

# Molecular Weights and Molecular Weight Distributions of Liquefied Wood Obtained by Acid-Catalyzed Phenolysis

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Received 17 May 1996; accepted 11 September 1996

**ABSTRACT:** By means of gel permeation chromatography analysis, the molecular weights and molecular weight distributions of liquefied wood obtained under various liquefaction conditions and species of catalysts were investigated in order to trace the change in the structural characteristics of the liquefied wood. The results indicated that during the liquefaction reaction, wood components were subjected to decomposition, phenolation, and recondensation. The intensities of these reactions depended greatly on the reaction conditions and the species of catalysts, and their competing result determined the structural characteristics of the resulting liquefied wood. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 351–357, 1997

**Key words:** liquefied wood; gas permeation chromatography; phenol; phenolysis; acid catalysis

## INTRODUCTION

In previous studies,<sup>1–4</sup> the liquefaction of wood in the presence of phenol under acid-catalyzed conditions and the properties of the resulting liquefied wood resins, such as flowing properties, curing behavior, and mechanical properties, have been investigated. It has been found that the properties of the liquefied wood depended greatly on the liquefaction methods, conditions, and the species of catalysts. For successfully realizing the practical application of this technique and developing this technique into a comprehensive science, systematic studies on the structural characteristics of liquefied wood and the liquefaction mechanism of wood have become very important.

However, as we know, wood is a complicated composite composed of three main components: cellulose (40–45%), hemicellulose (20–30%), and lignin (20–30%). Their different molecular

structures provide them with different reaction mechanisms and reactivities, which doubtless lead to considerable difficulties in understanding the structures of the liquefied wood. Therefore, recently, we have individually studied the structures of the liquefaction products and the liquefaction mechanism of the representative components of wood, such as cellulose<sup>5</sup> and lignin,<sup>6–8</sup> by using their model compounds. Under these circumstances, a general trace of the molecular weights and molecular weight distributions for the liquefied wood becomes substantially meaningful for understanding the general behavior of liquefaction.

Moreover, similar to the general polymeric materials, the molecular weights and molecular weight distributions of liquefied wood are also the fundamental structural parameters that can have a pronounced influence on the chemical and physical properties of the liquefied wood resins. Therefore, in this study, an attempt was made to inspect the molecular weights and molecular weight distributions of the liquefied wood and their dependencies on the reaction conditions, with the help of gel permeation chromatography (GPC) analysis.

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## EXPERIMENT

### Materials

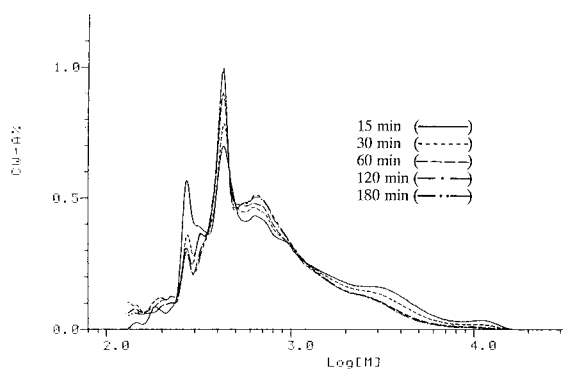
The wood meals used in the liquefaction were of 20–80 mesh prepared from birch chips (*Betula maximowiczii* regel). They were dried in an oven at 105°C for 8 h and then kept in a vacuum oven at room temperature before use. Tetrahydrofuran (THF), used as an eluting solvent for GPC, was of industrial grade and contained 0.03% 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. All of the other chemicals were of reagent grade.

