

Hard-to-remove water in cellulose fibers characterized by thermal analysis: A model for the drying of wood-based fibers

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ABSTRACT: A new parameter, hard-to-remove (HR) water content, was recently defined as the moisture ratio at the onset point between the constant and falling rate zones in an isothermal cellulose drying process and was further investigated with differential scanning calorimeter (DSC) characterization in this study. The linear relationship between the HR water content and the water retention value (WRV) was explained by the combined results of thermogravimetric analysis (TGA) and DSC. The drying order of different classes of water was *quantitatively* verified. We found that free water was evaporated first, followed by trapped water, freezing-bound water, and then nonfreezing-bound water, with some overlap. This was found for bleached, unbleached, and mechanical pulp. It was also found that the HR water mass is a combination of trapped water, freezing-bound water, and nonfreezing-bound water. Trapped water could be described as water that is not bound to the fibers, but is difficult to evaporate. For the pilot paper machine samples, all the water in the wet web after pressing and entering the dryer section, was found to be entirely HR water with no free water detected. Based on the results, a qualitative drying model of cellulose fibers is proposed with regard to decreasing moisture ratio. This model is valid for different types of wood-based cellulose fibers.

Application: This study demonstrates the drying behavior of water saturated cellulose fibers and could be applied to papermaking for a better understanding of fiber-water interaction during drying.

Papermaking is essentially a dewatering process. Most of the water in a wet fiber web should be removed during the papermaking process by gravitational and suction forces in the wire section, mechanical forces in the press section, and thermal energy in the dryer section. The web consistency (% solids) is typically 20% after the paper machine forming wire, 45% after the press section, and 95% after the dryer section. These consistencies correspond to the removal of 195 kg of water (per kilogram paper) in the wire section, 2.8 kg of water in the press section, and 1.2 kg of water in the dryer section. Although the dryer section is responsible for a small fraction of the total dewatering, it is the major energy consumer in the paper mill. This is because porous and hygroscopic pulp fibers have hard-to-remove water that is considered to be located in the fiber cell wall and trapped in the fiber network geome-

try. Thus, it is important to understand the interaction between fibers and water and the resulting impact on the fiber drying behavior to optimize the capital and operating costs of the dryer section. Further, the drying processes can have significant effects on the quality of products, including mechanical strength, smoothness, and dimensional stability.

In general, water in cellulose fibers is categorized into three types: unbound water, freezing-bound water (FBW), and nonfreezing-bound water (NFBW). Bound water (freezing and nonfreezing) is water associated with cellulose surfaces. Nonfreezing-bound water is defined as water that does not freeze and the first 1~3 layers of water adjacent to a surface are considered NFBW. This is because the motion of water structures is severely limited by the association with the surfaces [1]. FBW can freeze at a temperature lower than the usual freezing point. The

amount of FBW can be determined by measuring the amount of water with a depressed freezing (or melting) temperature. This phenomenon, called freezing point depression, has been extensively reviewed elsewhere [2].

Drying energy is used not only to vaporize the water molecule, but also to overcome the interaction between cellulose fibers and water. Water molecules are bound to the hydrophilic surfaces of cellulose fibers by hydrogen bonds. Water trapped in nano-scale pores could be considered NFBW [3]. Another view of the interaction between cellulose fibers and water is that the swollen fiber cell wall can be treated as a mixture of (a) partially water-soluble polymer and water [4] and (b) an insoluble polymer phase. This model has also been put forth by Pelton [5].

For a better understanding of the drying behavior of water in cellulose fibers, a parameter termed hard-to-remove (HR) water was introduced for a

