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ENVIRONMENTALLY FRIENDLY CELLULOSIC FIBERS FROM CORN STALKS

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Abstract

One of the main causes of global climate change is deforestation. Wood is largely used in construction, furniture, and pulp and paper industries, which consume hundred of millions of cubic meter of wood year by year. Forest surfaces decrease rapidly at global level and this reality is of crucial importance for world global ecological footprint. Shortage of pulpwood for paper industry became a great challenge and, for this reason, other raw materials must be taken into consideration. Recovered paper is the most important raw material for paper industry, but low paper grades can be produced only. Collection rate of recovered paper is high in most countries and there are no additional quantities to assure the large requirements of the paper industry. Today, nonwood plants are considered more and more important raw material for this industry. Wheat and rice straws are used for decades to produce chemical pulp in many Asian and European countries.

This paper investigates the possibility of replacing pulpwood with corn stalks as raw material in producing chemical pulp for paper. Corn stalks are abundant agricultural waste in Romania, since more than 12 million tones of stalks were generated in 2017. It was found that corn stalks contain less lignin than wood and can be delignified using less chemicals, at lower temperatures and in shorter time. Moreover, corn stalks can be processed using ordinary reagents like sodium hydroxide, and pulps with different yields and lignin content can result. Natron pulping of corn stalks offers pulps with reasonable strength properties which can replace wood pulp in obtaining papers for corrugated board.

Key words: corn stalks, pulping, paper, resources

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1. Introduction

Wood is a valuable raw material and large quantities are used in many industries like construction, furniture and pulp and paper. Wood is also an important fuel being more and more used today for household heating. Deforestation is currently a challenging problem, because about 26 ha of forest disappear every minute at global level (Piazza and Santanu, 2015). Extension of farming land, excessive wood harvesting, forest fires and urbanization are among the causes of deforestation. Other reasons of

deforestation are associated with overpopulation and poverty, as well as corruption in many countries which leads to immediate profit (Kissinger et al., 2012).

Increasing of carbon footprint and climate change are among the most important consequences of deforestation. The woodlands are the major terrestrial sink of carbon, so that deforestation disrupts carbon cycle at global level (Fortuna et al., 2012; Gavrilescu et al., 2017; Ladd et al., 2013; Ward et al., 2015). The key result is the rise of concentration of carbon dioxide. By cutting the forests, the soil cannot hold water and a drier climate become evident (Binkley and

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Fisher, 2012; Gimona et al., 2012). In the last decades, the woodland of EU countries has continually decreased and now its surface represents no more than 34% from the EU countries surface. (FAO, 2014).

Pulp and paper sector needs large volumes of wood. To obtain a tone of pulp, 5-6 m³ of pulpwood are necessary, so that a pulp mill consumes up to one million cubic meters of timber per year (Gavrilescu and Craciun, 2012; Hetemaki et al., 2013). According to Confederation of European Paper Industries (CEPI), around 150 million m³ of softwood and hardwood were consumed in 2016 by the pulp and paper sector of European Union countries (CEPI, 2017). This high level of wood consumption can not be overcome without serious environmental consequences. Wood has become deficient and expensive and, for this reason, paper producers have sought solutions to replace it. Recovered paper can replace wood pulp in production of many paper grades and this raw material is largely used by paper manufacturers (Bajpai, 2015; Ghinea et al., 2014; Puitel et al., 2014; Scott, 2011). However, recovered paper can be used in production of low quality paper grades and it is available in limited quantities.

Another solution involves the fabrication of chemical pulp from nonwood raw materials (Kassim et al., 2015; Leponiemi, 2008). Nonwood plants are of increasing interest as a potential cellulosic fiber resource and these include cereal straw (wheat and rice), flax, cotton, corn stalks, rapeseed stalks, bagasse, reed etc. (Marin et al., 2017; Gavrilescu et al., 2009).

Chemical pulp is largely obtained from wood by means of suitable delignification processes (Gavrilescu, 2013). Romania was a forest-rich country, but the forests surface decreased from 40% in 1900 to 28% in 1948. According to Romsilva, the surface of Romanian forests accounted 25% in 2013 (Romsilva, 2015). The main causes of deforestation in Romania in last decades were excessive logging and deficient reforestation. As a consequence, wood consumption in industry decreased year by year. Due to the lack of wood and the continuously increasing of pulpwood price, Romanian pulp mills were gradually closed, so that no pulp mill is working anymore today. For this reason, Romanian paper mills were obliged to replace the pulpwood with recovered paper as fibrous source (Vlase et al., 2012).

