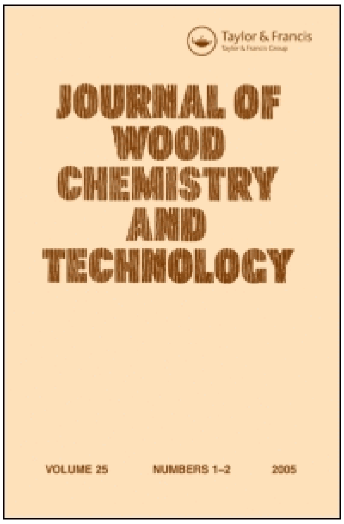

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UTILIZATION OF SOFTWOOD KRAFT LIGNIN AS ADHESIVE FOR THE MANUFACTURE OF RECONSTITUTED WOOD

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ABSTRACT

Reaction conditions for hydroxymethylation of pine kraft lignin (KL) were optimized by kinetic studies of the reaction. Characterization of the resulting hydroxymethylated kraft lignin (HMKL) indicated that about 0.36 mole of the -CH_2OH/C_9 unit was introduced into the lignin under the optimal reaction conditions, of which about 0.33 mole was introduced into C-5 of guaiacyl moieties via Lederer-Manasse reaction. This result was confirmed by ^{13}C-NMR spectrum of ^{13}C enriched HMKL prepared from KL and $^{13}CH_2O$ (about 7 atomic %) under the same reaction conditions. Lignin-phenolic resins were formulated by blending the HMKL with phenol-formaldehyde (PF). A 50/50 blending of HMKL/PF resulted in a bond strength of about 65 psi in laboratory boards made with sweetgum flakes. In general, bond strength increased with an increase in the PF. Studies on effects of process and wood variables indicate that such resin could yield satisfactory boards made with red oak, black gum, red maple, post oak and sweetgum flakes with: (a) hot press temperature of 410 °F, (b) hot press time of 8 minutes, and (c) minimum resin content of 5%.

INTRODUCTION

Increasing interest in better utilization of renewable resources has led to novel utilization of technical lignins produced in pulping processes (1-7). Some of these uses include partial replacement of phenolics in phenol resin binder systems, reinforcement in corrugation medium, and application in tertiary oil recovery in the petroleum industry.

The estimated annual production of lignosulfonates in the United States in 1980 is about 1.5 million tons, of which about 700,000 tons (about 47%) are used in manufacture of by-products (8). In contrast, the estimated annual production of kraft lignin in this country in the same year is about 20 million tons, of which only about 35,000 tons (about 0.2%) are recovered from the spend liquor, and are processed for production of technical lignins and chemically modified products (8). The remainder is burned in the form of spent liquor to provide energy for mill operation, and also to facile the recovery of pulping chemicals (9). Thus, the predominance of the kraft pulping process in this country makes kraft lignin a more logical choice as raw material for the future development of by-product utilization.

Recently, hydroxymethylated softwood kraft lignin has been widely used in formation of lignin-phenolic resins for fabrication of wood composites (1,3,4,7). However, no comprehensive studies have been conducted on the optimalization of reaction conditions for hydroxymethylation of kraft lignin and characterization of the resulting hydroxymethylated kraft lignin used in adhesive formulations, although Marton and co-workers (10) characterized hydroxymethylated kraft lignin in an earlier work.

The objective of this research project is, therefore, to study kinetics for hydroxymethylation of pine kraft lignin by condensation with formaldehyde in alkaline solution in order to elucidate optimal conditions for the reaction, to characterize the resulting hydroxymethylated kraft lignin produced under the optimal reaction conditions, and finally to study effects of process and wood variable in formulation of HMKL/phenolic resins for fabrication of particle boards.