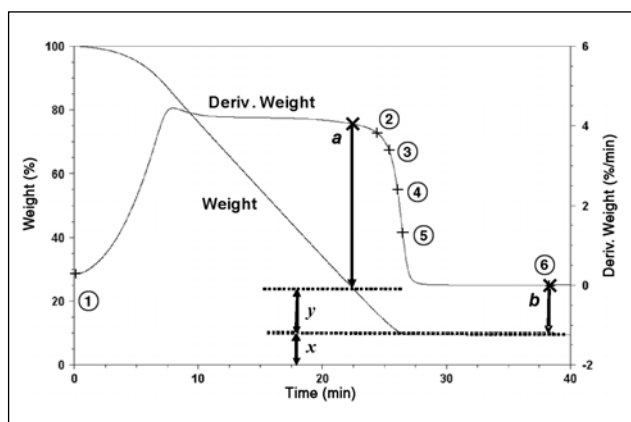
cellulose fiber and water system using high resolution isothermal thermogravimetric analysis (TGA) as described in an earlier study [6]. The study described here combines the concept of hard-to-remove water with that of bound water to develop the drying order of water from cellulose fibers. The drying order of water has been presented *qualitatively* for microcrystalline cellulose [7], but *quantitative* information was not found in the literature. In addition, pilot plant papers sampled from various locations on the paper machine were analyzed to compare with cellulose fibers dried in TGA chamber. It is expected that a proposed non-mathematical model can provide a simple, but insightful description to understand which types of water with different characteristics are removed from the fibers during isothermal drying.

MATERIALS AND METHODS

Sample preparations

Three types of pulps were investigated in this study. For bleached grades, softwood pine kraft unrefined pulp (International Paper) was used. For unbleached grades, laboratory-cooked softwood pine with a kappa number of 99 was obtained. Thermomechanical pulp (TMP) was obtained from Bear Island Paper (Ashland, Virginia). Nonporous glass fiber (Lauscha Fiber International, Summerville, South Carolina) was also investigated to compare the HR water content and the WRV with cellulose fibers. The average dimensions of the fibers were measured (Table I) using a Fiber Quality Analyzer (FQA, OpTest Equipment Inc., Hawkesbury, Ontario, Canada).

To compare TGA drying with paper machine drying, four samples were obtained from the pilot paper machine at North Carolina State University campus, Raleigh. Samples were taken from four locations: (1) headbox, (2) after presses, (3) after the first dryer cylinder, and (4) after the eighth dryer cylinder. The stock was composed of 20% bleached softwood and 80% bleached hardwood. Filler (18%, CaCO_3), retention aid (0.05%, Accurac 90 polyacrylamide), and sizing agent (0.20%, AKD Hercon 70) were added to the stock. Filler retention was about 50%. Paper was produced at the speed of 18.3 m/min with a basis weight of 77.8 g/m² and a reel width of 30 cm. Dryer cylinders were heated with 225.5 kPa of saturated steam and the web sheet temperatures were reported to be 14°C (after presses) to 80°C (after eighth dryer).



1. Drying response at isothermal temperature 90°C. Six points (+) are identified on the derivative curve of weight. The hard-to-remove (HR) water content is calculated as y/x .

Measurement techniques

The water retention value was calculated following SCAN test method (SCAN C102XE: 3000 g, 15 min and 1700 g/m²) and is the ratio of water to dry fiber mass after centrifugation (Centra CL3R with 958 swing-horizontal rotor, International Equipment Company). The HR water content was measured using a thermogravimetric analyzer (TGA Q500, TA Instruments) run isothermally at 90°C. The HR water content is the moisture ratio of the fibers at the transition between the constant rate zone and the falling rate zone, which is the weight of water at onset point (point *a* in Fig. 1) divided by the weight of dried fibers (point *b* in Fig. 1). The nitrogen gas flow rate was 40 mL/min for balance gas and 60 mL/min for sample gas. Wet samples having different initial moisture ratios and solid masses were prepared for the experiments. Detailed experimental conditions can be found elsewhere [6].

To determine the drying order of the different classes of water, the TGA and a differential scanning calorimeter (DSC Q1000, TA Instruments) were used. The TGA isothermal drying experiment (90°C) was interrupted at six different times. The samples were rapidly removed from the TGA furnace, placed into DSC pans (Part #900793.901 for bottom and Part #900794.901 for lid, TA Instruments) and sealed, and analysis

Samples	Length, mm	Width, μm	WRV, g/g	FSP, g/g	HR water, g/g	FBW, g/g	NFBW, g/g
Bleached SW	2.09	25.9	1.97	0.99	1.47	0.324	0.303
Unbleached SW	2.76	34.1	2.61	1.43	2.66	0.321	0.351
TMP	1.74	33.6	2.21	1.17	2.59	0.260	0.313
Glass fiber	2.04	25.1	1.05	0.00	1.03	0.222	0.000

I. Fiber characteristics. Legend: WRV is wave retention value; FSP is fiber saturation points; HR is hard-to-remove; FBW is freezing-bound water; NFBW is nonfreezing-bound water; TMP is thermomechanical pulp.

