MISCANTHUS GIGANTEUS AS AN AUXILIARY RAW MATERIAL IN NSSC BIRCH PULP PRODUCTION

JAN BOCIANOWSKI,[*] EWA FABISIAK,[**] KRZYSZTOF JOACHIMIAK,[***]
RENATA WOJECH[***] and ADAM WÓJCIAK[***]

[*]*Department of Mathematical and Statistical Methods, Faculty of Agronomy and Bioengineering, Poznań University of Life Sciences, 28, Wojska Polskiego, 60-637 Poznań, Poland*
[**]*Department of Wood Science, Faculty of Wood Technology, Poznań University of Life Sciences, 28, Wojska Polskiego, 60-637 Poznań, Poland*
[***]*Institute of Chemical Wood Technology, Faculty of Wood Technology, Poznań University of Life Science, 38/42, Wojska Polskiego, 60-637 Poznań, Poland*
✉ *Corresponding author: Adam Wójciak, adak2@neostrada.pl*

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This paper reports the results of neutral sulfite cooking of birch wood, with the addition of *Miscanthus giganteus* stalks as a complementary raw material. The results of the experiments indicate the potential use of miscanthus as an additive in industrial processes.

Keywords: birch wood, *Miscanthus giganteus*, NSSC cooking, degree of delignification

INTRODUCTION

For many years, pulp producers have faced the problem of raw material shortage for pulp production. An important factor in decisions regarding the use of supplementary materials is the economic aspect. Pulp and paper mills use supplementary raw materials in amounts ranging from 5 to 10%, as compared to the basic raw material, *e.g*. kraft pine pulps are manufactured with a 10% addition of spruce, despite the inferior paper properties of spruce as a raw material. Semi-chemical pulps are also produced with the addition of 5% or more of other hardwoods, including waste materials. The use of non-wood raw materials in the production of pulp goes back to the origins of papermaking, so the issue remains a valid one.[1-3]

Among the new species of plants with industrial importance, miscanthus, which is a fibrous perennial grass, has been gaining attention. A large increase in biomass qualifies this plant particularly for energy applications, but the possibility of its use in papermaking should be explored before assuming the creation of large-scale plantations. So far, relatively little research has been dedicated to obtaining pulp from miscanthus, including mainly *via* sulfate, sodium and high-yield TMP and CTMP processes.[4-9] The production of neutral sulfite pulps has been the subject of an even smaller number of studies.[10,11] The results of our previous comparative studies on neutral sulfite pulping of *Miscanthus giganteus* and birch wood indicated that this raw material is subjected to relatively rapid delignification and has a slightly lower pulp yield as compared to birch.[12] By using appropriate digestion conditions (low alkali doses, a low hydro module and short cooking time), we can obtain neutral sulfite pulps from miscanthus with a yield that is comparable to that of hardwood pulps.

The above-mentioned economic issues, which have prompted the search for new types of supplementary raw materials for the pulp and paper industry, have inspired us to commence research on the possibility of using *Miscanthus giganteus* stems for these purposes. The aim of this study was to assess the impact of selected technological factors (liquor to wood ratio, cooking time, content of *Miscanthus giganteus* as a complementary raw material) on basic chemical-technological and strength indicators of neutral sulfite pulps.

EXPERIMENTAL

Materials and studied parameters

For the research, stalks of *Miscanthus giganteus* straw hybrid GM-4 (the fraction of 0.1-1-3.5 cm – thickness-width-length) were acquired thanks to the cooperation with the Institute of Plant Genetics, Polish Academy of Sciences in Poznań. Industrial birch (*Betula verrucosa* L.) chips and sawdust (the fraction collected over screens >ϕ7 and >ϕ3 (according to SCAN–CM–40:94)) were used for all of the digestions.

Pulping methodology

The digestion process (with the exception of the preheating period) was carried out under isocratic conditions in Hägglund's laboratory autoclaves, immersed in a glycerin bath.

The experiments were performed in two variants: one-stage cooking without impregnation; and a two-stage process (impregnation of lignocellulosic material with vapors of neutral sulfite liquor in the first stage and cooking in the second stage).

