

Nitric Acid-Alkali Two-stage Pulping of Wheat Straw, Industrial Hemp, and *Miscanthus × giganteus*

Dariusz Danielewicz *

Index levels of the process of pulping wheat straw (WS), industrial hemp stalks (HS), and *Miscanthus × giganteus* (MS) using the nitric acid-alkali (NA–A) method (HNO₃/KOH and HNO₃/NH₄OH two-stage sequential delignification systems) were determined. The research showed, as a rule, a lower total yield of NA–A pulps than kraft pulps from WS, HS, and MS, and a lower level of the tensile index and tear resistance compared to the properties of soda-AQ and kraft pulps presented in other studies, as well as the author's own studies. Additionally, the levels of nitrogen (in different forms) and potassium in the combined post-pulping filtrate were determined. Their levels were found to be higher than in the fertilizer solution used to fertilize tomato crops grown on soilless substrates in greenhouses. However, application of filtrates from pulping of nonwoody plant straw using NA-A method requires determining the effectiveness of this type of fertilizer solution, its impact on the horticulture and agriculture plants, and the properties of their output including grains, tubers, and fruits.

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Contact information: Fibrous Papermaking Pulps Technology Team, Centre of Papermaking and Printing, Lodz University of Technology, Wolczanka 223 Str., 90-924 Lodz, Poland;

* *Corresponding author:* dariusz.danielewicz@p.lodz.pl

INTRODUCTION

The two-stage method of pulping plant fibrous raw materials (PFRM) consisting of the nitration (N) of lignin in the first stage with nitric acid and its extraction (E) with alkali in the second stage, *i.e.*, the nitric acid-alkali (NA–A) method, is a known method of obtaining fibrous papermaking pulps. This method of producing this type of pulp was first patented in Great Britain in 1861 (Kalish 1967). In 1937, using a similar method, the I. G. Farben concern in Wolfen (Germany) started the production of nitrogen cellulose from beech wood, called N-Zellstoff, which was to be a substitute for nitrocellulose from cotton linters. However, production of this product was discontinued after World War II (Kalish 1967). An example of an attempt to introduce the NA-A pulping process into industrial practice is also the Delbay process. The pulping of wood in this process was performed in a special lying-type reactor, which is divided into two parts. In the first one, called the nitrator, wood chips are treated with 42% nitric acid and then extracted/neutralized with NaOH (Brink 1961).

In 1961, Brink (1961) proposed the use of black liquors from the pulping of white spruce using the NA–A method (HNO₃/NH₄OH system) as fertilizer for agricultural purposes. In the second part of the paper under Brink's direction (Brink *et al.* 1961), the

authors completed several attempts to pulp white spruce with the use of a 10% nitric acid solution, *i.e.*, dosing of this acid at approximately 100% to oven-dry (o.d.) wood with the use of alkaline extraction with ammonia as the second stage of the process. The third part of work (Brink *et al.* 1962) concerned the balance of nitrogen in the process of pulping of white spruce with the NA–A method.

In the mid-1960s, pulping of softwood and hardwood using the NA–A method was discussed by J. H. Kalisch. He developed a new industrial-scale process for pulping this PFRM using this method in the so-called rapid cycle (NARC - Nitric Acid Rapid Cycle). In this process, the wood wafers were nitrated at two stages using 12.0 to 14.5% and 0.9 to 2.1% of HNO₃ solutions, respectively, washed, and extracted in the E stage (Kalish 1967). In contrast, Kurrle (1963) processed red spruce wood from the trunk, tips, roots, and branches of this species into NA–A pulps using HNO₃ water solutions with a concentration of 16 to 17% at a liquid-to-wood ratio of 6:1 (*i.e.*, using approximately 114 to 122% HNO₃ for wood), followed by alkaline extraction.

Relatively large amounts of HNO₃ on o.d. on PFRM were also used by Biyani *et al.* (1967), *i.e.*, 52.2% and 66.8% on o.d. of bamboo (the nitric acid concentration in the cooking liquor was 8 to 10%, cooking liquor-to-PFRM of 6:1). An important result of this study was that the pulping of bamboo using the NA–A method gives pulps that are stronger if the pulping temperature is lower, *e.g.*, 75 °C rather than 85 °C, and that NA–A pulps have low pentosane content, which predisposes the NA–A process to produce dissolving kinds of pulps.

In the 1970s, a method of pulping PFRM (wood, straw) using the NA–A method was developed in Poland (Nitramcel process), using the black liquor from such pulping as fertilizer. In this process, PFRMs were first impregnated with a solution containing 0.1% dimethyl oleic acid amide and 0.05% imidazolium inhibitor or ammonium nitrate for cellulose protection, then nitrated using of 15 to 18% nitric acid solution, and finally extracted with alkali (Kin 1990).

The issue of pulping wood by the NA–A method was also extensively studied in the Soviet Union. For example, Sorokin and Bakina (1977) studied the extraction of nitric acid-nitrated birch and poplar wood with different alkalis, while Gorbunova *et al.* (1993a,b,c) discussed the chemical composition of black liquors from NA–A pulping.

In 1990, Ngamveng and Ndikontar presented the results of pulping cassava stems (*Manihot esculenta* Crantz) using the NA–A method with concentration of nitric acid in the nitration stage of 7.5% (*i.e.*, about 32% o.d. PFRM) and extraction of nitrated PFRM with alkali.

