## Comparison of the Reaction Rates of the Alkali-Catalyzed Addition of Formaldehyde to Phenol and Selected Lignins

Douglas J. Gardner[a]; Gary D. McGinnis[b]

[a] Division of Forestry, West Virginia University, Morgantown, WV [b] Mississippi Forest Products Utilization Laboratory, Mississippi State University, Mississippi State, MS

## PLEASE SCROLL DOWN FOR ARTICLE

# COMPARISON OF THE REACTION RATES OF THE ALKALI-CATALYZED ADDITION OF FORMALDEHYDE TO PHENOL AND SELECTED LIGNINS

Douglas J. Gardner
Division of Forestry
West Virginia University
P.O. Box 6125
Morgantown, WV   26506-6125


Gary D. McGinnis
Mississippi Forest Products Utilization Laboratory
Mississippi State University
Mississippi State, MS   39762

## ABSTRACT

    A comparison of the reaction rates of the alkali-catalyzed addition of formaldehyde to phenol, Kraft lignin, and steam-exploded lignin was studied by monitoring the disappearance of formaldehyde at four temperatures to determine the Arrhenius parameters.   ¹H-NMR spectra of acetylated lignins and their hydroxymethylated derivatives and the  disappearance of formaldehyde during lignin-formaldehyde reactions were used to quantify the degree of formaldehyde substitution.  The rate of the addition of formaldehyde to phenol was faster than the addition of formaldehyde to lignin, although the lignin-formaldehyde reactions were essentially complete under the reaction conditions examined.  Both lignin-formaldehyde reactions had lower activation energies than the phenol-formaldehyde reaction.  Kraft lignin has a faster rate of reaction with formaldehyde than steam-exploded lignin and the rate of formaldehyde addition to lignin is dependent on the reactive site availability on the lignin molecules.

## INTRODUCTION

Lignin can be incorporated into phenol-formaldehyde (PF) resins in several ways:  1) it can be reacted with formaldehyde to provide methylol  functionalities and then mixed with a standard PF resin to act as an extender [1,2]; 2) it can also be directly condensed into a resin with phenol and formaldehyde[3,4]; and 3) it can be sequentially derivatized with formaldehyde and phenol to enhance its reactivity in PF resins.[5]  The most practical way to incorporate lignin into a PF resin is still a subject of debate.  More information is needed regarding lignin-formaldehyde (LF) reactions and PF-LF reactions to determine practical incorporation procedures.  One area of interest that has received insufficient attention is the difference in the reaction rates of formaldehyde addition between phenol and lignin.

Formaldehyde reacts with lignins in the presence of alkali by substituting both the free 5-positions in the phenolic (guaiacyl) nuclei (Lederer-Manasse reaction), and the side chains bearing carbonyl groups by the Tollens reaction[6].  Kraft lignin which contains catechol structures,[6,7] formed during the pulping process, can also react with formaldehyde at free 2-, 5-, and 6-positions on the phenolic nuclei.

Reactivity of different lignin preparations with formaldehyde will vary according to the severity of their isolation procedure, and also, to the genetic origin of the

lignin. Hardwood lignins which contain a high percentage of
syringyl units and highly condensed lignins have been shown to
have limited reactivity with formaldehyde.[5] The apparent
reactivity of lignins with formaldehyde may also be affected by
the quantity of extraneous materials; i.e., carbohydrates and
inorganics contained in the lignin preparations and by competing
side reactions such as the Cannizzaro reaction.[8,9]

The alkali catalyzed addition of formaldehyde to phenol,
substituted phenols,[10,11] and Kraft lignin[6] have been shown to
follow second-order kinetics. Most commercial resole PF resins
are alkali-catalyzed.

The purpose of this study is to determine the overall
reaction rate of the addition of formaldehyde to lignin as
compared to the addition of formaldehyde to phenol. A more
thorough understanding of the reaction rates will help in the
formulation of polymers using these raw materials.


## METHODS AND MATERIALS

Kraft lignin (Indulin AT, Lot 02261) was obtained from
Westvaco and used as received. Steam-exploded lignin from mixed
southern hardwood species was obtained from the Masonite
Corporation in Laurel, Mississippi. Steam explosion was carried
out at 225°C for one minute. The steam-exploded fiber was
extracted with aqueous alkali (2% NaOH) followed by acid
precipitation of the extract with sulfuric acid.[12] The lignin

precipitate was then dried in an oven at approximately 50°C

followed by grinding and ball-milling. The chemical composition

and elemental analyses of the lignins are shown in Table 1. The

elemental analyses and methoxyl content determination were

performed by Galbraith Laboratories, Knoxville, Tennessee. Both

lignin preparations were analyzed for ash content after ignition

at 700°C and for carbohydrate content after hydrolysis by gas

chromatographic (GC) analyses.[14]

Phenol (90%) was obtained from Fisher Scientific and used as

received. Formaldehyde (50%) was obtained from a Georgia Pacific

chemical plant in Louisville, Mississippi. The formaldehyde was

diluted to approximately 39%, carboxymethyl cellulose (10 ppm)

was added to inhibit the precipitation of paraformaldehyde, and

it was also titrated to a pH of 6.8 and stored at 40°C. The

formaldehyde solution contained 0.07% formic acid as determined

by titration and 0.5% methanol.

