

CELLULOSIC PULPS OF CEREAL STRAWS AS RAW MATERIAL FOR THE MANUFACTURE OF ECOLOGICAL PACKAGING

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The aim of this work was to study the potential application of four types of cereal straws: oats, maize, rapeseed, and barley, in order to obtain cellulose pulp through the Specel® process for use in the manufacture of 100% biodegradable and ecological packaging. Raw materials were chemically characterized to determine alcohol-extractives, ash, lignin, holocellulose, and α -cellulose. Cellulosic pulps obtained from raw materials were characterized to determine yield, Kappa number, and viscosity. Paper sheets made from cellulosic pulps were characterized to determine beating degree, tensile index, stretch, burst index, tear index, and brightness. Finally, the results were compared to the raw material used in the industrial manufacturing of packaging (wheat). The four studied raw materials (oats, maize, rapeseed, and barley) were judged to be suitable for use in the Specel® process to obtain cellulosic pulp suitable for production of ecological containers.

Keywords: Cereal straws; Packaging; Cellulosic pulp; Sodium hydroxide; Industrial

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INTRODUCTION

The concept of a sustainable economy is increasingly being put into practice in all social aspects and, of course, in the industrial production. An example of a sustainable economy is that based on a proper use of natural resources, such that one takes advantage of all of their components. One way of achieving this goal is through the valorization of byproducts or waste generated in agricultural or industrial activities. One of the aims of any industrial activity is to produce products that can satisfy new market needs. In these products, the ecological commitment is a very important factor; society is becoming aware and convinced of the need to consume products that have been obtained through environmentally respectful processes.

Europe produced 96.5 million tons of paper and cardboard in 2010, of which approximately 17% wt. came from non-wood fibers (Confederation of European Paper Industries, CEPI). The cellulosic fibers of non-wood species, such as residues of agricultural and agri-food industry, are very appropriate for the manufacture of papers with special characteristics due to their favorable morphology, composition, and heterogeneity (García Hortal 2007; González-García *et al.* 2010). So, to date, several residues of agricultural and agri-food industry have been studied (orange tree pruning, vine shoots, cereal straws, palm oil waste (EFB), *etc.*) (Berrocal *et al.* 2004; Navaee-Ardeh *et al.* 2004; Huang *et al.* 2006; Rodríguez *et al.* 2008; Jiménez *et al.* 2009;

Hosseinpour *et al.* 2010; Jiménez *et al.* 2010; Rodríguez *et al.* 2010; Chen *et al.* 2011; Ferrer *et al.* 2011; González *et al.* 2011; Hou *et al.* 2011; Fatehi *et al.* 2010).

Among all these non-wood raw materials, cereal straws are a very important source of raw material, since the world production of wheat, barley, maize, oats, and rapeseed was 1,742 million tonnes in 2009 (FAO). Considering that one kilogram of cereals generates approximately one kilogram of residue (straws) (Rodríguez *et al.* 2010), this agricultural activity creates a large quantity of residue each year. Such materials are used, nowadays, at best and in small quantities, as organic amendment and food for cattle, but mostly they are burned directly in the field, which causes pollution and fire risk.

Ecopapel S.L. company, which is located in Écija, Spain, manufactures cellulosic pulps from wheat straw that are used to produce packaging for various products, especially for the food and clinical industries. The pulping process, called Specel®, is versatile, allowing feedstock to consist of different types of cereal straws and other non-wood agricultural and/or forest waste. In this process, part of the lignin and hemicelluloses are solubilized from the straw, leaving a yield of about 65% to 70% by mass of dry straw. This is done through a reaction with sodium hydroxide as the only reactive chemical, without using either sulfur- or chlorine-containing compounds.

The production of wheat in Spain in 2009 was 4,724 t. Considering that the factory produces 20 t per day of cellulosic pulp, and the yield of the pulping is about 70% wt., it follows that 10,428 t per year of wheat straw would be required in order to guarantee the continuous operation of the plant and its economic viability. Taking into account that the Specel® process is adequate for all kind of cereal straws, and the annual production of oats, barley, rapeseed, and maize in 2009 in Spain was 11,775 t, it is really interesting to investigate the viability of the use of these raw materials in order to produce cellulosic pulps to obtain the above-mentioned packaging material.