### Liquefaction Reaction

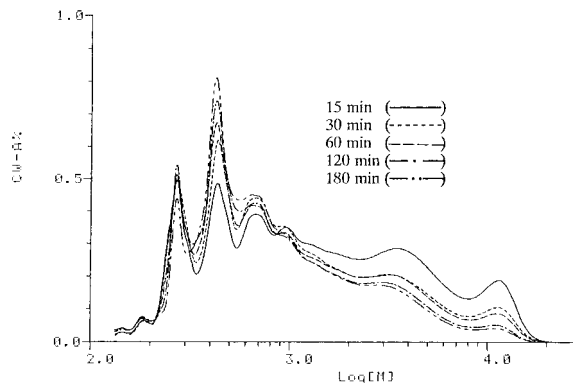
The liquefaction reaction of wood was conducted as demonstrated in one of our previous articles,<sup>1</sup> i.e., wood meal, phenol, and acid catalyst, in a desired ratio, were put into a 50-mL two-necked flask equipped with a stirring system and a reflux condenser, followed by being heated in an oil bath at 120–180°C. After the desired reaction time, the liquefaction mixture was cooled to room temperature and then diluted by THF for GPC analysis.

### Measurements

The molecular weights and their distributions of the liquefied woods obtained above were determined on a Toyo Soda HLC-8020 GPC system equipped with a refractive index detector with TSK gel -G. 2000 HHR and -G.1000 HHR columns connected in series. Measurements were done at 40°C with THF as a mobile phase at a flow rate of 1.0 mL/min. The concentration of the tested



**Figure 1** Effect of liquefaction time on the differential molecular weight distribution curves of the liquefied woods. Phosphoric acid, 6.8%; liquefaction temperature, 160°C; liquid ratio, 3.

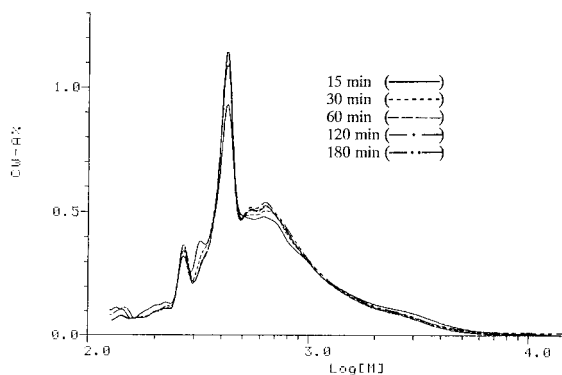


**Figure 2** Effect of liquefaction time on the differential molecular weight distribution curves of the liquefied woods. Phosphoric acid, 6.8%; liquefaction temperature, 120°C; liquid ratio, 3.

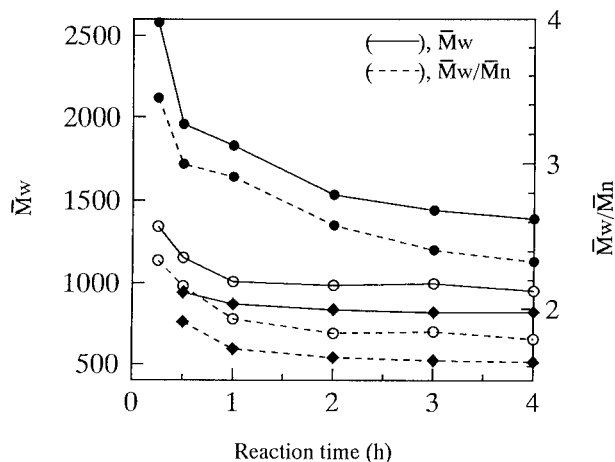
samples was 0.5–1 wt % in THF, and the injected amount was 300  $\mu$ L. The molecular weights of the samples were calibrated by monodisperse polystyrene standards. The molecular weight distributions were plotted as differential curves. The x-axis ( $\log[M]$ ) is the logarithm of molecular weight; the y-axis (CW-A%) is the differential area percentage on the basis of the total absorbing area.

## RESULTS AND DISCUSSION

The molecular weight distributions of the liquefied woods, obtained with phosphoric acid as a catalyst under three different reaction conditions, are shown in Figures 1–3. The corresponding



**Figure 3** Effect of liquefaction time on the differential molecular weight distribution curves of the liquefied woods. Phosphoric acid, 6.8%; liquefaction temperature, 160°C; liquid ratio, 4.