More recently, Yang *et al.* (2019) found that the optimal conditions for pulping birch wood (*Betula platyphylla*) in nitration stage are a nitric acid concentration of 9.2%, a liquor-to-wood ratio of 10:1 (*i.e.*, approximately 101% HNO₃ on o.d. PFRM), 85 °C, and 4.3 h. Even greater amounts of HNO₃ in the stage of nitration on o.d. PFRM [(black mustard (*Brassica nigra* L.) and camelina (*Camelina sativa* L.)], *i.e.*, approximately 127% to the o.d. PFRM (concentration of HNO₃ solution of 6%, with a cooking liquor-to-PFRM ratio of 20:1), were used by Hájková *et al.* (2021).

Attempts to pulp PFRM by the NA–A method were also performed with lower concentrations of nitric acid in the N stage. For example, Ivanow *et al.* (1978) showed that wood can be processed into pulp by the NA–A method using a concentration of nitric acid of 2 to 6% in the nitration stage, while Shishonok *et al.* (1997) that such effect can be obtained using concentration HNO₃ of 1 to 2% in this stage.

It was also proposed to use the NA–A method to obtain chemical-mechanical pulps from bagasse (El-Taraboulsi *et al.* 1983a) and rice straw (El-Taraboulsi *et al.* 1983b).

In the works mentioned above, the temperature and time conditions of the nitration and extraction processes, as well as the type of substance used for the extraction of lignin in the E stage, were also presented. The review of these conditions shows that in order to obtain the desired pulping degree of PFRMs, it was necessary to conduct these processes at temperatures elevated to the ranges 75 to 100 °C and 75 to 130 °C, respectively, for one to four hours. For the removal of lignin from the nitrated raw material, hot 1 to 5% solutions of alkali were used. As the source of alkali, sodium-containing alkalis (NaOH or in one work also Na₂CO₃, and NaHCO₃) were used. Only in works of Brink *et al.* (1961), Kin (1990), and Sorokin and Bakina (1977), NH₄OH was used instead of NaOH.

The current study aims to determine the level of basic processing indices of wheat straw (WS), industrial hemp (*Cannabis sativa* L.) stalks (HS), and *Miscanthus × giganteus* (MS) (*i.e.*, non-woody plant materials growing well in the northern temperate climate zone, such as in Europe) pulping using the NA-A method in temperature-time conditions described in works of other authors. In addition to the type of PFRM, this work is distinguished from the work of other authors by dosing of HNO₃ as percentage on the o.d. weight of PFRMs (*i.e.*, as in the case of industrial production of kraft pulps) at a liquor-to-PFRMs ratio at a constant level of 5, and by using KOH or NH₄OH as the alkalizing agents in the E stage. The difference is also the determination of the content levels of total nitrogen, nitrate nitrogen, ammonia nitrogen, and potassium in the combined post-cooking filtrate (CPF) obtained by combining the filtrates from the N, E and washing stages using contemporary analytical methods.

EXPERIMENTAL

Fibrous Raw Materials

Unsorted WS (with leaves and ears) cut into sections of approximately 20 mm, similarly cut MS stalks (without leaves), and HS stalks (also without leaves) cut into 3 to 6 mm sections were used in the study. The purpose of cutting fibrous raw materials was to facilitate the penetration of nitric acid into these raw materials and to remove nitrated lignin from them at the alkaline extraction stage. In the case of hemp stalks, their greater fragmentation was caused by the need to shorten the long hemp bast fibers to reduce their tendency to spin during the formation of paper handsheets and deteriorate their formation. These PFRM were obtained locally from small plantations owned by Polish farmers. Birch (*Betula pendula*) (B) and pine (*Pinus sylvestris*) (P) chips were obtained from one of the Polish pulp mills (Fig. 1).



Fig. 1. WS (A), HS (B), and MS (C)

Pulping of PFRM Using the NA–A Method

The pulping of WS, MS, and HS using the NA–A method was performed in a Hato rotary digester (LD8; Hato Oy, Helsinki, Finland) in autoclaves with a capacity of 3000 cm³, usually 100 g of o.d. of these raw materials. Nitric acid was dosed in terms of the pure compound in the amount of 5 to 30% on the o.d. of PFRMs (in most cases 10 to 30% on o.d. PFRM). The liquid-to-PFRMs ratio in these experiments was always 5. The range of concentrations of nitric acid in the digestion process was therefore in the range of 1 to 6% (in most cases of 2 to 6%). Before starting the heating, the fibrous raw materials were left in the autoclaves for 1 h to supersaturate them with a nitric acid solution on the principle of penetration. After this period, the digester heating was started. The time of heating to the maximum temperature (60 to 90 °C) was the same for all experiments and amounted to 1 h, while the time of pulping ranged between 2 or 3 h. After the nitration stage, the cooking acid was drained, and then the PFRM was poured twice with tap water in a pile and left for 3 h to wash the raw material from acid residues by diffusion (two stages of such washing) and filtered on a Buchner funnel lined with cheesecloth. After nitration and washing, the pulped material was subjected to alkaline extraction (E) with aqueous potassium hydroxide (KOH), or in selected experiments ammonia hydroxide (NH₄OH) to extract nitrated lignin from it. Extraction was also performed in a Hato rotary digester. The KOH and NH₄OH were dosed into these autoclaves in the amounts of 2 to 10% on the o.d. PFRM (in most cases 10% on o.d. PFRM). The liquid-to-PFRM ratio in the E stage was 5:1, while the concentration range of KOH or NH₄OH in the E stage was in the range of 0.4 to 2.0% (in most cases 2%). Extraction experiments were performed at 80 or 90 °C. Heating time and extraction time were respectively, 1 h and 2 to 3 h. After extraction, a strong alkaline filtrate was drained, and then the raw material was washed with tap water in a bucket, left for 3 h for diffusion washing (two stages of such washing), centrifuged, and stored in plastic bags for further research. After washing, pulped raw materials were disintegrated in a laboratory disintegrator and screened on a Weverk screen. Uncooked parts of raw materials, after separated from pulp, were refined in a laboratory Bauer disc refiner and then added to screened pulp. The pulp was then centrifuged, and after determining its dryness, it was stored in a wet condition in a refrigerator in closed polyethylene bags.