The impregnation time (the resulting temperature was 140 °C) lasted *ca.* 15 min. Comparative conditions of the digestions were controlled by the H factor (the cooking time was *ca.* 15 and 30 min). The maximum temperature during cooking was *ca.* 174 °C. Two industrial cooking liquors were used for all of the digestions. For the impregnation and cooking stage, neutral sulfite liquors with two different chemical charges were used, *i.e.* 97.97 g/dm^3 and 165.06 g/dm^3 for Na_2SO_3 and 66.04 g/dm^3 and 72.08 g/dm^3 for Na_2CO_3, respectively, with pH of 12.08 and 12.94.

For the proper cooking stage representing a simulation of real industrial conditions, "red" liquor (spent liquor obtained after NSSC pulping), with a density of 1.035 g/cm^3, was added to the portion of liquor introduced before the impregnation stage. Mass ratios (liquor to wood ratio – l/w) from 2 to 5 were used for all of the neutral sulfite cooking experiments. The alkali (Na_2SO_3) to wood (o.d.m.) ratio ranged from 7.4% on o.d. wood, which is similar to industrial conditions, to excessive charges, up to 49% on o.d. wood, thus making possible the appropriate refining of pulp and the formation of paper sheets for further strength tests. From two to four independent digestions were carried out for each experiment. After the digestion, the pulps were washed with running water until a neutral pH was reached. After washing, the pulps were stored and conditioned at room temperature for one week. Then, the moisture content and yield were determined. The data in Table 1 indicate that using initial impregnation and an alkali dosage of 7.4% under laboratory conditions allowed achieving similar rates of cooking liquor consumption as under industrial conditions.

Methods

The chemical composition of the lignocellulosic material (miscanthus stalks and birch sawdust) was determined before and after cooking. The following chemical constituents were determined: Klason lignin (PN-74/P-50092), Seifert's cellulose (PN-62/P-50099), holocellulose with sodium chlorine (PN-74/P50092), pentosans (Tollens' method), hot-water extractives (TAPPI T-207 om-88), cold-water extractives (TAPPI 207 om-88), benzene-methanol extractives (TAPPI 204), extractives with 1% NaOH (TAPPI 212 om-02) and 10% NaOH,[13] as well as ash content (TAPPI T 211 om-07). The yield, degree (dL/L) and selectivity of delignification (L/Hc – ratio of lignin to holocellulose; dL/dY – ratio of degree of delignification to yield loss) were determined for the pulps obtained after cooking.

For each of the technological parameters, the pulp samples were refined in a PFI laboratory mill to reach an appropriate level of 30 ºSR (according to the procedure described in the PFI manual, after refining each sample was subjected to the freeness test, and if the ºSR value was too low, the number of revolutions was increased until the correct value was reached). The pulps obtained after the cooking and refining process were analyzed for their fractional composition on a PulpExpert unit. After the Schopper-Riegler freeness tests (PN-EN ISO 5267-1, 2002), paper sheets were made from all of the pulp samples. Four strength properties were examined, namely SCT – Short Crush Test [EN/ISO 9895], CMT – Concora Medium Test [EN/ISO 7263], tear strength [EN 21974] and burst strength [EN/ISO 2758], for the dried and conditioned paper samples.

Table 1
Comparison of laboratory and industrial technological indices for the spent liquors for separate pulping of birch wood and *Miscanthus giganteus*[*]

Digestion	Raw material	Spent liquor pH	Residual alkali	Dry mass content (%)
Laboratory conditions	Miscanthus	7.97-8.87	14.5-18.3	17.7
	Birch	6.73	10.8	14.3
Industrial (PFI mill)	Birch	6.8-7.56	16.4-22.0	14.5

[*]7.4% Na_2SO_3 on o.d. wood, cooking time *ca.* 15 min, H 117)

Statistical analysis

For each of the tested parameters, the pulping experiments were repeated twice. The results of determining the chemical composition of the pulps are the arithmetic average of three or four determinations performed in parallel. Based on a series of analyses, spreads between the results of parallel and independent determinations were determined and standard deviations were calculated. Results differing over 1% for yield and over 0.4% for chemical composition (lignin, holocellulose) were assumed as statistically significant using the 2σ rule.

