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Role of Syringyl Moieties in Kraft Delignification of Hardwood

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Abstract

In order to elucidate the role of syringyl moieties in kraft delignification of hardwood, kraft pulping of Douglas-fir (*Pseudotsuga menziesii*) and sweetgum (*Liquidambar styraciflua*) 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, the structures of pulp residual lignins were analyzed by a combination of nucleus exchange and nitrobenzene oxidation. Syringyl moieties were revealed to facilitate the delignification of hardwood in the following manner: (a) Syringyl units induce the flexibility of lignin molecule because of high frequency of β-O-4 linkages. (b) Syringyl units are easily dissolved because of no condensed type linkages and no reactive sites on the nuclei for condensation reactions. (c) Syringyl units accelerate the cleavage of β-O-4 linkages, resulting in a fast dissolution of both syringyl and guaiacyl units. (d) The association of syringyl with guaiacyl units reduces the extent of condensation of guaiacyl units in protolignin, accelerating the dissolution of these guaiacyl units during pulping. (e) Syringyl units prevent further condensation of guaiacyl units through the formation of guaiacyl-syringyl type of diphenylmethane moieties.

Key words: Kraft delignification, Guaiacyl nuclei, Syringyl nuclei, Lignin condensation reactions, Diphenylmethane

Introduction

The comparison of the extent of dissolution of total phenyl nuclei or the reduction in lignin content has become the norm in the demonstration of the difference between delignification of softwood and hardwood. Using this approach, CHAND and SARKANEN[1] have compared the rate of kraft delignification of several species with different syringyl-to-guaiacyl (S/G) ratios and found that the rate of delignification is directly proportional to the S/G ratio. So far, this is probably one of the strongest evidences to demonstrate that the ease of delignifying hardwood is due to the presence of syringyl nuclei. However, based on the dissolution of total phenyl nuclei during the course of pulping, it is not possible to manifest directly the involvement of syringyl nuclei in facilitating the fragmentation of hardwood lignin. The dissolution of syringyl moieties has to be known. The fragmentation of lignin is known to be retarded by the competing condensation reactions[2] forming, for instance, diphenylmethane moieties. Consequently, it is apparent that the presence of syringyl nuclei is crucial in both fragmentation and condensation reactions for facilitating the overall degradation of hardwood lignin.

Current paper reveals the role of syringyl nuclei in both lignin fragmentation and condensation reactions

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occurred in kraft pulping of hardwood. This paper also deals with an in depth and quantitative analysis on the dissolution of various phenyl nuclei and the condensation reactions forming diphenylmethane moieties during kraft pulping of softwood (Douglas-fir) and hardwood (sweetgum). This is done by characterizing the quantity of various phenyl nuclei in residual lignin in the pulp obtained at different stages of pulping. The characterization applies two lignin degradation reactions, i.e. nucleus exchange and the well-known alkaline nitrobenzene oxidation reactions. The nucleus exchange reaction involves the use of boron trifluoride in excess phenol and is able to selectively and quantitatively cleave C_1-C_α linkages of phenylpropane units and methylene linkages of diphenylmethane type structure units[3,4]. The quantitation of each type of phenyl nuclei in residual pulp lignins is elucidated at length in the next section.

Structural Analysis of Pulp Residual Lignins by a Combination of Nucleus Exchange and Nitrobenzene Oxidation

Abbreviations

NEP: Nucleus exchange products
NEP_G: Nucleus exchange products from guaiacyl units
NEP_S: Nucleus exchange products from syringyl units
NEP_G^{110}: Nucleus exchange products from guaiacyl units at a reaction temperature of 110°C
NEP_S^{110}: Nucleus exchange products from syringyl units at a reaction temperature of 110°C
NOP: Nitrobenzene oxidation products
NOP_G: Nitrobenzene oxidation products from guaiacyl units
NOP_S: Nitrobenzene oxidation products from syringyl units

Hardwood lignin is composed of non-condensed guaiacyl (Ga), condensed guaiacyl (Gb) and non-condensed syringyl (Sa) units. When subjected to chemical reactions, such as kraft delignification, part of these units becomes dissolved and the non-dissolved units undergo rearrangements, forming so called residual lignin. It was suggested[2,5,6] that diphenylmethane type units were the major products associated with residual lignins in alkaline pulping as the results of condensation reactions. Consequently, in residual hardwood lignins (Fig. 1), guaiacyl units can be of non-condensed (Ga), diphenylmethane type non-condensed (Ga′), diphenylmethane type condensed (Gb′), and other type condensed (Gb). Syringyl nuclei can be of non-condensed (Sa) and diphenylmethane type non-condensed (Sa′). Possible diphenylmethane type structures (Types I-IV) formed under alkaline conditions are summarized in Fig. 2[6-10]. Likewise, phenyl nuclei in softwood protolignin can be classified into non-condensed (Ga) and condensed (Gb) guaiacyl units. In residual softwood lignins, guaiacyl units can be of non-condensed (Ga), diphenylmethane type non-condensed (Ga′), diphenylmethane type condensed (Gb′) and other type condensed (Gb) units. The condensation reaction at C_2 or C_6 position of phenyl nuclei is insignificant under alkaline conditions[11].

