

Portuguese Hemp Plant as Raw Material for Papermaking

By Cecília Baptista[‡], Natércia Santos[±] & Manuel Rosa^{*}

The objectives of this study were the physical and chemical characterization of Portuguese industrial hemp and the assessment of its suitability to produce kraft pulp. A comparison was established with a reference eucalyptus pulp, obtained by the same chemical process. Handmade paper sheets were prepared in the laboratory using hemp pulp, eucalyptus pulp and a blend of both fibres in order to compare final paper properties. The unbleached pulp was produced by batch kraft cooking (NaOH + Na₂S) and the evaluation of pulp bleachability was carried out under a D₀E₀D₁E₁D₂ sequence. The physical properties of laboratory papers prepared with different compositions (100% hemp, 100% eucalyptus, hemp/eucalyptus 50:50) were assessed according to International Standards. Hemp fibres present two fractions, bast and core (33% and 67% of the total stem mass, respectively) with distinct biometric characteristics and cell composition. The hemp plant allowed cooking yield overlapping the wood reference, with lesser uncooked fractions. The pulp exhibited a good bleachability, even better than the reference. Hemp plant allowed a pulp with a higher gain of brightness and lower loss of intrinsic viscosity than eucalyptus. Hemp pulp also showed a better beatability, superiority in tearing resistance and a lower air permeability. The paper sheets obtained with the hemp/eucalyptus mixture showed interesting properties, which predicts a suitable combination of these two raw materials for papermaking.

Keywords: Bleachability, Hemp plant, Kraft cooking, Papermaking, Physical properties.

Introduction

Hemp (*Cannabis sativa* L. var. *sativa*) is a non-woody plant originated from Central Asia (Hillig 2005), farmed worldwide and having a wide variety of applications, namely in food, cosmetics, construction, textile and paper industries. Actually, the largest European producer is France, where the main destination is the production of special papers; China is also an important producer (Bouloc et al. 2013, Amaducci et al. 2015).

There are many scientific studies focusing hemp in general, its chemical composition, physical and chemical characteristics, pulping and bleaching aptitude, potential as a reinforcing fibre with hardwood and softwood fibres (Aitken et al. 1988, Malachowska et al. 2015, Danielewicz and Surma-Ślusarska 2017, Danielewicz and Surma-Ślusarska 2019a). Different hemp plants from particular

[‡]Professor, Polytechnic Institute of Tomar, Portugal.

[±] Professor, Polytechnic Institute of Tomar, Portugal.

^{*}Professor, Polytechnic Institute of Tomar, Portugal.

regions were studied, mainly from Canada, Eastern Europe, Asia and Australia, but there are few studies on the Portuguese hemp or industrial hemp farmed in similar geoclimatic regions (Wong and Chiu 1995, Correia et al. 1998, Barberà et al. 2011). The plant is strongly affected by the climate and soil and, thus, the obtained results can be somewhat different. Hemp plant exhibits in the stalk two distinct regions and usually this feature implies an initial stem processing in order to separate both fractions. Most of the studies present the pulping results from these two isolated fractions.

Non-woody plants have been used in papermaking for several reasons. One of the most relevant motives is the reduction of wood dependence which became an increasing problem for paper industry in recent decades. Other reasons concern the technological process involved, once this raw material possess an interesting chemical composition (high polysaccharide and low lignin contents) allowing the improvement of some pulping and bleaching process variables and some paper properties, as well as, the reduction of chemical reactant needs and beating energy consumption. Among the most non-woody plants used for papermaking one can refer cereal straw, sugarcane bagasse, bamboo, sisal, abaca, kenaf, cotton, and hemp. Industrial hemp has been used for pulp production and as reinforcing fibres for hardwood kraft pulps (Correia et al. 2003, Danielewicz et al. 2018). Furthermore, this plant can be fractionated in different biorefinery approaches (Johnson 1999, Danielewicz and Surma-Ślusarska 2010, Lavoie and Beauchet 2012, Malachowska et al. 2015). Some studies use hemp plant in blend with other pulp and paper raw materials, such as pine and birch, to obtain bleached pulp, and the results were promising (Danielewicz and Surma-Ślusarska 2019a, Danielewicz and Surma-Ślusarska 2019b).