Paper recycling is environmental friendly, but involves large investment in new plants and implementation of appropriate technologies for paper production. Compared to the chemical pulp, secondary fibres represent an inferior raw material and only low-grades quality of paper can be produced. Because recovered paper is used several times in producing paper, the cellulosic fibres gradually lost their papermaking potential. Periodically, a certain quantity of secondary fibres must be replaced with virgin fibers (chemical pulp) in order to assure the required quality of fibrous raw materials. For this reason, addition of virgin fibers in the fibrous circuit

of paper manufacture is necessary (Gavrilescu et al., 2014).

Virgin cellulosic fibres are produced from pulpwood or nonwoods. Corn stalks are among the nonwood waste with great potential to be used as resource for virgin fibers. Romania is an important producer of corn among EU countries, since more than 14 million tones were produced in 2017 (Eurostat, 2018). The corn stalks yield was estimated at more than 12 million tones and represents a valuable agricultural waste. There are several traditional ways to use the corn stalks: to feed animals, for incorporation into soil to regenerate soil humus, or for household heating. A new direction refers to chemical processing of stalks to obtain bio-based chemicals (Puitel et al., 2012).

The goal of this paper is to investigate the possibility to replace wood with corn stalks as resource for fibrous materials required in the production of paper used in corrugated board manufacturing. Chemical composition of corn stalks collected from Moldova region of Romania was determined. Natron pulping using sodium hydroxide was selected in order to estimate its delignification potential. A large range of pulps in terms of yield and lignin content was obtained. The strength properties of pulps were determined and the possibility for their use in obtaining papers for corrugated board is discussed.

2. Materials and methods

Stalks from current production of corn (*Zea mays* L.) in Moldova region of Romania were naturally dried in laboratory and then chipped at 3-5 cm length. The average moisture of stalks was 10%. Chemical composition of stalks was determined, according to the standards listed in Table 1.

The corn stalks pulp was obtained using a 10L laboratory rotating digester with automatic control of temperature (Puitel et al., 2015). An amount of 400 g oven dried (o.d.) stalks was filled in the digester and 120-220 g o.d. pulp was obtained, depending on the pulping conditions. Cooking liquor was prepared in the laboratory by dissolving NaOH in tap water. The following cooking conditions were used:

- heating time: 25-40 min., depending of cooking temperature;
- sodium hydroxide addition: 12-16% on o.d. stalks;
- cooking temperature: 120-160 °C;
- time at cooking temperature: 30-90 min.

Table 1. Standards used for chemical composition of corn stalks

Component, %	Standard
Cellulose	TAPPI T 17 wd-70, 1970
Pentosans	TAPPI T 223 cm-01, 2001
Lignin	TAPPI T 222 om-02, 2002
Extractives	TAPPI T 204 cm-07, 2007
Ash	TAPPI T 211 om-02, 2002

After digestion, the brown stock was defibered and washed with water until no color in the resulting liquor was observed. Washed pulp was screened using a vibratory screen with 0.25 mm slots. The screened yield of pulps was gravimetrically determined and the screened pulps were analyzed for their lignin content expressed as Kappa number (TAPPI T 236 om-06, 2006). The pulps were refined in a Jokro mill and transformed in handsheets in accordance with the Rapid Köthen method (ISO 5269-3, 2008). The pulp handsheets were tested regarding their strength properties according to the standards listed in Table 2.

Table 2. Strength properties testing of natron pulp from corn stalks

<i>Strength property</i>	<i>Standard</i>
Tensile strength	ISO 1924:3, 2005
Bursting strength	ISO 2758, 2014
Corrugating Medium Test - CMT	ISO 7263, 2011
Short-span compression strength - SCT	ISO 9895, 2008

3. Results and discussion

The corn at maturity is composed of root, stalk, leaves, cobs and ear. After harvesting the cobs, the plant material taken from the field consists of stalks, leaves and ears, of which the stalks represent about 85% (by mass). Corn stalks contains pit, which represents up to 90% of the stalk volume. Chemical composition of the constituent parts of corn stalks is presented in Table 3.

Corn stalks have a similar chemical composition related to other pulping raw materials. A comparison with Romanian pulpwood main species reveals that corn stalks have less cellulose, less lignin and higher content of pentosans and ash (Table 4). Comparative to wheat straw, corn stalks contain less cellulose, more lignin and similar percentages of extractives and ash. The most important advantage of corn stalks is the lower lignin content than that of wood. This means that corn stalks can be delignified using less chemicals, lower temperatures and shorter time, compared with wood delignification.