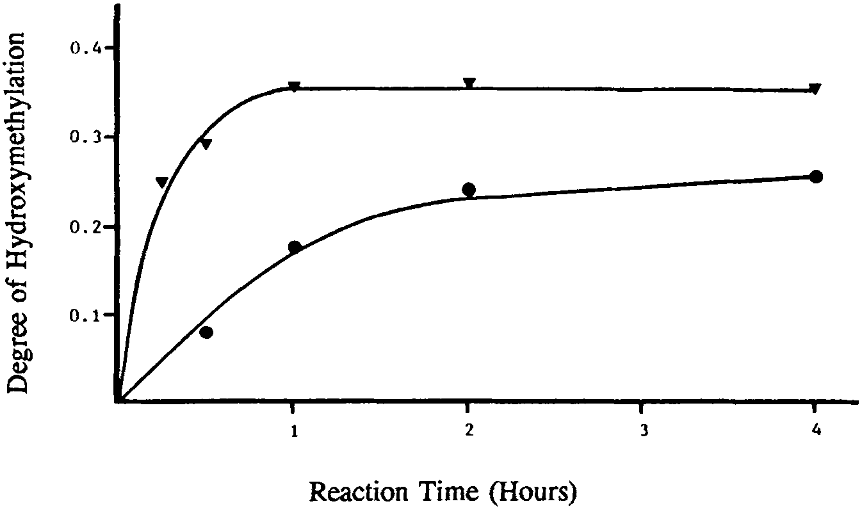

Figure 1. Degree of Hydroxymethylation Versus Reaction Time; Condensation of Formaldehyde with Pine Kraft Lignin ($HCHO/C_9$ Molar Ratio = 1.1) in Dilute NaOH Solution at pH 12.

● ● ● ● Reaction Temperature 25 °C.
▿ ▿ ▿ ▿ Reaction Temperature 50 °C.

RESULTS AND DISCUSSION

Kinetic Study

Degree of Hydroxymethylation vs. Reaction Temperature and Time

Purified pine kraft lignin (KL) was hydroxymethylated by condensation with formaldehyde in dilute NaOH solution at PH 12 and at room temperature (25 °C) and 50 °C, HCHO/KL (C_9-unit) molar ratio being 1:1. The hydroxyl content of original kraft lignin and resulting hydroxymethylated lignins were determined by acetylation, and subsequent acetyl determination of the resulting acetates by PMR spectroscopy as well as by procedure of Månsson (11). Any increase in the hydroxyl content of hydroxymethylated kraft lignins as compared to that of kraft lignin is assumed to be number of hydroxymethyl groups introduced into KL by the reaction. The increase of hydroxyl content is, thus, termed as the degree of hydroxymethylation, and is expressed by moles of -CH_2OH group (= HCHO) per C_9-unit.

Results of the study are given in Figure 1. It can be observed that formaldehyde condensed slowly with kraft lignin at room temperature (25 °C); the degree of hydroxymethylation was only about 0.27 mole -CH_2OH per C_9-unit under the reaction conditions at reaction time of 4 hours. When the reaction time was prolonged to 24 hours, the degree of hydroxymethylation increased marginally to about 0.30 mole -CH_2OH per C_9-unit. Further increase in the reaction time did not result in increase of the degree of hydroxymethylation. In contrast, formaldehyde condensed rather rapidly with the lignin at reaction temperature of 50 °C. The lignin took up about 0.36 mole -CH_2OH per C_9-unit at reaction time of 1 hour, and the degree of hydroxymethylation stayed almost constant hereafter. Thus, it is evident that reaction temperature of 50 °C, and reaction time of 2 hours are the optimal conditions for the reaction.

Degree of Hydroxymethylation vs Molar Ratio of Formaldehyde to Kraft Lignin (C_9-unit)

The effect of HCHO/KL (C_9-unit) on the hydromethylation of kraft lignin was studied. Purified kraft lignin was condensed with formaldehyde in dilute NaOH solution at pH 12, reaction temperature of 50 °C and reaction time of 2 hours, the HCHO/KL (C_9-unit) molar ratio being the variable. Results are shown in Figure 2. The degree of hydroxymethylation increased with increase in HCHO/KL (C_9-unit) molar ratio in the range of 0.25 to 1.1. At the HCHO/KL (C_9-unit) molar ratio of 1.1, the degree of hydroxymethylation was found to be 0.36 mole -CH_2OH per C_9-unit. Hereafter, increase in the HCHO/KL (C_9-unit) molar ratio did not result in an increase of the degree of hydroxymethylation. Thus, the optimal conditions for hydroxymethylation of pine kraft lignin have been determined to be HCHO/KL (C_9-unit) of 1.1, reaction temperature of 50 °C and reaction time of 2 hours in dilute NaOH solution at pH 12.

