PULPING OF CORN STALKS – ASSESSMENT FOR BIO-BASED PACKAGING MATERIALS

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The authors dedicate this paper to
Academician Bogdan C. Simionescu, on his 70th birthday,
to honor his fruitful and prodigious scientific activity, the expression of his continuous concern to pass on the advances and the most valuable research results to younger generations.

Agricultural residues resulting as side-streams from harvesting cereals have lately gained particular interest for pulping and papermaking due to their availability and low price. Corn (*Zea mays*) is one of the most important cereals and its harvesting yields amounts of stalks in the range of 1.7-4.5 t/ha. In the present paper, the chemical composition of corn stalks was determined and the obtained values represent an argument for their use as feedstock for papermaking fiber production. Furthermore, alkaline pulping processes using different cooking agents were tested for conversion of corn stalks to papermaking pulp. The obtained pulps were characterized with respect to yield, Kappa number and viscosity, and were then subjected to beating and handsheet formation. The mechanical properties (tensile and bursting strength, corrugating medium flat crush resistance and short span compressive strength) of the handsheets obtained with different beating degrees were determined in order to find out the optimum cooking and/or refining conditions and the most suitable cooking agents to obtain pulps with good papermaking properties. The findings of this study provide insights into new opportunities to utilize a low-cost raw material to produce high-value bio-based materials, resulting in significant savings for the pulp and paper industry.

Keywords: corn stalks, pulp, fibrous materials, bio-based materials, packaging

INTRODUCTION

The Europe 2020 Strategy identifies the bioeconomy as a key building block for smart and green growth in Europe, in which the research and innovation will allow improving the management of renewable biological resources and developing new and diversified markets for bio-based products.[1] Starting from two premises, that biomass is underexploited and that its potential can be upgraded, the bioeconomy strategy seeks synergies and creates complementarities between the agricultural sector (as biomass supplier) and the pulp and paper manufacturing sector (as biomass beneficiary).

Agricultural residues represent an important lignocellulosic biomass category resulting from crop cultivation and harvesting, composed mainly of three polymers: cellulose, hemicelluloses and lignin.[2] These materials may represent both an environmental burden, in areas where field incineration is a traditional practice, and monetary losses, considering the loss of extra-income for farmers.[3] Agricultural wastes are of primary interest as raw materials for pulp and paper production due to their high production yields per hectare, high availability, low costs and low lignin content, which allows pulp processing in totally chlorine free bleaching facilities.[4-6]

Several disadvantages of these raw materials, such as high ash content, low density and seasonal availability, have prevented the extensive use of these materials. The higher content of hemicelluloses, extractives and mineral substances in lignocellulosic agricultural waste is incriminated as causing low pulp yields and deposit formation on technological lines,[7] while the high ash and silicate content generates deposits in regeneration circuits of chemicals.[8] All these aspects contribute to reducing economic efficiency.

However, recent studies[9] have shown that agricultural waste is a feasible source of raw materials, if appropriate methods and process conditions are chosen. Besides the straws resulting from harvesting wheat, oats, barley or rice crops, other agricultural side-streams available at the farm gate may be used as virgin fiber supply for the pulp and paper industry.

Corn or maize (*Zea mays* ssp. *mays* L.) is a crop cultivated worldwide mainly for food, feed and bioenergy,[10] yet a substantial fraction of the plant remains unused or underused. Corn stover is the above-ground residue that remains after corn kernels are harvested. It consists of stalks and leaves, and makes up about half of the total biomass yield of a corn crop.[11] It is usually left in the fields and must be plowed under to prepare the land for the next crop. Farmers can collect it and use it as fodder for ruminants during the winter season, as litter for livestock, as a fuel source for production of bioenergy or as feedstock for bioproducts, fermentation to cellulosic ethanol, fibers, *etc*.

Corn cultivation reached 18.6% of the total cultivated cereals in the European Union in 2016[12] and accounted for corn yields in the range of 2.2-13.7 t/ha, based on 5-year averages, with the lowest value obtained in Romania in the year 2012, and the highest value – in the Netherlands in 2014.[13] For a total above-ground biomass residue, calculated on a 1:1 harvest index or ratio of residue to grain for corn, the hypothetical values for corn stover yields are predicted to reach almost 60 million tones in EU-28 in the year 2015.

