LIGNOCELLULOSIC AGRICULTURAL RESIDUES – A VIRGIN FIBRE SUPPLY SOLUTION FOR PAPER-BASED PACKAGING

ADRIAN CĂTĂLIN PUITEL,[*] NARCISA MARIN,[*] PETREA PUIU[**] and DAN GAVRILESCU[*]

[*]*Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, Iasi, Romania*
[**]*SC. Romwelle PM SA, Romania*
✉ *Corresponding author: Adrian Cătălin Puitel, puitelac@tuiasi.ro*

The current work focuses on determining the suitability of wheat and oat straws (*Triticum aestivum*, *Avena sativa*) as raw materials for papermaking pulp production. One of the first objectives of the study was to establish the chemical composition of these raw materials in terms of major constituents (cellulose, hemicelluloses, lignin) contents, as well as minor constituents (extractives and ash). The studied raw materials contain 70-75% holocellulose, 35-42% cellulose and 18-22% lignin. These values uphold their use as raw materials for pulping, which was the second step of this study. The yield, kappa number and viscosities of the obtained pulps have been determined. The obtained experimental values for pulp yield in soda pulping ranged from 35 to 45% and proved to be higher in sodium carbonate pulping. Finally, the strength properties of the pulp were evaluated for handsheets obtained before and after beating the pulp at 40 °SR.

Keywords: alkaline pulping, sodium carbonate, straw pulp, virgin fibres

INTRODUCTION

Pulp and paper industry is one of the best examples of the biorefinery concept, incorporating the production of materials, chemicals and energy through established technological processes, which maximize the value of lignocellulosic resources. This industry is relying on the recyclability, biodegradability and renewability of its most used resources – cellulose fibres. Although in the European Union, the recycling rate has reached 71.7%, according to the latest CEPI statistics (2014),[1] the industry is encountering a continuous need for virgin fibre resources to satisfy different market demands. Some of these demands are generated by the shift of the packaging industry towards green alternatives by replacing plastics with fibre based materials, such as paper and cardboard, which have lower environmental impact.[2] The constant need for virgin fibres is the direct consequence of the decline of fibre properties during the lifecycle of paper.[3] The contamination with a wide range of substances, the chemical components of mineral oils being the most important of them, and the rising concern on their migration into packaged foods may limit the application of recovered paper in the production of food paper-based packaging and thus may also lead to an increase in the virgin fibre demand.[4]

In the pulp and paper industry, wood is traditionally the most intensively used virgin fibre source, which causes forest overexploitation in certain parts of the world. In this context, the use of agricultural residues for the production of fibres deserves serious consideration. Nonwood fibre sources already represent an important raw material in Asian countries, such as China, India, and Vietnam.[5] There are some issues worth mentioning regarding the attractiveness of agro-wastes as raw material for papermaking pulp production. According to their origin, the sources of non-wood raw materials may be classified in the following manner: dedicated fibre crops, agricultural wastes as straws and stalks and spontaneous wild growing plants.[6,7] In the case of cereal straw yields of 1 to 3.5 tons oven dry straws have been reported, but the efficiency of collection and the cultivated species strongly influence the mentioned values.[8-10] The advantages of these fibre sources are both of environmental and economic nature; they include faster growing and harvesting costs covered by the main crop, abundant availability from grain processing in various regions of many countries, ecological footprint lower than those of woods.[11]

The most important disadvantages of nonwood and particularly agricultural wastes have been reported to be the lower density, susceptibility of rotting, higher content of hemicelluloses, ash and extractives, compared to wood.[11-23] Hemicelluloses content of some of these resources are responsible for low pulp yield due to degradation in the initial phases of pulping and alkali consumption. The low bulk density of these materials, susceptibility of rapid degradation by rotting and other storage associated phenomena, may limit their utilizations as raw materials for paper production. Lower density and susceptibility of rotting also affect the logistics of nonwood processing. Ash chemical components are the main cause of deposits in chemical recovery circuits.[12,13] Lipophilic extractives may generate multiple malfunctions as a result of pitch deposit formation, foaming. A number of effluent management problems have also been reported as being generated by extractives.[14]

The aim of this study was to investigate the possibilities of using agricultural residues, in particular wheat and oat straws, as raw material for the production of papermaking pulp by alkaline methods – soda pulping and sodium carbonate pulping. The experimental work was mainly focused on the use of sodium carbonate as pulping agent since this pulping method is appropriate for small facilities and eliminates the need of causticization in alkali recovery systems.