For the studied characteristics, the normality of distribution was tested using the Shapiro-Wilk normality test. One-way analysis of variance (ANOVA) was conducted to determine the effects of both *Miscanthus giganteus* and birch wood on CMT, SCT, tear and burst strength. The mean values, least significant differences (LSDs) and *p*-values were calculated, which allowed to create homogeneous groups for the observed traits. Data analysis was performed using GenStat 18.2.

RESULTS AND DISCUSSION

Miscanthus giganteus stems were selected for digestion since they constitute the main part of the plant mass (*ca*. 76% of the raw material) and ensure homogeneity of the fibrous fraction in pulps (leaf fibers differ morphologically from the stem).[6] Although the tested varieties of miscanthus and birch did not differ in terms of content of the main structural components (lignin, cellulose), there were some quantitative differences in the content of holocellulose, pentosans, extractives and minerals (Table 2). The relatively high cellulose (44.6%) and relatively low lignin (21.6%) content in the case of miscanthus is worth noting. According to Nieschlag *et al*.,[14] fibrous plants containing more than 34% of α-cellulose are suitable for papermaking, thus the high content of holocellulose (72.1%) also recommends this raw material for production of semi-chemical pulps.[7] The chemical composition analyses presented here are more or less similar to those reported in the literature.[4,6,15-18] The ash content of miscanthus, although higher than that of birch, was relatively low for grassy plants, and similar data have been reported in the literature.[4,6,17] The relatively low content of mineral substances should not be an obstacle for the pulping process, as it does not use the recovery of spent liquors in the same range as the sulfate method. The different composition of lignin and hemicellulose components in holocellulose in the two raw materials (birch and miscanthus) had an influence on the differences in the content of soluble substances in 1% and 10% NaOH. The high content of the latter substances in miscanthus stems (50.9%) determined this raw material's behavior during cooking.[4]

Previous studies on pulping with miscanthus stems only pointed to rapid delignification and significant loss of yield, even at a relatively low pH of the cooking liquor.[12] The pulp yield was above 80% when miscanthus stems were used as an additive in the range from 5 to 20% in relation to birch wood, even at a high liquid to wood ratio of 5 and an overdose of alkali (49% to o.d. mass) (Fig. 1). Despite these satisfactory results, a decrease in the selectivity of delignification is noticeable along with an increase in the share of miscanthus stems – the loss of lignin is clearly lower in relation to the carbohydrate losses. An explanation of this phenomenon may be the dissolution of hemicelluloses contained in miscanthus stems.

Cooking was done with and without impregnation in order to assess the effect of initial impregnation on the digested raw materials. The selectivity of delignification (L/Hc) was analyzed for various shares of *Miscanthus giganteus* in the reactor feed. The cooking process was performed at a lower liquor to wood ratio (l/w) – equal to 3, thus closer to the one that is used in practice (Fig. 2).

Table 2
Chemical composition of *Miscanthus giganteus* stems and birch sawdust

Content (%)	Miscanthus	Birch	Content (%)	Miscanthus	Birch
Lignin	21.6	21.1	10% NaOH	50.9	35.6
Cellulose	44.6	43.7	Cold H_2O	4.4	0.7
Holocellulose	72.1	68.7	Hot H_2O	6.0	1.6
Pentosans	29.1	23.5	Extractives	4.5	2.4
1% NaOH	35.3	15.8	Ash	1.6	0.4

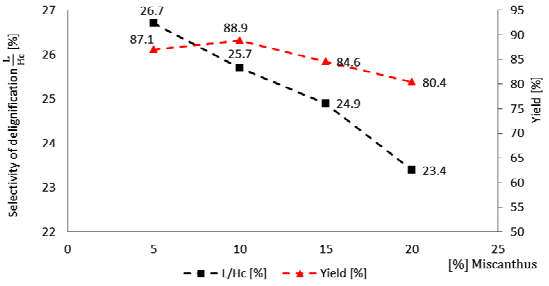

Figure 1: Influence of miscanthus content on the yield and selectivity of delignification of birch neutral sulfite pulps (initial impregnation, liquor to wood ratio of 5, cooking time *ca.* 15 min, 49% Na_2SO_3 on o.d. wood)