In the present study, oats, maize, rapeseed, and barley straws were chemically characterized to determine their ash, holocellulose, α - cellulose, and lignin content. These raw materials are subjected to the Specel® process too, operating under the same conditions as those used for wheat straw. The following characteristics were evaluated: the degree of refining (*i.e.* freeness), the Kappa number, the viscosity of cellulose in the pulps, and the tensile index, stretch index, burst index, tear index, and brightness of the obtained sheets from the pulps. Finally, the observed results were compared with those obtained from wheat straw in order to determine their potential application in the production of cellulose pulps for the manufacturing of containers.

EXPERIMENTAL

Raw Material

Oats, maize, rapeseed, and barley straws were provided by Ecopapel S.L. company from cooperatives of Écija, Sevilla, Spain. Because of the way in which these raw materials are harvested, it is necessary to sift and perform a manual screening in order to separate undesirable elements such as stones, plastic bags, seeds, dust, wires, *etc.*

Once these elements had been separated, the straw was dried to an approximate value of dryness, close to 90 %, and stored in plastic bags for proper conservation.

Raw Material and Pulp Characterization

The chemical properties of cereal straws and pulps obtained from these were determined in accordance with the respective TAPPI©1997 standards for the different components, namely: T-222 for lignin, T-203 0S-61 for α -cellulose, T-9m-54 for holocellulose, T-204 for ethanol-benzene extractives, and T-211 for ash.

Pulping of Raw Material

The cellulosic pulp of wheat straw, which is used as a standard for comparison of the results of other raw materials, was provided by the Ecopapel S. L. company and obtained under the following operating conditions: 7% sodium hydroxide, 100 °C, a 10 liquid/solid ratio, and a processing time of 150 minutes.

Pulps from other straws were obtained by using a 15-L batch cylindrical reactor that was heated by means of an electrical wire and linked through a rotary axle – to ensure proper agitation – to a control unit including a motor actuating the reactor and the required instruments for measurement and control of the pressure and temperature.

The raw materials were cooked using 7% NaOH, 100 °C, a 10 liquid/solid ratio, and a processing time of 150 minutes. These operating conditions are the same as those used in the Specel® process. Next, the cooked material was fiberized in a wet disintegrator at 1200 rpm for 30 min, and the screenings were separated by sieving through a screen of 0.14 mm mesh size. The pulp obtained was beaten in a Sprout-Bauer refiner.

Specel® Process

In Fig. 1, an outline of the process is shown. The bale of wheat straw is placed in a conveyor belt where strings are removed and slightly cleared.

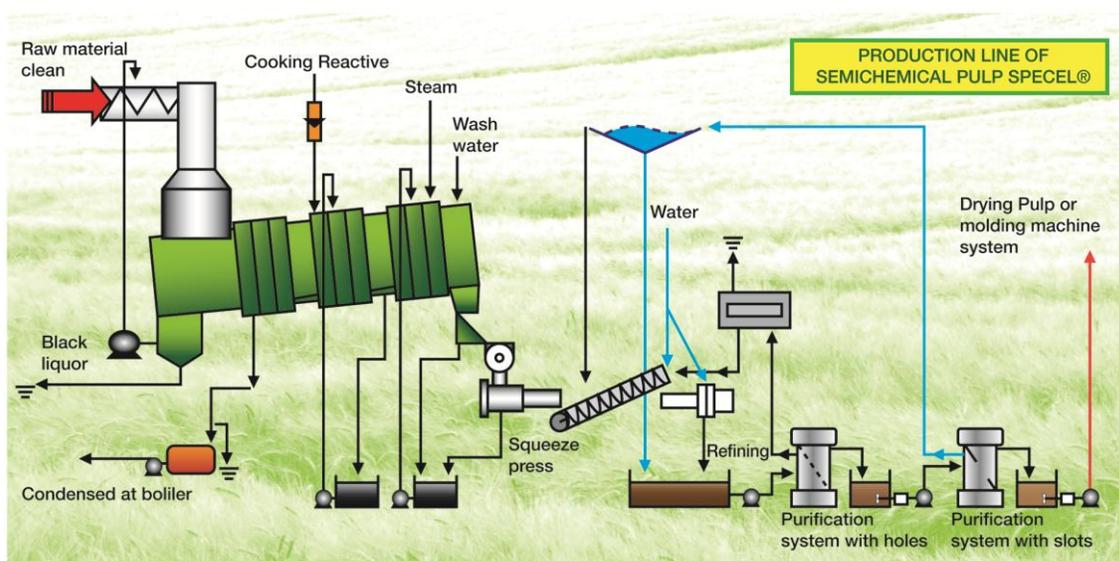


Fig. 1. The Specel® process

Then, by blowing, the undesirable elements that may accompany the straw are removed and, subsequently, wheat straw is put into the digester through the conveyor belt. Wheat straw moves through the digester crosscurrent to the cooking liquor, reducing its volume until one sixth of the initial one. Cooked pulp leaves the digester through a mechanical conveyor, which leads it to a twin screw press in order to extract the cooking liquor, which is passed forward to the digester to recover the alkali and fibers that it contains.

