

# Phenolation of Wood Using Oxalic Acid as a Catalyst: Effects of Temperature and Hydrochloric Acid Addition

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## SYNOPSIS

Birch wood meal has been phenolated in the presence of oxalic acid alone or its mixture with hydrochloric acid (HCl) at various temperatures ranging from 150 to 250°C under high pressure. The effects of high temperature, high pressure, and the addition of HCl in conjunction with oxalic acid on the amounts of wood residue and combined phenol have been investigated. In the case of the oxalic acid-catalyzed process, by increasing reaction temperature from 180 to 250°C, the amounts of wood residue could be considerably reduced, but the amount of combined phenol decreased. In comparison to a noncatalyzed process in the absence of water, the catalyzed one offered a relatively lower amount of wood residue and a higher amount of combined phenol. However, compared to a noncatalyzed process with water, particularly at a high temperature of 250°C, the catalyzed process gave significantly larger amounts of wood residue. In addition, with a small addition of HCl to an oxalic acid catalyzed system, the amount of wood residue was remarkably reduced compared to that of oxalic acid alone, and the amount of combined phenol could be increased significantly. Furthermore, the mechanical properties of the moldings prepared from the phenolated wood were sufficiently improved by the addition of a small amount of HCl to the oxalic acid-catalyzed system. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

With the increasing impetus for a more extensive utilization of abundant and renewable biomass resources, liquefaction of wood in the presence of phenol and its application to thermosetting materials have been studied intensively in our laboratory. Until now, phenolated wood resins with good processability and reactivity have been successfully prepared by various methods.<sup>1-8</sup> On the other hand, it has also been found that the liquefaction efficiency of wood, the thermoflow properties, and reactivity of the resulting resins were remarkably dependent on liquefaction conditions, such as the kind of catalyst and the temperature. Therefore, for a more comprehensive understanding of the liquefaction of wood and for further development of its application,

more extensive studies on the fundamental phenomena of the liquefaction should be accomplished.

As a result, in our recent study on the preparation of phenolated wood-based novolak type resins, we attempted the use of oxalic acid<sup>5</sup> as a catalyst for the phenolation of wood because it is less corrosive to processing equipment and less harmful to human health compared to strong acids, such as hydrochloric and sulfuric acid.<sup>9</sup> However, when we used an open system under moderate temperatures (150–170°C) for the phenolation of wood,<sup>5</sup> with respect to the amount of combined phenol, conversion rate of wood, processability of the phenolated wood-based resin, and so on, the catalytic effect of oxalic acid was found to be insufficient compared to that of relatively stronger acids, such as sulfuric<sup>4</sup> and hydrochloric (HCl) acid.<sup>1,2</sup>

As one of the resolutions to the aforementioned problems, a postresinification process applied after oxalic acid catalyzed phenolation using formaldehyde has been found to be efficient for improving the properties of the phenolated wood resins, as

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shown in our previous study.<sup>5</sup> However, in this case the amount of unreacted wood was still said to be high.<sup>5</sup>

Therefore, attempts were made in this study to reduce wood residues by increasing the reaction temperature under high pressure, or by additions of small amounts of HCl to the oxalic acid catalyzed system. The main goal of this study was to determine the effects of high reaction temperatures using oxalic acid as a catalyst, and the effects of the additions of small amounts of HCl as a catalyst together with oxalic acid on the typical parameters of the wood phenolation (e.g., the amount of wood residue, combined phenol, and so on).

## EXPERIMENTAL

### Materials

Wood meals (20–80 mesh) prepared from birch (*Betula maximowicziana* Regel) species, guaranteed reagent grade phenol (solvent), anhydrous oxalic acid, and 36.5% aqueous HCl acid (catalysts) were used for phenolation process. Moreover, commercial grade hexamethylenetetramine (HMTA) (curing agent), zinc stearate (lubricating agent), calcium hydroxide (accelerating agent), and wood flour (filler) were used as molding components for making novolak resin-type moldings, which were obtained from Hitachi Chemical Co. Ltd., Japan.

