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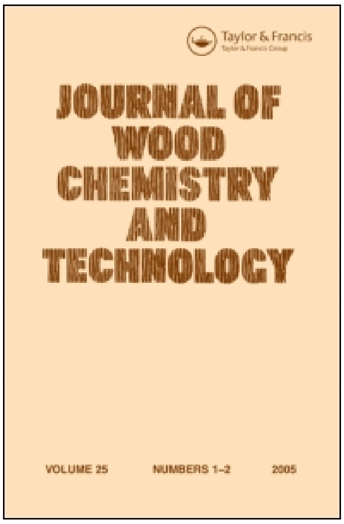

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CHARACTERIZATION OF METHYLOLATED LIGNIN BY H-NMR AND ^{13}C-NMR

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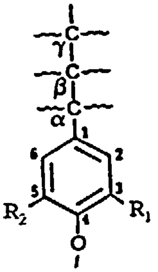
ABSTRACT

The hydroxymethylation of an ammonium based lignosulfonate (ALS) was done in the presence of alkali. In terms of their chemical structures, lignin and lignin derivatives were characterized and quantified by H-NMR and ^{13}C-NMR spectroscopy. Results indicate that two kinds of hydroxymethyl groups can be formed in the process of lignin methylolation. One kind is adjacent to the aromatic ring, the other is adjacent to the side chain. The amount of hydroxymethyl groups increases and of aromatic protons decreases with increasing methylolation time and levels off after 3 hours.

INTRODUCTION

Lignins are polydisperse, crosslinked, three-dimensional macromolecules made of phenylpropane (C9) units. Their main structural characteristics[1] are showed as follows:



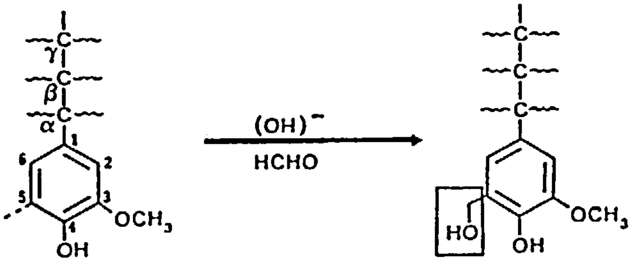
Guaiacyl: R_1=OCH_3, R_2=H

Syringyl: R_1=R_2=OCH_3

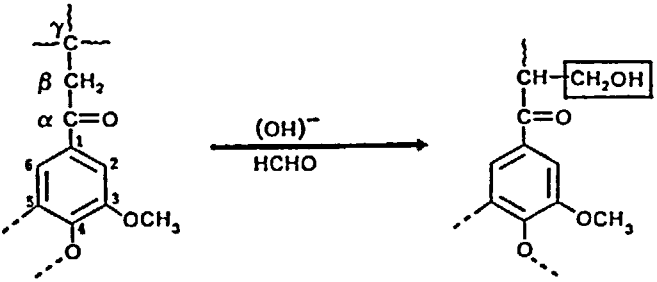
Lignins have several important chemical and physical properties. It is possible to prepare lignin derivatives that are useful prepolymers[2]. Methylolated lignin is one of the most important lignin derivatives. As early as 1929, Ross and Hill observed that lignin could react with formaldehyde[3]. A great deal of research has been published in characterization of lignins and lignin derivatives[4-6], NMR spectrocopy appears as the most successful analytical tool. This paper deals with the use of H-NMR and ^{13}C-NMR to evaluate the degree of methylolation of lignin.

An ammonium based lignosulfonate (ALS) whose phenylpropane structural unit is mainly guaiacyl was used since it is easily dissolved in water. When guaiacyl lignin is mixed with formaldehyde in the presence alkali, generally, two types of methylolation reaction are expected to occur between lignin and formaldehyde[7,8].

(A) Introduction of hydroxymethyl groups into the 5-position of the aromatic ring as illustrated by the following equation.



(B) Hydroxymethyl groups can be introduced into the neighboring position of the carbonyl groups or the double bonds by substituting their activated hydrogen atoms (Tollens reaction).



