NMR Imaging and Differential Scanning Calorimetry Study on Drying of Pine, Birch, and Reed Pulps and Their Mixtures

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ABSTRACT: Drying, water fractions, and water distribution were investigated for pine, birch, and reed pulps and pine–birch, pine–reed, and pine–birch–reed pulp mixtures. Gravimetrically determined drying times showed that the drying rates of the pulps decreased at two to four inflection points. Characterizations of the dried pulps by differential scanning calorimetry (DSC) showed a faster removal of free water than freezing and nonfreezing bound waters; all decreased simultaneously, however. DSC also revealed the critical water contents at which the free water and freezing bound water disappeared. The gravimetrically determined inflection points of the drying curves corresponded with the critical points determined by DSC. NMR line widths and images produced by ¹H-NMR imaging revealed the nature and regions of the pulp drying. The constant growth rate of the NMR line widths with decreasing water content appeared to change at two inflection points, which fell approximately in the same water content regions as the inflection points of the drying curves. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 937–945, 2006

Key words: differential scanning calorimetry; NMR; NMR imaging; pulp drying

INTRODUCTION

In addition to wood fibers, cotton, straw, cane, grass, hemp, and other plant fibers are used as raw materials for papermaking.[1] Before we can better utilize alternative plant fibers in papermaking, we need to have a thorough understanding of the microstructure and properties of the pulps.

The structure and flow behavior of cellulose are influenced by the presence of water, and thus the water content of cellulose in papermaking and the water content in paper play an essential role.[2] Drying of the paper web is also important. Removal of water from the paper web and the subsequent elimination of water vapor are energy-intensive operations.[1] During drying, the paper web tends to shrink and the mechanical properties of the paper are affected.[3]

Differential scanning calorimetry (DSC) has been found to be suitable for measuring different water fractions during pulp drying.[4–7] It has also been used to study the sorption of water in cellulose[8–13] and measure the pore size distributions of pulp fibers.[14–17]

NMR imaging is a powerful research technique in materials science[18,19] and it is ideally suited for observation of the drying of paper pulps. Water protons in pulp give strong and easily observable NMR signals that can be utilized to produce two- or three-dimensional NMR images. ¹H-NMR has been used to study water–cellulose interactions or the relation between water content and the line widths and shapes of NMR signals[2] or the relaxation times.[20] In addition, water distribution in cellulose fibers,[21–23] the flow of cellulose suspensions,[24–32] water transport processes in cellulosic cardboards,[33] and moisture distribution inside a pulp sheet[34,35] have been studied by ¹H-NMR imaging.

Our aim in this study was to compare the drying properties of pine, birch, and reed pulps and their pulp mixtures. We studied the drying of the pulps gravimetrically and determined the nature and amounts of water fractions during the drying process by DSC. We also investigated the drying of these paper pulps by NMR imaging by following the changes in the line widths and two-dimensional images.

EXPERIMENTAL

Pulp samples

The samples were pine, birch, and reed (canary grass) pulps and pine–birch, pine–reed, and pine–birch–

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TABLE I
Description of Pulp Samples

Pulp	Ave. fiber length (mm)	Orig. dry content (wt %)
Pine	2.06	7.3
Birch	1.2–1.3[a]	6.6
Reed	0.44	9.1
Pine/birch 50/50% (w/w)	1.29	8.3
Pine/reed 50/50% (w/w)	1.19	9.9
Pine/birch/reed 56/22/22% (w/w/w)	1.19	10.0

[a] Literature value.[34,35]

reed pulp mixtures, all produced by chemical sulfate pulping (Table I).

Fiber length measurement

The fiber lengths (Table I) were measured according to TAPPI standard T271 with a KAJAANI FSA on-line fiber length analyzer. The KAJAANI FSA-200 method is an optical method based on the ability of the fibers to change the degree of light polarization when they pass through a narrow capillary tube. The resolution is 50 μm over the entire measurement range, and the analyzer divides fibers into 144 length classes.[36,37]

Determination of water contents

The total water contents of the original pulps (Table I) were determined by weighing the pulp samples before and after oven drying (105°C, 24 h) to a constant weight. Alternatively, a Mettler Toledo LP 16 IR dryer was used to determine the total water content where the pulp sample was dried at 105°C until the weight loss was less than 2 mg during 120 s.

