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Quantification of accessible hydroxyl groups in cellulosic pulps by dynamic vapor sorption with deuterium exchange

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Abstract Dynamic vapor sorption (DVS) coupled with deuterium exchange was applied in determining the amount of hydroxyl (OH) groups accessible for deuteration in pulps and pure cellulose quantitatively. The samples studied with the method were different types of chemical pulps as well as microcrystalline and amorphous cellulose powders. The measurement sequence consisted of drying the samples first until the change in sample mass was less than 0.0005% min^{-1} followed by rewetting the sample with deuterium oxide (D_2O) vapor at set relative humidity (RH) of 95% for 600 min and then drying the sample again the same way as the initial drying was done. The method allows determination of the absolute amount of OH groups accessible to deuterium exchange in the samples fully automatically within 1 day. In addition, the equilibrium moisture contents (EMC) of the samples were measured at RH 95% without prior drying enabling the assessment of the EMC of the samples in as-received state without the need to assess the effect of drying. The accessibilities of chemical pulps were found to vary between 54 and 61% of the theoretical maximum, whereas the accessibilities of microcrystalline cellulose and amorphous cellulose were 51 and 63%, respectively. Interestingly, it was found that the accessible OH group content and the EMC of the samples in mol kg^{-1} correlated with each other and that, in fact, their ratio was close to one.

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Graphical abstract
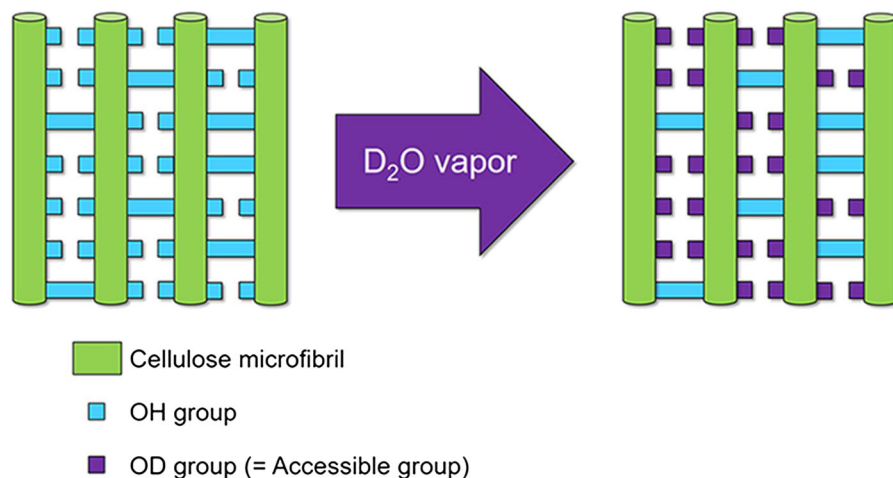
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Introduction

Cellulose plays a significant role in the on-going shift from fossil-based economies to renewable resource-based bioeconomies. As an abundant and renewable biopolymer, cellulose is in the key position when choosing sustainable raw materials. Manufacturing novel cellulosic products, such as cellulosic nanomaterials (Brinchi et al. 2013; Habibi et al. 2010), biofuels (Lienqueo et al. 2016; Sun and Cheng 2002) and regenerated cellulose materials (Stepan et al. 2016; Wang et al. 2016), requires in most cases chemical modification of cellulose or even its dissolution. The availability of the hydroxyl (OH) groups in cellulose is one of the main factors in cellulose treatment as the OH groups form the main reactive functionality in cellulose susceptible to chemical reactions. The availability of the OH groups has been related with the water uptake of cellulose fibers in aqueous environment. Thus, the means to assess the accessibility of the OH groups in cellulose for water has been a topical question for decades and remains to be so, perhaps more than ever, today.

The accessibility of OH groups in cellulose has been studied indirectly with several different

techniques including the water retention value (WRV) (Jayme 1944; Lovikka et al. 2016; Oksanen et al. 1997) and the fiber saturation point (FSP) (Maloney and Paulapuro 2000; Roselli et al. 2014; Stone and Scallan 1967) which provide information on the pore structure of the fiber wall in the wet state and the fibers' ability to swell. In addition to these techniques, the porosity of cellulose fibers has been studied with various experimental techniques (Berthold and Salmén 1997; Billosta et al. 2006; Ding et al. 2014; Fahlén and Salmén 2005; Grönqvist et al. 2014; Lovikka et al. 2016; Maloney et al. 1997, 1998; Moura et al. 2005; Östlund et al. 2010; Park et al. 2006; Reza et al. 2015; Stone and Scallan 1967, 1968; Tenhunen et al. 2017). Moreover, the accessibility of the OH groups in cellulose has been studied by analyzing deuterated samples with different techniques. Deuteration, or exposing cellulose to excess deuterium oxide (D_2O), provides a means to label and study OH groups in cellulose as it results in the exchange of hydrogen atoms to deuterium in those OH groups that are accessible to moisture and have the tendency to be exchanged. Deuterated samples have been studied before with Fourier transform infrared (FT-IR) spectroscopy (Hishikawa et al. 1999; Hofstetter et al. 2006; Jeffries 1963; Pönni et al. 2013, 2014a; Suchy et al. 2010a, b; Tsuchikawa and Siesler 2003a, b). Recently, Lindh et al. (2016) conducted a detailed study of the accessibility of the OH groups of cellulose fibrils by NMR and FT-IR spectroscopy of deuterated samples combined with molecular dynamics simulations. In

