Study on the Kinetics of Lignin Methylolation

W. PENG, B. RIEDL,* and A. O. BARRY

Centre de Recherche en Science et Ingénierie des Macromolécules, Département des Sciences du Bois, Faculté de Foresterie et de Géomatique, Université Laval, Ste-Foy, Québec, Canada G1K 7P4

SYNOPSIS

The kinetics of lignin (ammonium-based lignosulfonate and sodium-based lignosulfonate) methylolation were studied in solution by monitoring the rate of disappearance of formaldehyde and by using differential scanning calorimetry (DSC) techniques under an isothermal program, at 20, 40, 50, and 60°C, respectively. The kinetic parameters obtained from these two methods agree with each other. The results show that the degree of lignin methylolation depends on the number and availability of reactive sites per C_9 unit of lignin. Lignin methylolation has a lower activation energy and a lower preexponential factor than that of phenol methylolation. Lignins took a shorter time to reach complete methylolation than did phenol at the low temperatures used here. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Large volumes of wood composites are bonded with phenol–formaldehyde (PF). Since the increase in the cost of petrochemicals renders PF resin expensive, a way to reduce its relatively high cost is sought by industry.[1] Lignin is a renewable byproduct of the pulp industry. Its structure is similar to that of PF resin and much less expensive than PF.[2] Many studies have been done in the field of replacement of PF with lignin or lignin derivatives.[3-6] Methylolated lignin is one of the most important derivatives of lignin. More information is needed regarding the lignin–formaldehyde (LF) reaction and the PF–LF reaction. The kinetics of lignin methylolation has not been studied much. In 1988, Gardner and Moginnis[7] studied the methylolation rate and kinetic parameters of kraft lignin and steam-exploded lignin by monitoring the rate of disappearance of formaldehyde. These authors postulated the reaction of phenol molecules or C_9 units (both aromatic cycle and side chain) of lignin with formaldehyde as a second-order reaction. Generally, the reaction of phenol or phenol derivative molecules with formaldehyde is taken as second-order in the kinetic studies of their methylolation that have been done

by monitoring the rate of disappearance of phenol or phenol derivatives.[8-10] It is also possible to postulate the reaction of the active aromatic protons in phenol or phenol derivarives with formaldehyde as second-order by monitoring the rate of disappearance of formaldehyde.[11-15] The aim of this paper was to study the kinetics of ammonium-based lignosulfonate (ALS) and sodium-based lignosulfonate (SLS) methylolation, with the reaction of the functional groups in lignins with formaldehyde taken as a second-order reaction, by monitoring the rate of disappearance of formaldehyde and by isothermal DSC techniques.

EXPERIMENTAL

Methylolation of Lignin

Lignin, 46.65 g, was dissolved in 103.9 g of 6.69% sodium hydroxide solution. This solution was kept at 80°C for 75 min, then cooled down to 20, 40, 50, and 60°C, respectively. To keep constant the pH value of the lignin solution during methylolation, a buffer solution was employed by using $NaHCO_3$ to adjust the pH value to 10.5. Formaldehyde solution, 19.5 g (38.5%), was added. The solution was kept at these temperatures with continuous stirring. The amount of formaldehyde in the solution was measured periodically during lignin methylolation.

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* To whom correspondence should be addressed.

Determination of the Amount of Formaldehyde in Solution[16]

Two to three grams of the reaction mixture 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 ($1N$) was cooled to 4°C as solution B. Thymolpthaleine solution, 10–15 drops (0.01%), were added to solution A as indicator. The color was adjusted by using $0.1N$ HCl solution. Solution B was mixed to solution A and back-titrated by $1N$ NaOH solution.

Nuclear Magnetic Resonnance (NMR) Spectrometry

The reaction mixtures were freeze-dried and ground to powder. The samples were scanned at a concentration of 10–12% in DMSO-d_6. H-NMR spectra were recorded with an XL-200 Varian spectrometer at 200 MHz, 25°C.

Elemental Analysis Techniques

Elemental analysis was done with an elemental analyzer, Model 1106 (Carlo Erba). The amount of C, H, and N in the sample can be measured by this method.

Differential Scanning Calorimetry (DSC) Technique under Isothermal Program

The isothermal DSC technique also was used to study lignin methylolation. A 5–10 mg sample of solution was put into an aluminum pan for 120 min in a Mettler thermal analyzer, DSC-20. The temperature was set at 40, 50, and 60°C, respectively.

