RECYCLING OF CHEMICAL PULP FROM WHEAT STRAW AND CORN STOVER

Ulrike Tschirner,[a*] James Barsness,[b] and Tamara Keeler [c]

Handsheets produced from corn stalks and wheat straw soda AQ pulps were recycled in the lab. Pulping of corn stalks resulted in a low pulp yield, low bonding strength, and low recyclability. Conversely, wheat straw fiber had a better yield, very good tensile properties, and showed a considerably better response to recycling. The tensile index of wheat straw fibers retained 67% of its original value after four cycles. It could be shown that recycling caused only small changes in chemical composition, but that the crystallinity index increased considerably. To be able to understand the behavior of wheat straw fiber as part of a commercial papermaking furnish, a paper containing 20% wheat straw fiber was produced on a 24 inch pilot paper machine and was recycled using a handsheet mold with white water return. Chemical analysis of the control (no wheat fiber) and the wheat-containing paper demonstrated slightly higher xylan content for the wheat-containing material. Recyclability increased slightly with addition of wheat fibers to a commercial furnish.

Keywords: Wheat, Corn, Recycling strength loss, Crystallinity index, Chemical composition

Contact information: a: Department of Bioproducts and Biosystems Engineering, University of Minnesota, 204 Kaufert Lab, St. Paul, MN 55108 ; b: Donaldson Company Inc. P.O. Box 1299, Minneapolis, MN 55440, c: Donaldson Company Inc., P.O. Box 1299, Minneapolis, MN 55440
**Corresponding author: ulrike@umn.edu*

INTRODUCTION

In recent years, non-wood fibers have been increasingly considered as a potential source of papermaking raw material (Paavilainen 1997, Kramer 1998). While there is a large body of information available regarding different pulping conditions and characteristics of these fibers, there is limited information on the behavior of non-wood fibers during paper recycling. In this paper we are focusing on recycling properties of fully bleached chemical fibers produced from corn stalks and wheat straw. It is well known that all chemical fibers show a significant loss in strength properties upon recycling (Szwarcsztajn 1996; Phillips 1994; McKee, 1991; Nazhad and Paszner 1994). It is generally accepted that the loss of strength in low yield pulps during recycling is caused by "hornification," a loss of wet fiber flexibility and bonding ability caused by self association of cellulose microfibrills during drying (Jayme 1958). While this effect was originally thought to be caused by the removal of lignin (Scallan 1992), several researchers have found that the xylans present in the pulp fiber have a distinct impact on recycling behavior of wood fiber (Cao et. al 1998; Aravamuthar 1998). In pulps with high levels of xylans, loss of pulp strength during recycling was reduced (Cao et. al 1998). Since non-wood plant material tends to have high xylan content, it was expected that these fibers might show a good potential for recycling.

There have been limited studies on recyclability of non-wood chemical fibers. In addition, these studies have used lab handsheets. For example, Garg and Singh (2004) studied recyclability of bleached chemical pulps from wheat straw and bagasse. While wheat straw pulps showed relatively less strength loss during recycling, bagasse fiber had a low recycling potential. Aravamuthan and Greaves (1998) studied recycling behavior of handsheets containing up to 30% of wheat straw fibers, the remaining materials being softwood kraft fibers. They found that the presence of wheat straw did not significantly alter the recycling potential but did not offer an explanation. Interestingly, in several cases the handsheets made with the mixed fibers showed higher strength than the 100% softwood fiber. It also was observed (Aravamuthar and Greaves 1998) that unbeaten wheat pulp had a better recycle potential than beaten wheat pulp.

As mentioned before, the few recycle studies available all have been based on handsheets. It is known that there is a significant discrepancy between machine-made paper and handsheets with regard to recycling behavior (Eastwood and Clarke 1978; van Wyk et al. 1982). To address some of these issues, we produced a commercial type paper, containing typical amounts of fillers and wet end chemicals, on a pilot paper machine. A control paper sample contained a mixture of hardwood and softwood fiber (70% HW, 30% SW), while in the trial runs 20% of the wood fiber was replaced with bleached wheat straw fiber (56% HW, 24% SW). Both the control and the wheat trial paper were not coated, but did contain 14% PCC (Precipitated Calcium Carbonate) as filler.

