Peroxyformic acid pulping of nonwood plants by the MILOX method—Part 1: Pulping and bleaching

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ABSTRACT

Four nonwood plants (the grasses Festuca arundinacea, Phalaris arundinacea, Galega orientalis, and Phragmites communis*) were subjected to two-stage MILOX pulping comprising cooking with formic acid alone followed by reaction in a mixture of formic acid and hydrogen peroxide (80°C for 3 hours). Depending on the grass, the cooking temperature in the formic acid stage varied from 100 to 120°C, and the time varied from 60 to 120 min. Low kappa numbers and high viscosities were achieved using only 1.5% hydrogen peroxide on grass. The yields of unbleached MILOX grass pulps were 40–50%. These pulps were easily bleached to high brightness with alkaline hydrogen peroxide only.*

Application:

The MILOX method provides a good alternative for pulping nonwood raw materials. High-quality pulp can be produced without disturbing silicon compounds in the chemicals recovery.

FOR A LONG TIME, INTEREST IN USING straw and different grasses for papermaking was limited to countries with little or no wood reserves. Recently, however, interest has spread to Europe. In Finland, this is because the production of agricultural crops is predicted to fall due to current overproduction. The surplus land made available could be used for nonfood crops, e.g., agrofiber production. Another reason is that about 30% of the short-fibered wood material, mainly birch, used by the pulp industry is imported. Traditionally, nonwood materials have been cooked using the alkaline soda and kraft methods. Both yield pulp with good papermaking properties but involve problems with silicates during recovery of the cooking liquors. The silicates released from grasses disturb all stages of the recovery cycle, but major problems arise in the evaporators, where silicates form hard scales, causing a significant decrease in heat transfer *(1)*. On the contrary, in the slightly acidic Alcell method, only 17% of the silica originally present in the raw material dissolves during pulping *(2)*.

The MILOX method, which is based on formic acid and hydrogen peroxide as cooking chemicals, has been found to be suitable for both hardwoods and softwoods *(3, 4)*. With wood as raw material, the three-stage method, where a formic acid stage is sandwiched between two peroxyformic acid stages, has given the best results. The pulps are very reactive toward alkaline hydrogen peroxide and are easily bleached to high brightnesses. Grass material, however, behaves very differently, and the optimum conditions for wood are not necessarily the same for grasses. Even within grasses, there are great differences between species.

The aim of this work was to find suitable conditions for preparing papermaking pulp from four agricultural plants using the MILOX method. Milled grass lignins and MILOX lignins from the spent liquors were isolated to obtain further information about the pulping reactions.

EXPERIMENTAL

Raw materials. Tall fescue *(Festuca arundinacea)*, Goat's rue *(Galega orientalis)*, and Common reed *(Phragmites communis)* were obtained from the Agricultural Research Centre of Finland in Jokioinen, Finland. Reed canary grass *(Phalaris arundinacea)* was grown in the Oulu area in Finland.

Two-stage pulping. The following procedure was used for FA + PFA MILOX pulping. In the first stage, 50–100 g of grass (dry matter 85–90%) was impregnated in a vacuum with formic acid (technical grade ca. 83%) for 30 min followed by cooking for 45–180 min at 100–120°C. The spent liquor was removed by filtration, and the grass was defibrated in a laboratory blender. In the second stage, the defibrated material was heated in a mixture of formic acid and varying amounts of hydrogen peroxide on grass (0–5%, with 0% = formic acid pulp, FA + FA) for 180 min. This includes a 90-min heating period to a maximum temperature (80°C) and 60 min at the maximum temperature. The pulp was washed first with formic acid (technical grade ca. 83%) and then with water. The liquor-to-grass ratio was 5:1 in the first stage and 4:1 in the second, calculated on the dry weight of the grass at the start of the cook.

Two-stage pulping in reverse order (PFA + FA pulp) was carried out by cooking the grass first in a mixture of formic acid and hydrogen peroxide followed by cooking in formic acid alone. The cooking conditions were the same as those used in the two-stage MILOX pulping.