According to Barten,[14] the most important pathways for corn stover valorization and uses are animal bedding, combustion in power plants and chemical processing. Corn stover traditionally presents particular interest for saccharification and further cellulosic ethanol production by fermentative processes.[15] In such contexts, lignin and hemicelluloses are removed from the raw materials by various physico-chemical treatments, and the remaining solid residues, often impure carbohydrates, are considered as a raw material for sugar production and fermentation.[16]

Cornstalks have been traditionally pulped by alkaline processes, using cold or hot lime, soda or Kraft, in batch or continuous pulping, at atmospheric or elevated pressures. However, there are limitations in achieving the desired pulp quality caused by the presence of pith in corn stalks, which amounts to approximately 21%.[17] There has always been interest in the efficient removal of the pith from the fibrous portion of corn stalks, so that they could be used for making high-quality pulp and paper.

In previous research, it was observed that the pith could be efficiently removed by pre-extraction, which consequently increased the percentage of sugars in the pre-extracted liquor.[18] Corn stalk pith contains a high amount of hemicelluloses,[19] which are valuable raw materials for many value-added products. Thus, pre-extraction may serve several purposes: of pith removal and recovery of the valuable hemicelluloses for value-added products, but also of reducing the content of the amorphous compounds found in the stalk (*e.g.*, hemicelluloses, lignin and some other non-cellulosic materials).

Although, the first patents that explored the papermaking potential of corn stalks were issued as early as in 1837 in France[20] and in 1838 in the United States,[21] and at that time, various grades of paper products were already available on the market, the lack of continued supply and the problems associated with the preservation of raw materials all year long eventually led to the closure of the mills.

The objective of the current study is to process renewable biomass resources resulting as the by-product of agricultural activities into value-added products. The report presents the conversion of corn stalks into papermaking pulps by different methods and promotes their application in bio-based packaging products. The experimental work was focused on alkaline methods, due to their efficient lignin removal and the production of fibers with high strength properties.

Turning corn stalks into renewable fibrous materials, suitable for unbleached paper grades, paperboard (single- or multi-ply), board and molded pulp is seldom mentioned in literature studies, although significant quantities of this raw material are available annually and it can become an alternative supply to virgin fibers, recycled papers and plastics.

EXPERIMENTAL

Raw material

The raw material consisted in corn stalks collected manually from corn fields at local farms. The material was chopped and air-dried to atmospheric equilibrium and further cut into pieces of about 3-5 cm in length in order to facilitate impregnation. The results were reported on oven-dry weight basis. All reagents used were of analytical grade. No process or functional additives, or other chemicals were used to improve the manufacturing or the properties of the paper products.

Chemical composition analysis

A portion of the material was ground and prepared for chemical analysis according to the following methods: holocellulose (TAPPI T 9 wd-75, 1975); cellulose (TAPPI T 17 wd-70, 1970); pentosans (TAPPI T 223 cm-01, 2001); lignin (TAPPI T 222 om-02, 2002); acetone extractives (T 264 cm-07, 2007); hot water solubility (T 207 cm-99); 1% NaOH solubility (T 212 om-02) and ash (TAPPI T 211 om-02, 2002).[22]

Fiber morphology

The corn stalk pulp fibers were investigated to find the mean values of their length, diameter and cell wall thickness. Sample preparation was done as described in TAPPI T259-sp-09 – Species identification of nonwood plant fibers.[22] The coarse material was defibered by boiling in a 10% NaOH solution for approximately 30 minutes, followed by washing and vigorous shaking in water for complete individualization of the fibers. Samples from the fibrous suspension were placed on microscope slides and dried. The fiber mats were coated with gold and examined using a JEOL 5500 Scanning Electron Microscope, operating at an acceleration tension of 20 kV. The images obtained were analyzed using the ImageJ[23] software package for measuring the fiber parameters.

Pulping trials and analysis

Pulping trials were performed in a stainless steel laboratory rotating batch reactor, equipped with electric heating and automatic temperature control. Amounts of 400 g of raw materials (o.d. mass) corresponding to pulping liquor at a solid to liquid ratio of 5:1 were used. Six pulping experiments were carried out using different cooking agents, as shown in Table 1. For all six experiments, the following conditions were used: heating time of 30 min and cooking time of 60 min at a temperature of 170 °C.

In the case of the soda pulping experiments, the alkali charges were kept constant – of 18% NaOH (w/w, based on o.d. material). The white liquors were prepared by separately dissolving analytical grade reagents in tap water. In the case of the KOH/NH_4OH pulping trials, the liquor was obtained by dissolving equal equivalent amounts of potassium hydroxide and ammonium hydroxide corresponding to 18% NaOH.