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was subsequently conducted to characterize the freezing-bound water and unbound water [8]. A heating rate of 1°C/min was used. This technique is based on the melting temperature depression of freezing-bound water on cellulose fibers. non-freezing-bound water was calculated by subtracting the amount of freezing-bound water and unbound water detected by the DSC from the total water as measured by the TGA.

Fiber saturation point (FSP) was determined by the solute exclusion technique to measure the amount of water in the cell wall. This was accomplished by using a probe polymer, Dextran (Sigma-Aldrich D5376, MW of 2,000,000), following the procedure described elsewhere [9,10].

RESULTS AND DISCUSSION

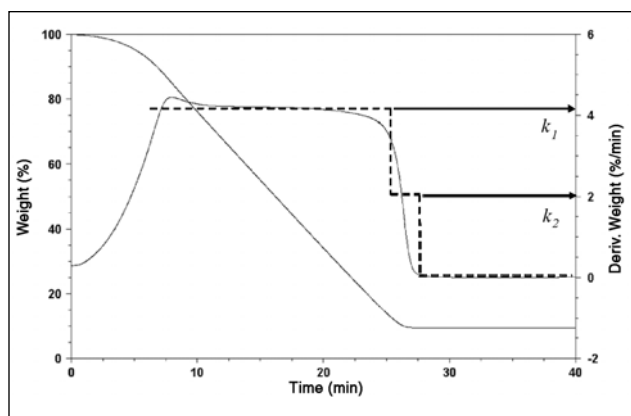
Mass transfer rate for the drying of fibers

It was experimentally shown that the WRV was correlated with the HR water content under specific experimental conditions with a high R^2 value when a softwood bleached kraft market pulp was used [6]. The reason why the HR water content determined by thermal energy has such a close relationship with the WRV determined by mechanical force (centrifugal force) is discussed here.

The drying process of cellulose fibers in the TGA chamber may be explained using two mass transfer rates (k_1 and k_2) and an additional assumption. The first mass transfer rate (k_1) is the evaporation rate of water from the exposed sample surface to the TG chamber. This rate k_1 represents the constant drying rate zone as a dashed line in Fig. 2. This was shown the same for the different types of fibers, but was sensitive to the experimental conditions such as isothermal temperature and initial total mass [6]. This makes sense, as this free water does not directly interact with the fiber surface.

The fraction of water evaporated with the mass transfer rate of k_1 can be designated as f_1 . A step decrease in the drying rate would then result at the transitions from the constant rate zone to the falling rate zone. The second mass transfer rate (k_2) is introduced as the transfer rate of water from the interior of the fiber or from the small spaces created by fiber-to-fiber network to the exposed sample surface. The rate k_2 is the limiting rate in the falling rate zone. For simplicity, k_2 is drawn constant in Fig. 2, but the rate k_2 is a function of moisture ratio and fiber type. While the mechanism of water removal is not well defined in this zone, this process may also be affected by a slow rate of heat transfer through the low moisture content fiber wall at lower moisture ratio. The fraction of water that is evaporated in the falling rate zone is designated as f_2 .

To explain the relationship between the HR water content and the WRV, it is assumed that the water fraction f_1 is evaporated first and the water fraction f_2 is removed later (the additional assumption). The WRV is a measurement of the fiber at a certain level of saturation at which the surfaces remain wet and the majority of water exists inside the fibers'

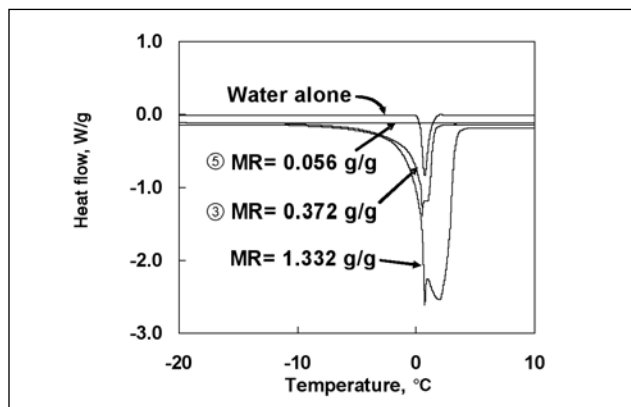


2. Two mass transfer rates (k_1 and k_2) for the constant rate zone and falling rate zone, respectively, represented by the dashed lines (---). Warming-up zone (initial heating to 90°C) was not modeled in this study.