the current work, the amount of accessible OH groups, i.e. cellulose accessibility, is defined by those OH groups that are exchanged to OD groups by deuteration.

The accessibility of cellulose is limited by the structure of cellulose consisting of highly ordered regions formed by hydrogen bonds. It depends on the origin of the cellulose as well as on what types of treatments have been applied. Thus, the accessibility of pulps originates from the intrinsic characteristics of the wood fibers and the various mechanical, chemical and/or physico-chemical treatments they have been subjected to. For example, the hemicellulose and acid group content of pulps as well as processing conditions, such as temperature, pH and moisture content, are known to influence the accessibility of pulps through microfibril aggregation (Fahlén and Salmén 2003; Lindström and Carlsson 1982; Maloney and Paulapuro 2000; Oksanen et al. 1997; Pönni et al. 2013, 2014a, b). In addition to microfibril aggregation, other structural characteristics, such as cellulose crystallinity, affect the accessibility (Strømme et al. 2003).

Despite the numerous techniques available for studying the accessibility of cellulose, the gravimetric determination of the OH groups exchanged to OD groups is the only method that enables direct quantification of the accessible OH groups in cellulosic materials. Dynamic vapor sorption (DVS) is an automated system employed in determining sorption rates gravimetrically with high precision mass measurement. The analysis is based on measuring the change in the mass of the sample when the vapor concentration (relative humidity, RH) of the air inside the measurement chamber is changed with a solvent of interest. The control of RH is precise and dynamic as the solvent is introduced to the chamber in a dry carrier gas, usually nitrogen, at a well-defined flow rate and temperature. When DVS is coupled with deuterium exchange, the RH of the measurement chamber is increased with D_2O vapor resulting in the exchange of the sample's accessible OH groups to OD. The DVS system allows exact quantification of the exchanged groups by monitoring the increase in the dry mass of the sample. The mass of the sample is measured with a highly sensitive microbalance of the DVS device, and the amount of exchanged groups is calculated from the difference between the dry mass of the sample before and after it has been exposed to D_2O vapor.

So far, DVS with deuterium exchange has been applied to determine the accessible OH group content mostly in wood (Beck et al. 2018; Kymäläinen et al. 2015, 2018; Popescu et al. 2014; Rautkari et al. 2013; Thybring et al. 2017), although some accessibility studies have been done to other cellulosic materials as well, e.g. bacterial cellulose (Lee et al. 2011). Thus far, only few DVS studies have been done to determine the accessibility of cellulose fibers (Borrega et al. 2018; Pönni et al. 2014b) and, to our knowledge, none for pure cellulose powders. The aim of this study was to apply DVS coupled with deuterium exchange in quantifying the amount of accessible OH groups in chemical pulps and pure cellulose. The method was applied to chemical pulps in both industrially dried and solvent exchanged states as well as to microcrystalline and amorphous, or non-ordered, cellulose powders. In addition, the equilibrium moisture contents (EMC) of cellulose samples were measured at the relative humidity of 95% without prior drying making it possible to study the EMCs of the samples in as-received state without the need of drying them before the experiment.

Experimental

Samples

The samples studied included several different kinds of pulps obtained from Finnish pulp mills as well as commercial microcrystalline cellulose powder (MCC; Avicel PH-101, ∼ 50 μm particle size, Sigma-Aldrich, Ireland) and amorphous cellulose (AC) prepared from the MCC using a modified method from Mormann and Wezstein (2009). In preparing the AC sample, 3 mol of hexamethyldisilazane (HMDS) was used per anhydroglucose unit (AGU) for the silylation and 1-ethyl-3-methylimidazolium acetate (EmimOAc) was used as the reaction medium with 10% MCC concentration. Desilylation was performed in a slightly acidic water reflux. The pulp samples were industrially dried, bleached softwood (SW) kraft and hardwood (HW) dissolving pulps as well as never-dried (ND) bleached HW kraft and dissolving pulps. Their moisture contents were 4.65%, 4.61%, 66.1% and 66.1%, respectively. All the pulps were produced from birch with the exception of the SW kraft for which the raw material was an approximately 85/15

mixture of Scots pine and Norway spruce. The accessibilities of the samples were studied in as-received state with the exception of the never-dried pulps which were predried with sequential solvent exchange followed by evaporation of the final solvent (CO_2) in its supercritical region. Sequential solvent exchange was used to minimize pore collapse and shrinkage of the cell wall. The method is described in more detail in Lovikka et al. (2016). Prior to the accessibility measurements, all industrially dried pulps as well as cellulose powders were stored in a desiccator whereas the predried ND pulps where analyzed immediately after the sequential solvent exchange.