The white liquor needed for Kraft pulping had the following characteristics (expressed in grams of NaOH per Liter): NaOH – 100; Na_2S – 20; sulfidity 20%.

Prior to some soda pulping trials, a pre-hydrolysis phase was carried out in order to remove the pith, as well as to extract some of the hemicelluloses present in the lignocellulosic material. The pre-hydrolysis was performed with water at 170 °C for 30 min and 100 °C for 1 h in the same reactor, as pulping trials; 400 g (o.d. mass) of raw material at a water to solid ratio of 5:1 was used. At the end of the pre-hydrolysis stage, the resulting fibrous material was washed, then crushed in a laboratory disintegrator and stored in plastic bags for further use in soda pulping processes.

A detailed characterization of the products dissolved in the water extracts was beyond the scope of this paper, so they will not be discussed further.

After cooking, the reactor was degassed and cooled to an appropriate temperature to allow removal of the pulp for disintegration, washing and squeezing for water removal up to a consistency of about 30%. Furthermore, total yield (gravimetric method), kappa number (ISO 302:2004), freeness of pulps (ISO 5267-1:1999), and intrinsic viscosity (ISO 5351:2010)[24] were determined.

Preparation of handsheets and analysis of their mechanical properties

The handsheets used for testing were prepared on a Rapid Köthen sheet former (ISO 5269-2:2004) and had a basis weight of 120 g/m^2. The pulps used to form the handsheets were beaten for different durations (2.5; 5 and 10 minutes) in a Yokro mill (ISO 5264-3:1979). The drainability of the pulp suspensions in water, in terms of the Schopper-Riegler (SR) number, was determined for each sample (ISO 5267-1:1999). The beating rate was calculated as the ratio between ΔSR and $\Delta\tau$, in which ΔSR is the variation of freeness expressed in SR degrees, and $\Delta\tau$ is the variation of time expressed in minutes. The handsheets were conditioned (23 °C, 50% relative humidity – ISO 187:1990) before testing. The following mechanical properties were determined according to their respective standards to best represent the performance of packaging materials in service: tensile strength (ISO 1924:2008); bursting strength (ISO 2758:2001); corrugating medium flat crush resistance (*i.e.* Concora Medium Test, ISO 7263:2011) and SCT – short span compressive strength (ISO 9895:2008).[24]

Table 1
Pulping trials

Sample notation	Pulping method	Cooking agent
ZM Soda	Soda	NaOH
ZM Soda B	Soda-butanol	NaOH + butanol
ZM ($KOH+NH_4OH$)	KOH/NH_4OH	$KOH + NH_4OH$
PH170(30) ZM Soda	Pre-hydrolysis (170 °C/30 min) + Soda pulping	Hot water/NaOH
PH100(60) ZM Soda	Pre-hydrolysis (100 °C/60 min) + Soda pulping	Hot water/NaOH
ZM Kraft	Kraft	$NaOH + Na_2S$

Table 2
Chemical composition of corn stalks and dimensions of isolated fibers

Properties	Units	Average	Range	Standard deviation
Chemical composition				
Holocellulose	%	64.4	62.5-67.7	2.71
Cellulose	%	38.7	34.6-42.1	2.49
Pentosans	%	19.5	17.6-20.7	0.99
Lignin	%	20.2	19.1-20.9	0.64
Acetone extractives	%	2.6	2.4-2.9	0.14
Hot water solubility	%	22.9	19.7-24.5	1.65
1% NaOH solubility	%	49.3	47.3-52.3	1.59
Ash	%	5.1	4.5-5.7	0.37
Fiber morphology				
Fiber length,	mm	0.93	0.63-1.38	0.25
Fiber width,	μm	22.9	16.1-30.8	4.87
Cell wall thickness,	μm	5.8	4.3-8.8	1.54

RESULTS AND DISCUSSION

Chemical composition

The chemical composition of corn stalks (Table 2) shows satisfactory results, compared to those of other common non-wood, softwood and hardwood raw materials. The stalks are mostly composed of carbohydrates: cellulose (~40%), pentoses (~20%) and hexoses (~20%), and are therefore of interest for technological developments to produce bio-based materials.