By combining the phenyl nucleus exchange reaction and nitrobenzene oxidation, the quantity of Ga, Gb, Ga′, Gb′, Sa, and Sa′ types of structural units in residual lignin can be calculated directly from wood and pulps[12-16]. The nucleus exchange reaction is a combination of alkylation and dealkylation reactions in the presence of boron trifluoride and excess phenol. In principle, this reaction allows the C_α-aryl carbon-carbon linkages in the phenylpropane units and the methylene linkages of diphenylmethane moieties to be cleaved

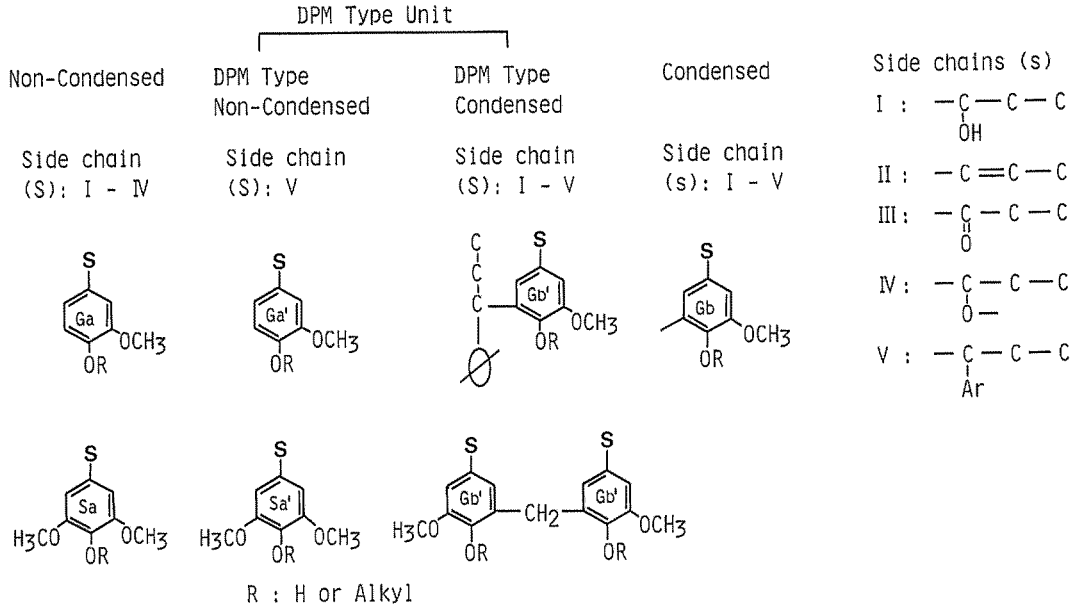

Fig. 1. Types of structural units in original and alkali-modified lignins.

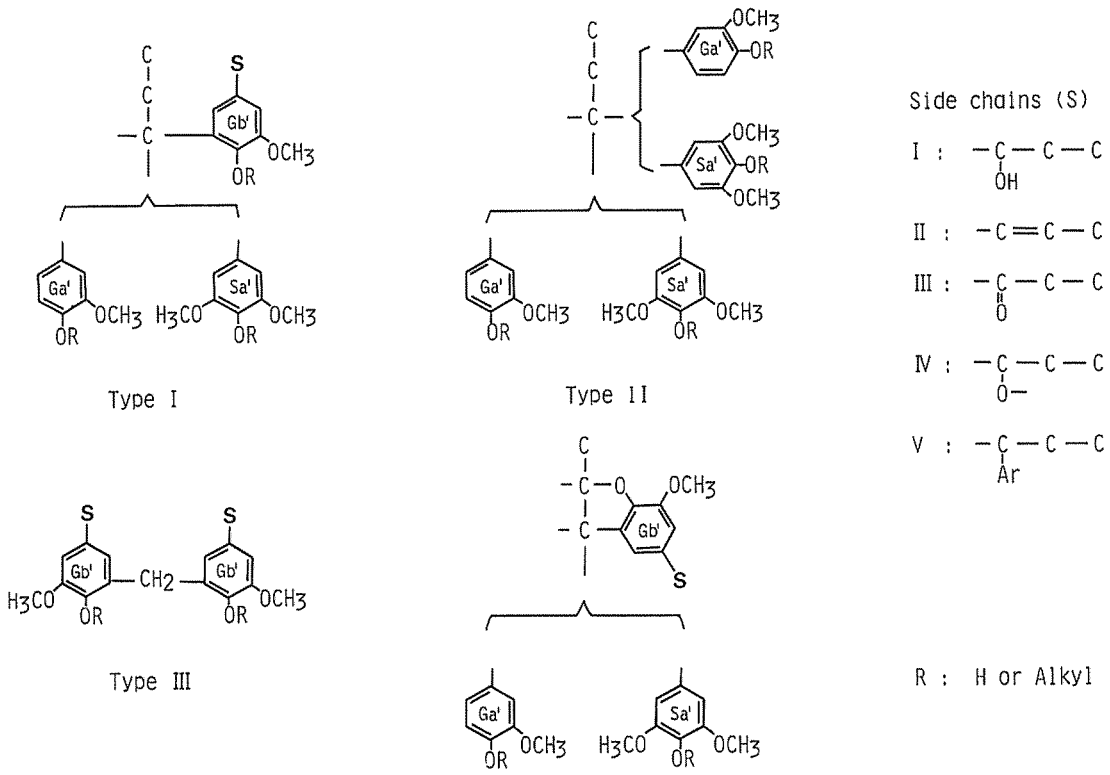

Fig. 2. Possible diphenylmethane type structures formed under alkaline conditions.

