An Isotopic Study of the Effects of Refining on Fiber

FRANCES L WALSH[*] and SUJIT BANERJEE[†]

[*]PhD Candidate, Institute of Paper Science & Technology and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology,
[†]Professor, Institute of Paper Science & Technology and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology
Georgia Institute of Technology, Institute of Paper Science & Technology,
500 Tenth Street NW, Atlanta, GA 30332, USA
sb@gatech.edu

ABSTRACT

Tritium has been used to directly measure the exchangeable hydrogen in bleached softwood kraft pulp. The hydrogen atoms associated with hydroxyl groups in pulp or with water contained in the pulp can dissociate and exchange with the hydrogen atoms in bulk water. Tritium is a radioactive isotope of hydrogen and behaves almost identically to it. The distribution of tritium between pulp and water (k_{pw}) can be easily measured and becomes an index of the protons available for hydrogen bonding.

Bleached kraft pulp was refined in a PFI mill to a range of freenesses. Tritiated water was added and the amount exchanged measured. There was a slight steady increase in k_{pw} until approximately 300 CSF; k_{pw} then rose sharply between 300 CSF and 100 CSF. This rise appears to correlate with FSP.

It is likely that the action of refining on the fiber reaches a threshold at about 300 CSF causing the fiber surface to break open creating exponentially more surface area. This theory is visually confirmed through light microscopy. The slow increase in fibrillation of the fibers above 300 CSF correlates with the increase in k_{pw}. Beyond the threshold of 300 CSF a dramatic difference in fibrillation is shown, also corresponding with the large increase in k_{pw}. The freeness difference around 300 CSF is small, but the change in fiber properties is extreme within this region. This change in properties could lead to sheet breaks and other disruptions when producing products around the threshold.

This study leads to a better understanding of how fiber changes during refining, resulting in a practical benefit of target freeness determination. Presently, freeness is selected based on product quality and on some measure of runnability. Yet, there are other considerations, demonstrated by the extreme change in fiber properties around 300 CSF.

INTRODUCTION

Refining of kraft pulp is a complex and somewhat understood process (Page 1989). Throughout the years many methods have been developed to further the understanding of beating or refining on fibers. With this study we introduce a new method developed to better understand the interaction between fiber and water. This paper focuses on the changing fiber/water relationship during the refining process with the objective of better understanding both.

Hydrogen isotopes have historically been used to study water accessible or crystalline/amorphous regions of pulp fibers (Dechant 1967; Guthrie and Heinzelman 1970; Child and Jones 1973). For these studies, deuterium was often used. While deuterium is an isotope of hydrogen, tritium used in this study can be easily and accurately measured. Thus, this new method provides a way to further the understanding of refining and the fiber/water relationship on the molecular level.

Most traditional methods employed to understand refining are limited by the scale of the method or the alterations to the system that must occur in order to access the data. Our method minimally affects the fiber/water system and allows exchange to occur without impacting the system. Thus, our method is able to quantify changes in fibers only before seen by microscopy.

These changes can impact the papermaking process through runnability and product quality.

EXPERIMENTAL

Never dried bleached softwood kraft pulp was obtained from Stora Enso's Wisconsin Rapids Mill, Wisconsin Rapids, WI USA. This pulp was refined in a PFI mill following CPPA Standard C.7 (IPST Procedure No. 401B) to a number of refining levels, ranging from unrefined to 15000 revolutions. The refined pulp was then subjected to tests to determine the fiber properties and characteristics of the pulp.

Tritiated water technique

The tritiated water technique is governed by equations 1-3. First, the pulp is equilibrated with the tritiated water, resulting in tritium being attached to the fiber, equation 1. Then the excess tritiated water, which is not attached to the fiber, is displaced from the fiber through the use of acetone (C_3H_6O), equation 2. Acetone is miscible with water but is also an aprotic solvent, thus it easily removes the excess water from the system without affecting the tritiated pulp. Acetone also swells the fiber to a much lesser extent than water, 43% compared to 373% with compressed samples (Mantanis, Young et al. 1995). Thus, the acetone addition should minimally affect or swell the already water saturated pulp pad. Once the free water is removed from the system, the pulp pad is re-equilibrated and washed with deionized water to remove the tritium from the system for analysis, equation 3.