Three-stage pulping. Three-stage MILOX pulping was carried out as described for softwood and hardwood *(4)*.

Bleaching. Pulp bleaching with alkaline hydrogen peroxide was carried out as described earlier *(4)*. The target pH at the end of a bleaching stage was 10.5.

Parameter	Tall fescue *(5)*	Reed canary grass
Cellulose, %	34	39
Arab. gluc. xylan, %	24	24
Lignin, %	19	23
Silica (SiO_2), %	3	3
Others, %	20	11

I. Calculated chemical compositions of Tall fescue and Reed canary grass

Raw material	1st stage, °C/min	Yield*, %	H_2O_2, %	Kappa no.	Viscosity, dm^3/kg
Tall fescue	100/180	33.7	5.0	8.4	590
Festuca arundinacea	100/120	39.2	5.0	7.5	-
	100/60	36.7	5.0	7.5	650
	100/45	37.2	5.0	9.6	660
	120/60	38.1	5.0	5.9	790
	100/60	36.7	3.0	10.1	710
	100/60	39.4	1.5	13.5	960
	100/60	39.3	0	22.2	1080
Reed canary grass	100/120	45.5	5.0	11.2	820
Phalaris arundinacea	100/60	50.9	5.0	13.4	840
	100/45	47.2	5.0	14.6	890
	100/60	45.6	1.5	24.0	950
Goat's rue	110/120	33.9	4.0	22.6	730
Galega orientalis	110/120	34.5	2.0	30.1	720
Common reed	100/60	45.0	2.0	18.9	1000
Pharagmites communis					

*Screened yield, reject less than 1% for all pulps

II. Two-stage MILOX pulping of grasses and the properties of the pulps

Phosphate pulp was kindly donated by Jan Janson and prepared according to the published method *(5)*.

Separation of lignins from spent liquors. The lignins were precipitated from the spent liquors with water and separated and washed according to the method described earlier for birch lignins *(6)*.

Milled grass lignin (MGL) from Tall fescue was prepared according to the Björkman method for milled wood lignin *(7)*. However, the grass powder was milled without solvent, and the extraction with dioxane–water was replaced by an ultrasonic extraction.

Pulp analysis. The polysaccharides were hydrolyzed to monosaccharides *(8)*, which were quantitatively determined by anion exchange chromatography with pulsed amperometric detection. Cellulose and arabinoglucuronoxylan contents were then calculated using a method described earlier for wood *(9)*.

The lignin content of the grass samples was determined by the published method *(10)*.

For the silicon content determination, the samples were incinerated, and the ashes were fused with a mixture of sodium carbonate and boric acid. The melts were dissolved in hydrochloric acid, and the silicon content was determined by atomic absorption spectrometry at KCL.

Other elemental analysis and methoxyl group determinations were performed at the Analytical Laboratories, Engelskirchen, Germany.

The FTIR spectra were obtained with a Nicolet 740 FTIR spectrometer (KBr technique).