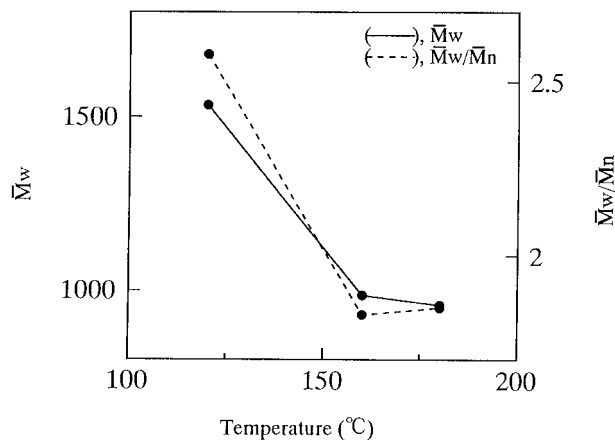


**Figure 4** Effect of liquefaction time on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied woods obtained with 6.8% phosphoric acid under (●) 120°C with a liquid ratio of 3, (○) 160°C with a liquid ratio of 3, and (◆) 160°C with a liquid ratio of 4.

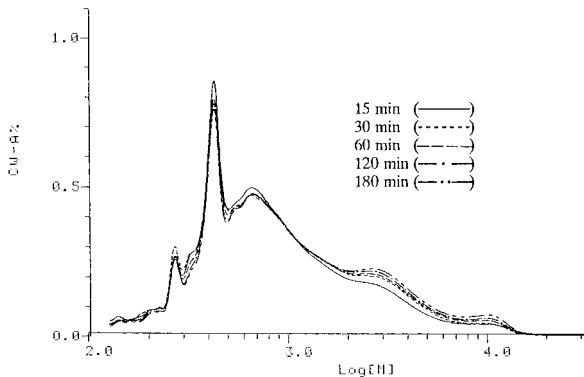
weight-average molecular weights ( $\bar{M}_w$ ) and the molecular weight dispersities ( $\bar{M}_w/\bar{M}_n$ ) obtained on the basis of these distribution curves are summarized in Figure 4. It can be seen from Figure 1 that under a typical liquefaction condition, i.e., 160°C/catalyst 6.8%/liquid ratio 3 (i.e., phenol/wood ratio is 3), the molecular weights of the liquefied woods disperse in a region approximately from 100 to  $1.5 \times 10^4$  with a main portion ranging from 300 to  $2.0 \times 10^3$ , which amounts to more than 80% of the total substance. Moreover, with an increase in the reaction time, the substances lying on both sides of the molecular weight distribution curves diminish, i.e., the liquefied wood obtained at a longer reaction time gives a narrower distribution curve. After 60 min, the molecular weight distribution approaches a steady state. The corresponding  $\bar{M}_w$ ,  $\bar{M}_w/\bar{M}_n$ , and their changing tendencies can be seen in Figure 4. As the reaction time increases from 15 to 60 min,  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  decrease from  $1.3 \times 10^3$  and 2.3 to about  $1.0 \times 10^3$  and 1.9, respectively, and then almost keep constant with a further increase in the reaction time.

Figure 2 shows the molecular weight distribution curves of the liquefied wood obtained at the same liquid ratio and acid content as shown in Figure 1, but under a lower reaction temperature, 120°C. It has been known that, at this temperature, both the liquefaction rate of wood and the amount of combined phenol in the resulting liquefied wood are much lower than those obtained at

160°C.<sup>1</sup> It can be found that the proportions of the substances with large molecular weights are obviously greater under this reaction temperature than those obtained at 160°C (Fig. 1) and that the ultimate molecular weight reaches a much larger value of  $2.0 \times 10^4$ . Moreover, similar to the case at 160°C, the substances with larger molecular weights diminish with an increase in the reaction time. However, the corresponding  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  values, as shown in Figure 4, are much larger than those obtained at 160°C. The effect of reaction temperature on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  is further demonstrated in Figure 5. It can be found that the effect of reaction temperature is similar to that of reaction time, i.e., with increasing the reaction temperature from 120 to 160°C,  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  rapidly decrease from  $1.5 \times 10^3$  and 2.6 to  $9.8 \times 10^2$  and 1.8, respectively, and then level off after 160°C. The above results indicate that the reaction temperature is a significant factor which affects not only the liquefaction rate of solid wood, but also the phenolysis reaction and the molecular characteristics of the liquefied wood obtained. From Figure 3, it can be seen that the molecular weight distribution curves of the liquefied woods, obtained under a larger liquid ratio of 4, quickly reach a steady state and fall in a lower and narrower molecular weight region compared with those shown in Figures 1 and 2. The corresponding  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  values, as shown in Figure 4, have already been low in the initial stage of the reaction, and after the small decreases within 60 min, they no longer change with further