$$\text{Pulp} + \text{HTO} \leftrightarrow \text{pulp-T} + \text{HTO}. \quad (1)$$

$$\text{pulp-T} + C_3H_6O \leftrightarrow \text{dry pulp-T} + \text{wet } C_3H_6O \quad (2)$$

$$\text{dry fiber-T} + H_2O \leftrightarrow \text{HTO} + \text{wet pulp}. \quad (3)$$

Throughout this technique, samples for scintillation counting are taken. The scintillation counter is able to quantify the amount of activity in each sample in terms of disintegrations per minute (DPM). The activity of the samples can then be utilized to calculate a fiber:water partitioning coefficient (k_{pw}).

Traditional techniques

Traditional techniques were employed to determine the validity of the tritiated water technique. These methods include freeness by TAPPI Standard Test Method T 227 (TAPPI 2000), solute exclusion, FSP, by the method of (Stone and Scallan 1967) as modified by (Böttger, Thi et al. 1983), water retention value, WRV, by TAPPI Useful Methods (TAPPI 1991), and fiber quality analysis. Scanning electron microscopy was preformed on selected samples to better understand the changing nature of the refined fibers. Britt jar measurements were also performed to determine fines generation during refining.

Scanning electronic microscopy

Scanning electronic microscopy (SEM) was performed at selected refining levels. Using a technique developed by Nanko and Pan, visual depiction of fiber cross sections as well as external and internal fibrillation and delamination were able to be detected (Nanko and Pan 2005). All SEM preparation and microscopy were performed by Shaobo Pan.

RESULTS AND DISCUSSION

This study initially consisted of five refining levels: unrefined, 2500, 5000, 7500, and 10000 revolutions. Pulps refined to 12500 and 15000 revolutions were also included for some aspects of the study.

During low levels of refining (up to 5,000 revolutions), k_{pw} appears to correspond with freeness, FSP and WRV (Table 1). However at 7500 revolutions, k_{pw} is almost an order of magnitude larger than results at lower levels of refining. The higher k_{pw} values continue with increased refining. This section will explore and explain the trend of k_{pw} during refining and hopefully will gain some insight into the effects of refining on fibers.

Water holding values for initial study

Refining level (rev)	Freeness (csf)	FSP (g/g)	WRV (g/g)	k_{pw} (g/g)
0	676	1.74	1.78	0.09
2500	464	2.26	2.14	0.22
5000	358	2.78	2.26	0.32
7500	261	2.52	2.32	2.02
10000	235	2.95	2.37	3.64

Table 1 Initial results

The maximum of the first trend in k_{pw} occurs at 5000 revolutions. At this point, assuming a k_{pw} corresponds to a monolayer of water covering the fiber surface, the surface area of the fiber is approximately 585 m^2/g. At 7500 revolutions, using the same assumptions, the surface area would increase to 3700 m^2/g. This area greatly exceeds previously published values and is a dramatic increase from the previous refining level. There is a high probability that k_{pw} refers to more than monolayer coverage at this stage in refining.

Fig. 1 illustrates the beater or refining curve for the complete study. The PFI Mill revolutions are shown across the x-axis with CSF, or freeness, along the y-axis. As shown, the fiber used in this study follows a standard refining curve for bleached softwood pulp. This curve confirms that the fiber used for this study and the refining performed on it is not out of the ordinary.

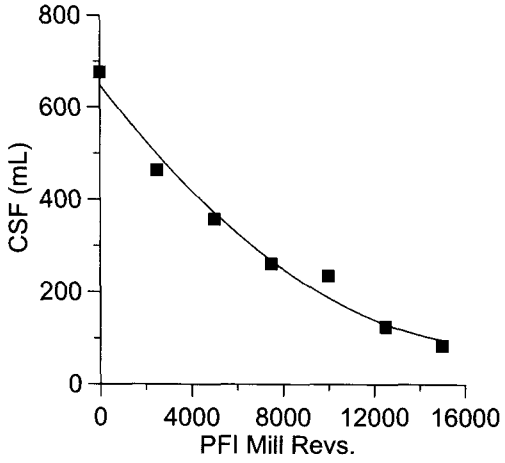

Figure 1 Standard beater curve

Fig. 2 compares WRV and FSP to freeness. Again, freeness is plotted along the y-axis with WRV and FSP plotted on the x-axis. WRV trends very well with CSF, while there is quite a bit of scatter within the FSP trend. The difference in these trends become more apparent when plotted versus k_{pw}, Fig. 3 and 4.