### Phenolation of Wood

Three grams of wood meal (oven dry), 6–9 g of phenol, 0.18–0.48 g of oxalic acid, and/or 0.15–0.67 g of 36.5% aqueous HCl acid were charged in a specially designed 300-mL reaction tube, as illustrated in Figure 1. The reaction tube was heated in an oil bath at a temperature range of 150–250°C for various reaction times.

After the end of the reaction time, the reaction was terminated by putting the reaction tube in ice-cooled water. The resultant mixture, consisting of phenolated wood, free phenol, and wood residue, was diluted with methanol and filtered with a glass-fiber filter (Toyo GA-100). The methanol-insoluble part (i.e., wood residue) was oven dried, and wood residue percent was determined. The methanol-soluble parts, after being sampled for high-performance liquid chromatography (HPLC) measurement of free phenol, were concentrated under reduced pressure (40 mm Hg) to remove the methanol and free phenol

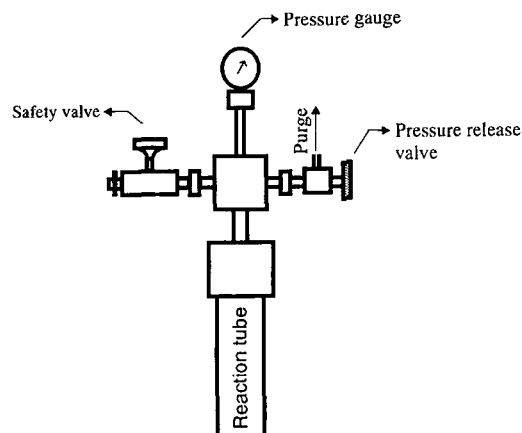


Figure 1 Reaction apparatus.

at 50 and 180°C, respectively, and then the phenolated wood was obtained.

### Preparation of the Moldings

For preparing the molding compound, the phenolated wood (37.7%) obtained as described earlier was dissolved in acetone and mixed with HMTA (9.4%), zinc stearate (1.0%), calcium hydroxide (2.4%), and wood flour (49.5%). After mixing thoroughly, the mixture was oven dried at 70°C for 1 h to remove acetone and then ground in a mortar to make fine powders.

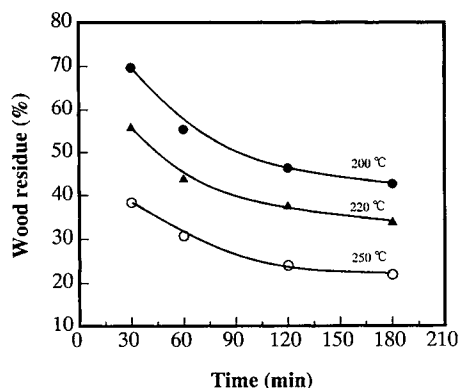
The powdered molding compound obtained as mentioned earlier was compression molded into test specimens in a die with a dimension of 4 × 10 × 80 mm. The molding conditions were as follows: temperature, 190°C; pressure, 39.2 MPa; time, 5 min. Then the specimen was removed from the die and cooled under a slight pressure from 190°C to an ambient temperature.

### Measurements

The extent of liquefaction was evaluated on the basis of the wood residue and the amount of phenol combined with wood components, the so-called combined phenol. The wood residue was calculated by the following equation:

$$R(\%) = \frac{W_r}{W_0} \times 100 \quad (1)$$

where  $R$  is the wood residue in percent,  $W_r$  is the oven-dry weight of the solid wood residue (g), and



**Figure 2** The effects of reaction temperature and time on the wood residue for the oxalic acid catalyzed process. Phenol/wood ratio (w/w), 2; oxalic acid concentration, 3%.

$W_0$  is the oven-dry weight of the starting wood meal (g).

The amounts of free phenol remaining in the methanol-soluble parts were measured by using HPLC (Shimadzu LC-10A series) equipped with a SPD-10A ultraviolet (UV)-vis detector and Shimadzu shim-pack CLC-ODS (M) column [4.6 mm (i.d.)  $\times$  150 mm]. The chromatographic zones were visualized under UV light (254 nm). Tests were performed at 40°C at a flow rate of 1 mL/min using methanol/water solution ( $\frac{1}{2}$ , v/v) as the mobile phase. In addition, a phenol solution of known concentration was used as a standard. For the measurements, the methanol-soluble parts were injected into the HPLC apparatus in the amount of 10  $\mu$ L. Then the amounts of free phenol in the methanol-soluble parts were obtained by comparing with those of the standard solution.