selectively and quantitatively. As a result, non-condensed (Ga), diphenylmethane type non-condensed (Ga′) and diphenylmethane type condensed (Gb′) guaiacyl nuclei can be quantitatively converted into guaiacol and catechol as nucleus exchange products (NEP_G, mol% of total phenyl nuclei). Likewise, non-condensed (Sa) and diphenylmethane type non-condensed (Sa′) syringyl nuclei are quantitatively converted into pyrogallol-1,3-dimethyl ether, pyrogallol-1-methyl ether and pyrogallol as nucleus exchange products (NEP_S, mol% of total phenyl nuclei).

In order to obtain quantitative yields of guaiacol and catechol from guaiacyl units, the reaction has to be carried out at 180°C for four hours[17,18]. However, much lower temperature such as 110°C should be used to obtain pyrogallol-1,3-dimethyl ether, pyrogallol-1-methyl ether and pyrogallol from syringyl units. At temperatures higher than 130°C, pyrogallol tends to undergo secondary modification, lowering the total yields of the products[14,19]. However, the quantity of products at 110°C (NEP_S^{110}) is only a fraction of the maximum yield of NEP_S from syringyl units. Consequently, the NEP_S^{110} should be multiplied by a factor of "f" to give the quantitative yield of NEP_S. Because of the similarity between guaiacyl and syringyl units in their responses to nucleus exchange reaction[19], the factor of "f" can be conveniently obtained from the ratio of quantitative NEP_G yield obtained at 180°C to NEP_G yield at 110°C (NEP_G^{110}).

$$(NEP_G/NEP_G^{110})=f \quad \text{Eq. 1}$$

NEP_S (quantitative yield of NEP from syringyl units)

$$=NEP_S^{110}\times f=NEP_S^{110}\times(NEP_G/NEP_G^{110}) \quad \text{Eq. 2}$$

Since there is essentially no diphenylmethane type of structural units in protolignin, the quantity of different units (Ga, Gb, Sa) can be easily obtained using nucleus exchange method alone.

NEP_G=Non-condensed guaiacyl units (Ga)
NEP_S=Non-condensed syringyl units (Sa)

Sweetgum lignin consists of 61, 22, and 17 mol% of non-condensed syringyl (Sa), non-condensed guaiacyl (Ga) and condensed guaiacyl (Gb) units, respectively. Douglas-fir lignin consists of 50 and 50 mol% of non-condensed (Ga) and condensed (Gb) guaiacyl units, respectively. However, for residual lignin after kraft delignification, not only the non-condensed guaiacyl (Ga) and syringyl (Sa) but the diphenylmethane type units (Ga′, Gb′, Sa′) are also converted to NEP_G and NEP_S. Therefore, in order to obtain the quantity of phenyl nuclei associated with DPM I-IV (Fig. 2), the quantities of NEP's from non-condensed units Ga and Sa have to be subtracted from NEP_G and NEP_S, respectively. Consequently, another means is needed to provide the information on the quantity of only non-condensed guaiacyl (Ga) and syringyl (Sa) units in residual lignins. This can be achieved by applying alkaline nitrobenzene oxidation reaction, since this reaction only converts non-condensed guaiacyl (Ga) and syringyl (Sa) units into vanillin + vanillic acid and syringaldehyde + syringic acid, respectively[20,21]. However, the yields of nitrobenzene oxidation products (NOP_G and NOP_S) do not represent directly the total amount of non-condensed guaiacyl (Ga) and syringyl (Sa) units, respectively, because of their low yields[22]. Assuming that the conversion rates of non-condensed guaiacyl (Ga) and syringyl (Sa) units to NOP_G and NOP_S in residual lignins are not so different from those in original lignins[23], the quantities of units Ga and Sa in residual lignins can be calculated as follows:

Non-condensed guaiacyl unit (Ga), mol%,

$$=NOP_G/(NOP_G/NEP_G)_{original} \quad \text{Eq. 3}$$

Non-condensed syringyl unit (Sa), mol%,

$$=NOP_S/(NOP_S/NEP_S)_{original} \quad \text{Eq. 4}$$

The values of NOP_G/NEP_G and NOP_S/NEP_S for sweetgum original lignin used in this study were 0.68 and 0.70, respectively. The value of NOP_G/NEP_G for Douglas-fir was 0.79. The following equations summarize the calculations of the quantities of various phenyl nuclei in original and residual lignins.

Total syringyl units (Sa+Sa′), mol%, $=NEP_S$ ..... Eq. 5

Diphenylmethane type syringyl units (Sa′), mol%,

$=NEP_S$−non-condensed syringyl units (Sa)

$$=NEP_S-(NOP_S/0.70) \quad \text{Eq. 6}$$

Total guaiacyl units (Ga+Ga′+Gb+Gb′), mol%,

$$=100-NEP_S \quad \text{Eq. 7}$$

Diphenylmethane type guaiacyl units (Ga′+Gb′), mol%,

$=NEP_G$−non-condensed guaiacyl units (Ga)

$$=NEP_G-(NOP_G/0.68) \quad \text{Eq. 8}$$

Other type condensed guaiacyl units (Gb), mol%,

$=$Total guaiacyl units$-NEP_G$ ..... Eq. 9

Equations 3 to 9 are used for sweetgum lignin. By substituting 0.68 with 0.79, equations 3, 8 and 9 are used for Douglas-fir lignin.

