

Kinetics of Wood Phenolysis in the Presence of HCl as Catalyst

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ABSTRACT: Monarch birch wood (*Betula maximowiczina* Regel) wastes were phenolated in the presence of HCl as a catalyst at 60–150°C for various reaction times. Typical kinetic parameters along with percent reacted wood and phenol were determined by using kinetic models. In addition, according to the transition-state theory the activation parameters of wood phenolysis was determined. The percent reacted wood wastes depicted that about 90% of the wood could be liquefied into phenol at a temperature of 150°C. However, about 30% of phenol was found to react with wood components. The kinetic studies showed that wood phenolysis with HCl catalyst at 60–150°C obviously followed a bimolecular type of second-order reaction. Activation energy was found to be 13.438 kJ mol⁻¹ from an Arrhenius plot. Furthermore, the findings related with activation enthalpy showed that the wood phenolysis had dominantly endothermic reaction nature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1098–1103, 2002

Key words: kinetics; catalysts; wood phenolysis

INTRODUCTION

As is known very well, a large amount of wood wastes remaining from the wood-processing industries, and forests have been considered as wastes having no economic value and essentially burned and dumped until recently. However, nowadays the effective utilization of the wood wastes becomes much more attractive for many scientists. It is a well-known fact that wood possesses three main natural polymers such as cellulose (40–50%), lignin (20–30%), and hemicellulose (20–30%). Because these compounds are of a

thermosetting nature, they cannot be molded easily like thermoplastic materials, glasses, and metal.¹

Therefore, for the last 5 decades, many attempts and efforts have been made to utilize wood wastes much more efficiently by applying chemical and biochemical processes and various techniques such as hydrolysis, liquefaction, modification, etc.^{2,3} Specifically, recent environmental pollution due to increased consumption of fossil sources, decreasing availability of the petroleum resources, decrease in useful land, and increases in the amounts of wood-based wastes caused the chemists and wood technologists to reconsider lignocellulosic biomass as a source of a variety of chemicals and materials.⁴

More recently, a number of scientists, especially Shiraishi and his coworkers, have inten-

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sively focused on the phenolysis of wood wastes in the presence of acidic catalyst at moderate temperatures of 120–150°C and the absence of a catalyst at elevated temperatures (about 250°C) to produce phenol–formaldehyde-type molding materials^{5–9} and adhesives.^{10–13} It was found that almost all the lignocellulosic biomass such as wood wastes, tree bark, coffee residue, bagasse, corn, wheat straw, etc., could be liquefied into phenol. Novolak-type moldings made from the phenolated wood showed the physical and mechanical properties comparabled to commercial novolak-based ones.⁶

On the other hand, there are several studies on the mechanism^{12–14} of the phenolysis of wood components and various properties on the moldings from it.^{6,15} It was reported that the phenolysis of wood components in the presence of an acidic catalyst resulted in dozens or even hundreds of different reactions that compete with each other. It was also reported that due to the cleavage of lignin in the presence of phenol, a variety of phenolic compounds such as guaiacol, coniferyl alcohol, vanilin, etc., were determined. For example, guaiacol formed from the cleavage of guaiacylglycerol-*b*-guaiacyl ether (GG), used as a model component of lignin, was found to condense with phenol and formaldehyde.¹⁴

However, no kinetic study of wood phenolysis in the presence of an acidic catalyst has been conducted so far. Therefore, in this study it was the aim to study the bulk kinetic of wood phenolysis carried out in the presence of HCl as a catalyst by using kinetic models.

EXPERIMENTAL

Materials

Wood meal of a sapwood part of Monarch birch (*Betula maximowiczina* Regel) species was used after being dried in a vacuum oven at 60°C for 8 h; 36.5% HCl aqueous solution was used as a catalyst. Phenol in crystal form was used as the main solvent in the wood phenolysis process. Methanol was used as solvent to dissolve the obtained reaction mixture and determine the amount of unreacted phenol. The chemicals were of reagent grade and used without further purification.

Phenolysis of Wood

The birch wood meals (20–80 mesh; 20 g) along with phenol (60 g) and 36.5% HCl acid (2.4 g,

based on phenol) were charged into a three-neck glass flask (500 mL) furnished with a reflux condenser, thermometer, and stirrer, followed by heating them in a silicon oil bath at 60–150°C for various reaction times, for example, 0.5, 1, 2, 4, and 6 h.

