

POROUS STRUCTURE OF NEVER-DRIED PULP FIBERS ANALYZED BY NITROGEN ADSORPTION METHOD

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ABSTRACT

Porous structures of never-dried pulp fibers were investigated by nitrogen adsorption method. A distinct bent-point in the desorption isotherms was observed at a 45% relative vapor pressure for both softwood and hardwood never-dried pulp fibers. The singular reduction in nitrogen adsorption volume was likely attributed to the presence of meso-pores formed via lignin removal in wood cell walls during pulping, which was indicated from the results of nitrogen adsorption/desorption isotherms for partially delignified wood powders. The specific surface area of a sufficiently delignified softwood powder was ~ 150 m²/g, slightly lower than 200 m²/g. These results indicate that $4 \times 4 = 16$ individual cellulose microfibrils (each of which is 3–4 nm wide) form one unit of cellulose fibril bundle and each bundle is surrounded by lignin thin layer in softwood cell walls. On the contrary, partially delignified hardwood powders had extremely small specific surface areas, whereas a hardwood pulp fiber showed a fairly large surface area. The specific surface areas of delignified hardwood powders were drastically increased after extraction with alkali to remove xylan. Thus, not only lignin but also xylan plays a significant role in the formation of pore structures for the hardwood pulp fiber and the delignified wood powders. The results of pore size distribution analysis using BJH and NLDFT

techniques showed that the sizes of principal meso-pores present in unbeaten pulp fibers were 3.2–3.7 nm and were increased by disintegration process.

1. INTRODUCTION

Attention of porous structures of pulp fibers has been paid in both papermaking industry and academia for long time, because printing, writing and wiping are all strongly related to liquid adsorption behavior of the fibers in paper [1–3]. Flexibility of the fibers attained by the internal fibrillation during beating process is also related to the formation of void structures in the fibers [3]. The properties of cellulosic materials, which have been raised in line with establishment of a sustainable green society [4], are also strongly influenced by porous structures of the cellulosic fibers. Thus, understanding of porous structures is significant for controlling properties and functions of cellulosic end products as well as their biodegradability behavior. Pore sizes of more than 50 nm or so-called “macro-pores” in cellulosic fibers or paper structure are usually determined by mercury porosimetry, while a nitrogen adsorption method is competent for determination of pore sizes ranging from 2 to 50 nm.

The formation and collapse of meso-pores take place in wood cell walls during pulping and paper making processes, which eventually influence various properties of the cellulosic fibers and paper materials. However, void structures of the pulp fibers have been analyzed mainly using calculation of specific surface areas obtained from BET plots in an early stage of nitrogen isotherm. In this study, other useful information obtained from total isotherms is presented to clarify the formation/collapse behavior of meso-pores in never-dried pulp fibers during pulping and drying processes. The experimental results obtained for softwood and hardwood fibers are separately discussed in this study.

2. EXPERIMENTAL

2.1 Sample

2.1.1 Wood chips

North American Douglas fir (*Pseudotsuga manziesii*) wood chip donated by Nippon Paper Co. Ltd, Japan, was used as a starting material for preparation of softwood kraft pulp fiber and partially delignified softwood powder. Eucalyptus (*E. globules*) wood chip donated by Oji Paper Mill was used for preparation of a partially delignified hardwood powder.

2.1.2 Preparation of laboratory-made kraft pulp

The wood chip was cooked under the following conditions: 20% active alkali, 25% sulfidity, 1/5 chip/liquid weight ratio, the highest temperature of 170°C, the reaching time to the highest temperature and maintaining of duration at the highest temperature of 90 min. The obtained pulp (43% yield) was bleached with sodium chlorite in water at pH 4–5 and 75°C.

2.1.3 Commercial never-dried kraft pulps

Never-dried softwood and hardwood bleached kraft pulps donated by Nippon Paper Co. Ltd. were used as representatives of commercial pulps.

