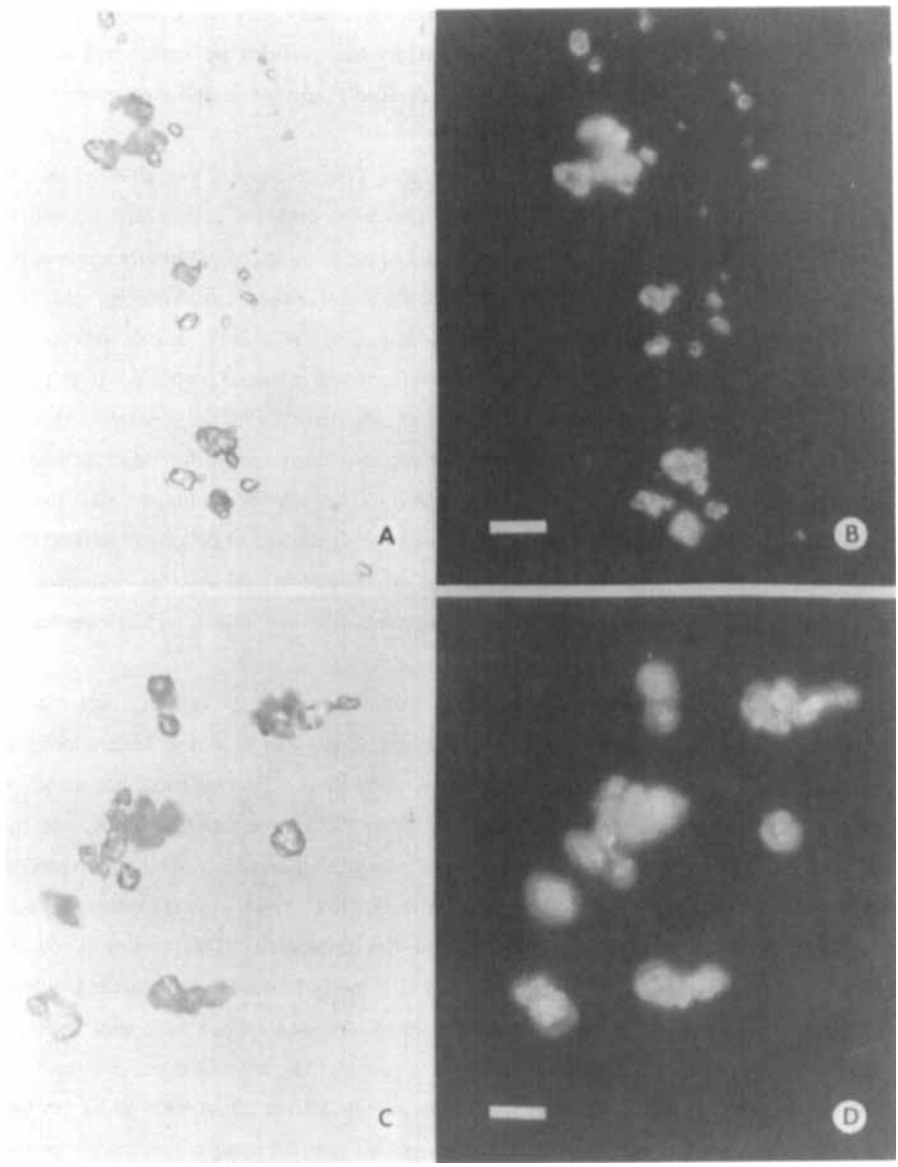

FIGURE 6. Transmitted bright field micrographs of (a) ML and (c) Sw particles and transmitted polarized light (crossed polars) micrographs of (b) ML and (d) SW particles; bars = 25 μm.

particles from either fraction at this magnification, nor were they visible at higher magnifications. Both middle lamella and secondary wall particles are unflattened and have round contours; the particles do not exhibit decidedly angular morphology nor are they flattened and/or flake-like.

Transmitted bright field light micrographs (Figure 6a and 6c) also indicate the physical similarity of the two fractions. Particles from both the middle lamella and the secondary wall appear bright (Figure 6b and 6d), i.e., the particles exhibit birefringence in both cases, despite the fact that fibrillar structures are not visible in the electron micrographs.