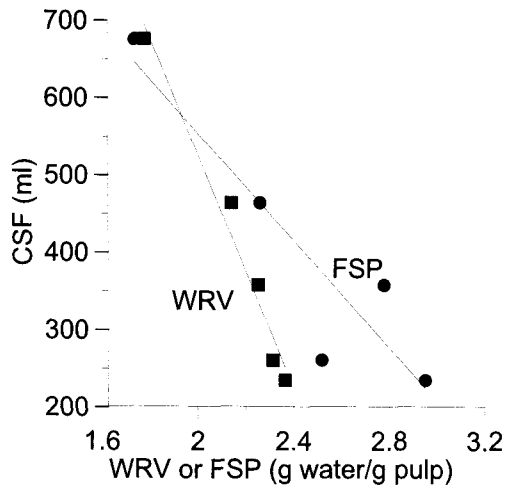

Figure 2 Comparison of WRV and FSP to freeness (CSF)

Fig. 3 confirms that WRV, indicated by the triangles, and freeness, indicated by the diamonds, are providing the same information about the water holding ability of the fiber used in this study. The consistency between WRV and freeness measurements is logical. Both measurements rely on gravitational pull to remove excess water from a pulp pad. Thus, WRV was dropped from the extended study and freeness was used as the comparison between k_{pw} and gravitational water measurements.

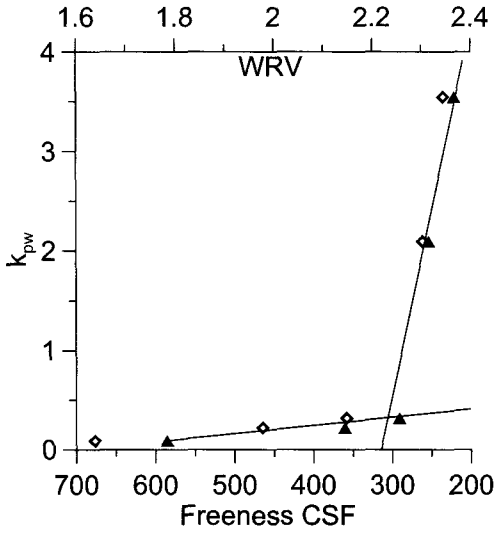

Figure 3 Comparison of Freeness and WRV to k_{pw}

What is extremely interesting in Fig. 3 is the two distinct trends formed during the refining curve. The first trend is created early during the refining curve. Within the first trend, k_{pw} slowly increases while there is a large decrease in freeness. The second trend appears later in the refining curve. In this trend, the opposite occurs k_{pw} quickly increases while freeness only decreases slightly. The transition between the two trends occurs at approximately 300 CSF and is caused by an almost order of magnitude increase in k_{pw}.

Fiber length and characteristics

refining level (rev)	% fines	fiber length (mm)	Mean Curl	kink index (1/mm)
0	1.61	2.11	0.095	1.47
2500	3.18	2.19	0.064	0.99
5000	3.61	2.16	0.081	1.19
7500	6.37	2.14	0.062	1.05
10000	8.05	2.19	0.056	0.83

Table 2 Fiber properties for initial study

The double trend is confirmed in Fig. 4, which compares FSP to k_{pw} in a similar manner as in Fig. 3. Again, two trends emerge. These trends split at the same point of the refining curve. Questions began to arise as to what changes are occurring within the fiber at 300 CSF. FQA results, Table 2, indicated an increase in fines content, while the other fiber properties had no consistent change at 300 CSF. The increase in fines content trends well with the FSP and freeness results. Could a doubling of the percent fines create such a large increase in k_{pw} when an earlier doubling of the fines content had minimal effect?

