Front. For. China (2006) 2: 214–218
DOI 10.1007/s 11461-006-0002-z

RESEARCH ARTICLE

Zhang Qiuhui, Zhao Guangjie, Chen Jinpeng

Effects of inorganic acid catalysts on liquefaction of wood in phenol

Abstract In order to obtain the effects of acid catalysts on wood liquefaction in phenol, we investigated the liquefaction of wood powder from Chinese fir (*Cunninghamia lanceolata*) and poplar (Triploid *Populus tomentosa* Carr) in the presence of phenol with the following weak inorganic acids as catalysts: phosphoric acid (85%), sulfuric acid (36%), hydrochloric acid (37%) and oxalic acid (99.5%). Results show that phosphoric acid (85%) and sulfuric acid (36%) are better than the other catalysts. It was found that lower residue ratios can be obtained under defined reaction conditions: phenol/wood ratio is 4, a 10% catalyst based on the weight of phenol, a temperature of 150°C for 2 h and phosphoric or sulfuric acid. The residue ratios are 3.2% and 4.0%, respectively.

Keywords wood liquefaction, acid catalyst, residue ratio

1 Introduction

Biomass is a biodegradable and reusable resource. Effective utilization of biomass plays an important role in the protection of natural resources and the environment. Liquefaction of wood material is a new technique, which aims to convert wood wastes from the wood industry into biodegradable polymer material and increases the rate of wood utilization. In recent years, investigators have liquefied chemical components of wood, such as celluloses, hemicelluloses and lignin into bioactive liquid material in order to produce biodegradable wood adhesives or molding materials (Shiraishis et al., 1985; Shiraishis, 1986; Shiraishi and Kishi, 1986; Morita et al., 1990; Zhang and Zhao, 2003). Chemically untreated wood can be liquefied, without any catalyst, at a high temperature and pressure, but these liquefactions require large quantities of energy and high-standard equipment (Pu and Shiraishi, 1993a, 1993b, 1994; Lin et al., 1997a, 1997b, 1997c; Lee et al., 2002). However, wood can be effectively liquefied with acid catalysts in phenol under atmospheric pressure and relatively moderate temperatures (Lin et al., 2000, 2001). At present, some investigators use inorganic acids as catalysts in phenol liquefaction of wood, such as strong sulfuric acid (97%–98%) (Lin et al., 1995a, 1995b; Yamata, 1996). But strong sulfuric acid corrodes equipments and causes partial carbonization during liquefaction. Some investigations used a weak acid as catalyst in phenol liquefaction of birch (Alma, 1995; Lin et al., 1994). But the results were restricted to this species and application areas are limited.

This paper deals with phenol liquefaction of softwood and hardwood species using four inorganic acids. The main goal of this work is to intensify research on phenol liquefaction of wood and to provide technical references for industrial application of wood liquefaction.

2 Materials and methods

2.1 Wood species and chemicals

Wood species: Chinese fir and poplar were, respectively, harvested from Jiangxi and Hebei Provinces, China. Both wood species were ground in a Wiley mill and collected by sieving through a 20–80 mesh. Samples were dried in an oven at 105°C for 12 h and stored in desiccators at room temperature before use.

Phenol was used as the liquefaction reagent. Sulfuric acid (98%) diluted to 36% sulfuric acid with distilled water, hydrochloric acid (36%), phosphoric acid (85%) and oxalic acid (crystal) were used as acid catalysts.

Methanol was used as thinner. All chemicals were analytical reagents and obtained from commercial suppliers.

