

Non-sulfur semichemical pulping of a red oak and wheat straw mixture

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ABSTRACT: The sodium carbonate (Na_2CO_3) semichemical delignification process was applied, using the same cooking conditions for all ratios of red oak and wheat straw. Increasing the wheat straw charge decreased the pulp yield (both total and screened), but the Klason lignin in pulp decreased only slightly. The degree of delignification, expressed as a percent of dissolved lignin, was significantly higher for wheat straw, compared to the red oak. The ratio between lignin and carbohydrates removal showed that the "solubility" of lignin and carbohydrates was similar for wheat straw during the delignification process.

Except for the apparent density and compressibility of the test handsheets, all properties of the pulp at 400 mL CSF increased up to a wheat straw charge of 30%-40%. A decreasing trend was evident when there was more than 50% wheat straw in the raw material mixture. Except for tear strength and compressibility, additional refining of wheat straw pulp (from 400 mL to 220 mL CSF) caused an increase in the strength properties to the level of 100% hardwood (red oak) pulp. The commercial semichemical pulp made from a mixture of hardwoods showed lower values for all strength properties, compared with the properties of laboratory red oak pulp, and much lower than those of wheat straw pulp additionally refined to a freeness of 220 mL CSF.

Application: Laboratory results suggest that wheat straw and hardwood chips can be pulped concurrently in sodium carbonate to produce a superior corrugating medium for board manufacture.

Unbleached semichemical pulp is the main raw material for corrugating medium production. Today, almost all corrugating medium in the United States is made from hardwood pulp and recycled fiber from old corrugated containers (OCC). In contrast to this, the world's largest semichemical, nonwood pulp mill (Zaragoza, Spain) uses pulp from wheat, rye, oat, and barley grain straw, along with secondary fiber (1, 2).

The neutral sulfite semichemical pulping process (NSSC) is most frequently used for the production of fluting for corrugating medium. To avoid the problems with the second stage of the chemical recovery system in NSSC pulp mills, pulping with green liquor instead of the regular sulfite cooking liquor has been tested (3). It is possible to produce pulp with mechanical properties similar to those of regular NSSC pulps, although the pulps obtained with green liquor contain more lignin at the same yield level. However, the residual lignin makes paper from this pulp very stiff, an important property for corrugating medium. Corrugating medium must have relatively high stiffness and resistance to crush, it must be inexpensive (4).

For many pulp mills, simpler, cheaper recovery systems and elimination of sulfur compounds from the cooking process were the incentives to introduce new, environmentally friendly delignification

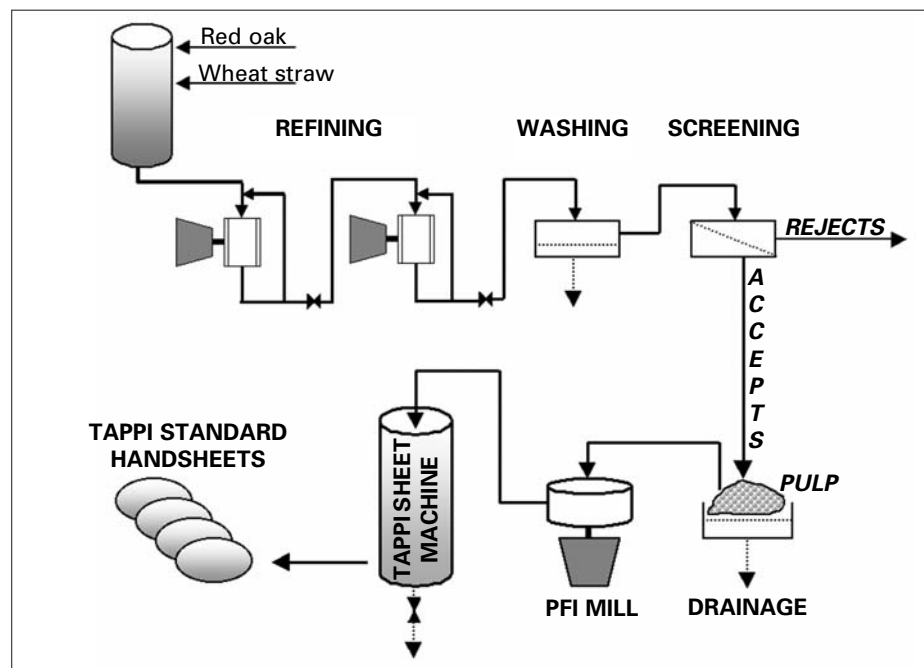
methods, e.g., the sodium carbonate process. Most U.S. and Canadian mills producing semichemical corrugating medium have replaced NSSC pulping with no-sulfur pulping since 1977. However, a few mills, including Owens-Illinois (Tomahawk, Wisconsin), which pioneered no-sulfur pulping in 1972, made the switch much earlier. Three major non-sulfur pulping processes are being practiced by semichemical mills: 1) the soda ash process, using sodium carbonate as the active pulping agent; 2) the Owens-Illinois process (O-I); and 3) the modified soda ash process, which uses a mixture of sodium carbonate and sodium hydroxide in different ratios. Spent liquor from the soda ash process has been successfully burned in a fluidized bed incinerator, and the recovered soda ash recycled back to the pulping process (5, 6).