CALCULATION OF KINETIC PARAMETERS[17–20]

Reactant Concentration Monitoring

For a reaction A + B → C, if the reaction order is 2 and reaction temperature is T, the reaction rate is as follows:

$$-d[A]/dt = k(T)[A][B] \qquad (1)$$

where $k(T)$ is the rate constant at temperature T; $[A]$ and $[B]$ are the molar concentration (mol/L) of A and B, respectively; and t is time (min).

To integrate eq. (1), it is convenient to define a progress variable x that measures the progress of the reaction to products as follows:

$$x = ([A]_0 - [A]_t) = ([B]_0 - [B]_t) \qquad (2)$$

where $[A]_0$ is the initial concentrations of reactant A; $[B]_0$, the initial concentrations of reactant B; $[A]_t$, the concentrations of reactant A at time t; and $[B]_t$, the concentrations of reactant B at time t.

The rate expression given by eq. (1) can then be rewritten in terms of x as

$$dx/dt = k(T)([A]_0 - x)([B]_0 - x) \qquad (3)$$

Equation (3) may be replaced by the standard integrated expression for a second-order reaction:

$$\frac{1}{([A]_0 - [B]_0)} \ln \frac{[B]_0[A]_t}{[A]_0[B]_t} = k(T)t \qquad (4)$$

In terms of eq. (4), the rate constant $k(T)$ can be yielded by plotting the left-hand side of eq. (4) against t.

Isothermal DSC Model

The reaction rate can be also ascertained by DSC techniques. In the isothermal method, the nth-order model assumes that the reaction rate obeys the following equation[21–23]:

$$d\alpha/dt = k(T)(1 - \alpha)^n \qquad (5)$$

where α is the fractional conversion after time t.

The rate constant and reaction order can be obtained, respectively, from the intercept and the slope of a log ($d\alpha/dt$) vs. log($1 - \alpha$) plot.

The parameters ($d\alpha/dt$ and α) can be obtained from the DSC exotherm. The reaction rate is obtained by dividing the peak height, dH/dt, at time t by the total heat of reaction, ΔH_0:

$$d\alpha/dt = (dH/dt)/\Delta H_0 \qquad (6)$$

The value of α is determined by measuring the partial heat of reaction up to time t, ΔH_p, and dividing by the total heat of the reaction:

$$\alpha = \Delta H_p/\Delta H_0 \qquad (7)$$

Finally, at least three isothermal runs are required to obtain kinetic parameters.

Arrhenius Relation

Reaction rate constant $K(T)$ can be treated by an Arrhenius relation:

$$k(T) = Ae^{-Ea/RT} \qquad (8)$$

where $k(T)$ is the reaction rate constant at temperature T; A, the preexponential factor; Ea, the activation energy; T, the reaction temperature; and R, the gas constant. A and Ea can be obtained by plotting $\ln k$ against $1/T$, where the slope is Ea and the intercept is A.

RESULTS AND DISCUSSION

Degree of ALS and SLS Methylolation

The chemical composition of lignin obtained by elemental analysis and NMR spectra[24] are listed in Table I. Table I shows that, for every C_9 unit, ALS has 1.1 aromatic protons at position 3 and 5, whereas SLS has 0.9. Figure 1 gives the relationship between the degree (number of hydroxymethyl groups in aromatic ring formed by methylolation, calculated by using the amount of reacted formaldehyde) of ALS and SLS methylolation with methylolation time at 50°C. The results show that, because ALS has more active aromatic protons than does SLS, it has a higher degree of methylolation per C_9 unit.

Table I   Analysis Results of Lignins (ALS, SLS)

Properties	ALS	SLS
Lignin content[a,b] (%)	62.32	63.36
Molecular weight per C_9 unit[b]	150.8	163.6
Carbohydrates[a] (%)	10.13	15.63
Humidity (%)	6.39	4.14
N (%)	4.64	0.00
C (%)	43.84	35.22
H (%)	5.60	4.46
OCH$_3$ (%)[a]	5.62	6.42
Molar ratio of aromatic protons with OCH$_3$ groups	4.97	3.00
No. of OCH$_3$ groups per C_9 unit	0.53	0.90
No. aromatic protons per C_9 unit	2.63	2.70
No. aromatic protons at 3 and 5 positions per C_9 unit	1.1	0.9