This plant was farmed in Portugal from the 14th to the 20th century to produce fibres for cloths and ropes. The tows were used for papermaking, for instance, the cigarette paper produced at the Matrena paper mill in Tomar (Portugal). Since the 1970's, the synthetic fibres development caused the loss of market competitiveness of this raw material for the textile industry. The seasonality of crops and the stems processing, which require specific equipment to separate bast and core fibres, impose some limitations on this production. However, from the 90's of the 20th century, the demand and the interest for its farming increased (Salentijna et al. 2015, Schluttenhofer and Yuan 2017), since this species is suitable for different climatic conditions, from the regions of temperate climate to areas of boreal climate (Pahkala et al. 2008).

In recent years there has been some interest in Portugal for the cultivation of industrial hemp for different purposes, from the food industry to the textile industry, but producers have encountered some difficulties due to the need for initial processing to separate the fibres from the outer and inner zone of the stems.

In the present research, the whole hemp stem was used to avoid the cost of initial processing and to allow the possibility of using the current wood chips cooking technology. Replacing wood kraft fibres with kraft fibres of whole hemp stem in papermaking would be the advantage of the industrial application of this study.

This work aims to characterize the industrial hemp produced in Portugal

(moderate Atlantic and Mediterranean climate area) and to assess the paper potential using the whole stalk, which avoids the use of specific equipment to sort bast and core fibres. The hemp plant was used in the conventional kraft cooking process without retting or decortication. The bleachability and beatability of the unbleached pulp were also studied. A systematic comparison was made with a conventional eucalyptus pulp and an equitable blend was produced with these two pulps (hemp and eucalyptus) in order to obtain a paper with the contribution of both fibres' intrinsic properties.

Materials and Methods

Raw Material

The hemp plant used in this study was produced in Mora (Alentejo) and was supplied as whole stems. The stems were washed with water, dried and cut with scissors into pieces of 2-3 cm length. The eucalyptus wood, in the form of industrial chips, was used as the reference raw material.

Morphological and Chemical Characterization

The stems pieces were cut with a length of approximately 1 cm and therefore distinguished in two different zones (the inner zone, woody-core fibres, and the outer zone, bast fibres) in order to analyse separately their morphology. A fraction of 1 g of each fibre was macerated in an oven (55 °C), during 48 h, in a 30 mL solution of hydrogen peroxide and glacial acetic acid (1:1). The solvent was renewed, and the maceration was repeated for a further period of 48 h. After stirring with a glass rod, the dissociated vegetable material was filtered through a crucible (porosity 2) and washed with boiling distilled water, until reach a neutral pH. An Olympus CH30RF200 optical microscope was used in the morphological characterization and the biometric analysis was carried out in a Morfi V7 9.5 analyser.

The stems were ground in a Retsch SM1 mill and the sawdust was classified in an Endecotts Octagon 200 sieve. The characterization was performed with the fraction retained in the 60-mesh screen. Two distinct texture fractions were identified in the sieving process; one of them was grainier (the core fraction) and the other one was fluffier (the bast fraction). A classical chemical characterization of the whole stem was carried out to determine the main chemical constituents after extraction of the material with ethanol/toluene (1:2). All the processes were carried out at least in duplicate and according to the following standards: Sampling and preparing wood for analysis - TAPPI 257 cm-85; Preparation of wood for chemical analysis - TAPPI 264 cm-97; Ash in wood, pulp and paperboard: combustion at 525 °C - TAPPI 211 om-93; Solvent extractives of wood and pulp - TAPPI 204 cm-97; Acid-insoluble lignin in wood and pulp - TAPPI T 222 om-02; Acid-soluble lignin in wood and pulp - TAPPI UM 250-85; Holocellulose content - peracetic acid method and Cellulose content - Kürschner and Hoffer method. A

DR Lange Cadas 100 spectrophotometer was used for the determination of soluble lignin. For further calculations, cellulose and lignin fractions from the holocellulose were determined, as well as, the ash content of insoluble lignin.

Raw Materials Cooking

The cooking liquor was prepared by dissolving NaOH and Na₂S in water and the cooking was carried out under the following operating conditions: active alkali - 22%; sulfidity - 30%; maximum temperature – 160 °C; time until the maximum temperature is reached - 90 min; time at the isothermal maximum temperature - 120 min; liquid-to-wood ratio - eucalyptus - 5:1 and hemp - 7:1. The reagents used for pulping were of high purity grade purchased from Sigma-Aldrich and Riedel-de Haën. The cooking was performed in a batch reactor “Haato-tuote oy” of 10 dm³.

The hemp pulping was performed with the entire stems (including bast and core), broken into pieces of 2-3 cm long.