Various chemical processes, including chemimechanical processes, are used for straw pulping. The lime or lime-soda processes are the classical methods for straw pulping and yield coarse pulps for the production of board, cheap packaging and wrapping papers, and corrugating medium. The soda, kraft, and neutral sulfite processes are employed for producing various types of pulps, ranging from high-yield semichemical to lightly bleached grades (7-9).

Wheat straw pulp is used primarily in blending with other kinds of pulp. Several reports show the beneficial effect of wheat straw pulp on the optical and strength properties of paper (10-13). Semichemical wheat straw pulp is used solely or in combination with waste paper to produce corrugating medium for boxboard manufacture. Other unbleached varieties, such as linerboard, test liners, machine-glazed (MG) imitation kraft, and grocery bags, are produced with straw pulp blended with long-fiber kraft pulp and selected wastepaper. Greaseproof papers, glassine, and toilet and other household tissue can be produced with up to 70% straw pulp. Excellent writing and printing papers and lightweight boards are produced using up to 80% bleached straw pulp in the fiber furnish. Due to the slow drainage of straw pulp and its short fiber length, addition of 15%-20% long-fiber wood pulp to the furnish assists greatly in operating the paper machine at optimum speed (7).

Wheat straw pulping with sodium carbonate as the sole cooking agent has been investigated on a laboratory scale (14). A bleachable grade of pulp from wheat straw, delignified with sodium carbonate, had similar strength properties to those obtained from kraft pulping at a similar yield (44%-45%) or kappa number (20-22.7). In one-stage carbonate pulping, when the lignin concentration and/or

PULPING



1. Scheme of laboratory-scale mix oak/wheat straw sodium carbonate delignification process.

alkalinity of the liquor are higher, lignin condensation reactions may occur. Thus, two-stage carbonate cooking (removal of the spent liquor or complete washing after the first stage) has been investigated, and a countercurrent process was suggested as being economically attractive. When sodium hydroxide (caustic) is used as a makeup chemical, its ratio to sodium carbonate (soda ash) is considered to be the critical factor, having a pronounced effect on the pulping properties, degree of delignification, refining horsepower, and pulp quality (5). Optimization of caustic-carbonate pulping of wheat straw for corrugating medium was carried out under laboratory conditions (15, 16). Refining energy was a constraint unless a higher caustic fraction (0.2) was used. Without the refining constraint, the caustic fraction could be reduced to near zero values. A beneficial effect of the high caustic fraction at low temperature and deterioration of strength properties at longer cooking times was also proven.

The lower lignin content in annual plants and agricultural residues, as well as the more open morphological structure compared to hardwoods and softwoods, allow milder cooking conditions and the application of a wider range of non-sulfur processes.

The objective of this study was to utilize existing pulping technology with a relatively simple recovery system (the sodium carbonate process), with complete or partial replacement of the wood with annual plants or agricultural residues as the raw materials. Another objective of this study was to evaluate the strength properties of laboratory-prepared pulps, including the basic delignification characteristics of the sodium carbonate cooking process with respect to different ratios of wheat straw to red oak wood. In addition to the strength properties, other papermaking characteristics (refining energy, drainage, etc.) were of interest. The laboratory pulps were compared with commercial, semichemical hardwood pulp for corrugating medium.