Given the morphology, size, and birefringence of the "middle lamella" fraction, it is apparent that some secondary wall material is included in these particles. It is equally apparent that the middle lamella is included, given the behavior in the separation media as well as the lignin contents. Other studies have also been unable to avoid inclusion of secondary wall in a segregated middle lamella fraction, but have been able to isolate particles having weak or no birefringence.[3,4,36,37] In particular, Boutelje and Erikson[36] isolated flake-like particles on the order of 100 X 150 μm which had a thickness (as determined by interference microscopy) of < 0.6μm. These fragments exhibited little or no birefringence, but probably included some primary and S_1 layers.

Comparison of the morphologies of particles isolated by various researchers by different methods shows that a variety of particle shapes and sizes can be produced and subsequently segregated based on sedimentation/flotation. For instance, Sorvari *et al.*[4] produced ribbon-like fragments approximately 50 to 100 μm long and by 1 μm wide from disintegrated TMP of spruce, while spruce wood meal yielded angular "flakes" approximately 4 to 15 μm in width and length by 0.2 to 1.5 μm thick. Both types were separated as middle lamella. The secondary wall fractions from both the disintegrated TMP and the wood meal were much larger than their counterpart middle lamella fractions and exhibited different morphologies. Whiting *et al.*[3] isolated middle lamella fragments which were large enough to include more than one pit structure, but were thin enough to be invisible under polarized light. Their secondary wall fragments were large (approximately 10 to 20 μm wide by 100 μm long) and resemble intact, birefringent cells. It is apparent that the sample preparation protocol employed influences the types of particles generated. Thus, comparison of results presented in the literature must be made with these considerations in mind.

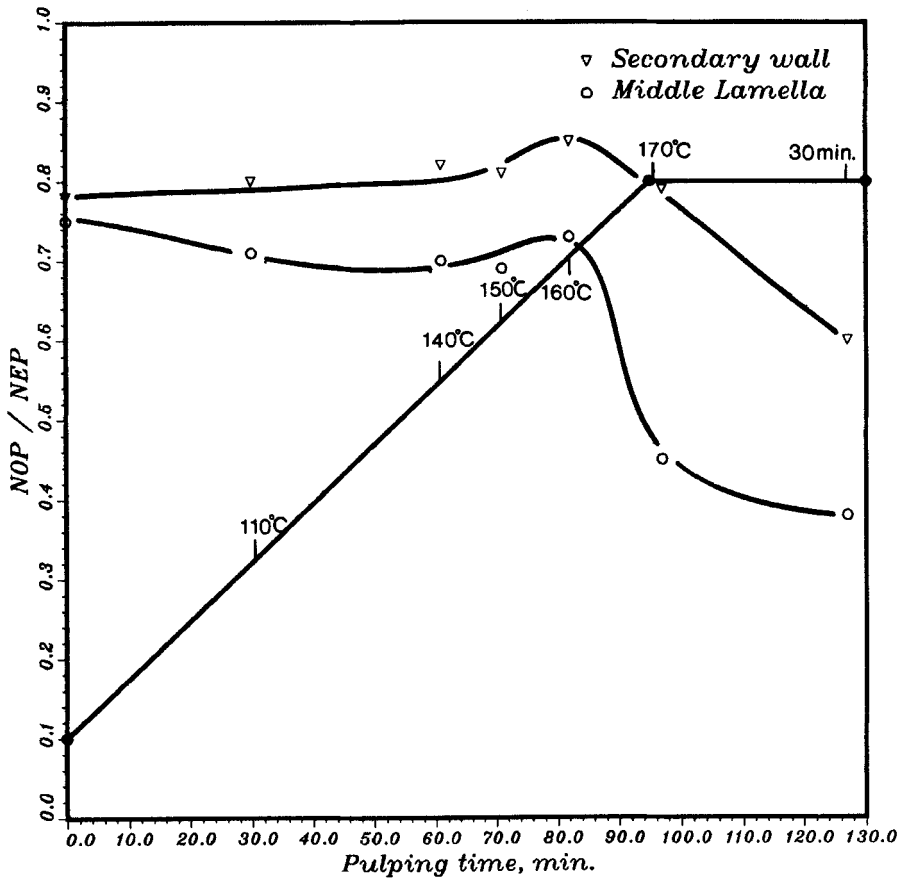

FIGURE 7. NOP/NEP as a function of pulping time.