After the end of the pulping time, the pressure in the digester was released and the cooked material was transferred to a three sequential screen device. The first filtration step occurred on a 64-mesh metallic screen for disaggregation of the cooked chips under water pressure while the second was carried out on a 400-mesh metallic screen that retains the washed fibres. The third screening level was performed on a double layer polyester wire with 2500-mesh, approximately, in order to retain the fines. The fibres and fines from the second and third filters were collected, remixed and dewatered before drying at room temperature.

The Portuguese Standard NP 3186:1995 was used for the determination of the kappa number, weighing about 2 g of eucalyptus pulp and 1 g of hemp pulp.

The determination of the intrinsic viscosity of the pulp followed the ISO Standard 5351/1: 1981, Part 1, Alternative A, using 0.05 g of cellulosic fibres (o.d.). The cellulose polymerization degree (DP) was calculated by equation (1), where $[\eta]$ is the pulp intrinsic viscosity value.

$$DP^{0.905} = 0,75 \times [\eta] \quad (1)$$

Pulp Bleaching

The unbleached pulps were bleached in an ECF (Elemental Chlorine Free) sequence of the type D₀E₀D₁E₁D₂. The oxidizing reagent (D) used was chlorine dioxide (ClO₂). The oxidation reaction occurred in acidic medium followed by an alkaline extraction (E) with NaOH to remove previously oxidized lignin fragments. All bleaching tests were performed with 6 replicates and a dry fibre mass of 10 g. During the tests, both pulps were subjected to the same conditions, differing only in the ClO₂ and NaOH amount used because they depended on the kappa number (KN) of the raw pulp. Steps D and E were carried out in plastic bags, kept in thermostatic water bath at 70 °C. Initial pH control was performed with the pH meter and the necessary adjustments were carried out with the addition of 0.1M HCl. The bags contents were manually homogenized at 15 minutes intervals and

the operating conditions are shown in Table 1. The bleaching agent ClO_2 was prepared in the laboratory by the reaction between NaClO_2 and concentrated H_2SO_4 , and subsequent absorption of the released gas in distilled water at 5-7 °C. The bleaching active agent (Cl_2) concentration in the prepared solution was determined by titration with a 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Table 1. Operating Conditions and Chemical Charges Applied during Bleaching

Conditions	D_0	E_0	D_1	E_1	D_2
Consistency (%)	10	10	10	10	10
Time (min.)	90	60	120	60	120
pH	2	11	4	11	4
Charge (%)	0.25KN/2.63	0.5 Cl_2 active D_0 + 0.15	1.5 Cl_2 active	1.0%	0.5 Cl_2 active

Properties of Paper Samples

Three samples of unbleached pulps were studied: hemp pulp, eucalyptus pulp and hemp/eucalyptus blend pulp 50:50.

Before the beating process, the two pulps were disintegrated using the British Pulp Evaluation Apparatus disintegrator according to ISO standard 5263:2004. Initially, the beatability of each pulp was assessed through the refining curves. Subsequently, 30 g of each pulp were refined in a laboratory refiner to reach a beating degree, performed in a beating and freeness tester – Schopper-Riegler type, between 35 and 40 °SR in order to produce 12 handsheets for each fibre composition. The handsheets were made according to TAPPI Standard sp 205-02 in a Lorentzen & Wettre handsheet former (TAPPI type) using standard stirrer and couch roller. The design of the drainage system of this device provides a uniform flow across the entire wire, thus permitting uniform sheets. Laboratory sheets with 200 cm^2 , prepared from the different pulp's suspensions were used for later physical properties determination. The handsheets goal basis weight was 60 g/m^2 and the sheet set was pressed in a AB Lorentzen & Wettre pneumatic press. Finally, handsheets were air-dried in accordance with the standard previously referred, using standard drying plates and rings.

Paper properties assessment was carried out, according to international standards for two types of tests, namely *i)* - *structural properties*: Thickness and Bulk - ISO 534:1988 Paper and board -- Determination of thickness and apparent bulk density or apparent sheet density; Bendtsen Roughness - ISO 8791-2:1990 Paper and board -- Determination of roughness/smoothness (air leak methods) -- Part 2: Bendtsen method; Bendtsen Air permeability - ISO 5636-3:1992 Paper and board -- Determination of air permeance (medium range) -- Part 3: Bendtsen method and *ii)* - *strength properties*: Tensile strength and stretch - ISO 1924-2:2008 Paper and board -- Determination of tensile properties -- Part 2: Constant rate of elongation method (20 mm/min); Tearing resistance - ISO 1974:2012 Paper -- Determination of tearing resistance -- Elmendorf method. These properties were evaluated using the three fibrous compositions handsheets.