EXPERIMENTAL

Raw material. Northern red oak (*Quercus rubra*) chips from Michigan were manually sorted. Selected chips, fresh and nondried, of approximately 2.0 x 2.5 x 0.3 cm, were used in the experiments. Wheat straw (*Triticum aestivum*) from the 1998 Michigan harvest was cut into 3-5-cm-long pieces and hand cleaned of sand and debris prior to pulping. The pieces of whole stems were used in the pulping experiments.

In addition to the pulps prepared in the laboratory, one sample of commercial sodium carbonate hardwood pulp was tested. This sample was screened on a laboratory slotted screen and beaten to a freeness of 400 mL CSF in a PFI mill (described below).

Chemical analysis. Basic chemical analysis and the moisture content in all samples were performed according to TAPPI Test Methods. The results obtained are shown in Table I.

Delignification. All cooks of the screened red oak chips, wheat straw, and of the mixtures were performed in a 6.5 L stationary batch digester (M&K Systems, Inc.) equipped with an electrical heat exchanger and a liquor circulation system. The following conditions were maintained: Na_2CO_3 charge [as sodium oxide (Na_2O)], 10% on o.d. material; liquor-to-wood (straw) ratio, 1:7; cooking temperature, 174°C; time to temperature, 25 min; time at temperature, 30 min. Each cook with a different wheat straw charge was performed twice. In the first set of the cooks, raw materials were well mixed before the cooking. In the second set, red oak chips and wheat straw were separated within the digester by a stainless wire. Separately cooked materials were used for the chemical and morphological analysis of the individual pulps (not included in this article).

Refining. High-yield pulps were refined immediately after cooking. The refining of the unwashed pulps was performed in the laboratory with a Bauer disc refiner (two cycles performed by varying the clearance between disks). The following refining was performed with the laboratory MEAD disc refiner with circulation of pulp stock for 20 sec at a consistency of approximately 1.5%.

To achieve the desired level of freeness (400 mL CSF), beating of the pulps was performed in a PFI laboratory mill at a consistency of 10%. Because the initial freeness of the 100% wheat straw sample before being beaten in the PFI mill was already 400 mL CSF, additional beating to 220 mL CSF was performed. Both samples, 400 and 220 mL CSF, were used to make handsheets.

Screening. The pulps after secondary refining were screened on a laboratory vibratory slotted screener. The accepts were collected on a 150-mesh screen and stored in cold room at a consistency of

approximately 30%. Total yield, screened yield, and rejects were determined.

Pulp testing. To evaluate the strength properties of the pulps, TAPPI standard handsheets with a basis weight of 60 g/m² were prepared and conditioned at standard conditions. For the ring crush test, handsheets with a basis weight of 130 g/m² were prepared. All tests were performed according to TAPPI Test Methods.

The scheme of the laboratory-scale delignification process is depicted in **Fig. 1**.

RESULTS AND DISCUSSION

Delignification experiments

The sodium carbonate semichemical delignification process was applied to produce fluting, using the same cooking conditions for all ratios of red oak and wheat straw. After screening the samples, rejects and the amount of Klason lignin in the accepts were determined. The pulp yield (both total and screened) decreased with a higher charge of wheat straw in the mixture. Screened yield had the same trend (**Table II**). The results obtained were not surprising because of the more open structure of wheat straw and the penetration conditions for the cooking chemicals. Hardwood chips have a comparatively denser structure and resist penetration by pulping chemicals. The screened yield for the 100% wheat straw was too low for production of corrugating medium. Thus there was an opportunity to optimize the delignification process and remove these shortcomings.

The amount of residual lignin and carbohydrates (mainly hemicelluloses) plays a substantial role in the properties needed for corrugating medium. Therefore, the Klason lignin in the accepts after screening was determined. The degree of delignification (DL in %) was calculated according to Eq. 1:

$$DL (\%) = 100 - (Y \cdot KL / KL_o) \quad [1]$$

where KL_o is the content of Klason lignin (%) in the raw material (red oak, wheat straw, or their mixtures), KL is the Klason lignin (%) of the pulp sample, and Y is the cooking yield (%).

While the values of Klason lignin in both red oak and wheat straw, as the raw materials, were analytically determined, the values of Klason lignin in their mixtures (KL_o) were calculated based on their proportions. From the results obtained (**Table II**) and plotted in **Fig. 2**, it was evident that the rate of delignification of wheat straw appeared to be significantly higher compared to the red oak alone. This resulted in the fact that the Klason lignin value in the wheat straw pulp was lower than the amount determined in the red oak pulp or in the mixed pulps.

