

# Reaction of Formaldehyde with Phenols: A Computational Chemistry Study

Tohru Mitsunaga

*Associate Professor, Faculty of Bioresources, Mie Univ., Tsu, Japan, and Visiting Scientist, Dept. of Chemical Engineering, Univ. of Wisconsin, Madison, WI*

Anthony H. Conner

*Project Leader, USDA Forest Service, Forest Products Laboratory, Madison, WI*

Charles G. Hill, Jr.,

*Professor, Dept. of Chemical Engineering, Univ. of Wisconsin, Madison, WI*

## Abstract

Phenolic resins are important adhesives used by the forest products industry. The phenolic compounds in these resins are derived primarily from petrochemical sources. Alternate sources of phenolic compounds include tannins, lignins, biomass pyrolysis products, and coal gasification products. Because of variations in their chemical structures, the reactivities of these phenolic compounds with formaldehyde vary in quite subtle ways. A method is needed for predicting the reactivity of phenolic compounds with formaldehyde in order to allow researchers to efficiently choose those compounds that might make the best candidates for new adhesive systems prior to conducting extensive laboratory trials.

Computational chemistry has been used to study the relationship between the reactivity of a number of phenolic compounds with formaldehyde in an aqueous, alkaline system, and charges calculated for reactive sites on the aromatic ring of the phenolic compound. Atomic-charges for each phenolic compound were calculated by *ab initio* methods at the RHF/6-31 +G level of theory using the ChelpG method. Reaction rate constants were determined from measurements of the concentrations of the phenolic compounds and formaldehyde as functions of time. The reaction rate constants varied over a wide range (approx.  $10^{-2}$  to  $10^4$  L mol<sup>-1</sup> hr.<sup>-1</sup>). An estimate of the reactivity per reactive site on the phenolic ring was determined by dividing the rate constant by the number of reactive sites. The charge per reactive site was estimated by summing the charges at all the reactive sites on the phenolic ring and dividing by the number of reactive sites. A strong correlation was

observed between the reactivity per reactive site and the average charge per reactive site.

## Introduction

In order to utilize phenolic adhesive systems more effectively and to develop new phenolic adhesives, it is important to understand the reactions of phenolic compounds with formaldehyde. To date, analytical studies on phenolic adhesives have concentrated mainly on kinetic studies (1-5). These studies involve not only the calculation of reaction rates but also complex processes for isolation and identification of intermediates, as well as reaction products. Recently, newer computational chemistry methods have been introduced that allow analysis of reaction mechanisms and prediction of the reactivities of chemical starting materials. Therefore, computational chemistry might be used to predict the reactivities of phenolic compounds with formaldehyde and thereby provide new insight into the reaction mechanisms. Such information would be useful in developing strategies for formulation and cure of phenolic adhesives. This insight would also serve to decrease the time needed for development of new adhesive systems.

Sprung (6) investigated the reactions of a series of methylphenols with formaldehyde. His kinetic measurements were based solely on the rate of disappearance of formaldehyde. As expected, differences in the reactivities of this series of phenolic compounds depended on subtle differences in chemical structure. Conner (7) demonstrated that the relative rates of these reactions could be correlated with electrostatic charges

at reactive positions in the phenolic-ring calculated using *ab initio* methods. Because of limitations on the analytical instruments in use at the time Sprung conducted his study, it was not clear whether either formaldehyde or the phenolic compounds were undergoing reactions other than those involved in hydroxymethylation. Moreover, Sprung's kinetic data were collected in non-aqueous systems rather than in the aqueous-based systems typically encountered in industrial applications of phenolic adhesives. Because of these limitations on the earlier work and the industrial significance of phenol-formaldehyde adhesives, we have employed aqueous-based systems to investigate the reactions of formaldehyde with a larger series of phenolic compounds (Table 1). These phenolic compounds included most of the phenols investigated by Sprung.

## Experimental

### Reaction of Phenols with Formaldehyde

Reactions of the phenolic compounds with formaldehyde were conducted in a three-necked flask fitted with a condenser and a thermometer. The reactions were conducted at 30°C. Two mmol of the phenols and 2 mmol of formaldehyde were dissolved in 20 percent aqueous dimethylformamide (DMF) solution with stirring. Sufficient 10 percent sodium hydroxide solution was added such that the pH equaled the pKa of the phenolic compound. The solvent volume was adjusted to give a solids concentration of 1 percent.