The lower content of cellulose, the high content of extractives and ash are the main drawbacks of corn stalks as a pulping raw material. Table 5 illustrates the pulping conditions and the main properties of natron pulp from corn stalks. As Table 5 shows, the yield and lignin contents of pulps strongly depend on pulping parameters. The pulp yield ranges between 29.7-55.1% and Kappa number between 21.4-64.4 units. Pulp yield correlates with lignin content as Fig. 1 shows. By using higher alkali addition (14-16%) and moderate temperatures (140-160°C), corn stalks can be delignified at low Kappa numbers (no more than 40 units), while the pulp yield ranges 30-40%. If the cooking is performed at low alkali addition (12% NaOH) and low temperature (120°C), pulps having higher lignin content (Kappa number 40-65 units) and yields (40-55%) are obtained, depending on the cooking time. It is obvious that to obtain pulps having better yields, low alkali addition and temperatures must be used.

It is known that lignin content is the one of main factor influencing pulp strength properties. Figure 2 presents the influence of Kappa number on tensile index of corn stalks pulp. It is evident that lignin content has a great influence on pulp tensile index. As Fig. 2 shows, tensile index records the best values at pulp Kappa number of 35-45 units. A similar behaviour was found regarding burst index of corn stalks pulps. As it is presented in Fig. 3, burst index values are the best at Kappa number of 30-45 units, and it is clear that tensile and burst indexes show the same dependence on the pulp lignin content.

It is already known that both burst strength and short span compression strength are the most appreciated among strength properties of papers for corrugated board (Campean et al., 2017; Gavrilescu and Toth, 2007). In addition, crushing resistance of the paper flutes is the key parameters of the corrugating medium (Gavrilescu, 2017). For these reasons, both short span compression strength (SCT) and crushing resistance (Corrugating Medium Test – CMT) were analyzed concerning their dependence on pulp lignin content. Fig. 4 shows the influence of lignin content on SCT index of pulp.

Table 3. Chemical composition of corn stalks constituent parts

<i>Component</i>	<i>Chemical composition, %</i>			
	<i>Cellulose</i>	<i>Lignin</i>	<i>Pentosans</i>	<i>Ash (SiO₂)</i>
Stalks	39.4	20.1	25.2	0.81
Pit	31.6	17.0	27.3	0.79
Leaves	31.3	17.4	21.2	7.0

Table 4. Comparison between chemical composition of corn stalk and other raw materials for pulping

<i>Raw material</i>	<i>Chemical composition, %</i>				
	<i>Cellulose</i>	<i>Lignin</i>	<i>Pentosans</i>	<i>Extractives</i>	<i>Ash</i>
Corn stalk	38.0	18.5	26.0	6.0	5.1
Wheat straw*	43.1	17.5	27.7	5.5	5.3
Softwood**	48-53	27-33	7-11	0.5-1.6	0.1-0.4
Hardwood**	44-50	18-25	11-20	0.1-0.6	0.2-0.6

* Data according to Puitel et al. (2012); ** Data according to Petrovici and Popa (1997)

Table 5. Natron pulping condition of corn stalks and pulp properties

No.	AA, %	Temp. °C	Time, min	Yield, %	Kappa number	TI, N.m/g	BI, kPa.m ² /g	CMT, N.m ² /g	SCT, N.m/g
1	12	120	30	55.1	64.4	52.1	2.2	2.40	37.3
2	12	140	30	47.3	48.8	60.3	2.5	2.34	36.5
3	12	160	30	41.1	45.4	63.2	2.4	2.26	35.5
4	12	140	60	42.2	45.7	66.0	2.9	2.22	34.8
5	12	160	90	40.0	42.0	68.3	3	2.20	33.5
6	14	120	60	39.5	41.8	68.1	2.8	2.14	33.8
7	14	140	30	38.3	41.4	67.4	2.8	2.12	33.5
8	14	140	60	35.0	35.7	65.0	2.9	2.12	33.0
9	14	140	90	31.7	26.8	65.0	3.0	1.84	31.7
10	14	160	60	32.9	29.3	64.0	2.8	1.96	32.5
11	16	120	90	33.1	30.1	64.0	2.8	2.00	29.5
12	16	140	30	32.3	27.5	60.2	2.8	1.94	29.2
13	16	140	60	30.8	23.6	60.5	2.6	1.84	27.2
14	16	160	30	29.7	21.4	54.0	2.3	1.68	25.4