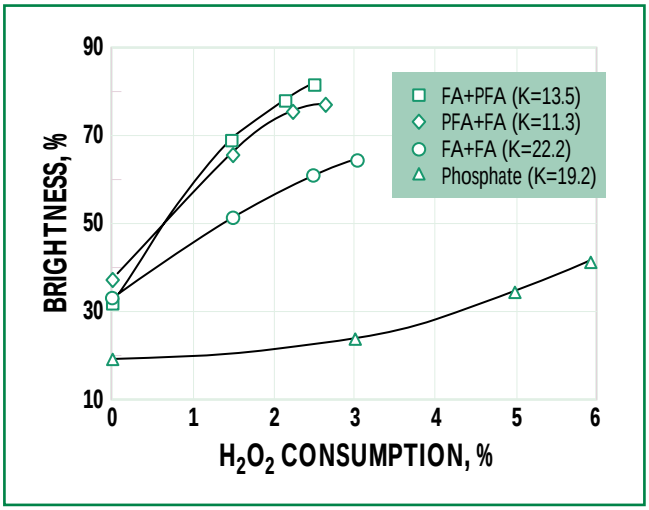
RESULTS AND DISCUSSION

Pulping

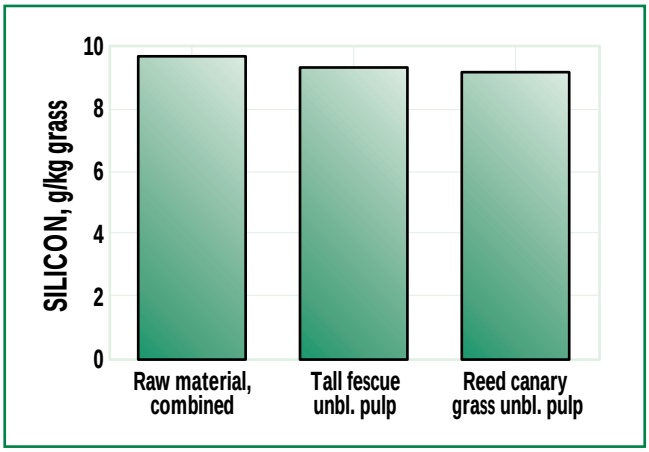
Tall fescue *(Festuca arundinacea)* and Reed canary grass *(Phalaris arundinacea)*, which are perennial grasses with good potential for growth in the Nordic countries and for use both as forage and as fiber raw material *(11)*, were chosen as the main raw materials for the MILOX pulping experiments. Neither of the grasses was fractionated before cooking. The calculated chemical compositions of the samples used are given in **Table I**. Some experiments were also carried out with Goat's rue *(Galega orientalis)* and Common reed *(Phragmites communis)*.

The effect of the cooking time in the first (formic acid) stage at 100°C, when 5% of the hydrogen peroxide on grass was used in the second stage, is shown in **Table II.** A cooking time of only 60 min was sufficient with Tall fescue to produce pulp with a kappa number of 7.5. Increasing the time to 180 min probably resulted in lignin condensation reactions, as can be seen from the higher kappa number. For Reed canary grass, the cooking time could be increased to 120 min without serious loss of viscosity. The kappa number of the pulp was low (11.2), and the screened yield was still very high (45.5%). The amount of rejects was less than 1% for all the pulps. An increasing amount of fines material was noticed when longer cooking times were used; this made dewatering of the pulps more difficult. Increasing the cooking temperature to 120°C had a similar effect. However, a very low kappa number (5.9) was obtained for Tall fescue pulp.

The amount of hydrogen peroxide used in the second stage has a significant effect on delignification (Table II). The kappa number increased as the hydrogen peroxide charge decreased, but even a charge as low as 1.5% led to kappa numbers of 14 and 24 for Tall fescue and Reed canary grass, respectively. Kappa no. 22 was



1. Reactivity of different Tall fescue pulps toward bleaching with alkaline hydrogen peroxide (FA = formic acid, PFA = peroxyformic acid)



2. Average silicon contents of Tall fescue and Reed canary grass and the respective unbleached MILOX pulps (g/kg of grass)

obtained for Tall fescue pulp cooked with formic acid alone, without hydrogen peroxide. The effect of hydrogen peroxide charge on yield was rather small. One reason for the easier delignification of Tall fescue is that its lignin content is lower than that of Reed canary grass. The higher yield obtained for Reed canary grass pulp compared to that for Tall fescue pulp at the same kappa number is due to the higher cellulose content of Reed canary grass.

Goat's rue is very difficult to cook with alkaline cooking methods *(11).* Even with high alkali charges, the amount of rejects is more than half of the total yield, and the kappa number is very high (40–70). With the two-stage MILOX method, it was possible to cook Goat's rue to kappa no. 23 using 4% hydrogen peroxide on grass by increasing the temperature in the first stage to 110°C and using a cooking time of 120 min. The yield was fairly low (34%), even when the raw material was fractionated and only the stem was used for cooking. The behavior of Common reed during MILOX pulping was quite similar to that of Reed canary grass.