In the bleachability study, pulps reflectance and ISO Brightness were

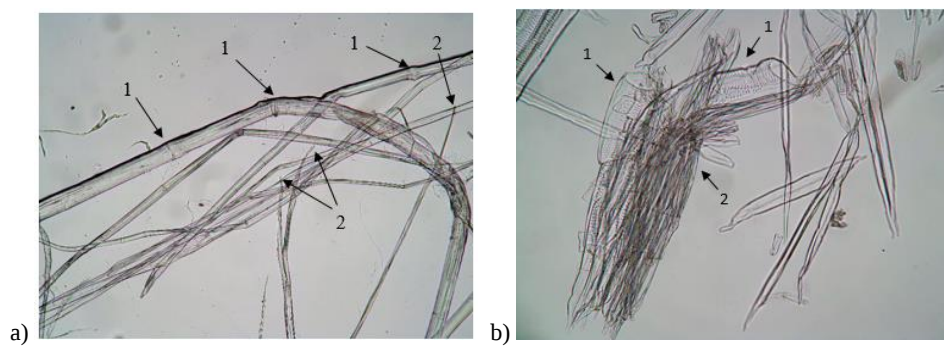
measured according to ISO 2470-1:2016 Paper, board and pulps — Measurement of diffuse blue reflectance factor — Part 1: Indoor daylight conditions (ISO brightness) using the Elrepho 0.7 colorimeter.

Results and Discussion

Morphological and Chemical Characterization

The morphological analysis gave rise to several microphotographs of the two different types of fibres and other plant cell elements, as depicted in Figure 1.

Figure 1. *Microphotographs of Hemp Fibres (Gx 100): A) Bast Fibres of the Stem Outer Zone - (1) Nodes and (2) Tapering Tips; B) Core Fibres of the Stem Inner Zone - (1) Vessel Elements and (2) Agglomerated Short Fibres*



The morphological analysis showed the two main types of fibres, the phloem (long) and xylem fibres (short), as it can be observed in Figure 1. Other cell types, namely vessel elements and wood fibres, are visible in the inner zone. In Figure 1a, it is possible to observe the rounded section of fibres and identify some nodes (1), typical and very common in hemp and linen lignified fibres. The fibres do not exhibit any twisted zones, as expected for this non-woody raw material, allowing an easy distinction from cotton. Besides most of the fibres are longer than the microscope image field, one can observe some tapering tips (2) in the smallest ones. The wood or xylem cells present different diameter vessel elements (Figure 1b) which show open perforation plates and multiple pitting. The clustered elements indicate a dissociation process which was not taken to limit.

Table 2 displays the results of the biometric characterization of hemp fibres. Bast fibre parameters were determined using four samples with a global number of 543484 counted objects. Core fibre parameters were determined using three samples making up a total number of 662701 counted objects.

Table 2. *Biometric Parameters of Hemp Fibres*

Parameters	Bast fibres (mean value $\pm$ s.d.)	Core fibres (mean value $\pm$ s.d.)
Length (mm)	1.28 $\pm$ 0.12	0.46 $\pm$ 0.01
Width (μ m)	25.1 $\pm$ 0.97	26.9 $\pm$ 0.05
Kink ($^{\circ}$)	115 $\pm$ 1.00	113 $\pm$ 0.50
Kinked fibres (%)	46.8 $\pm$ 2.56	6.0 $\pm$ 0.17
Curl (%)	12.3 $\pm$ 0.27	3.5 $\pm$ 0
Broken ends (%)	56.5 $\pm$ 5.81	26.6 $\pm$ 0.21

Bast fibres are much longer ($L_m = 1.28$ mm) than the core fibres ($L_m = 0.46$ mm), showing a length, at least, three times bigger than the core ones, although the obtained value may have been influenced by the cut imposed prior to the stem's dissociation. This cut also highly affects the standard deviation founded for the content of twisted fibres and broken ends. Eucalyptus has an average fibre length between hemp bast and core fibres (Foelkel and Zvinakevicius 1980). Despite the different length, the kink angles are similar varying between 112° and 116° . The widths (l_m) exhibited by the two types of fibres are more identical, $l_m = 25.1$ μ m and $l_m = 26.9$ μ m, respectively, for bast and core fibres, in accordance to the literature reference, $l_m = 25$ μ m, (Aitken et al. 1988). The percentage of kinked fibres, curl and broken ends are biometric parameters very different between bast and core fibres. The percentage of kinked bast fibres is eight times superior, while the curl is almost four times higher, which is certainly due to the smaller size of these latter cells, and consequently, less tendency to wind.