### Analysis of the Reaction Mixtures by High Performance Liquid Chromatography (HPLC)

Samples of the reaction mixture were taken at various times after the reaction was initiated. The amount of phenolic compound in the sample was analyzed using a Hewlett Packard 1050 series chromatograph containing an Inertsil ODS-3 column (25 by 0.46 cm). The mobile phase consisted of acetonitrile/0.01 percent aqueous trifluoroacetic acid (TFA). An elution gradient of 5 to 45 percent acetonitrile in 30 minutes was used for the analyses of the products of the reactions of formaldehyde with phloroglucinol, resorcinol, 5-methylresorcinol, and 5-methoxyresorcinol; corresponding gradients of 10 to 45 percent acetonitrile in 25 min. and 30 to 60 percent acetonitrile in 30 minutes were used for the reaction of phenol and the reactions of methylphenols and methoxyphenols, respectively. The eluants were detected by UV absorbance at 273 nm. The amount of each phenolic compound present was calculated using calibration curves describing the relation between concentration and peak area for that compound. Each phenolic compound formed during the reaction was assumed to be characterized by the same relative response as that of the starting phenolic compound.

**Table 1.**— Phenolic compounds used in this study.

| Phenolic compound     | Abbreviation |
|-----------------------|--------------|
| 2-methylphenol        | 2MP          |
| 3-methylphenol        | 3MP          |
| 4-methylphenol        | 4MP          |
| 2,3-dimethylphenol    | 23MP         |
| 2,4-dimethylphenol    | 24MP         |
| 2,5-dimethylphenol    | 25MP         |
| 2,6-dimethylphenol    | 26MP         |
| 3,4-dimethylphenol    | 34MP         |
| 3,5-dimethylphenol    | 35MP         |
| 2,3,5-trimethylphenol | 235MP        |
| 2-hydroxymethylphenol | 2HMP         |
| 3-hydroxymethylphenol | 3HMP         |
| 3-methoxyphenol       | 30MP         |
| 3,5-methoxyphenol     | 350MP        |
| 5-methylresorcinol    | 5MR          |
| 5-methoxyresorcinol   | 5OMR         |
| phenol                |              |
| resorcinol            |              |
| phloroglucinol        |              |

### Determining Formaldehyde by the Hydroxylamine Hydrochloride Method

The concentration of formaldehyde remaining in the reaction mixture was determined by the hydroxylamine hydrochloride method (8). One mL of sample was taken from the reaction mixture and poured into a weighing jar containing 3 mL of 0.02N hydrochloric acid solution. The solution was adjusted to pH 4 with 0.02N sodium hydroxide solution, and 3 mL of 0.5N hydroxylamine hydrochloride solution was added to convert the formaldehyde to hydroxime. After stirring the solution for 10 minutes, the sample was then back-titrated to pH 4 with 0.02N sodium hydroxide solution using an autotitrator FMS-201 (Fluid Management Systems, Inc.).

### Computational Methods

Optimized starting structures for each of the phenolic compounds were obtained with HyperChem (9) at RHF/PM3. The structures were further optimized at the RHF/6-31+G level of theory using Gaussian 98 (10). The final, optimized structures were used to calculate ChelpG (11) based on average charges obtained using Gaussian 98.

### Results and Discussion

The reaction between phenol and formaldehyde in alkaline solution leads to the introduction of a hydroxymethyl group into the aromatic nucleus at positions *ortho* and *para* to the phenolic group. The rate of the

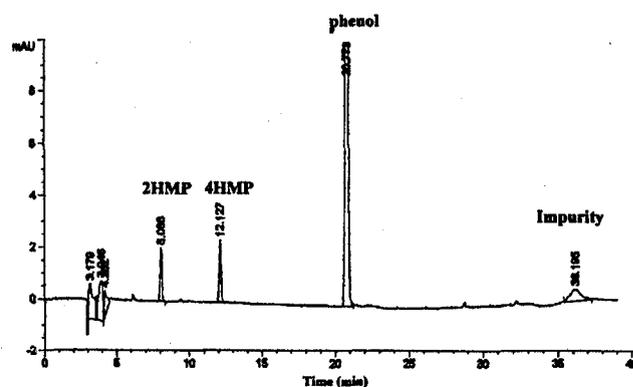
**Table 2.**—*pK<sub>a</sub>* values and dissociation constants of the phenolic compounds.