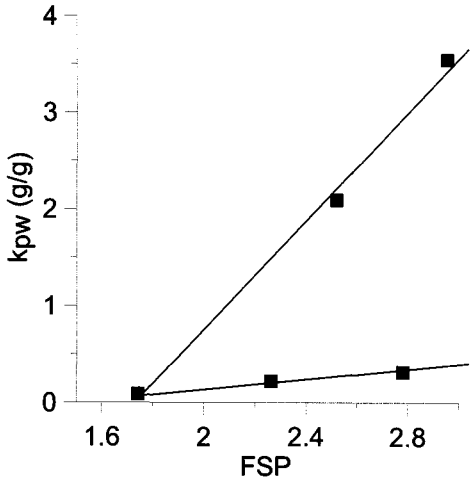

Figure 4 Comparison of FSP to k_{pw}

Figures 5 and 6 show a dramatic difference between fibers at 385 CSF, Fig. 5, compared to fibers only 100 points lower, Fig 6. The SEM pictures, taken by Shaobo Pan, illustrate the amount of internal delamination that is occurring between the cell walls. The interesting fact is that this delamination is minimal prior to 7500 rev and is not indicated by FSP or freeness. The delamination would also correspond with an increase in fines content. Page and De Grace discuss this delamination in their 1967 paper (Page and De Grace 1967). Their study determined that kraft, or sulfate, pulp splits into two to four layers upon beating, supporting the findings in this study.

In a refining study performed by Kibblewhite (1975), he observed cell wall removal during the refining process. In both the bleached and unbleached never dried softwood pulps, a significant increase, of S_2 exposure occurred between 4000 and 8000 revolutions in the PFI mill. An increase in fines content also occurred, which is consistent with cell wall removal (Kibblewhite 1975). The removal of the primary wall and S_1 layer increase the swelling within the fiber (Giertz 1957). This removal and the increased swelling could account for the large increase in k_{pw}. The internal delamination visible within the fiber may also cause acetone inaccessible, or hydrogen bonded cracks or pockets to form. These cracks are described by Caulfield (Caulfield 1977). The hydrogen bonded, water filled cracks may inflate the amount of water directly bonded to the fiber. The filled cracks may also falsely inflate the estimated surface area discussed earlier.

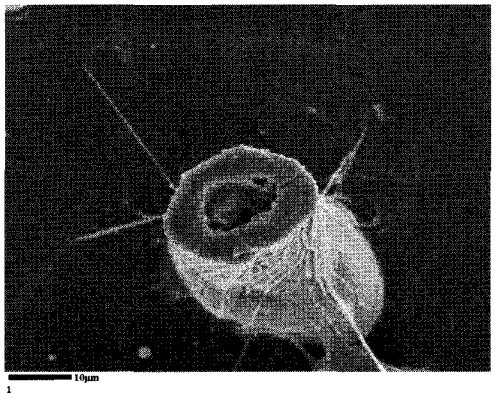

Figure 5 SEM image of a fiber – 5000 rev, 358 CSF

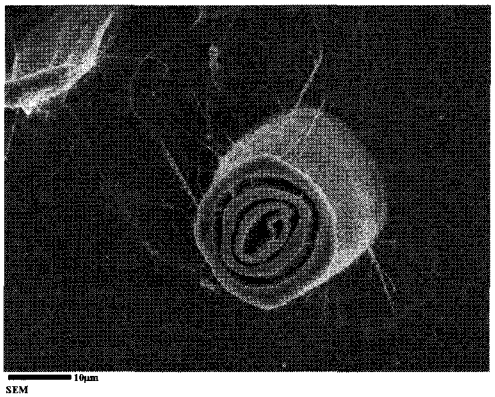

Figure 6 SEM image of a fiber - 7500 rev, 261 CSF

With the initial study, it appeared that the k_{pw} would continually increase after reaching the threshold at 300 CSF. To confirm this, two additional refining levels were added to the study, 12500 and 15000 revolutions, corresponding to freenesses of 125 and 84 CSF respectively. These two points created a new chaotic regime. Table 3 contains data for the initial study as well as the two additional points. For this portion of the study, FSP, fines %, freeness and k_{pw} were performed.

