Peroxyformic acid pulping of nonwood plants by the MILOX method

Part 2: Reed pulp for woodfree fine papers

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ABSTRACT

Peroxide-bleached Common reed (Phragmites communis) MILOX pilot pulp was used for laboratory-scale papermaking together with birch and pine kraft TCF mill pulps. Fiber furnishes contained 30% pine pulp and varying amounts of birch and grass pulps. From 30% to 50% of the short fiber material in the paper can be replaced with grass MILOX pulp without sacrificing paper strength. If the emphasis is on the optical properties, the proportion of grass pulp can be increased to nearly 70%. Bulk is increased with the grass pulp.

Application:

Pulps made from agricultural grassy crops can partially replace hardwood pulps in producing writing grades of paper with good strength and optical properties.

In Finland, short-fibered wood material for pulp production has been in short supply. On the other hand, agricultural crops are being produced in abundance. Not surprisingly, agricultural plants have been considered as a potential source of fiber. Nonwood fibers are quite different from wood fibers however. These differences affect the properties of the pulp as well as the properties of the paper made.

Nonwood raw materials contain less fiber than wood contains because of large amounts of nonfiber components that constitute the fines. In some species, the fiber length is about one third that of softwood fiber, and the nonfiber cell content is about 20 times greater *(1)*.

Understandably, strong paper cannot be made from grass pulps alone. By using grass pulp together with wood pulp, however, papermakers can combine the high strength and drainability of wood pulp with the better formation and superior optical properties of nonwood pulp.

In this work, the papermaking potential of MILOX grass pulp in fine papers was studied. The aim was to find the optimum amount of MILOX grass pulp that can be used instead of TCF birch kraft pulp in fine paper without any major impact on most of the paper properties.

BACKGROUND: COOKING METHODS FOR NONWOOD FIBERS

Traditionally, the cooking methods used for nonwood fibers have been the alkaline soda and kraft methods. Both methods yield pulps with good papermaking properties but involve problems with silicates during the recovery of the cooking liquors *(2)*. In the past few years, several new pulping methods for nonwoods have been introduced, including two using peracids as cooking chemicals *(3, 4)*.

One such method is the MILOX pulping method, in which formic acid and hydrogen peroxide are used as cooking chemicals *(3)*. The MILOX method includes two stages. In the first stage, the grass is subjected to cooking with formic acid alone, and in the second stage, cooking is carried out with a mixture of formic acid and hydrogen peroxide.

The MILOX method is suitable for several Nordic nonwood species. The optimum cooking parameters for these species can be found by changing the cooking time and temperature in the first stage. The main advantage of the MILOX method is that it can use the same chemical recovery system used for processing spent liquors from the pulping of wood. The silicon compounds in grasses remain in the pulp during the acidic cook rather than being released into the cooking liquor.

Another advantage is the excellent reactivity of the pulp towards alkaline hydrogen peroxide. High brightness can be achieved in bleaching with only two or three peroxide stages. In the alkaline bleaching stages, most of the silicon compounds dissolve. Depending on the target brightness, the silicon left in the pulp amounts to only 100–400 ppm *(3)*.

EXPERIMENTAL PROCEDURES

Pulps

Pulp from Common reed *(Phragmites communis)* was prepared on the pilot scale in a joint research project with Chempolis Oy (100–150 kg grass, dry matter 80–90%) using the two-stage MILOX method. As mentioned, grass is cooked first with formic acid alone and then with a mixture of formic acid and hydrogen peroxide.

Cooking times and temperatures were 75 min at 120°C and 1 h at 80°C in the first and second stages, respectively. In the second stage, the time to maximum temperature was 2 h. Hydrogen peroxide at 2.5% on grass was used in the second stage, and the liquor-to-grass ratios were 8:1 and 4:1 in the first and second stages, respectively.

Bleached pine and birch kraft pulps were supplied by a Finnish pulp mill. The totally chlorine-free (TCF) bleaching sequences included an ozone stage.

Test point	Grass pulp, %	Grass pulp, MJ/ton	Birch pulp, MJ/ton
1	0	100	200
2	25	100	200
3	50	100	200
4	75	100	200
5	100	100	200
6	0	100	400
7	25	100	400
8	50	100	400
9	75	100	400
10	0	100	600
11	25	100	600
12	50	100	600
13	75	100	600
14	25	400	200
15	50	400	200
16	75	400	200
17	100	400	200
18	25	400	400
19	50	400	400
20	75	400	400
21	25	400	600
22	50	400	600
23	75	400	600
24	50	400	200
25	50	400	200

Pine pulp: 30% of fibers, 600 MJ/ton.