The cooked and pressed straw is diluted to 8% to 10%, refined, and then purified. After the addition of a biocide to ensure its microbial stability, the obtained pulp is dried and stored for subsequent use in the manufacture of containers.

Pulp Properties

Treated pulp samples were characterized in terms of Kappa number, brightness, and viscosity according to TAPPI T236cm-85, TAPPI T525om-92, and TAPPI T230om-94, respectively. The Kappa number and viscosity were measured five times, and ten measurements of brightness were obtained in order to calculate a relative standard deviation, which was found to be ≤ 0.1 for the three properties mentioned.

Paper Sheets Characterization

Paper sheets were prepared on an ENJO-F-39.71 sheet machine according to TAPPI T205ps-95.

Paper sheets were characterized in terms of tensile index (TAPPI T494om-96), burst index (TAPPI T403om-97), and tear index (TAPPI T414om-98). Two measurements were obtained for each test from ten sheets. The total number of data points was 20 for each cellulosic pulp obtained.

Manufacture of Containers

Oven dry manufacturing process

In Fig. 2, an outline of the oven dry manufacturing process of packaging is shown. The pulp slurry with a consistency of 1.5% is placed in a cast in which the highest quantity of water is separated by gravity and subsequently moved by a conveyor belt to the oven, where it is dried. The production capacity of this molding machine is 2 t of cellulosic pulp per day.

Thermoformed process

Figure 3 shows a diagram of the thermoformed process. In the first stage of molding, a slurry of pulp with a consistency of 0.8% is poured over the cast, in which the greatest quantity of water is drained by gravity. Then it goes through two continuous thermoformed stages by applying pressure and temperature in order to remove the water from the container. The capacity of production of this molding machine is 1 t of cellulosic pulp per day.

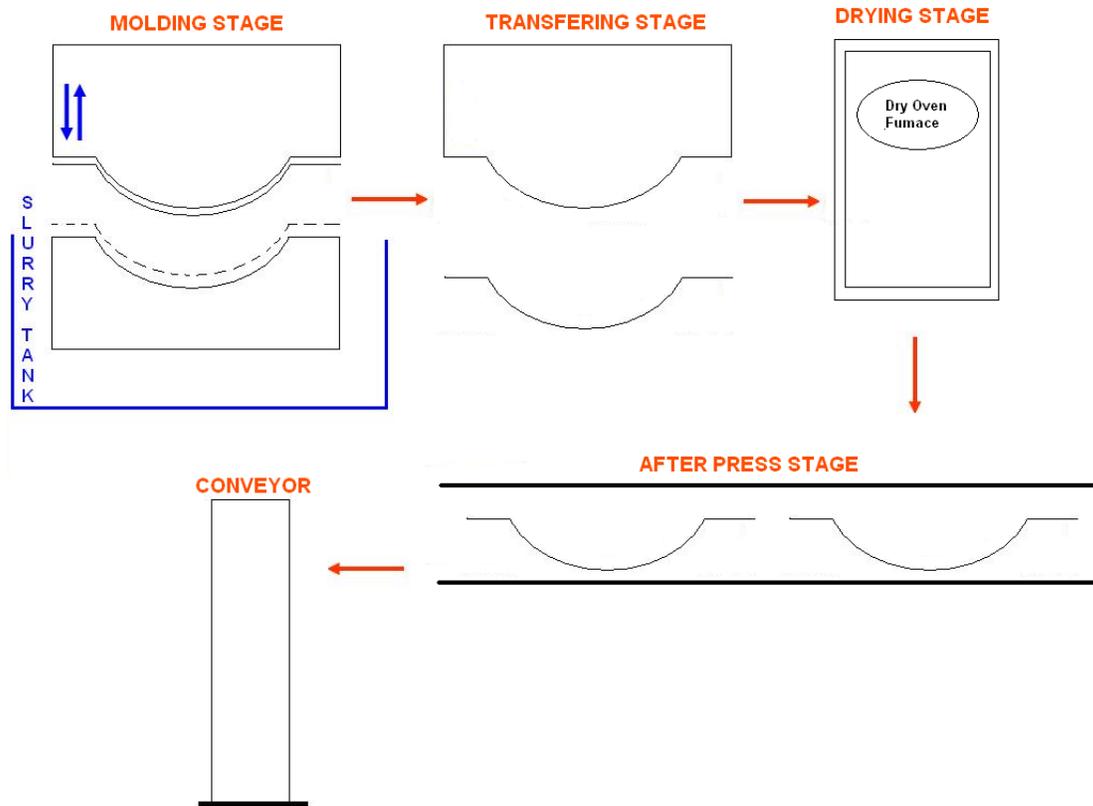


Fig. 2. The oven dry manufacturing process of containers manufactured from cellulosic pulps from cereal straw