Bases on the total original syringyl (Eq. 5) and guaiacyl (Eq. 7) units and their quantities in sweetgum residual lignins, the dissolved syringyl and guaiacyl units can be obtained by the following equations. Assuming,

GSol=Total guaiacyl units in solution, mol% of total nuclei in original lignin,
GOL=Total guaiacyl units in original lignin, mol% of total nuclei in original lignin,
GRL=Total guaiacyl units in residual lignin, mol% of total nuclei in residual lignin,
RL= Residual lignin content, % of original lignin content,

$$\text{then } GSol=GOL-(GRL\times RL\%) \quad \text{Eq. 10}$$

Similarly, assuming,
SSol= Total syringyl units in solution, mol% of total nuclei in original lignin,
SOL= Total syringyl units in original lignin, mol% of total nuclei in original lignin,
SRL= Total syringyl units in residual lignin, mol% of total nuclei in residual lignin,

$$\text{then } SSol=SOL-(SRL\times RL\%) \quad \text{Eq. 11}$$

Based on the above theory and equations, the quantity of guaiacyl and syringyl units in both residual and dissolved sweetgum lignins can be obtained. Thus the dissolution of these two types of units can be illustrated and compared. Furthermore, based on equations 6 and 8, the quantities of guaiacyl and syringyl units which are involved in the diphenylmethane moieties can also be calculated, revealing the condensation mechanisms during kraft pulping of sweetgum. Likewise, equation 8 gives the quantities of guaiacyl units in diphenylmethane

moieties of residual Douglas-fir lignins.

In the above calculation, it should be noted that the α-saturated units, if present, and the units with diphenyl ether linkages are grouped as the unit Gb in guaiacyl moieties, because both units do not give NEP. Furthermore, condensed guaiacyl units (Gb), even if associated with diphenylmethane moieties [Type (Gb)-C-Ar], are counted not as diphenylmethane types, but as other type condensed units (Gb).

Experimental

Kraft delignification

Douglas-fir (*Pseudotsuga menziesii*) and sweetgum (*Liquidambar styraciflua*) chips were used as the raw materials. The pulping of sweetgum was done with a liquor to wood ratio of 5 and sulfidity and effective alkali of 25 and 14% (as Na_2O), respectively, in 300 ml stainless steel autoclaves. For pulping of Douglas-fir, 17% (as Na_2O) effective alkali was used with the same liquor to wood ratio and sulfidity as for pulping of sweetgum. Thirty grams of wood (O.D. weight) were used for each pulping.

Following addition of pulping liquor to the wood chips, the autoclaves were sealed and set aside at room temperature for 1 hour to allow the liquor to impregnate the chips. After this preparation, the autoclaves were heated and oscillated in a cylindrical aluminum block preheated to 100°C. After the autoclave reached 90°C, the rate of heating was controlled at 1°C/min to a final temperature of 170°C. Pulping was maintained at the final temperature for various times. At the completion of the pulping at selected temperatures and times, delignified woods or pulps were filtered off, followed by thorough washing and air drying. The samples (woods or pulps) were ground to pass 80 mesh. The meals were extracted with ethanol-benzene (1 : 2) for 48 hours and dried over P_2O_5.

Isolation of milled wood lignin (MWL) and determination of lignin content of wood and pulp

About 10 grams of extractive- and moisture-free wood meal (80 mesh pass) was milled for 45 days in a rotating porcelain jar (0.5 gal in volume) half-filled with equal-weight of two different sizes (1/4″ and 1/2″) of stainless steel balls. The isolation and purification of the MWL's were done according to LUNDQUIST et al[24].

Lignin content of the cooked chips or pulps was obtained by determining Klason lignin and acid-soluble lignin contents according to TAPPI T222 om-83 and TAPPI UM250, respectively. The procedures of JOHNSON et al.[25] and MARTON[26] for the determination of acetyl bromide lignin were followed.

Based on the elemental analysis on the sweetgum and Douglas-fir MWL's, the empirical formulae per C_9 unit were $C_9H_{8.00}O_{3.08}(OCH_3)_{1.56}$ for sweetgum and $C_9H_{9.00}O_{3.24}(OCH_3)_{0.84}$ for Douglas-fir.