The chemical analysis revealed a Klason lignin content around 20%, which is in the range of that found for other annual plants. The values of its principal components make corn stalk a suitable material for papermaking pulps, which does not require additional cooking time or chemical charge compared to other non-wood raw materials. Also, the amounts of extractives and ash are comparable to those reported for other annual plants or agricultural crops.[6]

Fiber morphology

The average dimensions of isolated cornstalk fibers are listed in Table 2. Compared with the dimensions of wood and other non-wood fibers found in the literature, the data show a wide variation in the characteristics of these non-wood fibers.[25]

Typical fibers are fairly narrow and thick-walled, while vessel elements are pitted and very wide. Other cells similar to tracheids, saclike parenchyma cells and epidermal cells were found, but very scarce, as seen in Figure 1.

The fiber length is similar to that of other short-fiber hardwoods, and the diameter of the fiber is small, resulting in lower pulp coarseness. These fiber dimensions provide an insight into the potential usefulness of these pulps in pulp and papermaking:[26] good fibers suitable for papermaking and good pulp strengths.

Pulping studies

The results obtained after the analysis of the pulps in terms of total yield, Kappa number, freeness and viscosity are presented in Table 3. The characteristics of celluloses are different and depend on the cooking agent, because the temperature and duration have been kept constant for all six pulps: yields ranging between 27 and 47%, Kappa number between 19 and 99 units and viscosity between 750 and 1100 units. The soda and kraft pulps (ZM Soda, ZM Soda B and ZM Kraft) are the most delignified ones (with the lowest lignin content), but also have the lowest yields of celluloses (35.9-41%).

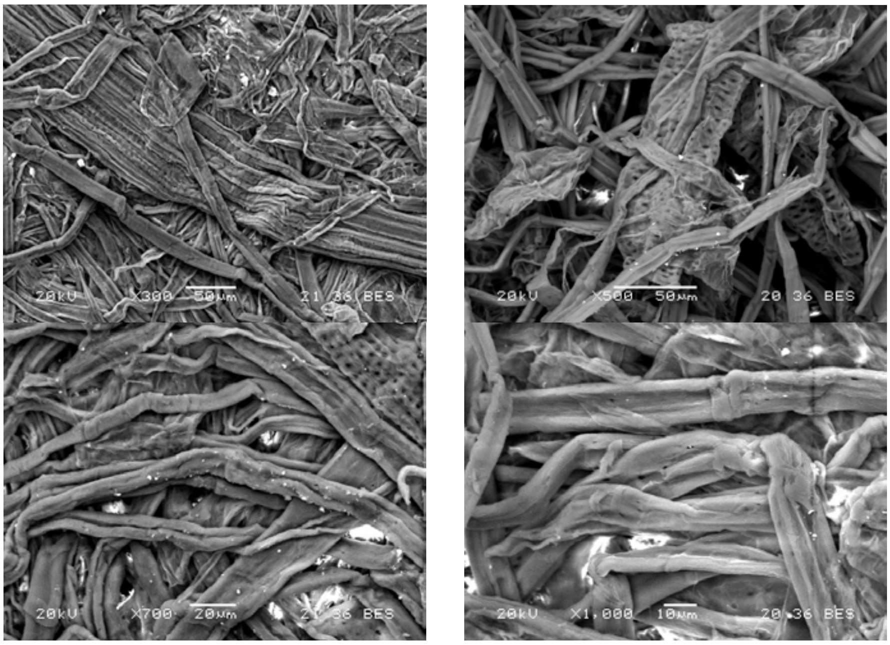

Figure 1: Micrographs of corn stalk fiber obtained by SEM (with different magnification)

Table 3
Pulping results: total yield, kappa number, intrinsic viscosity and initial freeness

Cellulose type	Total yield, %	Kappa number	Viscosity, mL/g	Schopper Riegler, °SR
ZM Soda	35.9	19.2	866	19
ZM Soda B	41.0	22.4	799	22
ZM ($KOH+NH_4OH$)	47.1	99	750	26
PH170(30) – ZM Soda	33.2	46.9	946	20
PH100(60) – ZM Soda	34.9	22.5	1022	20
ZM Kraft	37	32.4	1100	24

The highest pulp yield (47.1%), along with a high lignin content (Kappa number 99), has been obtained for the ZM($KOH+NH_4OH$) pulp, but, in this case, the pulp also exhibits advanced cellulose depolymerization, as illustrated by its lowest viscosity value. This demonstrates a lower selectivity of the delignification process with $KOH+NH_4OH$, in comparison, for example, with the ZM Kraft pulp, which appears to have been obtained by the most selective process of the tested pulping trials.