AA - Alkali Addition; TI - Tensile Index; BI - Burst Index; CMT - Corrugating Medium Test index; SCT - Short-span Compressive Test index

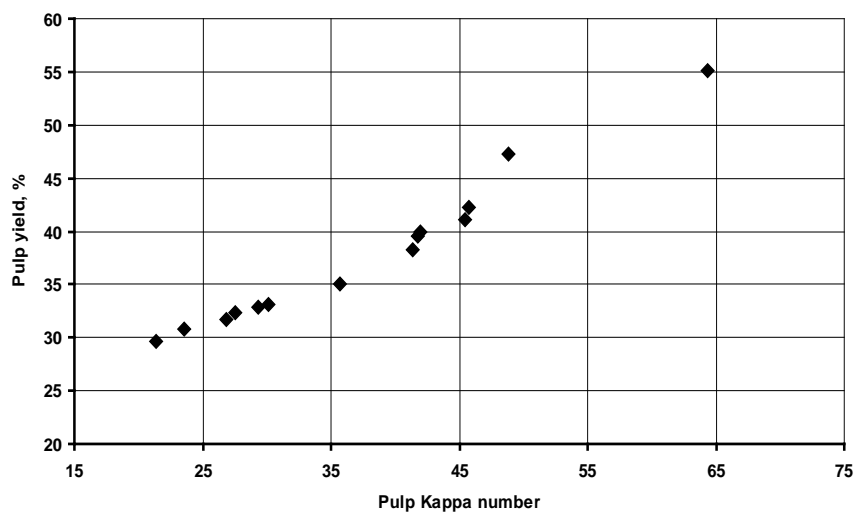
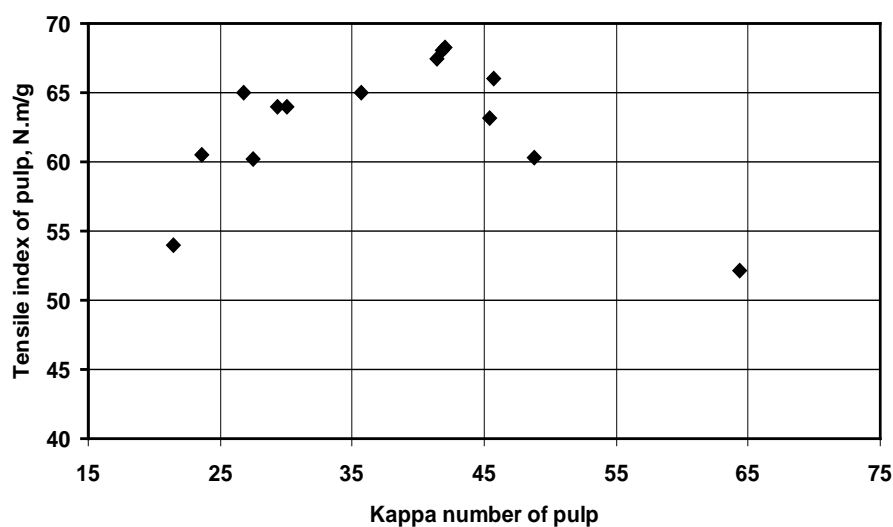
**Fig. 1.** Influence of corn stalk lignin content on pulp yield**Fig. 2.** Influence of corn stalk lignin content on tensile index of pulp

Fig. 4 reveals that, by increasing pulp lignin content, SCT index of the pulp handsheets increases, but no maximum values is recorded. The same evolution undergoes the dependence of CMT index on pulp lignin content (Fig. 5). CMT index of pulp continuously increases as the lignin content of pulp increases too. Comparing Figs. 4 and 5 it is unequivocal that SCT and CMT indexes of pulp depend in a similar manner on lignin content. The explanation of this behavior is that the rigidity of cellulosic fibres boosts as lignin content increases, and this determines the enhancing of handsheets rigidity.

This fact is of particular importance for the paper used in corrugated board manufacture. It is obvious that handsheets having higher SCT and CMT indexes are obtained from lignin-rich pulps, as resulted from Figs. 4 and 5.

The strength properties of corn pulp presented in Figs. 3 and 4, comparative with the recommended values of burst and SCT indexes listed in Table 5 prove that corn straws pulp can be a valuable fibrous source in producing of papers for corrugated board. In this respect, corn pulp can be an attractive solution for Romanian paper sector.