PFRMs Pulping by the Sulfate Method (Kraft Pulping)

To compare the total yield of NA–A and kraft pulps from WS, HS, MS, B, and P, kraft pulps were obtained as a result of the pulping of these raw materials by the sulfate method (kraft pulping). Kraft pulping experiments of PFRM were made in a laboratory Santasalo-Sohlberg digester using 11.5 to 18.5%, 14 to 18%, 12 to 18%, 18 to 26%, and

18 to 26% of active alkali to o.d. raw material, respectively. The sulfidity of white liquor in these experiments and the liquor-to-wood ratio were 25% and 5:1 for WS, HS, and MS, and 4:1 for wood samples, respectively. The time of heating to the pulping temperature (165 °C) and the time of pulping at this temperature were 90 min in each case. After pulping, pulped PFRMs were washed with water preliminarily on a wire mesh, then by diffusion overnight in a bucket, and finally disintegrated in a laboratory disintegrator. Uncooked parts of raw materials, after separated from the pulp, were refined in a laboratory disc refiner and then added to screened pulp. The pulp was then centrifuged, and after determining its moisture content, it was stored in a wet condition in a refrigerator in closed polyethylene bags.

Content of Lignin and Cellulose in PFRMs and Pulps Properties of in Loose Form

The content of lignin and Seifert cellulose in WS, HS, and MS were determined according to PN-74/P-50092 (1992) standard. As for pulps, the degree of pulping, *i.e.*, kappa number (KN) and intrinsic viscosity (η_{CED}) of pulps were determined. The KN was determined according to the PN 85/P 50095.02 (1985) and ISO 5351-11 (1981) standards.

Pulp Properties in the Form of Handsheets

The pulps KN 8.9 WS NA-A pulp (obtaining conditions Table 1, row 5), KN 8.9 HS NA-A pulp (obtaining conditions Table 1, row 14), and KN 11.5 MS NA-A pulp (obtaining conditions Table 1, row 20) were used for these tests. The handsheets properties of these pulps were compared with the properties of handsheets of KN of 9.4 B kraft pulp and KN of 22.5 P kraft pulp. The beating of these pulps was completed in the Jokro mill according to the PN-EN 25264-3 (1999) standard. Before beating, the pulp samples were soaked in water for 18 h. The freeness of beaten pulps was expressed as Schopper-Riegler freeness (S-RF), measured according to the PN-EN ISO 5267-1 (2002) standard. After beating, the pulp sample was transferred to the laboratory distributor and diluted to a consistency of 2%. This slurry was used for making handsheets of paper with a basis weight of 75 ± 3 g/m² in standard Rapid-Köthen apparatus according to PN-EN ISO 5269 (2001). The mechanical properties of pulps in the form of paper handsheets in static (*e.g.*, tensile strength, stretch at break) and dynamic conditions (*e.g.*, tear strength) were determined after their conditioning according to the PN-EN 20187 (2000) standard. Testing of these properties was conducted according to the PN-EN ISO 1924-2 (2008) and the PN-EN ISO 1974 (2012) standards using tensile strength tester BZ2.5/TN1S (Zwick/Roell, Ulm, Germany) and ProTear tester (Thwing-Albert, West Berlin, NJ, USA) apparatuses. For the measurement of the thickness of the handsheet, the papermaking micrometer was used with an accuracy of 0.001 mm.

Total Nitrogen, Nitrate Nitrogen, Ammonium Nitrogen, and Potassium Contents in the Combined Post-Cooking Filtrate

The fertilizing substances content was determined in filtrates from pulping of two samples of WS using the NA-A method, performed using 15% HNO₃ to o.d. PFRM in the nitration stage and alkaline extraction with 10% KOH (experiment 5) and 10% NH₄OH on o.d. WS. These tests were made with 50 g o.d. WS. The time and temperature conditions in these experiments corresponded to the conditions of experiment no. 5 and no. 13 from Table 1. For these tests, the filtrates from the nitration and alkaline extraction stages and

from the process of washing the pulp WS twice after these processes with water in the amount of 250 mL in each of its stages were preserved, giving a total of six aliquots of filtrates from one pulping experiment. The filtrates from each of the two NA–A pulping experiments were then combined and neutralized to pH 7 using KOH or NH₄OH. This gave approximately 1500 mL of combined post-cooking filtrate (CPF). This filtrate was analyzed for the content of total nitrogen (N_T), nitrate nitrogen (N-NO₃), ammonium nitrogen (N-NH₄), and potassium (K). N_T was determined using the conductometric method according to Dumas (method symbol PB-08) using the TruSpec CNS analyzer (LECO Europe BV, Geleen, Netherlands). N-NO₃ and N-NH₄ were determined potentiometrically. Potassium was determined by inductively coupled plasma atomic emission spectrometry (ICP-OES) (Optima 2000 DV ICP; Perkin-Elmer Inc., Waltham, MA, USA). The tests were carried out in Institute of Horticulture in Skierniewice (Poland).