[a] Ref. 25.
[b] Sulfonate groups and salt counterion are not included in the calculation.
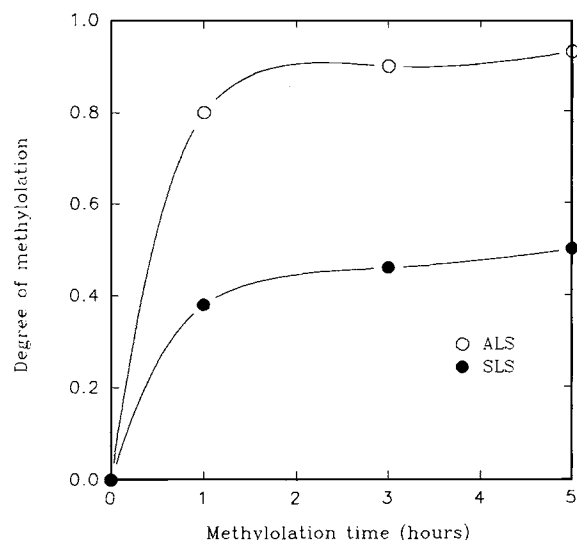

Figure 1 The degree of methylolation (no. protons methylolated, per C_9 unit) of ALS and SLS vs. methylolation time at 50°C.

Study of Kinetics of Lignin Methylolation by Monitoring the Rate of Disappearance of Formaldehyde

When lignin methylolation is done in alkaline conditions, generally two types of reaction are expected to occur[26,27]: (A) Hydroxymethyl groups are introduced into position 3 and, to a lesser extent, into position 5 of the aromatic ring. (B) Since there are carbonyl groups or double bonds in various positions of the side chain of the lignin, hydroxymethyl groups can also be introduced into the neighboring position by substituting their active hydrogen atoms. The main methylolation reaction still occurs on the aromatic ring[26] where the number of reactive aromatic protons is much higher than that in the side chain. For simplicity, only the reactive aromatic protons in lignin are thought of as functional groups to calculate apparent kinetic parameters of lignin methylolation.

Table II lists reaction components and respective amounts in the methylolation reaction media of phenol, ALS, and SLS. The variation of formaldehyde concentration in ALS, SLS, and phenol methylolation solution with methylolation time at 60°C is showed in Figure 2. A control experiment with only formaldehyde in the buffer solution (blank) shows that the concentration of formaldehyde does not change with time. This means that almost no Cannizzaro reaction occurs and no formaldehyde is lost to atmosphere under the experimental reaction conditions chosen. Therefore, the decrease of the

Table II   Reaction Components of Methylolation of Lignin and Phenol

Name	Weight[a] (g)	Molecule (mol)	Reactive Site (mol)[b]	NaOH (g)	NaHCO$_3$ (g)	Formaldehyde (g)	(mol)	pH
Phenol	15.1	0.161	0.483	2.5	1.8	19.5	0.25	10.5
ALS	46.65	0.193	0.212	6.95	5.0	19.5	0.25	10.5
SLS	46.65	0.181	0.162	6.95	10.0	19.5	0.25	10.5

[a] ALS and SLS contain humidity and other substances, as given in Table I.

[b] A phenol molecule has 3 reactive aromatic protons, ALS has 1.1 reactive aromatic protons per C$_9$ unit, and SLS has 0.9 reactive aromatic protons.

formaldehyde concentration in the lignin-formaldehyde solution can be assumed to be the amount of formaldehyde reacted.

The data in Figure 2 were treated by using the integrated expression of a second-order reaction [eq. (4)]. Figure 3 was obtained by plotting the left of eq. (4) vs. reaction time. Observing Figure 3, one finds that, at initial 5 min, the curve slope in lignin methylolation is higher than that at longer times. However, this phenomenon is absent in phenol methylolation. This illustrates that lignin has a fast initial reaction. This initial reaction is too fast to calculate its kinetic parameters in the fashion done in this case. Also, it is difficult to explain what kind of reaction occurred in this period. Gardner and Moginnis[7] observed this phenomenon. These authors think that this might be due to the catechol structure formed during the pulping procedure. Neat catechol reacted under these reaction conditions

showed an initial uptake (5 min) of formaldehyde, which was faster than with phenol and slower than with kraft lignin.[7] Lignosulfonates do not have catechol-like structure, but also show this phenomenon.

The points in Figure 3 follow a straight line, except for the initial 5 min in lignin methylolation. Similar results were obtained at other temperatures. Thus, the kinetic data of phenol and lignin methylolation follow a second-order reaction relation, and it is suitable to treat those data by eq. (4). The kinetic data, except at initial period 0–5 min in lignin methylolation, are used to calculate the reaction rate constant $k(T)$.

