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HIGH RESOLUTION THERMO-GRAVIMETRIC ANALYSIS OF PULP DRYING

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ABSTRACT

A method is described that classifies water in a cellulosic fiber and water system. Thermogravitmetric analysis (TGA) is used to determine *hard-to-remove (HR) water* from an isothermal drying curve. The *HR water content* is defined as the moisture ratio (g of water / g of oven dried sample) of the fiber-water system at the transition between the constant rate zone and falling rate zone of an isothermal drying curve. The TGA instrument provides tightly controlled drying conditions that allow one to distinguish small differences in drying behavior. The exact value of the HR water content was found to be influenced by the initial moisture ratio, solid mass, and isothermal drying temperature. Experiments at optimal conditions showed that the HR water content is linearly correlated with the water retention value. This correlation was examined in terms of the similar states of the fibers (*i.e.* minimum saturation point) when the HR water content and water retention value are measured. The dependence of the HR water content on the solid mass of the sample revealed two constants, y-intercept and slope. The y-intercept is considered to be linked with instrumentation and the slope is to be associated with the fiber. Once the HR water content measurements are adjusted for these constants, experiments may be conducted at any solid mass down to a few milligrams. The dependence of the HR water content on the isothermal drying temperature was linked to differences in the drying rate of the constant rate zone. It is proposed that the higher drying rate for higher isothermal temperatures results in the transport of water internal to the fiber becoming an important factor at higher moisture content. This results in a higher HR water content being observed. It was also found that the pulp yield affected the HR water content. At the same water retention value, the highest HR water content was found for mechanical pulp followed by unbleached chemical pulp, and bleached chemical pulp. These differences may be attributed to differences in chemistry, pore size and volume, and the dynamics of pore collapse during drying. This method can be performed on extremely small samples and provides a convenient and insightful characterization technique for cellulosic fibers.

INTRODUCTION

The interaction between cellulosic fiber and water has a significant impact on the papermaking process in terms of drainage rate, press solids, and drying energy. This interaction is linked to the fiber flexibility and fibrillation, which contributes to the final strength of the paper products. In the paper industry, two of the common methods used to characterize fiber-water interactions are water retention value (WRV) [1] and freeness [2]. The WRV is defined as the ratio of water to dry fiber after centrifugation of a fiber pad under standard conditions and is used as a measure of fiber swelling [3]. Fiber swelling is accompanied by an increase in fiber flexibility, which is important in developing fiber-fiber bonds in paper. The freeness of a pulp slurry is a measurement of the drainage rate of a pulp slurry under controlled conditions. This measurement is used as an indicator of drainability on the papermachine, and as a process-monitoring tool for refining.

A technique that uses small samples to characterize the papermaking fibers may be useful in forest biotechnology applications. Water retention value and freeness require about 0.5 grams and 3 grams of dry fiber mass, respectively. By papermaking standards, this is a relatively small amount of fiber, but these sample sizes are too large for the limited amount of fibers produced from genetically modified trees grown in greenhouses. These modified trees hold the potential to revolutionize pulp and paper production. Thus, techniques need to be developed to analyze saplings at early stages of development using extremely small samples. Furthermore, standard techniques that can be easily automated would be useful for reducing variability between tests and improving quality control. One disadvantage of utilizing such a small sample is the vulnerability to sampling error. Thus, proper sampling is critical for accurate and repeatable results.

Different classes and amounts of water associated with cellulosic fibers have been determined by methods such as solute exclusion, differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR). Each of these tests creates a means for characterizing fiber-water interaction, but precise interpretation of the physical meaning of these values is complicated by the fact that the boundary between fibers and water is not well defined. Solute exclusion, DSC, and NMR techniques also use fully saturated samples. However, hygroscopic porous materials like cellulosic fibers can alter their structure upon drying [4]. Thus, a technique that examines the fibers at various moisture ratios may provide insight into the papermaking properties.

Solute exclusion has been used since its inception in the 1960s to measure the amount of water in the cell wall. Using the solute exclusion technique, the fiber saturation point (FSP) can be determined [5, 6]. This is accomplished by using a probe polymer, *e.g.* dextran, of appropriate size, which does not interact with the fibers and is too large to penetrate into the cell wall. Water is classified as accessible and inaccessible water based on the accessibility of the probe polymer into fiber pores. By using a series of different size probes, the distribution of accessible pores can be calculated [6, 7].

A DSC method characterizes bound water in fibers, subcategorized as non-freezing and freezing bound water [8, 9, 10]. Non-freezing bound water is defined as water that is not detected during a DSC measurement and can be determined by the difference of the total water measured gravimetrically less the waters detected in a DSC analysis. It is reasonable to expect that the first 1~3 layers of water adjacent to a surface do not freeze, because the motion of water structures is severely limited by the association with the surfaces [11]. The hindrance of the water motion is considered not only due to the hydrogen bonds between the surface and the water, but also due to the presences of nano-cavities in fibers [12].

Freezing bound water is determined by measuring the amount of water that has its melting temperature depressed. This phenomenon, called freezing point depression, has been explained in several ways. First, this may be due to the effect of macromolecules and membranes [13]. The hydration interaction between the hydrophilic surfaces and water molecules increases the stability of water molecules and non-freezing bound water can be observed at the surfaces. The strength of hydration interaction decreases with the distance from the surface, and water molecules associated with the surface may be frozen at depressed temperatures. Second, the freezing point depression might be explained by considering the consequences of fibers being porous materials. If it is assumed that a pore in a cell wall is cylindrical [14], the pressure is increased within the pore according to the Kelvin equation shown below:

$$\frac{p_o}{p} = e^{\left(-\frac{2\sigma}{r\rho_l RT}\right)} \tag{1}$$

where p_o is the vapor pressure of a planar liquid surface, p is the vapor pressure of a liquid surface with radius of curvature r, σ is the surface tension of the liquid, ρ_l is the liquid density, T is the temperature and R is universal gas constant. This increase in pressure results in the freezing point being depressed. The third explanation is that partially soluble fiber and water can be viewed as a hydrated gel system [15]. In this situation, the freezing point depression is caused by a lowered activity and increased entropy of water in the fiber-water gel system.

A ^{1}H NMR method has been used to determine the amount and properties of non-freezing bound water [16, 17]. The non-freezing bound water was characterized by experimental free-induction-decay based on the molecular dynamics of the water molecules. The liquid-like signal at the freezing temperature is interpreted to originate from non-freezing bound water. NMR relaxation and self-diffusion analysis revealed the detailed properties of non-freezing bound water in fibers.