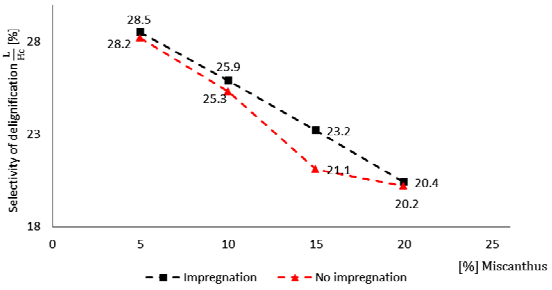

Figure 2: Effect of initial impregnation on the selectivity of birch wood delignification with the use of *Miscanthus giganteus* stems (cooking time *ca.* 15 min, H 131, l/w = 3, 41% Na_2SO_3 to o.d. mass)

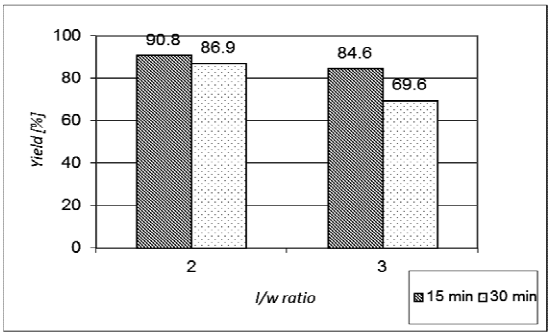

Figure 3: Effect of liquor to wood ratio (l/w) on pulp yield (10% miscanthus and 90% birch wood; initial impregnation, 31% Na_2SO_3 on o.d. mass)

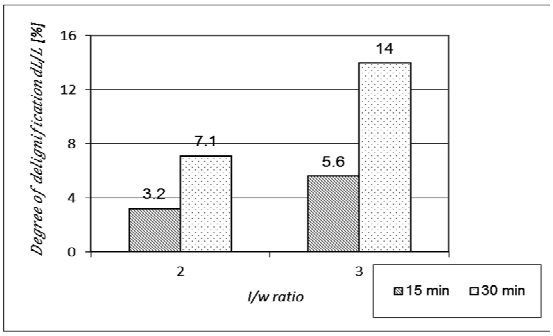

Figure 4: Effect of liquor to wood ratio (l/w) on delignification level (10% miscanthus and 90% birch wood; initial impregnation, 31% Na_2SO_3 on o.d. mass)

Similar relationships were obtained for selectivity of delignification to those resulting from the tests carried out at a higher hydro module (Fig. 1).

In this experiment, there were no clear differences between the results of digestion with and without this initial step. The initial impregnation had a slight effect on intensifying delignification or dissolving the hemicelluloses, but it did not change the mutual quantitative relations between delignification and carbohydrate degradation. The impregnation process, on the other hand, caused softening of the raw material and affected some of the tested pulp's strength properties.

Neutral sulfite pulping is a process that mildly interferes in the chemical composition of wood. Its chemistry is based on sulfonation of lignin, which is primarily subjected to softening and less to permanent removal, *i.e.* delignification. The aim of the process is to obtain pulp with the highest possible yield, which will be suitable for refining and production of fluting, *i.e.* paper with specific strength properties, where stiffness is a priority. In order to approximate the cooking conditions used in industrial practice, subsequent experiments were carried out at lower liquor to wood ratio (2 and 3), while maintaining the two-stage process (initial impregnation and main digestion).