I. Experimental program showing grass pulp as a percentage of total short fiber and showing refining energies for grass and birch pulps at each test point

	Unbl.	Bleached
Kappa number	28.1	0.65
Viscosity, dm^3/kg	760	730
Brightness, %	31.8	87.3
Carbohydrates, %	93.2	100
Dichloromethane extractives, %	0.47	0.06

II. Properties of unbleached and bleached Common reed MILOX pulp

Bleaching

The reed pulp was subjected to chelation in the laboratory at 60°C for 60 min to eliminate the effect of metal ions originating from the grass itself or introduced into the pulp from the process waters prior to the peroxide stages. The consistency in the chelation stage was 3%. EDTA was charged at 0.2% on pulp. The pH was set between 4.5 and 5.0.

The peroxide stages were carried out with the pulp at medium consistency in a rotating fiberglass vessel placed in an air bath at 85°C. The reaction times were 2 h in the first stage and 4 h in the second stage. Radical reactions were inhibited with 0.2% DTPA and 0.2% $MgSO_4 \cdot 7H_2O$ on pulp. The peroxide charges were 3% and 2% in the first and the second stages, respectively. The final pH was 10.0–10.5.

Carbohydrate analyses

The polysaccharides were hydrolyzed to monosaccharides *(5)*. The quantity of monosaccharides was determined by anion exchange chromatography with pulsed amperometric detection.

Morphological analyses

Fiber widths and cell wall thicknesses were measured using a light microscope connected to a Vidas image analyzer. The equipment is not fully automated. A Kajaani FS 200 was used to measure the fiber length and coarseness.

Refining

Pulps were refined with both a PFI mill and an Escher Wyss laboratory refiner. In Escher Wyss refining, we used a specific edge load of 2 J/m for both the birch and pine pulps at 4% consistency and a load of 1 J/m for the grass pulp at 6% consistency. Based on prerefining experiments, we chose a single refining energy for pine pulp (600 MJ/ton), three different refining energies for birch pulp (200, 400, and 600 MJ/ton), and two refining energies for grass pulp (100 and 400 MJ/ton).

Pulp mixtures

Paper handsheets were prepared containing 30% pine pulp along with birch pulp and grass pulp in different proportions. The 25 test points of the experimental program, including three replicates, are listed in **Table I**. For each test point, the table presents the amount of grass pulp used as a percentage of total short fiber. The refining energies for each test point are also given for the grass and birch pulps. ISO standard procedures were used for testing the paper handsheets.

Statistical analyses

Based on the results from handsheet testing, regression models were constructed to describe the relationships between the measured paper properties and the process variables included in the experimental program. Optimization with the regression models was achieved by emphasizing either the strength properties or the optical properties of the paper.

RESULTS AND DISCUSSION

Morphology and pulp properties

The harvesting time, the geographical location, and the population affect the morphology and chemical composition of the grasses, which can also be affected by plant breeding. The chemical and physiological composition changes as the plant develops *(6)*; as a result, pulping properties also change with the harvesting time.

The pulp yield increases as the plant matures, with the highest yields being achieved if harvesting is delayed until the following spring. Both the stalks and leaves of reeds are used for papermaking in Asia, but the leaves have a low fiber content and are rich in parenchyma cells *(1)*. The fibers are located chiefly in the stalk. It would be beneficial for the pulp properties, as well as for chemical consumption, to delay the harvesting time until the following spring or to fractionate the raw material prior to cooking to remove the leaves.

	Common reed	Wheat straw[a]	Birch[b]
Fiber length, mm			
Raw material	0.7	1.4	1.2
Unbleached pulp	0.5	0.8	0.9
Fiber width, µm			
Raw material	…	15	14–34
Unbleached pulp	12	…	25
Cell wall thickness, µm			
Raw material	…	…	5
Unbleached pulp	4	…	3
Coarseness, mg/m			
Raw material	0.07	0.09	…
Unbleached pulp	0.13	…	0.10
Fines, %			
Raw material	45	…	…
Unbleached pulp	55	40	13

[a]Refs. 6 and 12.
[b]Refs. 6 and 13.