Phenyl nucleus exchange reaction[3,18]

The degradation reagent was prepared by mixing 19 parts (by volume) of phenol, 10 parts of xylene and 4.5 parts of boron trifluoride-phenol complex. About 28 mg of extractive- and moisture-free wood meal (80 mesh pass) and 1 ml of the reagent were placed and sealed into a 1.5 ml stainless steel autoclave. The autoclave was heated at 180 or 110°C for 4 hours in a rocking aluminum block. After the reaction, the autoclave was cooled to room temperature and the reaction mixture was transferred quantitatively into a beaker with ethyl ether. A known amount of internal standard (dibenzyl in benzene) was added. Ether insoluble materials were filtered and washed with ethyl ether. The filtrate and washing were combined in a separatory funnel to which sodium

chloride saturated water was added. The funnel was shaken vigorously for a few minutes and allowed to set for about 20 minutes. This was repeated 3 times. The ether layer was separated and concentrated to about 10 ml by film evaporation. The ether solution was dried over anhydrous sodium sulfate overnight. Fifty μl of the ether solution was transferred into a small reaction vial to which a few drops of pyridine and 0.1 ml of N,O-bis(trimethylsilyl)acetamide were added. After one hour derivatization reaction at room temperature, the TMS derivatives were analyzed quantitatively using gas chromatography. A Hewlett Packard 5890 A Gas Chromatograph equipped with a computerized integrator (HP9122+HP3393 A) was used. The separation was carried out on a 50 m crosslinked methyl silicone capillary column (Hewlett Packard HP-1, 50 m$\times$0.2 mm$\times$0.33 μm) and an FID was used as detector. After 14 minutes at 170°C, the column temperature was raised to 180°C at a rate of 5°C/min. After 8 minutes at 180°C, the column was again heated to a final temperature of 270°C at a rate of 30°C/min. The injector and detector temperatures were 250 and 275°C, respectively. Helium was used as the carrier gas.

Alkaline nitrobenzene oxidation

Extractive- and moisture-free wood meal (10 mg, 80 mesh pass), 2 N sodium hydroxide (0.8 ml) and re-distilled nitrobenzene (0.05 ml) were placed in a stainless steel autoclave (1.5 ml in volume) and heated at 170°C in a rocking aluminum block for 3 hours. After the reaction, the mixture was extracted 3 times with ethyl ether. To the aqueous solution, a known amount of internal standard (2,6-dimethoxyphenol in dioxane) was added and then acidified to pH 2 with 18% hydrochloric acid. The acidic solution was saturated with sodium chloride and extracted 3 times with ethyl ether. The ether solution was then dried over anhydrous sodium sulfate overnight. After the evaporation of ethyl ether, the products were converted to their trimethylsilyl derivatives with N,O-bis(trimethylsilyl)acetamide in pyridine and analyzed by gas chromatography. The same gas chromatograph system as described above was used. However, the column temperature was 160°C initially and was raised after 14 minutes to the final temperature of 270°C at a rate of 5°C/min.

Results and Discussion

The sweetgum used in this study had a syringyl-to-guaiacyl ratio (S/G) of 1.6 (Eqs. 5 and 7). However, unlike most of the other studies, the current method is quantitative and able to use wood materials with intact lignin structure. Thus, the value of 1.6 is the true ratio of syringyl-to-guaiacyl contents and differs from the conventional syringaldehyde-to-vanillin (S/V) ratio.

Based on equations 5 and 7, the S/G ratios of residual lignins were obtained. Likewise, according to equations 11 and 10, SSol's and GSol's were calculated, respectively, and their ratios (SSol/GSol) represented the corresponding S/G ratios of dissolved lignin. The S/G ratios of residual and dissolved lignins as well as the S/V ratios of residual lignins are given in Table 1. As indicated in this figure, the S/G ratios of residual lignins were, in general, rather constant during the heat-up period. However, there was a dramatic decrease of S/G values from 140 to 170°C-10 min, suggesting that a major part of the syringyl units was dissolved at this point. These types of quantitative information can only be obtained by the current method. The conventional S/V ratios for modified lignins are not quantitative and misleading, since these values reveal the relative quantities of only non-condensed phenyl nuclei.

During early stages of pulping (below 150°C), the total lignin dissolution patterns were about the same

Table 1. S/G Ratios of residual and dissolved lignins and conventional S/V ratios of residual lignins during kraft pulping of sweetgum

Samples analyzed	S/G*1		Conventional S/V*2
	Residual Lignin	Dissolved Lignin	Residual Lignin
Original wood	1.6	—	2.82
at			
110°C, 0 min	1.8	0.3	3.16
120°C, 0 min	1.8	0.3	3.16
130°C, 0 min	1.7	0.9	3.23
140°C, 0 min	1.9	1.0	3.73
150°C, 0 min	1.9	1.0	3.73
160°C, 0 min	1.7	1.4	3.20
165°C, 0 min	1.4	1.8	3.01
170°C, 0 min	1.0	2.0	2.75
170°C, 10 min	0.5	2.0	2.30
170°C, 20 min	0.5	1.9	2.53
170°C, 30 min	0.2	1.9	1.95
170°C, 60 min	0.1	1.8	2.21
170°C, 120 min	0.1	1.7	3.87

