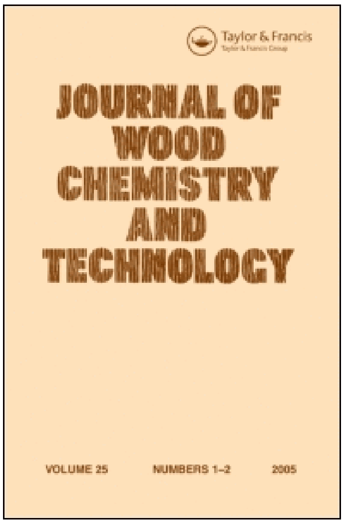

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TCF BLEACHED PULPS FROM *MISCANTHUS SINENSIS* BY THE IMPREGNATION RAPID STEAM PULPING (IRSP) PROCESS

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ABSTRACT

The production of bleached cellulose pulps from elephant grass (*Miscanthus sinensis*) via a two-stage soda pulping process and a TCF bleaching sequence is evaluated in this work. The impregnation rapid steam pulping process (IRSP) involves impregnating of the lignocellulosic material with the pulping liquor, withdrawing the excess liquor and rapidly steaming the impregnated material at 180–200°C for a short

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time. In this paper the process variables and their effect on the kappa number, yield and viscosity of the unbleached pulps are discussed. Bleaching by an ozone-based TCF sequence was tested, and the papermaking properties of the bleached pulp were determined. A kappa number of 19 was obtained by impregnating at an alkali charge of 30 + 0.1% anthraquinone carboxylic acid (AQCA) and pulping at 180°C for only 15 min. Kappa was reduced to 16 by extending pulping time to 26 min. The alkali consumption during impregnation and pulping was 10.2 g NaOH/100 g of dry *Miscanthus*. Screened pulp yield, viscosity and brightness for this pulp were 54.6%, 913 mL/g and 37.3%, respectively. After bleaching, the pulp had an ISO brightness of 87.4% and a viscosity of 700 mL/g. Refining in a PFI mill provided optimal strength properties of the bleached pulp at 4500 revolutions (71°SR): breaking length 7.2 km, tensile index 72 N m/g, and burst index 4.3 kN/g. Tear index was 7.9 mN m^2/g at this degree of refining.

Key Words: Miscanthus sinensis; Soda pulping; Impregnation; TCF bleaching

INTRODUCTION

Miscanthus sinensis, or elephant grass, is a species from East Asia that belongs to the *Monocotyledoneae* group and *Gramineae* family. It was first introduced into Europe as an ornamental plant during the 1930s. More recently it has attracted considerable attention as an energy crop and a source of cellulose pulp, mainly because of its adaptability to different soils and climates, its high productivity and its resistance to low temperatures.[1] High quality cellulose pulps produced from fast-growing annual crops that are rich in cellulose, like *Miscanthus sinensis*, are an interesting option from the environmental point of view and also because of the scarcity of wood sources in several regions of the world. Using *Miscanthus sinensis* to produce paper has been evaluated with established pulping processes such as kraft and sulfite. However, pulping by innovative chemical processes is relevant for achieving process options based on sulfur-free and chlorine-free technologies.[2] Several chemical processes have been investigated in recent years for *Miscanthus* pulping, such as organosolv processes,[3–5] soda[5,6] and soda/AQ[7] pulping, and NS/AQ pulping.[7] This paper explores the production of high-quality bleached cellulose pulps from *Miscanthus sinensis* by the impregnation-rapid-steam-pulping (IRSP) process.[8] The process is based on impregnating of the chips with alkaline liquor followed by pulping by direct steaming at high temperature and for a short time. The pulps were bleached by a totally chlorine-free (TCF) process based on ozone bleaching and an adequate pretreatment of the pulp to avoid excessive degradation of cellulose.[9] Advantages of the IRSP process are a smaller reactor for a specified production capacity than in a conventional pulping process, due to the short cooking times, and the environmental benefits obtained by the absence of organic solvents and a consumption of alkali that is lower than for other pulping processes.

MATERIALS AND METHODS

Analytical Methods

The chemical composition of *Miscanthus sinensis* was determined by the following standard methods: ASTM D-1348 for moisture content; TAPPI T 15 os-80 for ash content; ASTM D-1111-84 for hot water extractives, modified ASTM D-1107-84 for ethanol/toluene extractives. Lignin content was measured as Klason lignin (ASTM D-1106-84). Holocellulose content was determined by sodium chlorite delignification,[10] and α-cellulose was measured in the hollocellulose samples following TAPPI T-203 om-93. Residual lignin in unbleached and bleached pulps was determined by the Kappa number method (TAPPI T-236 cm-85). The intrinsic viscosity of the pulps was measured according to the ISO 5351-1-1981 standard.