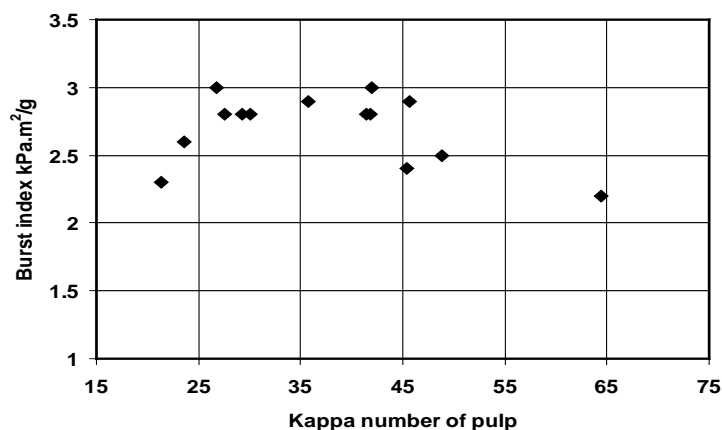


Fig. 3. Influence of corn stalk lignin content on burst index of pulp

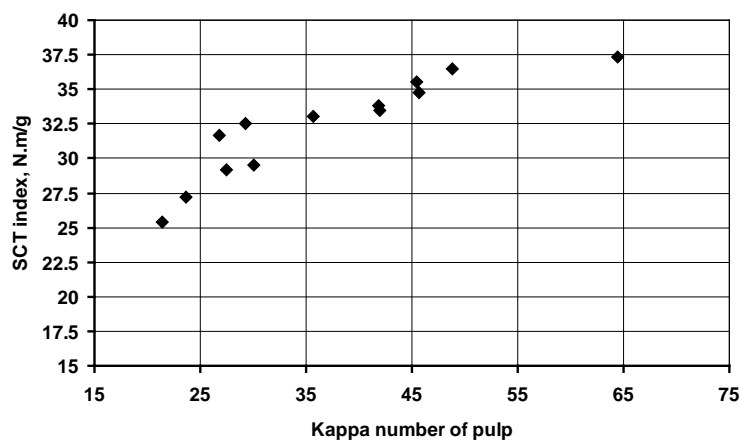


Fig. 4. Influence of lignin content on SCT index of pulp

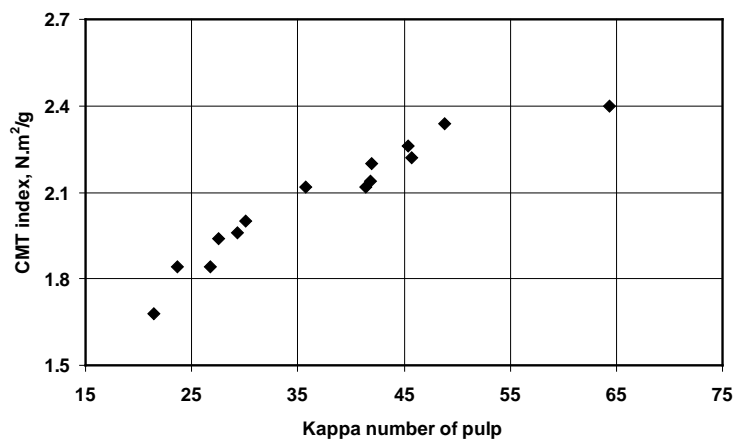


Fig. 5. Influence of lignin content on CMT index of pulp

Table 5. Recommended values of strength properties of paper used for production of corrugated board (ECO, 2012)

<i>Paper grade</i>	<i>Burst index, kPa.m²/g</i>	<i>Short span compression index (N.m/g)</i>
Testliner 1	More than 3.0	More than 17.5
Testliner 2	2.5-3.0	15.5-17.5
Testliner 3	2.0-2.5	13.5-15.5

4. Conclusions

Corn stalks can replace pulpwood in the production of fibrous materials for paper industry. The main advantages refer to the fact that corn stalks contain less lignin than wood and can be delignified using less chemicals, lower temperatures and shorter time. The high content of extractives and ash are the main drawbacks of corn stalks as a raw material for pulp manufacture.

Natron pulp yield strongly correlates with lignin content and the values depend on pulping parameters. It is obvious that to obtain pulps having better yields, low alkali addition and temperatures must be used.

The relatively high strength properties of corn pulp prove that corn straws pulp can be a valuable fibrous source in producing of papers for corrugated board. In this respect, corn natron pulp can be an attractive solution for Romanian paper sector.

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