The water contents of the pulps were measured gravimetrically as a function of the drying time. These drying measurements were carried out using the drying setup of the NMR imaging probe, so that knowledge of the drying rates could be utilized in the actual NMR imaging. A pulp sample was wrapped in cotton gauze and hung with the aid of a cotton string inside the NMR tube, which was then placed inside the NMR imaging probe. The bottom of the NMR tube was cut off so that the sample could be dried with the aid of flowing air. Flow of compressed air through the sample and removal of the released moisture were ensured by punching small holes in the plastic plug of the NMR tube. The drying conditions were exactly the same in the final and actual NMR imaging: room temperature and a flow rate of dry compressed air of 100 L/h.

Drying curves were fitted with the aid of Curve Expert 1.3 software, and inflection points were determined using Origin 6.0 software.

DSC

DSC measurements were made with a Mettler Toledo DSC 821^e instrument. Before the measurements, the water contents of the pulp samples (pine, birch, reed, and three mixtures) were adjusted by drying them to five different moisture contents: 68–73, 45–52, 35–42, 30–35, and 22–27 wt %. After reaching the target moisture content, the pulp samples (weight = 3–10 mg) were sealed in standard 40-μL aluminum capsules and equilibrated at +4°C for at least 24 h. In the DSC measurement, the sample was quickly frozen to −30°C and held for 4 min. After attaining this isothermic condition, the sample was heated to 15°C at a rate of 3°C/min. Thereafter the sample was frozen to −70°C at a rate of −5°C/min. After this cooling–heating–recooling cycle, the sealed capsule containing the pulp sample was reweighed to ensure that no water had evaporated. The capsule was carefully pierced and the pulp sample was dried at 105°C for 24 h. The dried pulp in the capsule was cooled in a desiccator and reweighed in order to obtain the accurate dry weight of the sample for the calculation of the moisture ratio (MR) (g H_2O/g dry pulp) of the original DSC sample.

NMR imaging

NMR imaging measurements were performed on a Bruker AMX-400 MHz spectrometer equipped with a 9.4-T vertical bore superconducting magnet and a microimaging accessory. The proton signal was picked up with a 10-mm diameter Helmholtz coil. Measurements were carried out with a spin-echo two-dimensional pulse sequence with a spin-echo time of 8.32 ms and a repetition time of 1000 ms. The read gradient varied from 18.07 to 23.49 G/cm and the slice gradient was 11.75 G/cm. The gradient in the phase dimension was from 14.58 to 46.08 G/cm. The pixel resolution ranged between 39.1 and 50.8 μm. The slice thickness was 500 μm and the matrix contained 256 × 256 data points.