The pulps were beaten in a PFI mill according to ISO 5264-2-1979 and the freeness (°SR) of the refined pulps was measured by the ISO 5267-1999 standard method. Laboratory sheets were prepared following ISO 5269-2-1998, and conditioned according to ISO 187-1990. The properties of the laboratory sheets were then determined by the following methods: ISO 9184-3-1990 for fiber furnish analysis, ISO 534-1988 for thickness and apparent bulk, TAPPI UM256 for water retention value (WRV), ISO 536-1995 for grammage, ISO 5636-3-1992 for permeability, ISO 2758-1983 for burst index, ISO 5626-1993 for folding endurance, ISO 1974-1990 for tearing resistance, ISO 1924-1-1992 and ISO 1924-2-1994 for tensile properties, and ISO 3688-1999 and ISO 2470-1999 for brightness. Bleached papers were aged at a temperature of 80°C and a relative humidity of 65% in a climatic chamber, according to the ISO 5630-3-1996(E) standard method. Ageing by light exposure was determined with the Suntest. The spent liquors of the bleaching process were collected and analyzed for chemical oxygen demand (COD) following the ASTM D1252-95 standard method, and for color according to the method ASTM D1209-79.

Pulping Procedure

All experiments were carried out using a batch of *Miscanthus sinensis* harvested in Galicia, northwest Spain. The moisture content of the batch as received was 8%. Its chemical composition was established by triplicate analysis using the aforementioned standard methods. Table 1 lists the average composition in percentages of w/w of dry *Miscanthus*. Its chemical composition is similar to cane bagasse.[11,12] The IRSP pulping sequence involved of a two-stage process: impregnation and high-temperature vapor-phase pulping. The pulp was then screened to remove uncooked fragments (knots and shives) and bleached using a TCF sequence. Figure 1 is a schematic of the process that lists the main operating conditions.

Impregnation

In the first stage of the process, elephant grass was impregnated with an alkali solution at room temperature. The impregnation step was performed at atmospheric pressure using extended impregnation times of several hours, but the process can be reduced to less than 5 min by applying pressure with identical results.[8] The liquor-to-solid ratio was 10 : 1 in all cases. Two alkali charges were tested: 20 and 30 wt% (based on dry *Miscanthus*). Some experiments were also performed at the alkali charge of 30% by adding 0.1 wt% (based on dry *Miscanthus*) of anthraquinone carboxylic acid (AQCA) as catalyst. After the impregnation period, the

Table 1. Chemical Composition of the Sample of *Miscanthus sinensis* Used in This Study

Component	% w/w (dry basis)
Ashes (TAPPI T15 os-80)	0.7 ± 0.01
Organic extractives (ASTM D-1107-84)	3.1 ± 0.3
Hot water extractives (ASTM D-1111-84)	9.1 ± 0.2
Klason lignin (ASTM D-1106-84)	19.9 ± 0.3
Hollocellulose (chlorite delignification)[10]	72.5 ± 0.2
α-Cellulose (TAPPI T-203 om-93)	42.2 ± 0.1

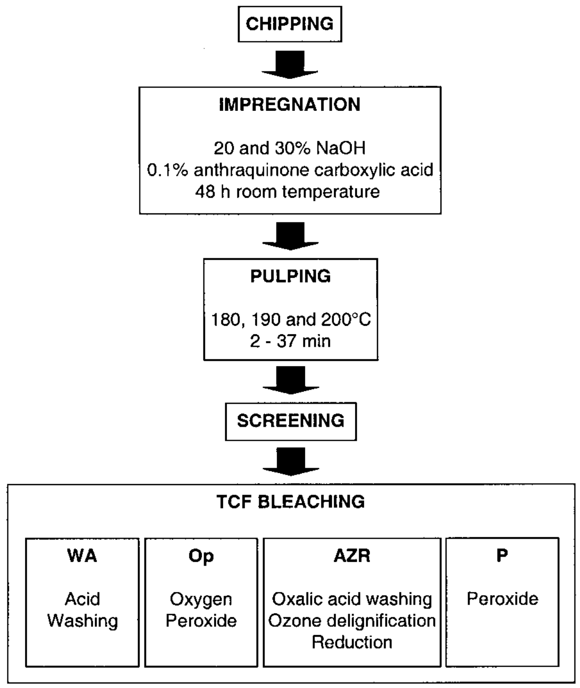

Figure 1. The IRSP pulping process for producing TCF bleached pulps from *Miscanthus sinensis*.

excess liquor was drained off and measured, and the concentration of alkali in the liquor measured by titration with standardized HCl. The impregnated material was collected, weighted and immediately transferred to the pulping reactor. The amount of alkali consumed during the impregnation stage by reaction with the acidic groups in wood (AI), the alkali introduced into the chips with the impregnation liquor (AL) and the total alkali consumption (TAC) were calculated as follows:

$$\mathrm{AI}\left[\frac{\mathrm{g\ NaOH}}{100\,g\ \mathrm{dry}\ \mathit{Miscanthus}}\right] = 4005\frac{V_0(C_0 - C_t)}{M_{\mathrm{Mis}}} \tag{1}$$

$$\mathrm{AL}\left(\frac{\mathrm{g\ NaOH}}{100\,\mathrm{g\ dry}\ \mathit{Miscanthus}}\right) = 4005\frac{(V_0 - V_t)C_t}{M_{\mathrm{Mis}}} \tag{2}$$

$$\mathrm{TAC}\left(\frac{\mathrm{g\ NaOH}}{100\,\mathrm{g\ dry}\ \mathit{Miscanthus}}\right) = 4005\frac{(V_0C_0 - V_tC_t)}{M_{\mathrm{Mis}}} = AI + AL \tag{3}$$

where

C_0 initial alkali concentration (gmol/L)
C_t final alkali concentration (gmol/L)
M_{Mis} mass of *Miscanthus* (g, dry basis)
V_0 initial volume of impregnation solution (L)
V_t final volume of impregnation solution (L)

The effect of *Miscanthus* preparation before impregnation was also considered. Experiments were performed using stems of *Miscanthus* cut to a maximum length of 10 cm, since this was effective for wheat straw pulping.[8] Other experiments used stems cut to 10 cm length and chipped to open them up in the axial direction. This second procedure not only impregnated the material better, but also had the extra advantage of removing a substantial amount of pit during chipping, and this improved the quality of the pulps.