Good linear relations are yielded when plotting ln $k(T)$ (obtained from monitoring the disappearance of formaldehyde) against $1/T$ (Fig. 4). The slope obtained is the activation energy, Ea, whereas the intercept obtained is Ln A (A is the preexponential factor). Values are listed in Table III.
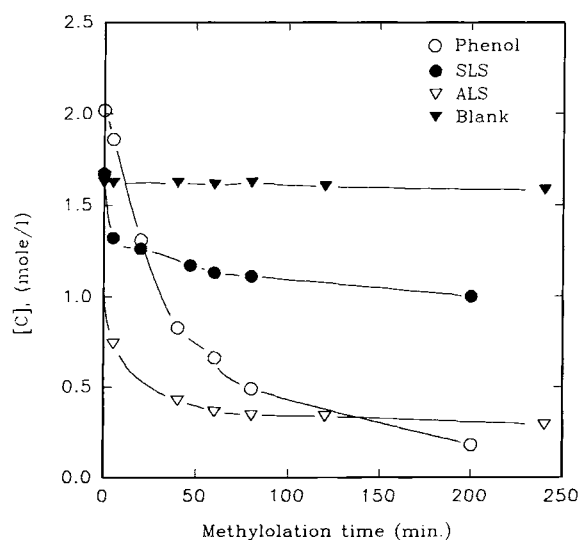

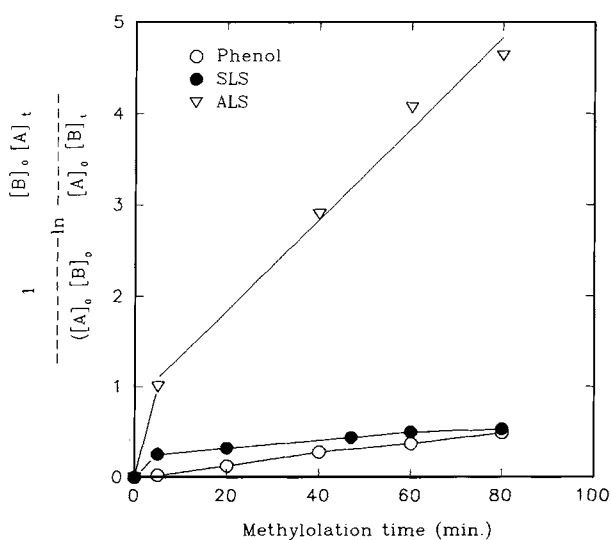**Figure 2**   The variation of formaldehyde concentration with methylolation time at 60°C.

Figure 3 $(1/\{([A]_0 - [B]_0)\})$ ln $([B]_0[A]_t)/([A]_0 [B]_t))$ [as in the eq. (4)] vs. methylolation time at 60°C.
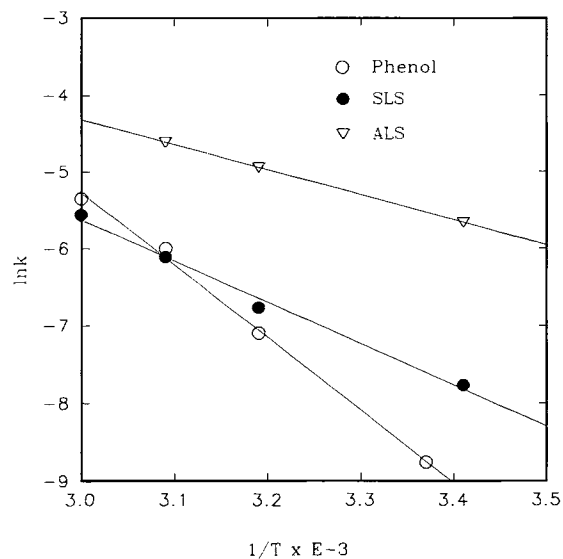
Figure 4 In $k(T)$ (obtained from monitoring disappearance of formaldehyde) vs. $1/T$.

Study of Kinetics of Lignin Methylolation by DSC Techniques

It is important, in the isothermal DSC technique, that the reaction be eventually complete, in order to have a proper baseline. It is seen in Figure 2 that, as described before, phenol methylolation does not reach reaction completion after 4 h or after a longer time, such as a few days.[15] Thus, it is not convenient to study its kinetics by isothermal DSC techniques. But lignin methylolation is practically complete after 2 h at these low temperatures, and it is thus possible to study its kinetics by this technique.