The pre-hydrolysis of corn stalks contributes to pulps with higher viscosity values – PH170(30) ZM Soda and PH100(60) ZM Soda. Also, the pre-hydrolysis under conditions of low temperature and long duration (100 °C/60 min) *versus* high temperature and short duration (170 °C/30 min) seems to be more effective in this regard. Instead, regarding the delignification degree, the pre-hydrolysis does not appear to be effective in this case, although the literature[27,28] mentions that hot water hydrolysis favors slightly the delignification process during subsequent pulping, which may be due to the increased reactivity of lignin.

The beating degree is relatively low for all the celluloses (19-26°SR), this being an important parameter for further pulp process operations, for example, pulp washing efficiency. The pre-hydrolyzed pulps (PH170 – ZM Soda and PH100 – ZM Soda) were obtained with the same

Schopper-Riegler beating degree as ZM Soda, although it was expected to have a lower amount of fine material resulted from the pith and consequently a lower Schopper-Riegler beating degree.

Pulp beating rates

As can be seen from Table 3, all six celluloses are obtained with a relatively low beating degree (around 20-24 °SR), so they can still be further subjected to beating to improve their papermaking properties (to around 35 °SR).

The beating rate of *Zea mays* pulps, regardless of the cooking agent, is not constant over time (Table 4): it has higher values at first, which then slightly decrease; the evolution being almost similar for all the pulps, regardless their lignin content (Kappa number between 19 and 99). We can conclude that the pulps from corn stalks are easy to beat due to both the high hemicelluloses content and their fiber length, requiring a short period of time (between 2.5-5 min) to reach a freeness of 30-35 °SR. This is definitely an advantage of these types of pulps, as low energy consumption is required to obtain papermaking pulps with improved characteristics.

Table 4
Beating rate of different types of corn stalk pulps

Sample	Kappa number	Beating duration, min	Beating rate, °SR/min
		0-2.5	3.6
ZM Soda	19.2	2.5-5	2.8
		5-10	3.4
		0-2.5	2.0
ZM Soda B	22.4	2.5-5	4.8
		5-10	2.8
		0-2.5	3.2
ZM(KOH+NH_4OH)	99	2.5-5	1.6
		5-10	2.4
		0-2.5	3.6
PH170(30)ZM Soda	46.9	2.5-5	0.8
		5-10	2.4
		0-2.5	4.0
PH100(60)ZM Soda	22.5	2.5-5	3.2
		5-10	2.4
		0-2.5	3.6
ZM Kraft	32.4	2.5-5	4.0
		5-10	2.2

Characterization of handsheets

In the second part of the work, we focused on investigating the properties of the fibrous material relevant to their possible use in papermaking applications as bio-based packaging materials.[23-31]

As mentioned in the experimental section, handsheets were formed from pulps beaten in a Jokro mill for different durations: 2.5; 5 and 10 minutes, and their mechanical properties, namely, tensile and bursting strength, corrugating medium flat crush resistance and short span compressive strength, were determined.

Tensile strength

Figure 2 shows the tensile index of the handsheets as a function of the beating degree of the pulps. A similar evolution of this parameter is observed for all six pulps: the tensile index evolves positively with an increase in the beating degree, records a maximum value around 30-35 °SR and then decreases. This evolution can be explained by the removal of the primary wall from the fibers in the initial stage of the beating process (2.5-5 min), which facilitates fiber bonding, followed by the reduction of the fiber length by excessive beating, leading to a decline of the tensile index.

The tensile index of the handsheets formed from unbeaten pulps ranges between 27-44 Nm/g. So, even in unbeaten form, the corn stalk pulps have satisfactory resistance characteristics. We can remark the high initial resistance of the pre-hydrolyzed pulp (PH100(60)-ZM Soda), compared with that of the un-hydrolyzed pulp

(ZM Soda). However, this situation is reversed after increasing the beating degree, the behavior of these two pulps being possibly caused by the different content of hemicelluloses. The presence of hemicelluloses enhances the formation of bonds between cellulose fibers, giving the pulp superior mechanical performance, therefore a small content of hemicelluloses is not beneficial in the production of high-quality pulps.[32]

The tensile index of the handsheets made from pulps beaten for 2.5-5 min reaches its maximum – around 56-59 Nm/g, with the highest tensile index recorded for the ZM Kraft pulp, followed by ZM Soda. The paper sheets made from ZM ($KOH+NH_4OH$) exhibited the slightest increase in tensile index with increasing beating degree, possibly because of its low viscosity value, but also its high lignin content (Kappa number of 99), which resulted in its high resistance to beating.