Structural carbohydrates

The carbohydrate composition of the samples was determined according to the standard NREL/TP-510-42618 (Sluiter et al. 2008). The samples were acid-hydrolyzed to their constituent monosaccharides that were then quantified with high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 system (Thermo Fisher Scientific, Sunnyvale, USA). The carbohydrate contents were calculated according to the procedure reported by Janson (1970). The

carbohydrate contents of the samples are shown in Table 1.

DVS with deuterium exchange

The accessibility of the samples was measured with a DVS Advantage ET (elevated temperature) apparatus (Surface Measurement Systems Ltd., UK). The measuring accuracy of its microbalance is 0.1 μg. The measurement sequence consists of three steps all measured at 24 ± 0.5 °C. The samples were first dried at RH 0% with dry nitrogen gas (99.95%, Oy AGA Ab, Finland) with a flow of 200 cm^3 min^{-1} until the change in the mass of the sample was less than 0.0005% min^{-1} for 10 min. Then, the RH of the measurement chamber was raised with D_2O vapor (99.9 atom- % D, Sigma Aldrich, St. Louis, USA) and kept constant for 600 min to allow equilibrium to be reached. In the case of the AC sample the time of the rewetting stage was 2460 min. The set RH was 95%. The actual RH reached by the DVS instrument was 87 ± 0.6% measured by the optical vapor concentration detector of the instrument, and it took on the average 21 min to reach the maximum RH after it was set. To complete the measurement sequence, the sample was dried again in the same way as in the first step. Each sample was prepared and measured in triplicate and the amount of sample analyzed in each

Table 1 Characterization of the studied samples

Pulp/cellulose type	Wood source	Drying	CEL (%)	XYN (%)	GLM (%)	OH content[a] (mol/kg)	A[b] (mol/kg)	EMC$_{D2O}$ (mol/kg)	EMC (mol/kg)
Dissolving	Birch	Never dried	94	6	1	18.4	N.D.	N.D	21.0
Dissolving	Birch	CPD	94	6	1	18.4	10.3 ± 0.3	11.5 ± 0.1	12.6
Dissolving	Birch	Industrial	94	6	0	18.4	9.9 ± 0.2	9.0 ± 0.0	9.8
Kraft	Birch	Never dried	74	25	1	17.6	N.D.	N.D	19.4
Kraft	Birch	CPD	74	25	1	17.6	10.7 ± 0.4	11.2 ± 0.0	12.1
Kraft	Spruce + pine	Industrial	81	10	9	18.1	11.0 ± 0.3	9.7 ± 0.3	10.4
MCC	N.D.	N.D.	96	2	2	18.5	9.4 ± 0.4	8.4 ± 0.0	8.9
AC	N.D.	N.D.	99	0	1	18.5	11.6 ± 0.2[c]	13.6 ± 0.0	14.0

The OH group contents are calculated according to the relative amounts cellulose (CEL), xylan (XYN) and glucomannan (GLM) in each sample and the accessibilities are shown as averages of three measurements with their standard deviation

[a] Theoretical maximum OH group content based on the structural carbohydrate composition of the samples

[b] Accessible OH group content of the samples based on the DVS measurements

[c] The accessibility of the AC sample is calculated from DVS measurements with 2460 min rewetting step

experiment was 10–11 mg. Figure 1 shows an example of the DVS accessibility measurement for the industrially dried SW kraft pulp.

The accessible OH groups were quantified according to Eq. 1

$$A = \frac{m_f - m_i}{m_i * (M_D - M_H)} * 1000 \left(\text{mol kg}^{-1}\right), \qquad (1)$$

where A is the accessible OH group content in dry mass of the sample, m_i is the dry mass of the sample before exposing it to D_2O vapor (g), m_f is the dry mass of the sample after the D_2O exposure (g), M_D is the molar mass of deuterium (2.014 g mol^{-1}) and M_H is the molar mass of hydrogen (1.008 g mol^{-1}).