The components of the PF and LF reactions are shown in Table

2. The addition of the lignins to the sodium hydroxide (NaOH)

solution required sonication (1 to 2 hours) to ensure complete

solubilization. Sodium bicarbonate buffer was added to the

component solutions to prevent a change in pH during the course

of the reactions. Sodium bicarbonate was chosen as the buffer

salt because the bicarbonate ion ($pK_a$ 10.36) provides adequate

buffering capacity at a pH of 10.5.[16] A pH of 10.5 was chosen

for running the reactions to ensure lignin solubility, minimize

TABLE 1

Analysis of Lignin Preparations Examined.

| Lignin preparation | Lignin[a] | Ash | Carbohydrates | Total[b] | Elemental and methoxyl group composition[c], % | | | |
| | weight % | | | | C | H | $OCH_3$[d] | S |
|---|---|---|---|---|---|---|---|---|
| Kraft lignin | 94.0 | 2.5 | 0.4 | 96.9 | 61.51 | 5.96 | 13.98 | 1-3[e] |
| Steam-exploded lignin | 89.0 | 7.0 | 2.0 | 98.0 | 54.98 | 5.82 | 19.46 | — |

a Klason and acid soluble lignin.
b A portion of the material unaccounted for could include uronic acids and degraded carbohydrates.
c Correction made for ash content.
d Correction made to account for true lignin content.
e Sjostrom.[13]

TABLE 2

Reaction Components of the PF and LF Reactions

| Component | Dry weight (g) | Moles[a] | Moles reactive sites | NaOH solution (g) | Sodium Bicarbonate buffer (pH 10.5) (g) | Formaldehyde (moles) Experimental | Calculated | pH |
|---|---|---|---|---|---|---|---|---|
| Phenol | 4.5 | 0.048[b] | 0.144 | 50(0.7)[e] | 25 | 0.067 | 0.057 | 10.5 |
| Kraft lignin | 10.0 | 0.053[c] | 0.021 | 50(0.5) | 25 | 0.062 | 0.057 | 10.5 |
| Steam-exploded lignin | 10.0 | 0.049[d] | 0.010 | 50(0.45) | 25 | 0.063 | 0.057 | 10.5 |
| Formaldehyde[f] | 1.76 | 0.057 | 0.057 | — | 50 | 0.054 | 0.057 | 10.5 |

[a] Weights used provide for approximate molar equivalency if lignins are based on C-9 unit molecular weight. Kraft lignin 190 g/mole, steam-exploded lignin 205 g/mole.

[b] 3 reactive sites/mole phenol.

[c] 0.4 reactive sites/C-9 unit.

[d] 0.4 reactive sites/C-9 unit x 0.5 (guaiacyl units) for hardwood lignins.

[e] The normality of the NaOH solution added was determined empirically to obtain a pH of approximately 10.5 with the components added before addition of the buffer.

[f] This reaction was run to determine if the Cannizzaro reaction was occurring under the reaction conditions.

the Cannizzaro reaction, and yet, have pH conditions similar to resole resin formulations.

The PF and LF reactions were run in stoppered 250-mL Erlenmeyer flasks which were placed in a constant temperature shaker bath. The reactions were run in duplicate at 30°, 40°, 50°, and 60°C for various lengths of time. The average difference between the duplicate readings was 2.8%. Reactions of formaldehyde and buffer at 50° and 60°C were run to determine the extent of the Cannizzaro reaction. The flasks were placed in the constant temperature bath for at least 10 minutes before the formaldehyde was added, and time zero was recorded from the time the formaldehyde was added to the flasks.

The disappearance of formaldehyde during the course of the reaction was determined by a slightly modified hydroxylamine hydrochloride method.[8] For each reaction series, a stock solution of 12.5 g of hydroxylamine hydrochloride in 500 mL of reagent grade methanol was made, and this stock solution was titrated to a pH of 4 with a 0.5N NaOH solution.

Five g of PF or LF reaction solution were removed at a designated time during the reaction and added to a 250-mL beaker followed by dilution with 50 mL of distilled water. This solution was titrated to a pH of 4 with 0.1N hydrochloric acid (HCl). Fifty mL of the hydroxylamine hydrochloride stock solution were added to the PF or LF solution with continuous stirring. The resulting solution was allowed to stand for 5

minutes. The solution was then titrated to a pH of 4 using 0.5N

NaOH until a stable pH reading was obtained. The formaldehyde

content of the samples were calculated as follows:

$$\% \text{ formaldehyde} = \frac{\text{mL of NaOH x normality of NaOH x 3.003}}{\text{weight of sample}}$$

The purpose of this simplified procedure was to allow the sample

analysis to be run quickly during the course of the reactions.

## Formic Acid Analysis

Two mL of the remaining reaction solution was mixed with 2

mL of 1N HCl and centrifuged. This neutralization procedure was

performed to remove precipitated lignin and convert any formate

ions present to formic acid. The supernatant (0.5 mL) was passed

through a small reverse-phase column (Waters C-18 SEP-PAK No.

51910) followed by 3 mL of distilled $H_2O$. The eluate was

analyzed for formic acid using a cation-exchange column (Bio-Rad

HPX-87).[17]

## Hydroxymethylation

Kraft and steam-exploded lignin (10 g each) were added to 50

g of 1N NaOH in a 250-mL Erlenmeyer flask and sonicated for 2

hours. Five and one-half grams of formaldehyde (39%) was added

to the solution and allowed to react with agitation for 72 hours

at ambient temperature. After the reaction, the solution was

precipitated by addition of acid and washed by centrifugation

with several changes of distilled water until the supernatant
appeared clear.