III. Morphological properties of Common reed (stem + leaves), wheat straw (stem), and birch

Mesh	MILOX reed pulp, %	Wheat straw soda pulp,[a] %	Birch kraft pulp,[b] %
> 30	2-3	3-10	22
30-200	67-70	62-78	62
< 200	28-30	15-35	16

[a]Values from Refs. 8, 9, and 14.
[b]Values from Ref. 8.

IV. Bauer-McNett distributions for the MILOX reed pulp, wheat straw soda pulp, and lightly beaten birch kraft pulp, all unbleached

The Common reed used in these experiments originated from the Oulu area in the north of Finland and was harvested in autumn 1994. The raw material was not fractionated prior to cooking. The grass was pulped with the two-stage formic acid–peroxyformic acid method on the pilot scale. The kappa number of the pulp was 28, which was higher than that obtained for a laboratory pulp, even under milder pulping conditions *(3)*. On the pilot scale, more efficient washing would probably result in lower kappa numbers *(7)*.

The total carbohydrate content of the grass MILOX pulp was 93.2% (**Table II**). The pulp carbohydrates were composed of 96.0% glucose and 4.0% xylose. Most of the hemicelluloses had dissolved during pulping. The hydrolyzing effect of formic acid depends to a great extent on the temperature and duration of the acid stage *(7)*—the first pulping stage in the case of grasses.

Because it is difficult to determine the yield of a pilot cook accurately, the same cooking conditions as were used for the same raw material in the laboratory. The yield in the laboratory MILOX cook was as high as 43.2% (kappa no. 12.4), and the yield can be expected to be even higher if the grass were harvested in the spring. The MILOX pulp was bleached to high brightness (87.3%) and low kappa number (<1) in a two-stage peroxide bleaching sequence. The decrease in pulp viscosity during bleaching was negligible (Table II). The extractives content of the bleached pulp was low.

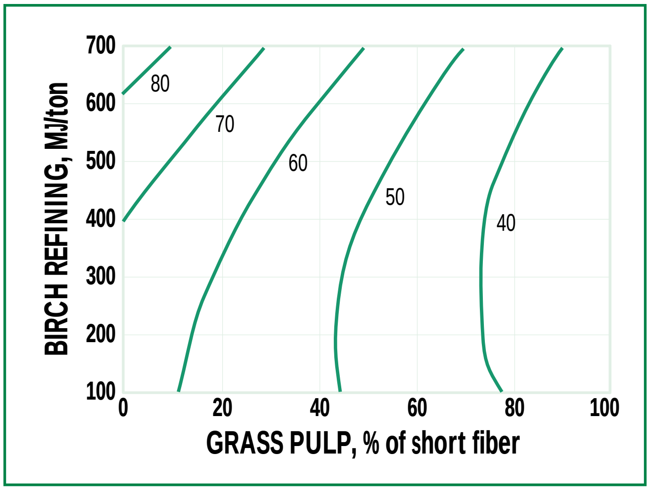
Table III presents the dimensions of the fiber raw material and unbleached MILOX pulp. For the sake of comparison, values are also listed for some other short-fibered raw materials and their corresponding unbleached pulps. Because both the stalk and the leaves of the raw material were used in pulping, the fiber length was determined for unfractionated material. The length-weighted length of Common reed fibers is half of that of birch fibers, mainly as a result of the high fines content of the leaves. The high amount of fines (with fiber length less than 0.20 mm) in the raw material is also attributable mainly to the high fines content of the leaves.

Compared to birch kraft pulp fibers, the fibers of Common reed MILOX pulp are short and narrow. The cell wall thicknesses of the two pulps are similar. As seen under a light microscope, Common reed pulp fibers are round, which made it difficult to determine the cell wall thickness. Common reed MILOX pulp is also slightly more coarse than wheat straw pulp and birch pulp. The amount of fines in MILOX pulp is fairly high, which is a typical feature of nonwood pulps. Delaying the harvesting time or fractionating the raw material would probably lower the amount of fines in the pulp.