Burst strength

The handsheets behave differently with regard to their bursting strength, compared with the tensile strength. Thus, the burst strength index has a positive, almost linear evolution, with the increase of the beating degree (more pronounced for PH100, PH170 and ZM Kraft pulps) (Fig. 3). The pre-hydrolysis of the corn stalks in this case does not have a positive effect on the initial burst strength, but instead a noticeable improvement is observed with increasing beating degree. One can also remark the lowest burst strength index of the ($KOH+NH_4OH$) pulp, both for no beating and with increasing beating degree. Thus, regarding the tensile and burst indices, one can conclude that both the beating degree and the lignin content of the pulps are important.

Corrugating medium and short span compression tests

The corrugating medium test (CMT) permits the evaluation of fibrous materials before they are fabricated into packaging materials, and can be used as a basis for judgment of fabrication efficiency, while the short span compressive strength (SCT) can be used to predict the compressive strength of bio-based material and products.[33]

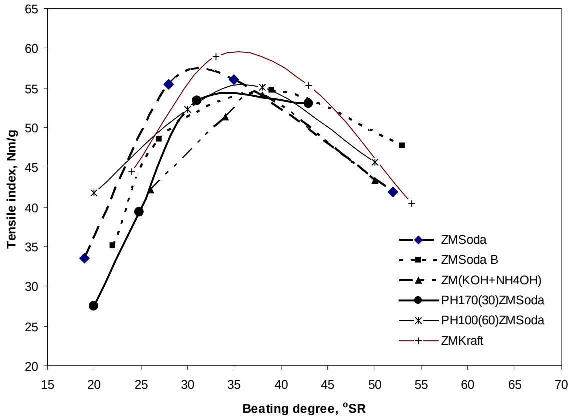

Figure 2: Tensile index of corn stalk paper sheets

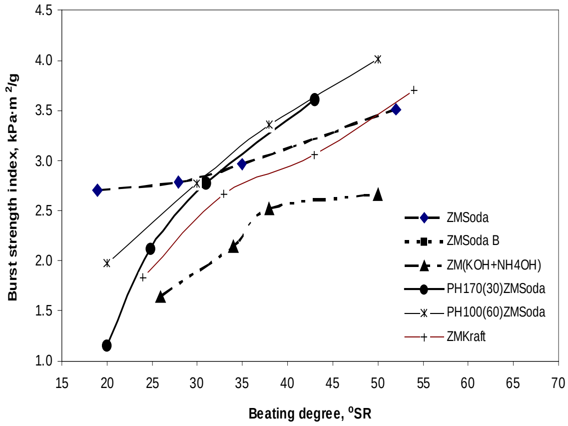

Figure 3: Burst strength index of corn stalk paper sheets

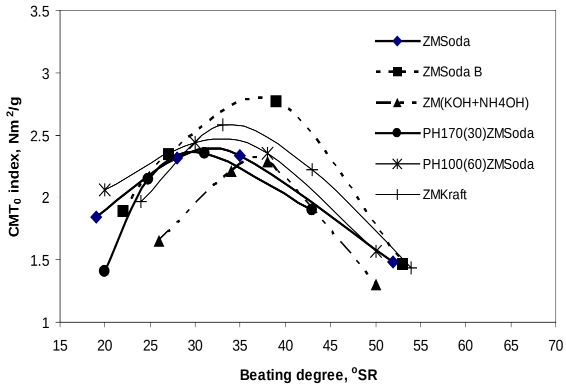

Figure 4: CMT_0 index of corn stalk paper sheets

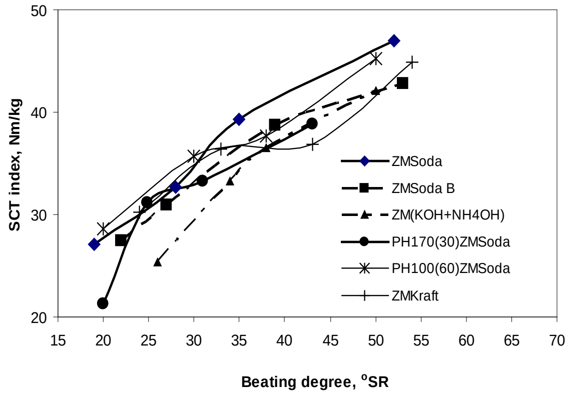

Figure 5: SCT index of corn stalk paper sheets

Having in mind the use of the prepared materials in liner, fluting, Schrenz and Wellenstoff types of papers, it is necessary to assess properly the performance and quality of the fibrous materials to determine their suitability for such uses. To find out how the fibers will perform in traditional packaging materials, they were tested by CMT and SCT methods, which are used to estimate two of the most important strength properties, which indicate strength performance and flexibility during conversion and usage.

All the samples performed well at CMT, reaching values above 1.3 Nm^2/g, the minimum standard value for the desired application,[34] but also superior values to those of similar products manufactured industrially and available on the market.[35] The CMT_0 index (Fig. 4) recorded a similar evolution to that of the tensile index: it rose with an increasing beating degree, but only up to a certain value, and then decreased for all pulp types. One can remark that the maximum value was recorded at the same beating degree (around 30-40 °SR).

The smallest CMT values were obtained in the case of the pre-hydrolyzed pulps, subjected to the delignification process with $KOH+NH_4OH$, showing that a process yielding good fibers and a spent liquor enriched with dissolvable compounds found in the stalk (*e.g*., hemicelluloses, lignin and some other non-cellulosic materials) is not feasible. It is possible to obtain either fibrous materials with good packaging properties, or the fraction of fermentable sugars, but not both. The deficiencies in strength can be overcome with increased refining, but only up to a certain beating degree, beyond which the properties deteriorate.