The chemical composition of the two individualized fractions was determined, as well as, the whole stem composition, reconstituted according to the experimentally determined proportions (33% bast and 67% core fibres). The results are shown in Table 3.

Table 3. *Chemical Constitution of Hemp Plant*

Chemical components	Bast + Core (% $\pm$ relative error %)	Bast (% $\pm$ relative error %)	Core (% $\pm$ relative error %)
Holocellulose	72.80 $\pm$ 0.06	86.40 $\pm$ 1.62	72.00 $\pm$ 0.22
Cellulose	53.25 $\pm$ 0.91	55.66 $\pm$ 0.53	47.34 $\pm$ 0.64
Total Lignin	21.80 $\pm$ 0.21	8.89 $\pm$ 0.22	25.35 $\pm$ 0.22
Extractives	2.00 $\pm$ 4.03	1.55 $\pm$ 2.32	1.79 $\pm$ 1.12
Ashes	2.59 $\pm$ 0.77	2.09 $\pm$ 2.04	2.53 $\pm$ 0.40

The results obtained for the different fractions are compatible with the literature values (Stevulova et al. 2014) or slightly lower with respect to the polysaccharides content, counterbalanced by the higher content of lignin (Gümüşkaya et al. 2007, Tutuş et al. 2014). The variability imposed by the plant growth conditions can justify the found discrepancies and, also, the similarities verified for plants grown in the Iberian Peninsula (Barberà et al. 2011). It should be noted the similarity with the chemical composition of the national *E. globulus*: Holocellulose - 72.0%; Extractives - 1.7%; Lignin - 22.1%; Ashes - 0.3% (Pinto et al. 2005); Lignin content: low - 20.5% and high - 23.0% (Cardoso et al. 2011),

particularly with regard to the determined lignin content (21.8%), which is atypical for a non-woody plant. This high content is determinant for any delignification process. However, the hemp plant ash amount is greater than eucalyptus wood, which is not a relevant fact for chemical pulping.

Raw Materials Cooking

The efficiency results of the kraft pulping processes performed to the whole hemp stalk and eucalyptus chips are presented in Table 4, which also exhibits the main unbleached pulp characteristics.

Table 4. *Cooking Process Results*

Unbleached pulp properties	Hemp	Eucalyptus
Pulp yield (%)	45.2	45.1
Uncooked pulp (%)	3.68	10.01
Kappa number	44.4	23.5
Intrinsic viscosity (mL/g)	991	1016
Degree of Polymerization	1489	1530

After carrying out the first hemp cooking, it was found that it was not possible to maintain the liquid-to-wood ratio of 5:1, possibly due to the structure and low density of the stems which have absorbed the entire cooking liquor, leaving no liquid phase for the circulation, essential factor for good impregnation and uniform heating of the cooking liquor. The lack of retting is another possible reason for this occurrence. Under these conditions it was chosen to increase the liquid-to-wood ratio to 7:1, and it was found that this volume of liquor was better suited to the cooking of this species. The cooking yields were similar for the two cooking essays, being 45.2% for hemp and 45.1% for eucalyptus. In previous studies carried out in Croatia and Spain the yield for hemp tow cooking with conventional kraft processes was 40% (Wong and Chiu 1995). Other authors from Poland reached total yields of 57.7% and 48.4% for whole stalks and woody-core fibres, respectively (Danielewicz and Surma-Ślusarska 2017), despite these values included pulp and fiberized uncooked knots. In the present study, the percentage of uncooked material (chips and knots) in the case of eucalyptus (10.1%) was higher than in the case of hemp, where the percentage of this material was residual (3.7%), probably due to the higher eucalyptus wood density.