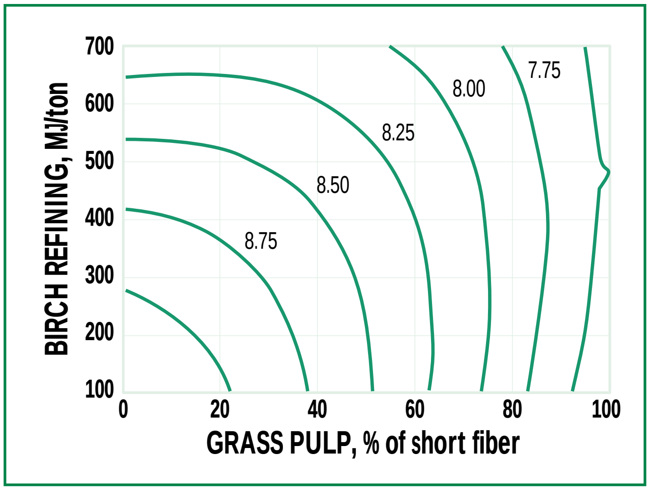
The Bauer–McNett distributions of **Table IV** also show a high amount of fines particles in Common reed and wheat straw pulps, compared to the birch pulp. The fiber fractions of the MILOX pulp are similar to those of wheat straw pulp made by the alkaline soda method *(8)*. Nonwood pulps have considerably more fines and less long fiber than birch kraft pulp has. The reason is that nonwood pulps have a high content of nonfibrous cells, even though some of the nonfibrous material is probably removed in the pulping process *(8)*.

Nonwood pulps show a high degree of swelling. The water retention values (WRV) are high for the Common reed pulp (169% at a Schopper–Reigler number of 26°SR) and straw pulp (176–210% at 34–42°SR) *(8, 9)*. The high fines content may be mainly responsible for the high water retention value of the pulps *(9)*, because the unfractionated whole straw pulp has a much higher water retention value than the fiber fraction of the same pulp.

Another reason for the swelling of wheat straw soda pulp is its high hemicellulose content *(9)*. Common reed MILOX pulp had a fairly low hemicellulose content, which may explain the difference in the water retention values of the two nonwood pulps. The pronounced swelling of nonwood pulps and short fibers with



1. Response of tensile index, in N•m/g, to the percentage of MILOX pulp added and the refining of birch kraft pulp



2. Response of tear index, in mN•m²/g, to the percentage of MILOX pulp added and the extent of the refining of birch kraft pulp

large specific surface area together results in slow drainage of nonwood fiber pulps *(10)*.

Papermaking properties of the pulp

To improve paper quality, the fibers should be treated mechanically. Therefore, three unbleached Common reed MILOX pilot pulps were subjected to PFI beating. At a tensile index of 50 Nm/g, the pulps ranged from 3.8 mN x m^2/g to 4.1 mN x m^2/g in tear index. Out of these three MILOX pulps, the one with the best strength properties was the one we chose for further experiments.

Common reed MILOX pulp showed no visible external fibrillation on the fiber surfaces after beating, as verified by light microscopy. On the other hand, the number of wrinkles and microcompressions increased with increased beating. The generation of wrinkles and microcompressions points to greater fiber flexibility *(9)*. No obvious external fibrillation has been reported during the beating of other grass and straw pulps either. The lack of observable external fibrillation is probably attributable to the morphological structure of the fibers. In general, grass fibers have relatively thick walls and a small lumen. The fibrils in the S_1 layer are arranged laterally like a protective shell around the fiber, shielding the fibrils of the S_2 layer from the action of the beater *(1)*. However, internal fibrillation of grass fibers occurs more easily than in wood fibers *(1)*. In general, paper made from nonwood fiber pulps is stiff and smooth but not strong. Furthermore, it is more brittle and is less stable in water than paper made from wood fibers *(11)*.

KEYWORDS
Betula, carboxylic acids, formic acids, grasses, nonwood fibers, paper grades, peroxy acids, pinus, phragmites, plant fibers, properties, pulping, reeds.

Bleached Common reed MILOX pulp (87.3% brightness), birch kraft TCF pulp (83.9% brightness), and pine kraft TCF pulp (83.4% brightness) were subjected to beating in an Escher Wyss laboratory refiner to find the optimum beating conditions to be used in the furnish experiments. Unlike the unbleached pulp, the Schopper–Reigler number of the bleached grass pulp did not increase substantially during beating. Because slight beating of the pulp (specific edge load of 1 J/m) improved its strength properties somewhat, two levels of beating were used for grass pulp in the final experiments (100 and 400 MJ/ton of refining energy).