2.1.4 Preparation of partially delignified wood powders

The sieved and coarse wood powders were prepared from Douglas fir and Eucalyptus wood chips. Partially delignified and never-dried wood powder samples having different Klason lignin contents were prepared from extracts-free wood powders by repeated treatment with NaClO₂ in water at pH 4–5 and 75°C for 1 h (according to the Wise method) up to 6 and 5 times for softwood and hardwood samples, respectively. The delignified softwood powder prepared by the above treatment for 6 times, for example, was coded as PDL5-6.

2.2 Sample preparation for measurement of nitrogen isotherm

The never-dried wood powder and pulp samples were dried after a sequential solvent-exchange treatment. The water in a never-dried sample/water suspension was carefully replaced with ethanol by repeated filtration using a buffner funnel and re-immersion in fresh ethanol using a polypropylene capsule. Here, in each step, the sample immersed in fresh ethanol in the capsule was shaken on a rotamax 120 shaker for 12 h. This solvent-exchange was repeated 3 times. Then the ethanol was replaced with Zeorora® H supplied by Nippon Zeon Co. Ltd, Japan. The solvent exchange from ethanol to Zeorora was also repeated 3 times, in which the shaking time was set for 12 h. This solvent-exchange procedure had to be carefully carried out so as not to expose the sample directly to an ambient air, especially when the sample immersed in Zeorora was filtered. Zeorora is easily vaporized, and takes up heat from the sample, resulting in partial and local freezing. Thus, water vapor in atmosphere might locally adsorb in the sample due to temperature drop, which induces reduction of surface area of the sample. The chemical structure and its main properties of Zeorora® H are shown in Figure 1. A super critical point drying using carbon dioxide seems to be one of the most

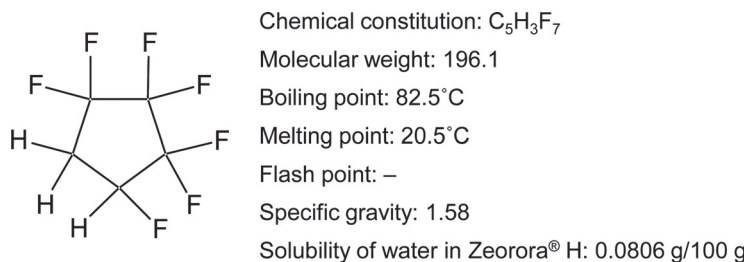


Figure 1. Chemical constitution and representative features of Zeorora® H.

reliable methods suitable for pulp fibers and wood powders, because no surface tension acts on the samples. High specific surface areas of the cellulose aerogels prepared using Zeorora have been reported, and the values were comparable to those obtained using super critical point drying [5].

2.3 Apparatus

A Nova 4200e type apparatus (Malvern Co. Ltd., UK) was used for the measurement of nitrogen isotherm with a NovaWin2 data processing system. This apparatus needs very stable atmospheric pressure during the measurement. Any gas emission from the samples pronouncedly affects the obtained specific surface areas, and thus this should be avoided. Hence, a pre-conditioning of the samples under vacuum was carefully carried out. The sample in a glass vessel was vacuum-dried at room temperature for 24 h and then heated at $90^{\circ}C$ for 3 h followed by heating at $105^{\circ}C$ for 5 h before the measurement. This apparatus requires some conditions for sample loading. The value of specific surface area (unknown before the measurement) \times sample weight should be more than 2 m^2 as an attainable assurance level suggested by the supplier. Since the maximum weight of cellulosic samples loadable in the specified glass vessel was $\sim 1\text{ g}$, the specific surface areas of the samples should be more than $2\text{ m}^2/\text{g}$. The validity of the obtained results were evaluated by confirming the following two points; 1) each BET plot has a clear linearity, and 2) the desorption isotherm is always positioned higher than or almost equal level to the adsorption isotherm in the whole range of relative pressure.