Equilibrium moisture content

The equilibrium moisture contents of the samples were measured with a DVS Intrinsic system (Surface Measurement Systems UK Ltd) at 25 ± 0.03 °C following the same sequence as applied in the accessibility studies omitting the initial drying step. The RH of the measurement chamber was first set to 95% with Milli-Q water (Millipore Corporation, resistivity 18.2 MΩ cm) and kept constant for 600 min. The actual RH reached by the DVS instrument was 94 ± 0.8%, and it took on the average 20 min to reach the maximum RH after it was set. After the wetting step, the samples were dried with a flow of dry nitrogen gas until the change in the masses of the samples was less than 0.0005% min^{-1} for 10 min. The moisture contents of the samples were calculated in percentage relative to the final dry mass
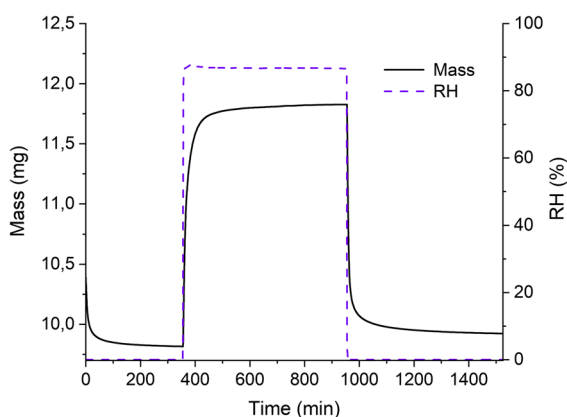

Fig. 1 Dynamic vapor sorption of industrially dried SW kraft pulp during one accessibility measurement

of the samples. The amount of sample analyzed in each experiment was 10–11 mg and each sample was prepared and measured once, which is a common practice for moisture sorption measurements. To evaluate the error in the EMC measurements, the EMCs of the samples were also calculated from the accessibility experiments after 600 min rewetting with D_2O.

Results and discussion

Accessibility of OH groups

The DVS system with deuterium exchange has been commonly used to determine the accessible OH group content in wood. In these studies, several drying-rewetting-drying cycles have commonly been applied (Kymäläinen et al. 2015; Popescu et al. 2014; Rautkari et al. 2013). Although, the most recent accessibility studies for wood have been done with only one cycle (Kymäläinen et al. 2018; Thybring et al. 2017). For determining the accessibility of the pulps and cellulose powders, only one drying-rewetting-drying cycle was applied in this work to minimize hornification, i.e. cellulose microfibril aggregation, associated with drying of the samples. The extent of hornification upon drying has previously been observed to be greater in chemical pulps compared to wood (Suchy et al. 2010a). Recently, the extent of hornification in wood has been questioned by Thybring et al. (2017). Moreover, in a study of the accessibility of birch kraft pulps, Pönni et al. (2014b) observed a decrease in the wet masses of the samples, i.e. the equilibrium moisture contents, with time during several consecutive drying-rewetting-drying cycles as well as a decrease in the time to reach the EMC at high humidity. They suggested drying induced hornification as a possible reason for these observations.

When the DVS system is employed in determining the EMCs from moisture sorption measurements or the accessibility of the OH groups in wood and cellulosic materials, the criterion for drying of the samples is typically set with a mass stability criterion so that the rate of change in sample mass (moisture content) with time is less than 0.002% min^{-1} over a 10-min time period (Hill et al. 2009; Kymäläinen et al. 2015; Pönni et al. 2014b; Popescu et al. 2014; Xie et al. 2011a, b). However, Glass et al. (2017, 2018) have recently

reported based on moisture sorption studies that this stability criterion leads to unacceptably high errors in EMC especially for wood. According to Glass et al. (2017), the moisture sorption data at short times is consistent with previous measurements, however the data at extended times exhibit slow sorption behavior which affects the final moisture content. It should be noted here that the study of Glass et al. (2017) was done with 5% MC steps which is common practice in moisture sorption studies whereas the OH accessibility in the current work is measured by raising the RH from 0 to 95%. It has been reported previously that the halftime to moisture equilibrium is inversely proportional to the swelling pressure, i.e. smaller RH change leads to longer time to reach equilibrium (Christensen 1959).

Yet, a true equilibrium is difficult to define in a DVS experiment, and as Glass et al. (2018) discuss, a reasonable approximation of equilibrium in a DVS measurement would be to apply a criterion for the change in mass over time that is similar in magnitude to the drift of the instrument, over a reasonably long time period. As a general guideline for studying the moisture sorption of lignocellulosic materials, Glass et al. (2018) suggest the mass stability criterion to be 0.0003% min^{-1} calculated over 2 h. However, currently, the most common commercial DVS instruments do not allow automatic calculation of the slope of mass change over longer times than 10 min. Glass et al. (2018) also studied the difference between the mass stability criterion of 0.0003% min^{-1} and the longest possible hold time restricted by the drift of the instrument. With this criterion, they reported the error to be 0.08% MC for the moisture absorption at RH 90–95% for holocellulose extracted from wood, 0.35% MC for moisture desorption at RH 95–90% for MCC and 0.35% MC and 0.75% MC for wood moisture absorption and desorption, respectively. They also showed that holocellulose extracted from wood and MCC exhibit faster moisture sorption kinetics than wood, and thus the error caused by a shorter drying period is smaller for them compared to wood. For MCC, they reported the error in the desorption at RH 95–90% to be 0.15–0.35% MC with different mass stability criteria ranging from 0.002% min^{-1} over a 10-min time period to 0.00005% min^{-1} over a 6-h time period. For the accessibility measurements of pulps and cellulose powders with the DVS system in the current work, the drying criterion was set