Characterization of SW and ML from Wood and Pulps by Nucleus Exchange and Nitrobenzene Oxidation Reactions

Figure 7 shows a plot of NOP/NEP vs. pulping time. The values of NOP/NEP for ML and SW enriched fractions isolated from the non-delignified Douglas-fir were 0.75 and 0.78, respectively. These values were used as indexes to indicate the structure changes in side-chain and phenyl nuclei of residual lignins in ML and SW regions. For instance, any value of NOP/NEP from residual lignins in ML or SW regions greater than 0.75 or 0.78, respectively,

indicates structure changes in the side-chain of phenylpropane units, resulting in the formation of such units that are known to give high yields of vanillin and vanillic acid (NOP).[25,38] A value that is smaller than 0.75 or 0.78 indicates a decreased amount of non-condensed units due to the formation of diphenylmethane moieties from these units which would otherwise yield guaiacol and catechol (NEP).[25]

As shown in Figure 7, below the pulping temperature of 150°C, the values of NOP/NEP from SW fractions were slightly higher than the value of 0.78, indicating that, up to this stage of pulping, there were some changes in side-chain structures of residual lignins in SW region. A significant change in side-chain structure of residual lignin in SW region was observed at 160°C. At this temperature, the dominant lignin fragmentation reaction is the cleavage of β-aryl ether linkages in non-phenolic units releasing free phenolic units.[32] Consequently, these liberated free phenolic units in the residual lignin can undergo rearrangement to form conjugated structures in side-chains[39,40] of residual lignin yielding high yield of NOP.[38] These conjugated structures would also promote addition reactions, resulting in the formation of various diphenylmethane types of subunits.[29-32] As shown in Figure 7, the value of NOP/NEP for SW fraction became less than 0.78 and decreased rapidly after 170 °C, indicating a rapid formation of diphenylmethane subunits in residual lignin in SW region after this temperature was reached. However, the diphenylmethane subunits in ML enriched fractions were detectable already at early stages of pulping, as indicated by the values of NOP/NEP being lower than 0.75 below a temperature of 150°C.

In order to illustrate the disappearance of non-condensed (NC) and condensed (C) phenyl units at various stages of pulping, the ratio of (NC+DPM)/C is plotted as a function of pulping time (Figure 8). Since the disappearance of non-condensed units is due to (1) the dissolution of these units and (2) the conversion of these units to diphenylmethane (DPM) moieties, the term (NC+DPM) thus represents the total phenyl nuclei which are of originally non-condensed types remained in the residual lignin. Consequently, the quantity of (NC+DPM) at any stage of pulping should always be different from and less than the quantity of the originally non-condensed units, and the difference represents the amount of dissolved non-condensed units. Therefore, the ratio of (NC+DPM)/C can be viewed as a rate ratio of the dissolution of non-condensed units to the dissolution of condensed units. As shown in Figure 8, at early stages of pulping (below 110°C), the dissolution of non-condensed phenyl nuclei in SW region proceeded much faster than the dissolution of condensed nuclei, as indicated by the rapid decrease in values of (NC+DPM)/C. Assuming the extent of