| Phenolic compound | <i>pK<sub>a</sub></i> |            | <i>K<sub>a</sub></i> |
|-------------------|-----------------------|------------|----------------------|
|                   | Literature (12)       | This study |                      |
| phenol            | 10.0                  | 10.3       | 4.9E-11              |
| resorcinol        | 9.4                   | 9.7        | 1.9E-10              |
| phloroglucinol    |                       | 9.2        | 6.0E-10              |
| 2MP               | 10.2                  | 10.6       | 2.5E-11              |
| 3MP               |                       | 10.4       | 4.3E-11              |
| 4MP               | 10.2                  | 10.6       | 2.5E-11              |
| 23MP              |                       | 10.9       | 1.1E-11              |
| 24MP              |                       | 10.9       | 1.1E-11              |
| 25MP              |                       | 10.7       | 2.0E-11              |
| 26MP              | 10.2                  | 10.9       | 1.1E-11              |
| 34MP              |                       | 10.7       | 2.0E-11              |
| 35MP              |                       | 10.5       | 3.0E-11              |
| 235MP             |                       | 11.1       | 7.9E-12              |
| 2HMP              |                       | 10.1       | 7.9E-11              |
| 3HMP              |                       | 10.1       | 7.9E-11              |
| 5MR               |                       | 9.9        | 1.2E-10              |
| 30MP              |                       | 9.9        | 1.2E-10              |
| 50MR              |                       | 9.4        | 4.3E-10              |
| 35OMP             |                       |            | 2.5E-10              |

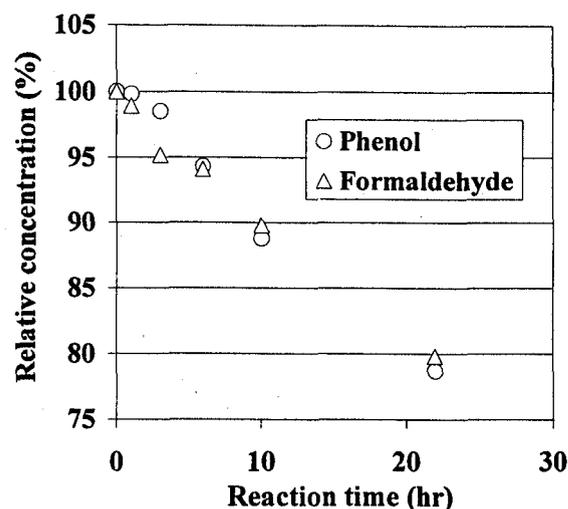
hydroxymethylation reaction is proportional to the concentration of the corresponding phenol anions. Consequently, the reactions of the phenolic compounds with formaldehyde were conducted at conditions such that each phenolic compound studied was characterized by the same concentration of its corresponding anion, i.e., at a pH equivalent to the *pK<sub>a</sub>* of that individual phenolic compound.

An aqueous solution containing 20 percent (w/w) DMF was needed for completely dissolving the methylphenols and phloroglucinol. Hence, this solvent system was used in all our studies. The *pK<sub>a</sub>* values of the phenolic compounds determined in the indicated aqueous DMF solution are shown in Table 2. The *pK<sub>a</sub>* determined in a solution containing organic solvent is generally higher than the corresponding *pK<sub>a</sub>* in water. The *pK<sub>a</sub>* values for phenol measured in water (12) and 20 percent DMF solution were 9.98 and 10.31, respectively. These results indicate that DMF has only a small effect on the extent of ionization of phenol and by inference is presumed to have minimal effect on the extent of ionization of the other phenols.

The chromatogram for the HPLC analysis of the products from the reaction of phenol with formaldehyde for 22 hours is shown in Figure 1. Inspection of this chromatogram indicates the presence of two products and residual initial phenol. The two products of



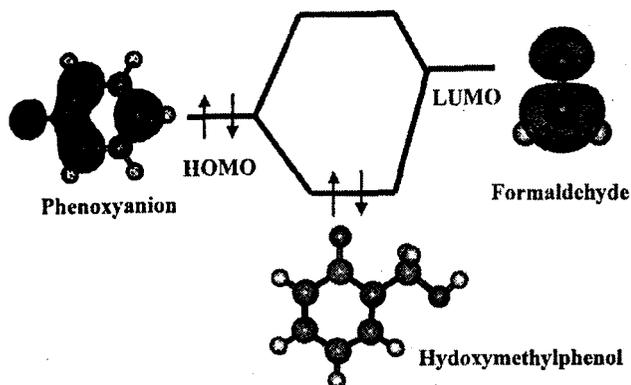
**Figure 1.**—Chromatogram resulting from HPLC analysis of the products of the reaction of phenol with formaldehyde for 22 hours.