The SCT index increases linearly with the increasing beating degree for all the pulps, as it may be observed from Figure 5. The best values were obtained for soda pulps.

In general, it seems that the bonding capacity of fibrous materials is essential for the compression properties, CMT and SCT, of the pulps.

CONCLUSION

The findings of the present study are of help either in filling in the blanks existing in the related literature or offering another perspective, different from that of other previous similar studies.

The chemical analysis of corn stalks revealed that this type of raw material is adequate for pulping. The proposed pulping trials yielded six different types of pulps, in terms of yield and properties. Soda and Kraft pulping processes appeared to be the most interesting of the tested pulping methods.

Also, the corn stalk pulps proved to be easy to beat due to both their high hemicelluloses content and their fiber length. This is definitely an advantage of these types of pulps, as their processing requires low energy consumption.

All the investigated mechanical properties were improved upon beating at up to 30-35 °SR for all the types of the pulps. The burst strength and SCT indexes were found to increase almost linearly with the beating degree, but above the mentioned limit (30-35 °SR), the tensile CMT_0 indexes decreased significantly. Regarding the studied mechanical properties, both the beating degree and the lignin content of the pulps are important.

The findings provide insights on new opportunities to utilize a low-cost raw material to produce high-value bio-based materials, which would result in significant savings for the pulp and paper industry.

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REFERENCES

[1] European Commission, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, Innovating for Sustainable Growth: A Bioeconomy for Europe, Brussels, 2012, available on-line at http://ec.europa.eu/research/bioeconomy/pdf/official-strategy_en.pdf

[2] R. Kannaiyan, N. Mahinpey, V. Kostenko and J. R. Martinuzzi, *Chem. Eng. Commun*., **204**, 803 (2017).

[3] N. D. Yilmaz, M. Sulak, K. Yilmaz and F. Kalin, *J. Nat. Fibers*, **13**, 397 (2016).

[4] A. C. Puitel, N. Moisei, B. M. Tofanica and D. Gavrilescu, *Environ. Eng. Manag. J*., **16**, 1027 (2017).

[5] B. M. Tofanica, E. Cappelletto, D. Gavrilescu and K. Mueller, *J. Nat. Fibers*, **8**, 241 (2011).

[6] D. Gavrilescu, B. M. Tofanica, A. C. Puitel and P. V. Petrea, *Environ. Eng. Manag. J*., **8**, 429 (2009).

[7] A. Leponiemi, *Appita J*., **61**, 235 (2008).

[8] H. Theliander, in "Pulp and Paper Chemistry and Technology", vol. 2, edited by M. Ek, G. Gellerstedt and G. Henriksson, Walter de Gruyter, 2009, pp. 297-333.