to be 0.0005% min^{-1} over a 10-min time period in order to minimize the error caused by too short drying time and yet to be able to complete a measurement in 1 day. To estimate the error in MC, the dried kraft pulp sample was also studied with the drying criterion set to 0.0001% min^{-1} over a 10 min time period (which corresponded to the drying criterion of 0.0003% min^{-1} over the time periods of 7.4 and 9.2 h for the initial and final drying, respectively). The error in the moisture contents after the initial and the final drying between the measurements with the drying criterion of 0.0005% min^{-1} over 10 min and 0.0001% min^{-1} over 10 min are 0.11% MC and 0.22% MC, respectively. The time that it takes to complete one accessibility measurement for the dried kraft sample with the drying criteria of 0.0005 and 0.0001% min^{-1} are 26.1 and 55.2 h, respectively.

Moreover, the previous drying history is known to affect the sorption behavior as well as the accessibility of wood and other cellulosic materials (Christensen and Hergt 1969; Thybring et al. 2017). This is an inherent factor of the accessibility measurements as the samples need to be dried before and after they are wetted. Thus, the initial conditions for the first and the second drying are not the same. To evaluate the effect of this on the moisture removal, the DVS sequence was applied to the dried kraft pulp rewetting the sample with water instead of D_2O. The difference in the dry masses of the sample before and after rewetting was 0.014% corresponding to an error of 0.14 mol kg^{-1} in accessibility.

The RH chosen for the rewetting of the samples was 95% as it should be enough to result in complete exchange of the accessible OH groups to OD groups as it is well over RH 60% above which no further deuteration occurs (Taniguchi et al. 1978). As the length of the rewetting step, 600 min was chosen based on a test measurement in which birch kraft pulp was analyzed with a rewetting step which lasted for 10,000 min (1 week). According to the experiment, ca. 98% of the OH groups are exchanged to OD groups during the first 600 min of D_2O exposure (Fig. 2). During the experiments, the AC sample showed different behavior compared to the pulps and the MCC. It took more time to reach equilibrium in both the drying and the rewetting steps for the AC sample compared to the other samples. Thus, it was decided to further study the effect of the duration of the rewetting step of the amorphous cellulose. The accessibility of
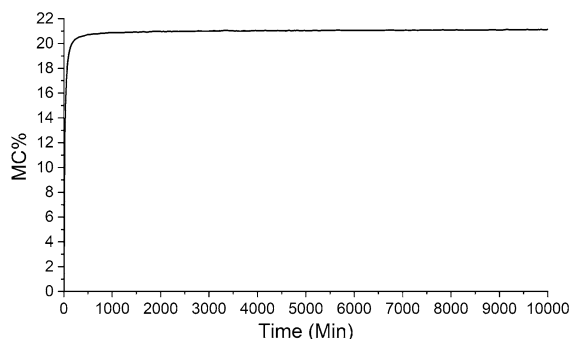
Fig. 2 Development of the moisture content during the rewetting step of a test run in which birch kraft pulp was exposed to D_2O vapor for 10 000 min (1 week)

the AC sample was studied rewetting it for 600 min, 1110 min and 2460 min. It was found that 600 min rewetting results in an error of 4% in the accessibility compared to 2460 min rewetting. The error with 1110 min rewetting compared to 2460 min rewetting was 0.3% which is within the standard deviation of the accessibility measurements. Nevertheless, 2460 min was chosen as the duration of the rewetting for the AC sample to ensure complete exchange of the accessible OH groups.

Table 1 shows the average accessibility values and their standard deviations measured for each sample. The accessibilities of the studied pulps are between 9.9 and 11.0 mol kg^{-1}, which is 54–61% of the theoretical maximum accessible OH group content (total OH group content) in these pulps. The theoretical maximum accessibilities are calculated from the relative amounts of cellulose, xylan and glucomannan in each sample when the theoretical maximum OH group contents in cellulose, xylan and glucomannan are 18.5 mol kg^{-1}, 15.1 mol kg^{-1} and 18.5 mol kg^{-1}, respectively. The accessibilities of the MCC and AC samples are 9.4 mol kg^{-1} (51%) and 11.6 mol kg^{-1} (63%), respectively. The exchange of OH to OD is far from being complete in the case of all the studied samples. This result is in agreement with the theory as well as with previously reported studies. When water is brought into contact with cellulose, water molecules diffuse into the non-crystalline domains in the structure swelling the structure and forming new hydrogen bonds (Hofstetter et al. 2006). When cellulose is exposed to D_2O vapor, the accessible OH groups are exchanged to OD. The exchange is almost complete in the non-crystalline regions but in the crystalline