EXPERIMENTAL

Methylolation of Lignin (ALS)

ALS (31.1 g) was dissolved in 60 mL of 8% sodium hydroxide solution. This solution was kept at 80 °C for 75 min, then cooled down to 50 °C, and 13 g of formaldehyde solution (37%) were added slowly. The solution was kept at 50 °C with continuous stirring for 1, 3 and 5 h, respectively, to complete the methylolation reaction.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The reaction mixtures were freeze-dried, and grinded to powder. The samples were examined at a concentration of 10-12% in DMSO-d6. H-NMR spectra and ^{13}C-NMR spectra were recorded with a XL-200 Varian spectrometer, set at 200 MHz to obtain H-NMR spectra and at 50 MHz to obtain ^{13}C-NMR spectra. In both cases spectra were recorded at 25 °C.

Determination of Free Formaldehyde[9]

The reaction mixture (2-3 g) was added to 100 mL of water and cooled to 4 °C as solution A; 25 mL of Na_2SO_3 solution (1M) with 10 mL of HCl solution (1N) were cooled to 4 °C as solution B. 10-15 drops of thymolpthaleine solution (0.01%) were added to the solution A as indicator. The color was adjusted by using 0.1N HCl solution. Solution B was mixed with solution A and back-titrated by 1N NaOH solution.

DATA TREATMENT

Proton NMR Spectra[10, 11]

a. The percentage of aromatic protons in lignin, C, can be calculated from the following equation:

$$\frac{A}{B} \times 100\% = C \qquad (1)$$

where:

A: average number of aromatic protons before methylolation (there are 2.6 armatic protons in ALS[12]), per C9 unit

B: average number of all protons (including protons of OCH_3 and others) before methylolation, per C_9 unit

b. Calculation of the degree of lignin methylolation in aromatic ring from loss of aromatic protons H-NMR signal (range 1, as defined in Fig. 2)

After methylolation, the percentage of aromatic protons in lignin, Y_1, is given by the following expression:

$$\frac{A - X_1}{B + 2(X_1 + X_2)} \times 100\% = Y_1 \qquad (2)$$

where:

X_1: number of aromatic protons reacted with formaldehyde per C_9 unit

X_2: number of active protons on the side chain reacted with formaldehyde per C_9 unit

The loss of one aromatic proton or one active proton in the side chain will create three new protons ($-CH_2OH$). Thus, X_1 aromatic protons and X_2 active protons in the side chain reacting with formaldehyde can form $3(X_1 + X_2)$ new protons. The number of protons in the whole C_9 unit will be $B + 3(X_1 + X_2) - (X_1 + X_2)$, which is equal to $B + 2(X_1 + X_2)$, after methylolation.

c. The degree of methylolation on the aromatic ring can also be calculated from the increase of methylene protons H-NMR signal (range 3, as defined in Fig. 2) of hydroxymethyl groups in aromatic ring

After methylolation, the percentage of methylene protons of hydroxymethyl groups adjacent to aromatic ring, Y_2, is given by the following expression:

$$\frac{2X_1}{B + 2(X_1 + X_2)} \times 100\% = Y_2 \qquad (3)$$

The same method is used to calculate the degree of methylolation in the side chain.

RESULTS AND DISCUSSION

Amount of Formaldehyde

The amount of formaldehyde in the methylolation solution of lignin is inversely related to the degree of methylolation. The higher the effectiveness of the methylolation is, the less the amount of formaldehyde in the solution is. Fig. 1 presents the relation of the amount of formaldehyde in the methylolation solution

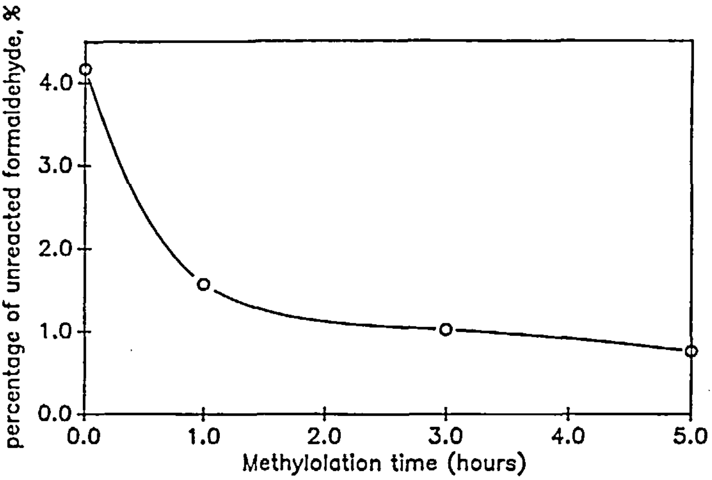


FIGURE 1 The relation between the amount of free formaldehyde in the methylolation solution and methylolation time