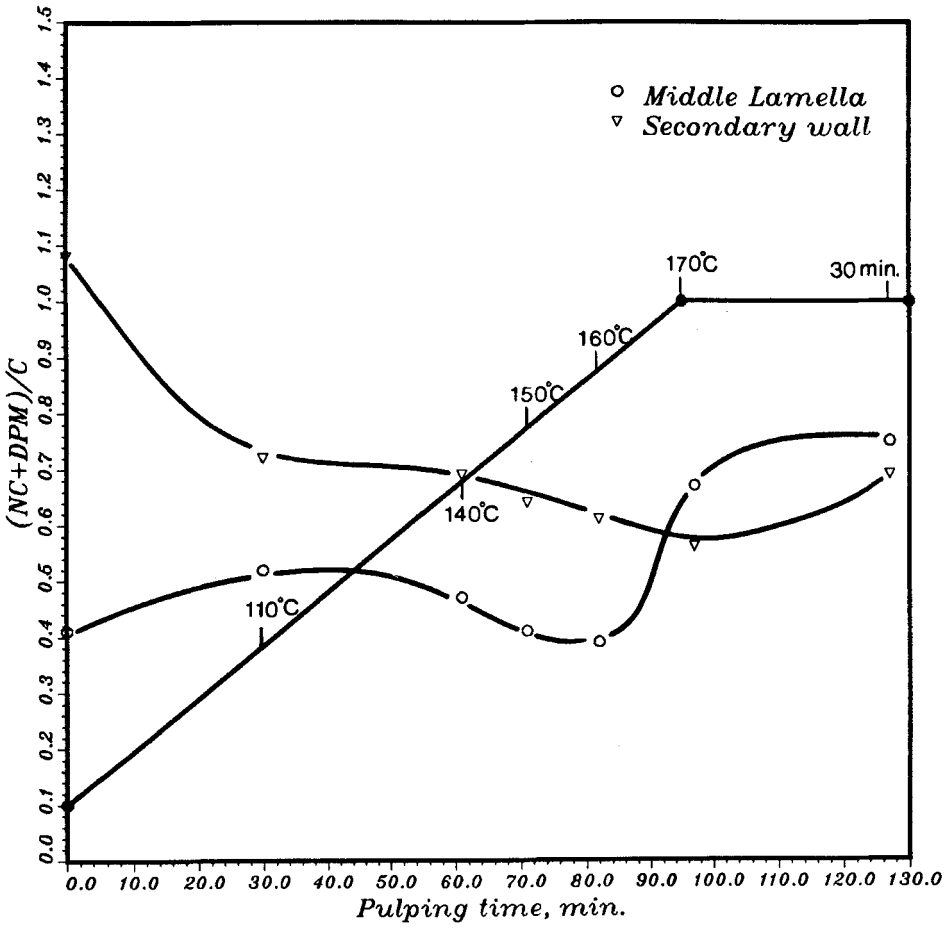

FIGURE 8. (NC+DPM)/C as a function of pulping time.

delignification of SW lignin is about the same as the delignification of total lignin, it can be estimated that, at 110°C, over 30% of the non-condensed phenyl nuclei were dissolved, whereas the condensed phenyl nuclei remained intact.

Between the temperatures of 110 and 170°C, it seemed that there was no dramatic difference between the dissolution of non-condensed and condensed phenyl nuclei in SW region. However, after the temperature reached 170°C, the conversion of non-condensed

