

# Liquefaction of Wood in the Presence of Phenol Using Phosphoric Acid as a Catalyst and the Flow Properties of the Liquefied Wood

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## SYNOPSIS

The liquefaction of wood in the presence of phenol using phosphoric acid as a catalyst and the flow properties of the obtained liquefied wood were investigated. It was found that phosphoric acid is a satisfactory catalyst for liquefying wood. The amount of phenol that reacts with the liquefied wood components (i.e., combined phenol) increases with an increase in liquefaction temperature, liquefaction time, catalyst content, or liquid ratio. By removing the free phenol, the resulting liquefied woods become novolaclike resins. The measurements of the flow properties of these liquefied woods reveal that the melts of liquefied woods behave as pseudoplastics and their flows obey the Ostwald de Waele power law equation. The amount of combined phenol within the liquefied wood and the presence of filler in the liquefied wood have great influence on their flow properties. The flowing temperature, activation energy, and zero shear viscosity of the liquefied woods show tendencies to increase with an increase in combined phenol. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The effective utilization of wood has become increasingly important in recent years. Actually, there is much woody biomass that has still not been utilized and is usually disposed. The main problem for the effective utilization is lack of techniques by which biomass can be converted into materials with high additional values. Thus, to find and develop novel processings, especially chemical processings, for this purpose is most important in order to open the wide fruitful landscape for utilizing the huge amounts of biomass unused. The liquefaction of wood in the presence of some organic solvents is one of the techniques that should be improved.<sup>1-3</sup> Especially, the liquefaction of wood in the phenol by using sulfuric acid as a catalyst has been intensively studied in recent years,<sup>4,5</sup> and the resulting liquefied woods appear as novolaclike resins and can be converted into adhesives,<sup>6,7</sup> moldings,<sup>8,9</sup> fibers, and car-

bon fibers,<sup>10</sup> etc. However, the use of sulfuric acid will lead to many negative results such as the serious corrosion of equipment and environmental pollution. Therefore, it is meaningful to find a more reasonable catalyst. From this point, liquefaction of wood using various catalysts other than sulfuric acid, such as hydrochloric acid, phosphoric acid, oxalic acid, and acetic acid, should be accomplished. In this study, a relatively weak catalyst, phosphoric acid, was used instead of sulfuric acid. The influence of liquefaction conditions on the liquefaction process of the wood and the flow properties of the obtained liquefied woods were investigated and are reported in this article.

## EXPERIMENTAL

### Materials

Wood samples used in the liquefaction were 20–80 mesh wood meals of birch (*Betula maximowiczii Regel*). They were dried in an oven at 105°C for 8

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h and then kept in the vacuum oven at room temperature before use. Wood powders used as fillers in the liquefied wood compounds were of 200 mesh pass size from the Hitachi Chemical Co. All other chemicals were of reagent grade.

### Liquefaction of Wood and the Preparation of the Liquefied Wood Concentrate

The procedures for the liquefaction of wood and the preparation of the liquefied wood concentrate are shown in Figure 1. The liquefaction reaction was

carried out in a 500 mL separable three-branch flask equipped with a stirring system and a reflux condenser in the oil bath at 120–180°C. After the desired reaction time, the reactant was diluted by a great excessive amount of methanol and then filtrated through Toyo GA100 glass filter paper. The volume of filtrate was adjusted by adding methanol to 500 mL and then was sampled for the measurement of the free phenol. The residue was dried at 105°C to a constant weight. The percent residue of the wood after liquefaction and the amount of phenol that combines with the liquefied wood components