Values of Klason lignin and pulp yield allow calculation of the lignin/carbohydrate ratio (L/C), the ratio of percent of lignin and carbohydrate dissolved. This ratio was calculated according to Eq. 2:

$$L/C (\%) = ((100 - (Y \cdot KL / KL_o)) / ((100 - Y \cdot (100 - KL) / (100 - KL_o))) \quad [2]$$

where the symbols are identical to the symbols in Eq. 1.

Results based on Eq. 2 are shown in **Fig. 3**. When red oak alone is delignified, the percent of lignin dissolved is more than

ANALYSIS		RED OAK	WHEAT STRAW
Moisture	%	30.1	8.3
EtOH-Benzene extract	%	5.2	3.7
Klason Lignin*	%	23.7	18.3
Total Ash*	%	0.4	5.3

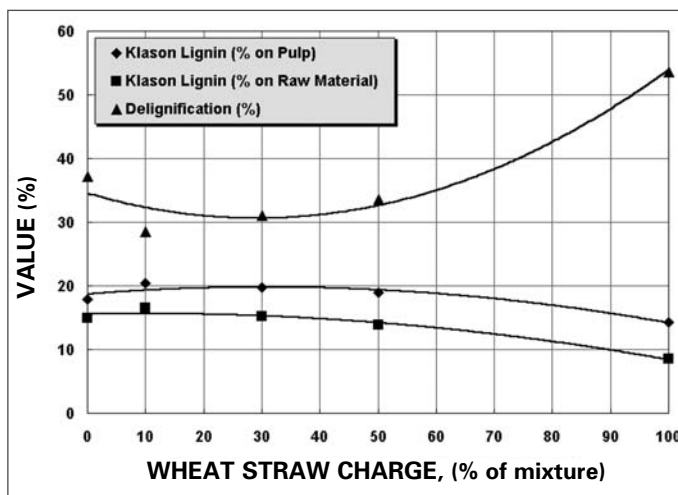
* extractive-free material basis

I. Chemical composition of raw materials.

CHARGE OF					KLASON
RED OAK	WHEAT STRAW	YIELD		REJECT*	LIGNIN
(%)	(%)	TOTAL	SCREENED	(%)	(% ON PULP)
100	0	83.3	78.9	4.4	17.9
90	10	81.1	77.0	4.1	20.5
70	30	77.1	73.5	3.6	19.8
50	50	73.4	70.2	3.2	19.0
0	100	59.3	57.9	1.4	14.3

* reject at 0.006" vibratory slot screen

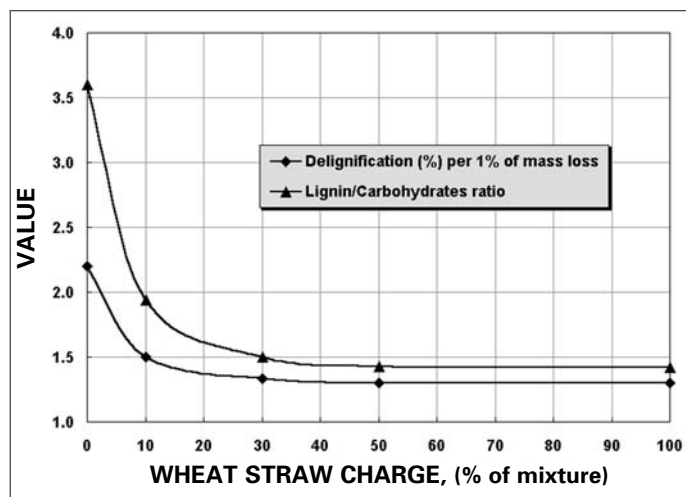
II. Yield, rejects, and Klason lignin for laboratory delignification experiments.



2. Klason lignin and delignification efficiency.

3.5 times higher than the percent of carbohydrate dissolved. Lignin is being removed more selectively. It was evident that with up to 30% of wheat straw in the mixture, this ratio decreased and reached a value of approximately 1.5. When wheat straw was delignified alone, the L/C ratio reached the value 1.4. This means that during the delignification of wheat straw alone, the extent of lignin and carbohydrates removal was very similar. Higher delignification selectivity of 100% red oak compared with the 100% wheat straw cooking is evident also from the curve depicting delignification (%) per 1% of mass loss.