Even though DSC and NMR techniques provide extensive information about the fiber-water interaction, interpretation of the raw data may require significant training and the equipment can be prohibitively expensive. In this study, an alternative method to characterize the water associated with cellulosic fibers is described using high-resolution thermogravimetric analyzer (TGA). Fibers are dried isothermally under tightly controlled conditions and three different zones are observed during the drying of fibers, *i.e.* warm-up, constant rate, and falling rate zones [18]. From the results of isothermal drying experiments, a classification of water is proposed, termed "*hard-to-remove (HR) water*", consisting of the water associated with the fibers at the transition between the constant rate zone and the falling rate zone. In this study, the HR water content is defined and examined under different experimental conditions such as isothermal temperatures, initial input masses and initial moisture ratios. The HR water content is further studied with a variety of fiber sources to investigate the interaction between fiber and water.

MATERIALS AND METHODS

Sample preparations

Softwood bleached kraft market pulp (Albacell, International Paper) was used to examine the relationship between the HR water content and WRV. The pulp was beaten using a Valley Beater (Valley Iron Works, Appleton, WI, Tappi Method T200 sp-96). Samples were withdrawn from the beater at nine different time intervals. Samples at each level were then decrilled using a Bauer McNett Classifier (CE Bauer, Canada) with 48-mesh screen. Two decrilled samples, unbeaten and beaten (30 min with 4.5 kg load) samples, were subjected to drying/wetting cycles in the laboratory. Laboratory drying/wetting was performed to model the effect of fiber recycling. The laboratory drying/wetting cycles involved the following steps: hand-sheet making, wet pressing (345 kPa for 5 min and then 2 min after changing blotter papers), oven drying (unrestrained drying at 105°C, over night) and disintegration in a British disintegrator (Lorentzen & Wettre, Sweden). The drying/wetting procedure was performed for 1, 2, and 3 cycles. Thus, twenty-four samples were produced by different treatment conditions from the original softwood bleached kraft market pulp.

In addition to the samples above, a variety of other pulps were tested. Hardwood bleached kraft market pulp (Georgia Pacific) was used. Laboratory prepared unbleached chemical fibers were also used. These pulps include hardwood (birch, aspen), softwood (pine, unknown species), and non-wood (wheat by kraft, wheat by soda). TMP (pine) was obtained from a commercial source. Commercial recycled pulp, produced from a mixture of old newspapers and old magazines, was also used. Of these samples, laboratory softwood (pine) and commercial TMP (pine) were never dried pulps. Glass fiber (C-50-R) was obtained from Lauscha Fiber International Corp. (Summerville, SC).

Measurement techniques

The water retention value was performed following the SCAN Method (3000 g, 15 min and 1700 g/m^2) [1] and is defined as the ratio of water to dry fiber mass after centrifugation (Centra CL3R with swing-horizontal rotor, International Equipment Company). Freeness of a fiber pad is a measure of the drainage rate at atmospheric pressure and was performed according to the Tappi Method [2].

A high-resolution thermogravimetric analyzer (Q500 TGA, TA Instruments) was used to record the weight loss during drying. A schematic diagram of the TGA instrumentation is shown in Figure 1. For the TG analysis,

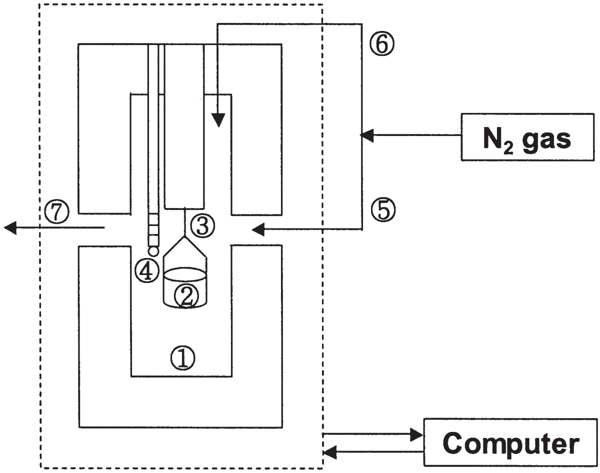

Figure 1 Schematic diagram of thermogravimetric analyzer (TGA). ①: furnace, ②: platinum sample pan, ③: wire connected to a balance, ④: thermocouple, ⑤: sample gas-in, ⑥: balance gas-in, and ⑦: gas-out.

wet samples having different initial moisture ratios and solid masses were prepared and placed in the TGA furnace. Experiments were run isothermally at 30°C, 50°C, 70°C, 90°C, and 110°C to dry the samples until the weight change was less than 0.001 %/min in the derivative of the weight loss. The sample moisture contents at those points were less than 1% for all isothermal temperatures. Therefore, the weight at the point where the derivative curve of the weight loss is less than 0.001 %/min can be used as the oven dried (OD) weight. Platinum sample pans (Part #952018.906, TA Instruments) were used and have dimensions of 2 mm in height and 10 mm in diameter. Dry nitrogen gas was used at a flow rate of 40 ml/min for balance gas and 60 ml/min for sample gas.

Freezing bound water and unbound water were measured using a differential scanning calorimeter (Q1000 DSC, TA Instruments) during a 5°C/min heating ramp according to Weise *et al* [19]. This technique is based on the freezing point depression of bound water on cellulosic fibers. Non-freezing bound water was calculated by subtracting the amount of freezing bound water and unbound water detected by DSC from the total water as measured by TGA.

RESULTS AND DISCUSSION

Different drying regimes

Drying kinetics revealed three different drying regimes, which are a warm-up zone, a constant rate zone and a falling rate zone [20]. These three zones are observed by examining the first derivative curve in Figure 2 from an isothermal drying experiments using TGA. When the sample is initially placed in the TGA furnace, the drying rate increases as the sample warms up, indicating a warm-up zone. The evaporation rate then remains relatively constant up to the time where point ⓐ corresponds. The nature of the constant rate zone existing over a relatively lengthy duration of time was addressed independently by Belhamri [21] and Schlünder [22]. These researchers indicated that if movement of water from the interior of a material is sufficient to keep the exposed surface 'wet', then a constant rate zone should be observed over a wide duration of time. Schlünder [23] showed mathematically that the condition for a sufficiently wet surface is fulfilled if the pores are evenly distributed and the pore diameter is small compared to the thickness of the viscous sub-layer formed by the gas flow past the surface.