Elaboration of Results

The determination of Y_T, KN, η_{CED} , and S-RF of pulps was performed twice for each pulp. Therefore, the results of the determination of these properties presented are the average of the two determinations. The standard deviations of the measurements of these properties ranged in the following intervals: 0.4 to 0.8%, 0.3 to 0.7 units, 10 to 23 cm³/g, and 0.5 to 1.0 °SR, respectively. From WS, HS, and MS NA–A pulps and from B, and P kraft pulps, two sets of eight paper handsheets were prepared. The paper formation was then visually examined against a light source to choose two sets of six handsheets each, representing the best-formed paper samples. These two sets of paper handsheets for each pulp sample were then used for the determination of the mechanical properties of pulp and bulk. Ten determinations of these properties were performed for each set of handsheets, so after the testing, there were two mean values for each property. In Table 2, the arithmetic average of these two values is presented. The standard deviations of the measurements of these properties ranged in the following intervals: 3.1 to 6.7 N·m/g, 0.2 to 0.5 mN·m²/g, 0.1 to 0.3 %, and 0.021 to 0.056 cm³/g, respectively.

RESULTS AND DISCUSSION

Table 1 shows the conditions for processing wheat straw into NA–A pulps and their KN. This Table shows that under the conditions of the WS pulping using the NA–A method described in rows 1 to 4 of Table 1, the splinter-fibrous (S-F) form of WS was obtained after mechanical fiberization, indicating that the sufficient high point of fiber liberation of the WS for pulps and a low residual lignin content in this case was not obtained due to too mild conditions of the NA–A pulping process. For this reason, the KN of the resulting fiber intermediates was not determined. This situation was marked in Table 1 as an F-S shortcut. For greater certainty of obtaining well-pulped pulps from WS in subsequent experiments, the amount of HNO₃ was increased to 15 to 30% of HNO₃ on o.d. WS and the amount of KOH to 10% on o.d. of this PFRM. This change brought the desired effect because, in this case, after mechanical fiberization, fibrous semi-finished products were obtained, in which most of the WS could be defibrated to single fibers, which made it possible to determine the kappa number by the standard and to prepare paper handsheets of pulps.

The data in Table 1 show that the pulping of WS described in row 5 allowed for the preparation of KN 8.9 NA–A pulp. Experiments conducted in similar time and temperature

conditions (experiment no. 6) but with the use of 20% HNO₃ on o.d. WS made it possible to obtain a pulp with an even lower KN, *i.e.*, 6.6 units. For trials conducted with 20% HNO₃ on o.d. WS, the effects of pulping with the amount of KOH reduced to 5% and 2% in the E stage were also examined due to the separation of black liquor from WS after pulping in the N stage and double washing of nitrated material. However, it seems that such amounts of KOH used for the E stage were too small, because the KN of the obtained NA–A pulps increased to 26.9 and 34.3 units, respectively. Considering the observed increased level of splinters in WS digester pulp when the KN of the pulp was 26.9 to 34.3, it can be concluded that such a level of lignin content may be too high. Therefore, the amount of KOH in the E stage should be more than 5% on o.d. PFRM, *i.e.*, for example, 10% on o.d. PFRM.

Table 1. Conditions of Processing WS, HS and MS into NA–A Pulps and Their KN

O.n.	Nitration (N), % HNO ₃ on the o.d. of WS	Temp. (°C/h)	Extraction (E), % Alkali on the o.d. of WS	Temp. (°C/h)	Pulp Form or KN
WS					
1	5	60/3	KOH, 2%	80/3	S-F
2	10	60/3	KOH, 2%	80/3	S-F
3	10	70/3	KOH, 3%	80/3	S-F
4	10	80/3	KOH, 5%	80/3	S-F
5	15	90/2	KOH, 10%	90/2	8.9
6	20	90/2	KOH, 10%	90/2	6.6
7	20	80/3	KOH, 5%	80/3	26.9
8	20	80/3	KOH, 2%	80/3	34.3
9	30	80/3	KOH, 10%	80/3	5.3
10	30	80/3	KOH, 6%	80/2	14.9
11	30	80/3	KOH, 5%	80/3	15.4
12	30	80/3	KOH, 3%	80/3	21.0
13	15	90/2	NH ₄ OH, 10%	90/2	19.7
HS					
14	15	90/2	KOH, 10%	90/2	8.9
15	20	90/2	KOH, 10%	90/2	4.6
16	20	80/3	KOH, 10%	80/3	13.3
17	30	80/2	KOH, 10%	80/2	5.3
18	20	90/2	NH ₄ OH, 10%	90/2	14.2
MS					
19	15	90/2	KOH, 10%	90/2	28.9
20	20	90/2	KOH, 10%	90/2	11.8
21	20	80/3	KOH, 10%	80/3	17.5