In the experiments, despite the relatively low liquor to wood ratios, an overdose of alkali (31% and 41% on o.d. mass) was still used to facilitate sawdust fiberization in the laboratory mill and then to form the paper sheets to determine the strength properties. The results of the experiments for a short cooking time (15 min) indicate a relatively small reduction of yield with the increase of the liquor to wood ratio. Extending the cooking process up to 30 min already caused a significant loss of mass from the raw material charge (Fig. 3). Yield changes were reflected in the delignification levels (Fig. 4). Increasing the liquid to wood ratio and the cooking time almost

doubled the increase of the delignification level. The absolute lignin losses for a liquor to wood ratio of 2 and for a shorter cooking time (15 min) were still low (*ca*. 0.7%), similar to the effects of digestion in a Bauer digester under industrial conditions. This proves that it is possible to approximate the industrial conditions (continuous digestion) under laboratory conditions (batch cooking). Extending the cooking process time from 15 to 30 min, for the liquor to wood ratio of 3, resulted in an almost threefold increase in the degree of delignification (from 5.6% to 14%). Considering the dosing of reagents, it appears from the data that the cooking time determined the pulp yield and delignification level, and to a lesser extent the increase in alkali charge. To a certain extent, this tendency is confirmed by the results of the delignification selectivity level (calculated as the ratio of lignin and holocellulose content changes), which indicate a significant increase in non-lignin losses due to the interaction of the cooking time and the increased alkali charge (Fig. 5). Increasing the dosage of alkali, along with a short cooking time (15 min), did not change the relationship between the loss of lignin and carbohydrates.

A slightly different relationship is shown in the analysis of delignification selectivity changes in relation to the loss of yield (Fig. 6). Although the decrease in selectivity, along with the increase in alkalinity of the liquor, confirms, to a certain extent, the previous experiments (Fig. 5), a higher liquor to wood ratio caused a decrease in the selectivity of delignification for a short digestion time as well, *i.e.* 15 min. This result may consist of yield losses not only for the carbohydrate components (including easily soluble oligosaccharides, not determined along with the holocellulose), but also for other non-carbohydrate extractives. The results shown in Figure 6 also confirm previous observations, which indicated a deeper delignification with extending the cooking time, regardless of the dose of alkali.

Figure 5: Effect of liquor to wood ratio (l/w) on delignification selectivity (10% miscanthus and 90% birch wood; initial impregnation, 31% Na_2SO_3 on o.d. mass)

Figure 6: Effect of liquor to wood ratio (l/w) on delignification selectivity (10% miscanthus and 90% birch wood; initial impregnation, 31% Na_2SO_3 on o.d. mass)

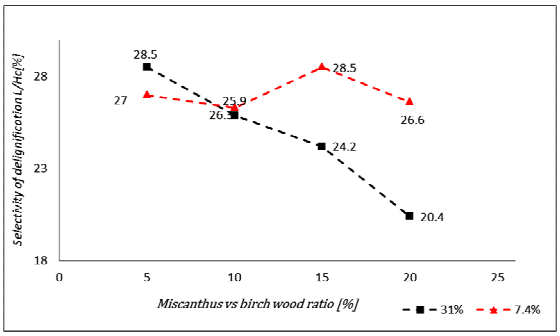

Figure 7: Influence of *Miscanthus giganteus* content on delignification selectivity for 31% Na_2SO_3 on o.d. mass and 7.4% Na_2SO_3 on o.d. mass; (initial impregnation, cooking time 15 min, H 131)