During the constant rate period, the drying rate should be controlled by

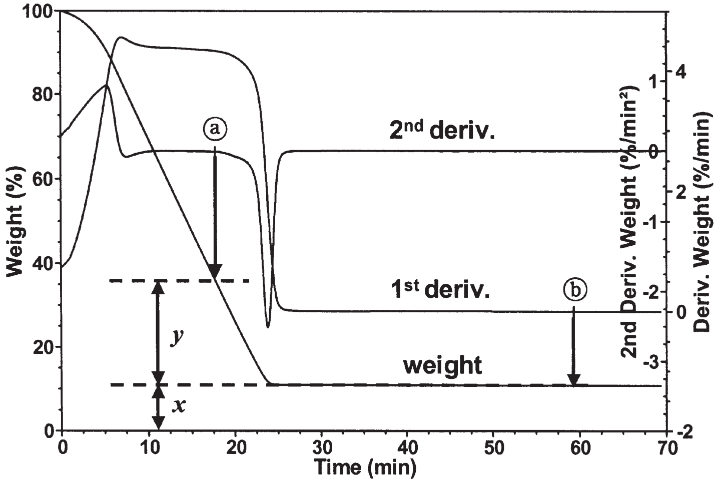

Figure 2 Drying response at isothermal temperature 90°C. The hard-to-remove (HR) water content is the moisture ratio at the transition between the constant rate zone and the falling rate zone. The HR water content is calculated as *y*/*x*.

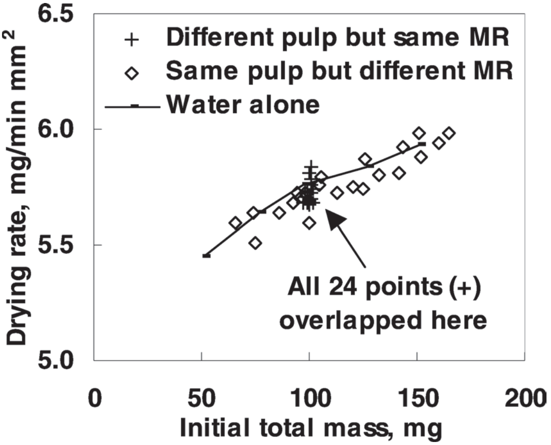

Figure 3 Effect of initial total mass on the drying rate, mg/min·mm^2, of the constant rate zone. Legend (+): 24 different samples having the same moisture ratio (MR) (~9 g/g) and initial total mass (~100 mg). Legend (◇): 20 samples that are different in moisture ratio and initial total mass, but are all from the same fiber sample.

experimental conditions such as sample surface area (pan diameter), relative humidity in the TGA furnace (relative humidity of gas), gas flow rate, and isothermal temperature. Since the same sample pan and gas flow rate of dry nitrogen were used in all experiments, the sample surface area, relative humidity, and gas flow rate were considered as constants. Figure 3 shows the drying rate of the constant rate zone at the isothermal temperature of 90°C as a function of the initial total mass. The drying rate was found to increase as the initial total mass of samples increased. The dependency of the drying rate in the constant rate zone on the initial total mass may be related to the differences in gas flow pattern over the sample pan, which could be changed due to the different levels of sample pan filling.

Using the same sample (softwood bleached kraft, 30 min beating with 4.5 kg load) that has different moisture ratio and initial total mass (legend ◇), the drying rate of the constant rate zone is well matched with the drying rate of water alone. Furthermore, the drying rate of the constant rate zone for all twenty-four different fibers (legend +, softwood bleached kraft) overlapped each other when the same initial total mass is used. This indicates that fiber processing does not affect the drying rate within the constant rate zone. All twenty-four samples were prepared from the different combinations of beating/decrilling/drying cycle. However, this finding is in contrast to Maloney *et al.* [24], who reported that the unbeaten fibers did not maintain a constant rate zone. These authors explained that rigid unbeaten fibers provided a high surface macro-roughness and a poor ability of the structure to transport water. It is speculated that the unbeaten fibers in their work may have been prepared at lower moisture ratio compared to other samples, thus the constant rate zone was not observed. The effect of initial moisture ratio on the constant rate zone will be discussed later.

After point ⓐon Figure 2, a decrease in the drying rate was observed. This is the beginning of the falling rate zone. The moisture ratio at the onset of this decrease is considered to be related to the fiber characteristics. Even though some studies found a second falling rate zone [24, 25], none was observed in this study.

Definition of hard-to-remove water

The decrease in the drying rate in the falling rate zone can be attributed to a change in the mechanism of drying. In the constant rate zone, the exposed fiber surface remains 'sufficiently wet'. In the falling rate zone, however, it is proposed that the internal diffusion of water to the exposed fiber surface is no longer sufficient to keep the surface wet, and this causes the rate of drying to fall. It is likely that the drying is then governed by the internal diffusion of water, which is dependent on fiber properties such as fiber type, pore volume and geometry, fiber wall thickness, and moisture ratio. Thus, the determination of the starting point of the falling rate zone has the potential to be used to characterize fibers.

A parameter, the hard-to-remove (HR) water content, is defined as the moisture ratio (g of water/g of OD sample) of the fibers at the transition between the constant rate zone and the falling rate zone. The HR water content is the weight of water at point ⓐdivided by the weight of the dried fiber (point ⓑ), *i.e.* y divided by x in Figure 2. The term critical moisture content describes the same quantity as the HR water content [22], but for the critical moisture content a systematic approach to determine the starting point of the falling rate zone has not previously been described.

The transition between the constant rate zone and the falling rate zone is smooth with respect to time and the points ⓐand ⓑmust be defined by a systematic method. Point ⓑis defined as the time at which the derivative of the weight loss curve equals 0.001 %/min. Point ⓐwas determined for each isothermal temperature by doubling the average value of the second derivative in the constant rate zone and then identifying the time at which the second derivative reaches this value. This methodology allowed for the identification of the boundary between the constant rate zone and the falling rate zone with a single definition that could be used for all isothermal drying temperatures.

Effect of experimental conditions on the HR water content: Part I

It is of interest to determine the sensitivity of the HR water content to experimental conditions such as initial moisture ratio and solid mass. Using the same type of fibers (softwood bleached kraft, 30 min beating), the initial moisture ratio and solid mass placed into the TGA furnace were varied. The HR water content was determined at the isothermal temperature of 90°C. The HR water content decreases slightly with increased initial moisture ratio at the same solid mass as shown in Figure 4. This may be attributed to a number of factors including differences in the fiber network structure created from the different initial moisture ratios, small differences in the drying conditions, and instrument artifact created by changes in the available water to be removed. The HR water content is also influenced by the solid mass. The measured HR water content decreased with the increased solid mass at the same initial moisture ratio in the range of 3.1 mg to about 8.7 mg of solid mass. For dry fiber masses greater than 8.7 mg, however, the HR water content is less sensitive to the solid mass.