O.n. – ordinal number; F–S: fibrous-splinter from of pulp preventing marking of KN

Tests were also conducted with the dosing of 30% HNO₃ on o.d. WS in the N stage. These tests were completed with the temperature of the process reduced to 80 °C. For experiment No. 9, an increase in the amount of HNO₃ dosed made it possible to obtain a KN 5.3 pulp. Subsequent tests with this amount of dosed HNO₃ were made to check how reducing the amount of KOH in the E stage at the increased dose of HNO₃ affects the effects of delignification. These studies have again shown that by reducing this amount from 10% to 6%, 5%, and 3%, the KN of final pulp again increases from 5.3 units to 15.4,

14.9, and 21.0 units, respectively. These experiments confirm the necessity of dosing the appropriate amount of KOH in stage E (approximately 10% on o.d. PFRM) to fully use the oxidation potential of HNO₃.

Table 1 shows also the conditions for processing HS and MS into NA–A pulps and their KN. These data show that by performing pulping of HS using the NA–A method under the conditions shown in the row 14, a well-pulped KN 8.9 pulp can be obtained. Increasing the amount of HNO₃ dosed from 15% to 20% on o.d. HS, maintaining the remaining process parameters as in experiment No. 1, resulted in the deepening of the delignification of the NA–A Hs pulp to KN 4.6 units. When the KN of pulps after pulping by the NA–A method in the range of 5 to 10 units is too low (what may happen, *e.g.*, because of the negative effect of too deep delignification at elevated temperature on the strength properties of the fibers), it can be increased to the range of 10 to 15 units by lowering the process temperature from 90 °C to 80 °C and extending the duration of the N and E stages (experiment 16, Table 1). Experiment no. 17 from Table 2 shows that increasing the amount of nitric acid from 20% to 30% in the N stage while reducing the time of the N and E stages to 2 h deepens the delignification of these stalks to KN 5.3, *i.e.*, as much as can be obtained by increasing the temperature of the Hs NA–A pulping by 10 °C at 20% HNO₃ on the o.d. Hs (experiment No. 15).

It was also checked how the delignification of WS and HS is affected by the replacement of KOH with NH₄OH in the E stage (experiment no. 13 and no. 18, Table 1), which can be considered a lignin extractor for the need to obtain fertilizer solutions from black liquor with a higher nitrogen content. The test results indicate, however, that in such a case, less delignified pulps should be expected due to the lower capacity of NH₄OH than KOH to extract nitrated lignin (the kappa numbers of WS and HS NA–A pulps were 19.7 and 14.2, respectively, compared to 6.6 and 4.6 using the HNO₃/KOH delignification system).

Table 1 shows also the conditions for processing MS into NA–A pulps and their KN (rows 19–21). These data indicate the possibility of obtaining MS NA–A pulps with residual lignin content corresponding to pulps intended for full bleaching from hardwood, *i.e.*, KN 11.8 to 17.5, when pulping is completed under conditions presented in rows 20 and 21. These data indicate a lower efficiency of MS delignification in the N stage performed at a lower process temperature, *i.e.*, 80 °C.

According to the Introduction section, only Shishonok *et al.* (1997) have so far discussed the processing of real non-wood fiber raw materials for European papermaking located in northern temperate climate zone (*i.e.*, rye straw) into pulps with a low lignin content using the NA–A method. However, it is possible that no one has yet processed WS, HS, and MS into NA–A pulps. Regarding the work of Shishonok *et al.* (1997), the authors state that when using HNO₃ solution of a concentration of 1 to 2%, liquor-to-PFRM ratio of 10:1 (and therefore approximately 11 to 22% HNO₃ on o.d. of rye straw), a temperature in N stage of 80 to 90 °C, a time of this process of 3 to 4 h, and using alkaline extraction of nitrated rye straw with a 1.5% NaOH solution, KN 11–35 NA–A pulps can be obtained. Therefore, these results seem to be similar to those obtained in this work for WS. These results also demonstrate that KOH can be used as an extractor for nitrated lignin instead of NaOH.

The data in Table 1 also enable the performance of a preliminary comparison of the susceptibility to delignification of WS, HS, and MS using the NA–A method. They indicate a slightly better susceptibility to delignification of WS and HS than MS using this method,

despite a slightly higher lignin content in WS than HS and MS (22.2% versus 18.2% and 20.6%, respectively). In the case of WS, this may be due to a much better availability of native and nitrated lignin for HNO₃ and KOH, respectively, than in the case of HS and MS (small thickness of the walls of wheat straw stalks compared to the thickness of HS and MS stalks), while in the case of HS, a significant share (25 to 35%) of hemp bast in hemp stalks containing a small amount of lignin (3.0 to 9.7%) (Kovacs *et al.* 1992, Zomers *et al.* 1995).

Figure 2 shows a comparison of the total yield (Y_T) of WS, HS, and MS NA–A pulps compared to the Y_T of kraft pulps from these PFRM and B and P woods.