EXPERIMENTAL

Raw materials

The raw materials (oat straws – *Avena sativa L.* and wheat straws – *Triticum aestivum L.*) used in the study were provided by some Romanian farms. These materials were pre-conditioned by drying up to 8-10% moisture. Before pulping trials, the straws were analyzed for main chemical components.

Chemical composition analysis

The chemical characterization of the straws was performed in triplicates according to standard or methods reported in the literature. Moisture content was measured according to TAPPI T 664 om-88 standard method. Other procedures were: cellulose,[15] holocellulose,[16] lignin (TAPPI T222 om-02), extractives (TAPPI T204 om-88); ash (TAPPI T211 om-85). The total contents of hemicelluloses and polyuronic acids were calculated by difference between holocellulose content and cellulose content.

Pulping trials and analyses

The second part of our work involved cooking experiments aiming at obtaining papermaking pulps by alkaline pulping using sodium hydroxide (soda pulping – S samples) and sodium carbonate (sodium carbonate pulping – SC samples) as alkali sources. The pulping trials were performed in a 10 L stainless steel laboratory rotating batch reactor, equipped with electric heating and automatic temperature control. Amounts between 300 and 500 g of raw materials (o.d. mass), corresponding to a pulping liquor:solid ratio of 5:1, were used in regular cooking experiments. The heating time was 30 minutes, while cooking time was established at 60 minutes at a temperature of 160 ºC.

During the experiments, the alkali charges were varied (16% and 20% expressed as NaOH units or 12.4% and 15.5% expressed as Na_2O units both for soda pulping and also for sodium carbonate pulping trials. White liquors were prepared in the laboratory by separately dissolving analytical grade sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3), respectively, in tap water. After cooking, the reactor was degassed and cooled to an appropriate temperature to allow removal of pulp for disintegration, washing and squeezing for water removal up to a consistency of about 30%. Furthermore, yield (gravimetric method) kappa number (ISO 302:2004) and intrinsic viscosity (ISO 5351:2010) were measured.

Obtaining laboratory sheets and mechanical properties analysis

The obtained pulp samples were further used for laboratory sheet forming before (~20 ºSR) and after beating (~40 ºSR). Laboratory beating was performed according to ISO 5264-3:1979 procedure in a Yokro mill, 750 rpm. Handsheets were obtained according to ISO 5269-2:2004 on a Rapid Köthen laboratory sheet former. The following mechanical properties were analyzed: tensile strength (ISO 1924:2008); bursting strength (ISO 2758:2001); corrugating medium flat crush resistance test (also called Concora Medium Test, ISO 7263:2011) and SCT – short span compression test (ISO 9895:2008).

RESULTS AND DISCUSSION

Chemical composition of straws

The chemical composition of the studied raw fibre sources (Figure 1) shows similarities with other raw nonwood virgin fibre sources, such as reed, and relatively close values to those presented in the literature for hardwoods.[14-17] The ash and extractives contents of the studied straws are higher than those of common beech (*Fagus sylvatica*) and reed (*Phragmites communis*).[17] It is known that the ash content of most nonwoods and in this case agricultural residues is higher than that of hardwoods and softwoods. In particular, oat straw has a higher content of extractives than wheat straw. The cellulose content of wheat straw is higher than that of oat straw and even higher than the average content of beech reported in the literature.[14] However, it is known that the chemical composition of cereal straws has a wide variability.

Lignin contents of both materials are lower than those of reed and beech, indicating the possibility of an easier delignification and lower alkali consumption. Hemicelluloses contents of both types of straws are relatively close to those of reeds and beech. In particular, wheat straws had the highest hemicelluloses content and the determined value is similar to that of beech. The determined values for the main chemical components are consistent with the values presented in other studies[5,6,10] and show the possibility of using them as raw materials for pulping by sulphur free pulping methods.

