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Porosity of wood pulp fibers in the wet and highly open dry state



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ABSTRACT

The porosity of kraft and dissolving pulp samples with different drying histories were studied in the wet (Water Retention Value, Solute Exclusion) and dry state (N_2 sorption, Scanning Electron Microscopy) and the results were compared. An efficient drying protocol was created to minimize porosity loss upon water removal for dry analyses. The samples were first solvent exchanged by dialysis to dry acetone and then critical point dried (CPD) from CO_2 .

It was found out that even after reaching relatively high specific surface areas of 200–300 m^2/g for CPD pulp, the samples had shrunk and most of the micropores were not detectable until rewetting. However, the dry state mesoporosity correlated well with the wet state values. SEM was used to examine the pore structure and fibril arrangement of the CPD fiber sample. The kraft pulps were found to have a larger specific pore volume and surface area than the dissolving pulps as measured by N_2 sorption. However, SEM analysis of the samples showed the dissolving pulps had a more homogenous and more open surface porosity than the kraft samples. The kraft pulp showed less hornification after drying and rewetting than the dissolving pulp. Heating of kraft pulp to 100 °C during drying increased the irreversible pore closure. Pores were often arranged in chain-like formations and signs of surface fibril aggregation were detected.

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1. Introduction

Lignocellulosic materials are under intense research for biofuel conversion and sustainable material applications. In a range of different processes, lignocellulosic materials are broken down, dissolved or chemically modified before conversion into the final product. The reaction rate or dissolution efficiency of a particular grade of pulp is often described by the somewhat ill-defined term “reactivity”. While a number of fiber properties may influence pulp reactivity, the pore structure of the fiber wall is of particular importance. This is a complex topic, since the pores in the cell wall are open when the fibers are suspended in water but completely collapse when the water is removed from the cell wall by traditional drying methods.

In solid containing reactions the reactivity is proportional to the substrate accessibility [1–4] which is a function of the porosity and the effective surface area of the material. Specifically with wood fibers, the closure of the meso- and macropores (2–50 nm and >50 nm respectively) has been found to be detrimental for

chemical and enzymatic treatments [3,4]. The closure of the pores can be caused by various pressure inflicting actions as exemplified by research done on pressing [5], drying [6] and heating the pulp during drying [7]. This is unfortunate since different methods of drying are used to improve cellulose transferability and storability before further refining.

Pulp as a material is not simple in drying behavior, which makes its drying challenging if high porosity and information from the wet state are to be preserved. This is troublesome also for pulp analysis, since there are powerful porosity analysis methods that require dry state, including mercury intrusion porosimetry, AFM (Atomic Force Microscopy), SEM (Scanning Electron Microscopy) and gas sorption. The best methods for preparation of well-preserved dry pulp samples have been limited mostly to three options: evaporation from a low surface tension solvent, freeze-drying and critical point drying (CPD) [8,9]. The most promising drying method is CPD because it avoids capillary effects of the evaporation drying and phase separation of the freeze-drying method. Freeze-drying can compete with CPD but only in some ideal cases [10].

When a dry fiber aerogel is prepared from a wet pulp fiber sample, it is likely that the pore structure will distort in some way and that the small scale details of the structure will be altered. To a certain extent, a higher dry specific surface area (SSA) for a given

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sample implies a better preserved pore structure in the dry state. In the literature, the values between different sample types can be very large but this may be more affected by the applied drying method than the sample properties. For softwood (SW) kraft pulp, values up to 230 m²/g and 185 m²/g have been reported for unbleached and bleached pulps, respectively [11]. However, more recently some authors stated that 80–190 m²/g would be an expected SSA for never dried pulp fibers [12–14]. Higher specific surface areas are usual in pretreated, nanofibrillated (NFC) or regenerated cellulose (RC) samples where SSAs of 200–375 m²/g have been observed [10,15–19]. In some extreme cases values around 400–500 m²/g have been reported for NFC [8] and RC [20] which still does not imply fully accessible fibrils but instead, in average, 2 × 2 fibril aggregations in the sample [14].