Then the amount of combined phenol was calculated as follows:

$$CP(\%) = \frac{P - FP}{W_0 - W_r} \times 100 \quad (2)$$

where CP is the amount of combined phenol in percent,  $P$  is the amount of starting phenol (g), and FP is the amount of free phenol remaining in the liquefaction mixture (g).

### Mechanical Properties

Mechanical properties—the modulus of rupture (MOR) and modulus of elasticity (MOE)—of the phenolated wood-based moldings were measured according to the JIS (Japanese Industrial Standard) K 7203 standard. The tests were performed on a

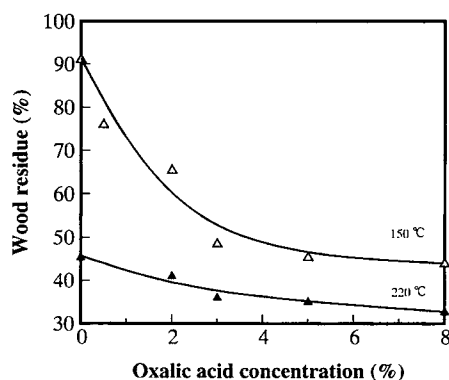
Shimadzu Autograph DCS R-500 universal testing machine. The samples were conditioned at  $20 \pm 2^\circ\text{C}$  and  $60 \pm 5\%$  relative humidity (RH) for 2 weeks before testing. The MOR and MOE values were calculated from the load-deflection curves by the equations available in the standard.

## RESULTS AND DISCUSSION

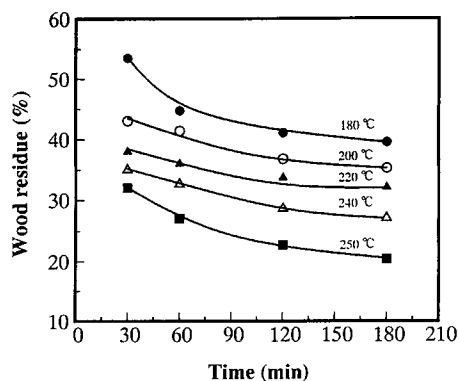
### The Effects of Reaction Temperatures and Times on Wood Residue

Figure 2 indicates the effects of reaction temperatures and times on the amounts of wood residue for oxalic acid catalyzed process. It is evident that the amount of wood residue decreases significantly with the increase in the reaction temperature. An 70°C-increase in the reaction temperature results in about a 20% decrease in the wood residue. However, as shown in Figure 2, the wood residue decreases somewhat sharply until reaction time reaches 120 min and then slows down in all cases. A relatively small amount of wood residue, about 20%, can be obtained at 250°C for 180 min. It is also worthwhile to mention that for the oxalic acid catalyzed phenolation process using an open system at a temperature range of 150–170°C, the amount of wood residue could not be reduced below about 50%, as discussed in our previous study.<sup>5</sup>

Figure 3 illustrates the effect of oxalic acid concentration on the amount of wood residue at two different reaction temperatures, 150 and 220°C. It is found that the influence of oxalic acid concentration on the wood residue is more drastic at the former temperature compared to that of the latter one. As shown in Figure 3, at a temperature of 150°C with



**Figure 3** The effect of oxalic acid concentration on the wood residue as a function of reaction temperature. Phenol/wood ratio (w/w), 3; time, 2 h.

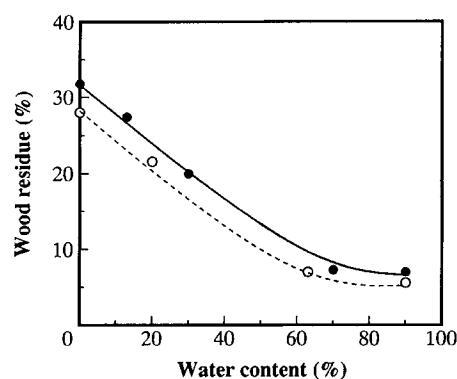


**Figure 4** The effects of reaction temperature and time on the wood residue for the noncatalyzed process. The other reaction conditions are the same as in Fig. 2.

an increase in oxalic acid concentration from 0 to 4.5%, the amount of wood residue descends significantly and then almost levels off with a further increase in the concentration of oxalic acid. This is attributable to the much more decreases in pH values at elevated temperatures (e.g., 250°C) (Fig. 11).