regions, only OH groups located at the surfaces of the crystallites or at imperfections are exchanged (Frilette et al. 1948; Jeffries 1963). In a recent study, Borrega et al. (2018) reported the OH accessibility of bleached birch kraft pulp to be 11.2 ± 0.4 mol kg^{-1} which is very close to the accessibilities of the bleached kraft pulps determined in the current study. In a study of the accessibility of spruce pulp with dynamic FT-IR spectroscopy coupled with deuterium exchange, Hofstetter et al. (2006) reported that deuteration only occurs in more or less non-load-carrying parts of cellulose, i.e. only the OH groups on the surfaces of cellulose fibrils are accessible to moisture. Frilette et al. (1948) reported the exchange to be close to 60% for cotton. Based on NMR and FT-IR spectroscopy of deuterated MCC, Lindh et al. found that only two of the three available OH groups on the surface of cellulose fibrils exchange hydrogen with the surrounding water molecules. The finding was verified and explained with molecular dynamics simulations which demonstrated that the OH(2) and OH(6) groups of the constituting glucose units act as hydrogen-bond donors to water whereas the OH(3) groups behave exclusively as hydrogen-bond acceptors from water donating hydrogen to their intra-chain neighbors, O(5) hence being unreactive to hydrogen exchange with water. Therefore, the ability of the OH group to donate its hydrogen to a water molecule in their connecting hydrogen bond is a prerequisite for hydrogen exchange (Lindh et al. 2016).

Comparing the previously reported accessibilities of non-crystalline cellulose shows that there is considerable variation between the observed values. Based on a FT-IR spectroscopy study of a cast non-crystalline cellulose film, Hishikawa et al. (1999) observed that ca. 87% of the OH groups was exchanged to OD during deuteration in saturated D_2O vapor. In contrast, Lee et al. (2011) found the accessible OH group content in bacterial cellulose (BC) films to be 1.24 per AGU, (i.e. 41%), measured with the DVS. In the current work, 63% of the theoretical maximum for the AC sample was exchanged indicating that not all hydrogens in the OH groups are exchanged to OD. The somewhat smaller accessibility reported by Lee et al. compared to the accessibilities observed in this study may be attributed to the structural differences between BC and plant-derived cellulose, such as the degree of crystallinity, crystallite size, degree of polymerization and

hemicellulose content. In addition, the sample preparation method (freeze-drying in the case of the BC films) has an effect on the accessibility. Nevertheless, the fact that the accessibility of the non-crystalline cellulose is far from the theoretical maximum accessibility suggests that the sample is not completely amorphous, or without a structure, but instead has a partly organized (paracrystalline) structure. The model for the amorphous regions in cellulose being partly interacted by intermolecular hydrogen bonds has been proposed by Kondo and Sawatari (1996) and evidence of this type of structure has been reported by Hishikawa et al. (1999).

Comparing the accessibilities in Table 1 against each other brings out some interesting features of the samples. Drying decreases the accessibility of HW dissolving pulp by 0.4 mol kg^{-1}. This decrease in accessibility is caused by hornification, which refers to stiffening of the polymer structure upon drying through an increase of intermolecular hydrogen bonding (Minor 1994) or intramolecular esterification (Fernandez Diniz et al. 2004). It has been suggested that hornification is related to irreversible collapse of pores in the cell wall, microfibril aggregation and loss of individual microfibrils at the fiber wall surface (Billosta et al. 2006; Oksanen et al. 1997; Pönni et al. 2012; Stone and Scallan 1968) thus decreasing the swelling capability of the fibers and cutting down the fiber surfaces accessible to water. Lower OH accessibility for dried cellulose microfibrils compared to never-dried microfibrils has also been reported previously, e.g. in a Raman spectroscopic study by Atalla et al. (2014). Moreover, the accessibilities of the kraft pulps are higher than the accessibilities of the dissolving pulps (Table 1). The higher accessibilities of the kraft pulps may be related to the higher hemicellulose contents of the pulps as well as the harsher conditions in the production of the dissolving pulp. The pulping and bleaching treatments remove most of the hemicellulose and lignin from the wood fibers resulting in broadening of the pores between fibril aggregates in the fiber wall (Fahlén and Salmén 2005). On the other hand, hemicelluloses located at the interfibrillar spaces of fiber walls are reported to hinder the hornification of the kraft pulps as the removal of hemicelluloses increases contact between cellulose fibrils and favors the formation of aggregates between the fibrils especially during drying (Billosta et al. 2006; Duchesne et al. 2001; Hult et al. 2001;

Oksanen et al. 1997; Pönni et al. 2012). Comparing the results shown in Table 1 to the accessibilities of the alkaline treated birch kraft pulps published by Pönni et al. (2014b), the alkaline treatment is shown to increase the accessibility of pulps. However, due to differences in the experimental conditions (i.e. extent of drying, number of DVS cycles and duration of D_2O exposure) the results are not directly comparable.