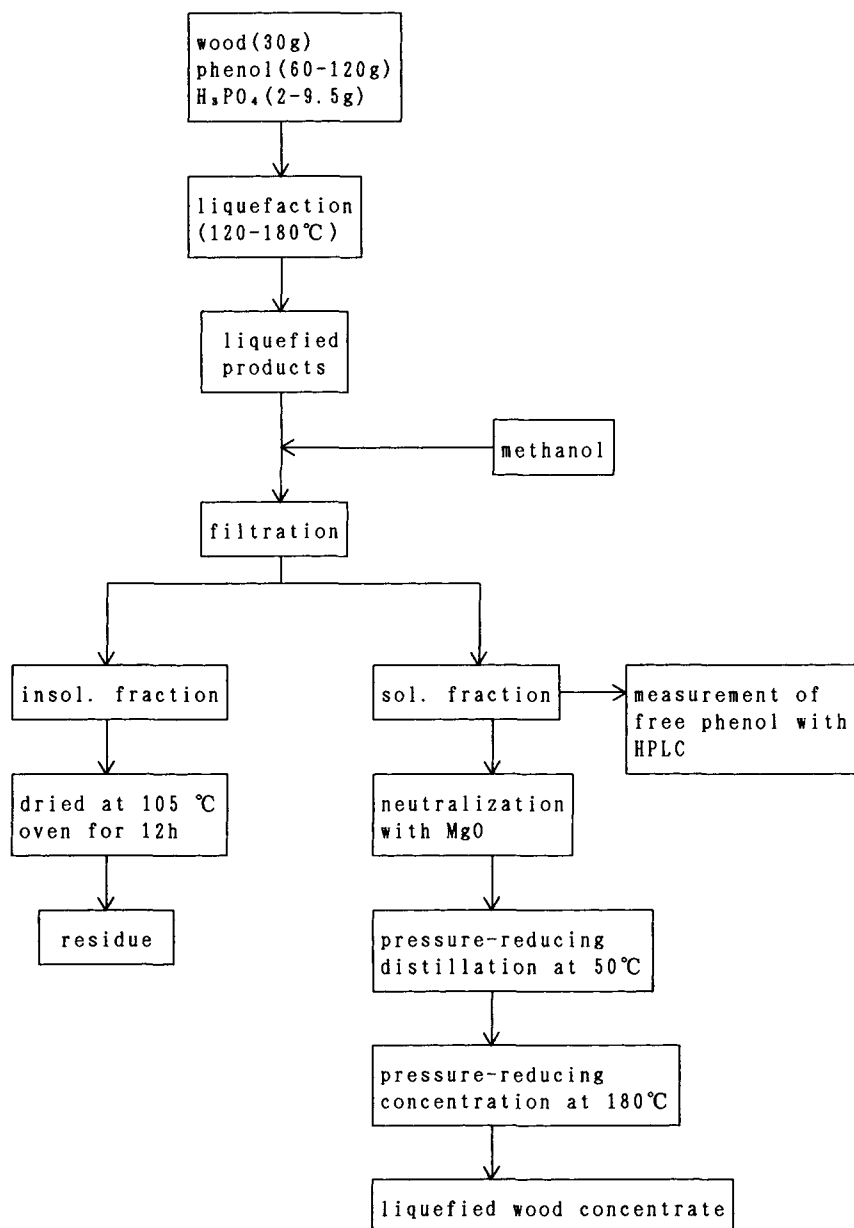


Figure 1 Preparation chart of the liquefied wood.

(combined phenol) were calculated by the following two equations:

$$\text{Percent residue} = \frac{W_r}{W_0} \times 100\%$$

$$\text{Combined phenol} = \frac{W_1 - W_2}{W_0 - W_r} \times 100\%$$

where  $W_0$  is the weight of the wood meals used in liquefaction;  $W_r$ , the weight of the wood residue;  $W_1$ , the weight of phenol used in liquefaction; and  $W_2$ , the weight of phenol still unreacted after liquefaction (free phenol). The above diluted liquefaction mixture was finally concentrated by pressure-reducing evaporation (about 20 mmHg) at 55 and 180°C successively to remove all the diluting solvent and free phenol, and then the liquefied wood concentrate (henceforth called liquefied wood) was obtained.