pore structure for cellulose fibers [11]. Thus, this saturated state should correspond directly in qualitative and quantitative manners to the drying transition between the constant rate zone and the falling rate zone based on the description above, if the assumption is appropriate. This assumption is proved reasonable based on the experimental evidence gathered using a combination of the DSC and the TGA, which will be discussed in the following section.

Drying order for water classes in fibers

To determine the drying order of the different classes of water existing in a fiber-water system during the drying of fibers, the TGA isothermal drying experiment was interrupted at different times indicated by points 1~6 in Fig. 1. Softwood bleached fibers were used for these experiments. DSC



3. DSC melting curve for fiber-water system at a heating rate of 1°C/min. Points (3, 5) are identified in Fig. 1. Water alone is also included as a comparison, but not scaled to y-axis. Endothermic heat flow is indicated downward.

by DSC	Unbound water		Bound water: Freezing	Bound water: Nonfreezing	Total water
by TGA	Easy-to-remove water (Constant rate zone)	Hard-to-remove water (Falling rate zone)			
Description	Free water	Trapped water	Bound water: Freezing	Bound water: Nonfreezing	•
①	8.265	0.795	0.324	0.303	9.687
②	0.000	0.134	0.311	0.296	0.741
③	0.000	0.070	0.099	0.273	0.442
④	0.000	0.000	0.009	0.132	0.141
⑤	0.000	0.000	0.005	0.051	0.056
⑥	0.000	0.000	0.000	0.000	0.000

* Points ① ⑥ are identified in Figure 1. All units are g water/g dry fiber mass.

II. Classification of water in bleached softwood fibers.

by DSC	Unbound water		Bound water: Freezing	Bound water: Nonfreezing	Total water
by TGA	Easy-to-remove water (Constant rate zone)	Hard-to-remove water (Falling rate zone)			
Description	Free water	Trapped water	Bound water: Freezing	Bound water: Nonfreezing	•
•	6.082	1.987	0.321	0.351	8.741
•	0.000	0.145	0.316	0.348	0.809
•	0.000	0.017	0.117	0.309	0.443
•	0.000	0.000	0.021	0.107	0.128
•	0.000	0.000	0.010	0.062	0.072
•	0.000	0.000	0.000	0.000	0.000

III. Classification of water in unbleached softwood fibers.

melting curves for some of these samples are plotted in **Fig. 3**. The small, sharp peak at the low temperature portion of the melting curve indicates that a fraction of the water has a depressed melting temperature. This class of water is known as freezing-bound water. The larger peak at higher temperature is unbound water. The peak temperatures of freezing-bound water were observed as 0.75°C and 0.54°C for moisture ratios 1.33 g/g and 0.37 g/g, respectively, which are higher than 0.00°C. This was caused by thermal delay with the heating rate of 1.0°C/min used in this study. It is of interest to observe that the peak temperatures for freezing-bound water shift to lower temperatures when low moisture ratio samples were used. This could be explained by the Gibbs-Thomson equation [12,13] and pore collapse during drying [14]. Pores are closed during the drying of fibers in the TGA and the decrease in average pore size of fibers causes the melting temperature to be depressed.

The combined results of the TGA and the DSC showed that the water in a simple fiber-water system could be classified into unbound water, freezing-bound water, and non-freezing-bound water by the DSC and easy-to-remove water

and hard-to-remove water by the TGA. The amounts of each water classification are listed in **Table II** for points 1–6. HR water mass is the combination of trapped water, freezing-bound water, and nonfreezing-bound water. The existence of this additional category of water, i.e. trapped water (HR water but not bound water), could be described as water that is not bound to the fibers but is difficult to transport to the exposed surface. These definitions of water are not “microscopic,” but “operational” classifications, based on experimental evidence.