3. RESULTS AND DISCUSSION

3.1 Softwood

Generally, materials possessing only macro-pores or no void in the structure show isotherms categorized to the second type of BDDT's classification or

BET type [6]. Isotherms of once-dried cellulosic fibers and paper samples are classified to this category. Figure 2 shows isotherms for the commercial and the laboratory-made never-dried unbeaten softwood bleached kraft pulp fibers. The unit in vertical axis, STP, is the adsorbed nitrogen gas volume converted to that at 1atm and 273K. It is noteworthy that each desorption curve showed a drastic change in the nitrogen adsorbed volume at the relative vapor pressure of ~ 0.45 . In the range of relative vapor pressure < 0.45 , both adsorption and desorption curves were completely overlapped. Moreover, in higher vapor pressure range, a distinct hysteresis between adsorption and desorption isotherms was observed. These isotherms are different from those of the second type of BDDT's classification described above. These phenomena are explainable in terms of a typical "inkbottle" type isotherm pattern [7].

Differences in isotherm between the BDDT second type and the result in Figure 2 are due to different drying history between them. In order to clarify the structures corresponding to the result in Figure 2, the nitrogen adsorption measurement for partially delignified softwood powders (from PDL5-1 to PDL5-6) was carried out. Figure 3 shows the result for PDL5-4 as a representative among a series of the model delignified softwood powder samples. A clear bend point on the desorption isotherm at relative pressure of $\sim 45\%$ was observed. Although the results for all the PDL5 samples are not listed in Figure 3, the bent behavior at relative vapor pressure of $\sim 45\%$ was quite similar. As shown in Figs. 2 and 3, the same behavior as that of the commercial and laboratory-made never-dried pulp fibers was observed.

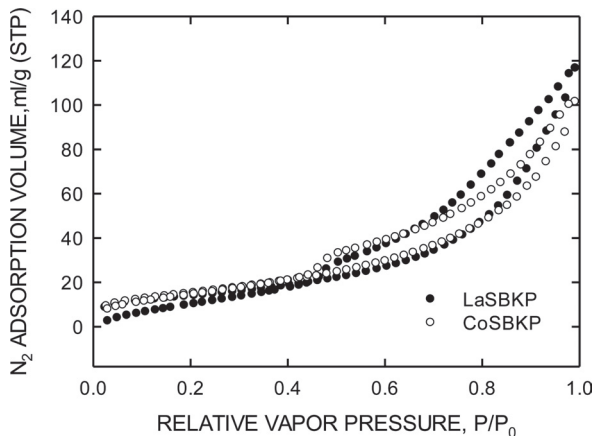


Figure 2. Nitrogen adsorption isotherms for commercial and laboratory-made never-dried softwood bleached kraft pulp.

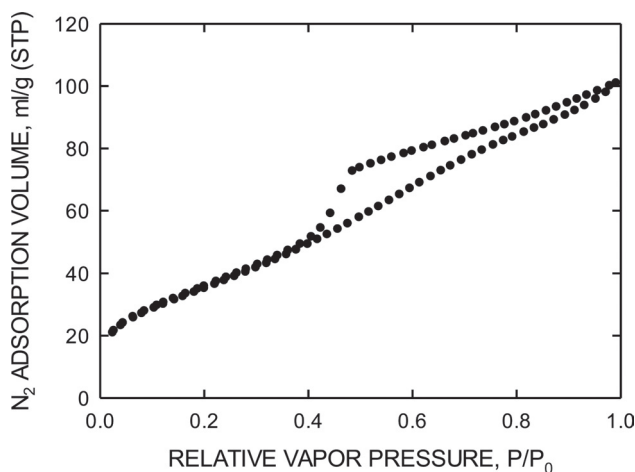


Figure 3. Nitrogen adsorption isotherm for PDLS-4.

Another characteristic point in Figure 3 was that no steep increase was observed in the nitrogen adsorption volume at higher relative pressures. This result was also distinguishable from those of isotherm patterns for the well-known BDDT's second type. Since the NaClO₂-delignified softwood powder samples had almost no macro-pores detectable by the nitrogen adsorption method, condensation of nitrogen gas at higher relative vapor pressures did not take place at all (Figure 3) even after the partial lignin removal.