Pulping results

Figures 2 and 3 present the results of the laboratory pulping trials for the yield and kappa number, while Figure 4 displays the results on the viscosity of the obtained pulps. An increase of alkali charge from 16% to 20% NaOH units leads to a decrease in yield and kappa number, as well as in viscosity. In the case of soda pulping, the yield suffers a significant drop with an increase in the alkali charge: for wheat straw pulps the yield drops by 3.3%, while for oat straw the difference is much higher (15.2%). Yield drops with the increase of alkali charge also occur in the case of the samples resulted from sodium carbonate pulping: 1.8% for wheat straw and 14.2% for oat straw. These values indicate that wheat straw pulps are more suitable for pulping. The obtained yield values are also explainable by the chemical composition of the straws, including by the reported high content of hot water solubles.[23] The presence of such chemical components, which are dissolved in the initial stage of pulping and react with the active alkali, limits the efficiency of pulping.

Kappa number of the obtained pulps decreases as the alkali charge increases in both types of pulping experiments. In the case of soda pulping of wheat straw, kappa number decreases from 14.9 at 16% NaOH to 11.5 at 20% NaOH, and from 26.1 to 14.9 for oat straw pulps for the same alkali charge. As expected, the use of sodium carbonate as active alkali results in higher kappa number pulps.

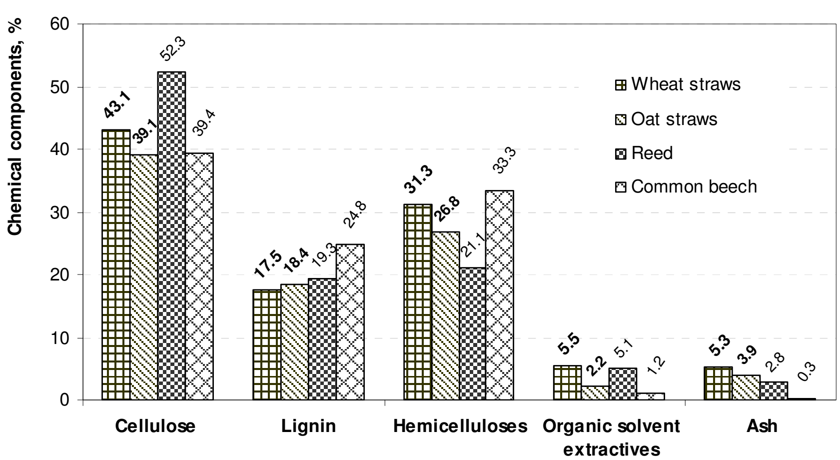

Figure 1: Chemical composition of raw materials used in the study. For the sake of comparison, values for reed[17] and common beech[14] are also presented

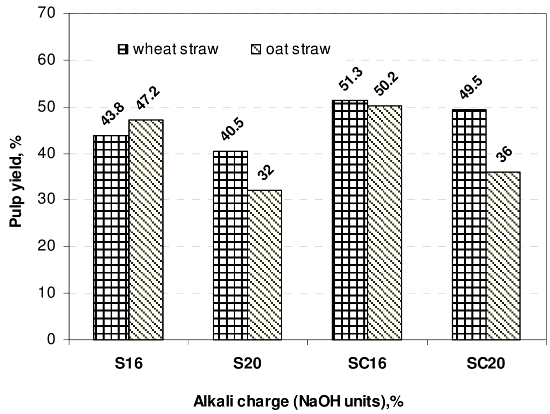

Figure 2: Yield of obtained pulps (S – pulps obtained by soda pulping, SC – pulps obtained by sodium carbonate pulping, 16 and 20 – % alkali charge)