Translated from *Journal of Beijing Forestry University,* 2004, 26(5)
[译自:北京林业大学学报, 2004, 26(5)]

Zhang Qiuhui (✉), Zhao Guangjie, Chen Jinpeng
College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China
E-mail: qhzhang18@sohu.com

2.2 Methods

Wood, Chinese fir and poplar in the ratio of 1:1 (2.5 g), phenol (20 g) and catalyst (0.6–2.0 g) were charged into a 100 ml three-neck flask and immersed in an oil bath preheated at fixed temperatures (120°C, 150°C, 180°C) with constant stirring at a rate of 1,000 r/min and reflux for 120 min. At the end of the reaction, the resulting mixture was diluted with methanol (Yao et al., 1994), followed by filtration with a glass filter (G2) under vacuum pressure (0.1 MPa) to separate wood residue (methanol-insoluble part) from the methanol-soluble part (Lin et al., 1995a). The residue was oven dried at 105°C to a constant weight. The residue ratio was calculated by the following equation:

$$R\ (\%) = (W_r / W_0) \times 100$$

where R is the residue ratio, W_r the weight of residue (g) and W_0 the initial weight of wood (g).

3 Results and discussion

3.1 Effects of phosphoric acid

Figure 1 shows the effect of phosphoric acid on the residue ratio during liquefaction of wood at different temperatures. The amount of phosphoric acid was effective for the reaction at the same temperature. With an increase in the amount of phosphoric acid, the residue ratios decreased. However, the residue ratio was 99.2% at 120°C without the catalyst and the wood power could hardly be liquefied. There were noticeable changes in the liquefaction result when the amount of phosphoric acid was below 6%. It meant that the amount of phosphoric acid had significant effects. But the rate of decline was not great when the phosphoric acid exceeded 6%. Under the conditions of three different temperatures, the curves show similar trends. The changes were most remarkable at 180°C. At high temperatures and the amount of phosphoric acid lower than 6%, the residue ratio was relatively more sensitive to changes in the amount of phosphoric acid (Alma, 1995). When the amount of phosphoric acid increased from 3% to 10%, the residue ratio at 180°C and 120°C decreased by 27% and 14%, respectively. The differences illustrate that the effects increase with an increase in temperature.

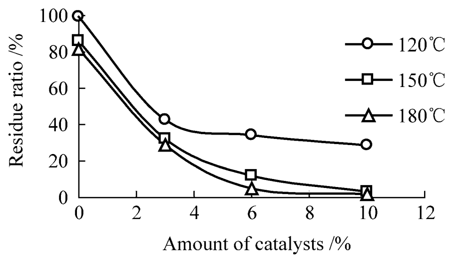

Fig. 1 Effect of phosphoric acid on liquefaction of wood (Chinese fir/poplar=1:1) in phenol at different temperatures

3.2 Effects of sulfuric acid

Figure 2 shows the relationship between the amount of diluted sulfuric acid and residue ratios at different temperatures. Although the effects of the amount of diluted sulfuric acid displayed similar trends, their extent was different. With increasing amounts of catalyst, the residue ratio decreased especially in the range from 0 to 3%. But there were only minor or no changes at all when the amount of catalyst was large enough. This characteristic corresponded with the effect of strong sulfuric acid. By comparing the three curves of different temperatures, we find that rates of changes of residue ratios decrease with the increase of temperature. When the amount of sulfuric acid increased from 3% to 10%, the rate of the change of residue ratio declined. This phenomenon can be attributed to the relatively high moisture content in sulfuric acid (36%). When the amount of sulfuric acid is increased, the amount of water in the reaction system increased and weakened the catalysis of the acid. The superfluous water caused the temperature of the liquefaction system to fall and resulted in a decline of the effect of the catalyst. At the same time, if the amount of the sulfuric acid exceeded 6%, we observed the phenomenon that the declining effect of sulfuric acid was the same as that of phosphoric acid. It implied that the effect of the catalyst was not in direct proportion to the amount of the catalyst and the extent of the effect of the amount of the catalyst on liquefaction was limited. All the residue ratios in the nine experiments were lower than 20%; when the amount of sulfuric acid exceeded 5%, both residue ratios at 150°C and 180°C were lower than 10%. It illustrates that diluted sulfuric acid can completely liquefy wood under the condition of a suitable temperature and amount of sulfuric acid.