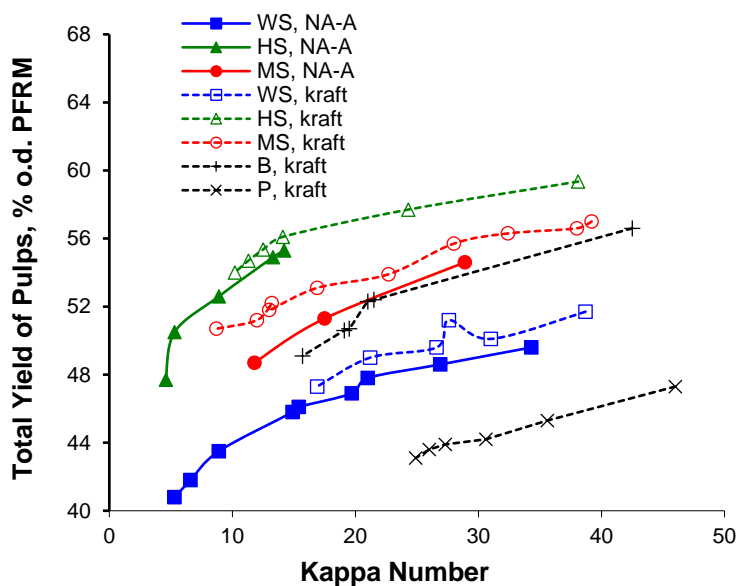


Fig. 2. Comparison of Y_T of WS, HS, and MS NA–A pulps with Y_T of WS, HS, MS, B, and P kraft pulps

These data indicate that the Y_T of NA–A pulps was slightly lower than the index of WS, HS, and MS kraft pulps at the KN 10 to 20 unit range. For the values of KN < 10, the Y_T index of NA–A pulps decreased more per unit of the KN reduction than for KN 10 to 20 NA–A pulps, indicating a decrease in the delignification selectivity in the KN < 10 range. Again, it can be stated that the obtained levels of Y_T of NA–A pulps from WS are comparable to the values of this index of NA–A pulp from rye straw presented by Shishonok *et al.* (1997), which were in the range of 42 to 49%. The higher yield of NA–A pulp from HS can be explained by its higher cellulose content (46.9%) than in the case of WS and MS (41.5% and 40.5%, respectively), resulting from the presence of hemp bast fibers in former PFRM. In turn, the lower yield of NA–A pulps from WS than MS is explained by the well-known higher content of mineral substances and hemicelluloses in WS among PFRMs and the greater susceptibility of considerable part of these chemical components to extraction or hydrolysis/extraction processes compared to cellulose and lignin.

As part of the work, the goal was to determine the level of properties of handsheets prepared from selected WS, HS, and MS NA–A pulps. Moreover, the results determining these properties were compared with the values of the properties of soda-AQ and kraft

pulps from these PFRM, presented by other authors, and B kraft and P kraft pulps. The results of these studies are presented in Table 2.

The data in Table 2 indicate that WS, HS, and MS NA–A pulps showed different S-RF after beating in a Jokro mill for 4 and 16 min. This was due to the different contents of primary fine fraction particles in the initial raw materials, which is much higher in WS and HS than in MS, B, and P pulps (Guo *et al.* 2009; Fišerova *et al.* 2013; Danielewicz and Surma-Ślusarska 2019). The S–RF of these pulps, however, seems high enough for the possibility of obtaining the high tensile strength of these pulps. For example, Guo *et al.* (2009) report that the breaking length of the WS soda-AQ pulps in the range of 30 to 50 °SR is 6.0 to 7.2 km, and Maddern and French (1989) report that with the S-RF of 45 to 55 °SR, the tensile index of the WS kraft pulp is 63 to 65 N·m/g. Similar values of the breaking strength of HS, soda–AQ or kraft pulps, *i.e.*, at the level of 60 to 80 N·m/g, were reported by Fišerova *et al.* (2013) and Danielewicz and Surma-Ślusarska (2017). In turn, for MS kraft pulps with an S-RF of 20 to 35 °SR, this property was in the range of 55 to 65 N·m/g (Danielewicz and Surma-Ślusarska 2019). Therefore, it can be concluded that the tensile strengths of the WS, HS, and MS NA–A pulps obtained in this work are lower than the values of the indices of this strength of the soda-AQ and kraft pulps obtained by other authors (they reach the level of 27.3 to 47.1 N·m/g), constituting only 47 to 76 % and 41 to 54% of the breaking strength of B, kraft and S, kraft pulps.

Table 2. Determining Selected Properties of Handsheets of NA–A and Kraft Pulps after Their Beating in a Jokro Mill for 4 min and 16 min

Pulp/Property	η_{CED} (cm ³ /g)	S-RF (°SR)	Tensile Index (N·m/g)	Tear Index (mN·m ² /g)	Stretch at Break (%)	Bulk (cm ³ /g)
Beating time 4 min						
WS NA–A, KN 8.9	663	29	36.0	4.3	1.50	1.947
Hs NA–A, KN 8.9	539	47	37.9	4.3	1.17	1.827
Ms NA–A, KN 11.5	687	20	27.3	5.0	0.97	1.925
B Kraft, KN 9.4	823	16	49.6	6.0	1.79	1.897
P Kraft, KN 22.5	795	15	57.4	8.7	1.82	1.650
Beating time 16 min						
WS NA–A, KN 8.9	A.a.	49	47.1	4.2	1.59	1.634
HS NA–A, KN 8.9		70	42.0	4.9	1.04	1.421
MS NA–A, KN 11.5		25	35.9	5.9	1.33	1.667
B Kraft, KN 9.4		30	80.4	6.8	3.25	1.398
P Kraft, KN 22.5		25	87.7	8.1	2.06	1.385