*1 Calculated from nucleus exchange products (NEP) Total syringyl units/Total guaiacyl units
*2 Calculated from nitrobenzene oxidation products (NOP)
(Syringaldehyde+Syringic acid)/(Vanillin+Vanillic acid)

between these two species, as shown in Fig. 3. According to GIERER[10], the main lignin degradation reactions during this period of pulping are the cleavage of phenolic α- and β-aryl ether linkages. Consequently, the similar lignin dissolution pattern between kraft pulping of Douglas-fir and sweetgum in the early stages of pulping suggests that the frequency and amounts of phenolic α- and β-aryl ether linkages are about the same in these species. Above 150°C or during the bulk phase delignification, the dissolution of sweetgum lignin proceeded much faster than that of Douglas-fir lignin. Since the cleavage of arylglycerol-β-aryl ether linkages is the main reaction in the bulk phase delignification[10] and the high frequency of these types of linkages is associated with syringyl units[27], the fast dissolution of syringyl units is expected. As shown in Fig. 4, in the early stages of pulping of sweetgum (110 to 140°C), the dissolution of one guaiacyl unit was accompanied by a removal of 1.4 syringyl units. In the main portion of the bulk phase delignification, every removal of a guaiacyl unit resulted in a dissolution of 3 syringyl units. These findings were in good agreement with model compound studies which showed that the presence of syringyl units in arylglycerol-β-aryl ether moieties provides a 2 to 4 times faster hydrolysis of these ether linkages in alkali than the hydrolysis of the linkages connecting only guaiacyl units[28,29]. It is therefore conceivable that the involvement of syringyl nuclei in guaiacyl-syringyl lignin facilitates the cleavage of β-aryl ether linkages and thus the dissolution of syringyl as well as guaiacyl nuclei. All the above observations suggest that with the aid of syringyl nuclei, the dissolution of guaiacyl units in pulping of hardwood should proceed faster than the dissolution of guaiacyl units in softwood pulping. This is clearly illustrated in Fig. 5. The dissolution of guaiacyl units in pulping of sweetgum indeed proceeded faster than the dissolution of guaiacyl units in pulping of Douglas-fir during the initial and particularly the bulk phase delignifications. The rate

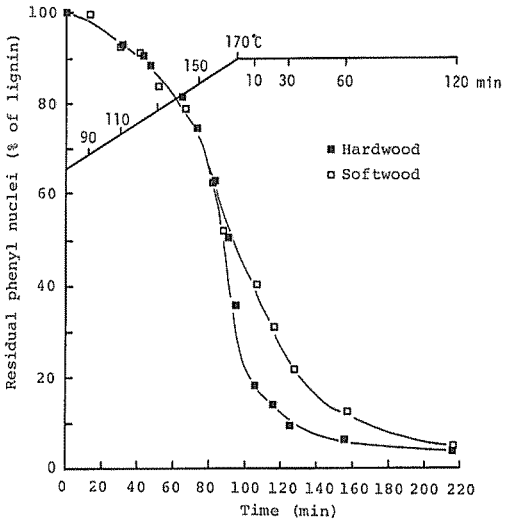

Fig. 3. Dissolution of total phenyl nuclei during kraft pulping of sweetgum and Douglas-fir.

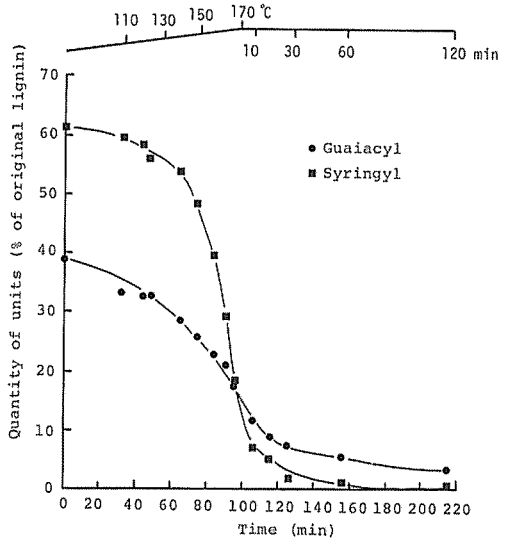

Fig. 4. Changes of guaiacyl and syringyl contents in pulp residual lignins during kraft delignification of sweetgum.

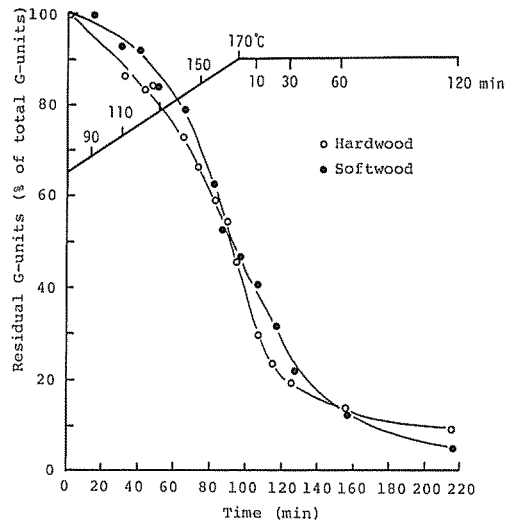

Fig. 5. Dissolution of total guaiacyl (G) units during kraft pulping of sweetgum and Douglas-fir.