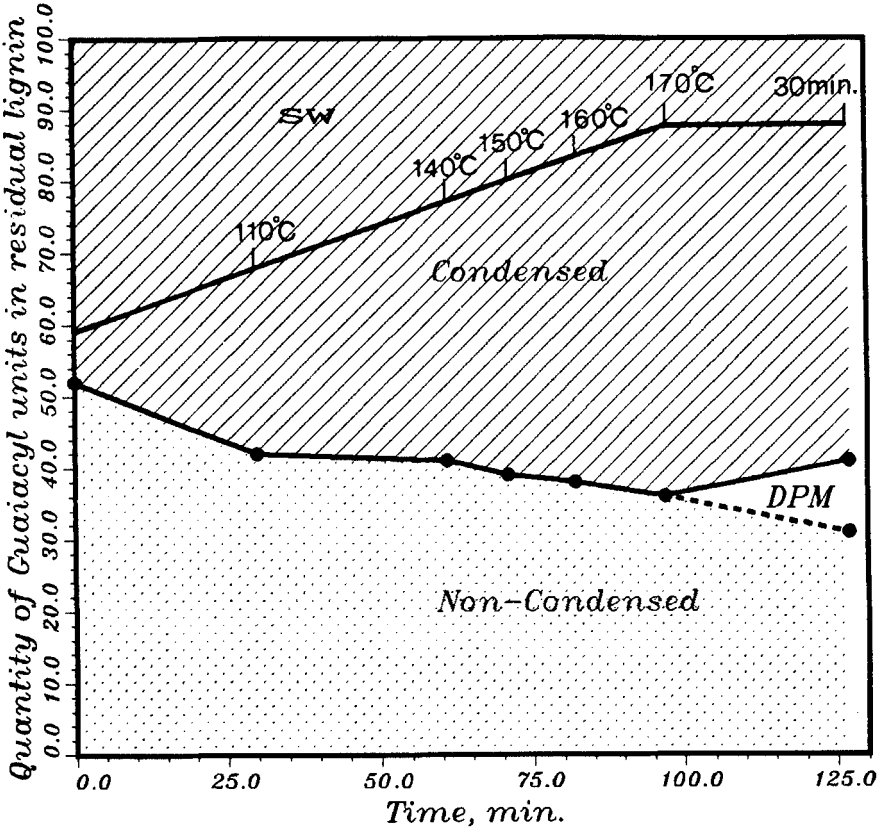

Figure 9. Composition of various types of guaiacyl nuclei in residual lignin of secondary wall.

units to diphenylmethane moieties occurred concurrently with the dissolution of non-condensed units and the dissolution of condensed units probably continued in SW, resulting in a gradual increase in (NC+DPM)/C.

Based on the expression of (NC+DPM)/C being a rate ratio of the dissolution of non-condensed units to the dissolution of condensed units, the increase in values of (NC+DPM)/C in ML region at the early stages appeared to indicate that a faster dissolution of condensed units as compared to the dissolution of non-condensed units occurred in the ML

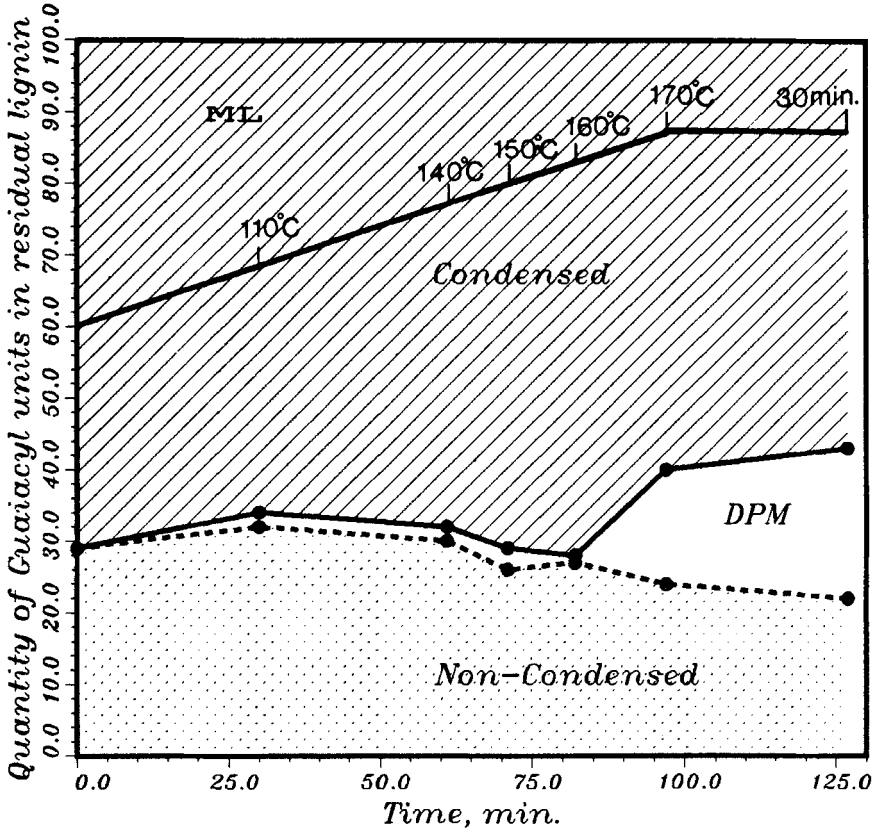

Figure 10. Composition of various types of guaiacyl nuclei in residual lignin of middle lamella.