It is also worth noting that the HR water content abruptly collapses to zero

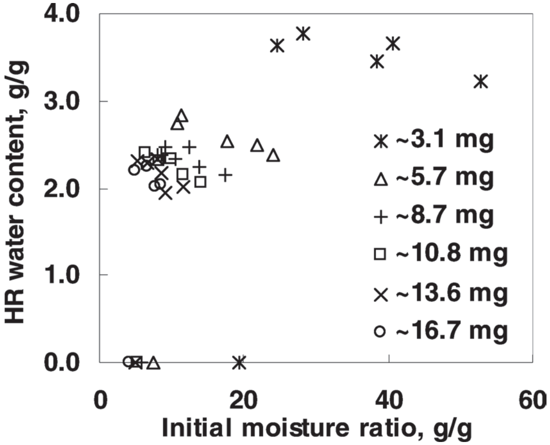

Figure 4 Effect of solid mass and initial moisture ratio on the HR water content. The legend indicates the solid mass. The HR water content is less sensitive to the solid mass at values greater than 8.7 mg.

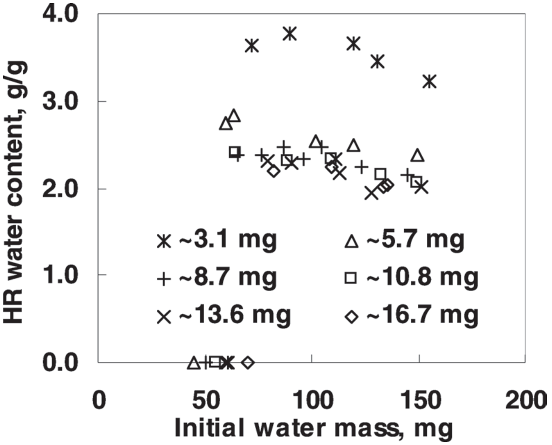

Figure 5 Effect of solid mass and initial water mass on the HR water content. Below 60~70 mg in initial water mass, the HR water content is not determined. The legend indicates the solid mass.

at a low moisture ratio for the different solid masses. By plotting the HR water content *versus* water mass in Figure 5 using the same data as Figure 4, it can be observed that there must be a minimum amount of water mass for this measurement to detect the HR water content. Below this minimum amount, the constant rate zone was not apparent and thus the HR water content could not be evaluated. Therefore, to compare changes in the HR water content, it is best to use a single solid mass, preferably above 8.7 mg, and a single water mass, preferably above 75 mg. For the remainder of the experiments in this work, approximately a 10 mg solid mass with 90 mg of water (~9 g/g moisture ratio) is used unless otherwise noted.

Correlation between the HR water content and WRV

With the specific experimental conditions of ~9 g/g moisture ratio, ~10 mg solid mass and 90°C isothermal temperature, the method described can be used successfully to characterize fibers which have been processed differently. The HR water content is plotted together with both the WRV and Freeness *versus* beating time for decrilled fibers in Figure 6. As beating proceeds, the fibers are known to change their structure, *i.e.* internal and external fibrillation, fiber shortening, and formation of fines. These structural changes of fibers result in changes of fiber properties such as the fiber flexibility, swelling,

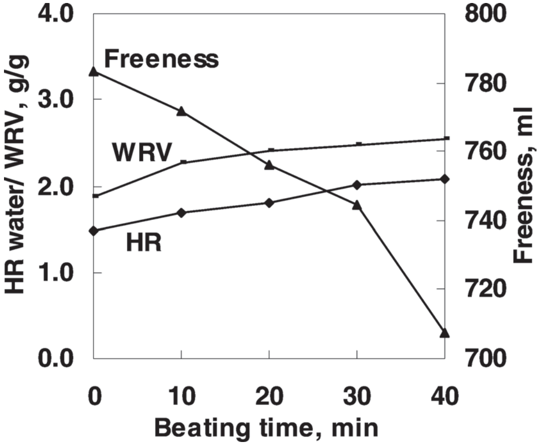

Figure 6 Effect of beating time on the HR water content, WRV, and Freeness. Both WRV and the HR water content increase and Freeness decreases with beating time.

and water holding capacity. Figures 7 (a) and (b) show microscopic images of unbeaten and beaten fibers. It is clearly observed that external fibrils are developed during beating and cover the surface of fiber. Both the HR water content and WRV increased and the Freeness decreased with beating time. Since the samples in Figure 6 were fines-free fibers, the results could be explained by the fibrillation and delamination of the internal structure of the fibers [26] and the development of specific surface area [27] with beating time. A t-test was performed to provide 90% confidence intervals (CI) for the three different methods. The 90% CIs were +/– 2.8 ml, +/– 0.031 g/g, and +/– 0.079 g/g for Freeness, WRV, and the HR water content, respectively. The CIs were based on data from unbeaten fiber (decrilled) and beaten fiber (whole). The HR water content was measured five times and WRV and Freeness were measured seven times.

The impact of drying/wetting cycles on the HR water content of unbeaten and beaten fibers is shown in Figure 8. As expected, the HR water content significantly decreased with successive drying/wetting cycle. This is the well-known phenomenon of hornification, which describes the physical and chemical changes to cellulosic fibers during drying and re-wetting [4, 28, 29]. It is known that drying causes an irreversible physical contraction of the fiber cell wall, and thus a cellulosic fiber swells to a much lower extent after it has been dried and re-wetted. The largest drop in the HR water content and WRV is observed after the first cycle of drying/wetting as shown in Figure 8. Further,

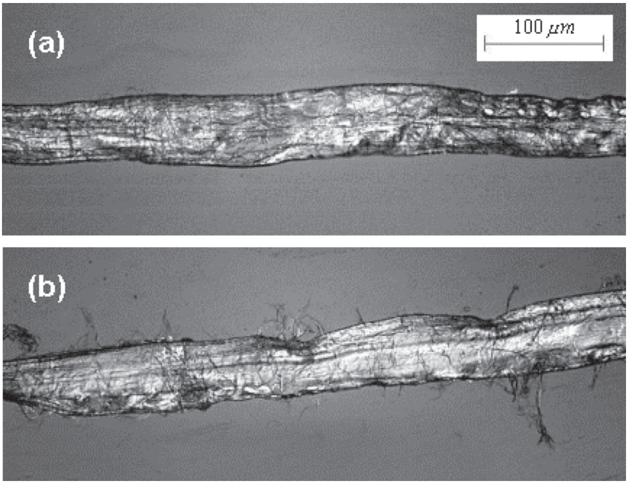

Figure 7 Microscopic images of softwood beached fibers. (a) Unbeaten fiber (WRV: 1.97 g/g). (b) Beaten fiber (WRV: 3.14 g/g). External fibrils are developed during beating and cover the surface of the beaten fiber.

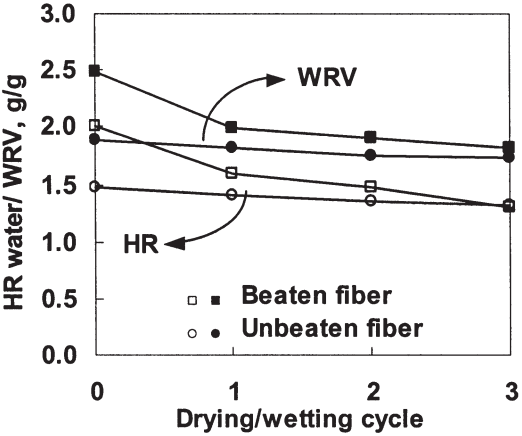

Figure 8 Effect of drying/wetting cycles on the HR water content. Drying/wetting cycles decrease both the WRV and the HR water content. The largest drop is observed after the first drying/wetting cycle.