**Figure 2.**—Consumption of phenol and formaldehyde as functions of time.

the reaction were identified as 2-hydroxymethylphenol (2HMP) and 4-hydroxymethylphenol (4HMP) by corresponding HPLC analyses of standard samples of these pure compounds. The plots in Figure 2 indicate the percentages of the initial phenol and initial formaldehyde which remain at various times. Almost equivalent molar amounts of phenol and formaldehyde are consumed as the reaction proceeds as is expected for a reaction in which the stoichiometric coefficients of phenol and formaldehyde are identical.

The reaction of phenol with formaldehyde corresponds to an electrophilic aromatic substitution (Fig. 3). Under alkaline conditions, phenol forms phenoxyanion. Phenoxyanion is generally considered to be the phenolic form that reacts with electrophilic compounds like formaldehyde. In terms of frontier molecular orbital theory (13), the reaction is envisioned to involve the highest occupied molecular orbital (HOMO) of the



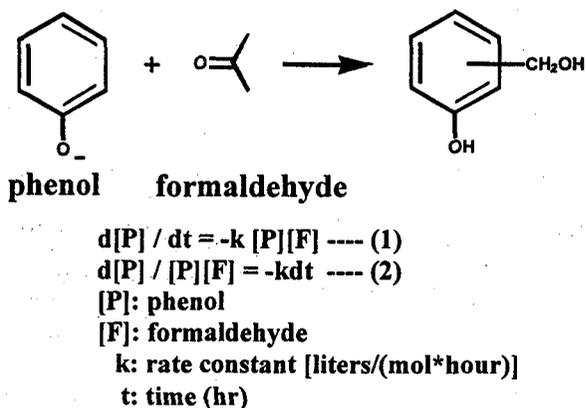
**Figure 3.**—Molecular orbital theory representation of the electrophilic substitution of phenol with formaldehyde. HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital.

phenoxyanion and the lowest unoccupied molecular orbital (LUMO) of formaldehyde. The HOMO of the phenoxyanion is distributed at the *o*- and *p*-positions of the aromatic ring. The LUMO of formaldehyde is located on the carbon atom. In addition, chemical computational methods predict that the carbon atom of formaldehyde bears a positive charge, while the *o*- and *p*-positions of the aromatic ring bear negative charges. Because there are no apparent steric factors to prevent reaction, one predicts that formaldehyde will react with phenol at the *o*- and *p*-positions, as is observed experimentally. Thus, the electrons in the HOMO orbital of the phenoxyanion are in effect shared with the LUMO orbital of formaldehyde to form a bond, giving the two indicated hydroxymethylphenol derivatives. The reaction of formaldehyde with other phenolic compounds can be envisioned as taking place in a similar fashion and could serve as the basis for a method of predicting the reactivity of formaldehyde with phenolic compounds.

The general method used to estimate the average charge per reactive site and a simple method of accounting for gross steric hinderance are represented in Figure 4. This example indicates the distribution of atomic charges on the 2,5-dimethylphenol anion (25MP) calculated using the CHelpG method. The total of all the atomic charges equals  $-1$ , as is required for an anion bearing a net charge equal to that of a single electron. Large negative charges are located at the C2, C4, and C6 positions of the aromatic ring. The HOMO orbital is also located on these same sites. Consequently, one expects the positively charged carbon of formaldehyde to be capable of reacting at these three sites. However, because a methyl group is attached at C2, access of formaldehyde to this site is more sterically hindered than is its access to the C4 and C6 positions. As a result, it is assumed that reaction of 25 MP is possible

| No.A  | Charge |                                                                    |
|-------|--------|--------------------------------------------------------------------|
| 1C    | 0.820  | Unsubstituted carbon with HOMO (UH)                                |
| 2C    | -0.209 |                                                                    |
| 3C    | -0.110 |                                                                    |
| 4C    | -0.482 | Substituted carbon with HOMO (SH)                                  |
| 5C    | 0.299  |                                                                    |
| 6C    | -0.654 |                                                                    |
| 7O    | -0.962 |                                                                    |
| 8C    | 0.010  |                                                                    |
| 9C    | -0.040 |                                                                    |
| 10H   | 0.101  | 2,5-dimethylphenol anion                                           |
| 11H   | 0.114  |                                                                    |
| 12H   | 0.163  |                                                                    |
| 13H   | -0.036 |                                                                    |
| 14H   | 0.003  |                                                                    |
| 15H   | 0.003  |                                                                    |
| 16H   | 0.008  |                                                                    |
| 17H   | -0.014 |                                                                    |
| 18H   | -0.014 |                                                                    |
| Total | -1.000 | Average $q = \text{sum of } q \text{ at UH} / \text{number of UH}$ |