region. This, however, is unlikely. The interpretation of the changes in (NC+DPM)/C for the ML or SW lignins must be made with the consideration of the fact that the delignification was done on whole wood rather than separately on the ML and SW enriched fractions. SW lignin, as such, is more flexible and reactive than ML lignin which has a higher degree of condensation (condensed units/non-condensed units = 2.45/1). Within the more flexible and reactive structure of SW lignin, the release of non-condensed phenyl nuclei could proceed conceivably faster than that of condensed nuclei. Consequently, a part of non-condensed units released from SW lignin would be transferred into ML region to condense with ML lignin

prior to the fractionation of the pulped wood into SW and ML enriched fractions. Therefore, it was most likely that the increase of (NC+DPM)/C in ML region at early stages was due to (1) the transfer of non-condensed units from SW region into ML region and (2) the condensation of these transferred non-condensed units in the ML region, resulting in the increase of DPM subunits in ML region. After 160°C, a sudden increase in (NC+DPM)/C (Figure 8) indicated a rapid formation of diphenylmethane subunits in ML region. This is probably due to the liberation and transfer of a large amount of non-condensed units from SW region at high temperatures.

The overall changes in quantities of various type phenyl nuclei in residual lignins in SW and ML regions are illustrated in Figures 9 and 10, respectively. There was a rapid disappearance of non-condensed phenyl nuclei in SW region (Figure 9) at early stages of pulping. The disappearance of these units continued as results of dissolution and conversion to condensed type subunits. The formation of diphenylmethane moieties in SW occurred at around 170°C. After 30 minutes at this temperature, when 60% of the lignin (based on total or SW lignins) was removed, the residual SW lignin consisted of 65, 25, and 10% condensed (type B, Figure 1), non-condensed (type A), and diphenylmethane type (types A'& B') phenyl nuclei, respectively. Small amounts of diphenylmethane units were already formed in residual ML lignins during early stages of pulping. Significant amount diphenylmethane units occurred earlier (160°C) in ML (Figure 10) than in SW . When 60% of the total lignin or 70% of the ML lignin was removed after 30 minutes at 170°C, the residual ML lignin consisted of 58, 22, and 20% condensed (type B), non-condensed (type A) and diphenylmethane type (types A'& B') phenyl nuclei, respectively.

CONCLUSIONS

(1) Lignin in ML has higher amount of condensed phenyl nuclei than lignin in secondary wall. The ratios of condensed/non-condensed phenyl nuclei are 2.45/1 and 1/1 for ML and SW lignins, respectively. This suggests that the frequencies of β-5, 5-5, and 4-O-5 types of linkages are higher in ML lignin than in SW lignin and the lignification process in ML region is of bulk-type polymerization..

(2) At early stages of pulping (below 110°C), the removal of phenyl nuclei in SW region is due entirely to the dissolution of non-condensed phenyl nuclei. At this temperature, about 30% non-condensed phenyl nuclei are dissolved. After the temperature reaches 170°C,

the conversion of non-condensed units to diphenylmethane moieties occurs concurrently with the dissolution of non-condensed units.

(3) Below the temperature of 140 C, some non-condensed phenyl nuclei released from SW region are probably transferred into ML region and condensed with ML lignin to form diphenylmethane subunits. A rapid formation of diphenymethane moieties in ML occurs after 160°C.

(4) When about 60% of the total lignin is removed, the residual SW lignin consists of 65, 25, and 10% condensed, non-condensed and diphenylmethane types condensed phenyl nuclei, respectively. At the same extent of delignification, the residual ML lignin consists of 58, 22, and 20% condensed, non-condensed and diphenylmethane types condensed phenyl nuclei, respectively.

ACKNOWLEDGEMENTS

The authors wish to thank Professors Kyosti V. Sarkanen, Joseph L. McCarthy and Bjorn F. Hrutfiord of the University of Washington, Seattle, Washington for their constructive criticism. The authors are grateful to the Weyerhaeuser Company and Michigan Research Excellence Funds for their financial support.

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