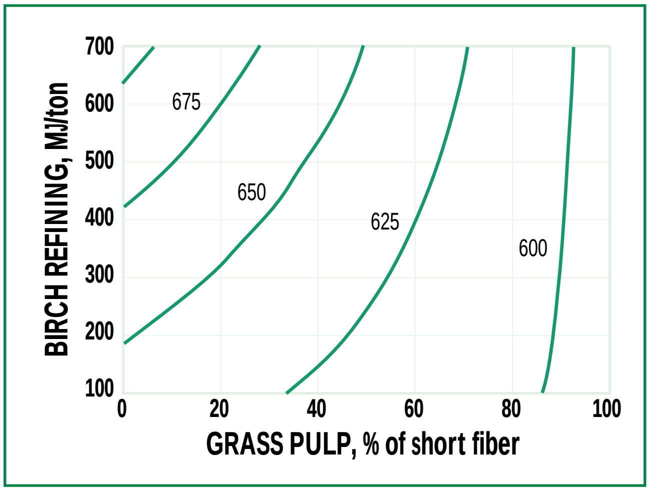
The tensile index of the bleached grass pulp was considerably lower than that of the birch pulp and that of the pine pulp. Although the grass pulp did not reach its maximum tear index, the value was only slightly lower than the tear index of the birch pulp. In nonwood pulps, the fines particles are probably poorly bonded to fibers, which affects the strength properties of the paper. The optical properties of the grass pulp were superior to those of the birch and pine pulps. The light scattering coefficient of the MILOX pulp was more than 20 units higher than that of the birch pulp. Refining produced only a slight deterioration in the optical properties of the grass pulp.

As mentioned, we chose two levels of refining for the grass pulp, three levels for the birch pulp, and only one for the pine pulp. The pulps were mixed according to the experimental program presented in Table I.

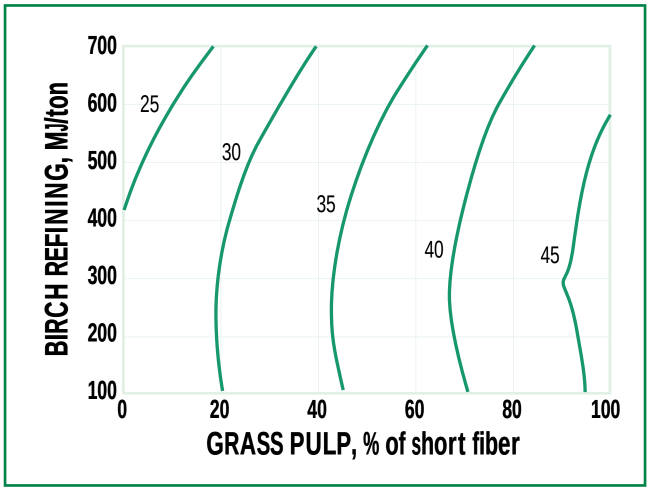
Paper properties

For grass pulp refined at 100 MJ/ton, increasing the amount of the grass pulp in the furnish affected all the paper properties, some negatively and some positively. The figures show these results graphically. Both the tensile strength and the tear strength of the paper decreased as the proportion of grass pulp in the furnish increased, as **Figs. 1 and 2** illustrate.

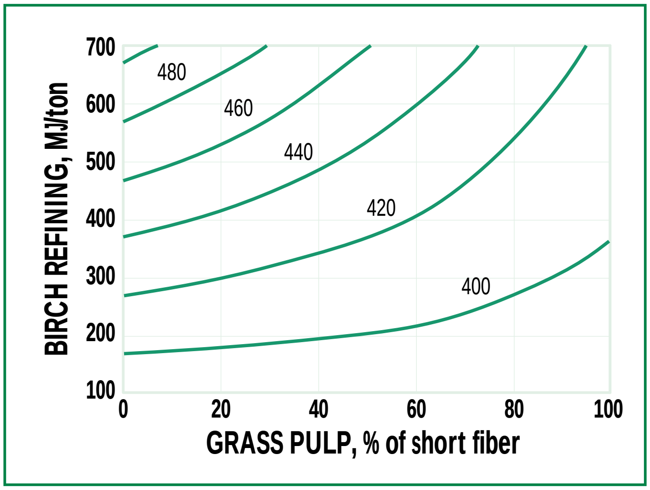
As we expected from the preliminary results, the effect on tensile strength was more drastic than the effect on tear strength. However, both