When the cooking was carried out with the two-stage method in the reversed order (PFA + FA), a somewhat lower kappa number and higher brightness were obtained compared to the MILOX pulp made otherwise under the same conditions (**Table III**). The yield of the PFA + FA pulp was slightly lower. The reversed cooking order was also used for nonwood raw material in a study made at the University of Oulu *(12);* however, no bleaching experiments were carried out with the pulps.

Method	Kappa no.	Viscosity, dm^3/kg	Brightness, %	Yield, %
FA+PFA	13.5	960	32.2	39.4
PFA+FA	11.3	990	37.6	37.7

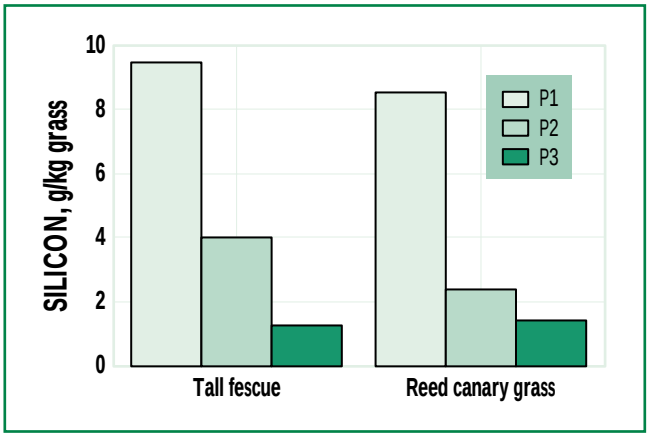
III. Properties of Tall fescue pulps made with the two-stage MILOX method (FA+PFA) and the reversed two-stage method (PFA+FA). FA stage: 100°C/60 min; PFA stage: 1.5% H_2O_2

The three-stage and two-stage MILOX methods gave very similar results with the same hydrogen peroxide charge for both Tall fescue and Goat's rue. The kappa numbers were slightly lower with the three-stage method, but the yields were also somewhat lower.

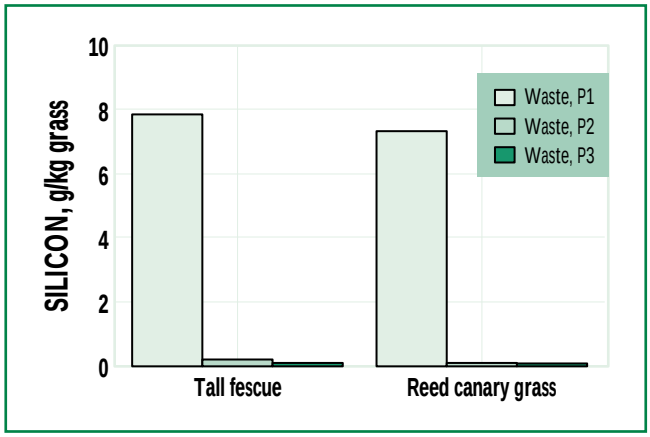
Bleaching

The grass pulps made with the two-stage MILOX method were easily bleached to the target brightness (80–85%) with alkaline hydrogen peroxide only (**Fig. 1**). Full brightness was achieved by increasing either the peroxide charge, the bleaching time, or the bleaching temperature. The bleaching yields were nearly 85%. A long cooking time in the first stage and a high peroxide charge in the second stage of the cook had very little effect on the final brightness of the pulps.

Figure 1 compares the alkaline peroxide bleachabilities of Tall fescue pulps made by different acid and alkaline cooking methods, when the target brightness was 80%. With a 2.5% consumption of hydrogen peroxide, the two-stage MILOX pulp, cooked first with formic acid followed by the peroxyformic acid stage (FA + PFA pulp), achieved 83% brightness. In spite of the higher initial brightness and lower kappa number, the pulp cooked first with peroxyformic acid followed by cooking in formic acid (PFA + FA) reached lower final brightness than the MILOX pulp. This is in agreement with the results obtained earlier *(13)* for pine pulps. Using the same bleaching conditions, the final brightness of the formic acid pulp (FA + FA) was only 65%. The phosphate pulp was chelated before bleaching but could only be bleached to 45% brightness,



3. Average silicon contents remaining in Tall fescue and Reed canary grass MILOX pulps after bleaching with alkaline hydrogen peroxide (calculated as g/kg grass). P1, P2, and P3 are the first, second, and third bleaching stages, respectively.