The results were supported by the fact that wheat straw contains less cellulose than wood, but the total holocellulose (cellulose plus hemicelluloses) content is almost the same. A lower content of cellulose is counterbalanced with a higher content of hemicelluloses, mainly pentosans, which are easily



3. Selectivity of lignin vs. carbohydrates removal.

SAMPLE	FREENESS (ML CSF)		PFI COUNTS (REV.)
	INITIAL	FINAL	
Mixed HW commercial	735	400	5700
0% Wheat straw	700	400	3000
10% Wheat straw	680	400	2950
30% Wheat straw	655	400	2200
50% Wheat straw	635	400	2000
100% Wheat straw	400	400	0
100% Wheat straw	400	220	1500

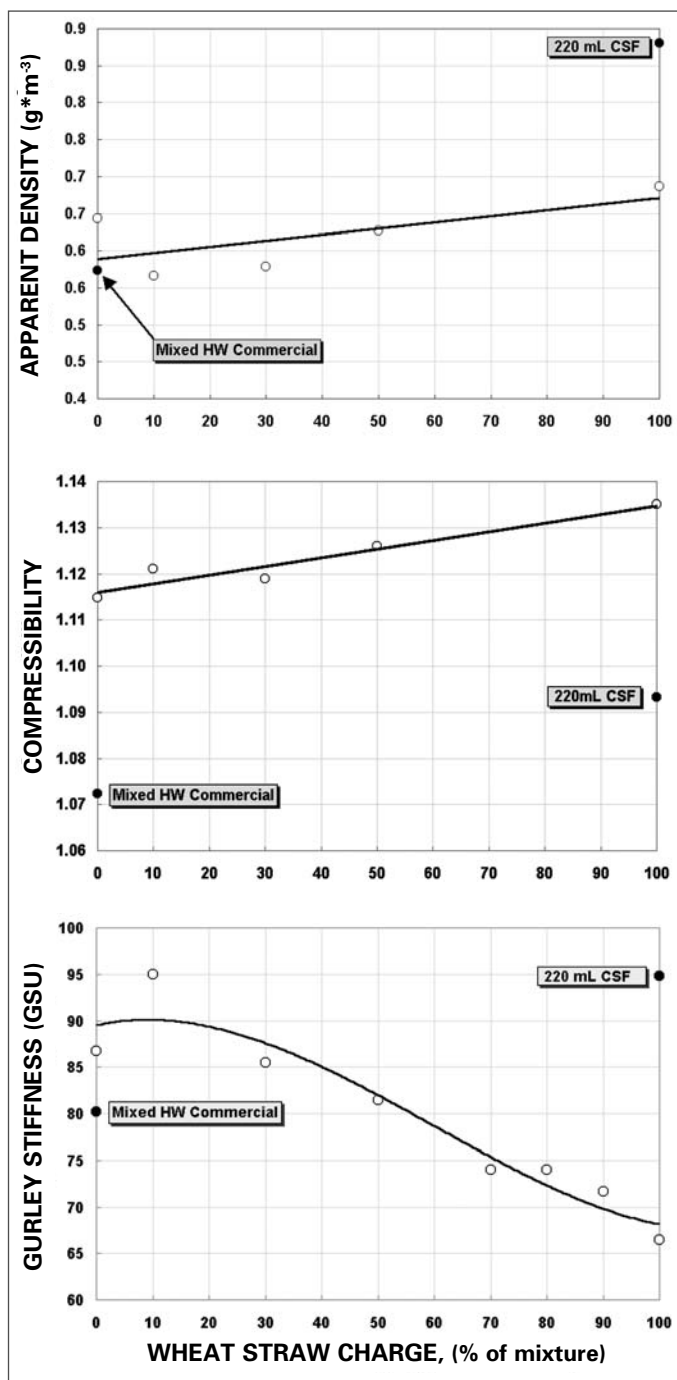
III. Refining of mixed red oak-wheat straw pulps in the PFI mill.

dissolved and extracted with alkali. All of these phenomena result ultimately in a decreasing pulp yield with an increasing charge of wheat straw into the furnish at relatively stable values of Klason lignin in the pulps.