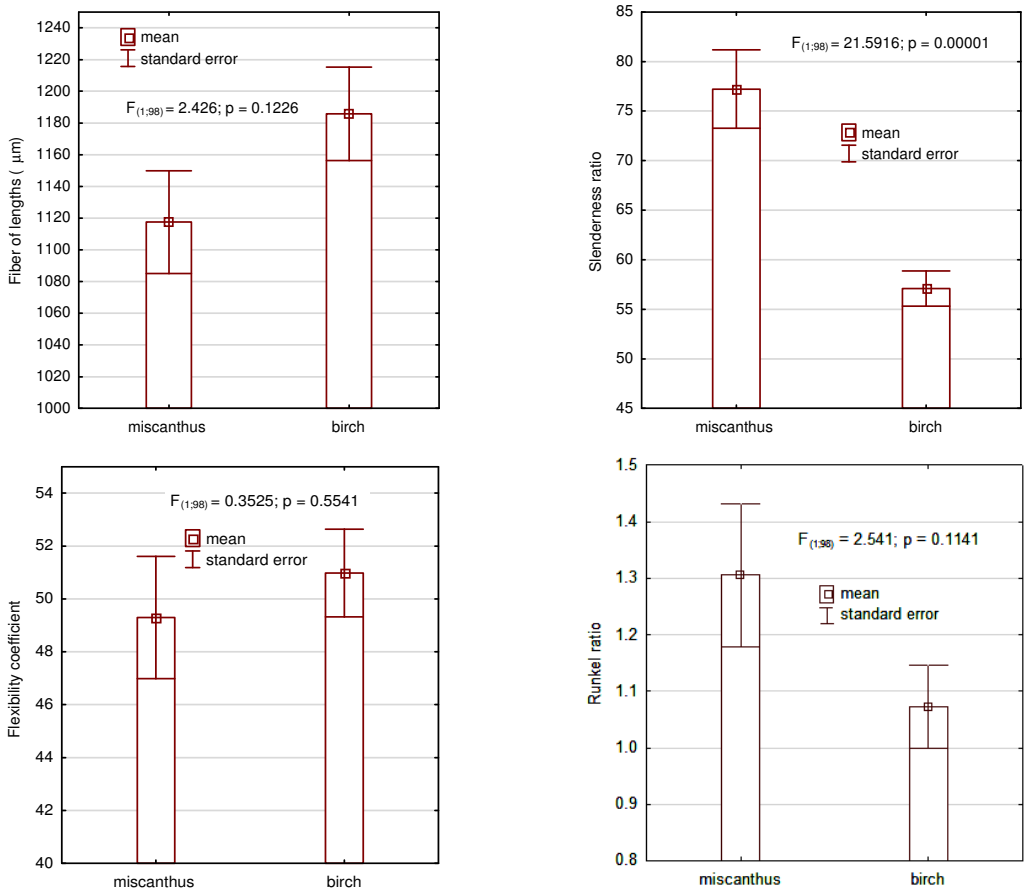

Figure 8: Comparison of fiber length, slenderness, flexibility and Runkel coefficient for birch wood and miscanthus stems (before digestion)

The manner in which the alkali charge dose, along with the cooking liquor, influenced birch wood processing, with the addition of miscanthus stems, is indicated by the experiments carried out with Na_2SO_3 doses similar to those used in industrial practice, *i.e.* 7.4% on o.d. wood (Fig. 7). The use of a low dose of alkali reduced the dissolution of lignin and of some of the hemicelluloses contained in miscanthus. Despite this raw material's increasing share in the feed of the digester, the presence of miscanthus stems in an amount of up to 20% did not affect the selectivity of delignification.

The results of the chemical composition (lignin and holocellulose) analyses of laboratory neutral sulfite pulps from birch wood with the addition of miscanthus stems, obtained under conditions similar to those for industrial processing (Fig. 7), indicate the possibility of using *Miscanthus giganteus* stems as a supplementary raw material in the process of neutral sulfite processing of birch wood.

The practical suitability of a raw material for the production of paper products is influenced not only by that raw material's chemical composition, but also by its anatomical structure. Microscopic analysis of the morphological features of fibrous elements was started by conducting a comparison of the raw materials before digestion. A comparison of the fiber length indicated no significant differences between the tested raw materials (Fig. 8). However, the diameters of miscanthus fibers and lumens were smaller than those of birch fibers. The average lengths of miscanthus fibers (1185.8 µm), fiber diameters (16.2 µm) and lumens (8.64 µm) were similar to those reported in the literature data.[9,17] The results obtained for the measurements of the mean values for the slenderness coefficient (77.2), flexibility (49.3) and Runkel coefficient (1.3) were also similar to those in the paper by Ververis *et al.*[17]

Comparative statistical analyses showed that the miscanthus fibers were characterized by similar flexibility and Runkel coefficient, but had a higher slenderness index than that of birch fibers. The average value of Runkel coefficient was higher for miscanthus, but differences in the cell wall thickness resulted in measured values that were characterized by a high coefficient of variation (Fig. 8).