Table 1 shows weight loss and Klason lignin content for PDLS samples repeatedly treated with sodium chlorite under acidic condition. Both, the weight and Klason lignin content of the samples linearly decreased with the cycle number of the delignification treatment. Moreover, the sums (a+b) of Klason lignin content and weight loss in Table 1 were 29–30% and almost constant irrespective of the cycle number; the weight losses were attributed to delignification or partial removal of lignin in the softwood powders.

The once-air-dried PDLS-4, for example, remarkably decreased in its surface area to lower than 2 m²/g. At lower relative vapor pressures, the nitrogen adsorption volumes in the desorption curve were anomalously lower than zero, although a linear relation of the BET plots in the adsorption curve was maintained. The specific surface area of this sample was calculated to 0.62 m²/g.

Pore size distributions have generally been determined from N₂-adsorption/desorption isotherms for porous materials using some special techniques. The BJH analysis [8] was selected first to calculate the pore size distribution in this

Table 1. Klason lignin content and weight loss of delignified softwood powders (PDLS) repeatedly treated by the Wise method

Repetition number	Klason lignin content, %, (a)	Weight loss, %, (b)	(a)+(b), %
0	29.3	0	29.3
1	22.1	6.8	28.9
2	17.4	12.1	29.5
3	12.9	17.4	30.3
4	7.7	21.7	29.4
5	2.9	26.6	29.5
6	0.8	28.8	29.6

study. The BJH method is based on Kelvin’s equation on the assumption that shapes of all voids in a material are cylindrical. However, according to a ultra-structural model of wood cell walls [9], the meso-pores have rather slit-like structures. Then, NLDFT (nonlocal density functional theory) method was also applied to the samples. This method has been developed for slit-like thin layered materials composed of carbon [10–12]. Thus, pore size distributions were calculated by the above two techniques in this study.

Figure 4 shows the BJH plots for the commercial the laboratory-made never-dried softwood bleached kraft pulp together with PDLS-3 and PDLS-5. The pronounced sharp peaks observed for all PDLS samples were detected ~3.7 nm

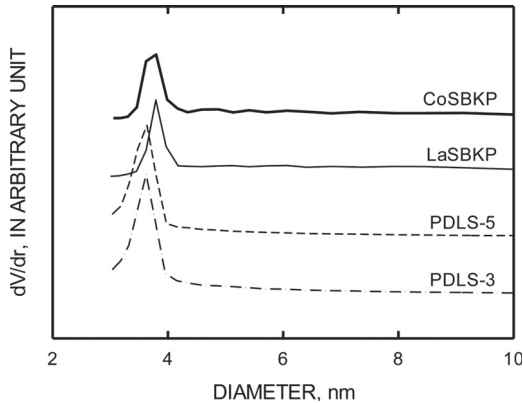


Figure 4. BJH plots for PDLS-3, PDLS-5, and commercial and laboratory-made never-dried softwood bleached kraft pulp.

when the cylindrical model was used. The other PDLS samples had similar plot patterns. The bent curve at the relative pressure of ~45% for PDLS-4 in Figure 3 and the sharp peaks for PDLS-3 and PDLS-5 in the BJH plots in Figure 4 are likely to be attributed to some voids formed in the wood cell walls by the partial removal of lignin. The sharp peaks were observed also in the BJH plots for the commercial and the laboratory-made never-dried pulp fibers, although the peaks were broader and slightly shifted to the large diameter side. Almost the same tendencies as shown in Figure 4 for PDLS samples were obtained by the NLDFT method, although the sharp peaks in the pore size distribution curves shifted to a narrower side, ~3.2 nm. The pore sizes obtained by the two methods cannot be directly compared because of difference in basic assumption constructed in these theories. Moreover, the pore sizes obtained here are not reflected by actual spaces formed from removal of lignin thin layers, and pores are expanded to reach equilibrium between osmotic pressure and elasticity of the cell walls after lignin removal. A size of the meso-pore calculated here is comparable with that detected by the solute exclusion method [2,3].