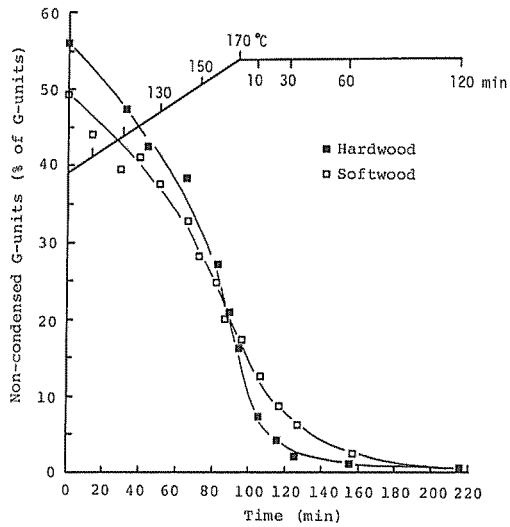

Fig. 6. Dissolution of non-condensed guaiacyl (G) units during kraft pulping of sweetgum and Douglas-fir.

of dissolution of sweetgum guaiacyl units became lower than that of dissolution of Douglas-fir guaiacyl units only in the final phase of delignification started after 20 minutes at 170°C. This is simply due to the facts that (a) at this stage (170°C, 20 min), over 96% of the syringyl units were removed from the residual pulp lignin, as indicated in Fig. 4 and (b) low alkalinity in pulping of sweetgum as compared to Douglas-fir pulping[30]. Consequently, the delignification of residual sweetgum lignin after 20 minutes at 170°C was essentially a case of delignifying softwood-like lignin with low alkalinity.

In order to further compare the difference in dissolution of guaiacyl units between pulping of Douglas-fir and sweetgum, these units are divided into non-condensed (Ga), diphenylmethane (Ga′ and Gb′), and condensed (Gb) types. Fig. 6 illustrates the relationship between the quantities of non-condensed guaiacyl units (Ga) in residual lignins and pulping times. The disappearance of non-condensed guaiacyl units (Ga) proceeded in a rather similar pattern between softwood and hardwood pulping. However, during the bulk phase delignification (started from around 140°C) a faster rate of removing non-condensed guaiacyl units (Ga) in pulping of sweetgum was observed. The most significant difference between kraft pulping of Douglas-fir and sweetgum was in the formation and dissolution of condensed units. As shown in Fig. 7, condensed guaiacyl nuclei (Gb) in sweetgum dissolved rapidly in the initial and bulk phase delignification and the dissolution became ineffective at the point (170°C, 30 min) where 90% of these units were dissolved. However, in the case of Douglas-fir pulping, the quantity of condensed guaiacyl units (Gb) in residual lignins was essentially unchanged during early stages of pulping (90 to 130°C) (Fig. 7). The removal of Douglas-fir lignin in the early stages of pulping is due entirely to the dissolution of non-condensed units (Fig. 6) through the cleavages of phenolic α- and β-aryl ether linkages. This implies that the phenolic α- and β-aryl ether linkages are mainly associated with non-condensed guaiacyl units in Douglas-fir lignin. The dissolution of the condensed units became effective only at temperatures higher than 140°C. Consequently, the difference between pulping of Douglas-fir and sweetgum in dissolution of guaiacyl units during early stages of delignification was that both condensed and non-condensed guaiacyl uints in sweetgum lignin were dissolved rapidly, whereas only the dissolution of non-condensed guaiacyl units in Douglas-fir lignin was effective.

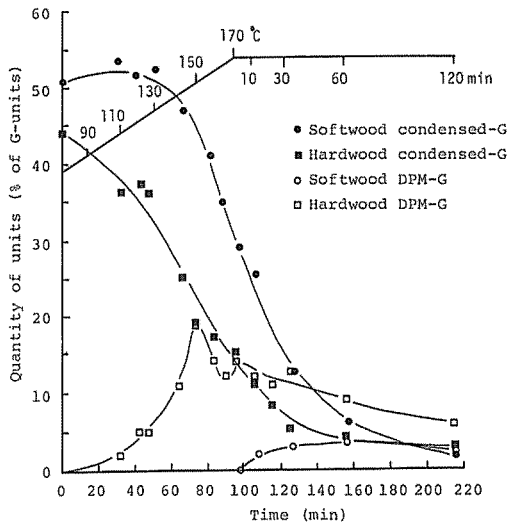

Fig. 7. Dissolution of condensed guaiacyl (G) units and the formation and dissolution of diphenylmethane (DPM) moieties during kraft pulping of sweetgum and Douglas-fir.

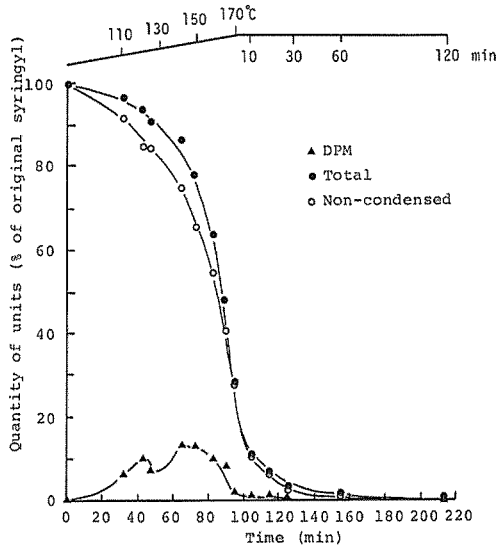

Fig. 8. Syringyl contents of the residual sweetgum lignins at various stages of pulping.