Pulping

The impregnated chips were transferred to the pulping reactor. This was a 10 L batch reactor made of ANSI 304-L and 316 stainless steel. After the chips were loaded, saturated steam was passed through the bottom of the reactor to heat the chips to the desired temperature. Pulping temperatures of 180, 190 and 200°C and reaction times of between 2 and 37 min were studied. At the end of the scheduled reaction time, the discharge valve at the bottom of the reactor was opened; this caused a flash decompression of the reactor and the cooked chips were completely defibrated by the sudden pressure release. The defibrated chips were collected in a closed 100 L vessel connected to the expansion valve. The pulp was then washed with water at room temperature until neutrality and screened through a 0.2 mm mesh in a WEVERK laboratory screen to eliminate uncooked fragments. The yield of screened pulp was calculated from the oven dry weight of pulp and raw material, which was determined by triplicate analysis. The amount of rejects was established in the same way.

Bleaching

A totally chlorine-free (TCF) bleaching sequence was applied to pulps with Kappa numbers below 20. The sequence was: acid washing (WA), delignification with oxygen and hydrogen peroxide [Op],[13] oxalic acid washing, ozone delignification and reduction [AZR],[14] and finally peroxide

Table 2. Conditions for Each Stage of the Bleaching Sequence (Op(AZR)P)

Conditions	Op	Z	R	P
Time (min)	90		60	150
Temperature (°C)	100	room	room	85
Consistency (%)	10	40	10	10
O_3 (% dry pulp)		0.5		
O_2 (kg/cm^2)	6			
H_2O_2 (% dry pulp)	3			2
NaOH (% dry pulp)	2			1.8
DTPA (% dry pulp)	1			0.2
$MgSO_4$ (% dry pulp)	0.5			1
Oxalic acid (% dry pulp)				
Na_2CO_3 (% dry pulp)			1	
$NaBH_4$ (% dry pulp)			2	

bleaching [P].[15] Table 2 shows the specific conditions and charge of chemicals that were applied at each stage.

RESULTS AND DISCUSSION

The IRSP process relies on achieving a uniform distribution of the pulping chemicals within the lignocellulosic structure before the chips are heated to the pulping temperature. Efforts during the first experiments were therefore focused on achieving a correct impregnation. The internodes of the stem of elephant grass are completely filled with pith, which stops the fibers from being correctly saturated with the pulping chemicals. Figure 2 shows the average yields of unscreened and screened pulps for *Miscanthus*, which was impregnated at 20% NaOH and pulped at 200°C for different lengths of time, either as whole canes or as chipped and depithed canes. Results show that the yield of screened pulp is higher when the elephant grass is chipped before impregnation, and that the amount of uncooked fragments appears to be lower. Chipping removes part of the pith and allows a better contact between the fibers on the inner side of the cane and the impregnation liquor, thus ensuring a uniform distribution of chemicals within the fibers. When the whole canes were used, screening rejects were mainly large uncooked fragments derived from the cane nodes. Uncooked fragments were dark brown after cooking, which contrasted with the light brown coloring of the pulp. When chipped canes were pulped, the rejects were much smaller and lighter in color, which indicates

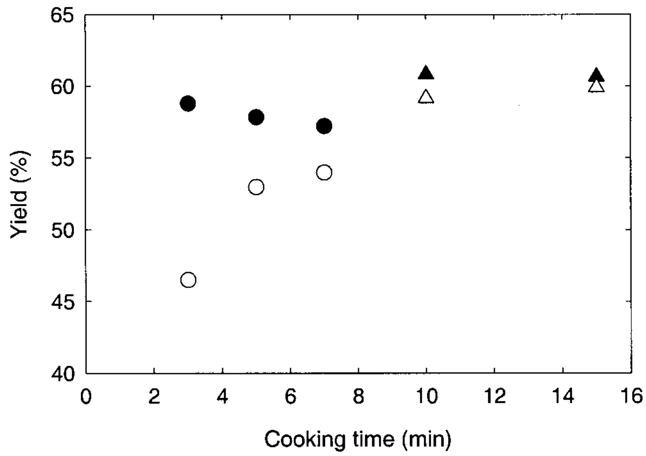

Figure 2. Effect of chipping and depithing on the yield of unbleached pulp. Impregnation with 20% NaOH and pulping at 200°C. Whole cane: unscreened yield (●), screened yield (○). Chipped cane: unscreened yield (▲), screened yield (△).

a better impregnation and better cooking. Therefore, the next experiments were all performed with chipped and depithed canes.