[9] V. I. Popa, "Pulp Production and Processing: From Papermaking to High-Tech Products", Smithers Rapra Technology Ltd., 2013.
[10] B. D. Solomon, J. Birchler, S. L. Goldman and Q. Zhang, in "Compendium of Bioenergy Plants – Corn", edited by S. L. Goldman and C. Kole, CRC Press, 2014, pp. 1-32.
[11] D. Glassner, J. Hettenhaus and T. Schechinger, in "Perspectives on New Crops and New Uses", edited by J. Janick, ASHS Press, 1999, pp. 74-82.
[12] EUROSTAT – European Union, Agriculture, Forestry and Fishery Statistics – 2016 Edition, Publication Office of the European Union, 2016.
[13] FAOSTAT database collections, Food and Agriculture Organization of the United Nations, Rome, Italy, URL: http://faostat.fao.org, accessed on 31.08.2017.
[14] T. J. Barten, PhD Thesis, Iowa State University, 2013.
[15] U.S. Department of Energy, 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy, vol. 1: Economic Availability of Feedstocks, Oak Ridge National Laboratory, 2016.
[16] B. Gikonyo, "Fuel Production from Non-Food Biomass – Corn Stover", Apple Academic Press, Boca Raton, 2015.
[17] J. E. Atchison, in "Pulp and Paper Manufacture", vol. 3, Joint Textbook Committee of the Paper Industry, 1987, pp. 4-6.
[18] M. S. Jahan, M. A. N. Russel, S. A. N. Shamim, A. I. Mostafa and M. A. Quaiyyum, *Ippta J.*, **16**, 13 (2004).
[19] H. Cheng, Q. Feng, D. Wang, P. Wang, H. Liu *et al*., *Cellulose Chem*. *Technol*., **51**, 215 (2017).
[20] R. Young, in "Paper and Composites from Agro-Based Resources", edited by R. M. Rowell and J. Rowell, CRC Press, 1997, pp. 135-248.
[21] H. A. Webber, *Ind*. *Eng*. *Chem*., **21**, 270 (1929).
[22] TAPPI Test Methods, Technical Association of the Pulp and Paper Industry, Peachtree Corners, GA, USA, URL: http://www.tappi.org, accessed on 31.08.2017.
[23] W. S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, available online at https://imagej.nih.gov/ij/, 1997-2016.
[24] ISO Standards Test Methods, International Organization for Standardization, Geneva, Switzerland, URL: http://www.iso.org, accessed on 31.08.2017.
[25] M. S. Ilvessalo-Pfäffli, "Fiber Atlas – Identification of Papermaking Fibers", Springer, 1995.
[26] M. C. Area and V. I. Popa, "Wood Fibres for Papermaking", Smithers Rapra Technology Ltd., 2014.
[27] T. Rauhala, A. W. T. King, G. Zuckerstätter, S. Suuronen and H. Sixta, *Nord*. *Pulp Pap*. *Res*. *J*., **26**, 386 (2011).
[28] S. H. Yoon and A. van Heiningen, *Tappi J*., **7**, 22 (2008).
[29] M. J. Kirwan, in "Paper and Paperboard Packaging Technology", edited by M. J. Kirwan, Blackwell Publishing, 2005, pp. 1-49.
[30] D. Chamberlain and M. J. Kirwan, in "Handbook of Paper and Paperboard Packaging Technology", second edition, edited by M. J. Kirwan, Wiley-Blackwell, 2013, pp. 1-49.
[31] D. Twede, S. E. M. Selke, D.-P. Kamdem and D. Shires, "Cartons, Crates and Corrugated Board. Handbook of Paper and Wood Packaging Technology", second edition, DEStech, 2015.
[32] S. Heinemann and J. Blechschmidt, in "Handbook of Paper and Board", second, revised and enlarged edition, vol. 1, edited by H. Holik, Wiley-VCH, 2013, pp. 34-47.
[33] C. J. Biermann, "Handbook of Pulping and Papermaking", second edition, Academic Press, 1996.
[34] CEPI – Confederation of European Paper Industries, Harmonised Structure for Raw Material and Products, 2014, URL: http://www.cepi.org/system/files/public/documents/publications/statistics/2014/CEPI%20Definitions%20-%20Annexes%20Full%20Package.pdf.
[35] VRANCART S.A. Adjud, Romania, Paperboards Mill Products, URL: https://www.vrancart.ro/index.php?lang=en&m=5&p=produse_hartie, accessed 31.08.2017.