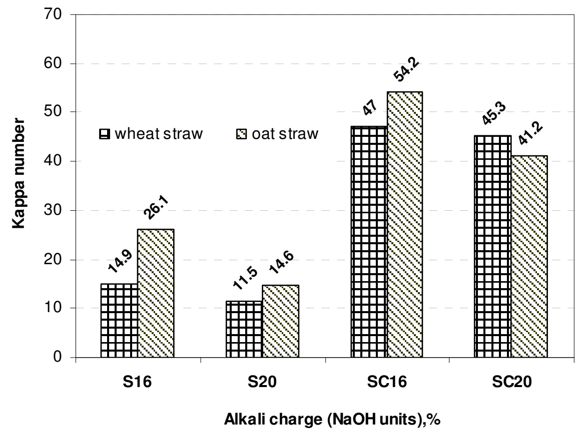

Figure 3: Kappa number of obtained pulps

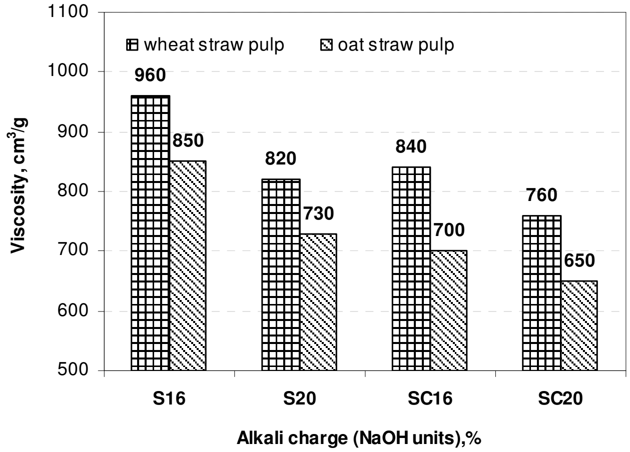

Figure 4: Viscosity of straw pulp samples

This evidences the lower efficiency of Na_2CO_3 as active alkali in pulping, as compared with sodium hydroxide. The reduction of kappa number with the increase of the alkali charge was from 47 to 36 in the case of wheat straw pulps and from 54.2 to 41.2 for the oat straw pulps.

The intrinsic viscosity of a pulp is in a direct correlation with the degree of polymerization of cellulose. In soda pulping – the viscosity losses are of 140 cm^3/g for soda pulping of wheat straw and 120 cm^3/g for soda pulping of oat straw. In the case of sodium carbonate pulping samples, the results are similar – viscosity loss is of 80 cm^3/g for wheat straw pulp and 50 cm^3/g for the oat pulps. The lower viscosity values obtained for the sodium carbonate pulp samples do not necessarily mean that these pulps are more degraded than soda pulps. It should be taken into account that intrinsic viscosity is a measure of medium molecular mass of polymers and the lower value may suggest the presence of a low molecular mass fraction. On the other hand, the reduction of yield and viscosity are the direct result of an increase in the kinetic rate of the destruction reactions of polysaccharides (peeling and alkaline hydrolysis) over the delignification reactions with increasing alkali charges.[24]

The most likely explanation for the higher yields and kappa number of pulps obtained by sodium carbonate pulping is the lower pH achieved during the experiments and a much limited cleavage of α-aryl ether bond in lignin.[25,26] A clear advantage of the usage of sodium carbonate as active alkali is an increased yield of cooking, which was up to about 50% in our experiments. A technological and economical advantage of using sodium carbonate as pulping active alkali is a simplified alkali recovery circuit, suitable for smaller facilities.

Mechanical properties of obtained pulp

Refining is an important technological process in papermaking, which influences final paper properties. Generally, the straw pulps are characterized by a relatively high initial refining degree, fast refining rate and low specific energy input, and thus allowing important savings in energy consumption.[21,30] The aim of refining in the current study was the improvement of sheet formation. As expected and reported previously,[17] these pulps showed a rapid increase of beating degree – about 38-40 ºSR was obtained after 750 rotations (5 minutes of beating in a Jokro mill). The notation 0 stands for unbeaten pulps (20-22 ºSR), while 5 stands for 5 min beaten pulps. The rapid increase of beating degree of these pulps is a direct consequence of the pulp composition in terms of fibres, cell types and their distribution.[27-29] Chemical composition and especially hemicelluloses content also play an important role in the high refining capacity of straw pulp.[28] As demonstrated by other authors,[23,28] the straw pulps are characterized by the presence of a high fraction of parenchyma cells and fine fibres.

The values for tensile strength and burst index are comparatively presented in Figs. 5-6. The results are in similar ranges with the data reported in the literature for other nonwoods and are close to those obtained for hardwood species pulps.[17,28-31] The tensile and burst indexes of soda pulps are both negatively affected by the increase of the alkali charge, while in the case of sodium carbonate pulps the increase of the alkali charge generates a slight increase of the tensile index values.

