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Micropore structure of wood: change in micropore structure accompanied by delignification

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Abstract In our preceding study, we clarified that liquids having similar molecular sizes to ethanol were mainly adsorbed onto lignin among the major constituents of wood. This suggests that most micropores or adsorption sites loosely hydrogen-bonded to each other, which are accessible to these liquids, exist in lignin. In the present study, to examine micropores in wood and lignin, micropore distribution was measured by CO_2 gas adsorption at ice–water temperature (273 K). Dry samples prepared by gradual delignification from wood meal were used as adsorbents. The pore-size distributions were determined by analyzing adsorption isotherms using the Horvath–Kawazoe method. It was found that the number of micropores decreased with the decrease in residual lignin, and micropores were hardly found in cellulose and hemicellulose. It is considered that most micropores smaller than 0.6 nm in wood exist in lignin.

Key words Micropore structure · Lignin · Pore-size distribution · HK method

Introduction

Wood is a porous material, and the pores in wood are classified into two categories: macropores enclosed by the cell wall, ranging from 0.1 μm to a few hundred micrometers (cell lumens, intercellular spaces, pits, etc.); and fine pores measuring 0.1–1 nm in the cell-wall substance.

Sawabe et al.[1] examined the pore structure in the cell wall by nitrogen adsorption using the *t*-plot method (*t*-method) and modelless method (ML method). However, at that time, it was technically difficult to analyze the pore structure to obtain detailed findings for the micropore structure below 1 nm.

On the other hand, Morisato and coworkers[2–4] studied the adsorption of four kinds of organic liquids from dilute benzene solutions onto dry and preswollen wood; it was suggested that adsorption sites showed loose hydrogen bonding between and/or within the molecules of wood constituents, or that pores that could easily adsorb liquids of a similar size to methanol exist on dry wood. The authors have already examined the adsorption of some organic liquids onto the main constituents of wood[5] and partly delignified wood,[6] and obtained the following results; ethanol and dimethyl sulfoxide (DMSO) were adsorbed much more onto dry wood meal than onto dry holocellulose and cellulose, and the amount of adsorption of ethanol and DMSO onto dry samples decreased remarkably as the delignification progressed, while the amount of adsorption of methanol hardly decreased. These results suggested that most of the above pores or sites exist in lignin, and those pores or sites are accessible to ethanol and DMSO.

This study sought to obtain more information about micropores in dry wood. Micropore distribution was measured by CO_2 adsorption at ice–water temperature (273 K), for which the required time for adsorption equilibrium was shorter than for higher temperatures used in earlier methods.[1] Pore-size distributions were determined using the Horvath-Kawazoe method (HK method),[7] which is suitable to measure micropore structure below 2 nm. In addition, to clarify the relation between the amount of residual lignin and the number of micropores, the change in the number of pores during the delignification process was examined.

Materials and methods

Adsorbents

Preparations

Wood meal of 60–83 mesh (177–250 μm) was obtained from mature wood of the heartwood of Japanese cypress

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(*Chamaecyparis obtusa*). This was placed into a column with a glass filter and water was forced upward through the column to remove fine particles of wood meal that may hinder adsorption measurement. Organic extractives such as oils and fats in the wood were then removed with an alcohol–benzene mixture (1 ethanol: 2 benzene) in a Soxhlet apparatus. After air drying in a draft for 1 week, the extracted wood meal was kept in a dry desiccator until delignification or the adsorption experiment.

Delignification

The extracted wood meal was delignified by the following methods; 1 g of sodium chlorite, 0.2 ml glacial acetic acid, and 150 ml of distilled water were added to 2.5 g of the extracted wood meal, and the mixture was allowed to react for 1 h at 75°C with gentle stirring to obtain a slightly delignified sample. To obtain more thoroughly delignified samples, the above operation was repeated once, twice, or three times; thus, four samples with different levels of residual lignin were obtained. These samples were washed thoroughly with distilled water. After air drying in a draft for about 1 week, they were kept in a dry desiccator until the adsorption experiment. Lignin content was determined by the sulfuric acid method.[8]

Cellulose

Dissolving conifer pulp kindly supplied by Nippon Paper Chemicals and purified cotton wool were used as adsorbents. The alpha cellulose contents of the pulp and cotton were 92.3%, and 98%–99.5%, respectively. They were washed thoroughly with distilled water, and, after air drying in a draft for about 1 week, they were kept in a dry desiccator until the time of the adsorption experiment.

Analysis of micropore structure

About 1 g of any one of the samples obtained was put into a sample cell for measurement of CO_2 adsorption, and the sample was degassed for 15 h or more under a high vacuum ($<1 \times 10^{-7}$ mbar) at 105°C. The amount of adsorbed CO_2 was measured at ice–water temperature (273 K) with an automatic gas adsorption device AUTOSORB-1 (Quantachrome, USA). The pore-size distribution of micropores below 0.6 nm was determined using the HK method from the adsorption isotherms obtained.