As described above, the wet pulp sample was enclosed in cotton gauze and hung in a bottomless NMR tube for NMR imaging. The sample was dried to the appropriate water content in the imaging probe, with the dry compressed air flowing at a rate of 100 L/h. To ensure an accurate measurement, the dry compressed air flow was shut off during the image acquisition for 4 min and 23 s. A spectrum, a profile, and a two-dimensional image were acquired from the middle of the sample in the direction of the magnetic tube (zxy orientation in NMR imaging), which was also the
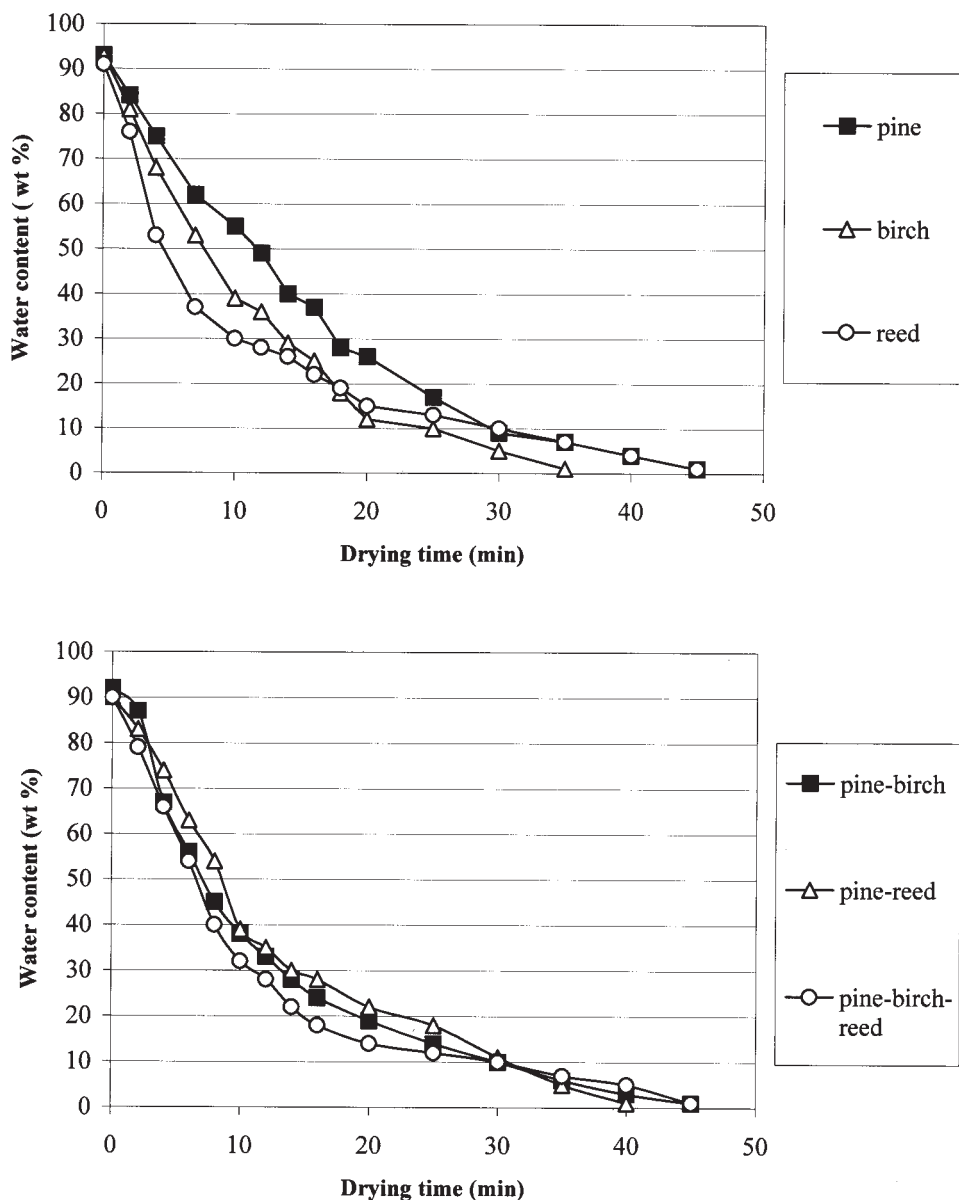
Figure 1   The water content of pure pulps and pulp mixtures as a function of the drying time as determined gravimetrically.

direction of the NMR tube and the air flow. The measurement was done at eight moisture levels down to a water content of 30 wt %, which was the limit for obtaining accurate images.

RESULTS AND DISCUSSION

Drying of pulps

The pulp drying was investigated with the use of dry compressed air in an experimental setup similar to the one employed in the NMR imaging. At the start of the drying, the pulps had water content of 90–93 wt % (i.e., MR = 9.0–13.3 g water/g dry pulp). With one exception, the water contents decreased relatively fast down to a first inflection point of the drying curve at

a water content of 56–60 wt % (MR = 1.27–1.50; Fig. 1, Table II). The exception was the reed pulp, which dried fast and uniformly down to a first inflection point at 28.0 wt %. The second inflection point of the pulp drying curves, except for the reed and pine–birch–reed pulps, appeared in the region of 35–39 wt % (MR = 0.54–0.64).

The drying rate of the pulps, with the exception of the pine–birch pulp, decreased once again when the water content fell below 26–30 wt % (MR = 0.35–0.43). A final inflection point at about 20 wt % water content (MR = 0.25) was found for the reed and pine–reed pulps.