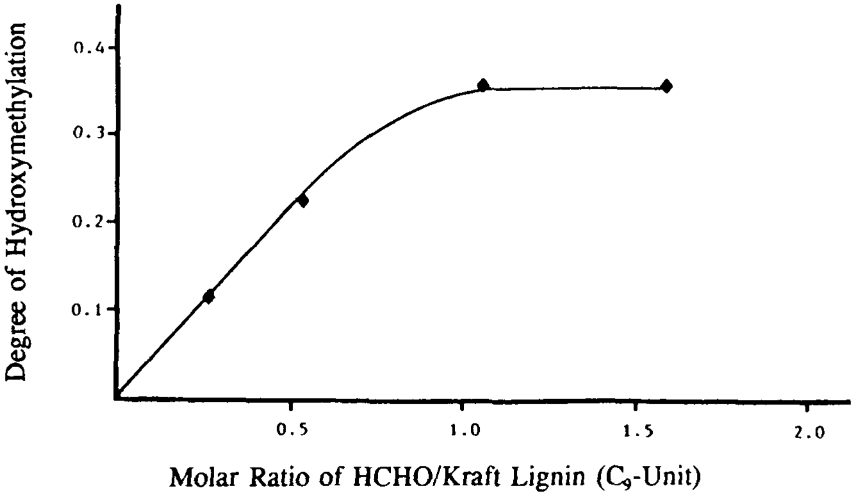

Figure 2. Degree of Hydroxymethylation Versus Molar Ratio of Formaldehyde/Kraft Lignin (C_9-Unit).

Reaction Conditions: In Dil. NaOH solution (pH 12), Heated at 50 °C for 2 Hours.

Characterization of Hydroxymethylated Kraft Lignin

Hydroxymethylated kraft lignin produced under the optimal conditions was characterized by elemental analysis, functional analysis and ^{13}C NMR spectroscopy.

Determination of Hydroxyl Content and Site of Hydroxymethyl Groups Introduced

Table 1 shows results of the hydroxyl content determinations of purified kraft lignin (KL), $NaBH_4$-reduced kraft lignin (RKL) and their hydroxymethylated products (HMKL and HMRKL). The methods for determination of hydroxyl content in lignin-preparation have been described in the previous section.

TABLE 1. Hydroxyl Contents of Kraft Lignin Preparations (per C_9-unit).**

Lignin Preparation*	Phenolic OH	Aliphatic OH	Aliphatic OH Introduced
KL	0.58	0.72	----
HMKL***	0.57	1.08	0.36
RKL	0.57	0.84	0.12
HMRKL***	0.56	1.17	0.33

* KL = Kraft Lignin; HMKL = Hydroxymethylated Kraft Lignin; RKL = $NaBH_4$-Reduced Kraft Lignin; HMRKL = Hydroxymethylated $NaBH_4$-Reduced Kraft Lignin

** C_9-Formula for Acetylated Kraft Lignin: $C_9H_{6.83}O_{2.12}S_{0.11}(OCH_3)0.85(COCH_3)_{1.29}$

*** Reaction Conditions for Hydroxymethylation: HCHO/KL or RKL (C_9) Molar ratio = 1.1 in 0.1N NaOH solution at pH 12, Reaction Temperature 50 °C and Reaction time 2 hours.

Since kraft lignin contains α-carbonyl groups in side chains, hydroxymethyl groups can be also introduced side chains at C-ß by Tollens' reaction under the reaction conditions, in addition to C-5 of uncondensed guaiacyl groups, namely ortho to phenolic hydroxyl groups, by Lederer-Manasse reaction. In order to stop Tollens' reaction during the hydroxymethylation reaction, kraft lignin was treated with sodium borohydride in alkaline solution at pH 10 to reduce a α-carbonyl groups to corresponding α-hydroxyl groups. The resulting $NaBH_4$-reduced kraft lignin (RKL) was then hydroxymethylated under the optimal reaction conditions to obtain hydroxymethylated $NaBH_4$-reduced kraft lignin (HMRKL). The difference in the aliphatic hydroxyl contents between HMRKL and RKL, 0.33 mole $-CH_2OH$ per C_9-unit, can be regarded as the maximal degree of hydroxymethylation at C-5 of uncondensed guaiacyl moieties. Thus, the data given in Table 1 indicate that the hydroxymethylation of KL under the optimal reaction conditions resulted in the introduction of about 0.36 mole -CH_2OH per C_9-unit, of which about 0.33 uncondensed guaiacyl moieties. Thus, the data given in Table 1 indicate that the hydroxymethylation of KL under the optimal reaction conditions resulted in the introduction of about 0.36 mole -CH_2OH per C_9-unit, of which about 0.33 mole -CH_2OH per C_9-unit were introduced into C-5 of uncondensed guaiacyl moieties via Lederer-Manasse reaction. Only about 0.03 mole -CH_2OH per C_9-unit were introduced into side chains via Tollens' reaction.