η_{CED} – determined in unbeaten state; A.a. – as above

For the tear resistance, it was defined for WS, HS, and MS soda-AQ or kraft pulps at the level of 3.3 to 4.2 mN·m²/g at an S–RF of 30 to 50 °SR (Maddern and French 1989; Guo *et al.* 2009), 6 to 15 mN·m²/g at an S-RF of 50 to 70 °SR (Fišerova *et al.* 2013), and 7.0 to 8.2 mN·m²/g at an S-RF of 20 to 35 °SR (Danielewicz and Surma-Ślusarska 2019). Therefore, the tear resistance of WS, HS, and MS NA–A pulps was comparable with these values only for WS NA–A pulp, while for HS NA–A, and MS NA–A pulps it was lower. The WS, HS and MS NA–A pulps were also worse compared to the more deeply delignified B kraft pulp (Tables 21). For WS and HS pulps beaten more intensively (*e.g.*, up to S–R–F 70 °SR), this is may not be a disadvantage, because Guo *et al.* (2009) also found almost twice lower tear index values of WS soda-AQ pulp than eucalyptus kraft pulp

at S–RF of 40 to 65 °SR. Fišerova *et al.* (2013) showed quite low tear resistance of the unbleached HS soda–AQ pulps (only approximately 6 mN·m²/g) with its S–RF of 75 °SR. The lower values of the breaking strength of WS, HS, and MS NA–A pulps in comparison to WS, HS, and MS soda–AQ or kraft pulps may be because the lower fiber strength of the first set of pulps than the second one, resulting from their lower intrinsic viscosity, which was low, especially for HS NA–A pulp (Table 2). Further reasons for this may be the reduced content of hemicelluloses, the increased content of cellulose in NA–A pulps, and lower degree of polymerization of hemicelluloses. Some authors claim that the NA–A method is a good method for obtaining dissolving pulps, *i.e.*, with a reduced content of pentosans and an increased content of cellulose (Biyani *et al.* 1967; Kalish 1967). This indicates the need to optimize the NA–A pulping process of WS, HS, and MS. Some indication for this here may be the results of Ivanov *et al.*'s (1978) work concerning the production of NA–A pulps from wood, indicating that these pulps obtained at a concentration of 2.0 to 2.5 % HNO₃ in the N stage but at temperature maximum of 81 °C in this stage are characterized by significantly higher viscosity than pulps obtained at an HNO₃ concentration of 6 %. It should also be checked whether it is possible to obtain pulps of low KN at even lower temperatures in the N stage, including room temperature. This would probably involve the need to increase the concentration of HNO₃ in the N stage. Such a modification of the process conditions could be beneficial from the point of view of the possibility of obtaining a higher concentration of nitrogen in CPF and the simplification of the pulping process in small, locally operating pulp mills. Another possibility is the use of special substances that limit cellulose depolymerization in the nitration process, as described by Kin (1990) or assumption of the use of NA–A pulps for other purposes (such as dissolving pulps or pulps intended for the production of nanocellulose) that do not require such high strength properties as in the case of kraft pulps.

As already mentioned in the experimental section, in this work the levels of the fertilizing elements were also determined, *i.e.*, nitrogen and potassium in combined post-pulping liquor (CPF), including nitrogen in the form of total nitrogen (N_T), nitrate nitrogen (N–NO₃), and ammonium nitrogen (N–NH₄). These determinations were performed for two pulping experiments of WS using the NA–A method, especially for this purpose. The results of these determinations are presented in Table 3.

Table 3. Nitrogen and Potassium Content in CPF from WS Pulping Experiments in HNO₃/KOH and HNO₃/NH₄OH Systems

Content of the Fertilizing Component	N _T	N–NO ₃	N–NH ₄	K
Type of Pulping Process	%	mg/dm ³		
Exp. no. 5, Table 1	0.1 ± 0.05	645 ± 34	238 ± 25	1644 ± 34
Exp. no. 13, Table 1	0.3 ± 0.03	1470 ± 44	1420 ± 52	212 ± 17

The data in Table 3 indicate that for filtrates from the pulping and washing of WS under the conditions of experiments No. 5 and 13 from Table 1, the content of N–NO₃ nitrogen, N–NH₄ nitrogen, and K was obtained at the levels of 645, 238, and 1644 mg/dm³, respectively, while for pulping in the HNO₃/NH₄OH system, the contents of these fertilizing elements were at levels of 1470, 1420, and 212 mg/dm³, respectively. The data in Table 3 also indicate that the use of alkaline extraction of the nitrated PFRM using NH₄OH instead of KOH increases the level of total nitrogen content in the PFP sample twice, the N–NO₃ nitrogen content 2.28 times, and the N–NH₄ nitrogen content 5.97 times.