Short-fibered nonwood pulps have been found in drainage tests to resist water removal as a result of the

TABLE II
Inflection Points of Curves of Water Content Versus Drying Time Determined Gravimetrically, NMR Line Widths Versus Water Content, and Critical Points of Water Fraction Curves Determined by DSC

	Inflection points of drying determined gravimetrically (total water content, wt %)			
	1	2	3	4
Pine	57.0	38.6	26.0	NF
Birch	57.9	37.5	26.9	NF
Reed	NF	NF	28.0	20.5
Pine–birch	56.0	35.5	NF	NF
Pine–reed	59.0	35.0	28.0	19.5
Pine–birch–reed	60.1	NF	30.0	NF

	Inflection points of NMR line widths (total water content, wt %)		Water fractions by DSC (total water content, wt %)	
	1	2	1cp	2cp
Pine	62	41	30.1	18.0
Birch	68	41	31.0	18.2
Reed	62	38	31.9	17.4
Pine–birch	67	45	31.0	18.9
Pine–reed	61	39	30.9	—
Pine–birch–reed	66	37	32.0	—

NF, Not found; (—) Could not be exactly extrapolated.

large surface area, high swellability, and large amount of fines.[38,39] In our study, the drying of the reed pulp to 30 wt % moisture (MR = 0.43) was faster than the drying of the pine and birch pulps and the pulp mixtures. However, the drying time of the reed pulp to a water content of 10 wt % and lower was as long as for the pine pulp and the pulp mixtures and longer than the drying time of the pure birch pulp (Fig. 1).

The pulp mixtures contained pine, birch, and reed in known ratios. Although the mixture of the three pulps dried more effectively down to a water content of 10 wt %, the residual moisture was tightly bound and the total drying time was as long as for the pine–birch pulp and 5 min longer than for the pine–reed pulp (Fig. 1).

Water fractions of drying pulp

The main water fractions of the pulps [bulk or free water (FW), freezing bound water (FBW), and non-freezing (bound) water (NFW)] were determined by DSC.[4–17] FW occurs in large pores (macropores) and comprises the interfiber FW in pores between fibers and intrafiber FW in cell cavities (lumens) of fibers. These macropores of chemical pulps are formed because of the dissolving of lignin and hemicellulose in the cell walls. The total amount of the inter- and intrafiber bulk waters can be determined as FW by DSC, but the two types of water cannot be differentiated because of their similar thermodynamic properties. Bound water appears as FBW and NFW. FBW in micropores of the fiber wall has a depressed melting temperature.[3–9,16,40] NFW is hydrogen bonded to the

hydroxylic and carboxylic acid groups in the micropores of fibers[40] and it shows no DSC signal down to −170°C.[16] However, the amount of NFW can be calculated.[3–9,16,40]

In our study, the FBW and FW fractions of the pulps were quantified from the DSC melting curves[5,6]:

$$\text{water fraction (g water/g dry pulp)} = \frac{\Delta H_{\text{DSC signal}}}{H_f \cdot W_{\text{dry}}}$$

(1)

where ΔH is the energy of the melting signal, H_f is the heat of fusion of water (334 J/g), and W_{dry} is the dry content of the pulp sample. FBW gave an endotherm at a temperature 0.1–3.2°C lower than that given by FW. Quantification of FBW and FW had to be done carefully, because the melting peaks partially overlapped.

NFW can be calculated by subtracting the total freezing water (FW + FBW) from the MR (g H_2O/g dry pulp): NFW = MR − (FW + FBW). The sum of NFW and FBW is called the total bound water (TBW). The distributions of the water fractions of the pine, birch, and reed pulps at different MRs can be seen in Figure 2.