In this article, an efficient method for analytical fiber drying is presented. The collected data was analyzed to compare pulps for their different pore classes in the wet and dry states. SEM and N₂ sorption techniques were applied to understand the pulp porosity changes upon water removal. Different pulp types were compared according to their drying history and hemicellulose content. Attention was also paid to reduce unnecessary or potentially harmful steps during the drying process. For example, the heating may cause rearrangements at 50 °C [21] and amplify hornification even below 100 °C [22] where moisture is known to cause softening of the matrix [23], and thus the samples were not heated to no more than 35 °C during CPD. Also, reports about solvent exchange series of more than 3 solvents before the drying step have been reported in the literature [18,24,25]. It is unclear whether prolonged exchanging is useful but based on the final results its possible advantages are likely dwarfed by the effects of the other drying steps.

2. Materials and methods

2.1. Samples and chemicals

Finnish mill produced bleached kraft and dissolving pulps were studied (Table 1). The pulps were either used as never dried, rewetted after drying (“machine dried”) or rewetted after oven treatment (40 °C and 100 °C). All samples were birch except for a softwood (SW) sample that was an approximately 85/15 mixture of Scots pine and Norway spruce. The total hemicellulose content of the pulp is shown in Table 1.

The pulps were all washed thoroughly in deionized water prior to evaluation. The acid group counter-ions were not adjusted. All water used was deionized water. Research quality dextran T5 and T2000 were provided by Pharmacosmos A/S. Acetone (WVR International) was at least of 99.8% purity. CO₂ (Oy Aga AB) was at least 99.8% pure.

2.2. Carbohydrate analysis

The carbohydrate composition of the pulps was determined by quantitative saccharification upon acid hydrolysis according to the standard procedure reported by Sluiter et al. [26] The monosaccharides were determined by high performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 system (Sunnyvale (CA), USA). The contents of cellulose, glucomannan and xylan were calculated from the monosaccharide contents using the procedure reported by Janson [27].

2.3. Solvent exchange and critical point drying

In order to prepare dry fibers with intact pore structure a critical point drying method was used. In this approach the water in the pulp is exchanged for an intermediate organic solvent that is miscible with water and CO₂. The solvent is then exchanged with liquid CO₂ which is brought above its critical point, where surface tension is zero, and then evaporated. This way the pore collapse, which happens when water saturated fibers are dried, can be avoided.

The pulp samples (10% solid content) were placed into 50 kDa molecular weight cut-off (MWCO) regenerated cellulose membrane tubings. Some water was added along with the samples for air bubble removal. The pulp was solvent exchanged by dialysis into >99.5% acetone for 45 h. The volumetric proportion of acetone to the wet pulp was minimum 10:1. The solvent was changed four times. The batch was agitated continuously with a magnetic stirrer. The acetone was later exchanged to liquid CO₂ in a critical point drier (Leica EM CPD300) over 25 cycles (1 h). No sample holders or free space fillers were used during CPD. The CO₂ was heated to 35 °C under ca. 75 bar pressure in order to bring it into the supercritical state. The fluid was removed slowly until only carbon dioxide gas at atmospheric pressure remained for the fluid phase. The CPD program from the first CO₂ addition onwards took approximately only 1 h for CO₂ exchange and 0.5 h for CO₂ removal but it was found to be effective enough for all the samples in this study since small temporal increases to the method did not cause any notable effect to the sample porosities. Some reference samples were prepared by doing the first dialysis step against MeOH or DMSO instead of acetone.

2.4. N₂ sorption

It is important to measure the specific surface area (SSA) of the samples immediately after CPD drying with minimal exposure to humidity of high temperature as the samples are unstable and the pores can partially collapse. The following procedure was used.

SSA and pore volumes were measured by nitrogen sorption apparatus Tristar II (Micromeritics) and the data was analyzed using Tristar 3020 (Micromeritics). The sample holders were 3/8 flat

Table 1
The samples of this study.

Name	Wood	Type	Drying	Hemicellulose content (%)
HW-d-ND	birch	dissolving	never dried	6.6
HW-d-d	birch	dissolving	machine dried	6.0
HW-d-100	birch	dissolving	oven (100 °C)	6.1
HW-K-ND	birch	kraft	never dried	26.1
HW-K-40	birch	kraft	oven (40 °C)	26.2
HW-K-100	birch	kraft	oven (100 °C)	26.0
SW-K-ND	spruce + pine	kraft	never dried	18.0

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