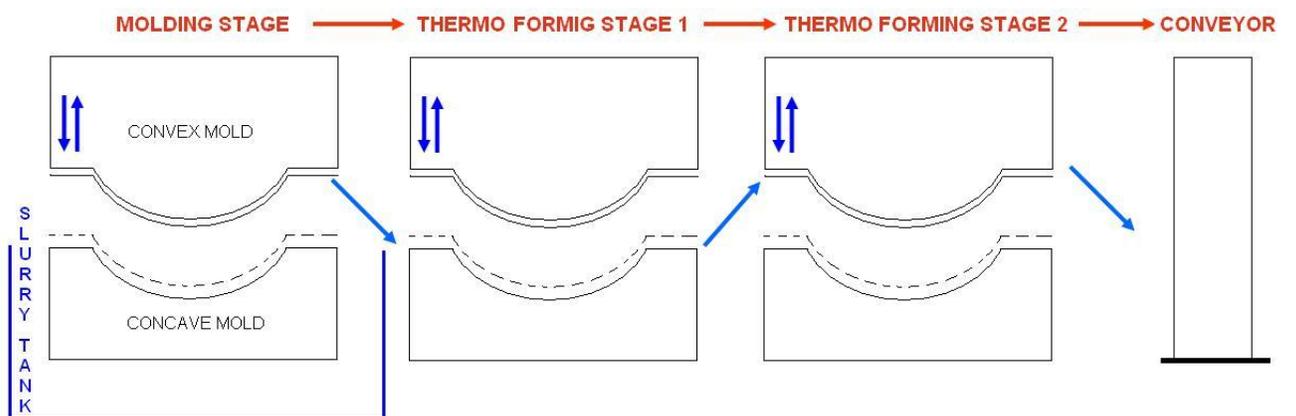


Fig. 3. The thermoformed process of containers manufactured from cellulosic pulps from cereal straw

RESULTS AND DISCUSSION

Raw Material

Table 1 shows the results obtained from the characterization of the raw materials under study as well as wheat straw samples. Ash can cause abrasion and inlays in the system. For that reason, it is very interesting to work with raw materials that have a low content in ash. It can be observed that the measured ash contents were similar or lower than the corresponding value for wheat straw (7.72%) except for the case of barley (9.49%), which value has the same order of magnitude as rice straw (9.2%) (Rodríguez *et al.* 2010), which can be used in the Specel® process without having any problem of abrasion.

Lignin is a hydrophobic constituent, which is the reason why a high proportion in pulp would inhibit the water absorption, making the refining difficult. However, a small quantity of lignin in pulps confers upon them relatively high values of specific volume, dimensional stability, and stiffness (García Hortal 2007), which are very valuable properties in the manufacturing of packaging. The lignin contents of the considered raw materials were similar to that of the wheat straw (17.7%). The hemicelluloses, unlike lignin, are very hydrophilic, favoring the swelling of fibers, increasing the plasticity, flexibility, and ability to link, and resulting in an improvement of the density of the sheet and of all the physical-mechanical properties (García Hortal 2007). The hemicelluloses content of the considered raw materials were of the same order of magnitude as the content presented by wheat straw (30.6%).

Table 1. Chemical Characterization of Oats, Maize, Rapeseed, Barley, and Wheat Straw

Raw Material	Alcohol Extractives, %	Ash, %	α -cellulose, %	Hemicellulose, %	Lignin, %
Oats	6.4	7.00	37.9	37.7	16.6
Maize	6.8	5.95	44.0	30.7	18.2
Rapeseed	7.9	6.38	37.0	36.5	17.2
Barley	8.1	9.49	34.0	27.7	16.3
Wheat	5.2	7.72	39.7	30.6	17.7

In view of the results obtained, the compositions of these four types of raw materials were judged to be suitable for pulping by means of the Specel® process. The materials considered were found to have similar values of alcohol extractives, ash, α -cellulose, holocellulose, and lignin in comparison to wheat straw. The Specel® process was successfully used with this raw material, so it could be concluded that these raw materials (oats, maize, rapeseed, and barley), from the point of view of its chemical composition, are suitable to be used with the Specel® process.