#### Preparation of Liquefied Wood Compounds for Measurement of Flow Properties

A formulation containing 37.7 wt % liquefied wood, 9.4 wt % hexamine, 49.5 wt % wood powder (fillers), 2.4 wt %  $\text{Ca}(\text{OH})_2$  (calcium hydroxide), and 1.0 wt % zinc stearate was used. Except for the liquefied wood, all the other ingredients were premixed in a mortar for about 2 min, followed by an addition of an acetone solution of the liquefied wood, and then the mixing was continued until a uniform mixture was obtained. The resulting mixture was dried in an oven at 70°C for 1 h, then reground to powders and kept in a desiccator before measurement.

#### Methods for Measurements

The flow properties of the pure liquefied woods were measured by GFT-500A Flow Tester (Shimadzu Co.). Preheating time was 200 s for all the samples and a heating rate of 10°C/min was used to measure the flowing point.<sup>11</sup> The compounds of the liquefied woods filled with wood powders and other additives that are used for the preparation of moldings are also measured by the same conditions.

The amount of free phenol in the liquefied mixture before concentrating was measured with high-performance liquid chromatography (HPLC) using a Model 6000A Waters chromatography system equipped with a Model 440 Waters UV absorbance detector and a Shimadzu Shim-pack CLC-ODS(M) 4.6 mm i.d.  $\times$  150 mm column. The eluent was composed of 70% phosphoric acid buffer solution (pH

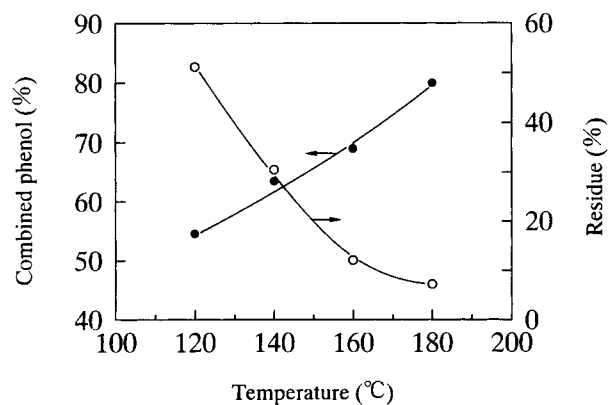
2.6) and 30% acetonitrile. The flowing rate of the eluent and the injecting amount of samples were 0.9 mL/min and 2  $\mu\text{L}$ , respectively. The concentration of tested samples was 0.05–0.1 wt %, and the solvent was methanol. The phenol solution of known concentrations was used as standards to evaluate the phenol concentrations of the tested solution. The molecular weights and their distributions of the liquefied woods were determined by use of the same apparatus as described above, except for the use of a Waters differential refractometer R401 detector and linearly linked Shodex GPC KF802 and KF803 columns. The eluent solvent was THF and the flowing rate was 1 mL/min. The concentrations of the tested samples in the THF solutions were 0.2–0.5 wt % and the injecting amount was 100–150  $\mu\text{L}$ . Monodisperse polystyrene was used as the standard for the calibration of the molecular weights.

## RESULTS AND DISCUSSION

### Liquefaction of Wood and Its Affecting Factors

#### Effect of Temperature

Figure 2 shows the relationship between liquefaction efficiencies and liquefaction temperature. It demonstrates that the temperature has a great influence on both the percent residue and the amount of combined phenol, i.e., as the temperature of the oil bath increases, the amount of combined phenol increases and the percent residue decreases rapidly. When the temperature of the oil bath is 160°C, the percent residue becomes relatively low (12%), and a further increase in temperature results in a depressed decrease in percent residue. Additionally, it was found



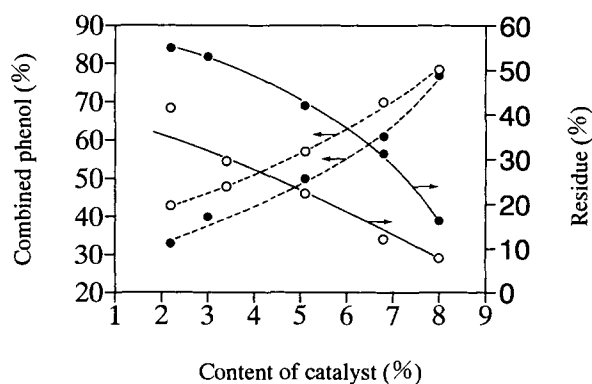
**Figure 2** Effect of liquefaction temperature on the amounts of combined phenol and residue. Liquefaction time, 2 h; liquid ratio, 3; catalyst content, 6.8%.

that there is a difference in temperature between the oil bath and the liquefaction reactant, which results from the reflux of evaporated substances. The higher the oil bath temperature, the larger the difference in temperature. Furthermore, this figure shows that at a 160°C reaction temperature a satisfactory liquefaction result can be obtained. Accordingly, in the following liquefaction experiments, the oil bath temperature was fixed at 160°C.