From the results calculated by the two methods, the drastic decrease in nitrogen adsorption volume at the relative vapor pressure of ~45% for the commercial and the laboratory-made never-dried fibers were also attributed to the inkbottle-type pores existing in the fibers as remainder spaces of lignin removal. Since the isotherm of PDLS-4 in Figure 3 did not show any steep increase in nitrogen adsorption volume at higher relative vapor pressures as described before, this sample possesses almost no macro-pores. In this case, the BJH method gives a mean pore radius, r_p from liquid nitrogen adsorption volume at the highest relative vapor pressure, V_{liq} and a specific surface area, S , that is,

$$r_p = 2V_{liq}/S \quad (1)$$

Here, V_{liq} is calculated by the following equation from STP unit in Figure 5,

$$V_{liq} = P_a V_{ads} V_m / RT \quad (2)$$

where V_{ads} is the adsorbed volume of nitrogen gas, P_a is the atmospheric pressure, and V_m is the molar volume of liquid nitrogen, 34.7 mL/mol. Figure 5 shows the calculation results for all the PDLS samples. The average value of the mean pore radius was ~2.8 nm (~5.6 nm in diameter). The mean diameter of the meso-pores of PDLS samples was higher than the peak diameter of inkbottle type meso-pores in Figure 4.

The surface area of one cellulose microfibril bundle accessible to nitrogen molecule was roughly estimated from the corresponding specific surface area of delignified and pulp samples. One individual cellulose microfibril has been

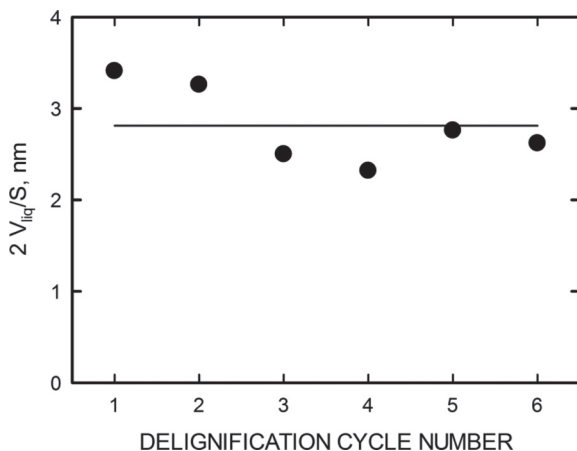


Figure 5. Mean meso-pore diameters for all PDL S samples.

recognized as a crystalline nanofiber having a square cross-section [9,13,14] and consisting of $6 \times 6 = 36$ cellulose chains regularly aggregated in parallel manner to the microfibril direction [14]. The specific surface area of completely individual cellulose microfibrils having the cellulose I crystal structure is calculated to be $\sim 800 \text{ m}^2/\text{g}$. When four individual cellulose microfibrils aggregate to form one fibril bundle having a square cross section, the surface area reduces to half. In a similar manner, when 16 individual cellulose microfibrils aggregate to form one larger fibril bundle having a square cross section, the specific surface area decreases to one fourth from that of the individual cellulose microfibril. The relationship between specific surface area and shape of cross section for cellulose microfibril and bundles was shown in Figure 6.

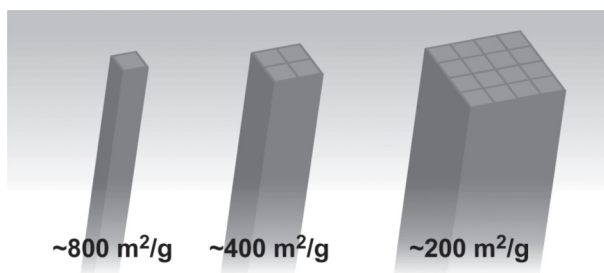


Figure 6. Modeled microfibrils and their surface areas.