## Acetylation and ^{1}H-NMR Spectrscopy

The Kraft and steam-exploded lignins and hydroxymethylated
derivatives were acetylated 24 hours at ambient temperature in a
1:1 mixture of pyridine and acetic anhydride.  The acetylated
lignins were precipitated with 0.1N HCl and washed by
centrifugation with several changes of distilled water until the
supernatant appeared clear.  The acetylated lignins were dried in
an oven at 45° to 50°C.  ^{1}H-NMR analysis was performed on the
acetylated lignins dissolved in deuterated chloroform ($CDCl_3$)
with 1% tetramethylsilane using a Varian FT-80A nuclear magnetic
resonance spectrometer.


## RESULTS AND DISCUSSION

Plots of the PF and LF reactions at 30°C and the PF, LF and
formaldehyde reactions at 60°C are shown in Figures 1 and 2.
These data are plotted as second-order reactions (reciprocal
concentration (moles/100 ml) formaldehyde (HCHO) remaining
against time.  Formaldehyde reacted in the buffer solution
(Figure 2) shows no indication of the Cannizzaro reaction
occurring under the experimental reaction conditions chosen.  No
formic acid was formed during the reactions which also support
this result.  Therefore, the decrease in the formaldehyde

FIGURE 1.  Plot depicting the reactions of phenol and
           formaldehyde (HCHO), Kraft lignin and HCHO, and
           steam-exploded lignin and HCHO at 30°C as
           determined by the disappearance of HCHO over
           time.

concentration over time can be assumed to be the amount of

formaldehyde reacted with each component during the course of the

reaction (Table 3).

    As the PF reaction proceeds, the rate increases (Figure 1).

This result agrees with Freeman and Lewis[10] and others[11] who
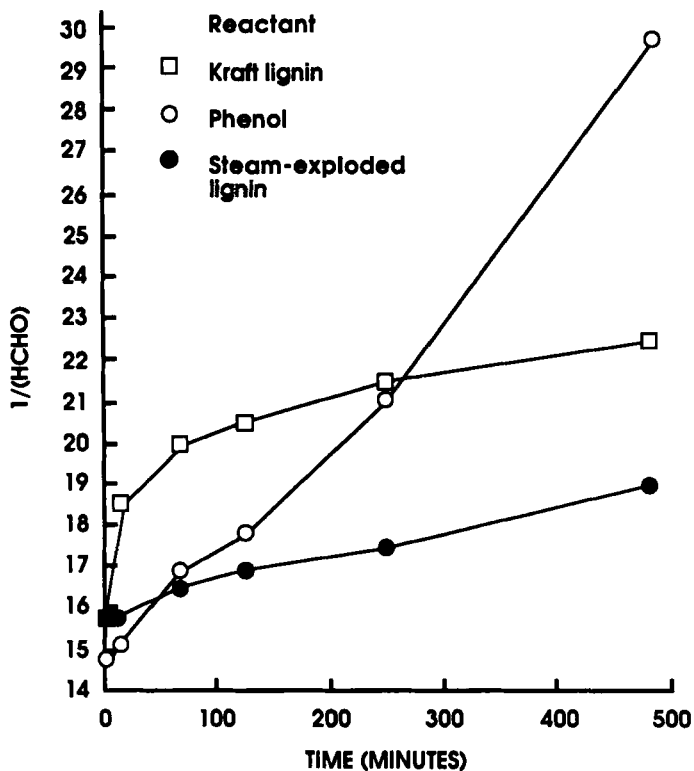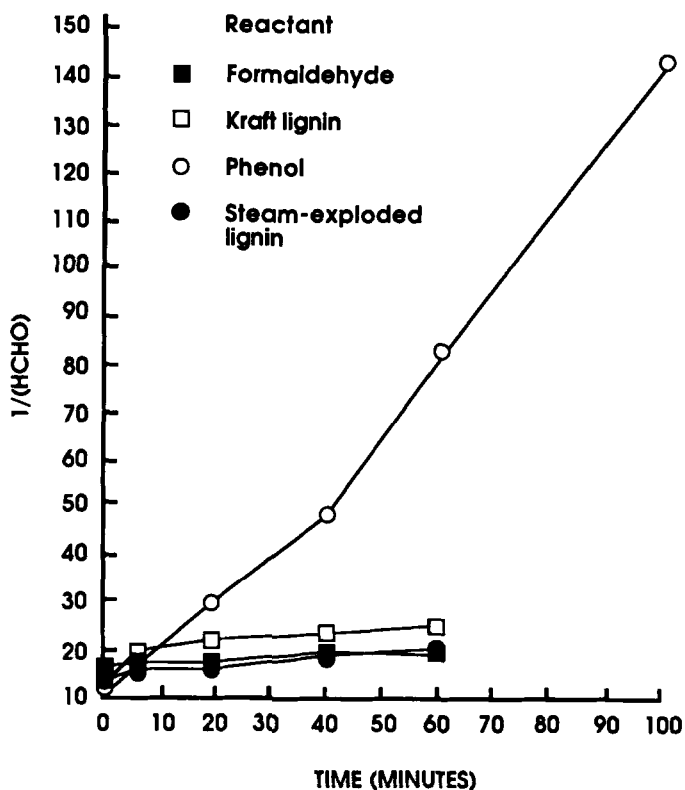
FIGURE 2.   Plot depicting the reactions of phenol and
            formaldehyde (HCHO) Kraft lignin and HCHO and
            steam-exploded (STE) lignin and HCHO and HCHO by
            itself at 60°C as determined by the disappearance
            of HCHO over time.

showed that as the phenolic molecule becomes partially

substituted, there is a subsequent increase in the rate of

reaction of the partially substituted molecule with formaldehyde.