EXPERIMENTAL

Lab Experiments

For the handsheet experiments both corn stover and wheat straw were processed in an M/K digester with 12% NaOH and 0.1 % anthraquinone (AQ). The liquor to wood ratio was 10:1 and the maximum temperature was 160 ^{o}C. Cooking time was 90 minutes. The pulps were screened and bleached to 87.5% ISO brightness (wheat pulp) and 88.9 % ISO (corn stalks) using a DED sequence. All paper was recycled using a sheet mold with white water recirculation, discarding the first 10 sheets while building up fines concentration in the white water system. For each cycle a portion of the pulp was used to produce standard handsheets according to TAPPI Method T205, including pressing and restrained drying on drying rings under controlled humidity. These sheets were used for testing purposes only (not recycled). The remaining sheets were dried on a hot plate under restraint and were reslushed in a British disintegrator to be used for the next cycle. Tensile index, tear index, ash content, burst index, opacity and brightness were determined using standard TAPPI test methods T 220, T 211, and T 453. Data presented in this paper are average numbers of at least two repeats.

Pilot Plant Runs

Pulping of wheat straw for the pilot paper machine run was done in a rotary globe digester. The total fiber charge for each cook was 36 kg (based on dry fiber weight) at a liquor-to-wood ratio of 8:1. The chemical addition rate was 14% NaOH and 0.1 % AQ (based on o.d fibers). Time to temperature was 60 minutes and time at temperature was

35 minutes. A maximum cooking temperature of 160 ^{o}C was used. Pulp was bleached using a DED sequence. The pilot paper machine runs were conducted using a Fourdrinier machine with a wire width of 24 inches and a speed up to 200 ft/min. The selected control furnish contained a mixture of fully bleached softwood and hardwood chemical pulps at the ratio of 3:7. In addition, the furnish contained 14 % of precipitated calcium carbonate (PCC) and a typical mixture of wet end chemicals (internal size, starch, retention aid). For the trials with wheat fiber, 20 % of the fibers were replaced, retaining the ratio of softwood: hardwood. All other conditions were kept constant.

Analytical Procedures

Solid-state ^{13}C NMR was used to determine cellulose crystallinity. Cellulose shows separate signals for the C4 carbon of the glucose in crystalline regions of cellulose (88 ppm) and amorphous regions (84 ppm) (Liitiae et al. 2003, Witter et al. 2006), which makes it possible to calculate the crystallinity index based on the intensity of these two peaks. The NMR experiments were carried out on a Varian VNMR spectrometer (Palo Alto, CA) operating at a resonance frequency of 150.8 MHz for ^{13}C. The temperature was maintained at 25 ^{o}C and the spinning speed was regulated at 5 kHz ±3 Hz. Carbohydrate and Klason lignin analyses were performed using the HPLC procedure proposed by Sluiter et al. (2006). Fiber length was determined using an Optest^{TM} fiber analyzer. Fines content was determined using a Britt Jar and TAPPI Method T261.

RESULTS AND DISCUSSION

Recycling of Lab Handsheets

There was a distinct difference noticeable between corn stalk and wheat straw Soda AQ pulps. As seen before, the use of corn stalks in the pulping process results in a lower fiber yield (30%), as well as a shorter fiber length. The average length weighted fiber length for corn stalk pulp was determined to be only 0.43 mm. Wheat fiber showed an average length weighted fiber length of 0.9 mm, very similar to the fiber length of hardwood. As expected, this resulted in superior strength properties for wheat pulps (higher tear, tensile and burst index) (Table 1, Fig. 1). In addition, as the pulp was formed into handsheets and recycled, corn stock fibers showed a larger strength loss than wheat straw fibers (Fig. 2). The difference in recyclability increased with continued recycling. After the first cycle, paper produced from corn fiber retained 69% of its tensile strength and wheat fiber 73%. While the strength loss leveled off fairly quickly for wheat straw paper (at around 67% of the original tensile strength), corn fiber paper continued to lose strength in subsequent cycles and reached a total strength loss of around 50% after three cycles.

Due to the loss in bonding properties, tear index increased slightly during recycling for both corn and wheat straw fibers. While both pulp types started at a similar tear index of 4.8 and 4.9 mNm^2/g respectively, wheat pulp tear index increased up to 6.5 mNm^2/g, maintaining this value through cycle four. Corn pulp, on the other hand, reached a maximum at 5.5 mNm^2/g tear index and started to decrease at cycle three.

TAPPI Opacity increased for both pulps during recycling, most likely due to increased generation of fines.