In general, unbound water is removed from the fibers first followed by freezing-bound water and then nonfreezing-bound water as found by DSC. At point 2 of Fig. 1, most of the unbound water has been removed and freezing-bound water begins to be removed. Also near point 4, most of the freezing-bound water has been removed and non-freezing-bound water begins to be removed. Finally, no water is left at point 6. Therefore, we concluded that free water is generally evaporated first followed by trapped water, freezing-bound water, and then nonfreezing-bound water, with some overlap.

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by DSC	Unbound water		Bound water: Freezing	Bound water: Nonfreezing	Total water
by TGA	Easy-to-remove water (Constant rate zone)	Hard-to-remove water (Falling rate zone)			
Description	Free water	Trapped water	Bound water: Freezing	Bound water: Nonfreezing	•
•	6.562	2.017	0.260	0.313	9.152
•	0.000	0.154	0.234	0.317	0.705
•	0.000	0.030	0.021	0.307	0.358
•	0.000	0.000	0.018	0.161	0.178
•	0.000	0.000	0.011	0.080	0.091
•	0.000	0.000	0.000	0.000	0.000

IV. Classification of water in thermomechanical pulp (TMP).

by DSC	Unbound water		Bound water: Freezing	Bound water: Nonfreezing	Total water
by TGA	Easy-to-remove water (Constant rate zone)	Hard-to-remove water (Falling rate zone)			
Description	Free water	Trapped water	Bound water: Freezing	Bound water: Nonfreezing	•
Headbox (a)	193.295	1.115	0.420	0.248	195.078
After presses (b)	0.000	0.657	0.389	0.241	1.287
After 1st cyl. (c)	0.000	0.336	0.367	0.226	0.929
After dryer	0.000	0.000	0.000	0.056	0.056

V. Classification of water in samples obtained from pilot paper machine.

The same experiments were conducted with unbleached pulp and thermomechanical pulp. The HR water content is different for the different fiber types (Table I). However, the same sequences of water exit were found for the different samples as shown in Table II and **Tables III and IV**. Based on the drying order of the different classes of water, a strong correlation between the HR water content and the WRV is expected.

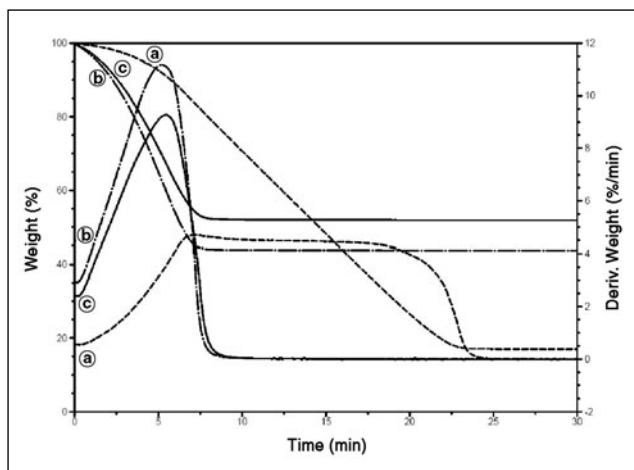
For comparison with cellulose fibers, the HR water content (1.03 g/g) and the WRV (1.05 g/g) were determined for the non-porous glass fiber (Table I). Since glass fibers are non-porous but hydrophilic, it is expected that water exists in the inter-fiber matrix rather than within the individual fibers. This idea was verified by a fiber saturation point (FSP) measurement of the glass fiber, which resulted in a value of 0.00 g/g, indicative of no water inside the glass fiber. This finding indicates that a significant amount of the water measured in a WRV or HR water content measurement exists in the inter-fiber matrix. This has been determined previously for WRV [15]. Further the glass fibers were determined to have 0.222 of FBW and 0.000 of NFBW, indicating that most HR water is trapped water, i.e., a type of HR water that is classified as unbound by a DSC measurement. Trapped water can exist inside and outside the fiber wall. For glass fiber, this water is outside the fiber wall. The wood-based cellulose fibers also

have a significant portion of the HR water existing external to the fiber walls. This is demonstrated by the FSP measurements that the water in the fiber wall (FSP) is less than the HR water content (Table I).