The rate of formaldehyde addition to both Kraft and

steam-exploded lignins decreased as the reaction proceeded

TABLE 3

Amount of Formaldehyde Reacted with Each Component During the Reaction Run at Various Temperatures

| | Phenol | | | Kraft lignin | | | Steam-exploded lignin | |
|---|---|---|---|---|---|---|---|---|
| Time | Moles HCHO Consumed | | Time | Moles HCHO Consumed | | Time | Moles HCHO Consumed | |
| (min) | A | B | (min) | A | B | (min) | A | B |
| | | | | | -30°C- | | | |
| 5 | 0.001 | 0.007 | 5 | 0.009 | 0.429 | 5 | — | -- |
| 60 | 0.007 | 0.049 | 60 | 0.013 | 0.619 | 60 | 0.002 | 0.200 |
| 120 | 0.010 | 0.069 | 120 | 0.014 | 0.667 | 120 | 0.003 | 0.300 |
| 240 | 0.019 | 0.132 | 240 | 0.016 | 0.762 | 240 | 0.005 | 0.500 |
| 480 | 0.033 | 0.229 | 480 | 0.018 | 0.857 | 480 | 0.010 | 1.000 |
| | | | | | -40°C- | | | |
| 5 | — | — | 5 | 0.009 | 0.429 | 5 | — | -- |
| 30 | 0.005 | 0.035 | 60 | 0.013 | 0.619 | 30 | 0.001 | 0.100 |
| 60 | 0.012 | 0.083 | 120 | 0.016 | 0.762 | 60 | 0.002 | 0.200 |
| 120 | 0.024 | 0.167 | 240 | 0.017 | 0.810 | 120 | 0.007 | 0.700 |
| 240 | 0.037 | 0.257 | 480 | 0.020 | 0.950 | 240 | 0.011 | 1.100 |
| | | | | | -50°C- | | | |
| 5 | — | — | 5 | 0.010 | 0.476 | 5 | — | — |
| 30 | 0.021 | 0.146 | 30 | 0.014 | 0.667 | 30 | 0.005 | 0.500 |
| 60 | 0.038 | 0.264 | 60 | 0.017 | 0.810 | 60 | 0.008 | 0.800 |
| 90 | 0.048 | 0.333 | 120 | 0.019 | 0.905 | 120 | 0.010 | 1.000 |
| 120 | 0.054 | 0.375 | 180 | 0.023 | 1.095 | 180 | 0.013 | 1.300 |
| | | | | | -60°C- | | | |
| 5 | 0.007 | 0.049 | 5 | 0.010 | 0.476 | 5 | — | -- |
| 20 | 0.032 | 0.222 | 20 | 0.015 | 0.714 | 20 | 0.005 | 0.500 |
| 40 | 0.046 | 0.319 | 40 | 0.017 | 0.810 | 40 | 0.009 | 0.900 |
| 60 | 0.054 | 0.375 | 60 | 0.020 | 0.950 | 60 | 0.012 | 1.200 |
| 100 | 0.060 | 0.417 | 80 | 0.022 | 1.047 | 80 | 0.014 | 1.400 |

A = moles HCHO consumed for approximate molar equivalency.
B = moles HCHO consumed/moles reactive sites.

(Figure 1). This trend should be expected since the side-chain

sites which are substituted via the Tollens reaction react at a

slower rate than the aromatic sites which are substituted via the

Lederer-Manasse reaction[6]. To make comparisons between the

lignins and phenol, the formaldehyde reactions were run with

approximately equivalent moles of lignin (based on C-9 units) and

phenol. Thus, the number of reactive sites on the lignins was a limiting factor.

Kraft lignin exhibited a fast initial reaction with formaldehyde (Figure 1 and Table 3). This initial reaction occurred within the first five minutes. The phenol and steam-exploded lignin did not exhibit this trend.

Explanations for the fast initial reaction of formaldehyde with Kraft lignin might be because of chemical structures formed in Kraft lignin during the pulping process or isolation procedures. Catechol structures are formed in Kraft lignin during the pulping procedure.[6] Lignin-based catechol compounds have been shown to be more reactive toward formaldehyde than their phenolic analogues under alkaline conditions.[18,19,20] However, other studies dealing with the reactivity of catechol compounds related to bark extractives have shown the catechol-type structures to have no reactivity with formaldehyde in the pH range 4.9 to 9.0.[21,22] Neat catechol reacted under the experimental conditions used in this study showed an initial uptake (5 minutes) of formaldehyde which was faster than phenol, but slower than Kraft lignin. It should be emphasized that there might be other undefined factors affecting Kraft lignin's initial fast reactivity with formaldehyde.

In both the PF and LF reactions, there is a deviation from a straight line plot which is the ideal case for a second-order reaction. These deviations occur because simultaneous reactions

TABLE 4

Kinetic parameters for the PF or LF Reactions

| Component | Rate Constant $k(10^{-2} M^{-1} min^{-1})$ ---Temperature °C--- | | | | Preexponential factor A $(min^{-1})$ | Activation energy Ea(kcal/mole) |
|---|---|---|---|---|---|---|
| | 30 | 40 | 50 | 60 | | |
| Phenol | 2.12 | 6.65 | 24.9 | 79.4 | $5.8 \times 10^{15}$ | 24.2 |
| Kraft lignin | 1.44 | 1.83 | 5.50 | 11.3 | $3.25 \times 10^{8}$ | 14.5 |
| Steam-exploded lignin | 0.98 | 1.60 | 4.37 | 9.44 | $1.32 \times 10^{9}$ | 15.5 |

are taking place during the course of the component
reactions.[6,10]  The plots depicting the reactions are better
expressed in terms of a quadratic relationship.  However, in
calculating the reaction kinetics, the method of initial reaction
rates was used.  If a tangent line is drawn to the curve at the
beginning of the reaction, the initial reaction rate constant can
be approximated (Table 4).  Working from the initial reaction
rate also simplifies calculation of the kinetic parameters for
both the PF and LF reactions.  In calculating the reaction rate
for the Kraft lignin, the fast initial uptake of formaldehyde
(first five minutes) was ignored because the reaction occurred
too fast to observe any differences in the reaction rate over the
temperature range examined.