Characterization of Hydroxymethylated Kraft Lignin by ^{13}C NMR Spectroscopy

In order to verify the results discussed in the previous section, kraft lignin, hydroxymethylated kraft lignin and ^{13}C-enriched hydroxymethylated kraft lignin were characterized further by ^{13}C NMR spectroscopy. The ^{13}C-enriched hydroxymethylated kraft lignin was prepared from kraft lignin by condensation with ^{13}C-enriched formaldehyde (about 7 ^{13}C-atomic %) under the optimal reaction conditions. Figure 3 shows ^{13}C NMR spectra of the kraft lignin preparations.

In the spectrum of kraft lignin (spectrum A), very strong signal 3 at 115.3 ppm corresponds to C-5 of uncondensed guaiacyl moieties. In the spectrum of hydroxymethylated kraft lignin (spectrum B), the intensity of signal 3 is greatly reduced, indicating presence of a substitutional group at C-5. Furthermore, the spectrum exhibits strong signals 1, 2 and 4 at δ 142.8, 128.4 and 58.4 ppm, respectively. The signal 4 corresponds to C-atom of -CH_2OH group substituted at C-5 of guaiacyl moieties, while signals 1 and 2 correspond to C-4 and C-5 of 5-hydroxymethylguaiacyl moieties. In addition, no visible change in the intensity of the signals in the oxygenated alkyl carbon region between 50-80 ppm can be observed in the spectrum. The spectrum of ^{13}C-enriched hydroxymethylated kraft lignin (spectrum C) is similar to that of hydroxymethylated kraft lignin, except for enhancement of the signal 4. Consequently, the signal is unequivocally assigned to the C-atom of -CH_2OH group in 5-hydroxymethylguaiacyl moieties.

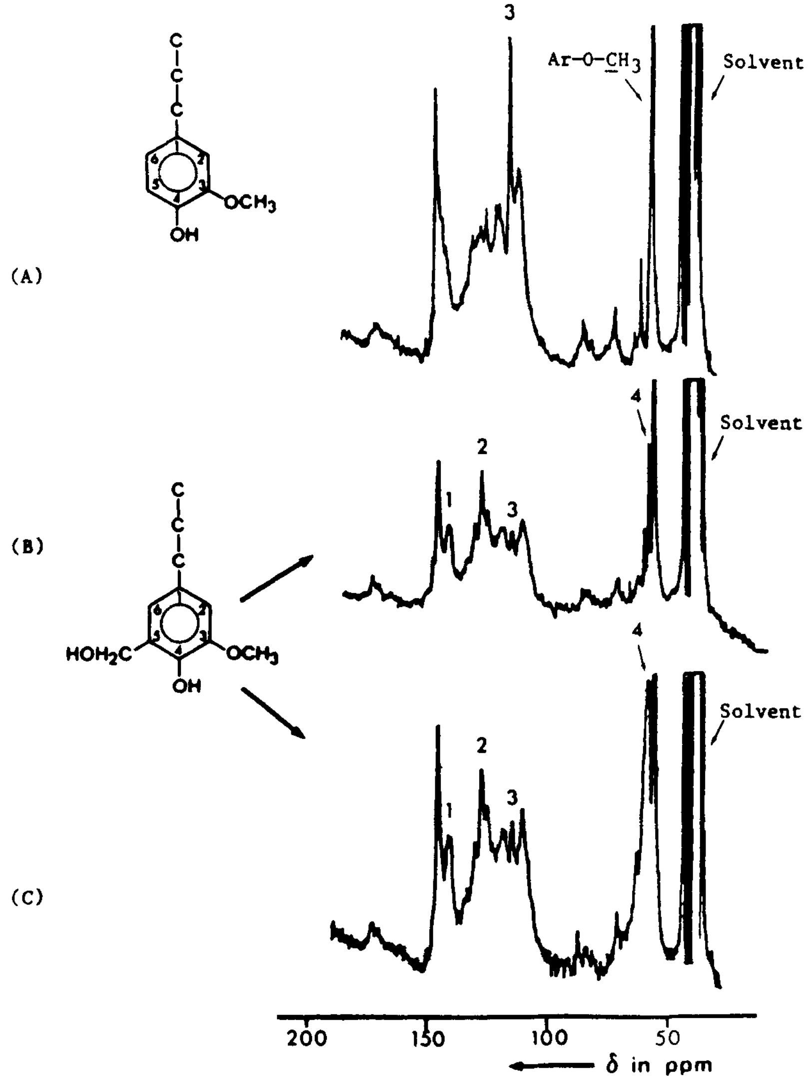

Figure 3. ^{13}C NMR Spectra of Kraft Lignin (A), Hydroxymethylated Kraft Lignin (B), and ^{13}C-Enriched Hydroxymethylated Kraft Lignin (C).