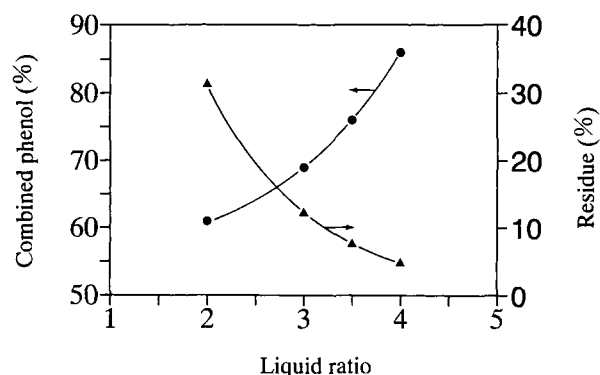
#### ***Effects of Content of Catalyst, Liquid Ratio, and Liquefaction Time***

The effect of catalyst content on the liquefaction efficiencies of wood at different liquid ratios is shown in Figure 3. It is observed that general shapes of the curves are similar for two kinds of liquid ratios studied, showing nearly linear increases in combined phenol and nearly linear decreases in percent residue. However, the slopes of the curves for liquid ratio 2 are greater than those for liquid ratio 3, indicating that the catalyst content has a greater influence on the liquefaction process at the lower liquid ratio conditions. In other words, in low liquid ratio conditions, increasing catalyst content is a more effective method to improve the liquefaction efficiencies.

The liquid ratio dependence of the liquefaction efficiencies is shown in Figure 4. The  $H_3PO_4$  content was fixed at 6.8%. It can be seen that the liquid ratio has a significant influence on both the percent residue and combined phenol. In more detail, the former (i.e., percent residue) is more sensitive in the lower liquid ratio region but the latter is more sensitive in the higher liquid ratio region. When the liquid ratio reaches 4, the amount of the combined phenol and the percent residue are 88 and 4.8%, respec-



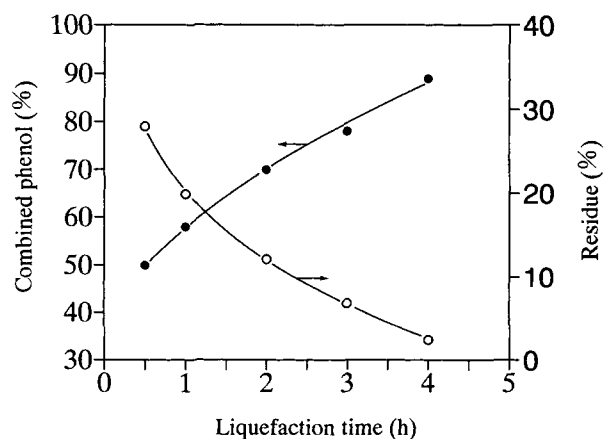
**Figure 3** Effect of catalyst content on the amounts of combined phenol and residue. Liquefaction time, 2 h; temperature, 160°C; liquid ratio: (●) 2; (○) 3.



**Figure 4** Effect of liquid ratio on the amounts of combined phenol and residue. Liquefaction time, 2 h; temperature, 160°C; catalyst content, 6.8%.

tively. The effect of liquefaction time on the liquefaction efficiencies is shown in Figure 5. With increasing liquefaction time, the combined phenol increases and the percent residue decreases monotonously. However, the changing extents of the percent residue and the combined phenol drop with increasing liquefaction time. In other words, the liquefaction efficiencies cannot be improved very much by increasing liquefaction time when the liquefaction time reaches a reasonable value.