The kinetics of the exchange have been monitored previously with FT-IR spectroscopy of deuterated samples (Hishikawa et al. 1999; Hofstetter et al. 2006; Jeffries 1963). According to the studies by Hofstetter et al. and Jeffries, a two-stage deuteration process has been observed. It is postulated that in the first, very short stage, hydrogens of the OH groups in the non-crystalline domains of cellulose are exchanged. The duration of this stage depends on several factors, such as the type and thickness of the sample, the mode of deuteration (i.e. vapor or liquid) and the environmental conditions including the RH and temperature. In the second, longer stage, the OH groups in the crystalline regions, particularly those ones at the surfaces of the crystallites or at irregularities are also affected. This stage is much longer and the exchange can take several hours or even days. The inside of the crystalline regions is inaccessible to deuterium exchange (Hofstetter et al. 2006; Jeffries 1963). Hishikawa et al. (1999) found three different domains for non-crystalline cellulose films and reported the exchange of D_2O to be almost completed in 10 h. Based on the DVS measurements of the current work, 10 h was observed to be enough to reach equilibrium during the exposure to D_2O vapor for pulps and MCC. The more detailed kinetics of the stages of the exchange cannot be confirmed based on this study as the weight increase in the DVS curves (Fig. 1) show two overlapping processes, i.e. moisture sorption and deuterium-hydrogen exchange.

Equilibrium moisture content

In the absence of liquid water, the moisture content of wood at a fixed temperature is dependent on the RH of the environment as well as the history of the sample (Glass et al. 2017). This is true also for pulps. The EMCs of the samples were measured in the current work without a pre-drying step in order to characterize the samples in as received-state without the effect of drying the samples beforehand. The EMCs of the

samples after 600 min at RH 95% are shown in Table 1. There is considerable variance between the EMCs of the samples. The EMCs of the never-dried dissolving pulp is 21.0 mol kg^{-1} (38% in EMC % of dry mass) whereas the EMC of the MCC is 8.9 mol kg^{-1} (16% in EMC % of dry mass). The errors in the EMCs were evaluated based on EMCs calculated from the accessibility measurements after 600 min rewetting with D$_2$O (EMC$_{D2O}$). The errors between the parallel samples were very small. The highest error was observed for the industrially dried SW kraft for which it was 0.3 mol kg^{-1}.

The moisture uptake of cellulosic materials depends on the chemical and morphological structures of the materials. In the case of natural cellulose fibers, water can be adsorbed onto the surfaces of microfibrils and into the nanopores in the inter-microfibrillar regions (Xie et al. 2011b). When water is adsorbed to a cellulosic material, the sorbed water exerts a swelling pressure against the cell wall matrix resulting in an increase in the volume of the material. The extent of water sorption stems from the balance between the swelling pressure and the resistance of the matrix to deformation (Rautkari et al. 2013; Xie et al. 2011a, b). An increase in the crystallinity of cellulose contributes to the reduction of EMC by hindering the access of water molecules into the bulk material. In a previous study of cellulose powders with varying crystallinity, Strømme et al. (2003) found that for highly crystalline cellulose materials, the interactions between cellulose and water take place mainly on the cellulose fibril surfaces that are adjacent to open pores causing no significant swelling of the material, while for less ordered celluloses the interactions take place inside the bulk material and the water uptake causes the pore volume to swell between 1 and 2 orders in magnitude. The effect of crystallinity can be clearly seen when comparing the EMCs of the AC and the MCC samples.

Similar values have been reported previously for the EMC of cellulose measured with the DVS apparatus. The EMC of the MCC sample measured here is close to the one measured by Xie et al. (2011b) for MCC at RH 95%, which was 16.9%. The small difference between these EMCs may be due to the fact that the MCCs are from different sources and they have undergone different chemical and mechanical pretreatments and thus e.g. the amount and the sizes of aggregates may vary between these samples. Xie et al. (2011a, b) have also measured the EMCs at RH 95%

for cellulose fibers, such as α-cellulose, cotton linter and filter paper with the reported EMCs of 20.6; 14.4 and 16.7%, respectively. The low EMC of the cotton linter has been attributed to a higher degree of crystallinity and a stiffer interfibrillar matrix while the α-cellulose has a lower degree of crystallinity as compared to the other cellulose materials and the crystallographic structure of cellulose II. (Xie et al. 2011b) The filter paper, and the pulps studied in the current work, comprise of a native cell wall multilayer network structure including crystalline and less ordered regions. The EMC of the filter paper measured by Xie et al. is close to the EMC of the industrially dried pulps measured in the current work.