Table 1: Properties of Bleached Corn and Wheat Straw Fiber during Recycling

	Tensile Index [kN/m]		Tear index [mNm^2/g]		Burst Index [kPa m^2/g]	
	Corn	Wheat	Corn	Wheat	Corn	Wheat
Starting	45.3	84.4	4.8	4.9	3.8	5.0
Cycle 1	31.4	61.4	5.0	6.2	2.5	5.0
Cycle 2	26.3	53.0	5.5	6.3	2.2	4.6
Cycle 3	23.2	57.4	4.5	6.5	2.0	4.8
Cycle 4		57.1		6.5		4.5

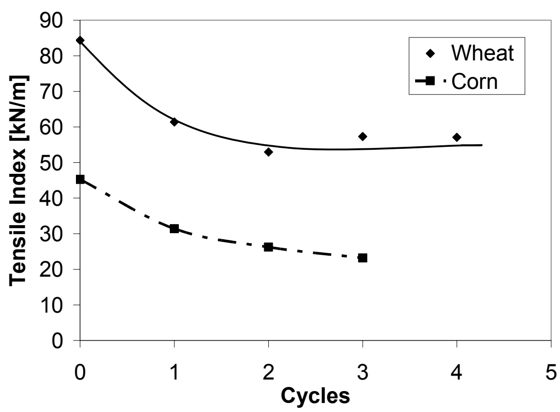

Figure 1. Tensile index changes during recycling of corn and wheat straw fiber

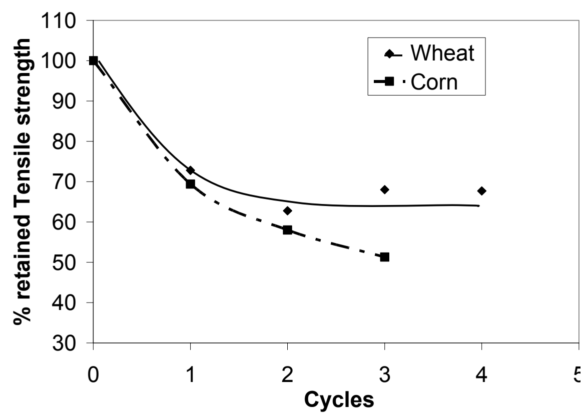

Figure 2. Loss of tensile strength properties during recycling of corn and wheat fiber

There have been discussions in the past regarding the significance of carbohydrate losses, specifically the loss of xylan during recycling (Sjöström et al. 1963; Eastwood et al. 1978; Bouchard et al. 1994; Cao 1997). Table 2 shows the chemical composition of bleached wheat straw fiber during recycling. All of these tests were run in duplicate.

No mannose could be detected during the analysis, and the Klason lignin content of the fully bleached pulp was below 0.5%. Examination of the bleached wheat straw fiber during recycling indicated a slight change in chemical composition, specifically during the first cycle. The glucan level increased from 68.1 % to 69.1% in the first cycle and reached 70.7 % during cycle four. While these differences are very small, they are statistically significant. Standard deviation for this test was determined to be +/- 0.25%. Xylan levels also increased slightly. This resulted in the fact that glucan/xylan ratio remained constant through all cycles.

It is generally accepted that the main reason for bonding strength loss during recycling is the effect called "hornification", a decrease in fiber flexibility caused by increased crystallinity. The crystallinity index of our wheat straw pulp was determined using ^{13}C NMR according to Liitiae and Witter. There was a significant increase in crystallinity index noticeable during recycling of wheat straw fiber. The crystallinity index increased from 38 % to 40.4% during the first cycle and showed a continuous increase to up to 49.7 % (Table 2). Clearly, changes in pulp fiber crystallinity index have a strong impact on the fibers during recycling.

Table 2: Chemical Composition and Crystallinity Index of Wheat Straw Pulp during Recycling

	Glucan [%]	Xylan [%]	Galactan [%]	Arabinan [%]	Crystallinity Index [%]
Starting	68.1	22.4	0.8	1.9	38.1
Cycle 1	69.1	23.7	1.1	2.1	40.4
Cycle 2	70.0	23.5	0.9	2.0	42.8
Cycle 3	70.0	23.1	0.8	1.0	48.3
Cycle 4	70.7	23.1	0.9	1.9	48.3
Cycle 5	69.9	22.9	1.0	2.1	49.7

Recycling of Pilot Plant Paper

The commercial type paper recycled for this part of our study was produced on a 24 inch pilot paper machine, using a softwood/hardwood furnish, filler, and wet end chemical levels typical for a commercial printing and writing grade paper. A control run used a fully bleached softwood and hardwood furnish (3:7 SW:HW ratio). For the wheat fiber trial, 20% of the wood fiber was replaced by fully bleached wheat pulp (replacement of equal amounts of softwood and hardwood). Since wheat straw produced with the above mentioned pulping and bleaching conditions continuously shows a very high tensile strength (Tschirner et al 2003), it was not surprising that the sample containing 20% wheat straw had a higher starting tensile index than the control.