It is known from Figures 2–5 that the amount of combined phenol of the liquefied woods up to 88% is obtainable, which is lower than the corresponding value (130%) obtained by the  $H_2SO_4$ -catalyzed method and is higher than the value (30%) obtained by the noncatalysis method.<sup>12</sup> Actually, in the present study, even if the liquefaction is carried out at 120°C, about one-half of the wood can be liquefied



**Figure 5** Effect of liquefaction time on the amounts of combined phenol and residue. Temperature, 160°C; liquid ratio, 3; catalyst content, 6.8%.

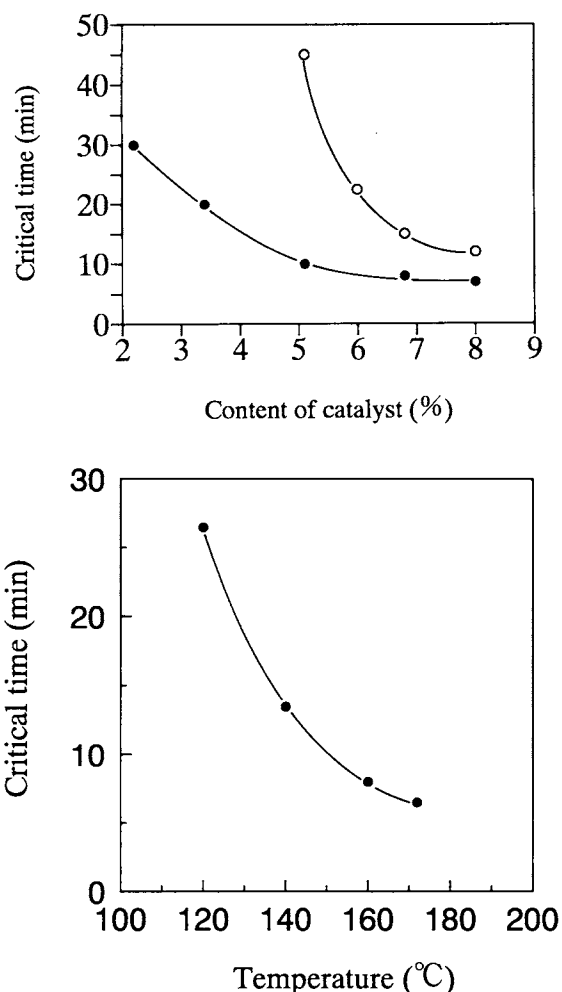
and the amount of combined phenol reaches 53% (as shown in Fig. 2).

### Critical Time of Liquefaction (CTL)

In the beginning of the liquefaction reaction, the liquefaction reactant is severely heterogeneous and the stirring efficiency is very poor. The liquefaction reaction cannot proceed well in this period because of the poor transference of the heat and mass. It was usually found that after a certain reaction time the state of the reactant rapidly changes from heterogeneous to apparently homogeneous. Only after this changing point, a liquid-state mixture can be obtained. Therefore, the time at which the state of reactant changes is expressed as the critical time of liquefaction (CTL). This period of time is a function of catalyst content, liquefaction temperature, and liquid ratio, as shown in Figure 6(a) and (b). In case of liquid ratio 2 and less than 5% catalyst content, the reactant remained in the solid state until the end of liquefaction. Therefore, CTL can be considered as one of the parameters affecting the liquefaction efficiencies of wood in certain conditions.