TABLE 1
The Degree* of Hydroxymethylation of ALS in the Aromatic Ring as Calculated with Different Methods

methods	1 hour	3 hours	5 hours
unreacted formaldehyde	0.83	1.00	1.05
increase of methylene protons of hydroxymethyl groups in aromatic ring from H-NMR	0.43	0.99	1.01
loss of aromatic protons from H-NMR	0.70	0.96	0.96

* number of aromatic protons reacted with formaldehyde per C_9 unit.

vs methylolation time. It shows that the amount of formaldehyde decreases with the increase of the methylolation reaction time and, inversely, the amount of methylolation increases with increase of the reaction time. After one hour of reaction, more than half of formaldehyde has been consumed. After 3 hours, this amount almost levels off. This shows that it is not necessary to methylolate the ALS for a period of time longer than 3 hours in the condition used here.

The degree of methylolation obtained by subtracting the formaldehyde in methylolation solution from the initial formaldehyde added into the solution is listed in Tab. 1. Due to the fact that the amount of formaldehyde cannot give a very precise indication about the position of methylolation, NMR spectrocopy appears to be a suitable technique which can give better information concerning these questions.

Proton NMR Spectra

The proton NMR spectra of lignin (ALS) and methylolated lignins (MALS) are showed in Fig. 2. The assignments of peaks, based on results as reported in the literature[10, 13, 14], are summarized in Tab. 2. These illustrate the existence of aromatic protons, side chain groups, methoxyl groups and double bond or carbonyl groups in lignin, which agrees with results reported in the literature.

Comparing the curves in Fig. 2, one can find that the percentage of protons in range 1 decreases, the percentage of protons in range 5 increases while other ranges are little affected after lignin is mixed with NaOH. Possibly, these come from the effect of ammonium groups in lignin. After methylolation, the peak due to protons adjacent to the double bonds or to the carbonyl groups at (1.8-2.3 ppm) and those associated to aromatic protons (>6.0 ppm) decrease and there appears some new peaks at 3.18 ppm, 3.22 ppm, 3.28 ppm and 4.55 ppm.

Because hydroxyl groups are always strongly affected by D_2O, the methylolated sample has been treated with D_2O before the NMR scan. Following this, only the peak at 3.28 ppm is shifted to 4.18 ppm, indicating that it is associated to hydroxyl protons. Comparing with the standard spectra of products with structures encountered in lignin reported by Aldrich Inc.[15], the peaks at 3.18 ppm and 3.22 ppm belong to the methylene protons of hydroxymethyl groups adjacent to the side chain while the peak at 4.55 ppm is related to the methylene proton of hydroxymethyl group adjacent to the aromatic ring.