In all cases, FW was removed from the pulps faster than the bound waters FBW and NFW, which nevertheless decreased from the start of drying. Usually, two significant points, a first critical point (1cp) and a second critical point (2cp), appear in graphs where different water fractions are presented according to moisture content.[3,4,6,16] At the 1cp the FW has totally
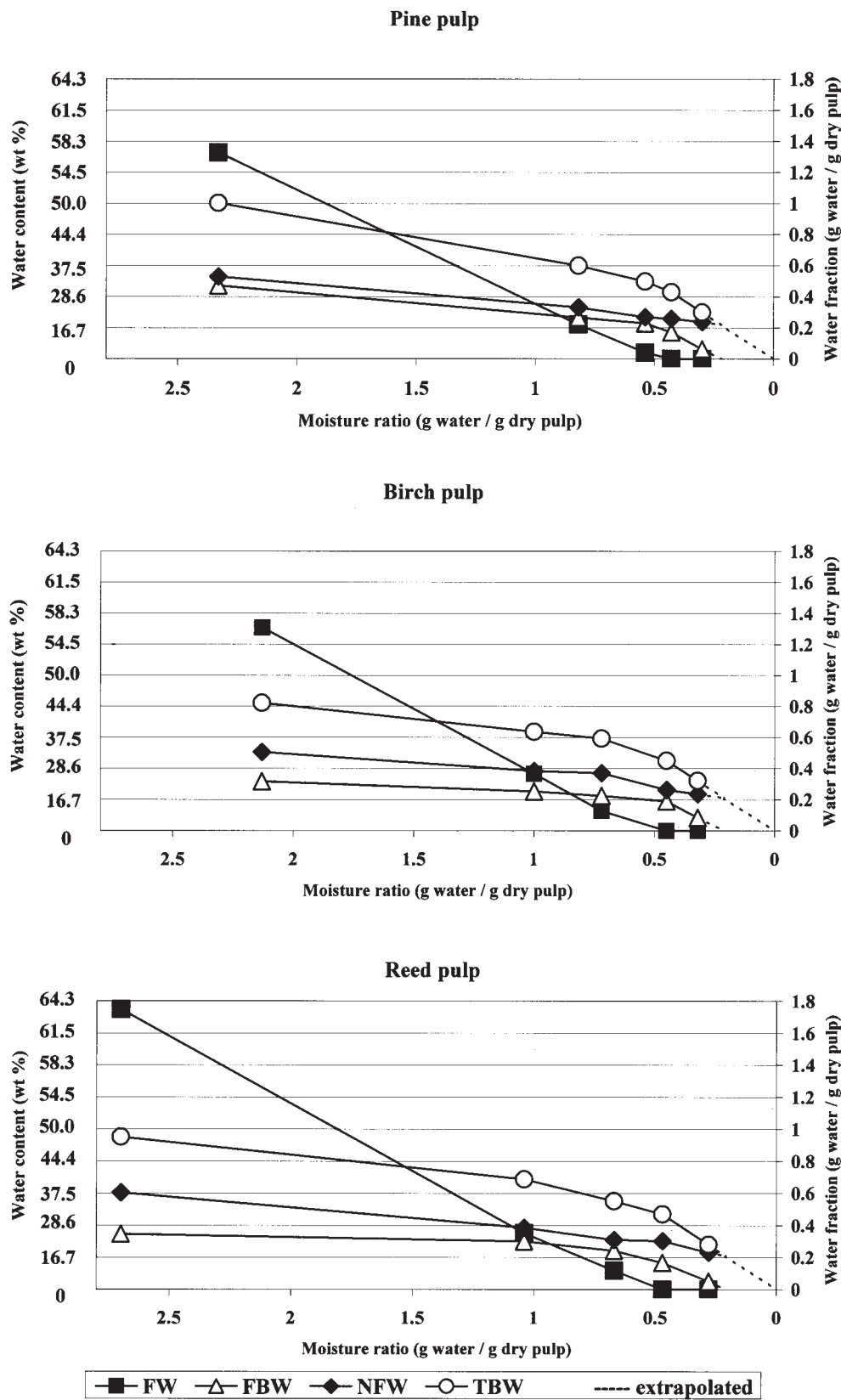
Figure 2 Water fractions of drying pine, birch, and reed pulps measured by DSC: free water (FW), freezing bound water (FBW), nonfreezing bound water (NFW), and total bound water (TBW) as a function of the moisture ratio.