### Flow Properties

The flow properties of the liquefied wood melts were measured by use of the flow tester under various temperatures and shear rates. The effect of the amount of combined phenol on flowing points is given in Figure 7. It is shown that with an increase in the amount of combined phenol the flowing point of the pure liquefied wood increases linearly. The change is so significant that in the range of the amount of combined phenol from 50 to 89% the flowing point increases from 97 to 159°C. Generally, the factors influencing rheological properties of polymers include molecular weight, molecular weight distribution, and molecular structure. However, it was found that the molecular weights and their distributions of the liquefied woods have no evident difference among the liquefied woods with various amounts of combined phenols, as shown in Table I. Thus, the flowing behavior shown in Figure 7 should be attributed to the molecular structures of the liquefied woods. It can be expected that with an increase in the amount of combined phenol increases in steric hindrance and hydroxy bonding among the resulting molecules occur because of the introduction of phenols by hydroxy phenylation as branches of the molecules,<sup>4</sup> which causes difficulties in molecular motions. Thus, with increasing the amount of combined phenol, the movements of the molecules be-



**Figure 6** (a) Effect of catalyst content on the critical time. Liquefaction temperature, 160°C; liquid ratio: (●) 3; (○) 2. (b) Effect of liquefaction temperature on critical time. Liquid ratio, 3; catalyst content, 6.8%.

come more difficult and, therefore, the flowing point of the pure liquefied wood shows a considerable change. This discussion can be supported by the activation energy for flow shown later in Table III.

The influence of the amount of combined phenol on the flowing point of the liquefied wood compounds filled with wood powders, however, is quite different from that of the pure liquefied wood. For the liquefied wood with low combined phenol, the introduction of fillers and the other additives greatly increases the flowing point, and the lower the combined phenol, the larger the degree of the influence. In other words, in the low combined phenol region, the flowing point of the liquefied wood compounds increases with a decrease in the amount of combined phenol. In compounding, 49.5 wt % of wood powders

are mixed to 37.7 wt % of the liquefied wood as described in the Experimental section. Thus, the appearance of flow has strong correlation with the interaction between wood powders and liquefied woods. In this flow process, wood powders are considered to maintain their solid shapes. The degree of interaction of thermoplastic resins with solid fillers directly reflect on wetting phenomenon between their interfaces. When there is small interaction between matrix resins and filler, wetting between their interfaces cannot be realized easily, requiring greater energy compared with the higher interaction cases. In the figure, the compounds composed of the liquefied wood with the lowest amount of combined phenol has the highest flowing temperature, revealing the poorest interaction between the liquefied wood and the wood powders. Increases in the amount of combined phenol of the liquefied woods result in rapid decreases in the flowing temperature of the compounds, suggesting an increase in the interaction between the liquefied wood melts and the wood powder fillers. At the same time, the matrix (pure liquefied woods) increases its flowing temperature with an increase in the amount of combined phenol. This trend is also superimposed on the interaction factor discussed above. Thus, with an increase in the amount of combined phenol, the flowing temperature decreases to a minimum value, then is followed by an increasing trend.

The apparent flow curves, shear stress  $\tau$  vs. shear rate  $\dot{\gamma}$  plots, of the liquefied wood melts with various amounts of combined phenol under a constant temperature are shown in Figure 8. All the flow curves are quite linear in the studied range of the shear rate, suggesting that the flow of liquefied wood melts obeys the Ostwald de Waele power law equation<sup>13</sup>:

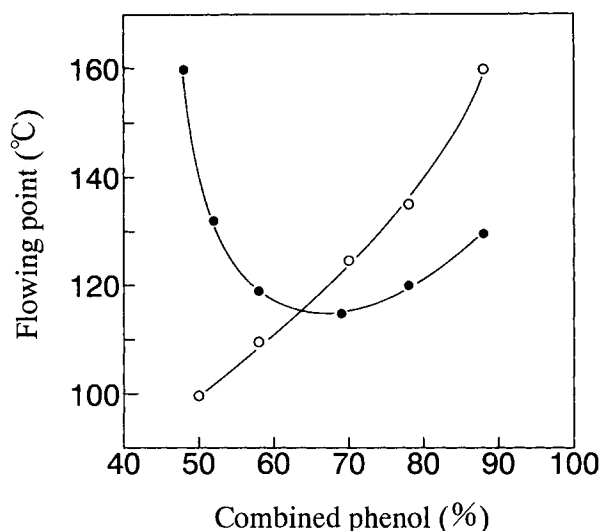
$$\tau = \eta \dot{\gamma} = k \dot{\gamma}^n$$

where  $\eta$  is the apparent viscosity;  $\dot{\gamma}$ , the shear rate;  $\tau$ , the shear stress;  $k$ , the shear viscosity coefficient;