Results and discussion

Examination of determining conditions

Pore-size distributions of porous materials are generally measured by nitrogen adsorption at liquid nitrogen temperature (77 K). However, it is difficult to accurately measure the pore-size distribution below 1 nm in wood by this method, because diffusion of the adsorbate molecules is so slow at liquid nitrogen temperature that a long time is required for adsorption equilibrium.[9] Little information is obtained from the measurement of nitrogen adsorption at higher temperatures at which the diffusion of nitrogen molecules is rapid enough to shorten the time for adsorption equilibrium, because the relative pressure is very low at atmospheric pressure, which is the upper limit for the apparatus used in this study.

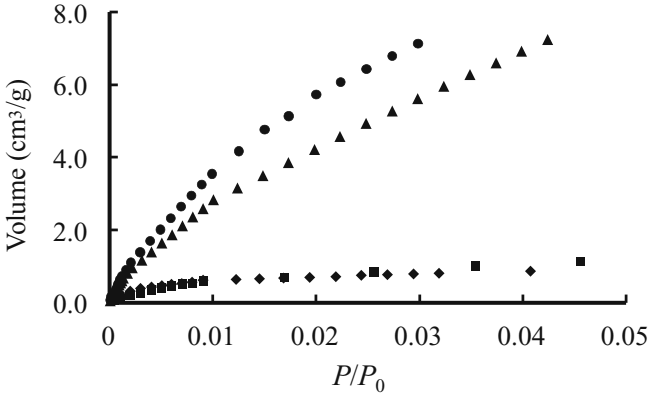

Fig. 1. Temperature dependence of adsorbed volume of carbon dioxide onto untreated wood. Adsorption equilibrium time was 5 min. *Circles*, 273 K; *triangles*, 269 K; *squares*, 230 K; *diamonds*, 195 K

From a similar viewpoint, the analysis of micropore structure of wood and bamboo charcoal was successful at dry ice–acetone temperature (195 K) and ice–water temperature (273 K) with carbon dioxide.[9] However, the same technique cannot always be applied to wood.

In this study, to determine the appropriate temperature to measure micropores in wood by adsorption of carbon dioxide, ice–water temperature (273 K), the temperature of ice–water with sodium chloride (269 K), dry ice–ethanol temperature (230 K), and dry ice–acetone temperature (195 K) were examined. Information about micropore distribution can be obtained at these temperatures up to 0.6 nm at 273 K, up to 0.8 nm at 269 K, up to 1 nm at 230 K, and up to 2 nm at 195 K. The results are shown in Fig. 1. The adsorption equilibrium time of each measurement point was set as 5 min for all of the temperatures examined.

Figure 1 shows that the amount of adsorption decreases with falling temperature. Because adsorption is an exothermic reaction, a decrease in the amount of adsorption with lower temperature cannot occur for gas adsorption onto a nonswelling adsorbent. Therefore, the result shown in Fig. 1 indicates that the relative pressure increased before reaching the adsorption equilibrium to determine the adsorption at the next measuring point.

Figure 2 shows pore-size distributions determined by carbon dioxide adsorption with 3 min, 5 min, and 10 min of adsorption equilibrium time at 273 K. If no pressure change occurred during the predetermined adsorption time, the measurement moved to the next measuring point. With 3 min of adsorption equilibrium time, there were fewer small pores than with 5 min or 10 min, and more large pores. The number of smaller pores increased slightly with the

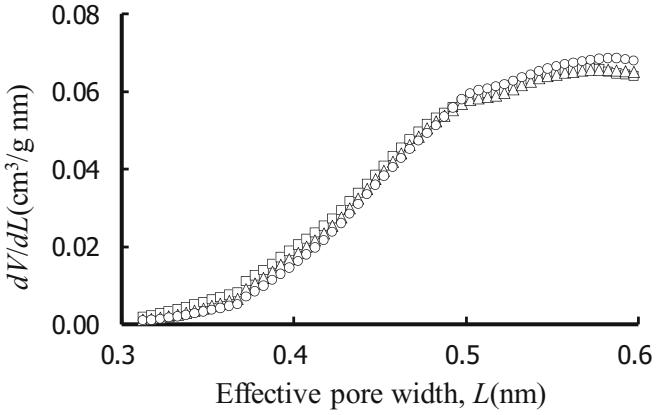

Fig. 2. Pore-size distributions determined by the adsorption of carbon dioxide at 273 K using adsorption equilibrium times of 3 min (*circles*), 5 min (*triangles*), and 10 min (*squares*)