In contrast, the content of potassium in CPF from the digestion of WS in the HNO₃/KOH pulping system was 7.75 times higher than the content of this element in CPF from the pulping in the HNO₃/NH₄OH system. The relatively high content of potassium in CPF from pulping using the HNO₃/NH₄OH system can be explained partially by the leaching of this element from WS in the process of NA–A pulping, whose content in rye straw is as high as 379 mg/dm³, as reported by Kaniszewski *et al.* (2010), and by using tap water to wash the pulps after N and A stages.

It seems that such filtrates could be used as fertilizer in horticulture, *e.g.*, for soilless cultivation of vegetables in greenhouses on various types of growing media (*e.g.*, Rockwood or Gordan-Master mineral wool). The content of fertilizing elements in filtrates from HNO₃/KOH pulping of WS is higher or similar to the content of N–NO₃ nitrogen and of K in the nutrient solution used in this type of crop for fertilizing tomatoes, amounting to 200 to 250 mg/dm³ and 280 to 380 mg/dm³, respectively (Kaniszewski *et al.* 2010) and the content of N–NO₃, N–NH₄, and K in the root zone of plants cultivated with this method, amounting to 400 to 600 mg/dm³, 0 to 60 mg/dm³, and 300 to 800 mg/dm³ (Dyśko *et al.* 2012).

If it is intended to use the filtrates from PFRMs pulping using the NA-A method in agriculture and other forms of horticulture than mentioned above, then it would probably be necessary to dewater and granulate the dry substance of the post-pulping filtrates to avoid their storage and enable their sale and more convenient use, what it was practically done by Kin (1990). The author of this article is not a specialist in the field of agricultural fertilizers, because the papermaking industry has not yet taken seriously the possibility of using black liquor from pulping to fertilize crops in horticulture or agriculture. Apart from that, it seems that this type of fertilizer could have an advantage over conventional fertilizers in that they can release nitrogen and potassium into the soil more slowly due to the ability to bind of nitrogen and potassium by lignin; enrich it with organic carbon of prepared organic matter of PFRMs with the action of HNO₃, what was suggested by Wrocławski (2014); and delay the drying out of the soil by the presence of hemicelluloses, which are known to have the ability to absorb water.

However, the application of filtrates from PFRM pulping using the NA-A method would require checking the impact of fertilizing cultivated plants with these filtrates on the properties of the plants themselves and their fruits, such as the color of leaves, the color of *e.g.* tomatoes or potatoes *etc.*, the content of harmful substances in them, and in the absence of them also the taste of vegetable or fruit. It is known that harmful substances (*e.g.* dioxins) may be formed as a result of chemical changes in lignin under the influence of some bleaching chemicals (*e.g.*, chlorine). In the case of pulping of PFRMs in the HNO₃ in the first stage, the possibility of producing a certain amount of HCN during the process should be taken into account. The possibility of formation of this type of chemical compound was mentioned by Gorbunova *et al.* (1993a). This fact and the possible inability to avoid the formation of HCN could significantly limit the applicability of this method in practice.

The transformation of cellulose into explosive cellulose nitrate during NA-A pulping seems to be the second disadvantage of the technology in question. However, it may be unlikely, because according to Heuser (1946), explosive cellulose would have to have a nitrogen content above 10%, and such celluloses are obtained using nitration solution which contains *e.g.*, 24.29% HNO₃, 65.8% H₂SO₄, and 9.91% water, *i.e.*, conditions that are very different from those used in this work for the processing of PFRMs into fibrous pulps using the NA-A method.

CONCLUSIONS

1. In this work, well-pulped WS, HS, and MS NA–A pulps (*i.e.*, of KN 5 to 20 units) were obtained with 10 to 30% of HNO₃ dosed on o.d. of these PFRM in the N stage and 10% of KOH or NH₄OH dosed on o.d. of these PFRM in E stage, conducting N and the E processed within 2 to 3 h and at 80 to 90 °C.
2. The yield of WS, HS, and MS NA–A pulps in the range of KN 10 to 20 showed slightly lower values compared to the yield of WS, HS, and MS kraft pulps. Below KN 10, however, the selectivity of the delignification of these raw materials by the NA–A method seemed to deteriorate.
3. The tensile strength and tear resistance of the handsheets made of selected WS, HS, and MS NA–A pulps were usually lower than the values of these indices of WS, HS, and MS soda-AQ or kraft pulps presented by other authors. One of the reasons for this is the lower intrinsic viscosity of the former pulps, especially HS NA–A pulp, but *e.g.* a lower content of hemicelluloses in NA-A pulps or their lower degree of polymerization may also contribute to this, as is the case with sulfite pulps.
4. The worse strength properties of WS, HS, and MS NA–A in comparison with soda–AQ and kraft pulps suggest the need for further research on the reduction of the hydrolytic effect of conditions of HNO₃ pulping on carbohydrates.
5. The contents of N–NO₃, N–NH₄, and K in CPF from the processes of WS pulping using the NA–A method were higher or comparable to the content of these fertilizing elements in the nutrient solution used to fertilize the growing media in soilless tomato cultivation in greenhouses. This makes it possible, in principle, to use these solutions for the nutrition of plants cultivated in horticulture and agriculture in the form of a solution or granules. However, this still requires determining the effectiveness of this type of fertilizer, its impact on the horticulture and agriculture plants, and the properties of their output, *i.e.*, grains, tubers, and fruits.

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