**Table I** Molecular Weights and Their Distributions for the Liquefied Woods

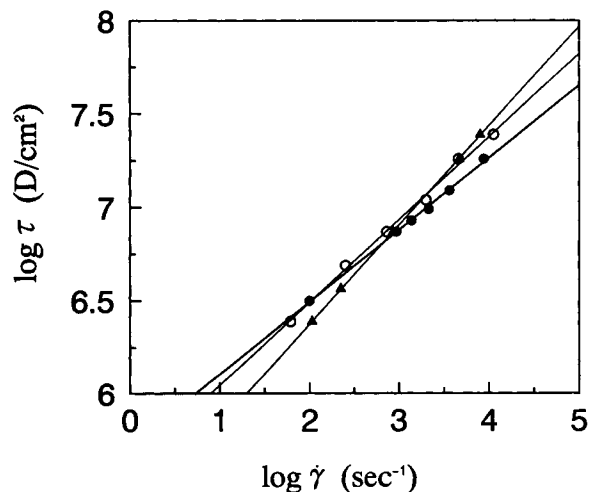
C. Ph. (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
58	872	1693	1.94
69	906	1648	1.81
78	853	1536	1.80
88	984	2120	2.15

C. Ph. is the amount of combined phenol.



**Figure 7** Effect of the amount of combined phenol on the flowing point: (○) pure liquefied woods,  $\tau 6.13 \times 10^6$  D/cm<sup>2</sup>; (●) liquefied wood compounds,  $\tau 4.9 \times 10^7$  D/cm<sup>2</sup>.

and  $n$ , the power law exponent. Values of the power law exponent “ $n$ ” evaluated by regression analysis of the data, as shown in Table II, reveal that all the  $n$  values are less than unity and decrease from 0.53 to 0.40 with increasing combined phenol from 43 to 87%, indicating that the liquefied wood melts are of pseudoplastic nature and the degree of pseudoplasticity increases with an increase in combined phenol of liquefied wood.



**Figure 8** Plots of  $\log \tau$  vs.  $\log \dot{\gamma}$  for the pure liquefied woods with different amounts of combined phenol: (●) 87%; (○) 77%; (▲) 43%. Temperature of measurement is 155°C.

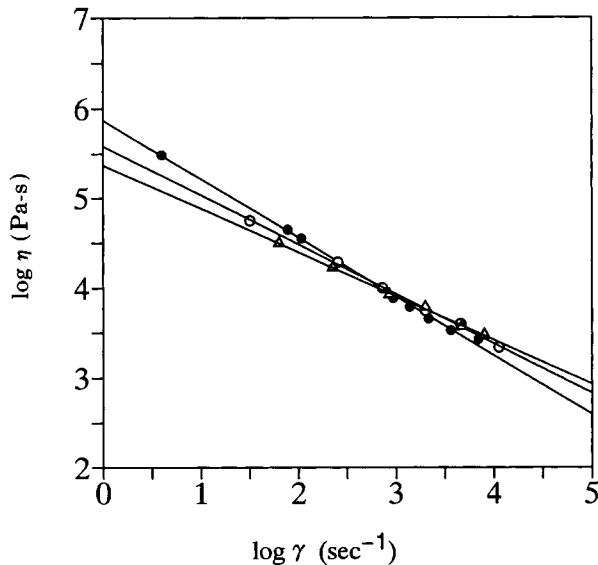
**Table II** Values of Power Law Exponent  $n$  and Zero Shear Viscosity  $\eta_0$