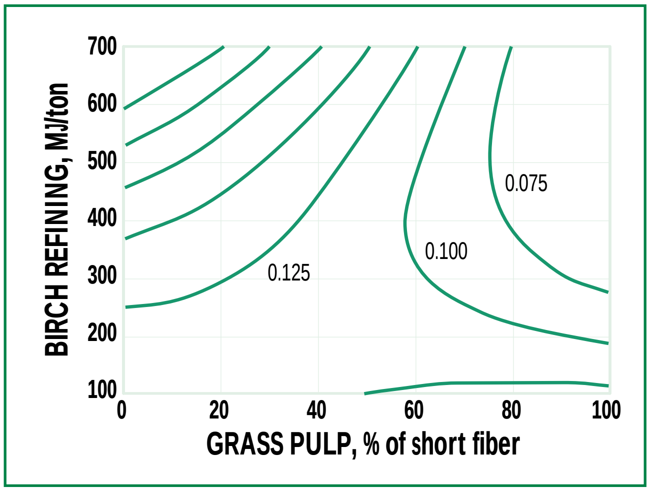
3. Response of density, in kg/m^3, to the percentage of MILOX pulp added and the refining of birch kraft pulp



4. Response of light scattering, in m^2/kg, to the percentage of MILOX pulp added and the refining of birch kraft pulp



5. Response of internal bonding strength, according to the Scott bond test, in J/m^2, to the percentage of MILOX pulp added and the refining of birch kraft pulp



6. Response of stiffness, in mN•m, to the percentage of MILOX pulp added and the refining of birch kraft pulp

values were affected by the amount of refining imparted to the birch pulp. In cases in which grass pulp represented 40% of the short fiber component of the pulp furnish, stepping up the refining of birch from 300 MJ/ton to 600 MJ/ton increased the tensile index by 8 units, from 52 N•m/g to 60 N•m/g. However, the increased refining also reduced the tear index by only 0.4 mN units, from 8.65 mN•m^2/g to 8.25 mN•m^2/g.

Paper density decreased as the proportion of grass pulp in the furnish increased, as **Fig. 3** shows. In other words, the paper produced had more bulk when more grass pulp was used. Paper density decreased from about 640 kg/m^2 to less than 600 kg/m^2 as the proportion of grass pulp increased from 0% to 100%. This feature of the grass pulp is important because high bulk is a requirement for high quality in copier paper.

All of the optical properties of the paper improved as more birch pulp was replaced with grass pulp. The effect on light scattering is shown in **Fig. 4**. For mixtures in which the birch was refined at less than 500 MJ/ton, increasing the proportion of grass pulp from 20% to 70% increased the light scattering coefficient from 30 m^2/kg to 40 m^2/kg. Some birch kraft TCF pulp should thus be replaced with grass pulp to achieve the optical properties required for woodfree fine paper.

According to the results for Scott bond tests, the internal bonding of the paper depends mainly on the amount of refining of the birch pulp. The curves for successive levels of bond strength in **Fig. 5** substantiate this finding. On every constant level of refining of the birch pulp, the internal bonding of the paper decreased slightly as the proportion of grass pulp in the furnish was increased up to 75%. Beyond 75%, an internal bond strength of 420 J/m^2 was the highest bond strength that could be achieved.

Paper stiffness decreased as the proportion of grass pulp increased (refining of birch pulp > 200 MJ/ton) and increased as the amount of refining of the birch pulp increased (grass

Property	Target	Calc.
Tensile index, N•m/g	50.0	51.7
Tear index, mN•m²/g	8.0	8.2
Light scattering, m²/g	35.0	35.0
Density, kg/m³	650	635
Air resistance, s	20–100	54
Brightness, %	83.0	83.7
Scott bond, J/m²	430	430
Stiffness, mN•m	0.10	0.13
Shrinkage, %	8.0	7.9

V. Calculated optimum fiber furnish

pulp < 50%). These results are shown in **Fig. 6**. Stiffness exceeded 0.1 mN•m when grass pulp represented 0–60% of all short fibers and birch pulp was refined at 350–700 MJ/ton. Stiffness was also greater than 0.1 mN•m when grass pulp represented 60–100% of all short fibers and birch pulp was refined at less than 350 MJ/ton.