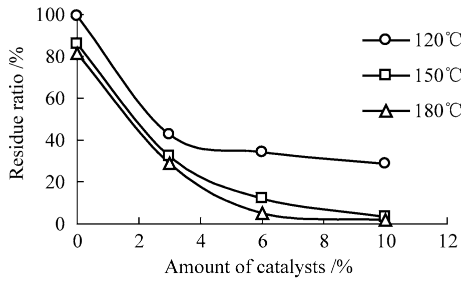

Fig. 2 Effect of sulfuric acid (36%) on liquefaction of wood (Chinese fir/poplar=1:1) in phenol at different temperatures

3.3 Effects of oxalic acid

Figure 3 indicates the effect of oxalic acid (crystal) on residue ratios during liquefaction of wood at different temperatures. As shown in the figure, initial residue ratios were high in the range of 45% and 72%. By increasing the amount of the catalyst, the residue ratios did not change much. It implies that oxalic acid has little effect on liquefaction. By comparing the three curves of different temperatures, the rates of the decline of residue ratios increased little with increasing temperature. At 120°C, when the amount of oxalic acid increased from 3% to 10%, the residue ratio decreased by 6.8%; at 180°C, however, the residue ratio decreased by 11.4% under the same changes in the amount of oxalic acid. It implies that the trend of the effect of oxalic acid as the catalyst on liquefaction of wood in phenol corresponds with those of other catalysts; however, the effect of oxalic acid was little and residue ratios were very high. This can be attributed to the fact that the oxalic acid is very weak and the pH value of the entire reaction system was close to neutral, which cannot move the reaction in the direction of the polymer degradation (Lee et al., 2002). Besides, compared with sulfuric acid, oxalic acid has no expansion characteristic and cannot expand the crystal region of cellulose, which is the most difficult component of wood to be dissolved. Therefore, the efficiency of liquefaction is low and oxalic acid is not suitable as the catalyst in phenol liquefaction of wood.

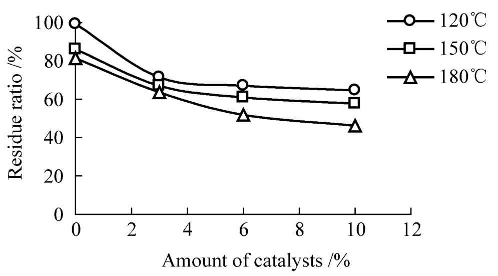

Fig. 3 Effect of oxalic acid on liquefaction of wood (Chinese fir/poplar=1:1) in phenol at different temperatures

3.4 Effects of hydrochloric acid

Figure 4 shows the effects of hydrochloric acid on liquefaction of wood in phenol at different temperatures. It shows that the residue ratio decreases with the increase in the amount of catalyst. Especially in the range of 0 to 6%, the effect of hydrochloric acid is remarkable. If the amount exceeds 6%, the effect diminishes considerably. Take 180°C, for example: the residue ratio decreased by 16.0% with the amount of catalyst increasing from 3% to 6%. When the amount continued to increase by 4%, the residue ratio only decreased by 3.0%. It should be noted that the residue ratio at 150°C was the lowest within the entire range of the amount of catalyst; at 120°C the next higher ratio was observed and the residue ratio at 180°C was the highest. This result does not correspond with the general law that liquefaction efficiency increases with increasing temperature (Lee et al., 2002). It can be attributed to the volatility of hydrochloric acid. These experiments were conducted under normal pressure, with hydrochloric acid volatilized as hydrochloric vapors under high temperatures. The higher the temperature, the larger the amount of hydrochloric vapors (Yamata et al., 1996). When the amount of hydrochloric acid was 6% at 150°C, the effect of the temperature on liquefaction was dominant. So the residue ratio at the temperature is lower than that at 120°C; however, at 180°C, volatilization of hydrochloric acid was dominant, which led to residue ratio lower than that at 120°C. Among these nine tests, all of the final residue ratios were between 35% and 60%, which is relatively high. Therefore, it is important to choose a suitable temperature range in the use of hydrochloric acid as the catalyst in phenol liquefaction of wood.