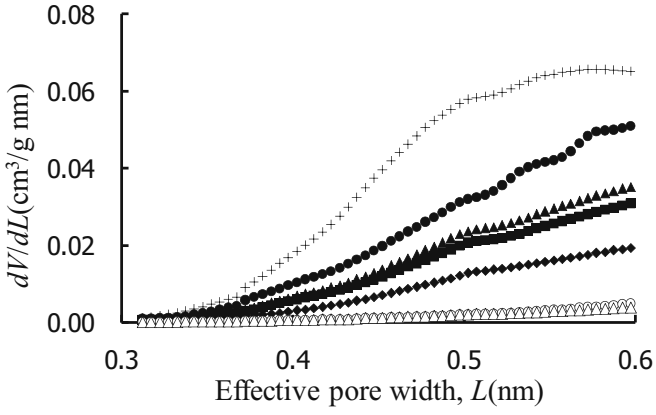

Fig. 3. Pore-size distributions in the range of 0.3–0.6 nm for all samples. *Crosses*, wood meal; *filled circles*, wood delignified once; *filled triangles*, wood delignified twice; *filled squares*, wood delignified three times; *filled diamonds*, wood delignified four times; *open circles*, wood pulp; *open triangles*, purified cotton wool

increase in the adsorption equilibrium time from 5 to 10 min, although the number of larger pores did not change much. From these results, it is interpreted that adsorption onto the surface of the small pores did not reach equilibrium within 3 min, and the amount adsorbed there added to the amount of adsorption onto large pores in measurements at higher relative pressures. Thus, this measurement suggested fewer small pores and more large pores than is the case. Consequently, the adsorption equilibrium time of 3 min was not sufficient to determine the pore-size distribution of wood at 273 K, and more time is required for adsorption at lower temperatures. However, if an excessively longer time will be set for the equilibrium time, the device will more frequently stop with an error message. For this reason, the temperature for determination of pore-size distribution of wood was set at 273 K. In addition, the 5-min equilibrium time was adopted because the reproducibility when using the same sample was high, and the difference in the pore-size distribution between the equilibrium times of 5 and 10 min was quite small, as shown in Fig. 2. Essentially, 5 min was considered to be close to the true equilibrium time. Although the pore distribution that can be obtained under these measuring conditions is currently limited up to 0.6 nm, reliable information about ultra minute wood pores was obtained for the first time.

Change in pore structure caused by delignification

Figure 3 shows pore-size distributions in the range of 0.3–0.6 nm of the samples, as determined from adsorption isotherms. The largest pore volume within this range was found in the nondelignified sample, and the volume decreased as delignification proceeded. The tendency of this decrease nearly corresponded to that of the decrease in the residual lignin caused by delignification, as shown in Table 1. The residual lignin decreased most remarkably from one to two delignification steps, and the pore volume also decreased markedly in this range. In addition, a similar tendency was found in the adsorbed amount of ethanol and dimethyl sulfoxide reported in the preceding report.[6] These

Table 1. Lignin content of delignified samples

Number of delignification treatments	Lignin content (%)
0	30.6
1	26.4
2	15.1
3	11.2
4	10.7

results suggest that pores below 0.6 nm are much more abundant in lignin than in the other main constituents of wood.

On the other hand, the pore volume in the sample that was delignified four times, which includes cellulose and hemicellulose, was much lower than that in the nondelignified sample, but was larger than in the cellulose samples. This is probably due the considerable amount of lignin that remains in the sample, even after four delignification steps, as shown in Table 1.

The change in the micropore structure in the delignification process should be considered. Stone and Scallan[10] reported that the number of pores in the range of 2–3 nm increased in the early stage of delignification, and then decreased as delignification proceeded. This is attributable to new pores caused by the removal of lignin. However, no increase in pore volume caused by delignification was seen below 0.6 nm in this study. It is considered that minute pores smaller than 0.6 nm do not develop with the removal of lignin, and a decrease in micropores with the progress of delignification is accompanied by the decrease in lignin. This decrease in micropores may be caused by the following: (1) a decrease in lignin with more minute pores than in cellulose and hemicellulose, and/or (2) a decrease in minute pores that originally existed in cellulose and/or hemicellulose with the progress of delignification. If the latter is dominant, change in pore size distribution would probably occur with the progress of delignification; however, pore size distribution was almost the same regardless of the progress of delignification. Therefore, it can be considered that the former is most probably dominant.

Pore volume below 0.6 nm was slightly different between wood pulp and cotton cellulose. This difference possibly resulted from the difference in crystallinity of both cellulose samples. More detailed discussion is not given in this report, because the pore volume below 0.6 nm was quite low in both cellulose samples.

Conclusions

Pore-size distributions below 0.6 nm in samples gradually delignified from wood meal, wood pulp, and cotton cellulose were determined by the adsorption of carbon dioxide at ice–water temperature (273 K). The results obtained were as follows:

1. Micropores smaller than 0.6 nm were found in dry wood, and the number of them decreased with the decrease in the amount of residual lignin.
2. Micropores were scarce in dry dissolving wood pulp and in cotton cellulose.
3. It is considered that micropores in dry wood mainly exist in lignin among the main constituents of wood.

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