After the desired reaction times, the reaction mixture, containing reacted wood, unreacted/liquefied wood, reacted phenol, unreacted phenol parts, and the catalyst, was cooled to an ambient temperature, diluted with methanol, and filtered using a glass-fiber filter (TOYO GA 100) to separate unreacted wood residue from the others. The methanol-insoluble parts were dried in an oven at 105 ± 2°C to a constant weight and weighed to determine the amount of reacted wood. On the other hand, the methanol-soluble parts were used for the determination of the amount of reacted phenol.

Determination of Percent Reacted Phenol

The amounts of free phenol remained in the methanol-soluble part were measured by using a high-performance liquid chromatograph (HPLC) (Shimadzu LC-10A series) equipped with a SPD-10A UV-vis detector and Shimadzu shim-pack CLC-ODS (M) column (4.6 mm i.d. × 150 mm). The chromatographic areas were visualized under UV light (254 nm). Measurements were performed at 40°C and a flow rate of 1 mL/min using a methanol/water solution (1/2, v/v) as the mobile phase. Additionally, pure phenol was used as a standard solution. For the measurements, the mixture without unreacted wood residue, obtained after the phenolysis process, with a concentration of 0.1% was injected into the HPLC apparatus in the amount of 10 mL. Then the amounts of the unreacted free phenol were determined in grams, and the amount of phenol reacted with the wood components (cellulose, lignin, and hemicellulose) and phenol itself, the so-called “percent reacted phenol” was determined by the following equation:

$$\chi_A(\%) = \frac{w_{A0} - w_A}{w_{A0}} \times 100 \quad (1)$$

where w_{A0} and w_A are the amounts of starting phenol (g) and phenol remaining after the liquefaction (g), respectively.

Determination of Percent Reacted Wood

To determine the percent unreacted wood, mixtures obtained at the end of wood phenolysis were

Table I The Values of Percent Reacted Phenol as Functions of Reaction Time and Temperatures

| Temperature (°C) | Reacted Phenol (χ_A) (%) Reaction Time (h) | | | | |
|---------------------|--|-------|-------|-------|-------|
| | 0.5 | 1 | 2 | 4 | 6 |
| 60 | 1.75 | 2.80 | 3.80 | 5.94 | 7.10 |
| 90 | 6.70 | 10.84 | 12.80 | 15.14 | 17.14 |
| 120 | 13.85 | 16.81 | 18.03 | 25.98 | 27.17 |
| 150 | 17.24 | 19.00 | 23.14 | 28.84 | 29.38 |

diluted with methanol and filtered as described above. Finally, percent reacted wood (χ_B) was determined by the following equation:

$$\chi_B(\%) = \frac{w_{B0} - w_B}{w_{B0}} \times 100 \quad (2)$$

where, w_{B0} and w_B are the amounts of starting wood material (g) and unreacted wood determined after the liquefaction (g), respectively.

RESULTS AND DISCUSSION

The Effects of Reaction Temperatures and Time on The Percent Reacted Phenol and Wood

Table I lists the percent reacted phenol determined at 60–150°C for five different reaction times, i.e., 0.5, 1, 2, 4, and 6 h. As presented in Table I, the percent reacted phenol obviously increases when increasing reaction temperatures from 60 to 120°C, and then almost levels off with a further increase. Under these experimental circumstances, the optimum reaction temperature and time are determined to be 120°C and 4 h in view of the greatest amount of reacted phenol, respectively. Moreover, the greatest percent reacted phenol (about 30%, based upon starting phenol) is determined for the temperature of 150°C and reaction times of between 4 and 6 h.

Table 2 depicts the percentages of reacted wood in the presence of HCl catalyst as functions of various reaction temperatures and times. The findings show that the percent reacted wood component increases exponentially with increasing reaction temperature and time. In view of the highest percent reacted wood, the reaction temperature of 120°C and 4 h are said to be optimum

values for the wood phenolysis at the conditions studied. At the reaction temperature of 150°C and times of 4–6 h, the reacted wood amounts reach about 86% (based on the starting wood meal), which is the greatest value determined here. It was also reported that about 95% of the wood wastes were converted into phenol in the presence of sulfuric acid as a catalyst, which is much more acidic than HCl.⁶

Kinetic of Wood Phenolysis

The kinetics of wood phenolysis can be considered as an irreversible bimolecular reaction:



where, A and B represent phenol reagent and wood wastes, respectively. The rate constant of reaction can be expressed in the following differential and integration forms:^{16,17}

$$\frac{d\chi}{dt} = k(w_{A0} - \chi_A)(w_{B0} - \chi_B) \quad (4)$$

$$\int_0^x \frac{d\chi}{(w_{A0} - \chi_A)(w_{B0} - \chi_B)} = k \int_0^t dt \quad (5)$$