**Figure 4.**—Charge distribution and average charges for 2,5-dimethylphenol.

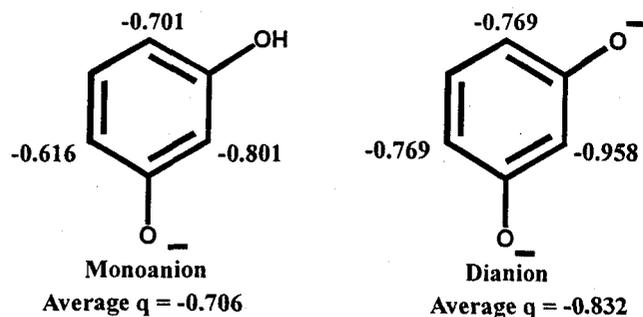


**Figure 5.**—Calculation of rate constant ( $k$ ) from consumption of phenol and formaldehyde.

only at two reactive sites, namely at C4 and C6. The average charge per reactive site ( $q_{\text{ave}}$ ) for 25 MP can be calculated by summing the charges at the unsubstituted carbons on which the HOMO orbital is located (UH) and dividing by the number of reactive sites. In the present case, the average charge is thus  $[-0.482 - 0.654]/2 = -0.568$ .

The base-catalyzed hydroxymethylation of phenol by formaldehyde in dilute aqueous solution is generally considered to be a second-order reaction (14). Thus the reaction follows the general rate expression given by Equation 1 in Figure 5, where  $P$  is the concentration of the phenolic compound and  $F$  is the concentration of formaldehyde at any time  $t$ . Equation 1 can be rearranged as shown in Equation 2 in Figure 5. By plotting the data in the form of the left side of Equation 2 vs.  $dt$ , one obtains a linear plot with slope  $k$ . This method was





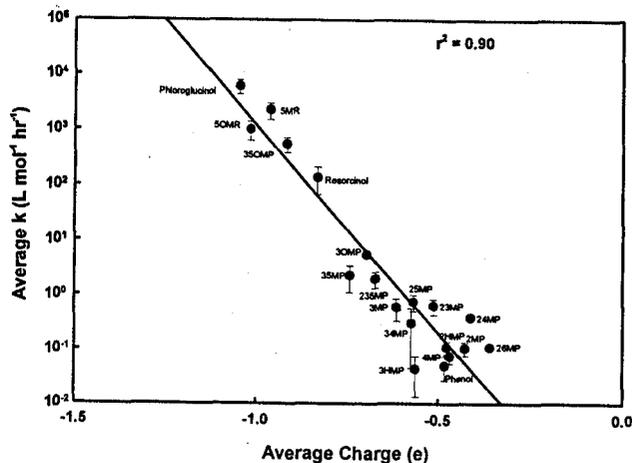
**Figure 8.**—Differences in the CHelpG charges for the monoanion and dianion of resorcinol.

tion conditions used in this study. The differences between the CHelpG charges on the monoanion and dianion of resorcinol are shown in Figure 8. Differences in the charges at the C2, C4, and C6 positions are reflected in the differences for  $q_{ave}$ . An alternative plot of the data in the form of  $k_{ave}$  vs.  $q_{ave}$  (calculated using average charge values for the dianions of the di- and tri-phenols) is shown in Figure 9. This approach results in a slightly stronger correlation ( $R^2 = 0.90$ ) between the experimental data and the calculated charges.

These correlations of the experimental data with the calculated values are not perfect because several other factors can also affect reactivity (e.g., steric hindrance). These other factors have not been adequately accounted for in the present study. However, the strong correlation that was observed indicates the predominate role that charge considerations play in determining the reactivity of formaldehyde with phenolic compounds. In addition, the method indicated above can be used to predict the relative reactivities of phenolic compounds with a wide variety of different chemical structures. Thus, the rates of reaction of resorcinol and phloroglucinol relative to phenol are on the order of 4,000 and 180,000, respectively. These relative reactivities are consistent with the experimental observations that a phenol-formaldehyde resin must be cured at elevated temperatures while a resorcinol-formaldehyde resin cures at room temperature and that resins made from compounds containing a phloroglucinolic sub-structure (e.g., pine tannins) cure almost instantaneously.