The influence of temperature on the PF and LF reaction rates
(k) was examined using the Arrhenius relation,

$$k = A \exp - Ea/RT$$

where A is the pre-exponential or frequency factor and Ea is the
activation energy.  The values of A and Ea for the PF and LF
reactions are shown in Table 4.

The initial reaction of formaldehyde with phenol involves
monosubstitution at either the ortho or para position on the
phenolic nucleus.  The slope of the the Arrhenius plot for the PF
reaction (Figure 3) gave an Ea of 24.2 Kcal/mole.  This does not
agree with the PF Ea's for monosubstitution obtained by Zavitsas,
et al.[11]  (ortho substitution 21.1 Kcal/mole and para substitution
20.6 Kcal/mole).  However, the Ea's calculated by using Zavitsas'
data were based on theoretical calculations obtained from
experiments run at only two temperatures.  Also, reaction
conditions used in this experiment were different, and this could
explain the different results obtained.

The Kraft lignin, ignoring the initial reaction, reacted with
formaldehyde at a faster rate than the steam-exploded lignin
(Table 4).  This is expected since the Kraft lignin was prepared
from a softwood (pine) and contains more reactive sites (guaiacyl
units) than the steam-exploded lignin which was prepared from
mixed hardwoods.  The slopes of the Arrhenius plots for both Kraft
lignin and steam-exploded lignin (Figure 3) gave Ea's of 14.5 and
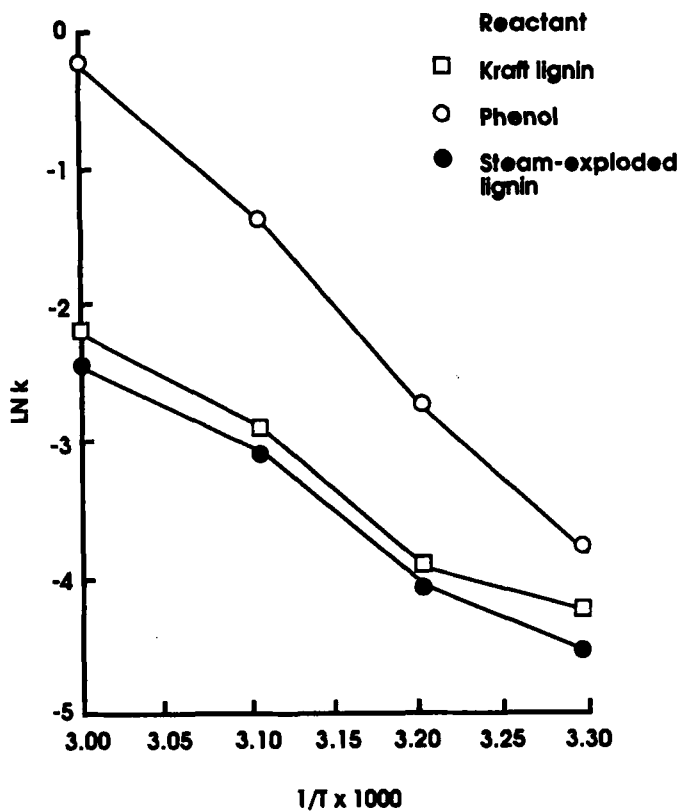
FIGURE 3.  Arrhenius plots of the reaction of formaldehyde
            (HCHO) with phenol, Kraft lignin, and steam-exploded
            (STE) lignin.

15.5 Kcal/mole, respectively.  Since no known Ea's for LF

reactions have been found in the literature, no further

comparisons could be made.

    Making comparisons between the PF and LF reactions for

Arrhenius parameters require examining both parameters A and Ea.

The parameter A has been designated in a number of rate theories[23]

as a factor related to molecular interactions occurring between

reactants in a chemical reaction. Simply stated, the parameter A

is related to the number of collisions occurring in a chemical

reaction that lead to the formation of products from reactants.

In the PF reactions, the number of collisions occurring between

the reactants as compared to the LF reactions is much greater and

this is reflected in the value of parameter A. Collisions

occurring between the LF reactants are limited because of steric

hindrances and reactive site availability on the lignin molecules.

The lower Ea's obtained for the LF reactions suggest that the

LF reactions should be faster than the PF reactions. This is not

apparent from examining the rate constants which show the PF

reactions to be faster than the LF reactions (Table 4). Also, the

influence of temperature on the component rate constants is

greatly enhanced for the PF reactions (Table 4, Figures 1 and 2).

However, if the PF and LF reactions are based on the moles of

formaldehyde reacted per moles of reactive sites (Table 3 Column

B), the lignins appear to be more reactive with the formaldehyde

than phenol. Since the original experimental conditions were not

designed to examine the moles of formaldehyde reacted per moles of

reactive sites for the lignins and phenol, calculating reaction

rates using this data would be invalid.

One possible explanation for the lower Ea's of the LF

reactions could be attributed to the increased reactivity of the

di-substituted phenolic nucleus on the lignin molecule. Relative

rate increases for formaldehyde substitution of phenol derivatives with methyl groups at the ortho- and para- positions have been reported.[24] 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 a methyl substituent.[25] This may explain the lower Ea's obtained for the LF reactions. However, it is difficult to make definitive conclusions about the lower Ea's obtained for the LF reactions without examining the reactions in greater detail, and future work in this area should address the lower Ea's of the LF reaction.