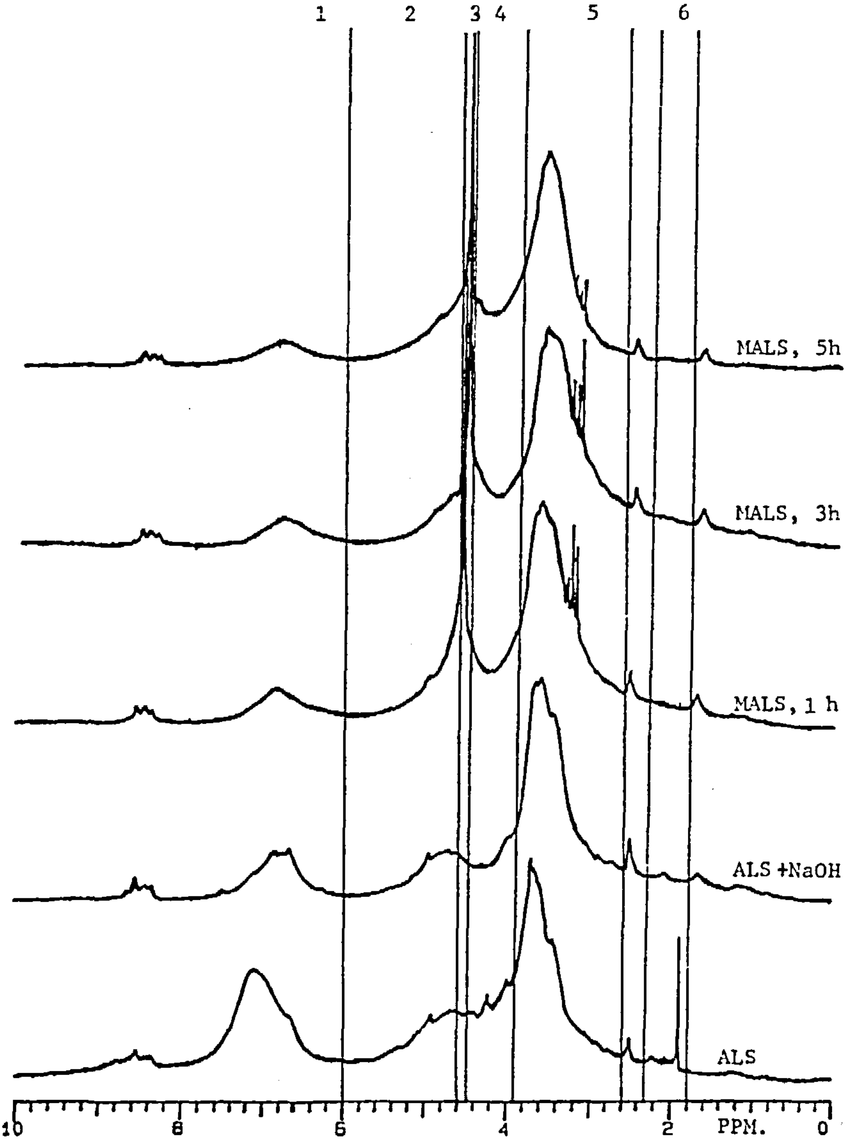


FIGURE 2 The proton NMR spectra of ALS (ammonium based lignosulfonate), ALS +NaOH and MALS (methylolated ammonium based lignosulfonate) after 1, 3 and 5 h methylolation, respectively, in DMSO-d_6 with ranges 1-6

TABLE 2
Protons Assignments and Distribution
of Lignin and Lignin Derivatives from H-NMR Spectra

Characteristics (ppm)	Percentage of protons,				
	ALS	ALS+NaOH	MALS,1h	MALS,3h	MALS,5h
range 1, aromatic protons (>6.0)	28.2	16.8	11.1	9.3	9.4
range 2, protons in side chain (4.6-6.0)	11.0	11.9	13.9	9.6	13.4
range 3, methylene protons of hydroxymethyl groups adjacent to aromatic ring, protons in the side chain (4.5-4.6)	1.5	1.5	6.4	11.0	11.4
range 4, protons in the side chain (3.9-4.5)	14.0	11.2	14.1	14.2	15.6
range 5, methoxyl protons, protons in the side chain (2.6-3.9)	42.4	55.2	51.9	53.3	48.9
methylene protons of hydroxymethyl group adjacent to side chain					
3.14-3.2	(1.2)	(1.5)	(1.9)	(2.3)	(1.9)
3.2-3.26	(1.1)	(1.5)	(2.6)	(2.3)	(1.6)
hydroxyl protons 3.26-3.3	(1.4)	(1.2)	(2.0)	(2.4)	(1.9)
range 6,methyl or methylene, protons adjacent to double bonds or carbonyl groups (1,8-2.3)	3.0	3.4	2.6	2.6	1.3

* The peaks at 2.3-2.6 ppm and 1.5-1.8 ppm belong to DMSO-d_6

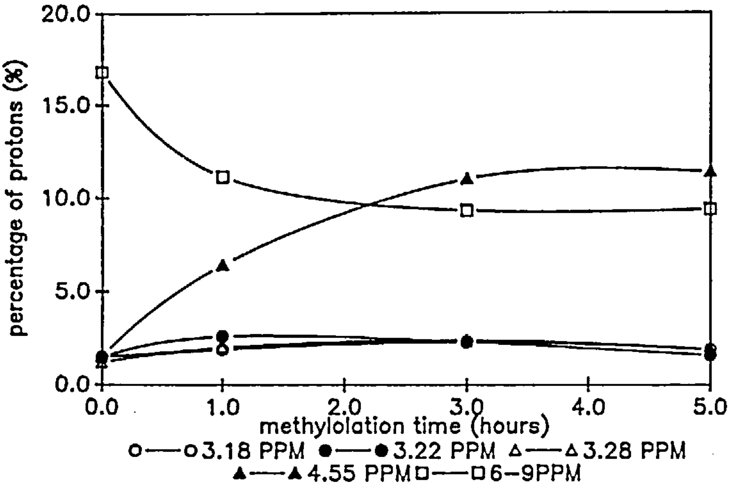


FIGURE 3 The relation between the amount of some important protons and methylolation time, from H-NMR