In addition, four samples obtained from a pilot paper machine were analyzed (**Table V**). The HR water content of the sample from the headbox was 1.783 g/g. The moisture ratio of the sample (sample b in **Fig. 4**) after the presses and before the dryer section, 1.287 g/g. Thus it is determined that all of the water in the paper web entering the dryer section is HR water. From this study, it is expected that some of this water is external to the fiber wall and some is internal. Isothermal drying was conducted in the TGA at 90°C for samples after the presses, first dryer cylinder, and eighth dryer cylinder and no free water was determined (Table V and **Fig. 4**). For the samples taken before the dryer (sample b) and after the first cylinder (sample c), only a warm-up zone and a falling rate zone were identified in the TGA (**Fig. 4**), the constant rate zone being absent. This indicates that the dryer section in a paper machine removes only HR water as measured by the TGA technique here, not free water.

Drying model

TGA isothermal drying is not identical to actual drying of paper in the paper machine. In the paper mill, the drying sec-



4. TGA isothermal drying (90°C) behavior of samples obtained from the pilot paper machine. (a) Sample from headbox. Sample was thickened using cheese-cloth to about 17% before measurement (original solids 0.51%). (b) Sample taken after the presses and entering the dryer section (solids 43.7%). (c) Sample taken after the first cylinder (solids 51.9%). Sample taken after the eighth dryer cylinder (solids 96.7%) is not shown in this figure.

tion consists of a number of internally steam-heated cylinders over which the web passes. A dryer fabric is used to increase contact between the web and the cylinder and hold the paper tight against the heated surface. In contrast, the TGA furnace is isothermally heated to 90°C and the unrestrained fibers are placed in the pan over which the nitrogen gas flows. Despite this, it is of value to provide a simple model to describe the drying occurring in the TGA that is in agreement with data in this study.

Considering the drying order of water and the fiber morphology, a conceptual qualitative drying model of fibers in a TGA furnace is proposed with regard to the moisture ratio (Fig. 5). When a fully saturated sample (point A in Fig. 5) is initially heated, the drying rate increases as the sample temperature increases. After reaching the isothermal temperature

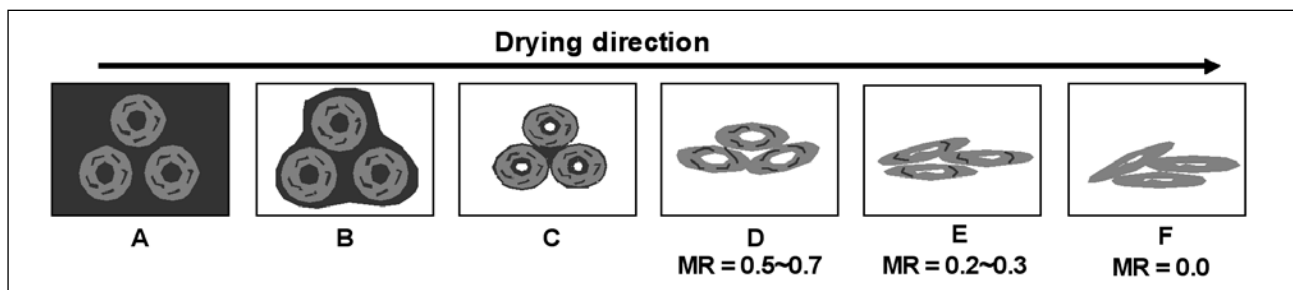
(90°C in this study), the evaporation rate remains constant at the mass transfer rate k_1 and free water is evaporated until the exposed surface is not wetted at its maximum value.

At point C in Fig. 5, there is no more free water left and the drying rate (mass transfer rate k_2) decreases, indicating the falling rate zone. Note that there is water on the outside of the fibers in the fiber-fiber network, reflective of water indicated by the WRV and HR water that exist for the glass fibers, for example. The movement of moisture to the exposed surface cannot replenish the water at the surface to support the drying rate measured in the constant rate zone. Wood-based cellulose fibers are considered to be irreversibly collapsed as the moisture ratio continues to decrease. More heat energy is required to evaporate the rest of the water and the mass transfer rate k_2 sharply decreases as shown in Fig. 2. Only bound water is left located in the micro-pores of fibers at point D. These pores are considered to be sizes of up to 144 nm [13] and 400 nm [14] in diameter. Fibers are contracted further due to the heat energy as described in point F for the fully dried fibers.