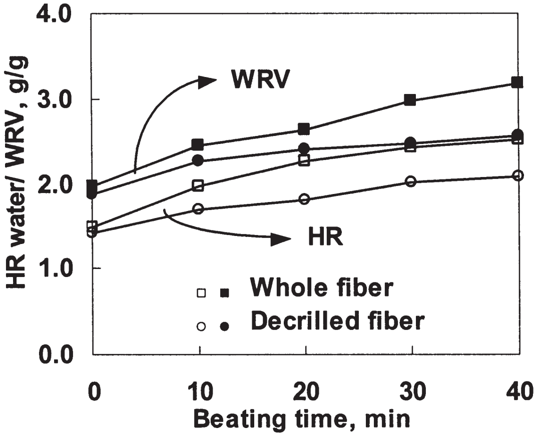

Figure 9 Effect of the removal of fines on the HR water content. Decrilled fiber has lower values in both the HR water content and WRV than whole fiber.

the beaten fibers have a large decrease in the HR water content and WRV when compared to the unbeaten fibers.

The effect of fines removal on the HR water content is shown in Figure 9. The decrilled pulp fibers have lower values in both WRV and the HR water content. This indicates that the HR water content measurement is sensitive to the loss of fines that have high specific surface area. The HR water content showed a close relationship with WRV in Figures 6, 8 and 9.

Finally, five different isothermal temperatures were investigated with all twenty-four softwood beached kraft samples. The HR water content at a given temperature was found to have a direct correlation with WRV as shown in Figure 10. A linear-regression analysis was performed for each temperature as shown in Table 1. When the y-intercept is set to zero, the coefficients of determination (R^2) ranged from 0.893 to 0.970 over the temperatures examined from 30°C to 110°C. Thus, it is realized that the HR water content could be used as a substitute for WRV, which is an indication of structural changes created by mechanical treatment for a given fiber. For the same fibers, the HR water content increases with isothermal temperature. This may be understood by noting that the drying rate in the constant rate zone is higher at a higher temperature than a lower one. It was proposed earlier in this paper that the onset of the falling rate zone is related to the internal transport of water being insufficient to keep the exposed surface sufficiently wet. If the internal transport of water is relatively unaffected by the increased

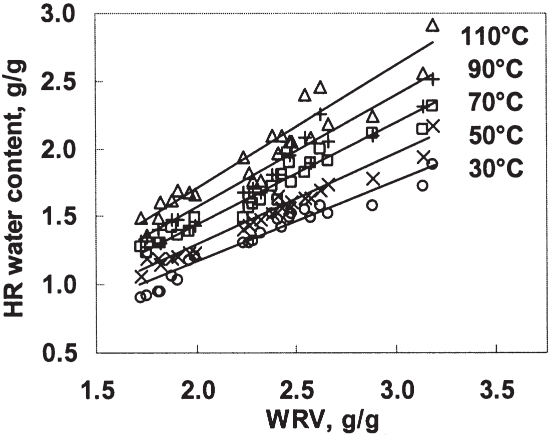

Figure 10 Effect of temperature on the HR water content and WRV for all twenty-four softwood bleached pulps. The HR water content has a linear relationship with WRV at a given isothermal temperature.

Table 1 Linear regression analysis using the data in Figure 10. If the y-intercept is set to zero, R^2 values are high enough to have significance.

Iso-temp., °C	Data points	Slope	y-int, g/g	R^2
30	24	0.58	0.00	0.930
50	24	0.64	0.00	0.970
70	24	0.72	0.00	0.955
90	24	0.77	0.00	0.931
110	24	0.84	0.00	0.893

temperature, then the onset point of the falling rate zone should occur at a higher moisture ratio as the isothermal temperature increases (*i.e.* drying rate in the constant rate zone increases).

Mass transfer rate for the drying of fibers

It was experimentally shown that WRV was correlated with the HR water content under specific experimental conditions having high R^2 value in Figure 10 and Table 1. It is of interest to investigate why the HR water content determined by thermal energy has such a close relationship with WRV determined by mechanical force (centrifugal force). Drying mechanisms of cellulosic fibers may be explained using two mass transfer rates, k_1 and k_2 and three additional assumptions. First, it is assumed that mass transfer rate (k_1) of water from the exposed sample surface to the TG chamber is constant at a given isothermal temperature. The fraction of water evaporated with mass transfer rate of k_1 can be designated as f_1. Second, the mass transfer rate (k_2) of water from the interior of the fiber to the exposed sample surface is introduced. The rate k_2 may be a function of moisture ratio and fiber type. It is assumed to be the limiting rate in the falling rate zone. The rate k_2 is assumed to be significantly smaller than k_1. The fraction of water that is evaporated in the falling rate zone is designated as f_2. For simplicity, k_2 can be assumed constant. A step function in the drying rate would then result at the sample transitions from the constant rate zone to the falling rate zone. This is shown as a dashed line in Figure 11. The third assumption is that the water fraction f_1 is evaporated first and then the water fraction f_2 is removed second. This assumption is reasonable based on the experimental evidence gathered using a combination of DSC and TGA, which will be discussed in the following section. Under these assumptions, a smooth drying curve could be realized

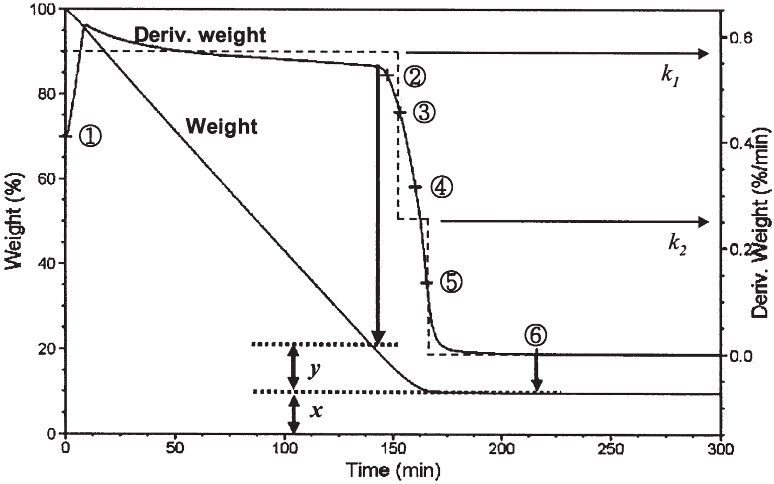

Figure 11 Drying response at isothermal temperature 30°C. The hard-to-remove (HR) water content is calculated as y/x. Six points (+) are identified on the derivative curve of weight. The dashed lines (---) represent a model step-wise function of derivative of weight.

when k_2 is expressed as a function of moisture ratio and/or the transition from the constant rate zone to the falling rate zone does not occur at precisely the same time throughout the entire fiber mass.