Figure 4 displays the effects of reaction temperature and time on the wood residue for the noncatalyzed process. It is evident from the figure that at the reaction temperatures studied, the changes of the wood residue become very slow after 30 min of the reaction time. On the other hand, as shown in the same figure, in comparison with the results obtained from the oxalic acid-catalyzed process (see Fig. 2), the noncatalyzed process gives a higher amount of wood residues at temperatures of 200 and 220°C but, slightly higher wood residues at temperatures of 250°C under the same experimental conditions. This can be explained by the variation of pH values with the reaction temperatures, as will be shown in Fig. 11. This is one of the advantages of an oxalic acid catalyzed process over a noncatalyzed one.

However, as can be seen from Figure 5, the addition of about 60–90% water (based on oven-dried wood meal) into a noncatalyzed process decreases the amount of wood residue very significantly even compared to the oxalic acid-catalyzed one. This is because at higher temperatures water provides steam, which acts as a hydrolyzing agent and heat transfer medium. On the other hand, as shown in the same figure, in the presence of both oxalic acid and water, the wood residues are somewhat lower than those of only with water, indicating that both water and oxalic acid catalyst contribute to the liquefaction.

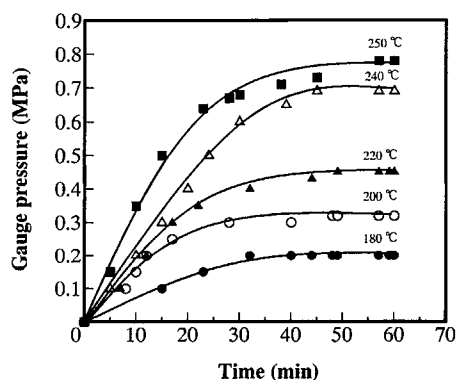


**Figure 5** The effect of water content on the wood residue at a reaction temperature of 250°C. (●): Noncatalyzed and water system; (○): oxalic acid catalyzed and water system (the fixed oxalic acid concentration, 3%). The other reaction conditions for both cases are the same as in Fig. 2.

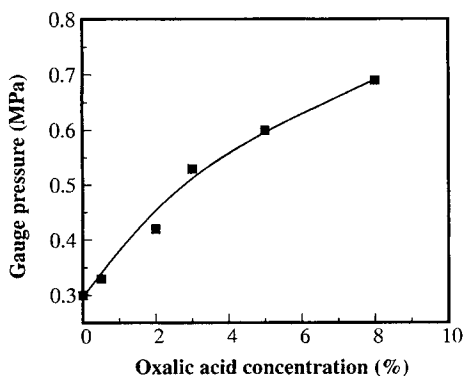
### Tube Pressure

The variations of tube pressures with reaction times and reaction temperatures are illustrated in Figure 6. It is obvious from this figure that the tube pressure rises along with the increase in the reaction time and temperature because of the presence of the volatile solvent (phenol) and the decomposition of wood components,<sup>10</sup> such as cellulose, hemicellulose, lignin, and oxalic acid itself to volatile substances (e.g., CO, CO<sub>2</sub>, and water).<sup>11</sup> However, with the increase in reaction time from 0 to 25 min, the pressure increases linearly and then slows down and almost levels off with further prolongation of reaction.

Figure 7 shows the relationship between the amount of oxalic acid concentration (based on starting phenol) and gauge tube pressure at 250°C. As shown in Figure 7, gauge tube pressure increases



**Figure 6** The effects of reaction time and temperature on the tube pressure for oxalic acid catalyzed process. The other reaction conditions are the same as in Fig. 2.