TABLE III
Water Fractions of Drying Pulps Measured by DSC

Pulp	MR (g water/g dry pulp)	FW (g water/g dry pulp)	FBW (g water/g dry pulp)	NFW (g water/g dry pulp)	TBW (g water/g dry pulp)
Pine	1.00	0.35	0.30	0.35	0.65
Birch	1.00	0.37	0.25	0.38	0.63
Reed	1.00	0.33	0.29	0.38	0.67
Pine–birch	1.00	0.40	0.30	0.30	0.60
Pine–reed	1.00	0.38	0.30	0.32	0.62
Pine–birch–reed	1.00	0.44	0.26	0.30	0.56
Pine	0.45	0.00	0.19	0.26	0.45
Birch	0.45	0.00	0.19	0.26	0.45
Reed	0.45	0.00	0.16	0.29	0.45
Pine–birch	0.45	0.00	0.27	0.18	0.45
Pine–reed	0.45	0.00	0.22	0.23	0.45
Pine–birch–reed	0.45	0.06	0.17	0.22	0.39

MR, moisture ratio; FW, free water; FBW, freezing bound water; NFW, nonfreezing bound water; TBW, total bound water.

evaporated, and at the 2cp the FBW has disappeared and TBW consists only of NFW.

The DSC endotherm of the FW disappeared when the MR reached 0.43–0.47 (30–32 wt % water). This 1cp obtained with the DSC measurements was more or less consistent with the results of the drying experiments, in which the drying rates of the pulps decreased significantly at water contents of 26–30 wt % (MR = 0.35–0.43). In contrast, the first critical point determined by DSC by Maloney et al.[4,16] for unbleached softwood and never dried kraft pulp was 0.71. The positions of the critical points are known to depend on the crystallinity and swelling properties of the pulp.[4,6,16]

According to the literature,[3,4,6,16] the second critical point appears when FBW is no longer present in a pulp. In our study, this extrapolated point appeared between 17 and 19 wt % (MR = 0.20–0.23). The inflection points in the drying curves of reed and pine–reed pulps at 20 wt % water content (MR = 0.25) probably correspond to this 2cp as well. Correspondingly, for their never dried kraft pulp, Maloney et al.[4] determined a 2cp value of 0.24 by DSC.

Some differences were found in the proportions of the water fractions of the pulps (Table III). At the MR of 1.0 (50 wt % of water), the pure pulps were found to contain minor FW fractions and more NFW and TBW than the pulp mixtures. The reed pulp had the highest (0.67 g water/g dry pulp) and pine–birch–reed pulp the lowest (0.56) content of TBW at the MR of 1.0. Below the MR of 0.45 (water content of 31 wt %) the FW fraction disappeared and there were no significant differences in the TBW contents of the pulps. However, the NFW fractions of TBW were higher for the pure pulps than the pulp mixtures.

NMR imaging of pulps

Drying of the six chemical pulps was followed and visualized with NMR signals and images collected at different stages of drying down to a water content of about 30 wt % (MR = 0.43).

The line width of the NMR signal is defined as the full width of a Lorentzian line at half-maximum, $\Delta \nu_{1/2} = 1/(\pi T_2)$.[19,41,42] The T_2 times of waterlike samples range from several hundred milliseconds to seconds, which results in a narrow signal line width. The line width of biological samples typically reaches a value of 100 Hz, which is a T_2 value of about 3 ms.[42]

In our study, the line widths of the NMR signals of the original pulps containing 90–93 wt % water ranged between 117 and 255 Hz. The narrowest signal (117 Hz) of these very wet pulps was for pine. The short-fibered birch (Fig. 3) and reed pulps with the same water content gave signals of 177 and 215 Hz, respectively, and the pulp mixtures gave values of 156–255 Hz.