C. Ph. (%)	$n$	$\eta_0$ (Pa-s)
43	0.53	233,114
77	0.45	427,819
87	0.40	749,561

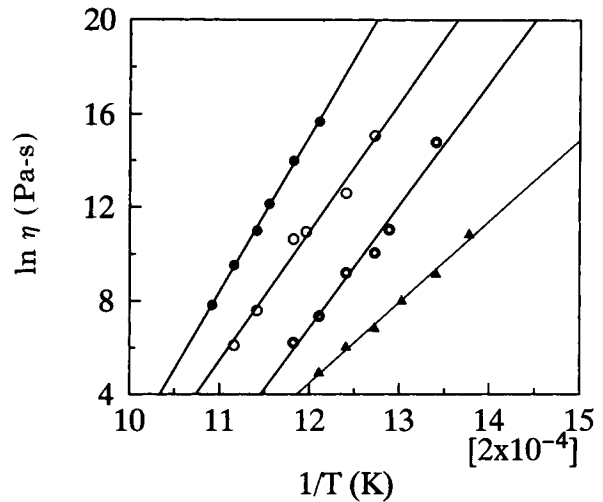
C. Ph. is the amount of combined phenol.

Viscosity ( $\eta$ ) of the liquefied wood melts as a function of shear rate ( $\dot{\gamma}$ ) for various combined phenols at constant temperature is shown in Figure 9. It can be seen that  $\log \eta$  decreases linearly with increasing  $\log \dot{\gamma}$ , indicating that the dependence of  $\eta$  on  $\dot{\gamma}$  also obeys the power law equation. The variation of slopes of plots,  $\log \eta$  vs.  $\log \dot{\gamma}$  with combined phenol, is consistent with the variation of  $n$  values mentioned above, indicating that the higher the amount of combined phenol, the more sensitive the  $\eta$  to  $\dot{\gamma}$ . As for the zero shear viscosity, it shows a tendency to increase with an increases in combined phenol, as shown in Table II.

Figure 10 is the plots of  $\log \eta$  vs.  $1/T$  at a constant shear stress. Under the given shear stress, the apparent viscosity of liquefied wood melts drops with increasing temperature, and the relationship be-



**Figure 9** Plots of  $\log \eta$  vs.  $\log \dot{\gamma}$  for the pure liquefied woods with different amounts of combined phenol: (●) 87%; (○) 77%; (△) 43%. Temperature of measurement is 155°C.



**Figure 10** Plots of  $\ln \eta$  vs.  $1/T$  for the pure liquefied woods with different amount of combined phenol: (●) 89%; (○) 85%; (○) 77%; (▲) 50%. Shear stress  $6.129 \times 10^6 \text{ D/cm}^2$ .

tween the  $\log \eta$  and  $1/T$  is linear, although the data is somewhat scattered. It means that the dependence of  $\eta$  on temperature roughly obeys the Arrhenius equation:

$$\eta = A \exp(E/RT)$$

where  $A$  is a constant that is related to material properties;  $E$ , the activation energy for flow;  $R$ , the universal gas constant; and  $T$ , the absolute temperature. According to the Arrhenius equation, the activation energies for flow of the liquefied woods with different amounts of combined phenol were calculated, and the results are shown in Table III. It is shown that the liquefied wood melts with higher combined phenol have a higher activation energy for flow. The variation of activation energy with combined phenol is consistent with the variation of flowing point.

**Table III** Values of Activation Energy for Flow

C. Ph. (%)	Activation Energy (kJ/mol)
50	14.39
77	21.81
85	22.93
89	27.65

C. Ph. is the amount of combined phenol.

## CONCLUSIONS

From the above results, it can be said that phosphoric acid is a relatively weak catalyst in the liquefaction of wood compared with sulfuric acid. However, satisfactory results can be obtained, i.e., liquefied woods with 50–89% combined phenol and 4–50% residue can be obtained. Somewhat higher residues are acceptable in practical use because they can be used as fillers. Furthermore, the measurement of flow properties of the liquefied woods reveals that the liquefied wood melts are of pseudoplasticity and their flow behavior obeys the Ostwald de Waele power law equation. The amount of combined phenol has a great influence on the flow properties of the liquefied woods and their compounds. The flowing temperature, the activation energy, and the zero shear viscosity of pure liquefied wood melts increase with an increase in the amount of combined phenol, showing that the cohesiveness of component molecules of the liquefied wood becomes large with an increase in the amount of combined phenol.

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