It is evident, therefore, that the hydroxymethylation of kraft lignin by formaldehyde predominantly proceeds via Lederer-Manasse reaction, resulting in introduction of hydromethyl groups into C-5 of uncondensed guaiacyl moieties in the lignin, and introduction of hydroxymethyl groups into side chains via Tollens' reaction is a minor reaction. The results of the ^{13}C NMR spectroscopic analyses are thus in good agreement with those of the hydroxyl content determinations.

Use of Hydroxymethylated Kraft Lignin-Phenol Adhesive Formulation for Fabrication of Wood Composites

Lignin-phenolic resins were formulated by blending hydroxymethylated kraft lignin (HMKL) produced under the optimal reaction conditions with phenol-formaldehyde resin (PF). Effects of process variables and wood variables during fabrication of wood composites were studied and evaluated.

Effect of HMKL/PF Ratio on Bond Strength

The HMKL was used in formulation of adhesive with or without phenol-formaldehyde resin for fabrication of laboratory particle boards made with sweetgum flakes, 5% resin content, hot press temperature of 410 °F, and press time of 6 minutes. Results are given in Table 2.

As expected, bond strength of laboratory boards increased as the phenol-formaldehyde resin content increased. A 50/50 (w/w) blending of HMKL/PF resulted in bond strength of about 65 psi in laboratory boards made with sweetgum flakes.

Effect of Wood Species on Bond Strength

The effect of wood species on bond strength of laboratory boards glued with the HMKL/PF resin (50/50, w/w) was studied. Results are given in Table 3.

Laboratory boards with satisfactory bond strength (i.e., exceeding the IB strength of 65 psi called for by U.S. commercial standard CS-236-66 for 2B1 board) were obtained when red oak, black gum, red maple, sweet bay, post

TABLE 2. Effect of HMKL/PF Ratio on Bond Strength*

HMKL/ PF (w/w)	pH	Panel Density (PCF)	IB (psi)
0/100	10.85	43	83
30/70	10.90	44	79
50/50	11.00	45	64
70/30	11.05	45	44
90/10	11.27	45	29
100/0	11.47	45	23

* Laboratory Boards made with Sweetgum Flakes; Resin Content, 5%; Hot Press Temp., 410 °F; Hot Press Time, 6 min.

Table 3. Effect of Wood Species on Bond Strength*

Wood Species	Panel Density (PCF)	IB (psi)
Red Oak	50	78
Black Gum	45	72
Red Maple	44	71
Sweet Bay	44	69
Post Oak	50	68
Sweetgum	45	67
Hickory	49	56
Ash	48	55
White Oak	48	50

* HMKL/PF Ratio, 50/50 (w/w); Resin content, 5%; Hot Press Temp., 410 °F; Hot Press Time, 6 min.

oakand sweetgum flakes were glued with the HMKL/PF resin. The board made with red oak flakes has a bond strength of about 78 psi, the strongest among the wood species investigated. Bond quality of laboratory boards made with hickory, ash and white oak flakes were slightly below the standard requirement. Nevertheless, rigorous separation of flakes by species is not likely in commercial practice, and in many situations a mixture of light and dense flakes would probably yield an acceptable board. The analysis is also supported by the data in that the overall average IB of the nine species is calculated to be at 65 psi.

Effect of Press Temperature and Press Time on Bond Strength

Studies were also conducted on effects of press temperature, hot press time, and resin content on bond quality of laboratory sweetgum boards using HMKL/PF resin with the ratio 50/50 (w/w) as adhesive. Results are give in Tables 4 and 5.