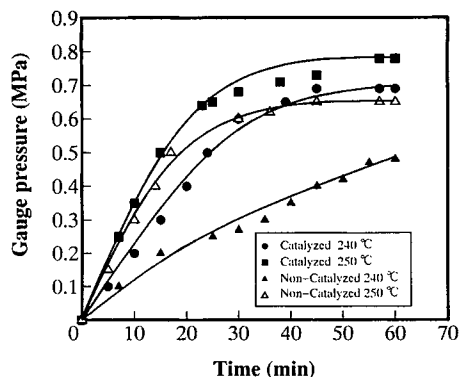


**Figure 7** The effect of the oxalic acid concentration on the tube pressure at a reaction temperature of 250°C. The other reaction conditions are the same as in Fig. 3.

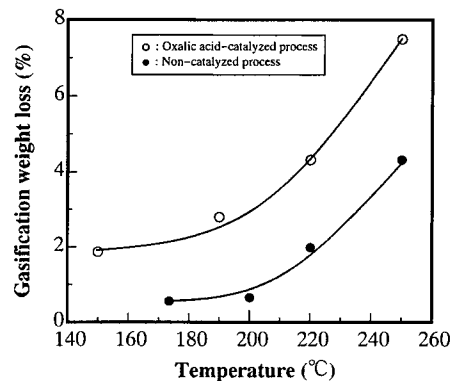
almost linearly with increasing oxalic acid concentration. This can be ascribed to the enhanced decomposition of wood components and oxalic acid itself at a higher oxalic acid concentration (also see Fig. 11).

Figure 8 shows a comparison of the gauge tube pressure for the oxalic acid-catalyzed process with that of a noncatalyzed one for different reaction times and temperatures. Once again, as shown in Figure 8, compared to a noncatalyzed system, an oxalic acid-catalyzed one shows higher tube pressure due to the decomposition of oxalic acid to CO, CO<sub>2</sub>, and water.<sup>11</sup>

This fact can also be confirmed in Figure 9, in which much higher gasification weight loss is observed for the oxalic acid catalyzed process in comparison with the noncatalyzed one. It is also found from the same figure that, especially when the reaction temperature becomes higher than 200°C, the



**Figure 8** The comparison of the tube pressure for the oxalic acid catalyzed process with that of the noncatalyzed one for different reaction times and temperatures. The other reaction conditions are the same as in Fig. 2.



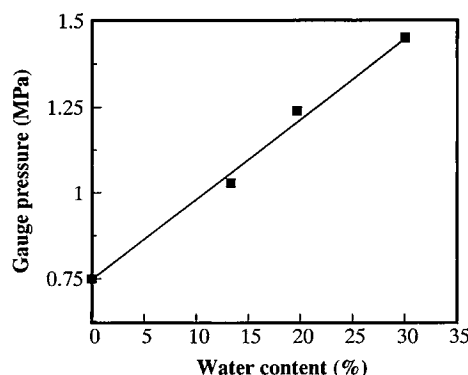
**Figure 9** The effect of reaction temperature on the gasification weight loss for both oxalic acid catalyzed and noncatalyzed processes. The other reaction conditions are the same as in Fig. 2.

weight loss due to gasification increases sharply for both catalyzed and noncatalyzed systems.

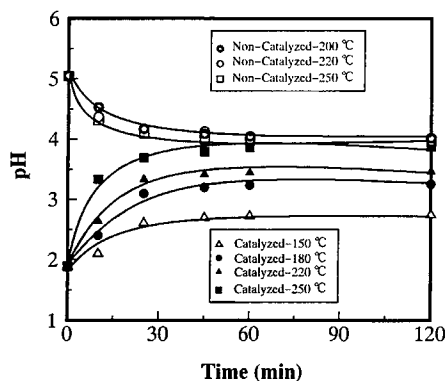
Figure 10 shows the effect of water content (based on the starting wood meal) on the gauge pressure for the noncatalyzed system at 250°C. As expected, the gauge pressure increases linearly with an increase in the amount of water due to its steam effect at elevated temperatures.

**pH**

Figure 11 depicts the variations of pH measured after the phenolation of wood with reaction temperatures and times for both the catalyzed and noncatalyzed processes. This figure reveals that in the case of the catalyzed process, the pH values increase with reaction time until 30 min of liquefaction, and then the trend slows down. In addition, with an increase



**Figure 10** The relationship between water content and tube pressure for a noncatalyzed process at a reaction temperature of 250°C. The other reaction conditions are the same as in Fig. 5.