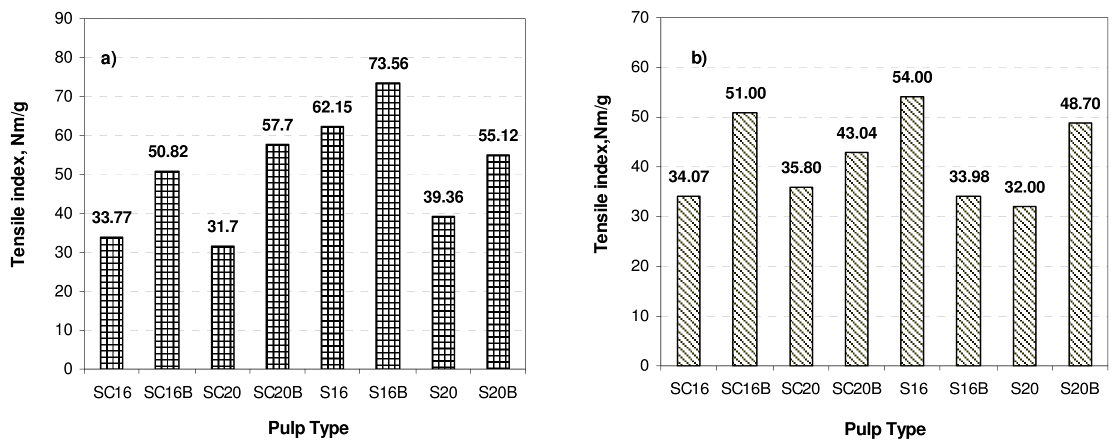

Figure 5: Tensile index of obtained pulps, before and after beating around 40 °SR: a) wheat straw pulps, b) oat straw pulps

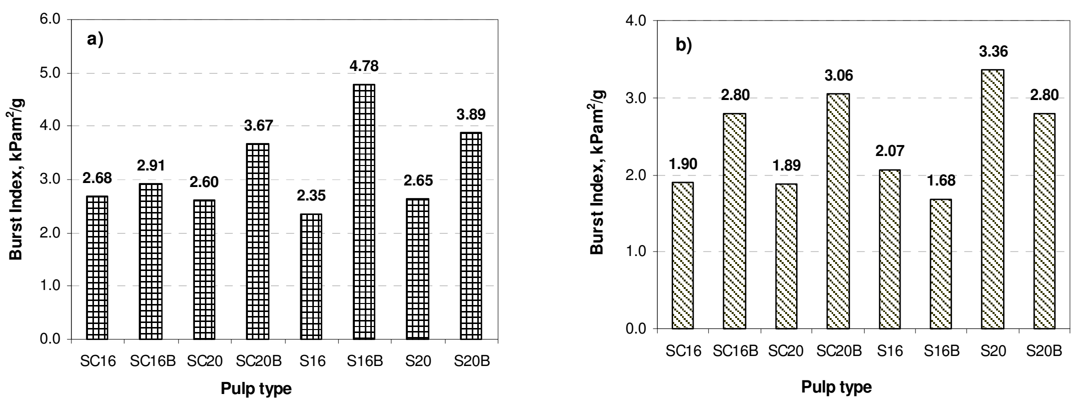

Figure 6: Burst index of obtained pulps: a) wheat straw pulps, b) oat straw pulps (S and SC have the same significance as in Figure 2)

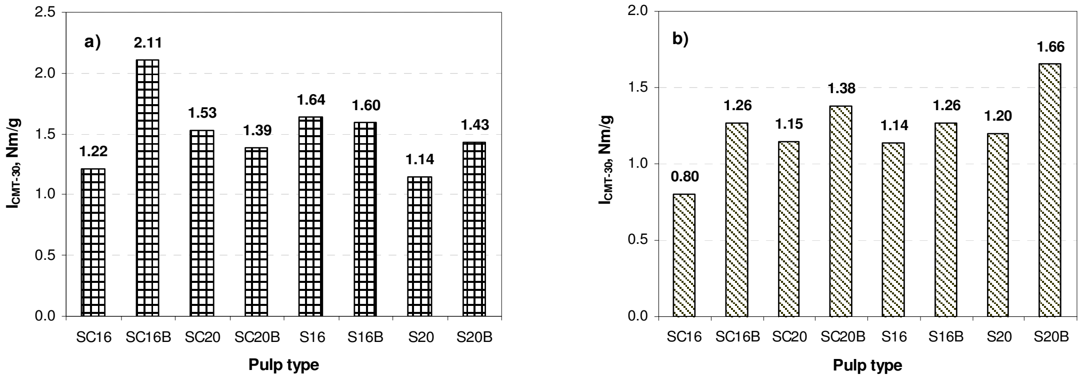

Figure 7: Corrugating medium flat crush resistance test index (I_{CMT-30}) of the obtained pulps: a) wheat straw pulps, b) oat straw pulps