Evaluation of the effects of press temperatures and press times on bond strength indicated that combination of either lower press temperature with longer press time (i.e. 390 °F and 11 minutes) or higher press temperature with shorter press time (i.e. 410 °F and 8 minutes) resulted in satisfactory glue bond strength of laboratory board made with sweetgum flakes. Bond strength increased about 5% as resin content increased slightly from 5% to 7% with press temperature of 410 °C and press time of 8 minutes. Thus, the results indicated that the HMKL/PC resin could yield satisfactory boards with hot press temperature of 410 °F, hot press time of 8 minutes, and minimum resin content of 5%.

CONCLUSION

Hydroxymethylated kraft lignin (HMKL) with the optimal degree of hydroxymethylation of 0.36 mole -CH_2OH per C_9-unit can be obtained under mild reaction conditions: with HCHO/KL (C_9-unit) molar ratio of 1.1 at 0.1N NaOH solution at pH 12, reaction temperature of 50 °C and reaction time of 2 hours. More than 90% of the hydroxymethyl groups are introduced into C-5 of

TABLE 4. Effect of Press Temperature and Press Time on Bond Strength*

Press Temp. (°F)	Press Time (min.)	Panel Density (PCF)	IB (psi)
390	5	45	24
	8	44	57
	11	45	79
410	5	44	35
	8	46	71

* Laboratory Boards made with Sweetgum Flakes; HMKL/PF Ratio, 50/50 (w/w); Resin Content, 5%.

Table 5. Effect of Resin Content on Bond Strength*

Resin Content (%)	Panel Density (PCF)	IB (psi)
5	46	71
7	46	74

* Laboratory Boards made with Sweetgum Flakes; HMKL/PF Ratio, 50/50 (w/w); Resin Content, 5%; Hot Press Temp., 410 °F; Hot Press Time, 8 min.

uncondensed guaiacyl moieties in kraft lignin (KL) via Lederer-Manasse reaction, and the remainder into side chains via Tollens' reaction.

A lignin-phenol resin formulated by blending of HMKL/PF in the ratio 50/50 (w/w) was used for fabrication of laboratory boards made with flakes of various wood species. Laboratory boards with satisfactory average bond strength of 80-65 psi were obtained by glueing red oak, black gum, red maple, post oak and sweetgum flakes with the HMKL/PF resin in decreasing order of the average bond strength, process conditions being resin content of 5%, hot press temperature of 410 °F and hot press time of 6 minutes. Evaluations on effects of process variables indicate that the resin can yield satisfactory boards with hot press temperature of 410 °F, hot press time of 8 minutes, and minimum resin content of 5%.

EXPERIMENTAL

Purification of Kraft Lignin

Pine kraft lignin used in this investigation was obtained from the Westvaco Corporation, Charleston, S.C. The lignin was of grade "Indulin AT", an acidified lignin with approximately 40% solids and ash content of less than 1%.

Indulin AT (30 g) was stirred mechanically with 100 mL of distilled water. The solid mass was centrifuged off, again stirred mechanically with 100 mL distilled water and centrifuged off. This procedure was repeated two more times. The final solid mass was stirred mechanically with 100 mL distilled water and filtered off. The wet mass was thoroughly washed with distilled water and dried in an air-ciculated oven at 105 °C for 24 hours. The dried solid mass (9.0 g) was dissolved in 40 mL 96% aqueous dioxane, filtered off any insoluble materials, and dropped into 400 mL Et_2O under mechanical stirring. The PPT was centrifuged off, stirred mechanically with 50 mL distilled water, then centrifuged off. The final PPT was suspended in 50 mL distilled water and freeze-dried to give purified kraft lignin which was dried under vacuum over P_2O_5 at 50 °C. Yield, 7.9 g.

Purified KL (2 g) was acetylated with acetic anhydride-pyridin (1:1, *v/v*) (10 mL) at room temperature in the usual manner to obtain acetylated kraft lignin.

Elemental Analysis

Purified Kraft Lignin:

Found: C%, 63.95; H% 5.66; S%, 2.24; $OCH_{3\%}$, 14.10.

Calculated as $C_9H_{7.86}O_{2.41}S_{0.13}(OCH_3)_{0.84}$;

C_9-unit weight, 184.80

Acetylated KL:

Found: C%, 63.86; H% 5.52; S%, 1.48; OCH_3%, 11.29; $COCH_3$%, 23.79.