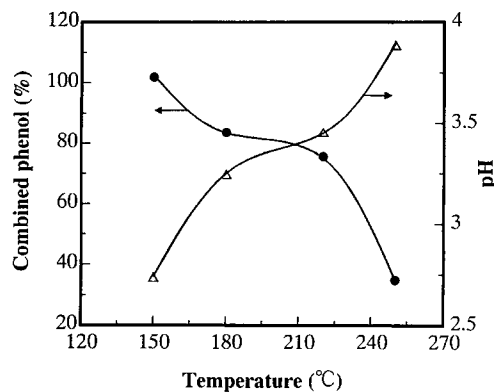
**Figure 11** The effects of reaction time and temperature on pH of the liquefaction solution for both catalyzed and noncatalyzed process. Phenol/wood ratio (w/w), 3; oxalic acid concentration, 3%; pH was measured in methanol-water solution (1/1, v/v).

in the reaction temperature, the pH values of the liquefaction solution rise distinctly due to the enhanced decomposition of oxalic acid to the neutral substances, such as water and gases. It is also interesting to note that pH tends to increase even at a 150°C reaction temperature.

Unlike oxalic acid-catalyzed process, the pH values for the noncatalyzed process decrease with an increase in the reaction time and temperature in the beginning 30 min of reaction time, due mainly to the decomposition of the acetyl groups (about 5–6% for hardwoods)<sup>12</sup> in hemicellulose to acetic acid.<sup>10,13</sup> However, this decrease does not change significantly with further altering reaction temperatures and times.

### The Effects of Reaction Temperatures on the Amount of Combined Phenol

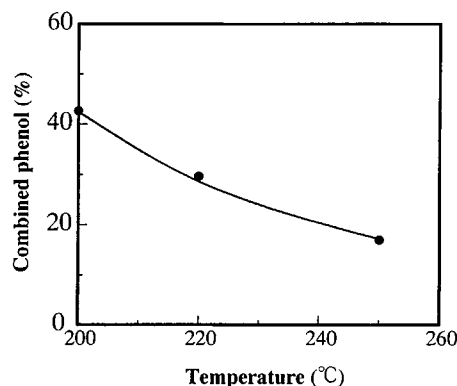
Figure 12 demonstrates the effects of the reaction temperatures on the amount of combined phenol and pH of the resultant reaction mixture in the case of catalyzed liquefaction. It is obvious from this figure that the amounts of combined phenol descend with an increase in the reaction temperature. This is understandable because the liquefaction mechanism at elevated temperatures is different from that at a moderate temperature. That is, the former is mainly dominated by a homolytic mechanism, which produces much smaller amounts of combined phenol compared with the latter, which was performed by a heterolytic mechanism.<sup>14</sup> Therefore, with increases in reaction temperature, the homolytic mechanism becomes more and more dominant in the liquefac-



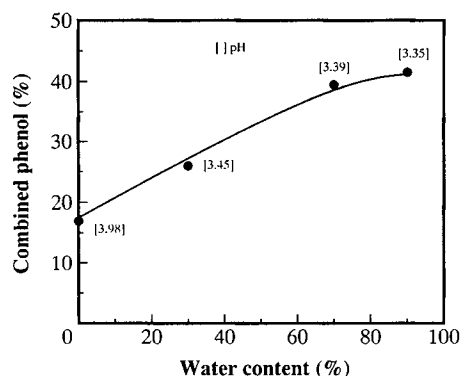
**Figure 12** The effects of the reaction temperatures on the amount of combined phenol and pH of the liquefaction mixture for the oxalic acid catalyzed process. The other reaction conditions are the same as in Fig. 11.

tion, and as a result, the amount of combined phenol decreases.