Pulping temperature is a key parameter in the process. Although the IRSP method tends to use a high temperature and a short pulping time, the practical range of values for both variables are determined by the quality of the pulp. If the temperature is too high, cellulose will degrade considerably even if the reaction time is reduced, and pulps with low viscosity will be produced. On the other hand, if pulping time is too short the chips will not reach a uniform temperature. Uncooked fragments and high kappa numbers of the screened pulp will then make the number of rejects excessive. A new group of experiments (sets #1, 2 and 3) were performed to test the effect of pulping temperature and time. Table 3 shows the pulping conditions and the screened yield and rejects for these experiments, which were performed with chipped canes impregnated at a constant alkali charge of 20% at 180, 190 and 200°C. Figure 3 shows the kappa number and the pulp viscosity of the screened pulps. At a pulping temperature of 180°C, the intrinsic viscosity decreased linearly from 1300 mL/g at a pulping time of 4 min to 840 mL/g after 37 min of cooking. When the temperature was increased to 190°C there was a much stronger degradation of cellulose, which had a viscosity of only 800 mL/g at a pulping time of 6.5 min. At 200°C cellulose degraded even faster, and viscosity fell to less than 600 mL/g in only 7 min. Pulping time

Table 3. Pulping at 180, 190, and 200°C of Chipped *Miscanthus sinensis* Impregnated at a 20% and 30% NaOH Charge (Screened Yield and Rejects at Different Pulping Times)

Set	Impregnation Alkali Load and Pulping Temperature	Pulp Yield (%)	Pulping Time (min)										
			3	4	5	6.5	7	8	11.5	15	16	26	37
1	200°C/	Screened	46.5		53.0		54.0						
	20% NaOH	Rejects	11.9		4.8		3.2						
2	190°C/	Screened				49.2			50.3		50.9		
	20% NaOH	Rejects				5.2			3.3		1.8		
3	180°C/	Screened		45.2				46.9		47.7		48.2	48.6
	20% NaOH	Rejects		9.5				7.4		5.9		5.0	4.1
4	180°C/	Screened		51.4				51.6		51.9		52.4	
	30% NaOH	Rejects		3.2				2.1		1.1		0.8	
5	180°C/	Screened		53.4				54.0		54.2		54.6	
	30% NaOH + 0.1% AQCA	Rejects		3.0				1.1		0.6		0.3	

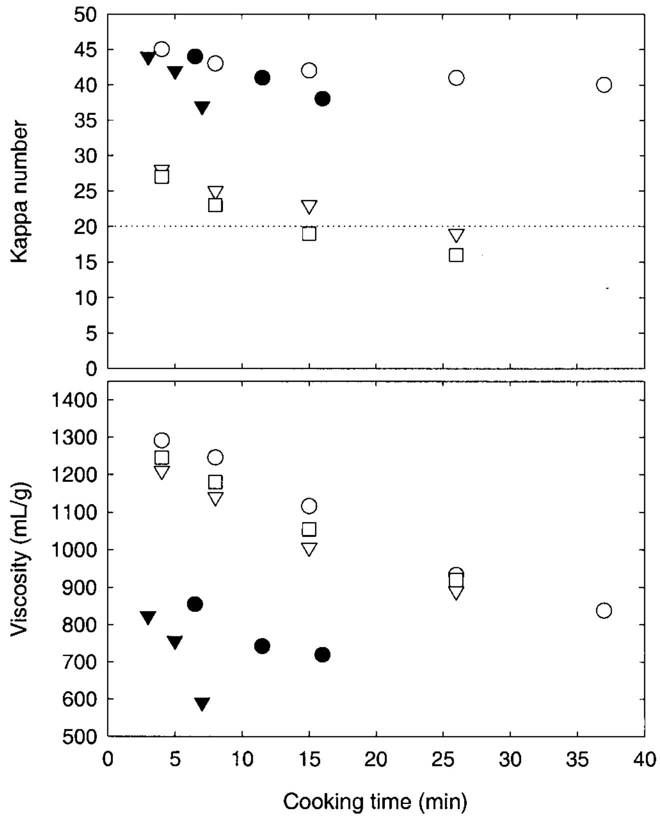

Figure 3. Effect of the impregnation conditions on the pulping of *Miscanthus sinensis* at different pulping temperatures: Kappa number (top) and pulp viscosity (bottom) against cooking time (○ 20% NaOH/180°C, □ 30% NaOH/180°C, △ 30% NaOH + 0.1% AQCA/180°C, ● 20% NaOH/190°C, and ▼ 20% NaOH/200°C. Dotted line in the top plot shows the target kappa number of 20).

also plays a significant role. Table 3 shows that when pulping time is below 5 min there is a high proportion of uncooked fragments in the pulp.