For papermaking with a standard press section, the drying that occurs in the dryer section corresponds only to points C-F in Fig. 5.

CONCLUSIONS

The relationship between the HR water content and the WRV was explained with two mass transfer rates and an additional assumption that water external to the fiber wall is removed prior to water internal to fiber wall. The assumption was verified experimentally by the combined results of TGA and DSC. It was found quantitatively that free water is evaporated first followed by trapped water, freezing-bound water and then nonfreezing-bound water, with some overlap. This was found for bleached, unbleached, and mechanical pulp. It was also found that the HR water mass is the combination of trapped water, freezing-bound water, and nonfreezing-bound water. The existence of this category of water, i.e. trapped water (HR water, but not bound water), could be described as water that is not bound to the fibers but is difficult to transport to the exposed surface. Thus, it was concluded that



5. Conceptual model of fiber drying. The fiber cell wall is saturated for pictures A, B, and C.

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the onset point on the TGA experiment represented a certain level of fiber saturation and this should be linearly related to the WRV. Based on the pilot plant samples taken from a paper machine, all the water in a typical wet web entering the dryer section is HR water and no free water is present. Considering the drying order of water, a conceptual qualitative drying model of fibers in TGA furnace is proposed with regard to the moisture ratio. **TJ**

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LITERATURE CITED

1. Berlin, E., Kliman, P.G., and Pallansch M.J., *J. Colloid Interface Sci.* 34(4): 488(1970).
2. Landry, M.R., *Thermochimica Acta* 433(1-2): 27(2005).
3. Liu, W.G., and DeYao, K., *Polymer* 42(8): 3943(2001).
4. Pouchly, J., Biros, J., and Benes, S., *Makromolekulare Chemie* 180(3): 745(1979).
5. Pelton, R., *Nordic Pulp Paper Res. J.* 8(1): 113(1993).
6. Park, S., Venditti, R.A., Jameel, H., et al., *Cellulose* 13(1): 23(2006).
7. Heng, P.W.S., Liew, C.V., and Soh, J.L.P., *Chem. Pharm. Bull.* 52(4): 384(2004).
8. Weise, U., Maloney, T., and Paulapuro, H., *Cellulose* 3(4): 189(1996).
9. Stone, J.E., Scallan, A.M., and Abrahamson, B., *Svensk. Papperstid.* 71(19): 687(1968).
10. Laivins, G.V., and Scallan, A.M., *J. Pulp Paper Sci.* 22(5): 178(1996).
11. Andreasson, B., Forsström, J., and Wågberg, L., *Cellulose* 10(2): 111(2003).
12. Furó, I., and Daicic, J., *Nordic Pulp Paper Res. J.* 14(3): 221(1999).
13. Maloney, T.C., and Paulapuro, H., *J. Pulp Paper Sci.* 25(12): 430(1999).
14. Park, S., Venditti, R.A., Jameel, H., et al., *Carbohydrate Polymers*, 66(1): 97(2006).
15. Maloney, T.C., Laine, J.E., and Paulapuro, H., *TAPPI J.* 82(9): 125(1999).

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INSIGHTS FROM THE AUTHORS

We chose this topic as an investigation of the nature of water in cellulose fibers to find possible energy savings in paper machine dryer sections. As noted in the paper, the drying order of different classes of water (free, trapped, freezing-bound, and nonfreezing-bound) in mechanical and chemical pulps was quantitatively verified and our findings resulted in a qualitative drying model for cellulose fibers.

The most difficult aspect of our research was achieving accurate measurement, which is challenging because fibers are not homogeneous. Using a pilot plant paper machine, one of our most interesting and surprising findings was that the web entering the drying section does not contain any free water as measured by TGA and DSC.

The information in this study can be used by papermakers to gain a better understanding of the



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nature and types of water present in cellulose fibers.

Our next step is to test our method with fibers having different lignin contents.

Jameel is a professor, Venditti is an associate professor, and Pawlak is an associate professor in the Department of Wood and Paper Science, North Carolina State University. Park is a post-doctoral research associate in the Forest Products Center of the University of Tennessee. Email Venditti at richard_venditti@ncsu.edu.