Further beating of grass MILOX pulp improved the tensile index of the mixed paper furnish. The Scott bond values also improved, and the paper furnish was slightly stiffer when the higher level of refining was used on the grass pulp. At the same time, however, slight deteriorations were observed in the tear strength and optical properties of the paper.

Paper containing larger proportions of grass pulp showed fairly high shrinkage at both energies of refining for the grass pulp. This feature is typical of nonwood pulps *(10)* and is caused by the high degree of swelling of the fines material in the pulp.

Optimization of the fiber furnish

Depending on where the emphasis is placed—whether on the strength properties, on the optical properties, or on the bulk of the final product—30% to nearly 70% of birch kraft TCF pulp can be replaced with grass MILOX pulp. **Table V** gives an example of a theoretically optimized fiber furnish for which the target strength properties are fairly high: a tensile index of 50 N•m/g and a tear index of 8.0 mN•m²/g. The values for other target properties are also shown in this table.

To achieve the given target properties, shown by the the calculated values, 50% of the birch kraft TCF pulp can be replaced with grass MILOX pulp. The amounts of refining to which the pulps should be subjected are 100 MJ/ton for the grass MILOX pulp and 450 MJ/ton for the birch TCF pulp.

CONCLUSIONS

Replacing birch kraft TCF pulp with grass MILOX pulp affects all of the paper properties. As the proportion of grass pulp in the furnish increases, the strength properties and the stiffness of the paper suffer somewhat. The change impairs the tensile strength more than it depletes the tear strength. At the same time, however, the optical properties improve, and the bulk of the paper increases.

Depending on the end use for the paper—that is, wether more importance is placed on the strength properties, the optical properties, or the bulk of the paper—from 30% to 70% of the birch kraft TCF pulp can be replaced with grass MILOX pulp.

The strength properties of the grass pulp could probably be improved even further by delaying the harvesting of the grass to the following spring or by fractionating the raw material prior to cooking. Pilot-scale cooking conditions and bleaching conditions may improve as more experience is gained in working with the raw material.

Based on the results obtained in this study, good quality woodfree printing and writing paper was produced on the pilot paper machine at The Finnish Pulp and Paper Research Institute in the spring of 1995. **TJ**

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LITERATURE CITED

1. Hua, W. J. and Xi, H. N., *Appita* 41(5): 365(1988).
2. Veeramani, H., *TAPPI Progress Report No. 8, Nonwood Plant Fiber Pulping*, 1977, TAPPI PRESS, Atlanta, p. 13.
3. Seisto, A. and Poppius-Levlin, K., *Proceedings of the 8th International Symposium on Wood and Pulping Chemistry*, Helsinki, 1995, Vol. I, p. 407.
4. Stewart, D. and Morrison, I. M., *Cellul. Chem. Technol.* 27(4): 419(1993).
5. Sjöström, E., Haglund, P., and Janson, J., *Svensk Papperstid.* 69(11): 381(1966).
6. Paavilainen, L. and Torgilsson, R., *TAPPI 1994 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, 1994, Book 2, p. 611.
7. Poppius-Levlin, K., Hortling, B., and Sundquist, J., *Proceedings of the 7th International Symposium on Wood and Pulping Chemistry*, Beijing, 1993, Vol. I, p. 214.
8. Fineman, I., Wågberg, L., Xiaoping, Z., Shi-Jun, K., and Nian, L. F., *Proceedings of the International Nonwood Fiber Pulping and Bleaching Conference*, Beijing, 1988, Vol. II, p. 618.
9. Zhao, X., Ödberg, L., and Risinger, G., *Tappi J.* 75(1): 153(1992).
10. Cheng, Z., *IPPTA* 6(2): 45(1994).
11. Cheng, Z., *Report C7*, Laboratory of Paper Technology, Helsinki University of Technology, Espoo, 1994.
12. Hamilton, F., Leopold, B., and Kocurek, M. J., *Pulp and Paper Manufacture*, Vol. 3: Secondary Fibres and Nonwood Pulping. 3rd edn., Harpell's Press Co., Quebec, 1987, p. 11.
13. Levlin, J–E., *Paper* 206(9): 28(1986).
14. Roy, T. K., Subrahmanyam, S. V., Godiyal, R. D., Panda, A., and Pant, R., *IPPTA Convention Issue* 49(1993–94).