An analysis of the fractional composition changes (Table 3) and strength properties (Figs. 9 and 10) was conducted for the birch pulps by increasing the addition of miscanthus stems from 5% to 20% milled at identical rotor speed of *ca.* 30 °SR. The fiberization index (Table 3) is the factor developed by authors to compare the refining ability of fibers. This index represents the relation of PFI revolutions to the ºSR value and describes how many revolutions of the laboratory mill were needed to achieve an increase of 1ºSR freeness. As expected, initial impregnation of the raw materials had a positive effect on the pulps' fiberization index, although no clear differences were found in the fractional composition of the pulps obtained with the impregnating process and without it. There was also no influence of the addition of miscanthus on the fractional composition of the pulps, with the exception of a slight decrease in the fraction of short and medium fibers for the pulps with a 20% share of miscanthus for both cooking variants.

Table 3
Fiber fractions in neutral sulfite pulps with various shares of *Miscanthus giganteus* and birch*

Measurements	Ratio of *Miscanthus giganteus* (%)							
	Digestion with initial impregnation				Digestion without initial impregnation			
	5	10	15	20	5	10	15	20
Fiberization (number of revolutions/°SR)	75	80	73.9	87.3	88.9	85.7	80	85.7
Basic weight (g/m^2)	130.6	129.7	130	130.6	128.7	129.7	132.5	130.9
PulpExpert								
Avg. fiber length (mm)	0.91	0.97	0.97	0.97	0.96	0.92	0.94	0.97
Curl (%)	8.7	8.4	8.6	8.5	8.2	8.2	8.6	8.6
Fine fibers (%)	5.6	4.5	4.8	5.4	4.2	4.8	5.3	5.4
Short fibers (%)	43.4	41.2	41.1	40.6	41.9	44.3	42.3	41
Middle fibers (%)	43.5	44.9	44.6	44.1	45.0	43.4	43.8	43.6
Long fibers (%)	7.6	9.4	9.4	9.8	9.0	7.5	8.6	9.9

*41% Na_2SO_3 on o.d. mass, liquor to wood ratio of 3, with and without initial impregnation, cooking time of 15 min, H 131

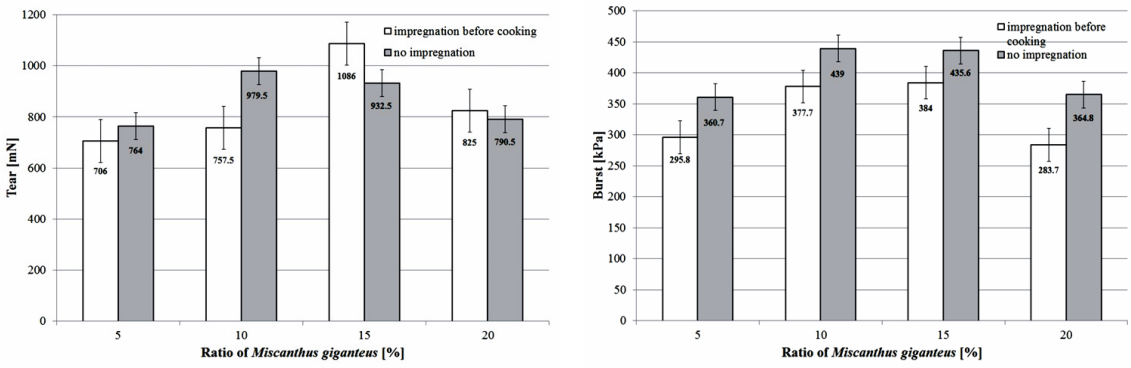

Figure 9: Effect of adding *Miscanthus giganteus* on tear and burst indices (cooking and beating as described in Table 3, 30 °SR)