On the basis of these results, a temperature of 180°C and a time above 4 min were selected. Although lower pulping temperatures can be applied, the goal is to obtain the shortest pulping times by using the highest temperature without degrading cellulose excessively. However, further optimization of the pulping process was still needed to achieve lower kappa numbers. Two new sets of pulping experiments were then performed at 180°C. In set #4 the alkali charge during impregnation was increased to

30%. In set #5 alkali charge remained at 30%, and 0.1% of anthraquinone carboxylic acid (AQCA) was added to improve delignification. The yield of screened pulp and the percentage of rejects for these pulps are also shown in Table 3, and Fig. 3 shows kappa number and pulp viscosity as a function of pulping time for both sets of experiments. When impregnation was performed with 20% NaOH, screened yield was 45.2% at a pulping time of 4 min. This rose to 48.6% at a pulping time of 37 min. This increase in screened yield was due to the fewer number of rejects, which decreased from 9.5% at 4 min of cooking time to 4.1% at 37 min. The kappa number of the screened pulp was 45 at a pulping time of only 4 min. Extending the pulping time to 37 min reduced kappa to 40. Moreover, viscosity decreased steadily from 1290 mL/g at 4 min of pulping, to 840 mL/g for 37 min of pulping. The high percentage of pulp rejects, the high kappa number of the pulp and the fact that it is independent of pulping time, strongly suggest that the amount of alkali introduced to the fibers during impregnation was not high enough to achieve a good delignification. The percentage of rejects and the kappa number dramatically decreased when *Miscanthus* impregnation was performed at an alkali charge of 30%. Screened yield was 51.4% at a pulping time of 4 min. This rose to 52.4% after 26 min of pulping. The number of rejects also decreased as pulping time increased, from 3.2 at 4 min to only 0.8 at 26 min. Kappa was 28 at for the sample pulped for 4 min; this decreased steadily to 19 when it was pulped for 26 min. In general, the pulps from *Miscanthus* impregnated at 30% alkali had a lower viscosity than those impregnated at 20%. The viscosity of the pulp at 4 min was 1210 mL/g, while it was only 890 mL/g for the pulp obtained at 26 min. Adding 0.1% AQCA in the impregnation liquor had a positive effect both on the yield of pulp and on its properties. In general, screened yield increased by more than 2% at all pulping times, while rejects decreased by roughly half when AQCA was used. When *Miscanthus* was impregnated with AQCA kappa numbers at all pulping times were lower than when it was impregnated without AQCA; the kappa number was 19 for a pulping time of only 15 min, and this became 16 when pulping time was extended to 26 min. Also pulps had higher viscosity when they were prepared with AQCA. For example, viscosity was 920 mL/g for the pulp which kappa number was 16.

Table 4 shows the alkali consumed during the impregnation stage and the alkali that was introduced in the chips. Total alkali consumption (TAC) accounts for the alkali that is retained by the solid (AL) and the alkali that it is neutralized by acidic species during impregnation (AI). Total consumption was 6.8 and 10.2% for the impregnation at 20 and 30%, respectively. The alkali retained after impregnation was 3.7% for the samples impregnated at 20% NaOH, and 6.9% for those impregnated at 30%. The spent impregnation liquor still retains a high concentration of alkali, and can be

Table 4. Alkali Consumption During Impregnation and Alkali Load in the Impregnated *Miscanthus* (g NaOH/100 g Dry *Miscanthus*)

Alkali in the Impregnation Liquor	Alkali Neutralized During Impregnation (AI)	Alkali Retained After Impregnation (AL)	Total Alkali Consumption (TAC)	Alkali Remaining in the Impregnation Liquor
20.0	3.1	3.7	6.8	13.2
30.0	3.3	6.9	10.2	19.8

reused by addition of fresh NaOH solution to adjust the concentration at the desired level.

The above experimental design provided a set of working conditions that were suitable for preparing chemical pulps from *Miscanthus sinensis* with kappa numbers of below 20 by the IRSP process. A batch of 2 kg (dry basis) of pulp was then prepared for studying the mechanical properties of the unbleached pulp and the pulp bleached by a TCF sequence. This batch was prepared by impregnating *Miscanthus* with 30% NaOH plus 0.1% AQCA and cooking it at 180°C for 26 min. After screening, the unbleached pulp had an average viscosity of 913 mL/g and an ISO brightness of 37.3%. After TCF-bleaching, pulp viscosity dropped to 700 mL/g and the ISO brightness rose to 87.4%. The loss of brightness by paper aging was tested in a climatic chamber and the results are presented in Fig. 4. After 144 h the brightness decreased approximately 7 units. Brightness reduction was also tested with the Suntest for 72 h, causing a brightness loss of 3.3 points. Comparison of the brightness reversion of *Miscanthus* pulps with that of kraft pulps from eucalyptus[16] and wheat straw[17] bleached with the same TCF sequence (Fig. 4), shows similar trends for all the pulps. The effluents of the bleaching process were analyzed for color and COD. The color of the effluents of the Op stage was 643 kg Pt/tdp, was much higher than those of the P stage (4.1 kg Pt/tdp). COD for both stages was 30.2 and 22.5 kg O_2/tdp, respectively.