Calculated as $C_9H_{6.38}O_{2.12}S_{0.11}(OCH_3)_{0.84(COCH3)1.29}$

Reduction of Kraft Lignin with $NaBH_4$ in Alkaline Solution

To a solution of purified KL (5 g) in 25 mL 1N NaOH was added drop-wise a solution of $NaBH_4$ (1 g) in 10 mL 1 N NaOH at room temperature under mechanical stirring. The solution was then stirred for 48 hours at room temperature. The reaction mixture was acidified to pH 3, and the resulting PPT was centrifuged off. The PPT was stirred mechanically with 25 mL distilled water, then again centrifuged off. This procedure was repeated twice. The final PPT was suspended in 25 mL water and freeze-dried. The crude product was dissolved in 5 mL dioxane, filtered off any insoluble materials, and the filtrate was dropped into 25 mL distilled water under mechanical stirring, then freeze-dried. The purified product was dried under vacuum over P_2O_5 at 50 °C for 48 hours.

Hydroxymethylated of Kraft Lignin at Room Temperature

To a solution of 2 g purified KL in 11 mL 0.1N NaOH was added 1.3 mL 37% HCHO aqueous solution (= 0.475 g HCHO; HCHO/KL (C_9) molar ratio = 1.1). The resulting solution was adjusted to pH 12 with 1N NaOH, then mechanically stirred at room temperature for 30 minutes. The reaction mixture was acidified to pH 3. The PPT was centrifuged off, stirred mechanically with 20 mL water for 15 minutes and again centrifuged off. This procedure was repeated twice. The final PPT was dissolved in minimal amount of dioxane, filtered off any insoluble materials. The resulting solution was dropped into 30 mL water under mechanical stirring, then freeze-dried. The purified product was dried under vacuum over P_2O_5 at 50 °C for 48 hours. Yield, 1.7 g.

The same reactions were conducted for reaction times of 60, 120 and 240 minutes, and 24, 48 and 96 hours.

Each product was acetylated with acetic anhydride-pyridine (1:1, v/v) (10 mL) at room temperature in the usual manner. The acetylated products were used for determination of hydroxyl contents.

Hydroxymethylation of Kraft Lignin at 50 °C

Purified KL was treated with HCHO in the same manner described in the previous section, except for reaction temperature of 50 °C and reaction times of 15, 30, 60, 120 and 240 minutes. Each product was acetylated in the same manner described in the previous section.

Hydroxymethylation of Kraft Lignin at 50 °C with various HCHO/KL (C_9-unit) Molar Ratios

Purified KL was treated with HCHO and acetylated in the same manner as described in hydroxymethylation of kraft lignin at room temperature, except for reaction temperature of 50 °C, reaction time of 120 minutes, and HCHO/KL (C_9-unit) molar ratio of 0.3, 0.6, 1.1 and 1.6.

Hydroxymethylation of Kraft Lignin with ^{13}C-enriched HCHO

^{13}C-enriched HCHO (1 mL; 99 ^{13}C-atomic %, 20% aqueous solution) was diluted to about 7 ^{13}C-atomic % by adding to 7.03 mL 37% HCHO aqueous solution (= 2.568 g HCHO). The resulting solution is about 34.4% HCHO aqueous solution. To a solution of 2 g purified KL in 11 mL 0.1N NaOH was added 1.38 mL of the ^{13}C-enriched HCHO solution (= 0.475 g; HCHO/KL (C_9) molar ratio = 1.1). The resulting solution was adjusted to pH 12 with 1 N NaOH, then heated at 50 °C for 2 hours under mechanical stirring. The reaction mixture was treated in the same manner as described in hydroxymethylation of kraft lignin at room temperature to obtain purified ^{13}C-enriched hydroxymethylated kraft lignin.

Hydroxymethylation of $NaBH_4$-Reduced Kraft Lignin

To a solution of 2 g $NaBH_4$-reduced KL in 11 mL 0.1N NaOH was added

1.3 mL 37% HCHO aqueous solution (= 0.475 g; HCHO/KL (C_9) molar ratio 1.1). The resulting solution was adjusted to pH 12 with 1N NaOH, and heated at 50 °C for 2 hours under mechanical stirring. The reaction mixture was treated in the same manner as described in hydroxymethylation of kraft lignin at room temperature to obtain purified hydroxymethylated $NaBH_4$-reduced kraft lignin (HMRKL).

Hydroxyl Content Determination

Hydroxyl contents of lignin preparations were estimated from elemental analysis of acetylated kraft lignin and comparison of area ratio between acetyl regions of aromatic acetate δ 2.50-2.19 ppm and aliphatic acetate 2.19-1.70 ppm in PMR spectra of acetylated lignin preparations, using the PMR spectrum of acetylated kraft lignin as standard.