Specific surface areas of PDLS-4, PDLS-5 and PDLS-6 after removal of significant amounts of lignin were $\sim 150 \text{ m}^2/\text{g}$ (Figure 7); these values are quite significant and meaningful for understanding of the relationship between degree of delignification of wood and the obtained cellulose fibril width in terms of wood cell wall architectures. The obtained values of $\sim 150 \text{ m}^2/\text{g}$ were slightly lower than $200 \text{ m}^2/\text{g}$. Many studies have been reported up to date for ultra-structures of wood cell walls [15]. According to some models proposed as microfibrils [16,17], the outside of one cellulose fibril (i.e. a bundle of cellulose microfibrils) is surrounded by thin lignin layer.

When the surface detected by the nitrogen adsorption method accounts for spaces formed by lignin removal, the following hypothesis is available; a thin layer of lignin covers the cellulose fibril or cellulose microfibril bundle consisting of $4 \times 4 = 16$ individual cellulose microfibrils (Figure 6). This hypothesis is well consistent with the results reported for cellulose nanofibers having 15 nm in width prepared from wood holocelluloses by mechanical disintegration in water [18]. In addition, lateral cellulose fibril aggregate dimensions from 15 to 25nm for wood and unprocessed pulp fibers detected by the various techniques have been reported [19–23]. Figure 8 shows a SEM image of disintegrated PDLS-4 prepared using a super high-pressure homogenizer in water. Nanofibers having 15–20 nm in width are observed, although the precise widths/width distribution was not measurable due to some thickness increases of the coated osmium layer.

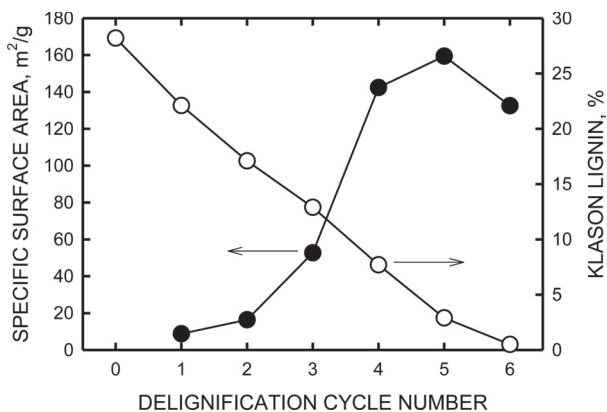


Figure 7. Plots for specific surface area and Klason lignin content against repeated delignification treatment number for PDLS.

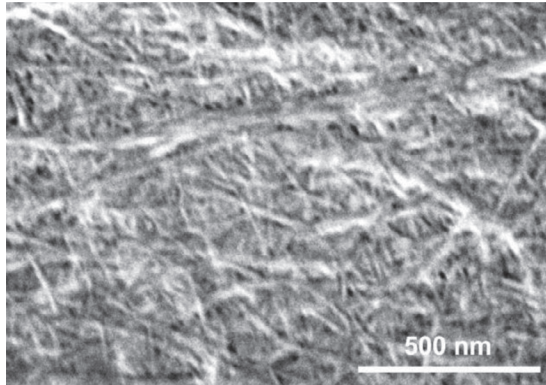


Figure 8. SEM image of PDLH-4, disintegrated by a super-high pressure homogenizer.