4. Average silicon contents of bleaching wastewaters after bleaching Tall fescue and Reed canary grass MILOX pulps with alkaline hydrogen peroxide (calculated as g/kg grass). P1, P2, and P3 are the first, second, and third bleaching stages, respectively.

while nearly 6% of the hydrogen peroxide was consumed. However, the pulp reached the target brightness when oxygen and ozone were included in the bleaching sequence *(5).* The results clearly show that placing a peroxyformic acid stage in front of the alkaline peroxide stage is a prerequisite for good pulp bleachability. Even 1.5% of the hydrogen peroxide in the second stage of MILOX pulping was enough to activate the residual lignin in the pulp toward alkaline hydrogen peroxide during bleaching. However, regardless of the low kappa numbers of the pulps, the grass pulps needed higher hydrogen peroxide charges to achieve the same level of brightness as wood MILOX pulps. This is believed to be due to differences in their lignin structures.

Pulps made using the three-stage method were bleached to about the same brightness under the same conditions as pulps made with the two-stage MILOX method.

Silicates

A high ash content, consisting mainly of silicates, is typical of grasses. The amount of silica in the grass depends on the harvesting time; the total ash and silica contents increase slightly when harvesting is delayed. At the same time, however, the homogeneity of the raw material improves, and the pulp yield increases *(14).* Most of the silica present in grass is located in the leaves. In Reed canary grass, the silica content of the stem is half that of the leaves *(15).* The amount of silica in the pulp is therefore highly dependent on the proportion of leaves in the raw material and may vary from cook to cook.

Figure 2 shows the average amounts of silicon found in the raw material (Tall fescue and Reed canary grass) and in the respective unbleached MILOX pulps. The silicon content of the raw material varied from 7.4 to 12.5 g/kg grass, depending on the harvesting time and the amount of leaves in the sample, because the raw materials were not fractionated prior to silicon analysis. The two raw materials contained very similar amounts of silicon. In MILOX pulping, the silicon present in grasses stays in the pulp during the acidic cook. Unbleached Tall fescue and Reed canary grass pulps contained 9.2–9.6 g/kg silicon calculated on grass.

The results were also verified by determining the silicon content of the pulping spent liquors from both the first and second stages. A silicon content of less than 0.01% on grass was found in the spent liquors, possibly originating from some fines material in the spent liquors. Thus, spent liquors from MILOX pulping of grasses, because they contain little or no silicon compounds, can be recycled in the same way as when wood is used as a raw material. During alkaline peroxide bleaching, most of the silicon compounds dissolve during the first bleaching stage (**Figs. 3 and 4**). After the first alkaline peroxide stage, the average silicon content was 0.9 g/kg calculated on grass, the corresponding bleaching wastewaters showing a high silicon content. In pulps bleached to 80–85% brightness, an average of 0.10–0.15 g silicon/kg grass was left in the pulp after the final bleaching stage. This corresponds to 300–400 ppm of silicon calculated on pulp. The amount was even less in pulps bleached to full brightness (100–200 ppm).

Milled grass lignins and MILOX lignins

To understand the chemical reactions occurring during the two-stage MILOX pulping of grasses and to be able to compare the pulping and bleaching behavior of grasses with that of wood, milled grass lignins (MGL) were prepared, and lignins from the MILOX spent liquors of Tall fescue and Reed canary grass were isolated and characterized.