Pulp testing

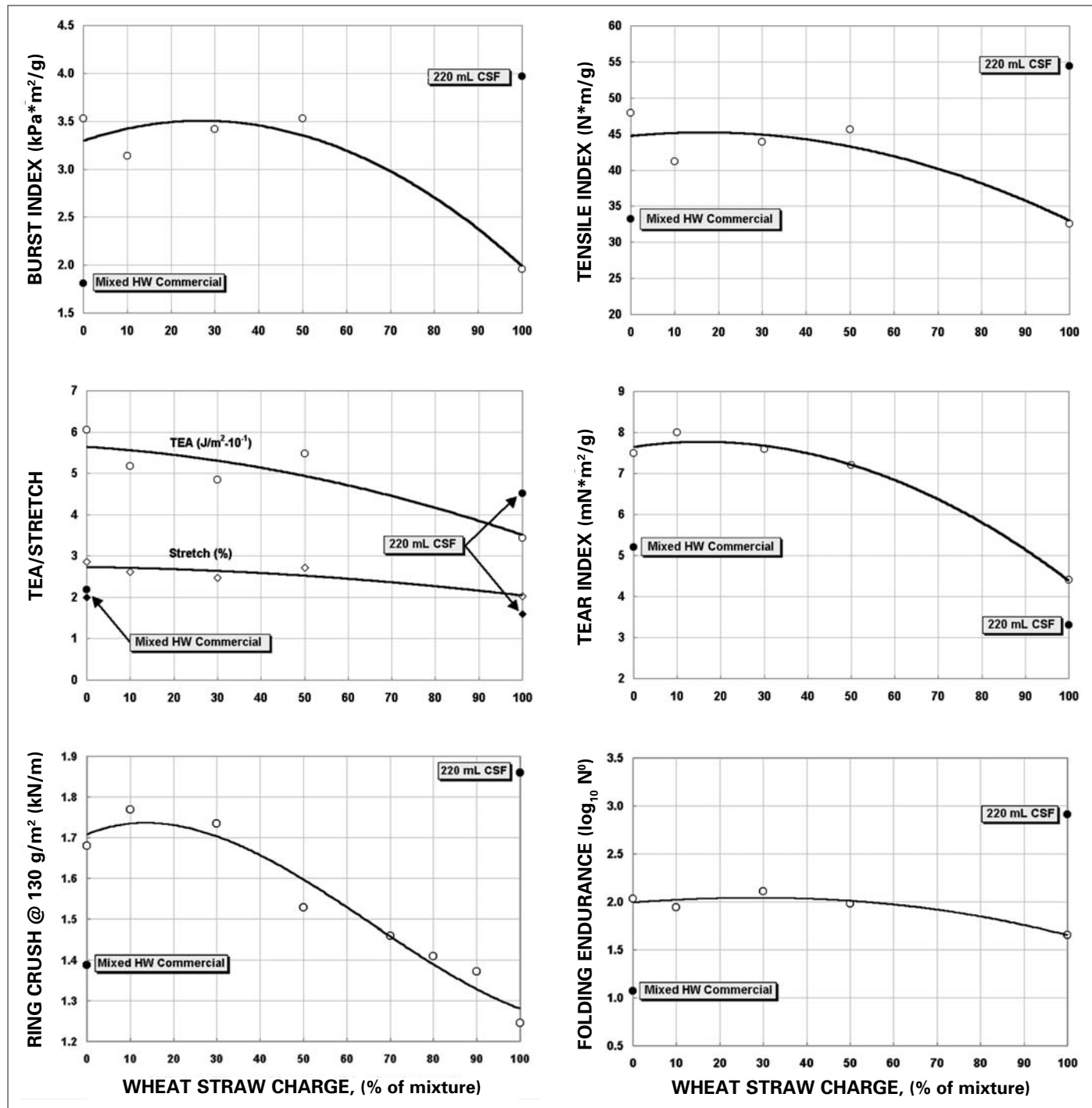
The strength properties of the pulps as a function of the wheat straw charge were evaluated and compared at the same freeness, 400 mL CSF. This decision was made to simplify the experimental design.

The amount of refining in a PFI mill, to obtain the same level of freeness (400 mL CSF), was reported as the number of revolutions. Although the results shown in Table III are not directly comparable to commercial scale refining, the relative results were considered valid. Two facts from this table are evident. First, freeness after the refining decreased with an increasing charge of wheat straw. Up to a 50% charge of wheat straw in the raw material furnish, the decrease in freeness was very moderate, being only 9.3% (from 700 to 635 mL). The protection of wheat straw fibers by the more resistant wood chips during the disintegration/refining is a possibility. Because the freeness of wheat straw pulp before refining in PFI mill was already 400 mL CSF, additional refining to a freeness of 220 mL was done. Second, the refining energy to achieve desirable freeness of 400 mL CSF decreased with an increasing charge of wheat straw in the raw material mixture.