Water holding ability and fines % for complete curve

Refining level (rev)	Freeness (csf)	FSP (g/g)	k_{pw} (g/g)	fines %
0	676	1.74	0.09	1.61
2500	464	2.26	0.22	3.18
5000	358	2.78	0.32	3.61
7500	261	2.52	2.02	6.37
10000	235	2.95	3.64	8.05
12500	125	2.09	0.94	8.57
15000	84	2.13	2.13	7.46

Table 3 Complete refining curve results

In this low freeness regime some unusual results were found. Both the FSP and k_{pw} decreased while the fines % stayed relatively constant. Figure 7 illustrates

the chaotic behavior found in the high refining / low freeness regime. As is shown, kpw proceeds through two fairly consistent regimes prior to entering the high refining region after 10000 revolutions.

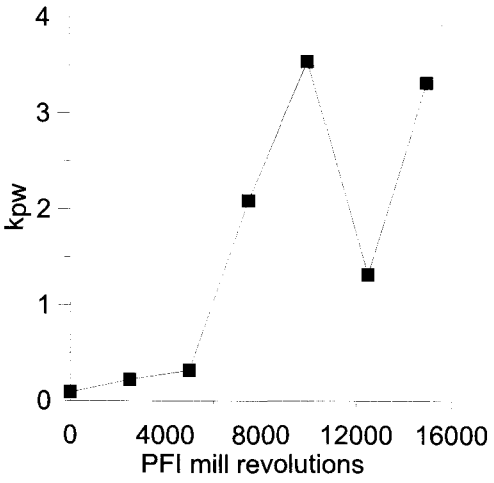

Figure 7 kpw refining curve

The three distinctive regimes are also present when plotting k_{pw} versus FSP. Through these graphs along with the SEM a hypothesis began to form. It appears that k_{pw} depicts the progression of refining through three distinct stages, Fig 8 and 9.

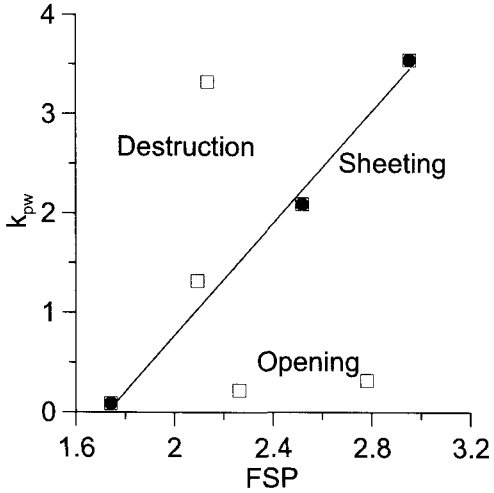

Figure 8 k_{pw} versus FSP

The first stage of refining removes the primary cell wall allowing the fibers to swell creating cracks in the fiber surface. These cracks increase the surface area of the fiber and thus the k_{pw}, causing the fiber surface to open up to the surrounding water and fiber. Hence this stage was dubbed *opening*.

As refining moves into the second stage, the cracks and new mobility of the fiber wall cause internal delamination to occur. Along with this delamination, the primary wall and S_1 layer begin to form sheets of microfibrils extending from the fiber surface. The sheet formation and internal delamination greatly increase the amount of water strongly associated with the fiber, as is reflected in the kpw. The water now strongly associated with the fiber may not be directly bonded to the fiber wall, but hydrogen bonded to other strongly bonded water molecules. Since, layers form within and surrounding the fiber during this stage we termed it *sheeting*.

The final and most chaotic stage of refining, *destruction*, occurs when the microfibril sheets and layers formed in the second stage begin to disassociate from the main fiber. This disassociation creates a very variable fiber mixture, most likely with fiber in all stages of refining present. Thus, the fiber/water relationship becomes chaotic as the fibers begin to destruct into microfibril sheets.