The total yields of MILOX Tall fescue and Reed canary grass lignins obtained by precipitation from the spent liquors were 11.3% and 13.0%, respectively, calculated on grass (**Table IV**). Taking into account the carbohydrate contaminants of the lignins and the amount of residual lignin in the pulps

Lignin[a]	Lignin yield on grass, %	Carbohydrate, % on lignin	ELEMENTAL ANALYSIS %C	%H	%O	%Si[b]	%OCH_3[c]	Empirical formula[d]
TF MGL	1.9	7.5	60.6	6.5	31.5	-	9.8	$C_9H_{10.6}O_{3.2}(OCH_3)_{0.6}$
TF 1S	10.7	5.3	58.3	5.9	32.5	0.53	9.5	$C_9H_{9.9}O_{3.4}(OCH_3)_{0.6}$
TF 2S	0.6	1.7	62.3	7.8	27.6	0.38	3.5	$C_9H_{13.2}O_{2.8}(OCH_3)_{0.2}$
RC MGL	-	3.1	58.7	5.6	35.2	-	15.4	$C_9H_{8.}O_{3.}(OCH_3)_1$
RC 1S	12.3	4.1	59.1	5.8	32.0	0.43	10.7	$C_9H_{9.6}O_{3.3}(OCH_3)_{0.6}$
RC 2S	0.7	2.9	60.3	7.0	29.1	0.36	6.5	$C_9H_{12}O_3(OCH_3)_{0.4}$

[a]TF=Tall fescue, RC=Reed canary grass, 1S and 2S = first and second stages of the MILOX method
[b]Detection limit for Si determination varies depending on the amount of sample. The MGL samples were too small for accurate determinations.
[c]Corrected for carbohydrate content
[d]Empirical formulas $C_xH_yO_z(OCH_3)_m$ were calculated as follows: x=(%C/12)–m; y=(%H/1)–3m; z=(%O/16)–m; m=%OCH_3/31

IV. Yields, carbohydrates contents, elemental compositions, and methoxyl group contents of the different grass lignins

(kappa nos. 13.5 and 24.0, respectively), most of the dissolved lignin was, however, precipitated with water. It can be assumed that the peroxyformic acid–stage lignin contains more hydrophilic groups, which render the lignin water soluble, than the first-stage lignin *(16).* Most of the lignin dissolved during the first pulping stage, which is thus the main delignification stage. However, the peroxyformic acid pulping stage is crucial to the structure of residual lignin and to the good bleachability of these pulps, as was shown in Fig. 1.

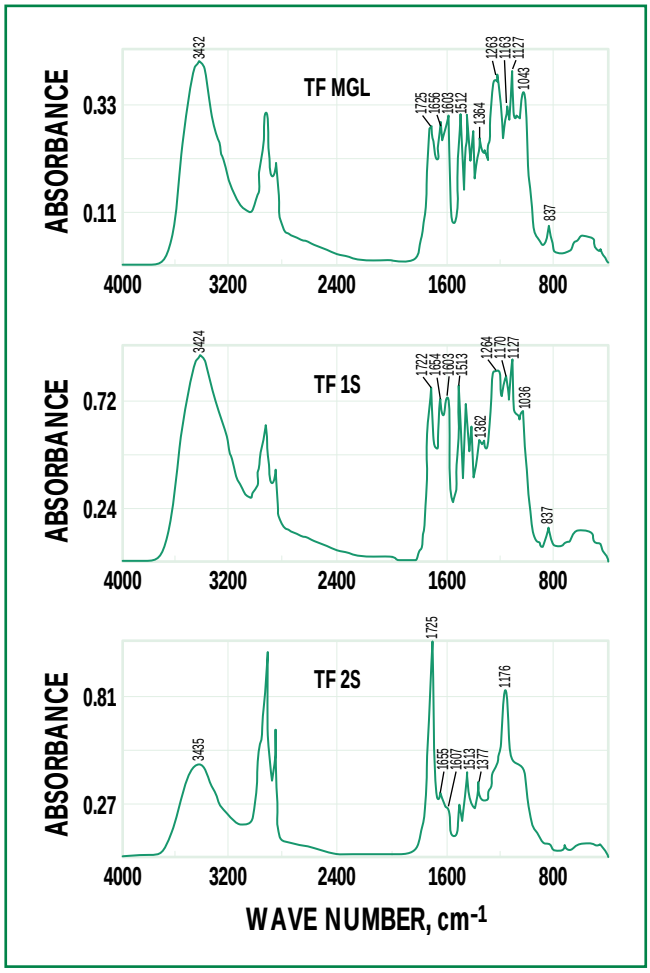
In general, the carbohydrate content of milled grass lignins, even after purification, is 5–10% *(17).* The unpurified MGL of Reed canary grass and Tall fescue did not contain more than 3% and 7.5% of carbohydrates, respectively. The carbohydrate contents of the second-stage MILOX lignins were lower than those of the first-stage lignins (Table IV); this is probably due to the higher selectivity of the peroxyformic acid stage compared to that of the formic acid stage.