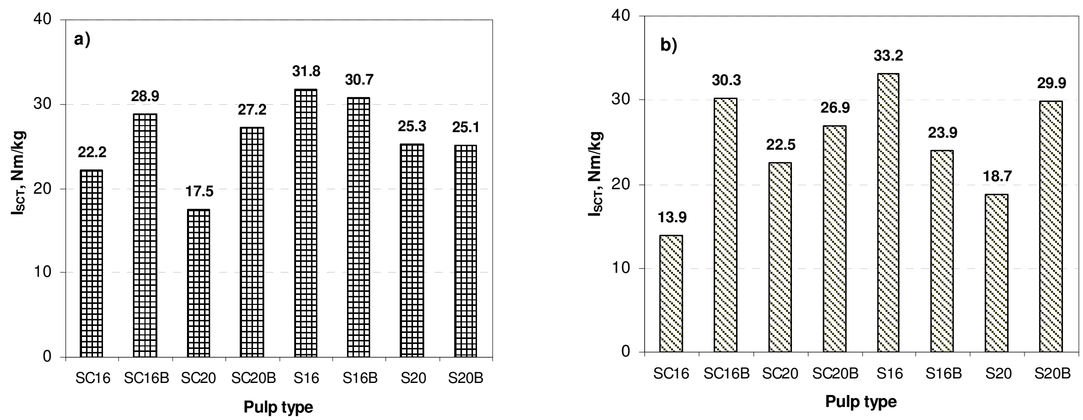

Figure 8: Short span compressive strength index (I_{SCT}) of obtained pulps; a) wheat straw pulps, b) oat straw pulps

The beating leads to an improvement of the mechanical properties for all the samples, with some minor exceptions. Tensile strength is a direct consequence of the intimate structure of paper and the properties of its individual fibres. The decrease of the strength properties in the case of soda pulps with the increase of the alkali charge is the consequence of cellulose depolymerisation and hemicellulose loss. In the case of sodium carbonate pulps a higher alkali charge leads to higher lignin removal, the main factor interfering in hydrogen fibre bonding.

Bearing in mind the potential utilization of the obtained pulps in packaging paper production, the results of the corrugating medium flat crush resistance test and the short span compression test are comparatively presented in Figures 7 and 8. The indexes I_{CMT-30} and I_{SCT} were calculated as the ratio between the determined values and the grammage of the pulp sheets. The rigidity of a fluting structure is particularly important during the conversion of the paper into flute structures and is reflected on the efficiency of the process of corrugated board production.[32] The values obtained for I_{CMT} generally decrease with the alkali charge increase in case of wheat straw pulps obtained by soda pulping and show an increasing trend in sodium carbonate pulping.

The short span compressive strength index (I_{SCT}) is one of the properties that reflect the compressive strength of the corrugated board and further the strength properties of the obtained boxes.[33] I_{SCT} of fluting made from OCC recycled pulps ranges from 10 to 16 Nm/kg at basis weight values of 80-120 g/m^2.[22] This indicates the potential use of straw fibres for blending of OCC and further strength increase. Literature data indicate that blending may reduce overall process energy consumption by 30%.[21] All values of I_{SCT} decrease with the alkali charge increase in both soda and sodium carbonate pulping. Pulp beating increases the short span compressive strength in the case of the sodium carbonate pulping samples and has minor effects or even lowers the I_{SCT}

values for the wheat and oat straw soda pulps. An overall comparison between the two types of the raw materials indicates that wheat straw gives better results in pulping, compared to oat straw.

CONCLUSION

Based on the experimental results, it can be concluded that straws can be pulped to different yields, kappa numbers and intrinsic viscosity values by using both soda and sodium carbonate as active alkali. Sodium carbonate used as alkali source for pulping leads to higher lignin content pulps.

The strength properties of the obtained paper sheets are also affected by the type of the active alkali source and also by the refining process. Having in mind the obtained results, straw these may become an economically feasible source of virgin fibre, if appropriate process conditions are selected. The proposed potential use of the obtained fibres is in the production of food packaging papers, the straw virgin fibres have the advantage of not being contaminated; the blending of recycled paper pulps for increasing the mechanical properties of corrugated medium. Other potential uses include blending with other virgin fibres for reduced energy consumption in refining.

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