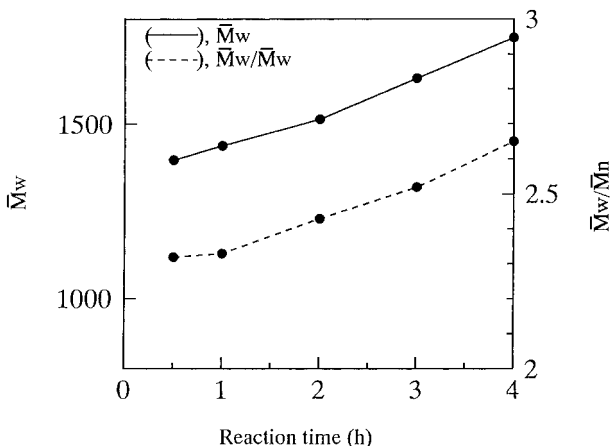
**Figure 5** Effect of liquefaction temperature on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied woods obtained with 6.8% phosphoric acid in a liquefaction time of 2 h with a liquid ratio of 3.



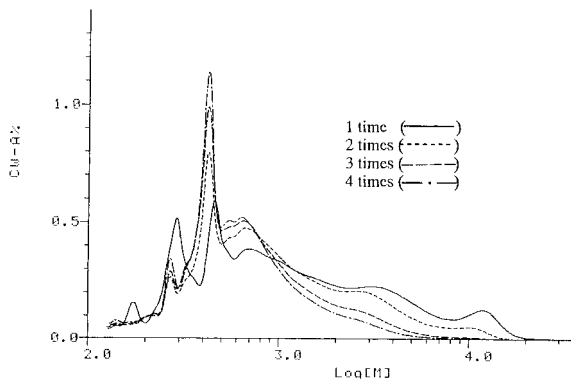
**Figure 6** Effect of liquefaction time on the differential molecular weight distribution curves of the liquefied woods. Phosphoric acid, 6.8%; liquefaction temperature, 160°C; liquid ratio, 2.

increasing the reaction time. These results indicate that in the presence of an excessive amount of phenol, the liquefied wood components are rapidly subjected to extensive phenolysis decomposition and phenolation and soon approach a dynamic equilibrium state, as indicated by the molecular weight.

Figure 6 shows the liquefaction results obtained under a lower liquid ratio (i.e., phenol/wood ratio), 2. It is interesting to find that the changing pattern of the molecular weight distributions with reaction time is reversed from those shown in Figures 1–3, i.e., with the progression of the reaction, the substances in the large-molecular-weight region increase, but those in the mid-region gradually decrease. The corresponding  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  values, as shown in Figure 7, in-

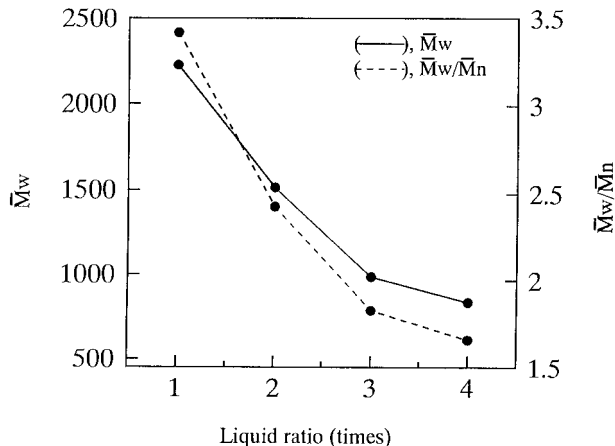


**Figure 7** Effect of liquefaction time on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied woods obtained under 160°C with a liquid ratio of 2 and an acid concentration of 6.8%.