Figure 13 demonstrates the effect of reaction temperature on the amount of combined phenol for the noncatalyzed system. As one can see from this figure, the amount of combined phenol decreases with an increase in the reaction temperature. This can also be explained by the homolytic nature of the reaction at elevated temperatures, as in oxalic acid catalyzed phenolation.<sup>14</sup> It is also evident from Figure 13 that the noncatalyzed process gives a similar trend of the amount of combined phenol versus reaction temperature compared to the oxalic acid-catalyzed one. However, by comparing Figure 12 with Figure 13, it appears that the absolute combined phenol values of the oxalic acid catalyzed process are significantly higher than those of the noncatalyzed one.



**Figure 13** The effects of the reaction temperature on the amounts of combined phenol for the noncatalyzed process. The other reaction conditions are the same as in Fig. 4.



**Figure 14** The effect of water content on the amount of combined phenol for a noncatalyzed process at a reaction temperature of 250°C. The other reaction conditions are the same as in Fig. 2.

Figure 5 indicates that the addition of water can significantly reduce the amount of wood residue. In this connection, Figure 14 displays the effect of water content on the amount of combined phenol. It is very interesting to notice that by increasing the amount of water from 0 to 90 wt % (based on the oven-dried wood meal), a 20% increase in the amount of combined phenol is observed. This is probably because of the obvious decrease in pH values, as shown in the same figure, which resulted from the hydrolyzing effect of water at high temperatures. However, it has been known that the mechanical properties of the moldings prepared from the phenolated wood mainly depend on the amount of combined phenol in the phenolated wood—that is, the mechanical properties increase significantly with increases in the amount of combined phenol and then level off when the amount of combined phenol reaches a certain value (e.g., about 150–160%) (unpublished data). Therefore, it is obvious that by this small amount of combined phenol (about 10–40%), sufficient mechanical properties cannot be obtained, as is also shown in Table I. For this reason, efforts must be focused on increasing the amounts of combined phenol in the phenolated wood to a sufficient level.

#### The Effect of HCl Addition along with Oxalic Acid

To increase the efficiency of the weak organic acids (e.g., oxalic and acetic acid) on the phenolation of wood, their combination with small amounts of strong acids (e.g., HCl, sulfuric acid) was thought to be an effective approach. In this study, we attempted to use oxalic acid, which is the most com-

**Table I** The Effect of HCl Addition along with Oxalic Acid on the Mechanical Properties for Phenolated Wood-based Moldings

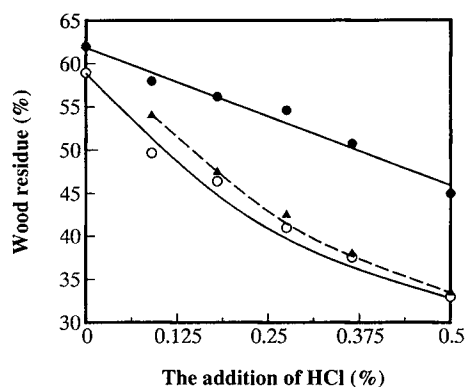
HCl <sup>a,b</sup> (%)	Modulus of Rupture, MOR (MPa)	Modulus of Elasticity, MOE (MPa)
0.00	42.67	74.69
0.09	65.93	76.48
0.18	71.63	81.42
0.27	77.83	88.36
0.37	79.12	91.86

<sup>a</sup> The other reaction conditions: phenol/wood ratio (w/w), 3; reaction time, 2 h; reaction temperature, 150°C.

<sup>b</sup> Based on the amount of starting phenol; the concentration of oxalic acid used was 5% (based on the amount of starting phenol).

monly used catalyst for commercial phenol-formaldehyde resin production, together with small amounts of HCl (which is inexpensive) on the phenolation of wood. Oxalic and HCl acids are compatible with each other from the viewpoint of their easy removal during the free phenol distillation at higher temperatures (e.g., 180°C).