Hydroxymethylated Kraft Lignins Prepared at Room Temperature

Results of the PMR analysis of acetylated hydroxymethylated KLs are shown in Tables 6 and 7.

Hydroxymethylated Kraft Lignins Prepared at 50 °C

Results of the PMR analysis of acetylated hydroxymethylated KLs are shown in Tables 8 and 9.

^{13}C NMR Spectra of Kraft Lignin Preparation

^{13}C NMR spectra of kraft lignin preparations were obtained with a JEOL FX 60 Fourier transform spectrometer. Deuterated dimethylsulfoxide (DMSO-$\underline{d}_6$) was used as solvent. The spectra were run in 10 mm (I.D.) glass tube with concentration of the samples about 400 mg in 2 mL DMSO-$\underline{d}_6$. The signal for the CD_3 group of DMSO-$\underline{d}_6$ was locked to the spectrometer. The signal had a value of 39.634 ppm relative to tetramethylsilane (TMS) which was used as

TABLE 6. Areas in Regions δ 2.50-2.19 and 2.19-1.70 ppm in PMR Spectra of Hydroxymethylated Kraft Lignins Prepared at Room Temperature*

Reaction Times (Minutes)	Area		Area Ratio (2.19-1.70/ 2.50-2.19)
	2.50-2.19 ppm	2.19-1.70 ppm	
0	25.8	32.6	1.26
30	24.0	33.8	1.41
60	23.0	35.6	1.55
120	22.0	37.0	1.68
240	23.0	40.0	1.73

* Reaction Conditions: pH 12; HCHO/KL (C_9) Molar Ratio = 1.1

TABLE 7. Hydroxyl Contents of Hydroxymethylated Kraft Lignins Prepared at Room Temperature* (per C_9-unit)

Reaction Times (Minutes)	Phenolic OH	Aliphatic OH	Aliphatic OH Introduced**
0	0.57	0.72	----
30	0.57	0.80	0.08
60	0.57	0.88	0.18
120	0.57	0.96	0.24
240	0.57	1.00	0.28

* According to Elementary Analysis, Purified Kraft Lignin has the Total Hydroxy Content of 1.29 Mole -OH per C_9-unit, hence the Phenolic and Aliphatic OH Contents of the Lignin are 0.57 and 0.72 Mole -OH per C_9-unit on the basis of the Area Ratio in Table 6, respectively; Aliphatic OH Content = 0.57 x Area Ratio.

** Aliphatic OH Introduced = Degree of Hydroxymethylation.

TABLE 8. Areas in Regions δ 2.50-2.19 and 2.19-1.70 ppm in PMR Spectra of Hydroxymethylated Kraft Lignins Prepared at 50 °C*

Reaction Times (Minutes)	Area		Area Ratio (2.19-1.70/ 2.50-2.19)
	2.50-2.19 ppm	2.19-1.70 ppm	
0	25.8	32.6	1.26
15	21.8	37.0	1.70
30	21.2	37.6	1.77
60	21.4	40.6	1.90
120	19.6	37.4	1.91
240	20.4	38.6	1.89

* Reaction Conditions: pH 12; HCHO/KL (C_9) Molar Ratio = 1.1

TABLE 9. Hydroxyl Contents of Hydroxymethylated Kraft Lignins Prepared at 50 °C* per C_9-unit)

Reaction Times (Minutes)	Phenolic OH	Aliphatic OH	Aliphatic OH Introduced**
0	0.57	0.72	----
15	0.57	0.97	0.25
30	0.57	1.01	0.29
60	0.57	1.08	0.36
120	0.57	1.09	0.37
240	0.57	1.08	0.36

* According to Elementary Analysis, Purified Kraft Lignin has the Total Hydroxy Content of 1.29 Mole -OH per C_9-unit, hence the Phenolic and Aliphatic OH Contents of the Lignin are 0.57 and 0.72 Mole -OH per C_9-unit on the basis of the Area Ratio in Table 6, respectively; Aliphatic OH Content = 0.57 x Area Ratio.

** Aliphatic OH Introduced = Degree of Hydroxymethylation.

internal reference. Data acquisition time was 1.0240 sec (pulse width: 10 μsec) with pulse repetition time of 2 sec. Number of accumulation was about 20,000 and the average accumulation time to obtain a lignin spectrum was about 17 hours.

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