The drying stage of the pulps can be conveniently followed with the aid of the line widths, as shown for birch pulp in Figure 3. The drying of the pulps, which is the decrease in water content and in proton concentration, affected the acquired signal line widths of both the pure pulps and pulp mixtures from the start; and the narrowest lines and highest intensities correlated with the highest water content. The constant growth rate of the NMR line widths as a function of the decreasing water content appears to have changed at two inflection points (Table II, 61–68 wt %, i.e., MR = 1.56–2.12; and 37–45 wt %, i.e., MR = 0.59–0.82), which were partially in the same regions as the first two inflection points in the drying curves. From the original line width of the wet pulp to the first inflection point, the line width value as a function of decreasing water content increased most slowly for the reed-containing pulps. After the first inflection point, the growth rates of the line widths with decreasing water content were not noticeably different for the six pulps. After drying of the pulps down to a water content of 30–40 wt %, the line widths increased to
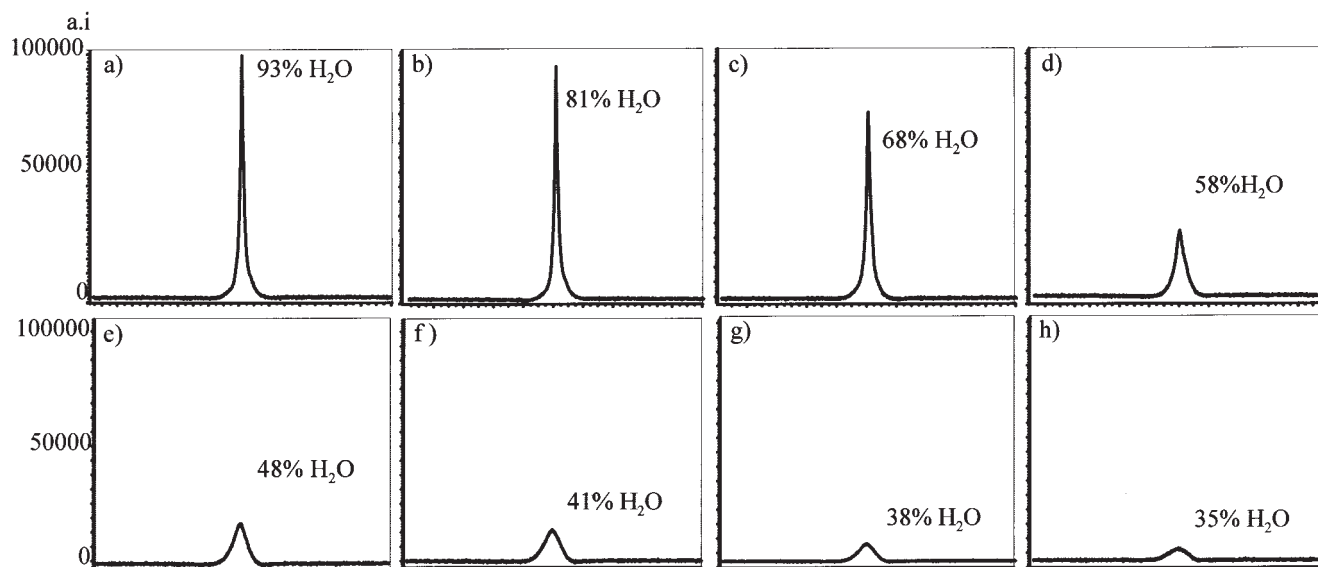
Figure 3 The NMR signal intensity and shape in response to the water content of birch pulp at drying times of (a) 0, (b) 1, (c) 3, (d) 7, (e) 9, (f) 10, (g) 14, and (h) 16 min; a.i., absolute intensity.

values of 1600–1690 Hz, with no appreciable differences among the pulps.

Drying of the pulps was also followed by recording two-dimensional NMR images (see Fig. 4 for birch pulp). The regions of the NMR sample in which the pulp drying began and where the residual water protons remained could be deduced from the images. The gray scale in Figure 4 describes the NMR signal intensity of the mobile protons: the brighter the image pixels are, the higher the proton concentration in this region.

In the case of the wet samples (water content = 90–93 wt %,), water distribution seemed to be fairly uniform and closely similar in the six pulps. Although water evaporated from the pulps at different rates during drying, it evaporated from similar regions. Residual detectable water seemed to be in pointlike proton-rich regions of the samples.

CONCLUSIONS

Of the six pulps studied (pine, birch, reed, pine–birch, pine–reed, pine–birch–reed), drying down to the 30 wt % moisture level was fastest for the reed pulp. The shortest drying time overall, with drying to 10 wt % water content and below, was recorded for the birch pulp.

The amounts of FW, FBW, and NFW in pulps during drying were determined by DSC. FW was removed faster than the TBW (FBW and NFW), which, however, decreased simultaneously from the start of drying. At a moisture content of 50 wt %, the pure pulps contained only minor FW fractions and more TBW and NFW than the pulp mixtures. Below a water

content of 31 wt %, FW was no longer present in any pulp and the TBW contents of the pulps were about the same.

NMR imaging was a powerful tool for the study of paper pulp drying down to a water content of about 30 wt %. The differences in the rates and regions of pulp drying could be seen from the NMR line widths and two-dimensional images. In the early stage of drying, the line widths as a function of water content increased most slowly for the reed-containing pulps; however, after the first inflection point no significant differences were evident in the growth rates of the line widths.