Cellulose Pulp

Table 2 shows the results of the chemical characterization of the obtained cellulosic pulps. Note that the rapeseed does not seem to be sufficiently delignified, since it gave the lowest value of α -cellulose and the highest one for lignin (even higher than the initial percentage of the raw material).

Table 2. Chemical Characterization of Cellulosic Pulps from Oats, Maize, Rapeseed, Barley, and Wheat Straw

Raw Material	Alcohol Extractives, %	Ash, %	α -cellulose, %	Hemicellulose, %	Lignin, %
Oats	0.89	2.50	69.2	16.4	13.1
Maize	0.86	1.36	71.0	20.0	8.9
Rapeseed	0.82	2.33	62.7	10.5	21.6
Barley	1.31	2.64	69.9	18.3	10.9
Wheat	3.37	10.90	73.0	16.3	2.8

Table 3 shows the values of yield, beating degree, Kappa number, and viscosity. Rapeseed gave the worst results of the four raw materials studied. The yield of wheat straw (70%) was higher than the values that other raw materials present, while the rapeseed raw material showed the lowest yield (63.1%). This data can be compensated by the low price of this feedstock (30€ / t) (Ecopapel S. L.).

Table 3. Characteristics of Cellulosic Pulps from Oats, Maize, Rapeseed, Barley, and Wheat Straw

Raw Material	Yield, %	Beating Degree, °SR	Kappa number	Viscosity, mL/g
Oats	66.9	36	71.5	465
Maize	65.5	47	56.7	996
Rapeseed	63.1	29	115.1	184
Barley	65.6	61	57.5	468
Wheat	70.0	51	38.6	536

The kappa number is a measure of delignification that the raw material has experienced. High values of kappa number imply that the pulp may not be well suited for carrying out bleaching of the pulps because of high cost; however, if whiteness is not fundamental in the container, the highest numbers of kappa which have been tested would not matter. Thus, the best value of kappa number for production of a bleached product was that of wheat straw (38.6), while the worst value was that shown by rapeseed straw.

The beating degree ranged between the lowest value, 29 °SR, for the pulp of rapeseed straw and the highest value, 61 °SR for the pulp of barley straw. The value of wheat straw pulp was between the previously cited values (51 °SR). A higher °SR value is often correlated to higher bonding strength of the resulting package, so in this case, rapeseed straw is not considered suitable for the packaging manufacturing process.

The viscosity values for the cellulose component in the obtained pulps were lower in all the cases, except for the obtained pulp from maize straw (996 mL/g), than that of wheat pulp (536 mL/g), noting the low value of the pulp obtained from rapeseed (184 mL/g). These low values of viscosity may be an inconvenience in cases where the brightness degree is an important feature in the packaging manufacture process (because in a bleaching processes there will be further degradation of the cellulose in the fiber, with a consequent further decrease in the viscosity value).

Paper Sheets

The values of the properties of the paper sheets (tensile index, stretch index, burst index, tear index, and brightness) (Table 4), were similar to those of the reference sheets, made by wheat straw pulp. The value of brightness in all the cases was not very high, but it is not a decisive property for manufacturing containers with these pulps because of the characteristics and uses that these have. All raw materials studied, except for rapeseed, yielded similar values of tensile index, stretch index, burst index, and tear index to the values obtained from the papersheets made from wheat straw. Therefore it can be said that oats, maize, and barley can be employed with the Specel® process for obtaining cellulosic pulps intended for the manufacture of packaging. The rapeseed, on the other hand, does not seem appropriate due to the significantly lower values of certain physical properties of the paper sheets.

Table 4. Characteristics of the Paper Sheets

Raw Material	Tensile Index, Nm/g	Stretch Index,%	Burst Index, kN/g	Tear Index, mNm ² /g	Brightness, %
Oats	64.0	1.84	2.966	2.049	57.1
Maize	68.2	1.85	3.284	2.837	60.2
Rapeseed	42.8	1.21	1.630	2.207	64.3
Barley	63.9	1.75	3.169	2.300	55.7
Wheat	43.5	2.71	2.330	2.620	60.0

CONCLUSIONS

The four studied raw materials (oats, maize, rape, and barley) were judged to be suitable to be utilized in the Specel® process in order to obtain cellulosic pulp for its use in the production of ecological containers. The obtained yields in the four cases were very similar to the reference case, which was wheat straw. Since the costs per ton of raw material were similar, the utilization of these materials can be recommended.

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