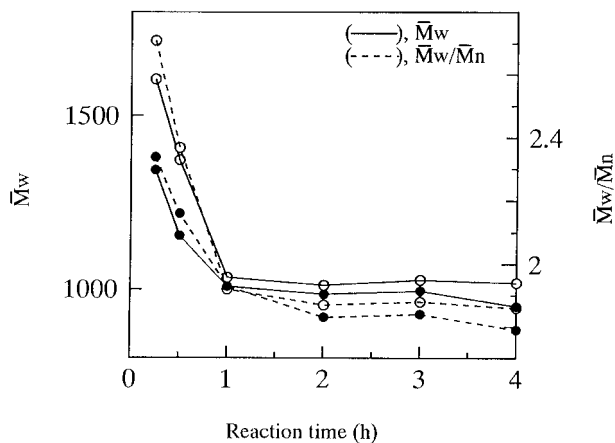


**Figure 8** Effect of liquid ratio on the differential molecular weight distribution curves of the liquefied woods. Phosphoric acid, 6.8%; liquefaction temperature, 160°C; liquefaction time, 2 h.

crease monotonously with an increase in reaction time. Figures 8 and 9 further demonstrate the effects of the liquid ratio on the molecular weight distribution curves of the liquefied wood and their corresponding  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  values, respectively. As demonstrated in Figure 8, with a decrease in the liquid ratio, the molecular weight distributions pronouncedly broaden toward the large-molecular-weight region, as a result, the  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  rapidly increase, as shown in Figure 9. The above results suggest that when the liquid ratio is lower than a certain value, the recondensation of the liquefied wood components will become the preferable reaction rather than phenolysis during the liquefaction. In other words, phenol can effectively promote the phenolation of



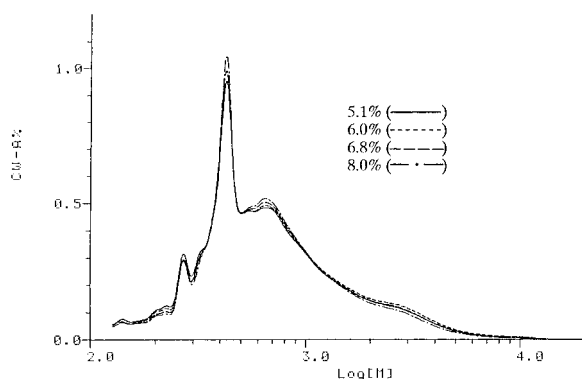
**Figure 9** Effect of liquid ratio on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied woods obtained under 160°C for 2 h with an acid concentration of 6.8%.



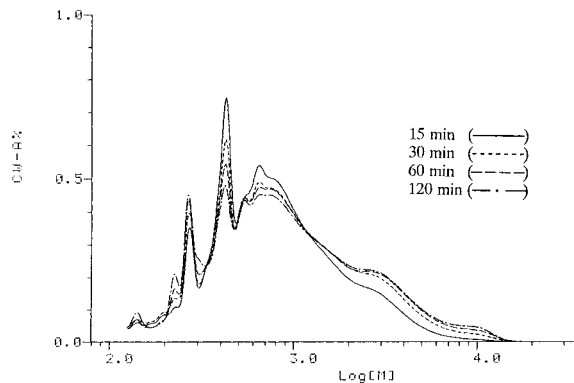
**Figure 10** Effect of liquefaction time on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied woods obtained under 160°C with a liquid ratio of 3 with phosphoric acid: (●) 6.8%, and (○) 5.1%, respectively.

the liquefied wood components, which therefore restrains their recondensation and prevents the extensive increase in the molecular weight of the resulting liquefied woods. Therefore, it is said that the liquid ratio is an important factor substantially affecting the liquefaction reaction and the characteristics of the liquefied wood resins.