The water distribution appeared to be uniform in all the wet pulps (water content = 90–93 wt %). Differences in water distribution during drying could be seen with the aid of NMR images. However, water was found to be released from similar regions of the pulps. Residual detectable water seemed to be in pointlike proton-rich regions of the samples. Because the outermost dimensions of the images of the pulps did not change during drying, we concluded that in no case did significant shrinkage of the pulp occur at moisture contents above 30 wt %.

From the drying curves based on the gravimetric measurements, inflection points were determined at 59, 35, 28, and 20 wt % water content for the pine–reed pulp; at 57–58, 38–39, and 26–27 wt % water content for the pine and birch pulps; at 56 and 36 wt % for the pine–birch pulp; and at 60 and 30 wt % for the pine–birch–reed pulp. In comparison, in curves where the NMR line widths were presented as a function of decreasing water content, the inflection points were at 61–68 and 37–45 wt % moisture content. The inflection
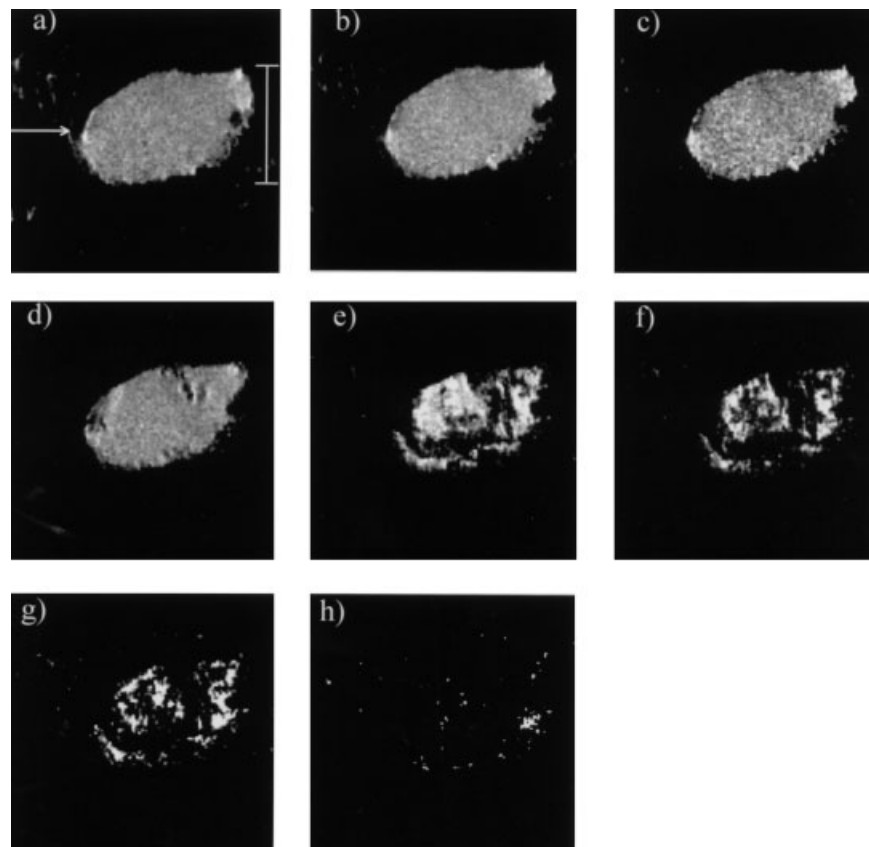
Figure 4 Two-dimensional NMR images of drying birch pulp at drying times of (a) 0, (b) 1, (c) 3, (d) 7, (e) 9, (f) 10, (g) 14, and (h) 16 min. (a) The arrow indicates the direction of air flow, and the vertical line indicates the size of the sample (9.54 mm).

points observed at 56–68 and 35–45 wt % in the gravimetric and NMR drying studies taken together have not been reported previously. Further, the DSC results showed the disappearance of FW at the first critical point of drying at 30–32 wt % water content, whereas FBW disappeared at the second critical point of 17–19 wt % water content. For four of the six pulps, these two DSC critical points correspond to the last two inflection points in the gravimetrically determined drying curves.

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