Strength properties were investigated for unbleached and TCF-bleached pulps. Unbleached pulp was refined with a PFI laboratory mill at 0, 500, 1000, 3000, 4500 and 6000 revolutions, while bleached pulps were refined at 0, 3000, 4500 and 6000 revolutions. Physical properties were then measured on laboratory sheets. The results for physical properties are shown as a function of the refining index (Shopper Riegler, °SR) in Table 5 for the unbleached pulp and in Table 6 for the bleached pulp. Both pulps have the same trend in the variation of the refining index with the number of

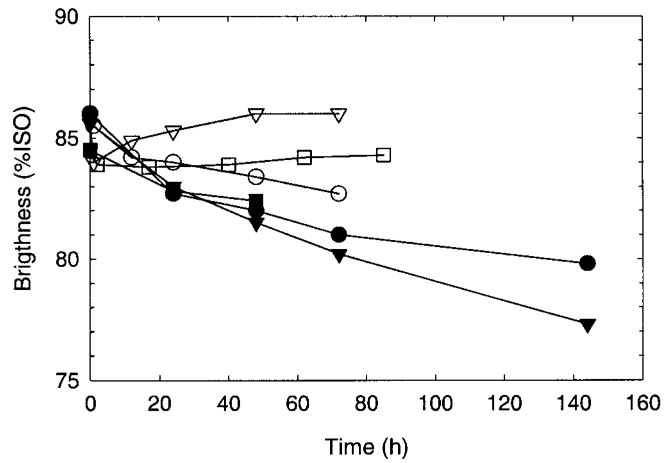

Figure 4. Aging of paper sheets prepared from TCF bleached pulps: IRSP pulps from *Miscanthus sinesis* prepared in this work (● climatic chamber, ○ suntest), eucalyptus kraft pulp[16] (▼ climatic chamber, ▽ suntest) and wheat straw kraft pulp[17] (■ climatic chamber, □ suntest).

Table 5. Properties of the Unbleached Pulp from *Miscanthus sinesis* at Different Degrees of Refining (Pulping at 180°C and 26 min; Impregnation with the 30% NaOH + 0.1% AQCA Liquor)

PFI (Revolutions)	0	500	1000	2000	3000	4500	6000
°SR	14	18	24	38	48	61	73
WRV (%)	115	125	134	145	150	160	169
Apparent density (g/mL)	0.51	0.56	0.60	0.64	0.65	0.69	0.75
Permeability (μm/Pa s)	43.7	29.9	19.1	7.30	3.20	0.89	0.36
Opacity (%)	98.5	99.5	97.6	98.4	97.0	96.7	97.5
Burst index (kN/g)	1.23	2.25	2.67	3.56	4.21	4.87	5.10
Tensile index (N m/g)	31.0	51.0	58.4	66.0	72.0	84.0	76.0
Breaking length (km)	3.2	5.2	6.0	6.7	7.3	8.6	7.7
Elongation (%)	1.4	2.2	2.5	2.7	2.8	3.5	3.2
Tear index (mN m^2/g)	10.1	11.5	11.3	10.5	10.0	9.1	8.4
Tear strength (mN)	848	946	911	839	780	421	705
Folding endurance (log)	1.56	2.32	2.83	3.19	3.26	3.41	3.40

Table 6. Properties of the TCF Bleached Pulp from *Miscanthus sinesis* at Different Degrees of Refining (Pulping at 180°C and 26 min; Impregnation with the 30% NaOH + 0.1% AQCA Liquor)

PFI (Revolutions)	0	3000	4500	6000
°SR	14	47	58	71
WRV (%)	96	147	159	168
Apparent density (g/mL)	0.49	0.68	0.71	0.76
Permeability (μm/Pa s)	53.6	2.4	0.7	0.2
Opacity (%)	80.1	78.2	72.3	69.9
Burst index (kN/g)	0.36	3.84	4.45	4.33
Tensile index (Nm/g)	14.8	64.5	71.7	70.8
Breaking length (km)	1.5	6.9	7.3	7.2
Elongation (%)	0.86	3.2	3.5	3.0
Tear index (mN m^2/g)	8.0	9.2	7.9	7.2
Tear resistance (mN)	597	643	554	511
Folding endurance (log)	0.88	3.04	3.1	3.4

revolutions in the PFI mill, and bleaching has no significant effect. Permeability decreases as refining is extended due to the compaction of the structure of the paper sheet. At the beginning of the refining process the bonded area between fibers is low, but this increases at higher refining degrees rising the resistance to air of the paper sheets. Permeability appears to be higher for the unrefined bleached pulp but both pulps tend to the same values of permeability when the pulp is refined to more of 45°SR. In general, extending the refining process produces pulps with better papermaking properties. Breaking length and tensile index show maximum values of 8.6 km and 84 N m/g at 61°SR for the unbleached pulp, while the maximum value for the burst index is 5.1 kN/g at 73°SR. The properties of the bleached pulp are inferior to those of the unbleached pulp due to the fiber modifications during the TCF bleaching sequence. The maximum values of breaking length, tensile index and burst index were 7.2 km, 72 N m/g and 4.3 kN/g at a refining index of 71°SR. Paper elongation has a tendency similar to that of the tensile index, and the maximum elongation was 3.5% for both the unbleached and bleached pulps at a refining index of around 60°SR. The trends for folding endurance are similar to those for breaking length. It rises from 1.56 for the unrefined pulp to around 3.41 at 61°SR, and extending of the refining does not change this parameter substantially. The folding endurance for the bleached pulp at a certain degree of refining is basically the same as that for the unbleached pulp. For the unbleached pulp, the tear index increases from 10 mN m^2/g for the unrefined pulp to 11.5 mN m^2/g (946 mN tear strength) at 18°SR, and then decreases steadily to a minimum of 8.4 mN m^2/g at 73°SR. Tear index values for the bleached pulp are significantly lower and they tend to decrease as the degree of refining increases.