After integrating the eq. (5), the following equation is obtained:

$$\frac{1}{w_{A0} - w_{B0}} \ln \frac{w_{B0}(w_{A0} - \chi_A)}{w_{A0}(w_{B0} - \chi_B)} = kt \quad (6)$$

If the equation is rearranged, the final form is

Table II The Values of Reacted Wood Percent as Functions of Reaction Time and Temperatures

| Temperature (°C) | Reacted Wood (χ_B) (%) Reaction Time (h) | | | | |
|---------------------|--|-------|-------|-------|-------|
| | 0.5 | 1 | 2 | 4 | 6 |
| 60 | 24.22 | 31.49 | 41.45 | 43.58 | 47.27 |
| 90 | 48.18 | 57.32 | 60.55 | 68.60 | 70.01 |
| 120 | 56.15 | 65.65 | 68.55 | 77.81 | 80.40 |
| 150 | 66.63 | 69.66 | 77.01 | 84.95 | 86.44 |

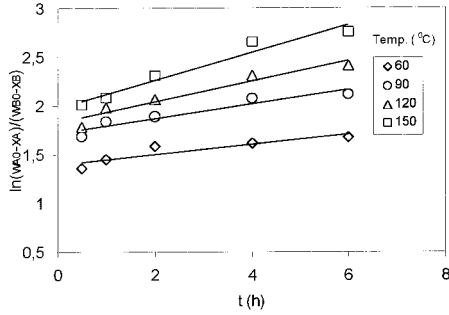


Figure 1 Second-order kinetic fit of wood phenolysis at different temperatures.

$$\ln \frac{(w_{A0} - \chi_A)}{(w_{B0} - \chi_B)} = \ln \frac{w_{A0}}{w_{B0}} + (w_{A0} - w_{B0})kt \quad (7)$$

where $(w_{A0} - \chi_A)$ and $(w_{B0} - \chi_B)$ are the weights of unreacted phenol and wood at time t , respectively. χ_A is reacted phenol (%) and χ_B is reacted wood (%).

The fact that the plots of $\ln \frac{(w_{A0} - \chi_A)}{(w_{B0} - \chi_B)}$ vs. t are linear has demonstrated that wood phenolysis process has a bimolecular second-order reaction kinetics (Fig. 1). The rate constants of reaction were determined from the slope of the straight line plots of $\ln \frac{(w_{A0} - \chi_A)}{(w_{B0} - \chi_B)}$ against t at different temperatures as shown in Figure 1. Equations given the data with regard to the characteristics of the correlation, i.e., the slopes, intercepts, and correlation coefficient, are presented in Table III.

It is seen from Table III that reaction rate constant varies between $1.2775 \times 10^{-3} \text{ h}^{-1}$ and $3.5625 \times 10^{-3} \text{ h}^{-1}$ when increasing temperature from 60 to 150°C. The rate constant of each wood phenolysis process increases with increasing reaction temperatures, thus indicating that the reaction occurs favorably at high temperature due to higher rate constants ($3.5625 \times 10^{-3} \text{ h}^{-1}$) and

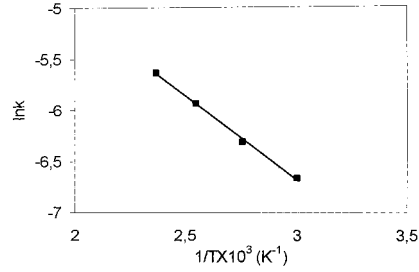


Figure 2 Arrhenius plot of wood phenolysis.

correlation coefficient (0.95) values at higher temperatures in comparison to others.

Relationship between $\ln k$ and $1/T$ was essentially linear having a correlation coefficient of 0.99 as shown in Figure 2. Thus, the dependence of rate constant of the phenolysis on temperatures can be described by using the Arrhenius equation:

$$k = k_0 \exp(-E^I/RT) \quad (8)$$

Then activation energy (E^I) of the reaction was determined from the slope of the Arrhenius plot of $\ln k$ vs. $1/T$, as shown in Figure 2. The E^I value determined is $13.438 \text{ kJ mol}^{-1}$.