Figure 5 shows isothermal DSC curves of ALS methylolation and SLS methylolation at 60°C. It shows that the methylolation rate of lignins decreases with reaction time and levels off after 60–

80 min. A similar result is observed in Figure 6, which is the curve of ALS methylolation rate vs. time at 60°C obtained from the concentration of reactant. To rule out pan leakage, isothermal DSC was done on MALS3H (ALS methylolated 3 h) solutions and formaldehyde solutions (Fig. 5). There is no evidence of such leaks, as the stable baseline shows. This illustrates that almost no small molecules are lost or no reaction occurs at this temperature. Thus, DSC techniques can show the thermal action of lignin methylolation and can be used to study the kinetics of lignin methylolation. Plotting In $k(T)$ (obtained from DSC curves) against $1/T$ (Fig. 7), a good linear relation also was observed. The kinetic parameters are listed in Table III.

The results in Table III show that kinetic parameters from the DSC technique and from monitoring the concentration of formaldehyde are comparable. The ALS methylolation has a lower activation energy than that of SLS methylolation. The methylolation rate constants of ALS appear higher than those of SLS. Lignin methylolation had a lower activation energy and lower preexponential factor than those of phenol methylolation. These results agree with the results of Gardner and Moginnis.[7] They calculated methylolation activation energy of kraft lignin and steam-exploded lignin and obtained an Ea of about 15 kcal/mol. This value is higher than ours (about 10 kcal/mol). The origin of this discrepancy may be in the different kind of lignin used and different postulates in the obtention of reaction order. The activation energy, Ea, of phenol methylolation obtained in our experiment (18.6 kcal/mol) is very near to that obtained by Zavitsas et al.[8,9] (17–19 kcal/mol) and by Eapen and Yeddanapalli[10] (about 16 kcal/mol), while all these are lower than that of Gardner and Moginnis[7]: 24.2 kcal/mol.

Table III   Kinetic Parameters for the PF or LF Reaction

Method	Component	−ln k (Rate Constant) (Temp °C)				Frequency Factor, A (min^{-1})	Activation Energy, Ea (kcal/mol)
		20	40	50	60		
1	Phenol	8.75[a]	7.10	6.00	5.35	7.98×10^9	18.6
	ALS	5.66	4.94	4.61	3.73	9.00×10^3	8.69
	SLS	7.76	6.76	6.11	5.65	3.30×10^4	10.6
2	ALS		8.03	7.56	7.15	2.76×10^2	9.20
	SLS		8.13	7.74	7.18	2.29×10^3	12.4

Method 1 is done by monitoring the disappearance of formaldehyde and supposing the reaction order as 2. Method 2 is done by isothermal DSC techniques.
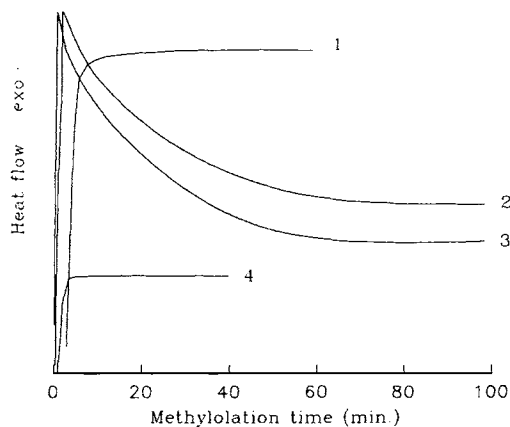
[a] Temperature is 24°C.

Figure 5 DSC curves of methylolation of ALS and SLS at 60°C. Curve 1 is MALS3H solution, curve 2 is solution of SLS with formaldehyde, curve 3 is solution of ALS with formaldehyde, and curve 4 is formaldehyde solution.

Figure 7 ln $k(T)$ (obtained from DSC techniques) vs. $1/T$.