The effect of hornification can be observed when comparing the EMCs of the industrially dried HW dissolving pulp and the rest of the HW dissolving pulps. According to these results, the EMC of dissolving pulp is reduced by 11.2 mol kg^{-1} (20%-points in EMC % of dry mass) by industrial drying compared to the never dried state. According to the results shown in Table 1, also the critical point drying has an effect on the EMC. This drying procedure decreases the EMC of the HW dissolving pulp by 8.4 mol kg^{-1} (15%-points) and the HW kraft pulp by 7.3 mol kg^{-1} (13%-points). In addition, the effect of drying can be seen when comparing the EMCs calculated from the accessibility measurements where the samples have undergone the initial drying step before wetting with the EMCs without prior drying. The EMC$_{D2O}$ values are smaller than the EMC values for each sample.

Figure 3 illustrates the ratio between the accessibilities and the EMCs of the studied samples. It seems that the accessible OH group content is close to the EMC in mol kg^{-1}, i.e. there is on the average approximately one water molecule per accessible OH group. There is, however, some scatter in the data and, depending on the sample, the accessibilities of some samples are slightly higher than the EMCs whereas for some samples it is the opposite. It has previously been reported that solely the accessible OH group content is not enough to describe the moisture uptake in wood (Rautkari et al. 2013). It has been suggested that at high RHs water adsorbs to the active sites created by the OH groups preferentially adsorbing to already hydrogen bonded molecules forming clusters and water bridges (Kymäläinen et al. 2015; Müller et al. 1996). It should also be noted that the
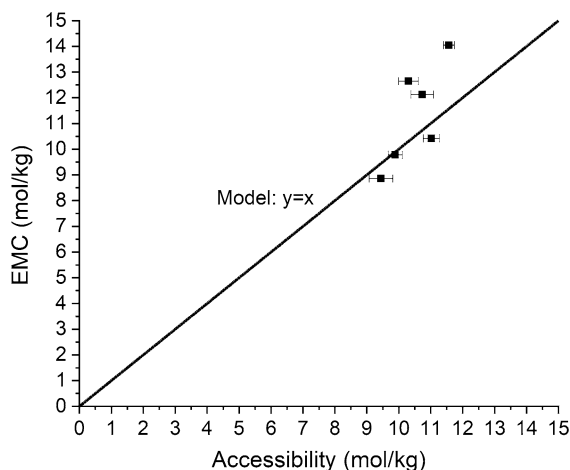
Fig. 3 The ratio between the accessibilities and equilibrium moisture contents of the studied samples with a reference line of y = x

accessibilities of the samples have been determined with initial drying of the samples whereas the EMCs of the samples have been determined without it. Although the drying was done at mild conditions (room temperature), it is possible that it causes structural changes, e.g. pore closure and microfibril aggregation, in the samples. These are possible explanations for the slightly larger EMC values compared to the accessibilities seen in the current work but it does not explain why the opposite is observed for some samples. The reason behind the small scatter in the ratios of the accessibilities to the EMCs of different pulps and pure cellulose samples remains to be discovered in the future work.

Conclusions

In this work, the amount of accessible OH groups in several different types of chemical pulps and pure cellulose samples was quantified based on DVS with deuterium exchange. The advantages of coupling DVS with deuterium exchange include minimal sample preparation, mild measurement conditions, utilization of a fully automated system and the relatively short duration of the measurements. However, the analysis of wet samples is not possible with the method as the calculation of the accessible OH group content is

based on comparing the dry mass of the sample before and after exposing the sample to D_2O vapor. Thus, in addition to the OH accessibilities, the EMCs of the samples were measured with the same DVS sequence omitting the initial drying step. This procedure enables the assessment of the EMC of the samples in as-received state without the effect of prior drying. It was found that the accessibilities of the pulps vary between 54 and 61% of their theoretical maximum accessibilities based on their relative cellulose and hemicellulose contents. The accessibilities of the MCC and the AC samples were found to be 51 and 63% of their theoretical maximum, respectively. This result suggests that instead of being completely amorphous, the AC sample has a partly organized (paracrystalline) structure. When the EMCs were compared against the accessible OH group contents of the samples, it was found that they correlated and that their ratio was, in fact, close to one. Some scatter was observed in the ratio between the different cellulosic samples studied in this work. For some of the samples, the ratio of the accessible OH group content to the EMC was slightly more than one and for some samples it was slightly less than one. The reason for the different behavior of the samples remains to be the task of future work.

Compliance with ethical standards

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