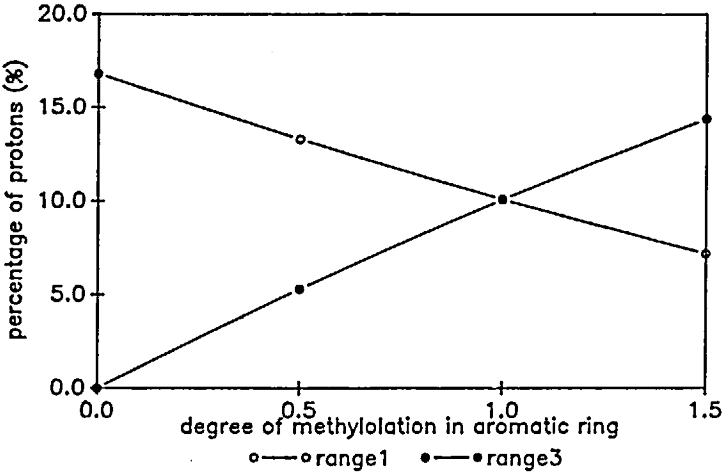


FIGURE 4 The calculated curves of degree of hydroxymethylation in the aromatic ring from the loss of aromatic H-NMR signal or the increase of H-NMR signal in methylene protons adjacent to the aromatic ring

The variation of the percentage of protons associated to methylolation as a function of the methylolation reaction time is represented in Fig. 3. As one can see from this figure, an increase of hydroxylmethyl groups content (at 3.18, 3.22, 3.28 and 4.55 ppm) with the increase of the reaction time is observed at up to 3 hours, after which time, all curves level off. Curve 5 shows the variation of the aromatic protons (>6 ppm) signal intensity vs the reaction time. It decreases as the methylolation reaction time increases and also levels off after 3 hours, as observed with the previous signal at 4.55 ppm and with amount of formaldehyde.

Degree of the Methylolation on the Aromatic Ring

Due to the fact that MALS contains NaOH, the mixture of ALS with NaOH was used as reference to calculate the degree of lignin methylolation. The number of all protons in C_9 unit, B, calculated from equation (1), is 15.65. The calculated curves of the degree of methylolation on aromatic ring obtained from equations 2 and 3 are showed in Fig. 4. From this figure, the degree of methylolation on the aromatic ring can be obtained by extrapolating the integration of range 1 or range 3. They are summarized in Tab. 1.

Comparing the data in Tab. 1, one can see that all results from these different methods of calculation have the same trend. The degree of hydroxymethylation increases with increase of the methylolation reaction time. After 3 h, for one C_9 unit, almost one aromatic proton was methylolated. It means that the methylolation of ALS is complete in this case. The results obtained from the remaining amount of formaldehyde seems somewhat higher than those obtained from the other methods mentioned above. Because some formaldehyde may react with active protons in the side chain, the degree of the methylolation on aromatic ring calculated from amount of formaldehyde is less precise.

Degree of Methylolation in the Side Chain

There are some active protons in the side chain as evidenced by H-NMR. The same method (H-NMR signal) was used to calculate the degree of hydroxymethylation in the side chain by calculating the loss of protons adjacent to carbonyl groups or to the double bonds, or by calculating the increase of methylene protons of hydroxymethyl groups in the side chain.

The number of active protons in the side chain per C_9unit in lignin is 0.53, as caculated from equation (1), by using (ALS + NaOH) as reference. The degree of methylolation calculated by using

TABLE 3
The Degree* of Hydroxymethylation of ALS in the Side Chain as Calculated with Different Methods from H-NMR

methods	1 hour	3 hours	5 hours
increase of methylene protons of hydroxymethyl groups in the side chain	0.15	0.16	0.05
loss of active protons in the side chain	0.09	0.09	0.34

* number of active protons in the side chain reacted with formaldehyde per C_9 unit.