The  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied wood as functions of reaction time obtained by using two different acid concentrations are shown in Figure 10. It can be seen that in the initial stage of reaction, the  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  values obtained by using 6.8% acid are smaller than those obtained with 5.1% acid. However, the differences diminish with increasing the reaction time and almost disappear after 60 min. Figure 11 further shows the molecu-

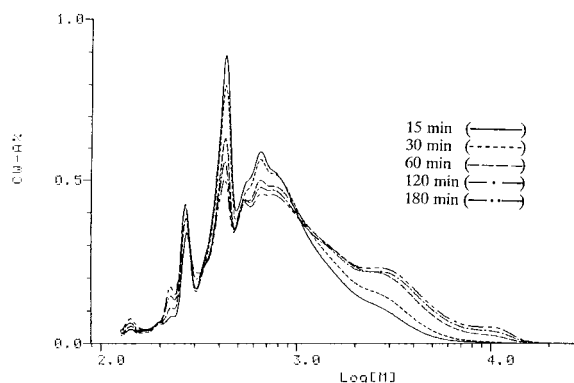


**Figure 11** Effect of phosphoric acid concentration on the differential molecular weight distribution curves of the liquefied woods. Liquefaction temperature, 160°C; liquefaction time, 2 h; liquid ratio, 3.

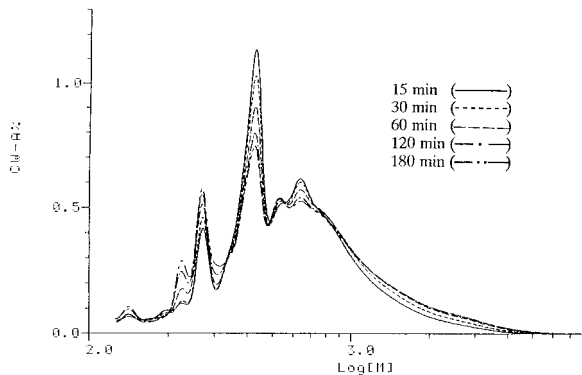


**Figure 12** Effect of liquefaction time on the differential molecular weight distribution curves of the sulfuric acid catalyzed liquefied woods. Sulfuric acid, 3%; liquefaction temperature, 160°C; liquid ratio, 3.

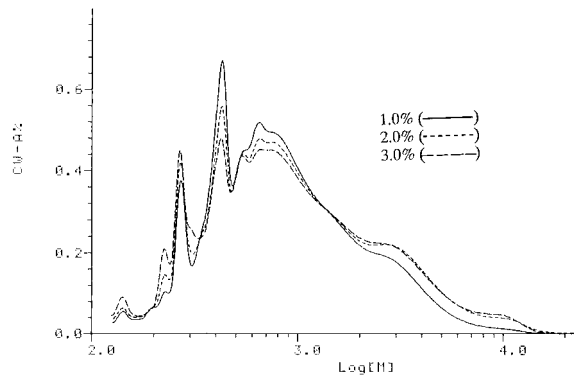
lar weight distribution curves of the liquefied woods obtained in the equilibrium state (i.e., in a liquefaction time of 2 h) with four different acid concentrations: 5.1, 6.0, 6.8, and 8.0%. It can be found that the molecular weight distributions of the liquefied woods obtained in the equilibrium state with various acid concentrations are almost superimposed on each other. These results suggest that an increase in the acid concentration can only accelerate the initial reaction of wood components but evidently not influence the reaction pattern and structural characteristics of the resulting liquefied wood in the range studied. This is probably because phosphoric acid is a relatively weak catalyst and the changing range from 5.1 to 8.0% is not large enough to substantially influence the reaction pattern of wood.



**Figure 13** Effect of liquefaction time on the differential molecular weight distribution curves of the sulfuric acid catalyzed liquefied woods. Sulfuric acid, 2%; liquefaction temperature, 160°C; liquid ratio, 3.



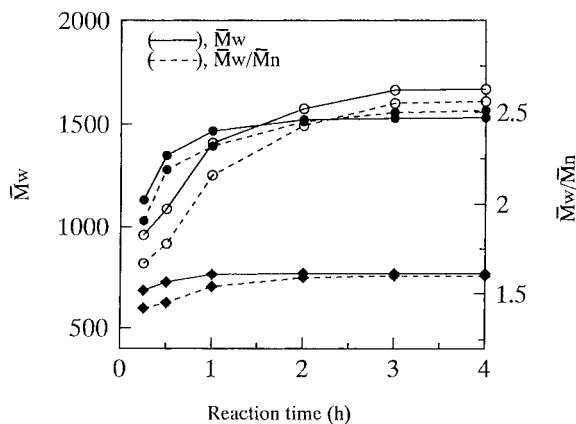
**Figure 14** Effect of liquefaction time on the differential molecular weight distribution curves of the sulfuric acid catalyzed liquefied woods. Sulfuric acid, 2%; liquefaction temperature, 160°C; liquid ratio, 5.