The extent of the PF and LF reactions over the temperature range examined is shown in Table 5. Although the reaction rates for the PF and LF reactions were different, the formation of LF derivatives was essentially complete under the conditions examined. From a resin formulation standpoint, the completeness of the LF reactions compared to the PF reactions indicates that the addition of formaldehyde to lignin is not prohibitively slow as has been generally believed by resin chemists. This "slowness" of the LF reaction encountered when formulating lignin into PF resins is probably due more to the limited number of reactive sites capable of condensing with phenolic moieties rather than the addition of formaldehyde to lignin.

Lignin analysis by ^{1}H-NMR spectroscopy was pioneered by Ludwig et al.[26,27] and adapted for lignin derivatives by Muller

TABLE 5

Extent of the PF and LF Reactions

| Component | Theoretical Moles Reactive Sites | Moles HCHO available | Moles HCHO consumed ---Temperature °C--- | | | |
|---|---|---|---|---|---|---|
| | | | 30 | 40 | 50 | 60 |
| Phenol | 0.144 | 0.067 | 0.033 | 0.037 | 0.054 | 0.060 |
| Kraft lignin | 0.021 | 0.062 | 0.018 | 0.020 | 0.023 | 0.022 |
| Steam-exploded lignin | 0.010 | 0.063 | 0.010 | 0.010 | 0.013 | 0.014 |

and Glasser.[5] The results of the ^{1}H-NMR analysis for the lignins
and hydroxymethylated lignins in percent of integration by ranges
are shown in Table 6. The peak assignments and range boundaries
established for the lignins and lignin derivatives are described
in the literature.[5,26,27] A ^{1}H-NMR spectrum for acetylated Kraft
lignin with range assignments for protons on the C-9 unit are
shown in Figure 4.

In the reaction of formaldehyde and lignin, the ranges of
interest in the ^{1}H-NMR spectra are ranges 2 and 4a. When the
lignin is substituted as the result of the reaction with
formaldehyde at the free-5 positions, a proton is removed from the
aromatic nucleus, thus reducing the signal response in range 2.
Subsequently, the formation of a methylol group on the aromatic

TABLE 6

$^1$H-NMR Analysis Results for Acetylated Lignins and Lignin Derivatives in Percent of Integration by Ranges[a]

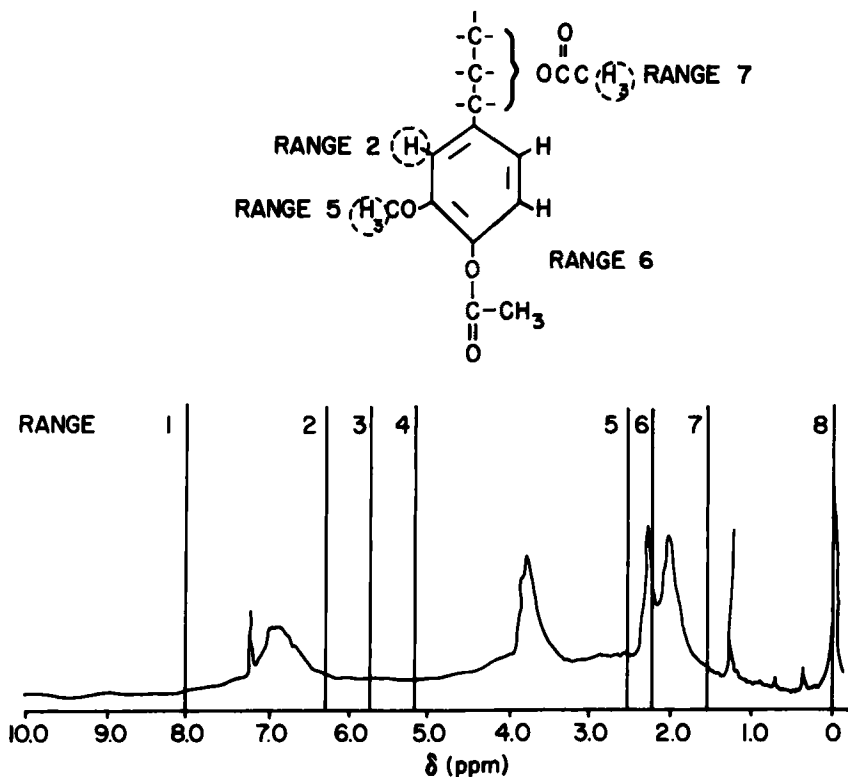| Lignin type | Signal response (% integration) | | | | | | | | |
| | Range | | | | | | | | |
| | 1 | 2 | 3 | 4 | 4a | 5 | 6 | 7 | 6+7 | 8 |
|---|---|---|---|---|---|---|---|---|---|---|
| Kraft lignin | 0 | 22.6 | 2.8 | 0.9 | 2.4 | 38.7 | 11.3 | 21.7 | 33.0 | 1.9 |
| Hydroxymethylated Kraft lignin | 0 | 17.3 | 3.3 | 2.0 | 6.6 | 40.0 | 6.7 | 25.3 | 32.0 | 5.3 |
| Steam-exploded lignin | 0 | 18.9 | 4.5 | 3.6 | 6.8 | 45.0 | 8.1 | 17.1 | 25.2 | 1.8 |
| Hydromethylated steam-exploded lignin | 0 | 15.9 | 4.8 | 3.7 | 7.5 | 48.6 | 6.5 | 17.8 | 24.3 | 2.8 |

[a] Reference 27.