3.2 Hardwood

Figure 9 shows a nitrogen isotherm for the commercial bleached hardwood pulp fiber. A drastic decrease in nitrogen adsorption volume at the relative vapor pressure of ~45% on desorption isotherm was observed also in this case. The size of open end in the ink-bottle type meso-pores was also close to that for the softwood pulp fiber. Then, further investigations using the partially delignified hardwood powders (PDLH samples) were carried out. Figure 10 shows nitrogen isotherms for PDLH-4. The whole isotherm shapes were almost identical to those of PDLH samples. However, the nitrogen adsorption volume at the highest vapor pressure was extremely

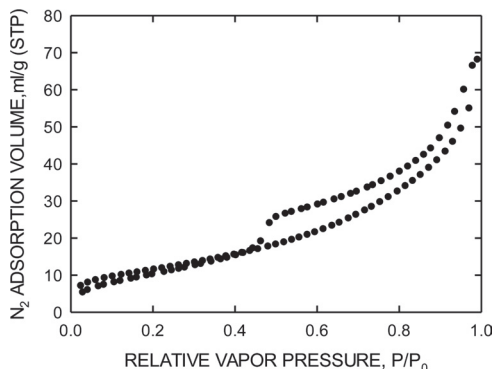


Figure 9. Nitrogen adsorption isotherm for commercial never-dried bleached hardwood kraft pulp.

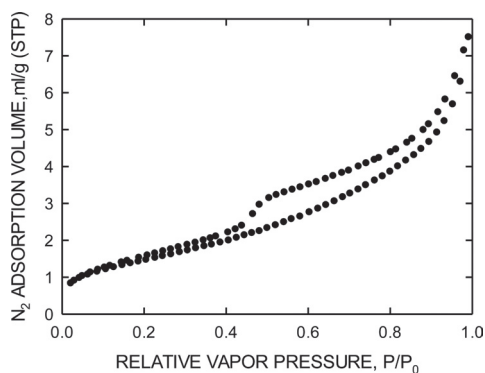


Figure 10. Nitrogen adsorption isotherm for PDLH-4.

smaller than that for the PDLs samples. Since the isotherm itself was similar to that for the softwood pulp fiber, the dimension of the open end of inkbottle type mesopores was likely to be almost the same. In contrast, the inkbottles of PDLH samples must be extremely shallow. The specific surface areas for all the PDLH samples are shown in Figure 11 together with the weight loss of each sample by the delignification. The specific surface areas for all the samples were not higher than 6 m²/g.

The residual lignin present in the delignified eucalyptus samples may have turned to extremely small particles during the sulfuric acid treatment. Such small lignin particles may have been partly filled in the used glass filter (1G P16 type) so that the filtration could not be completed. Then, the lignin contents in a series of PDLH samples were evaluated by the weight loss values of the samples after the NaClO₂ treatment.

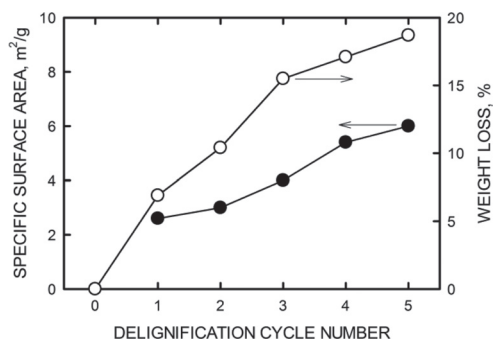


Figure 11. Plots for specific surface area and weight loss against repetition number of delignification treatment for PDLH

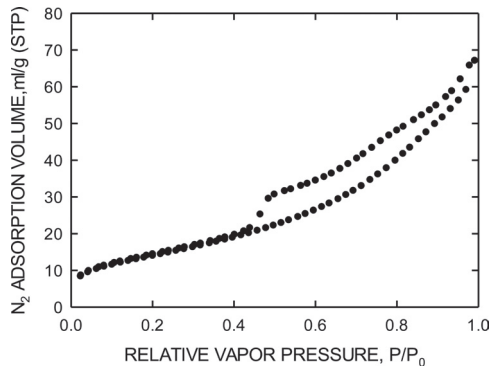


Figure 12. Nitrogen adsorption isotherm for PDLH-4, extracted with 4% NaOH.