TABLE 4
Assignments of ^{13}C-NMR Spectra and Intensity Ratio (peak at 55.6 ppm is used as reference)

Characteristics (ppm)	Intensity ratio			
	ALS	MALS,1h	MALS,3h	MALS,5h
179.0, carbon atoms of carbonyl	--	--	--	--
147.5, C-4 in guaiacyl	--	--	--	--
142.7, C-1 in guaiacyl ether	--	--	--	--
123.4, C-3/C-5 in β-hydroxyphenyl unit, C-6 in guaiacyl	--	--	--	--
114.3, C-5 in guaiacyl	--	--	--	--
88.7, Carbon atoms of $(CH_2O)_2H$ adjacent to aromatic ring	0	0.65	0.57	0.26
80.5, C-α in β-O-4 with α-C=O	0.37	0.43	0.37	0.32
73.8, carbon atoms of hydroxymethyl groups adjacent to aromatic ring	0.47	5.01	8.27	8.83
72.4, C-α in β-O-4 unit	0.78	0.58	0.60	0.58
71.2, carbon atoms of hydroxymethyl groups adjacent to the side chain	0.58	1.09	1.09	1.16
65.6, C-γ, C-β in β-O-4 unit	0.34	0.43	0.52	0.54
63.2, carbon atoms of hydroxymethyl groups adjacent to the side chain	0.47	0.54	0.72	0.96
61.6, C-γ, C-β in β-O-4 unit	0.51	0.47	0.46	0.54
55.6, carbon atoms of OCH_3	--	--	--	--

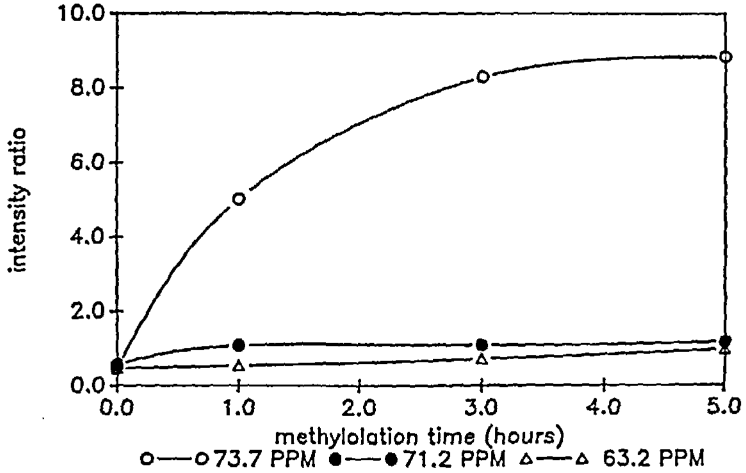


FIGURE 5 The relation between intensity ratio (peak at 55.6 ppm taken as reference) and methylolation time, from ^{13}C-NMR

equations similar to equations 2 and 3 is listed in Tab. 3. It shows that the degree of methylolation in the side chain is much lower than that in aromatic ring. As observed by Marton et al[7], in lignin methylolation, the reaction of formaldehyde with aromatic protons is easiler than with active protons in the side chain in alkaline condition.

13C-NMR Spectra

The peaks assignment based on reported results[13,16,17] of ^{13}C-NMR of the non-methylolated lignin are summarized in Tab. 4. It confirms the existence of aromatic ring, β-O-4 structure, methoxyl groups and carbonyl groups. These results agree well with the proton NMR spectra result summarized in Tab. 2.

As in the case of proton NMR spectra, ^{13}C-NMR spectra also reveals some changes after lignin methylolation. Due to the fact that methoxyl groups are not affected by the methylolation reaction of lignin[10], the peak at 55.6 ppm related to methoxyl groups was used as reference in the calculation of peaks height ratio. Tab. 4 presents these values for the non-methylolated as well as for the methylolated lignins. It shows that there is a new peak at 73.8 ppm after methylolation. This peak at 73.8 ppm is related to the carbon atoms of hydroxymethyl groups connected to the aromatic ring. The peaks at 71.2 ppm and 63.2 ppm increases in a lesser extent. They are related to carbon atoms of hydroxymethyl groups connected to the side chain. Fig. 5 shows the variation of peaks intensity ratio at 73.8 ppm, 71.2 ppm, 63.2 ppm vs the methylolation reaction time, respectively. They increase in intensity ratio with the increase of methylolation reaction time up to 3 hours after which it remains almost constant as observed from H-NMR.

CONCLUSION

1. The chemical characterization of the lignin and methylolated lignin can conveniently be performed by H-NMR and ^{13}C-NMR spectroscopy.
2. ALS can react with formaldehyde to form lignin derivative with hydroxymethyl groups. In the process of methylolation of ALS, two kinds of hydromethyl groups can be formed. One kind is adjacent to the aromatic ring and the other to the side chain; but the methylolation of aromatic ring is the main reaction.
3. The degree of hydroxymethylation have been calculated by amount of formaldehyde and by H-NMR. All results obtained agree well with each other and indicate an increase of the degree of the methylolation, as the methylolation reaction time increases, and levels off after 3 h of reaction.

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