The activation energy, Ea, can be thought as the amount of energy that must be supplied to the reactants to get them to react with each other. Preexponential factor A is related to the number of collisions occurring in the chemical reaction that led to the formation of products from reactants. The results in Table III show that lignin methylolation needs lower energy and occurs more easily than does phenol methylolation. One possible explanation for the lower Ea of lignin methylolation could be attributed to the increased reactivity of the disubstituted phenolic nucleus on the lignin molecule. A relative rate increase for formaldehyde substitution of phenol derivatives with methyl groups at the *ortho*-
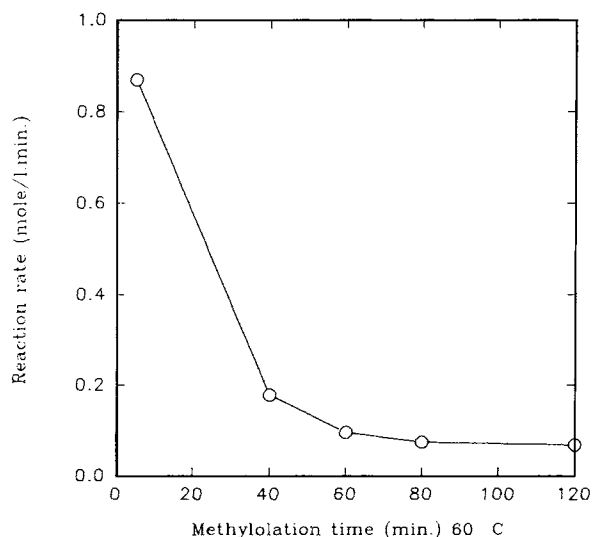

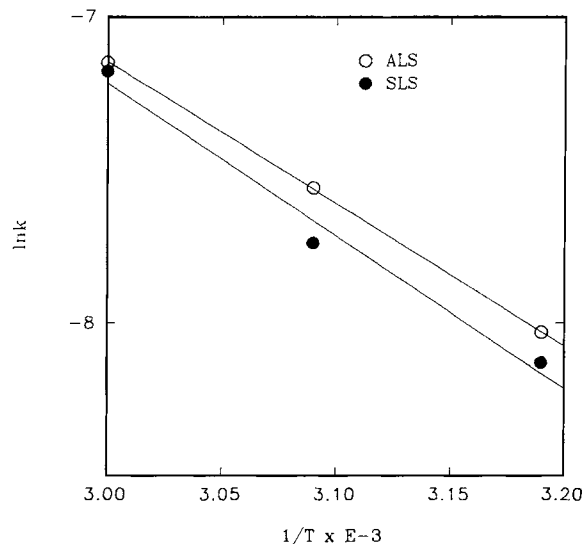**Figure 6** The reaction rate of ALS methylolation vs. methylolation time at 60°C.

and *para*-positions has been reported.[7-15] Similarly, in a study of the kinetics of base-catalyzed condensation reactions of lignin model compounds, the methylol group on the 5-position of lignin model compounds was activated to a greater extent by a propyl side chain than by a methyl substituent.[28] Since lignin is a macromolecule, it does diffuse more slowly than does phenol, and the opportunity for collisions between reactive groups, in lignin methylolation, is lower than that in phenol methylolation. Therefore, a lower preexponential factor A is obtained in lignin methylolation. The reaction rate constant is the result of the combination of these factors (Ea, A). The lower Ea obtained for the lignin methylolation suggests that lignin methylolation should be faster than the phenol methylolation at low temperature. Our results show that the reaction rate constants of ALS methylolation are higher than those of phenol methylolation at temperatures used here, whereas the reaction rate constants of SLS methylolation are higher than those of phenol methylolation at temperatures that are lower than 40°C. Gardner and Moginnis[7] expected but did not observe an apparently higher rate in lignin methylolation than in phenol methylolation.

Since lignin methylolation has a lower Ea, the methylolation of lignin can be done at lower temperature than that of phenol methylolation. For instance, ALS can be almost completely methylolated at 50°C for 2 h. But phenol cannot be methylolated well at so low a temperature. Its reaction rate constant is more sensitive to temperature. The reaction temperature is very important for phenol methylo-

lation. Generally, phenol methylolation is done at 70–90°C. Thus, it appears that difficulties involved in the lignin methylolation are not due to its slow rate of reaction but to it having a smaller amount of reactive sites.

CONCLUSION

1. The kinetic parameters obtained from monitoring the disappearance of formaldehyde and from DSC techniques agree with each other.
2. The degree of ALS methylolation is higher than that of SLS. The degree of lignin methylolation is then dependent on the availability and number of reactive sites in the C_9 unit of lignin.
3. Lignin methylolation achieves completion faster than does phenol methylolation at the low temperatures used here.
4. Methylolation of ALS and SLS had a lower activation energy and a lower preexponential factor than that of phenol. Because of the lower activation energy of lignin, the methylolation of lignin can be done at a lower temperature than that for phenol.

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