4. Effect of wheat straw charge on properties (nondestructive tests) of the pulps @ 400 mL CSF.

Strength properties of pulps from grass and agricultural residues, with the exception of the comparatively strong bamboo pulps, are generally inferior to wood pulps. The pulp qualities naturally vary with the raw material, the pulping process, and the conditions chosen. There are two major pulp categories. One is unbleached, coarse semichemical pulps for cheaper grades of paper and boards, such as corrugating medium, egg case filler board, and cheap packaging papers, where strength is not essential. The other is semibleached/bleached semichemical



5. Effect of wheat straw charge on strength properties of the pulps @ 400 mL CSF.

or chemical pulps for glassine and fine papers. In the former category, the yellow-straw pulp made by the lime or alkali processes predominates, and this is the largest use for straw pulps so far.

In this study, the delignification process for semichemical fluting production was evaluated, and the tests impor-

tant for evaluation of fluting quality were performed, including pulp stiffness, and the ring crush test. Other strength properties important for chemical pulps were also tested. All are plotted in Figs. 4 and 5. Except for the apparent density and compressibility of the test handsheets, all properties increased up to a wheat straw

charge of 30%-40%. A decreasing trend was evident when there was more than 50% wheat straw in the raw material mixture. The reason could lie in the refining process, which was not optimized for wheat straw pulps. It is evident that refining the wheat straw to freeness 220 mL CSF produced higher strength properties

SAMPLE	EMC(%)
Mixed HW commercial	7.9
0% Wheat straw	6.4
10% Wheat straw	6.4
30% Wheat straw	6.8
50% Wheat straw	6.7
100% Wheat straw	7.3

IV. Equilibrium moisture content (EMC) of test handsheets.

than 100% wood pulp. The exception is for tear strength and compressibility, which generally decrease after additional refining.

The ring crush test was done on samples with a basis weight of 130 g/m². Equilibrium moisture contents (EMC) of the conditioned samples are shown in Table IV. Increasing the charge of wheat straw in the raw material causes a moderate increase in the EMC values, but the pulp from wheat straw never reached the value of commercial mixed hardwood pulp.

The properties of the laboratory pulp samples were compared with those of commercial pulp made from a mixture of hardwoods. The results differed from those in other studies, presumably because of differences in the laboratory conditions, pulping process [a noncommercial process (sodium carbonate) for agricultural residues and annual plants], and the choice of hardwood (red oak). Samples of the commercial semichemical pulp were taken after brownstock washing (chemiwasher), then screened and refined to a freeness of 400 mL CSF. The results plotted in Fig. 4 show lower values of all strength properties in the commercial pulp compared with the properties of the laboratory red oak pulp, and much lower than those of wheat straw pulp refined to a freeness of 220 mL CSF.

CONCLUSIONS

The sodium carbonate semichemical delignification process commonly used to produce fluting for corrugating medium was applied in the laboratory to produce pulps from different ratios of wheat straw and red oak chips. The same cooking conditions for all ratios of red oak and wheat straw were used. Increasing the wheat straw charge reduced the pulp yield, both total and screened. The same trend was found for rejects. The Klason

lignin in the pulp decreased only slightly. The degree of delignification, expressed as percent of dissolved lignin, was significantly higher for wheat straw than for the red oak. The ratio of lignin-to-carbohydrates removal showed that the solubility of lignin and carbohydrates for wheat straw was very similar during the delignification process. This indicated a lower lignin selectivity for wheat straw, leading to the lower yield of wheat straw pulp.

Except for the apparent density and compressibility of the test handsheets, all properties of the pulp at 400 mL CSF increased up to a wheat straw charge of 30%-40%. A decreasing trend was evident when there was more than 50% of wheat straw in the mixture of raw materials. Except for tear strength and compressibility, additional refining of wheat straw pulp (to 220 mL CSF) caused an increase in the strength properties to the level of 100% hardwood (red oak) pulp. The commercial semichemical pulp made from a mixture of hardwoods shows lower values for all strength properties compared with the properties of laboratory red oak pulp, and much lower than those of wheat straw pulp after additional refining to a freeness of 220 mL CSF. **TJ**

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