Figure 15 shows the effects of HCl additions on the amounts of wood residue under a fixed oxalic acid content of 5%. It is obvious that the wood residue decreases significantly with increasing HCl addition for both phenol/wood ratios studied—that is, 2 and 3. Moreover, it is evident from the figure that HCl addition seems to be more effective at higher levels of phenol/wood ratios. As also can be seen from the same figure, in comparison with the HCl-



**Figure 15** The effect of HCl addition on the wood residue. (●): Oxalic acid concentration, 5%; phenol/wood ratio (w/w), 2; temperature, 150°C; time, 2 h. (○): oxalic acid concentration, 5%; phenol/wood ratio (w/w), 3; temperature, 150°C; time 2 h. (▲): only HCl; temperature, 150°C; phenol/wood ratio (w/w), 3; time 2 h.

catalyzed process, the oxalic and HCl combination system gives a somewhat smaller amount of wood residue. On the other hand, compared with sulfuric acid-catalyzed phenolation,<sup>4</sup> oxalic acid plus a small amount of HCl catalyzation shows higher wood residues but almost comparable wood residues in comparison with phosphoric acid catalyzation.<sup>6</sup>

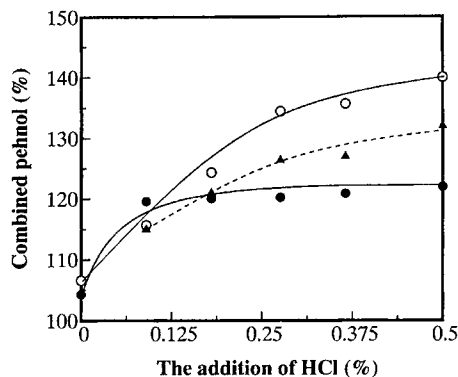
Figure 16 displays the effect of HCl addition along with oxalic acid on the amount of combined phenol at phenol/wood ratios (w/w) of 2 and 3. As shown in this figure, increasing HCl addition along with oxalic acid increases the amount of combined phenol. The influence of HCl addition on the amount of combined phenol at a phenol/wood ratio of 3 is more pronounced compared to that of a phenol/wood ratio of 2. Especially, the use of oxalic acid in combination with HCl at a phenol/wood ratio of 3 is more effective at providing much higher amounts of combined phenol compared to that of oxalic acid or HCl alone. However, the increases level off when the addition amount reaches a certain value (about 0.3% for a phenol/wood ratio of 3 and about 0.1% for a phenol/wood ratio of 2). This result indicates that the increases in the combined phenol are limited. On the other hand, the phenolation done by small amounts of HCl addition along with oxalic acid gives combined phenols lower than one performed by sulfuric acid<sup>4</sup> but comparable to one done by phosphoric acid.<sup>6</sup> Moreover, this trend is consistent with that of HCl-catalyzed phenolation performed under atmospheric pressure.<sup>2</sup>

Table I presents the effect of HCl addition to the oxalic acid-catalyzed system on the mechanical properties (i.e., MOR and MOE) for phenolated wood-based moldings. As indicated in this table, the mechanical properties increase significantly with an increase in the addition of HCl to some extent. This fact can be attributed to the increase in the amount of combined phenol.

It is interesting to note that an approximately 0.18% addition of HCl increases the MOR by about 70% and gives a MOR value of around 70 MPa, which is acceptable for commercial novolak resin-type moldings.<sup>15</sup> Furthermore, the processability of the molding compounds can also be improved by small additions of HCl due to good reactivity of the phenolated wood matrix.

## CONCLUSIONS

From the aforementioned results and discussion, the following conclusions can be drawn:



**Figure 16** The effects of HCl addition along with oxalic acid on the amounts of combined phenol. Legends and reaction conditions are the same as in Fig. 14.

1. The wood residue, as well as the amount of combined phenol, obtained by an oxalic acid-catalyzed phenolation process decreased significantly with an increase in reaction temperature from 180 to 250°C under high pressures.
2. In comparison with a noncatalyzed process without water, the catalyzed one gave somewhat lower wood residue and higher combined phenol; however, it gave higher wood residue compared to the noncatalyzed process with water. Moreover, the wood residues obtained by the oxalic acid catalyzed process with water were found to be relatively smaller than that obtained by the noncatalyzed one with water.
3. With a small addition of HCl in conjunction with oxalic acid, the wood residue could be remarkably decreased in comparison with the oxalic acid catalyzed process alone, and the amount of combined phenol could be significantly increased compared to either only HCl or oxalic acid.
4. The mechanical properties of the moldings from the phenolated wood resins were sufficiently improved by small additions of HCl.

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