The WRV is a measurement of the fiber at a point of saturation where the surfaces remain wet and the majority of water exists inside the fibers' pore structure. This state should correspond directly in a qualitative manner to the transition in the drying rate to the falling rate zone based on the description above. Thus, one would expect a strong correlation between the HR water content and WRV.

Drying order for different classes of water in fibers

To determine the drying order of the different classes of water existing in a fiber-water system during the constant rate zone and the falling rate zone, the TGA isothermal drying experiment (30°C) was interrupted at different times indicated by points ①~⑥ in Figure 11. The samples were quickly removed from the TGA furnace, placed into DSC pans and sealed, and DSC analysis was subsequently conducted. DSC melting curves for some of these samples are plotted in Figure 12. The small and 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. This phenomenon called freezing point depression is associated

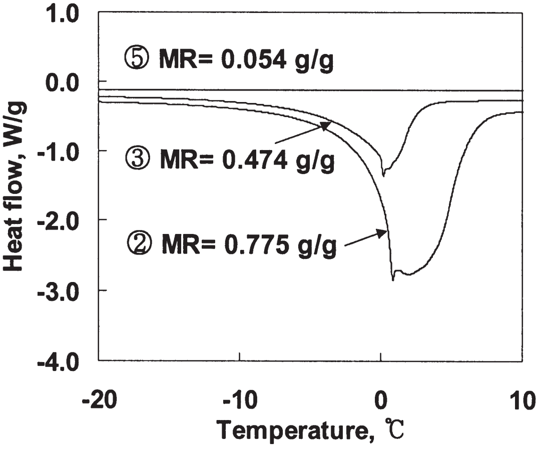

Figure 12 DSC melting curve for water-fiber at a heating rate of 5°C/min. Points (②, ③, ⑤) are identified in Figure 1. Endothermic heat flow is indicated downward.

with water interacting with fibers. The larger peak at higher temperature is unbound water. The small peak temperatures were observed as 0.88°C and 0.22°C for points ② and ③, respectively, which are higher than 0.00°C. This was caused by thermal delay with the fast heating rate of 5°C/min used in this study. When the heating rate of 1°C/min was used, the small peak temperature would be below 0.00°C (data not shown). It is of interest to observe that the small peak temperature shifts to the low temperature when low moisture ratio sample was used. This could be explained by the Kelvin equation, cf. Equation (1), and pore collapse during drying. Pores are closed during drying in the TGA and the pressure is increased within the pores due to the decreased pore diameter. Thus, this increase in pressure results in the melting temperature being depressed [14].

The combined results of TGA and 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 DSC and easy-to-remove water and hard-to-remove water by TGA. The amounts of each water classification are listed in Table 2 for points ①~⑥. As shown in Table 2, TG analysis combined with DSC results creates a different category of water. HR water mass is the

Table 2 Classification of water in fibers from the combined results of TGA and DSC.

by DSC	Unbound water		Bound water: Freezing	Bound water: Non-freezing	Total water
by TGA	Easy -to-remove water (Constant rate zone)	Hard-to-remove water (Falling rate zone)			
Description	Free water	Trapped water	Freezing BW	Non-freezing BW	
①	8.293	0.546	0.211	0.301	9.351
②	0.000	0.288	0.191	0.297	0.775
③	0.000	0.070	0.116	0.289	0.474
④	0.000	0.000	0.001	0.183	0.184
⑤	0.000	0.000	0.000	0.054	0.054
⑥	0.000	0.000	0.000	0.000	0.000

* Points ① ~ ⑥ are identified in Figure 11. All units are g water/ g dry fiber mass.

combination of *trapped water*, freezing bound water and non-freezing bound water. The existence of this category of water, *i.e.* 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.

As expected, unbound water is removed from the fibers first followed by freezing bound water and then non-freezing bound water. At point ② of Figure 11, most of unbound water has been removed and freezing bound water begins to be removed. At around point ④, most of freezing bound water has been removed and non-freezing bound water begins to be removed. Finally, no water is left at point ⑥. Therefore, it is concluded that free water is generally evaporated first followed by trapped water, freezing bound water and then non-freezing bound water, with some overlap in the time.

Effect of experimental conditions on the HR water content: Part II

Earlier in this study, the dependence of the HR water content on experimental conditions such as initial moisture ratio and solid mass was shown in Figures 4 and 5. However, it was not anticipated that the solid mass should influence the HR water content and this phenomenon is worth exploring further.

The same data from Figure 4 (softwood bleached kraft, 30 min beating) are plotted as water mass at the onset point of the falling rate zone *versus* solid mass in Figure 13. The water mass showed a linear relationship as a function of solid mass. To model this relationship, simple linear regression was applied to the data.

$$y = a + bx \tag{2}$$

Where, y is the HR water mass at the onset point of the falling rate zone expressed in mg, x is the OD solid mass in mg, a is the y-axis intercept in mg, and b is the slope of the line expressed as g water/ g OD fiber. This linear regression is further extended to the different pulps including bleached softwood and hardwood, unbleached softwood and hardwood, and glass fiber as shown in Table 3.

It should be noted that even pure water in the TGA sample pan exhibits a constant rate zone and a falling rate zone, consequently indicating a HR water mass. Water mass at zero solid mass was 10.33 mg as shown in Figure 13, which was greater than the a constant calculated from the linear regression. It is considered that when pure water is dried in the TGA, the drying rate is governed by a mass transfer rate, k_1, which is directly related to the exposed water surface area. The exposed area stays constant until the

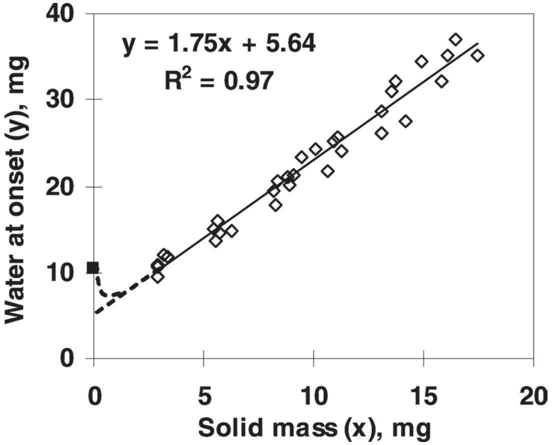

Figure 13 Linear relationship Abetween solid mass and water mass at onset point of the falling rate zone. Water mass at zero solid mass is 10.33 mg with a standard deviation of 0.86 mg. This is the average value for nine duplicate runs using about 100 mg of water without fibers.

continuous water film is broken. When continuous coverage no longer exists, it is observed that water gathers near the corner of the pan due to the high surface tension of water and the three-dimensional nature of the pan, resulting in a decrease in the exposed surface area of the water. Thus, the HR water mass for zero solids is a measure of the point at which a continuous film no longer covers the bottom surface of the pan. If, however, fibers are present in the pan, fibers prevent water from gathering in the corner of the pan due to the diffusion of water through the fiber network. A 'hook' shaped curve is expected below 3 mg of solid mass as shown as the dashed line in Figure 13.