**Figure 16** Effect of sulfuric acid concentration on the differential molecular weight distribution curves of liquefied woods. Liquefaction temperature, 160°C; liquefaction time, 2 h; liquid ratio, 3.

In order to probe the effect of the species of acid catalysts on the molecular characteristics of liquefied wood, an attempt was made to monitor the molecular weight distributions of the liquefied woods obtained under the catalysis of sulfuric acid, a strong catalyst. The results are shown in Figures 12–14. First, it can be seen that the molecular weights and their distributions of the liquefied woods prepared with sulfuric acid as a catalyst are basically similar to those obtained under the catalysis of phosphoric acid. However, the changing pattern of the molecular weight distribution with reaction time is reversed from those obtained under the catalysis of phosphoric acid

with a liquid ratio of 3 or higher but is similar to the case of lower liquid ratios. In other words, in the initial stage of reaction, with an increase in the reaction time, the distribution curves broaden toward the large-molecular-weight region (Figs. 12 and 13). This broadening tendency can be greatly-restrained by using a larger liquid ratio, as shown in Figure 14. From the  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  data summarized in Figure 15, it can be seen that in a liquid ratio of 3,  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  in the initial stage (15 min) are about  $1.0 \times 10^3$  and below 2, respectively, and are similar to the corresponding equilibrium values of the phosphoric acid-catalyzed ones (Fig. 4 or 10). However, with an increase in the reaction time, both  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  increase rapidly to about  $1.5 \times 10^3$  and 2.5, respectively, and then level off. On the basis of the finding<sup>8</sup> that the catalysis of sulfuric acid could give a much faster liquefaction rate and a much greater amount of combined phenol than those obtained under the catalysis of phosphoric acid, the above results suggest that the wood components had no sooner been dissolved in the liquid phase than they were decomposed into very low molecular weight substances under the catalysis of sulfuric acid. The decomposed components possessed more reactive sites, which provided many chances for the phenolation or recondensation of the liquefied wood components. As a result, the molecular weight of liquefied wood increased with a further increase in the liquefaction time. At the same time, this increasing tendency became slower and slower as these reactive sites were gradually saturated. On the other hand, an increase in the liquid ratio (i.e., the availability of



**Figure 15** Effect of liquefaction time on  $\bar{M}_w$  and  $\bar{M}_w/\bar{M}_n$  of the liquefied woods obtained under 160°C with sulfuric acid as a catalyst: (●) acid concentration of 3% and liquid ratio of 3; (○) acid concentration of 2% and liquid ratio of 3; (◆) acid concentration of 2% and liquid ratio of 5.

phenol) could significantly restrain the recondensation by blocking the reactive sites on the liquefied wood components and therefore prevent the further increase in molecular weight, as shown in Figures 14 and 15, where a higher liquid ratio of 5 was used for the liquefaction. The effect of the sulfuric acid concentration is demonstrated in Figure 16. It can be found that the effect of the acid concentration is similar to that of the reaction time, that is, with an increase in the acid concentration from 1 to 3%, the distribution curves broaden toward the high-molecular-weight region, and after 2%, the change becomes obscure, indicating that 2% sulfuric acid has approached the saturated value.

The above comparisons between two kinds of catalysts suggest that catalyst intensity greatly influences the liquefaction reaction patterns. In all cases, phenolation and recondensation are a pair of competing reactions which are significantly dominated by the availability of phenol and the species of the catalyst.

## CONCLUSIONS

During liquefaction, wood components were subjected to decomposition, phenolation, and recon-

densation. The intensities of these reactions depended on the species of the catalysts, the phenol/wood ratio, and the liquefaction temperature. The competition of these reactions dominated the whole dynamic liquefaction process and determined the structural characteristics of the liquefied wood.

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