There was a significant difference in the methoxyl group content of MGL from these two grasses. The methoxyl content of Reed canary grass MGL was 15% (corrected for carbohydrate content), and that of Tall fescue MGL was less than 10% (Table IV). The lower methoxyl group content of the grasses, i.e., the lower content of syringyl type structures than that of birch MWL [21.5% *(18)*], may partly explain the pulping results. These results showed that, in spite its lower lignin content, Tall fescue was no easier to delignify in the MILOX process than birch. The lignin contents of birch and Reed canary grass are roughly the same, but the delignification degree of the grass is lower. It is known *(19)* that syringyl structures are more reactive toward peroxyacids than guaiacyl structures, which in turn are more reactive than *p*-hydroxyphenyl structures. The significant demethylation caused by peroxyformic acid is shown in Table IV as a lower methoxyl content of the second-stage compared to the first- stage lignins.

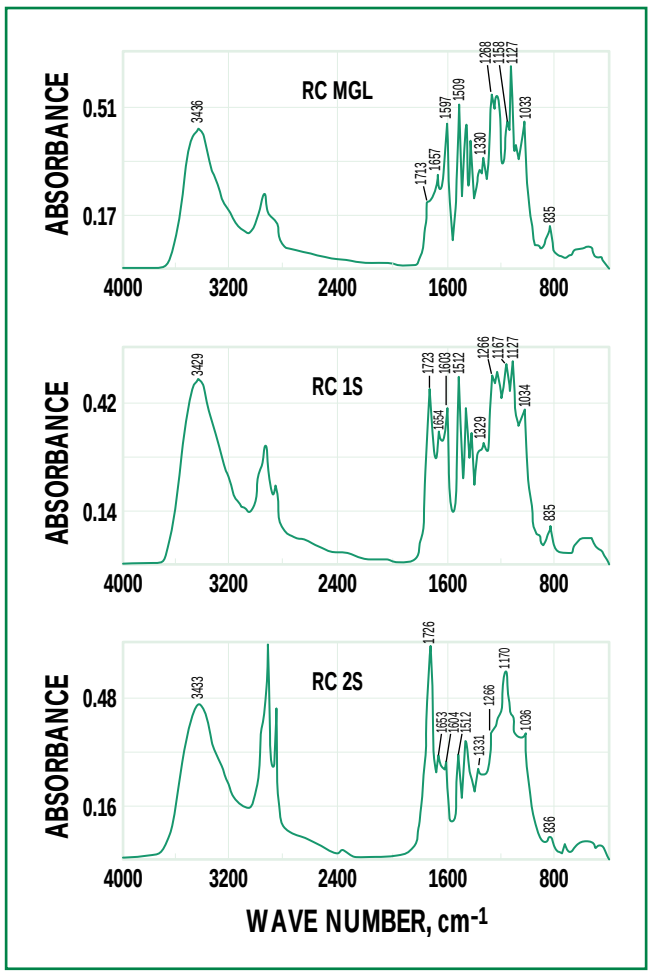
The empirical formulas for the different lignins were calculated from the results of the elemental analyses. The silicon content of the lignins was only 0.4–0.5% on lignin and does not affect the empirical formula. The amount of silicon compounds precipitated together with the lignins corresponds well with that found in the spent liquors.