FIGURE 4.  $^1$H-NMR spectra for acetylated Kraft lignin.

nucleus gives rise to increased signal response in range 4a
because of the protons on the methylol group.

The acetylated hydroxymethylated lignins exhibited limited
solubility in the CDCl$_3$ (approximately half of the material was
soluble).  Spectra of the acetylated hydroxymethylated lignins
were also run in a better solvent (deuterated pyridine).  Although
the lignin derivatives were more soluble in the deuterated

pyridine, the resulting spectra showed down field shifts of the
aromatic and methylene proton peaks as compared to the spectra run
in $CDCl_3$. Also, the spectra run in pyridine did not show a
clearly defined separation between the peak responses for acetates
of phenolic hydroxyl groups and the side-chain hydroxyl groups.
The percent integration by range technique requires similar peak
assignments and range boundaries to determine changes in signal
response between derivatized and underivatized lignins.
Therefore, the two solvent systems were not compatible for
comparing spectra integration ranges.

Plotting the percent integration values on a theoretical
model for estimating the degree of formaldehyde substitution (DS)
on both the Kraft lignin and steam-exploded lignin (Figure 5) gave
values similar to those reported in the literature (Table 7).
Kraft lignin and steam-exploded lignin had DS values of 0.38 and
0.18, respectively. The DS values obtained for the lignins also
support the kinetic results. Kraft lignin which reacted with
formaldehyde faster than steam-exploded lignin reacted with
formaldehyde also had a higher DS as determined by ^{1}H-NMR. Thus,
the rate of formaldehyde addition is directly related to the
number of available sites present on the lignin molecule (per C-9
unit).

The theoretical lines in Figure 6 were obtained by plotting
the values for  percent integration in both ranges, 2 and 4a, as
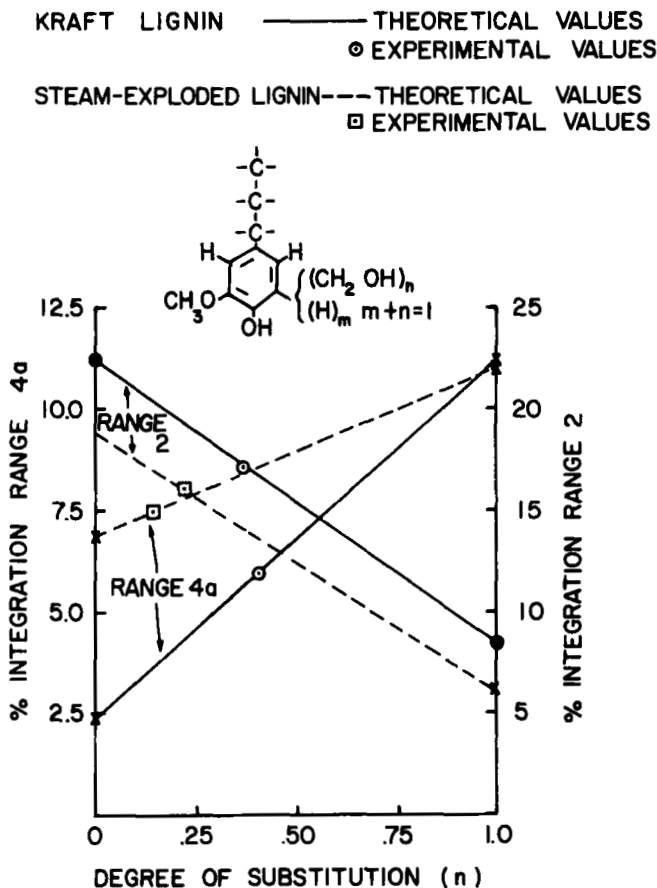determined by ^{1}H-NMR spectroscopy for the acetylated lignins (DS =

FIGURE 5.  Relationship between ^{1}H-NMR signal intensity (percent
integration in ranges 2 and 4a) and degree of
substitution for hydroxymethylated Kraft lignin and
hydroxymethylated steam-exploded lignin.

0), and by determining what the theoretical percent integration

values should be for DS = 1.  The theoretical model works on the

principle that when formaldehyde is substituted on the lignin

aromatic nucleus, there is a decrease in the aromatic proton

response and an increase in the methylol proton response.

TABLE 7.

Degree of Formaldehyde (HCHO) Substitution per C-9 Unit of Lignin
by Various Methods.

| Method | --Degree of formaldehyde substitution-- | |
| --- | --- | --- |
| | Kraft lignin | Steam-exploded lignin |
| HCHO uptake[a] | 0.39 | 0.25 |
| $^1$H-NMR | 0.38 (0.35)[b] | 0.18 (0.15-0.20) |
| $^{13}$C-NMR[c] | 0.42 | 0.27 |
| Hydroxyl group determination[d] | 0.40 | -- |

[a] Calculated from the results of this study.
[b] Values in parenthesis from Reference 5.
[c] Values from Reference 28.
[d] Values from Reference 6.

The theoretical percent integration values for DS = 1 were
obtained by determining an estimate for the total number of
protons (H's) available per acetylated C-9 (AC-9) unit for a
given lignin. For example, the total number of H's/AC-9 unit for
Kraft lignin and steam-exploded lignin were estimated by using
values reported in the literature,[29] and from values obtained
from elemental analysis of the lignin.