As expected, we could observe a strength reduction for both the control and wheat-fiber-containing papers during recycling. As demonstrated in most other recycling studies, the drop was most dramatic during the first cycles (Figs. 4 and 5). The first cycle was especially important in our study, since only the first cycle used a paper formed on a paper machine. The following cycles were again using handsheets. Interestingly, the wheat-containing material not only started out at a higher strength property, but it also showed a lower percent reduction in strength (Fig. 5). Wheat-containing paper retained 86% of its original tensile strength and was able to maintain this level through the subsequent stages. The control paper retained only 82% of its tensile strength after stage one and continued to show strength reductions to levels as low as 75% of the original. As before, the recycling experiments were run in duplicate, and the tests showed a very good repeatability. For tensile strength, the difference between two independent runs was only 1-4%.

There was no significant difference in tear index or change in tear index between the two papers. Fines content for the control sample was determined to be 7%, while fines content for the wheat containing paper was slightly higher (9.4%). Neither fines content nor average fiber length of the samples changed significantly during recycling. Table 3 shows the chemical composition of both types of paper used for this study. It is well known that wheat straw fibers have high xylan and silica content, so it was not surprising to find that the wheat containing paper machine paper had a slightly higher xylan and ash content than the control. The slightly improved recyclability of material with wheat straw fiber content agrees well with Cao's conclusion that higher levels of xylan promote resistance to bonding strength loss during recycling. Clearly, wheat pulp fiber, if added to commercial papermaking furnish, has the potential to retain comparable or slightly better strength properties than wood-derived fiber.

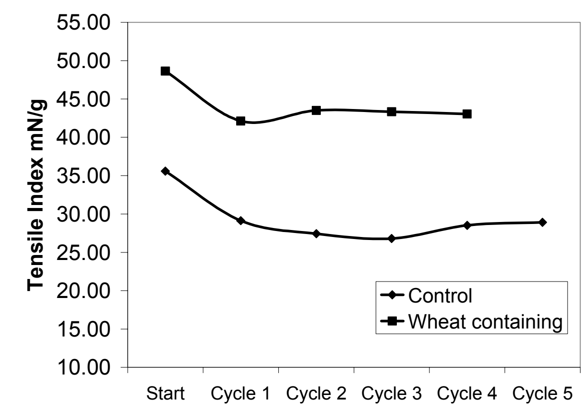

Figure 4. Changes in tensile strength during recycling of pilot plant paper

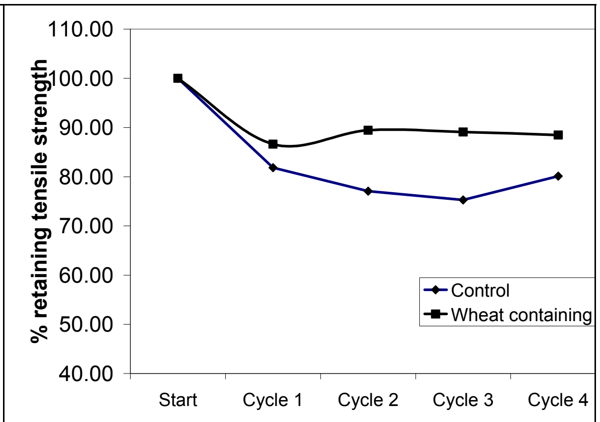

Figure 5. Percent tensile loss during recycling of pilot plant paper with/ without wheat fiber

Table 3. Chemical Composition of Control and Wheat-Containing Paper

	Control %	Wheat containing %
Glucan	71.2	70.1
Xylan	13.7	15.4
Galactan	0.0	0.0
Arabinan	0.4	0.7
Mannan	2.3	2.2
Lignin	0.4	0.4
Ash	7.7	8.5

CONCLUSIONS

1. Corn stover pulping resulted in unacceptably low pulp yield and up to 50% loss in bonding potential during recycling.
2. Wheat straw pulping produced pulp with high initial strength properties and greater resistance to strength loss during recycling.
3. The change in chemical composition of wheat straw during recycling was minor. The change in crystallinity index during recycling, on the other hand, was significant and clearly is the main contributor to loss in strength properties.
4. Commercial type paper produced on a pilot paper machine showed better resistance to strength loss during recycling than a control sample containing only hardwood and softwood fiber.

5. The improvement in strength retention during recycling of wheat-straw-containing fiber was most likely due to increased levels of xylan.

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