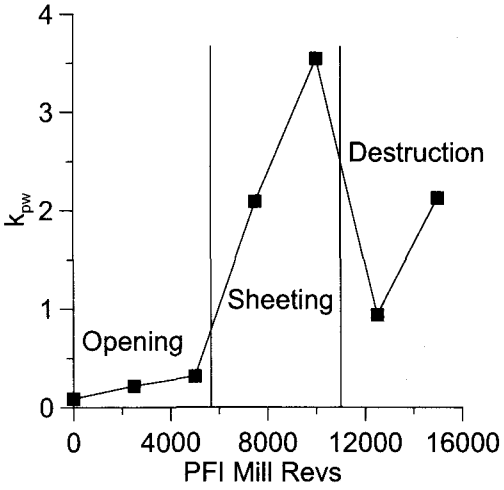

Figure 9 proposed stages of refining

CONCLUSIONS

The three distinct stages of refining can greatly affect the papermaking process. As refining increases the interaction with water changes traditionally increasing bonded area and drainage time. What becomes apparent through this study is that traditional measurements such as freeness, water retention value and solute exclusion cannot predict when these changes will occur. Often these changes can occur within small freeness ranges, approximately 100 points for this study, between both opening and sheeting, and sheeting and destruction. Adding additional refining levels may show that the change between the phases is even less. The differences between the fibers in these stages could easily lead to runnability and product quality issues, but are undetectable using traditional wet testing methods.

REFERENCE

Böttger, J., L. Thi, et al. (1983). "Untersuchungen zur Porenstruktur von Zellstoffasern." Das Papier **37**(10A): V 14 - V 21.

Caulfield, D. F. (1977). The effect of cellulose on the structure of water: view 2. Fiber-Water Interactions in Paper-Making, VIth Fun. Res. Symp., Oxford, FRC.

Child, T. F. and D. W. Jones (1973). "Broad-Line NMR Measurement of Water accessibility in Cotton and Woodpulp Celluloses." Cellulose Chemistry and Technology **7**: 525-534.

Dechant, J. (1967). "Eine Methode zur Bestimmung der Zuganglichkeit von Cellulose durch Deuteriumaustausch." Faserforschung und Textiltechnik **18**(6): 263-265.

Giertz, H. W. (1957). The effects of beating on individual fibres. Fundamentals of Papermaking Fibres, 1st Fundamental Research Symposium. F. Bolam. Cambridge, FRC: 389-409.

Guthrie, J. D. and D. C. Heinzelman (1970). "Determination of the accessibility of cellulose by use of $D_2{}^{18}O$ and mass spectroscopy." Textile Research Journal **40**(12): 1133.

Hernadi, A. (1984). "Accessibility and specific surface of cellulose measured by water vaper sorption." Cellulose Chemistry and Technology **18**: 115-124.

Herrington, T. M. and J. C. Petzold (1995). "Surface area of papermaking woodpulps used by the British paper industry." Cellulose **2**: 83-94.

Kibblewhite, R. P. (1975). "Interrelations between pulp refining treatments, fibre and fines quality, and pulp freeness." Paperi ja Puu **57**(8): 519-526.

Magne, F. C., H. J. Portas, et al. (1947). "A calorimetric investigation of moisture in textile fibers." Journal of the American Chemical Society **69**: 1896-1902.

Mantanis, G. I., R. A. Young, et al. (1995). "Swelling of compressed cellulose fiber webs in organic liquids." Cellulose **2**: 1-22.

Nanko, H. and S. Pan (2005). Personal Communication on SEM Techniques, IPST @ GT. F. L. Jacobson. Atlanta, GA.

Nelson, R. A. (1977). "The determination of moisture transitions in cellulosic materials using differential scanning calorimetry." Journal of Applied Polymer Science **21**: 645-654.

Page, D. H. (1989). The beating of chemical pulps - the action and the effects. Fundamentals of Papermaking, 9th Fundamental Research Symposium, Cambridge, FRC.

Page, D. H. and J. H. De Grace (1967). "The delamination of fiber walls by beating and refining." TAPPI **50**(10): 489-495.

Stone, J. E. and A. M. Scallan (1967). "The effect of component removal upon the porous structure of the cell wall of wood. II. Swelling in water and the fiber saturation point." TAPPI Journal **50**(10): 496-501.

TAPPI (1991). UM 256 Water Retention Value (WRV). TAPPI Useful Methods. Atlanta, GA, TAPPI Press: 54-56.

TAPPI (2000). 2000-2001 TAPPI Test Methods. Atlanta, GA, TAPPI Press.