The *a* constants for nine pulps calculated ranged from 4.82 to 6.51 mg. To check the significance among the *a* constants, 90% confidence intervals were determined. No significant differences were found for all *a* constants (data not shown), which indicates that one single value can be assumed for all samples. Thus, the *a* constants were averaged to 5.64 mg and this value was used for the linear regression of each sample as shown in Table 3. This single *a* constant may be interpreted as associated with instrumentation and experimental conditions (*i.e.* isothermal temperature, gas flow rate, and pan dimension), but not the sample itself.

The 90% confidence interval was also examined for the *b* constant. It is found that significant differences exist when significant difference in WRV

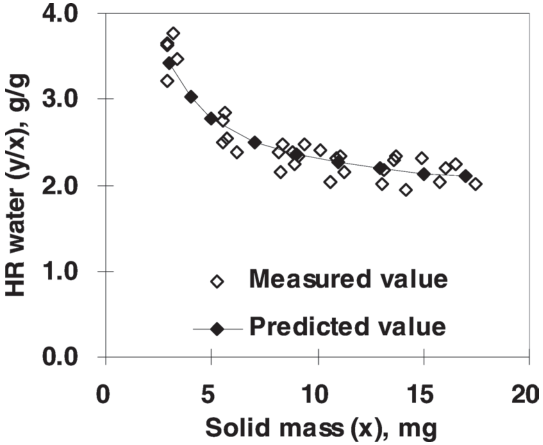

Figure 14 Effect of solid mass on the HR water content. Predicted values using two constants, *a* and *b*, fit well to the measured values.

also exist. The *b* constant times the solid mass is considered as the portion of HR water that is directly associated with the fiber. Re-plotting the data in Figure 13 as the HR water content *versus* solid mass, one observes that the linear regression closely predicted the experimental HR water content as shown in Figure 14. Unbleached softwood kraft unbeaten fiber (sample (1) in Table 3, WRV = 1.97 g/g) is compared to beaten fiber (sample (2) in Table 3, WRV = 3.14 g/g) in Figure 15. The predicted HR water contents are also shown on the figure. The *b* constants are 1.75 g/g and 1.11 g/g for the beaten and unbeaten fibers, respectively. A significant difference between the *b* constants for the beaten and unbeaten fibers is observed (58% difference). It is worth noting that the difference in the WRV for the beaten and unbeaten fibers was quite similar to the difference in the *b* constant (59% and 58%, respectively). For comparison, the *b* constant was analyzed for glass fiber and shows a low value (0.78 g/g) that corresponds to a low value of WRV (1.05 g/g)

Effect of different types of fibers on the HR water content

The HR water content was measured for various types of fibers. The data are plotted in Figure 16. The pulps can be separated into three main groups: mechanical pulp, unbleached chemical pulp, and bleached chemical pulp. Also two never dried pulps (TMP and Softwood Pine) are included in this

Table 3 Linear regression analysis of *b* constants.

	Sample description	WRV, g/g	HR water content, g/g	*b* constant, g/g	*90% CI for b constant, g/g*	R^2	Data points
(1)	Bleached SW (IP)	1.97	1.42	1.11	± 0.089	0.98	13
(2)	Bleached SW (IP)	3.14	2.31	1.75	± 0.104	0.97	32
(3)	Bleached HW (GP)	1.88	1.48	0.96	± 0.162	0.95	8
(4)	Bleached HW (GP)	2.16	1.71	1.09	± 0.155	0.97	7
(5)	Bleached HW (GP)	2.48	2.06	1.25	± 0.254	0.95	7
(6)	Unbleached SW (pine)	2.61	2.66	2.23	± 0.290	0.97	9
(7)	Unbleached SW (pine)	2.70	2.87	2.23	± 0.279	0.96	11
(8)	Unbleached HW (aspen)	1.98	1.88	1.38	± 0.060	0.99	6
(9)	Unbleached HW (aspen)	2.16	2.15	1.72	± 0.351	0.95	7
(10)	Glass fiber	1.05	1.03	0.78	·	0.90	9

* The *a* constant is set to 5.64 for all analysis

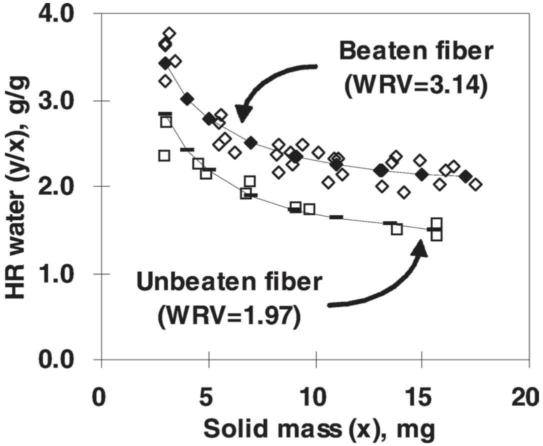

Figure 15 Comparison between beaten and unbeaten fibers. The constant value *b* was 1.75 and 1.11 for the beaten and unbeaten fibers, respectively.