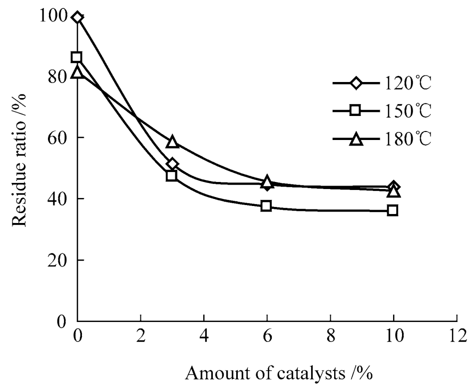

Fig. 4 Effect of hydrochloric acid（37%）on liquefaction of wood (Chinese fir/poplar=1:1) in phenol at different temperatures

3.5 Effects of temperature and type of catalysts

Figures 5–7 show the effects of the type of acid catalysts on phenol liquefaction of wood at 120, 150 and 180°C. Figure 5 indicated that at 120°C the effect of sulfuric acid (36%) on phenol liquefaction of wood for the lowest residue ratio. Others, in ordinal ranking were phosphoric acid, hydrochloric acid and oxalic acid. When the amount of sulfuric acid (36%) was 10%, the residue ratio was at a low level. Using suitable amount of sulfuric acid (36%) as the catalyst, we not only can obtain an ideal effect on phenol liquefaction of wood, but can also reduce the cost of liquefaction and the corrosion caused by strong acids in equipments. If oxalic acid or hydrochloric acid were used as

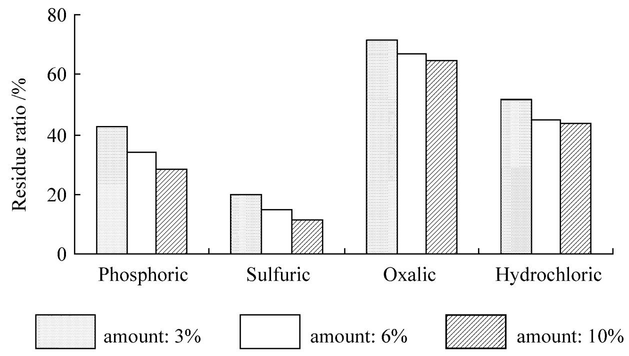

Fig. 5 Effect of the type and amount of acid catalysts on liquefaction of wood in phenol at 120°C

the catalyst, it would be difficult to get ideal liquefaction results even with an increased amount of catalyst.

As shown in Fig. 6, at 150°C, compared with phosphoric acid and sulfuric acid (36%), the catalyses of oxalic acid and hydrochloric acid were worse, with residue ratios exceeding 40%. But using phosphoric acid or diluted sulfuric acid as the catalyst, the effect of liquefaction at 150°C was markedly better than at 120°C. Even though the amount of phosphoric acid was 6%, the residue ratio was relatively low. When the amount was 10%, both residue ratios in the catalysis of phosphoric acid and that of diluted sulfuric acid were below 5%. Considering the acid corrosion in equipments and operational safety standards, the use of phosphoric acid as the catalyst is recommended.

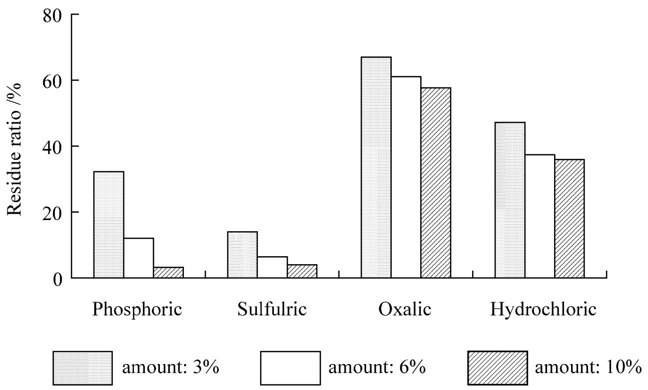

Fig. 6 Effect of the type and amount of acid catalysts on liquefaction of wood in phenol at 150°C