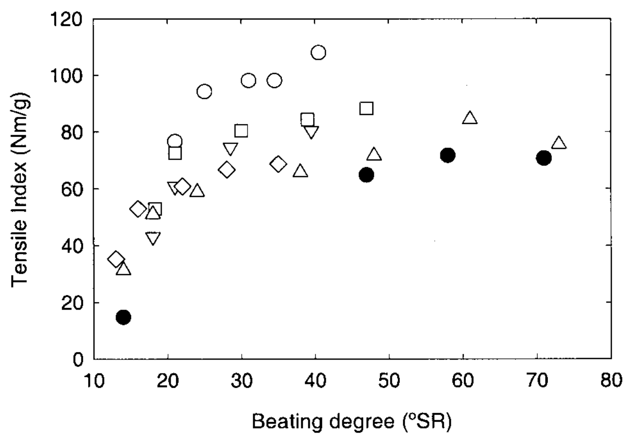

Figure 5. Pulps from *Miscanthus sinensis*: tensile index vs. beating degree. (Unbleached pulps: ○ ASAM,[5] ▽ NS/AQ,[7] □ Soda,[5] ◇ Soda/AQ,[7] and △ this work. Bleached pulp: ● this work).

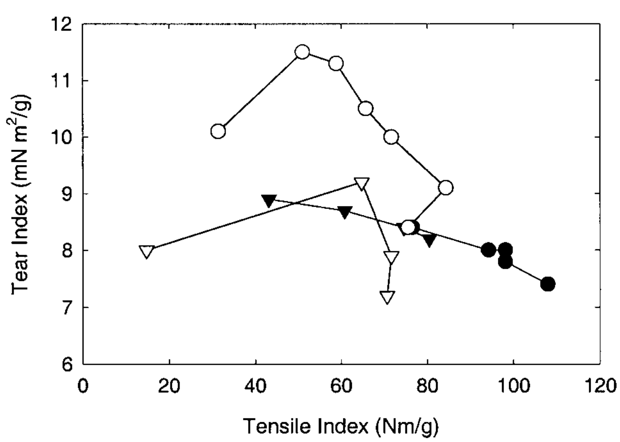

Figure 6. Pulps from *Miscanthus sinensis*: tear index vs. tensile index. (Unbleached pulps: ● ASAM,[5] ▼ Soda,[5] and ○ this work. Bleached pulp: ▽ this work).

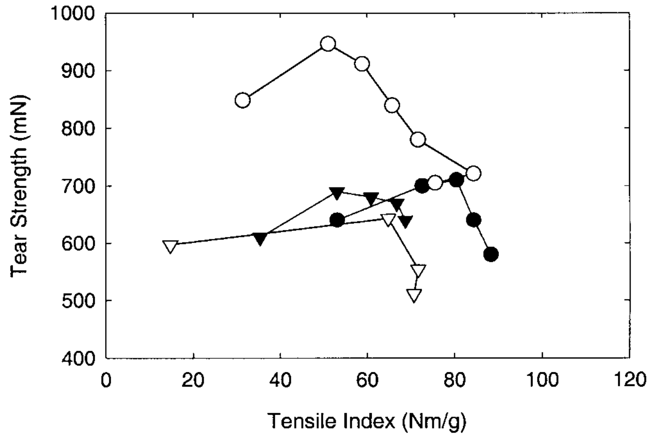

Figure 7. Pulps from *Miscanthus sinensis*: tear strength vs. tensile index. (Unbleached pulps: ● NS/AQ,[7] ▼ Soda/AQ,[7] and ○ this work. Bleached pulp: ▽ this work).

Comparison of the strength properties of the unbleached and bleached IRSP pulps from *Miscanthus sinensis* with unbleached ASAM,[5] NS/AQ,[7] Soda[5] and Soda/AQ[7] pulps is reported in Figs. 4, 5 and 6. Comparison of the tensile index among the different pulps (Fig. 4) shows that the IRSP pulps have tensile indexes equivalent to those of conventional soda[5] soda/AQ[7] and NS/AQ[5] pulps, although they are lower than the breaking length of the ASAM[7] pulp. The IRSP pulps have superior Tear properties, as shown in Fig. 5 (tear index) for the ASAM and soda pulps[5] and in Fig. 6 (tear strength) for NS/AQ and soda/AQ[7] pulps. Evaluation of the physical properties shows that unbleached IRSP pulps from *Miscanthus* are similar to conventional soda and soda/AQ pulps, and they are easily bleached by a TCF sequence based on ozone. Furthermore, brightness and the physical properties of bleached IRSP pulps from *Miscanthus* are similar to those of conventional eucalyptus kraft pulps.[14,15]