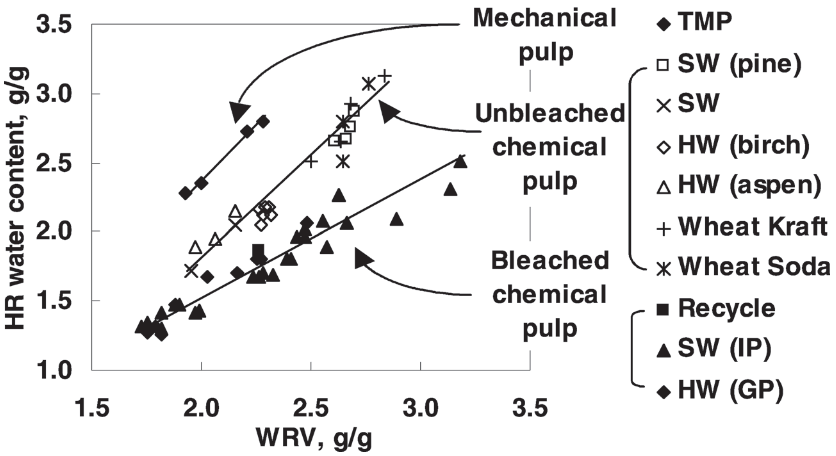

Figure 16 Effect of various types of fibers on the HR water content. High yield pulps show higher HR water content at the same WRV.

data. These three groups of pulps appear to show three different correlations with WRV. The mechanical pulp exhibits the highest HR water content at a given WRV followed by the unbleached chemical pulp, and the bleached chemical pulp, respectively. The difference in the correlation between the HR water content and the WRV for the different pulps may be linked to differences in fiber chemistry, pore structure, pore size, pore volume and changes in the pore structure as the fibers dry. Considering these results, the HR water content appears to characterize additional properties beyond the WRV. Therefore, the HR water content is not simply a substitute for the WRV, but a unique measurement that is sensitive to the same factors effecting WRV in addition to factors that do not influence the WRV.

CONCLUSION

Isothermal TGA weight loss curves for a cellulosic fiber and water system showed three different drying regimes, a warm-up zone, a constant drying rate zone, and a falling drying rate zone. From the isothermal drying experiment, a parameter termed "*hard-to-remove (HR) water content*" was defined as the ratio of water mass to fiber mass at the transition between the constant rate zone and the falling rate zone. The experiments were conducted at a variety of experimental conditions such as initial moisture ratio and solid mass to find optimal conditions for the experiments. The HR water content was found to be affected by the solid mass and initial water mass. Preferably the solid mass should be above 8.7 mg and the water mass should be above 75 mg.

The HR water content was correlated with the WRV at a variety of isothermal temperature. Results showed that the HR water content had a direct correlation with WRV for all isothermal temperatures investigated. This implies that the HR water content could be used as a substitute for WRV. An argument was presented that described the basis for the relationship between the HR water content and WRV. One of the critical assumptions of this argument was verified by DSC experiments. These experiments showed the primary order of drying is that unbound water is first removed from the sample, followed by freezing bound water, and non-freezing bound water. The HR water mass was found to include a portion of ‘unbound water’ as well as freezing and non-freezing bound water. This indicates that a portion of ‘unbound water’ is in some way inhibited, *or trapped*, from evaporating as readily as the remainder of unbound water.

Simple linear regression analysis of the HR water mass as a function of solid mass revealed two constants. The y-intercept, *a* constant, was associated with instrumentation and was considered to be independent of the fiber type used in the experiment. The slope, *b* constant, was the portion of the HR water mass associated with the fiber. It was shown that this constant changed with WRV. Thus, it was concluded that the *b* constant could be a indicative of the HR water content in the fiber.

Three distinct correlations between the HR water content and WRV were found when mechanical, unbleached chemical, and bleached chemical pulps were used. This suggests that the HR water content may be used to characterize additional properties beyond the WRV. Therefore, the HR water content is not simply a substitute for the WRV, but a unique measurement that is sensitive to the same factors impacting WRV in addition to factors that do not influence the WRV. Finally, this method can also be performed on extremely small samples and it provides a convenient and insightful characterization technique for cellulosic fibers.

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Transcription of Discussion

HIGH RESOLUTION THERMO-GRAVIMETRIC ANALYSIS OF PULP DRYING

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In your assumptions for the drying process there was no reference to the highly hydrated colloidal fines and polysaccharides which are associated with the pulp. Your model was essentially one in which the change in rate occurs as the onset of removal of moisture from the cell wall begins. I wonder if you would like to comment about how you see the role of these hydrated components of the pulp?

Joel Pawlak

Sure, I can comment on that. If we think about water and how water is associated with the structure of the fibre, it can be associated in a number of different ways. Of course, we can think of the water directly hydrogen bound to some sort of solid surface. We can think of the water as trapped within some sort of cavities inside the cell wall or we can think of the water as sort of a hydrated gel type system, as a colloid or something like that. I would like to emphasize here that this is not a perfect drying model. This is to give us some basic understanding of how the water is removed if you go through a drying process. If we think of the water transporting away from even a hydrated gel type system, we would assume that that water probably has more difficult time leaving that system as compared to free water that is moving around. So in effect, it would almost act as though that water was trapped inside the cell wall, and then moving to the outside of the cell wall, although, it indeed is not. Extending that and better understanding that are the things that we are going forward with. We want to understand why we do see such differences with different types of pulp and the amount of hard-to-remove water content even at the same water retention value and to better understand the influences of hydrated colloids.

Warren Batchelor Australian Pulp and Paper Institute

The typical hard-to-remove water values that you have are larger than the moisture content of a sheet going into the dryer section. So does that mean that all of your drying in the dryer section is going to be done in the falling rate zone?

Joel Pawlak

It is important here to be careful not to make the assumption that what is going on in the TGA represents paper drying exactly. We are not trying to model here what is going on in the dryer section of the paper machine. It is a very different type of drying, of course; there we have a very directional type of drying and directional type of heating. This is heating in an atmosphere or oven and also these are not paper samples but pulp samples. We observe that there are changes in the drying rate as a function of the temperature. So if you lower the overall drying rate of the sample, then you will observe a constant rate zone for a longer period of time. So essentially if you go back and say our drying rate is so low that the diffusion of water from inside the fibre to the external surface would not become a factor, we should not observe a falling rate zone. We have not extended this to the point of looking at what is going on in terms in the dryer section in the falling rate zone. We suppose that it goes back to two things: one the difference in the mechanism of drying and two, the overall drying rate and the way the heat is transferred to the sheet itself.

Anders Åström

Maybe I can take the opportunity and ask about the background to this technique that has been developed because you work with genetically modified wood and very small fibre samples. Have you done any work on such samples? Can you describe a little bit what it is that you will be looking for specifically?

Joel Pawlak

As you may or may not be aware, we are not able to grow genetically modified trees out in the wild yet. So we have to grow them in a greenhouse and our greenhouses are only about 14 feet (4.3 *m*) tall. So once they get to about 14 feet, we thereafter chop off the top or chop down the tree and that leaves us with the small amount of pulp that we will begin to analyse for a few different things like lignin content, chemical composition, fibre length and other sorts of things. The next stage in this is to try to extend this to say "what are the papermaking properties of these trees?". If we can plant these trees in the wild, they have these great properties that are optimized for the pulping operation, but have we optimized these properties or can we optimize these properties for the papermaking operation? Of course, we would like to analyse this in a short turn-around time. We do not want to have to wait 10 years or 5 years to grow a tree large enough to do pilot scale trials, so we have not got to the point yet of testing these samples, but we are trying to develop techniques where we can use just a few *mg* of fibre and try to get an idea of their papermaking characteristics.