Figure 7 shows that at 180°C, catalyses of hydrochloric acid and oxalic acid were not effective, which can be attributed to the significant volatilization of hydrochloric acid at high temperatures and to the low acidity of oxalic acid, respectively. But sulfuric acid and phosphoric acid were effective. When the amount of sulfuric acid was above 6%, the residue ratios were lower than 6%. In order to lower the corrosion caused by sulfuric acid in equipments, further reduction in its concentration should be considered. If the amount of phosphoric acid is 10%, effective phenol liquefaction of wood can also be obtained.

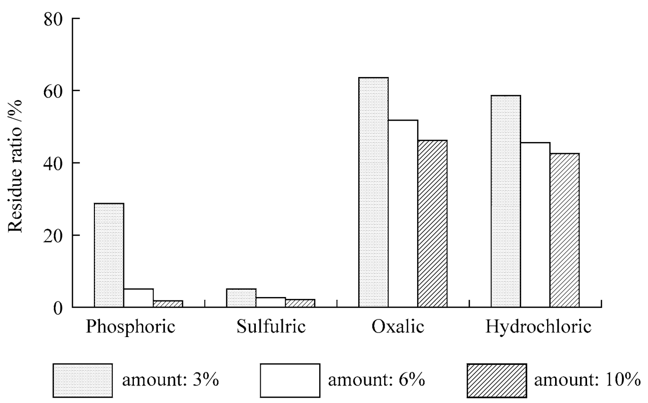

Fig. 7 Effect of the type and amount of acid catalysts on liquefaction of wood in phenol at 180°C

4 Conclusions

Among the four inorganic acid catalysts in our experiments, diluted sulfuric acid (36%) and phosphoric acid (85%) were effective in wood liquefaction in phenol at the given temperatures. Because of relatively strong volatility, catalysis of hydrochloric acid (37%) was not as good as the former two catalysts. This was particularly true when catalysis notably decreased at high temperatures. Catalysis of oxalic acid (99.5%) was the least satisfactory; even at 180°C it was difficult to achieve ideal results of liquefaction.

Using diluted sulfuric or phosphoric acid as catalyst, the effect of liquefaction at 150°C was not markedly different from that at 180°C, though an optimal liquefaction effect was obtained at 180°C. In order to minimize power consumption and costs, it is advisable to choose 150°C as the reaction temperature.

The amount of diluted sulfuric acid below 10% showed ideal catalyzsis during liquefaction. Temperatures above 150°C with a 6% amount of catalyst also produced ideal effects. Ideal liquefaction can be achieved using 10% amount of phosphoric acid as the catalyst, especially at 150°C.

Acknowledgements The authors thank the Key Research Program Foundation of the Ministry of Education of China for financial support.

References

Alma M.-K., Yoshioka M., Yao Y.-G. and Shiraishi N., Preparation and characterization of the phenolated wood using hydrochloric acid (HCl) as catalyst, Wood Sci. Technol., 1995, 30(1): 39–47

Lee S. H., Yoshioka M. and Shiraishi N., Resol-Type Phenolic resin from liquefied phenolated wood and its application to phenolic foam, J. Appl. Polym. Sci., 2002, 84(3): 468–472

Lin L., Yao Y. and Shiraishi N., Liquefaction mechanism of β-O-4 lignin model compound in the presence of phenol under acid catalysts—Part 2. Reaction behavior and pathways, Holzforschung, 2000, 55(6): 625–630

Lin L.-Z., Yao Y.-G. and Shiraishi N., Liquefaction mechanism of β-O-4 lignin model compound in the presence of phenol under acid catalysts—Part 1. Identification of the reaction products, Holzforschung, 2001, 55(6): 617–624