The FTIR spectra of the milled grass lignins show signals typical of nonwood lignin, consisting of *p*-hydroxyphenylpropane, guaiacylpropane, and syringylpropane units (HGS lignin, **Figs. 5 and 6**). The two bands at 1600 cm^{-1} and 1500 cm^{-1} are characteristic of aromatic compounds and are due to vibrations of the aromatic skeletal. The intensities of these two bands are approximately equal in the MGL of Tall fescue—a typical feature of hardwood and grass lignins. In MGL from Reed canary grass, the intensity of the 1600-cm^{-1} band is only slightly lower than that of the 1500-cm^{-1} band. The band at 1127 cm^{-1} is dominant and typical of GS lignins *(20).* The band at 1655 cm^{-1} indicates the presence of carbonyl groups in conjugated *p*-substituted aryl ketones. Note that the bands at 1725–1715 cm^{-1} show the presence of carboxylic acids and/or ester groups. The band at 1163–1158 cm^{-1} is typical of HSG lignins, indicating the presence of carbonyl groups in conjugated ester structures. An important spectral feature of the HSG lignins is the band at 836 cm^{-1}, which is due to the aromatic C–H "out-of-plain" vibrations in *p*-hydroxyphenylpropane units *(20).*

FTIR spectra of the lignins isolated from the spent liquor from first-stage cooking differ only slightly from those of the MGLs. The intensity of the band at 1720 cm^{-1} has increased slightly, indicating some formylation of the lignin. The intensity of the 1500-cm^{-1} band has increased slightly in relation to the 1600-cm^{-1} band, indicating that guaiacyl-type lignin has been dissolved in preference to the syringyl type. There are clear differences in the structures of the lignins precipitated from the spent liquor from the oxidative peroxyformic acid cooking stage. The intensity of the broad hydroxyl band (max. at 3430 cm^{-1}) has decreased relative to the intensity of the



5. FTIR spectra of Tall fescue: (a) MGL, (b) lignin precipitated from the first- stage cooking liquor, and (c) lignin precipitated from the second-stage cooking liquor



6. FTIR spectra of Reed canary grass: (a) MGL, (b) lignin precipitated from the first-stage cooking liquor, and (c) lignin precipitated from the second-stage cooking liquor

bands at 2930 and 2850 cm^{-1}, which indicates oxidation and/or formylation of the hydroxyl groups or ring cleavage leading to formation of lactones. The oxidation in the second stage also is seen as an increase in the intensity of the band at 1720 cm^{-1}, due to carbonyl groups probably from carboxylic acids, formiate groups, and muconic acids and their methyl esters. The relative decrease in intensity of the band at 1512 cm^{-1} compared to the band at 1720 cm^{-1} indicates the decomposition of aromatic structures. Similar changes were observed for birch lignins dissolved by peroxyformic acid during MILOX pulping *(16)*.

KEYWORDS

Bleaching, brightness, formic acid, grasses, hydrogen peroxide, infrared spectra, kappa number, lignins, mixtures, natural fibers, nonwood fibers, nonwood plants, pulping, performic acid, peroxides, peroxy acids, silica, temperature, time, two stage process, viscosity.

CONCLUSIONS

Unlike the case with wood species, two-stage MILOX pulping of agricultural plants is more effective than three-stage cooking. The overall cooking time is shorter, the yields are higher, and the pulping procedure is easier in practice because of the better impregnation in two-stage than in three-stage pulping. Both pulps are easily bleached to the target brightness (80–85%) with alkaline hydrogen peroxide, with no difference in the total consumption of hydrogen peroxide.

The differences in the lignin contents of the grasses and differences in the chemical structures of their lignins, compared both with each other and with wood lignin, are seen in their delignification behavior during formic acid/peroxyformic acid cooking. The *p*-hydroxyphenyl units present in grass lignins are less reactive than syringyl structures toward peroxyacids.

The MILOX process is a good way of pulping agricultural plants. Silicates, which are abundant in grasses, cause problems in the chemicals recovery in alkaline pulping methods, but these can be avoided in the acidic process. **TJ**

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