CONCLUSIONS

Good quality, bleachable-grade pulps can be produced from *Miscanthus sinensis* by a two-step sequence that involves impregnating the chips with the pulping chemicals, followed by fast pulping by directly steaming them at high temperature. Pulp quality and screened yield are improved if the impregnation is performed on *Miscanthus* canes that have been previously chipped and depithed. The concentration of alkali in the impregnation liquor determines the degree of delignification achieved during pulping: a kappa number below 20 is obtained by impregnation at an alkali charge of 30% NaOH + 0.1% AQCA and pulping at 180°C for 15 min. The resulting *Miscanthus* pulp is easily bleached by a TCF sequence based on ozone. The strength properties of the unbleached *Miscanthus* pulps obtained by the IRSP process are equivalent to those of conventional soda and soda/AQ pulps. The brightness and physical properties of the bleached pulps are similar to those of eucalyptus kraft pulps. The spent impregnation liquor still has a high concentration of alkali, and it can be reused by adjusting its concentration with fresh NaOH solution. Optimizing the impregnation conditions by applying pressure and temperature may further improve the kappa number and strength properties of the pulps.

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REFERENCES

1. Speller, C.S. Weed Control in *Miscanthus* and Other Annual Harvested Biomass Crops for Energy or Industrial Use. In *Proceedings of British Crop Production Conference*; 1993; 671–676.
2. Kordsachia, O.; Baum, N.; Patt, R. Elephant Grass—A Potential Raw Material for the Pulp and Paper Industry? Das Papier **1992**, *46*(6), 257–264.
3. *Miscanthus Handbook*, 94 MW 579; Hyperion Energy Systems Ltd., Main St. Watergrasshill, Co.: Cork, Ireland, 1997.
4. Iglesias, G.; Bao, M.; Lamas, J.; Vega, A. Soda Pulping of *Miscanthus sinensis*. Effects of Operational Variables on Pulp Yield and Lignin Solubilization. Bioresource Technology **1996**, *58*, 17–23.

5. Kordsachia, O.; Patt, R. Suitability of Different Hardwoods and Non-wood Plants for Non-polluting Pulp Production. Biomass and Bioenergy **1991**, *1*(4), 225–231.
6. Kishore, H.; Rawat, N.; Panda, A.; Roy, T.K.; Pant, R. Studies on Bleaching of Elephant Grass (*Miscanthus*) Pulp. IPPTA **1994**, *6*(3), 89–94.
7. Kordsachia, O.; Seemann, A.; Patt, R. Fast Growing Poplar and *Miscanthus sinensis*—Future Raw Materials for Pulping in Central Europe. Biomass and Bioenergy **1993**, *5*(2), 137–143.
8. Montané, D.; Jollez, P.; Salvadó, J.; Farriol, X.; Chornet, E. Rapid Soda Pulping of Wheat Straw by the Impregnation/Rapid Steam Pulping (IRSP) Process. Tappi Journal **1996**, *79*(3), 253–260.
9. Roncero, M.B.; Colom, J.F.; Vidal, T. Enhancing the Ozone Stage Selectivity in a TCF Sequence like XOZP. Part I. Using Pretreatments. Afinidad **2000**, *LVII*(486), 93–100.
10. Browning, B.L. *Methods in Wood Chemistry*; Interscience Publishers: New York/London, 1967; Vol. 2.
11. Casey, P. *Pulpa y Papel*; Editorial Limusa: México, 1990; Vol. 1.
12. Atchinson, J.E.; Bagasse. In *Secondary Fibers and Non-Wood Pulping*, 3rd Ed.; Malcolm, E., Grace, T.M., Kokurek, M., Eds.; Pulp and Paper Manufacture, Joint Textbook Committee of The Paper Industry: Atlanta/Montreal, 1989; Vol. 3, 22–67.
13. De la Rosa, A.; Vidal, T.; Colom, J.F. Optimización de la Etapa O y Op en los Procesos de Blanqueo de Pastas Químicas de Kenaf. In *Proceedings of CIACICYP*, Iguazü (Argentina), 2000; Vol. 1, 280–286.
14. Roncero, M.B.; Vidal, T.; Torres, A.L.; Colom, J.F. Use of Xylanase in the Totally Chorine-Free Bleaching of *Eucalyptus* Kraft Pulp. In *ACS Symposium Series 655, Enzymes for Pulp and Paper Processing*; Jeffries, T.W., Viikari, L., Eds.; 1996; 219–227.
15. Pedrola, J.; Vidal, T.; Colom, J.F. Optimization of Hydrogen Peroxide Stage in TCF Bleaching Sequences of Hardwood Kraft Pulps. In *Proceedings of the Tappi Pulping Conference*; Tappi Press, 1996; 551–557.
16. Martín, A.Ma.; Vidal, T.; Colom, J.F. Influence of New Bleaching Processes (TCF and ECF) on Pulp and Paper Performance. In *Proceedings of the 7th Mediterranean Congress of Chemical Engineering*; Barcelona, Oct. 22–24, 1996; 353.
17. Mir, M.; Roncero, M.B.; Colom, J.F.; Vidal, T. Comparison of TCF and ECF Sequences on Wheat Straw. In *Proceedings of the 6th European Workshop on Lignocellulosics and Pulp*; Burdeos, Sept 3–6, 2000; 473–476.