In pulping of sweetgum, the diphenylmethane type moieties (Ga′, Gb′ and Sa′) were formed already at the early stages (110–140°C) (Figs. 7 and 8). The formation of diphenylmethane type moieties at such early stages could be attributed to the involvement of syringyl nuclei within the lignin molecule. The involvement of syringyl

units makes the hardwood lignin become less condensed. This characteristic and the high frequency of β-O-4 linkages that associated with syringyl units induce the flexibility of the hardwood lignin. Furthermore, the presence of syringyl units in arylglycerol-β-aryl ether moieties always facilitates the alkaline hydrolysis of β-O-4 linkages in the temperature range of 110 to 140°C[28,29]. Consequently, due to the flexibility of hardwood lignin and to the impelled cleavage of β-O-4 linkages forming conjugated moieties in residual lignins, the condensation reactions were facilitated at an early stage. Based on the fact that the quantities of both guaiacyl (Fig. 7) and syringyl (Fig. 8) units that were associated with diphenylmethane moieties reached the maximum at 150°C, the diphenylmethane type units formed during the early stages of pulping should conceivably consist of mainly guaiacyl-syringyl moieties. The quantity of guaiacyl units that were associated with diphenylmethane moieties decreased rapidly after 150°C (Fig. 7). This decrease is most likely caused by the dissolution of guaiacyl-syringyl type diphenylmethane units because diphenylmethane type syringyl units (Sa′) also decreased dramatically (Fig. 8). This is possible since the phenyl nuclei in guaiacyl-syringyl type [(Sa′)-C-(Gb′)] diphenylmethane units are not condensed to any other units, making these units alkali-soluble. After 160°C, the quantity of guaiacyl units in diphenylmethane type moieties increased slightly first and then decreased slowly as pulping proceeded (Fig. 7). The slight increase in diphenylmethane type guaiacyl units from 160 to 170°C indicates the formation of guaiacyl-guaiacyl types of diphenylmethane structural units. This is in good agreement with the observation that the formation of diphenylmethane type units (Ga′, Gb′) in Douglas-fir pulping occurs at 170°C (Fig. 7). The diphenylmethane units in residual softwood lignins can be of guaiacyl-guaiacyl types. The (Ga′)-C-(Gb′) types of diphenylmethane moieties can be further condensed with other units. All these diphenylmethane type units remain insoluble as pulping proceeds (Fig. 7). No diphenylmethane type syringyl unit was detected in residual sweetgum pulp lignin at the end of pulping.

After 2-hour pulping at 170°C, the residual sweetgum lignin (at kappa ~20) consisted of 66 and 26 mol% guaiacyl units (Ga′, Gb′) that were associated with diphenylmethane type moieties and other types of condensed guaiacyl units (Gb), respectively. The residual Douglas-fir lignin (at kappa ~30) consisted of 54 and 37 mol% of diphenylmethane type guaiacyl units (Ga′, Gb′) and other types of condensed units (Gb), respectively.

Conclusions

In order to elucidate the role of syringyl moieties in kraft delignification of hardwood, the dissolution patterns of various phenyl nuclei during kraft pulping of Douglas-fir and sweetgum were compared.

The presence of syringyl units in arylglycerol-β-aryl ether moieties facilitates the cleavage of β-O-4 linkages and therefore the formation of conjugated moieties which offer reactive sites for condensation reactions. Conseqnently, during pulping of sweetgum, the condensation reactions occur already at early stages of delignification forming diphenylmethane moieties containing syringyl units. However, these types of diphenylmethane units become completely dissolved without the necessity of cleaving methylene linkages in these units after pulping at 170°C for 30 minutes. This is due to that, first, all syringyl nuclei are of non-condensed type and, secondly, the involvement of syringyl units in these moieties prevent further condensation between syringyl nuclei and other units since there is no reactive site on syringyl nuclei under alkaline conditions. Carbon-carbon linkages are possible only on propane side-chains of syringyl units. Without the presence of syringyl units, the diphenylmethane moieties in residual Douglas-fir lignins remained insoluble after the quantity of these condensed units reached its maximum at 170°C.

That is, the involvement of syringyl units facilitates the delignification of sweetgum in the following manner: (a) Syringyl units induce the flexibility of lignin molecule, because of high frequency of β-O-4 linkages. (b) Syringyl units are easily dissolved because of no condensed type linkages and no reactive sites on the nuclei for condensation reactions. (c) Syringyl units accelerate the cleavage of β-O-4 linkages, resulting in a fast dissolution of both syringyl and guaiacyl units. (d) The association of syringyl with guaiacyl units reduces the extent of condensation of guaiacyl units in protolignin, accelerating the dissolution of these guaiacyl units during pulping. (e) Syringyl units prevent further condensation of guaiacyl units through the formation of guaiacyl-syringyl types of diphenylmethane moieties.

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広葉樹クラフト脱リグニンにおけるシリンギル単位の挙動

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広葉樹クラフト脱リグニン過程における構成シリンギル単位の役割を明確にするため，Douglas-fir および Sweetgum のクラフト蒸解を行なった。パルプ残留リグニンの構造をリグニンを単離することなく定量的に解析し，パルプ化過程におけるリグニンの組成変化を両樹種間で比較検討した。クラフト蒸解における針葉樹および広葉樹間の最も重要な相違は，縮合型単位の生成と溶出にあることが明らかとなった。シリンギル単位はリグニン分子にフレキシビリティーを与えること，また，シリンギル—グアイアシル型ジフェニルメタン縮合構造の形成を通して，グアイアシル単位の高度な縮合を阻止することが示された。