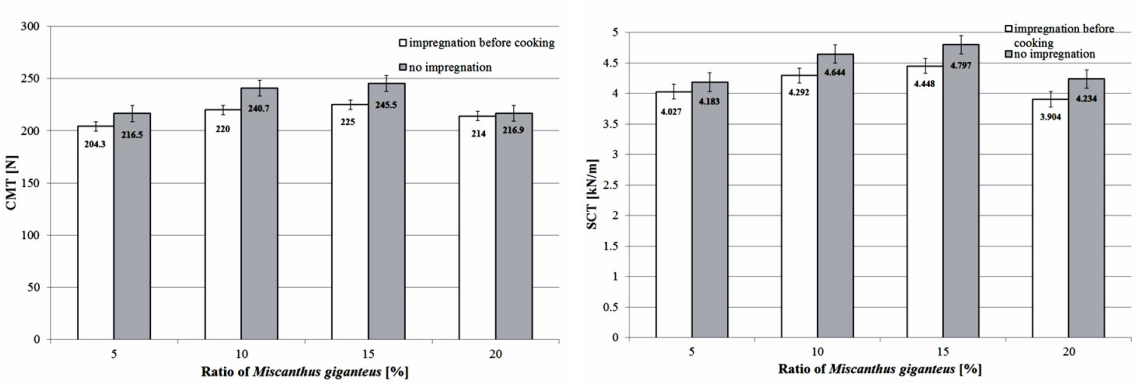

Figure 10: Effect of adding *Miscanthus giganteus* on CMT and SCT indices (cooking and beating as described in Tables 3, 30 °SR)

Although the reduction in the content of short and medium fibers was relatively small, it may have had an effect on reducing the strength properties of the pulps with a 20% share of miscanthus (Figs. 9 and 10). The general trend is that the strength properties increased with increasing miscanthus content up to 15% for tear resistance (tests with initial impregnation), and in the range from 10 to 15% for burst resistance (tests with and without initial impregnation). For tear resistance, there was no significant effect of initial impregnation on the strength of the paper sheets.

The burst tests showed increased resistance to bursting in the papers obtained from pulp produced without initial impregnation. This phenomenon cannot be associated with fiber length (tear resistance decreases with a shortening of fibers), although a slightly higher share of short fibers in the pulps obtained without initial impregnation may have had some significance as they constituted about half of the share of fibers with papermaking ability (short and long fibers constituted ca. 86-88% of all the fibers in the tested pulps).

Figure 10 shows the results of CMT and SCT tests performed for various miscanthus proportions in neutral sulfite birch wood pulp. The tests, once again, demonstrated an increase in the above-mentioned strength parameters for the miscanthus proportions in the range from 10 to 15%. However, when the proportion of the auxiliary raw material was increased up to 20%, all of the strength parameters under study were found to have decreased. An important finding is that the strength was higher in the samples prepared without initial impregnation, and statistically significant differences were noted between the tests performed with and without impregnation. The tested indicators were most probably influenced not so much by the fractional composition of the fibers as by the method of processing. The pulps obtained in the process without initial impregnation were slightly more deeply delignified and thus easier to refine. They also had a slightly higher share of holocellulose in the fibers, which could have affected the general papermaking properties and, as a result, their strength (Fig. 2).

CONCLUSIONS

The content of holocellulose and lignin in *Miscanthus giganteus* stems does not differ from that in birch wood (*Betula verrucosa* L.). The relatively high content of alkaline-soluble compounds in miscanthus stems requires the use of short cooking times and a low digesting liquor to wood ratio.

The results of the chemical composition analyses (lignin and holocellulose) and the delignification selectivity of the laboratory neutral sulfite pulps of birch wood with the addition of miscanthus, obtained using an alkali charge similar to the industrial charge (7.4% Na_2SO_3 to wood), showed the possibility of using *Miscanthus giganteus* stems as a raw material in the neutral sulfite cooking process of birch wood. Using a liquor to wood ratio of 2, initial impregnation and a main cooking time of 15 min allowed obtaining a neutral sulfite pulp with a yield exceeding 80%.

The highest strength properties were obtained for the neutral sulfite pulps comprising *Miscanthus giganteus* in the range from 10 to 15% in relation to birch wood. An overly high percentage of miscanthus fibers (20%) resulted in

lowering the strength property indicators, such as the SCT, CMT, burst and tear indices.

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