The results in Figure 11 are apparently inconsistent with those of lignin distribution in hardwood cell walls measured by ultraviolet photomicrography [24]. As the next step, hemicelluloses present in PDLH-4 were extracted with 4% sodium hydroxide for 30 min at room temperature under nitrogen atmosphere. The nitrogen adsorption isotherm of the alkali-extracted PDLH-4 (weight loss 32%) was shown in Figure 12. Although the shape of the total adsorption/desorption isotherms was fairly resemble to the original PDLH-4, the nitrogen adsorption volume remarkably increased, and the specific surface area was increased from 5.4 to 85.3 m²/g.

It is obvious that the removal of hemicelluloses from PDLH-4 is the predominant factor to increase in the specific surface area. These results indicate that the meso-pores of the original PDLH-4 were filled with hemicelluloses (mainly xylan) so that nitrogen gas could not penetrate into the pores. According to the model proposed by Salmen and Olsson [25], xylan exists in hardwood cell walls in association with lignin rather than with cellulose [24,25]. Xylan forms a complex with lignin in the cell wall of wood. [26,27]. Thus, xylan possibly spreads over the meso-pores after the lignin removal. Since the specific surface area of the highly delignified alkali-extracted PDLH did not reach the value around 150 m²/g, some structural changes in the cell walls may have taken place during the treatment.

Hence, it is likely that hemicelluloses behave as fillers in the meso-pores formed by the lignin removal; hemicelluloses in the cell walls play a role to decrease in the specific surface area of wood fibers. The disintegration treatment of PDLH-6 at 10,000 rpm for 15 min in water reduced its specific surface area from 132.5 to 42.1 m²/g. This indicates hemicellulose remained in meso-pore was expanded and partially filled in the pore by vigorous agitation in water, thus

preventing some extent nitrogen from penetration into the pore. Specific surface areas of the commercial and laboratory-made never-dried softwood bleached kraft pulp fibers in Figure 2 were 76.3 and 59.3 m²/g, respectively; these values are less than half those of the sufficiently delignified PDLs samples. Since the effect of hemicelluloses on specific surface areas of pulp fiber in paper making process including disintegration, refining and drying processes seems to be complicated, and further investigation is needed.

CONCLUSION

The never dried pulp fibers were found to possess large amounts of meso-pores in cell walls. The dimension of open end spaces of ink-bottle type meso-pores was likely to be uniform from the results of nitrogen adsorption measurement. Once the fibers were air-dried, the meso-pores were almost completely closed. Hemicelluloses in meso-pores influence pronouncedly the resulting specific surface areas of cellulosic fibers, although its behavior is fairly complicated. For example, the disintegration process remarkably reduced the specific surface area of the fibers originally having meso-pores. The results obtained in this study may provide some significant information to trace structural changes in cell walls of pulp fibers during pulping, beating, paper making, and drying processes.

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Transcription of Discussion

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Thad Maloney Aalto University

Thank you for a very interesting presentation. I am curious about the final solvent that you used in your solvent exchange procedure. Normally I have used some alkane, pentane, or hexane or sometime like that, which are not that pleasant and not that repeatable. What I am asking is: what was the final solvent that you used, why did you use that and does it have some special properties that help you with the solvent exchange?

Minoru Kimura

The main reason we decided to use a fluorine reagent is that it has no flash point and is not harmful to the human body. Zeorora has a very high specific surface area which is a comparable to that area using critical drying by carbon hydroxide.

Bob Pelton McMaster University (from the chair)

So I guess the surface tension is very low and so the Campbell forces are low, even compared to an alkane?

Discussion

Minoru Kimura

But the problem is that the cost is very high, 300 dollars for a few grams, but you can reuse it after purification.

Bob Pelton

There are many nitrogen adsorption isotherms in the literature on wood and fibres. Are there any others reported that have this discontinuity in them?

Minoru Kimura

As far as I know, no. In the 1950s and 1960s, there was much research on surface area using the nitrogen adsorption method, but they all use isotherms at the initial stage then calculate the surface area. They didn't attempt to measure over the full range of water vapour pressure and produce whole isotherms.