### Conclusions

1. Rate constants for the reactions of a large variety of phenolic compounds with formaldehyde in aqueous solution under alkaline conditions were obtained from experimental measurements. These data represent the largest available data base for the reactivities of different phenolic compounds with formaldehyde.



**Figure 9.**—Semilog plot of the average rate constant vs. average CHelpG charge calculated at the RHF/6-31 + G level of theory for the reactions of formaldehyde with various phenolic compounds. The compounds containing two and three phenolic groups are assumed to exist in solution as the dianions.

2. Resorcinol and phloroglucinol represent sub-structures often found in phenolic materials derived from natural sources. The ratio of the reactivities of resorcinol and phloroglucinol to phenol were estimated to be 4,000 and 180,000 times, respectively.
3. A strong correlation was obtained between  $k_{ave}$  determined experimentally for the reactions of phenolic compounds with formaldehyde and  $q_{ave}$  determined by calculations at the RHF/6-31 + G level using CHelpG.
4. The correlation of  $k_{ave}$  and  $q_{ave}$  was best when di- and tri-phenols were assumed to exist in solution as their respective dianions.

### References

1. Aldersley, J.W. and P. Hope. 1972. A study of the methylation of phenol using gel permeation chromatography. *Die Angewandte Makromolekulare Chemie*. 24:137-153.
2. Astarloa-Aierbe, G., J.M. Echeverria, J.L. Egiburu, M. Ormaetxea, and L. Mondragon. 1998. *Polymer*. 39:3147-3153.
3. Dijkstra, R., J. DeJonge, and M.F. Lammers. 1962. The kinetics of the reaction of phenol and formaldehyde. *Rec. trav. chim.* 81:285-296.
4. Grenier-Loustalot, M.F., S. Larroque, P. Grenier, J.-P. Leca, and D. Bedel. 1994. Phenolic resins: 1. Mechanisms and kinetics of phenol and of the first polycondensates towards formaldehyde in solution. *Polymer*. 35:3046-3054.
5. Grenier-Loustalot, M.F., S. Larroque, D. Grande, and P. Grenier. 1996. Phenolic resins: 2. Influence of catalyst type on reaction mechanisms and kinetics. *Polymer*. 37:1363-1369.
6. Sprung, M.M. 1941. Reactivity of phenols toward para-formaldehyde. *J. Amer. Chem. Soc.* 63:334-343.

7. Conner, A.H. 2000. Predicting the reactivity of phenolic compounds with formaldehyde under basic conditions: An ab initio study. *J. Appl. Polym. Sci.*
8. Meyer, B. 1979. Urea-formaldehyde resins. Addison-Wesley Publishing Co., Inc. pp. 123-126.
9. HyperChem 5.1; Hypercube, Inc.; Gainesville, FL.
10. Gaussian 98, Revision A.7. 1998. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople. Gaussian, Inc., Pittsburgh PA.
11. Breneman, C.M. and K.B. Wiberg. 1990. Determining atom-centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. *J. Comp. Chem.* 11:361-373.
12. Abe, I. and H. Ono. 1980. Effect of the acidity of some tropical wood extractives on the curing of the resol. *Mokuzai Gahishi.* 26:686-692.
13. Clark, T. 1985. *A Handbook of Computational Chemistry.* John Wiley and Sons. pp. 133-138.
14. Zavitsas, A.A., R.D. Beaulieu, and J.R. Leblanc. 1968. Base-catalyzed hydroxymethylation of phenol by aqueous formaldehyde. Kinetics and mechanism. *J. of Polym. Sci. Part A-1* 6:2533-2540.

# Wood Adhesives 2000

*June 22-23, 2000  
Harveys Resort Hotel & Casino  
South Lake Tahoe, Nevada*

*Sponsored by*  
The USDA Forest Service, Forest Products Laboratory

*in cooperation with*  
the Forest Products Society  
the Adhesion Society  
International Union of Forestry Research Organizations (IUFRO)  
the Japan Wood Research Society



**Forest Products Society  
2801 Marshall Court  
Madison, WI 53705-2295  
phone: 608-231-1 361  
fax: 608-231-2152  
[www.forestprod.org](http://www.forestprod.org)**