Total H's/AC-9 unit = aromatic H's + acetate of hydroxyl H's +
methylol H's + methoxyl H's + Estimated propyl chain H's

Kraft lignin:

Total H's/AC-9 unit = (2.51-1)+[(1.32+1)x3]+2+(.86)x3+4.5

Total H's/AC-9 unit = 17.6

Steam-exploded lignin:

Total H's/AC-9 unit = $(2.10-1)+[(1.01+1) \times 3]+2+(1.43) \times 3+4.5$

Total H's/AC-9 unit = 17.9

When the total number of H's/AC-9 unit was determined, the theoretical percent integration values were calculated.

For a DS = 1

Kraft lignin                               Steam-exploded lignin

Range 2

$$\frac{\text{aromatic H's}}{\text{Total H's}} = \frac{1.51}{17.6} \times 100 = 8.6; \quad \frac{\text{aromatic H's}}{\text{Total H's}} = \frac{1.10}{17.9} \times 100 = 6.1$$

Range 4a

$$\frac{\text{methylene H's}}{\text{Total H's}} = \frac{2}{17.6} \times 100 = 11.4; \quad \frac{\text{methylene H's}}{\text{Total H's}} = \frac{2}{17.9} \times 100 = 11.2$$

The experimental percent integration values for ranges 2 and 4a were plotted on the theoretical line, and thus, the DS value for the lignins could be estimated.

## CONCLUSIONS

1.  The rate of formaldehyde addition to phenol was faster than the addition of formaldehyde to lignin, although the lignin-formaldehyde reaction was not prohibitively slow.

2.  The extent of the lignin-formaldehyde reaction was essentially complete under the reaction conditions examined.

3.  Both the lignin-formaldehyde reactions had lower
    activation energies than the phenol-formaldehyde
    reaction.

4.  Kraft lignin has a faster rate of reaction with
    formaldehyde than steam-exploded lignin, and the rate
    of formaldehyde addition to lignin is dependent on the
    availability of reactive sites on the lignin molecule.

## ACKNOWLEDGMENTS

## REFERENCES

1.  A. J. Dolenko and M. R. Clarke, For. Prod. J., 28,
    41 (1978).

2.  K. G. Forss and A. Fuhrmann, For. Prod. J., 29, 39 (1979).

3.  J. W. Hollis and M. W. Shoenherr, U.S. Pat. 4,303,562 (1981).

4.  E. R. Janiga, U.S. Pat. 4,423,173 (1983).

5.  P. C. Muller and W. G. Glasser, J. Adhesion 17, 157 (1984).

6.  J. Marton, T. Marton, S. I. Falkheag, and E. Adler, In Lignin Structure and Reactions, Advances in Chemistry Series 59, p. 125-144, J. Marton, Sym. Chairman, Amer. Chem. Soc., Washington, DC, 1966.

7.  S. I. Falkheag, J. Marton, and E. Adler, In Lignin Structure and Reactions, Advances in Chemistry Series 59, p. 75-89, J. Marton, Sym. Chairman, Amer. Chem. Soc., Washington, DC, 1966.

8.  J. F. Walker, Formaldehyde, Reinhold Publishing Co., NY, 1964.

9.  R. J. L. Martin, Australian J. Chem., 7, 335 (1954).

10. J. H. Freeman and C. W. Lewis, J. Amer. Chem. Soc., 76, 2080 (1954).

11. A. A. Zavitsas, R. D. Beaulieu, and J. R. Leblanc, J. Polym. Sci. Part A-1 6, 2544 (1968).

12. D. J. Gardner, T. P. Schultz, and G. D. McGinnis, J. Wood Chem. and Technol., 5, 85 (1985).

13. E. Sjostrom, Wood chemistry, Fundamentals and Applications, Academic Press, New York, NY, 1981.

14. C. C. Chen and G. D. McGinnis, Carbohydrate Res., 90, 127 (1981).

15. P. C. Muller, S. S. Kelley, and W. G. Glasser, J. Adhesion, 17, 185 (1984).

16. R. A. Day and A. L. Underwood, Quantitative Analysis, 3rd ed., Prentice Hall, Inc., Englewood Cliffs, NJ, 1974.

17. G. D. McGinnis, S. E. Prince, C. J. Biermann, and J. T. Lowrimore, Carbohydrate Res., 118, 51 (1984).

18. G. E. Troughton, J. F. Manville, and S.-Z. Chow, For.
    Prod. J., 22, 108 (1972).

19. R. C. Gupta and V. K. Sehgal, Holzforschung und
    Holzverwertung, 30, 85 (1978).

20. T. Enkvist, Applied Polym. Symp. 28, 285 (1975).

21. A. Pizzi and P. Van Der Spuy, J. Polymer Sci:Polymer
    Chem. Ed., 18, 3447 (1980).

22. D. Rossouw, A. Pizzi, and G. McGillivray, J. Polymer
    Sci:Polymer Chem. Ed. 18, 3323 (1980).

23. J. H. Espenson, Chemical Kinetics and Reaction Mechanisms,
    McGraw-Hill Book Co., New York, NY, 1981.

24. K. C. Eapen and L. M. Yeddanapalli, Makromol. Chem., 119,
    4 (1968).

25. G. E. Troughton and J. F. Manville, Can. J. For. Res., 2,
    71 (1972).

26. C. H. Ludwig, B. J. Nist, and J. L. McCarthy, J. Amer. Chem.
    Soc., 86, 1186 (1964).

27. C. H. Ludwig, B. J. Nist, and J. L. McCarthy, J. Amer. Chem.
    Soc., 86, 1196 (1964).

28. D. J. Gardner, G. D. McGinnis, and L. W. Amos. (Submitted
    to) J. Wood Chem. Technol.

29. W. G. Glasser, C. A. Barnett, P. C. Muller, and K. V.
    Sarkanen, J. of Agric. and Food Chem., 31, 921 (1983).