On the other hand, a more detailed explanation for the transformation of reactants into products is given by the transition-state theory. According to the theory, reactants are first transformed an unstable intermediate form called the activation complex (transition-state), and then they are decomposed spontaneously into products as follows:



where, AB^* is the intermediate state at the top of the activation barrier. The probability of forming AB^* can be determined by the equilibrium constant. And then the activation free-enthalpy (ΔG^I)

Table III The Results of Rate Constant of Wood Phenolysis as a Function of Reaction Temperature

| Temperature (°C) | Rate Constant (k) $\times 10^3$ (h^{-1}) | Equation | R^2 |
|------------------|---|--------------------|-------|
| 60 | 1.2775 | $y=0.0511x+1.396$ | 0.82 |
| 90 | 1.8250 | $y=0.073x+1.7232$ | 0.89 |
| 120 | 2.6475 | $y=0.1059x+1.8227$ | 0.93 |
| 150 | 3.5625 | $y=0.1428x+1.9742$ | 0.95 |

Table IV Values of Activation Free Enthalpy (ΔG^I), Activation Enthalpy (ΔH^I), and Activation Entropy (ΔS^I) as Functions of Reaction Temperatures

| Temperature (°C) | ΔG^I (kJ mol ⁻¹) | ΔH^I (kJ mol ⁻¹) | $-\Delta S^I$ (J mol ⁻¹ K ⁻¹) |
|---------------------|---|---|---|
| 60 | 100.28 | 7.90 | 277.42 |
| 90 | 108.50 | 7.40 | 278.52 |
| 120 | 116.54 | 6.90 | 278.98 |
| 150 | 124.65 | 6.40 | 279.54 |

of the reaction was calculated by the Eyring equation, which gives the relationship between the reaction rate constant and activation free enthalpy as follows:^{17,18}

$$k = (k_B T/h) \exp(-\Delta G^I/RT) \quad (10)$$

where, k is the rate constant (h⁻¹), k_B is the Boltzmann constant (1.381×10^{-23} JK⁻¹) and h is the Planck constant (6.626×10^{-34} Js).

Furthermore, activation entropy and enthalpy were calculated from eqs. (11) and (12), respectively:

$$k = e^2(k_B T/h) \exp(\Delta S^I/R) \exp(-E^I/RT) \quad (11)$$

and

$$\Delta H^I = \Delta G^I + T\Delta S^I \quad (12)$$

The values of activation free enthalpy (ΔG^I), activation enthalpy (ΔH^I), and activation entropy (ΔS^I) of wood phenolysis done as functions of reaction temperatures are illustrated in Table IV. The activation free enthalpy for the wood phenolysis process increases steadily with increasing reaction temperature, as shown in Table IV. That is, a-30°C increase in reaction temperature gives about a 8-kJ mol⁻¹ increase in activation free enthalpy. The fact that ΔG^I has a higher positive value of 112.49 kJ mol⁻¹ on average demonstrates that the activated complex is quite unstable. The reaction rate is governed by the rate of decomposition of the intermediate state, thus revealing that the second step is the rate-controlling step.

It is evident from this table that the activation enthalpy is affected slightly by the reaction temperatures.¹⁷ That is, a-30°C increase in reaction temperature decreases by about 0.5 kJ mol⁻¹ in

activation enthalpy. It can also be understood from the enthalpy values that the wood phenolysis process has dominantly endothermic nature of reaction.

As shown in the same table, the activation entropy values of wood phenolysis as a function of reaction temperatures were almost the same as each other. This means that the motion of molecules is considerable slow. This can be attributed to the high concentration of reaction mixtures.

CONCLUSIONS

Wood wastes could successfully be phenolyzed in the presence of HCl as a catalyst at different temperatures and times. Typical kinetic parameters of wood phenolysis performed were studied. The results showed that about 90% of the wood could be liquefied into phenol, whereas 30% of phenol was found to react with wood components at a temperature of 150°C. The kinetic studies demonstrated that the wood phenolysis done at temperatures from 60–150°C obeyed a bimolecular type second-order reaction. Activation energy was found to be 13.438 kJ mol⁻¹.

Moreover, on the basis of the transition-state theory it was found that the second step of wood phenolysis reaction had a rate-controlling-step via the activated complex (transition-state) at a first step due to its higher activation free enthalpy values. Although activation enthalpy varied slightly with temperature, activation entropy almost did not change. Furthermore, the results with regard to activation enthalpy indicated that the wood phenolysis was of a dominantly endothermic reaction nature.

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