Lin L.-Z., Yoshioka M., Yao Y.-G. and Shiraishi N., Liquefaction mechanism of lignin in the presence of phenol at elevated temperature without catalysts—multi-condensation, Holzforschung, 1997a, 51(4): 333–337

Lin L.-Z., Yoshioka M., Yao Y.-G. and Shiraishi N., Liquefaction mechanism of lignin in the presence of phenol at elevated temperature without catalysts—reaction pathway, Holzforschung, 1997b, 51(4): 325–332

Lin L.-Z., Yao Y.-G., Yoshioka M. and Shiraishi N., Liquefaction mechanism of lignin in the presence of phenol at elevated temperature without catalysts—structural characterization of the reaction products, Holzforschung, 1997c, 51(4): 316–324

Lin L.-Z., Yoshioka M., Yao Y.-G. and Shiraishi N., Liquefaction of wood in the presence of phenol using phosphoric acid as a catalyst and the flow properties of the liquefied wood, J. Appl.

Polym. Sci., 1994, 52(11): 1,629–1,636

Lin L.-Z., Yoshioka M., Yao Y.-G. and Shiraishi N., Physical properties of moldings from liquefied wood resins, J. Appl. Polym. Sci., 1995a, 55(11): 1,563–1,571

Lin L.-Z., Yoshioka M., Yao Y.-G. and Shiraishi N., Preparation and properties of phenolated wood/phenol/formaldehyde cocondensed resin, J. Appl. Polym. Sci., 1995b, 58(8): 1,297–1,304

Morita M., Yamawaki Y., Shigematsu M. and Sakata I., Preparation and properties of a cyanoethylated wood latex, Mokuai Gakkaishi, 1990, 36(8): 659–664

Pu S. and Shiraishi N., Liquefaction of wood without a catalyst Ⅰ—time course of wood liquefaction with phenols and effects of wood/phenol ratios, Mokuai Gakkaishi, 1993a, 39(4): 446–452

Pu S. and Shiraishi N., Liquefaction of wood without a catalyst Ⅱ—weight loss by gasification during wood liquefaction, and effects of temperature and water, Mokuai Gakkaishi, 1993b, 39(4): 453–458

Pu S. and Shiraishi N., Liquefaction of wood without a catalyst Ⅳ—effect of a additives, such as acid, salt, and neutral organic solvent, Mokuai Gakkaishi, 1994, 40(8): 824–829

Shiraishi N. and Kishi H., Wood-phenol adhesives prepared from carboxymethylated wood, J. Appl. Polym. Sci., 1986, 32(1): 3,189–3,209

Shiraishi N., Onodera S., Ohtani M. and Masumoto T., Dissolution of etherified or esterified wood into polyhydric alcohols or bisphenol A and their application in preparing wooden polymeric materials, Mokuai Gakkaishi, 1985, 31(5): 418–420

Shiraishis N., Plasticization of wood, Mokuai Gakkaishi, 1986, 32(10): 755–762 (in Japanese)

Yamata T., Ono H., Ohara S. and Yamaguchi A., Characterization of the products resulting from direct liquefaction of cellulose Ⅰ. Identification of intermediates and the relevant mechanism in direct phenol liquefaction of cellulose in the presence of water, Mokuai Gakkaishi, 1996, 42(11): 1,098–1,104

Yao Y.-G., Yoshioka M. and Shiraishi N., Soluble properties of liquefied biomass prepared in organic solvents Ⅰ. The soluble behavior of liquefied biomass in various diluents, Mokuai Gakkaishi, 1994, 40(2): 176–184

Zhang Q.-H. and Zhao G.-J., Liquefaction of wood by using phenol or polyhydric alcohols, J. Beijing For. Univ., 2003, 25(6): 71–76 [张求慧, 赵广杰, 木材的苯酚及多羟基醇液化, 北京林业大学学报, 2003, 25(6): 71–76]