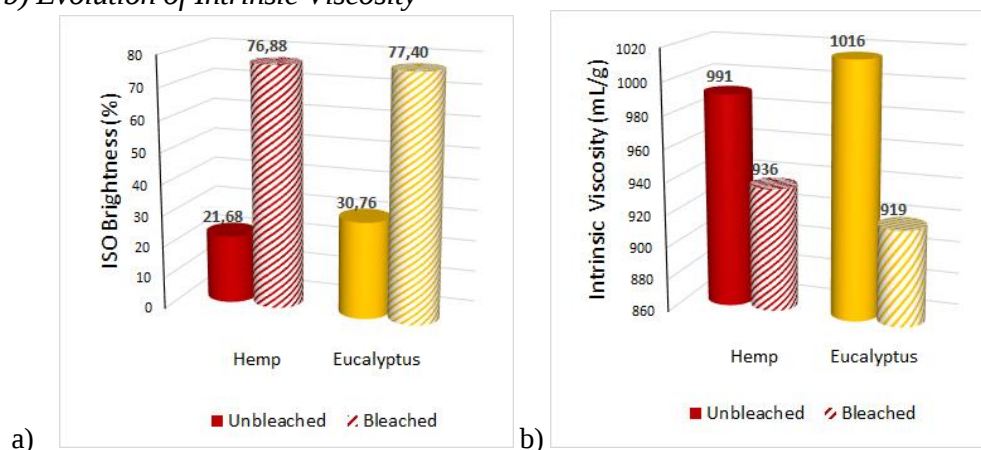
Starting with two raw materials with identical lignin contents, it is noted that the extent of cooking was lower in the case of hemp because the kappa number determined in the unbleached hemp pulp (44.4) is about twice of the eucalyptus kappa number (23.5). This fact presupposes that the hemp delignification is harder. This difficulty in cooking hemp has already been observed in previous studies (Danielewicz and Surma-Ślusarska 2010). The selectivity of the cooking process is clearly superior for eucalyptus because the degree of polymerization obtained was higher and corresponds to a lower lignin content (DP = 1530, kappa number = 23.5) than in the case of hemp (DP = 1489, kappa number = 44.4). This feature shows that, with eucalyptus, a more efficient delignification occurred with a lower degradation of the cellulose chains and less liquid-to-wood ratio. The presence of a

very high amount of core fibres (67%) must explain the slow lignin removal and the difficult delignification of hemp fibres, as reported in other studies (Correia et al. 1998, Correia et al. 2001). Nevertheless, the DP obtained for the hemp pulp is typical for unbleached wood pulps (Tutuş et al. 2016).

Pulp Bleaching

The bleaching effect is shown in Figure 2.

Figure 2. ECF Bleaching Results of Unbleached Pulps a) Evolution of ISO Brightness b) Evolution of Intrinsic Viscosity

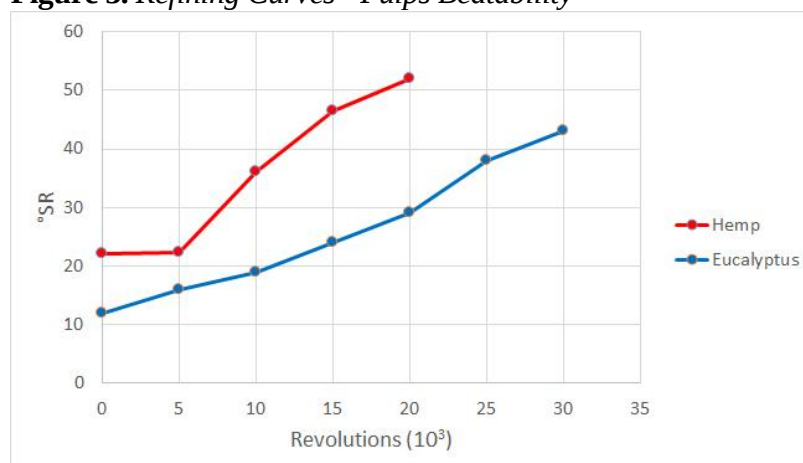


Hemp and eucalyptus bleached pulps show a similar ISO brightness as can be observed in Figure 2a. However, hemp pulp has a greater suitability for bleaching because it showed a higher increase in brightness (55.2%) compared to the increase attained for eucalyptus pulp (46.6%), since the reflectance of the unbleached pulp was initially lower. In United Kingdom, multi-step bleaching with chlorine dioxide was carried out for unbleached hemp tow pulp achieving a reflectance of about 24%, and final ISO brightness of 70% (Wong and Chiu 1995). In Poland, a hemp bleaching sequence with only two steps of chlorine dioxide and one alkaline extraction but preceded by an oxygen delignification, obtained a brightness of 88.6% (Danielewicz and Surma-Ślusarska 2017) revealing that an oxygen delignification stage before the first chlorine dioxide bleaching step really promotes a significant brightness improvement.

Pulps intrinsic viscosity variations are presented in Figure 2b and it is observed that the bleaching process led to a similar degradation of the polysaccharides (Smook 2016), being slightly higher in the case of eucalyptus (9.6%) than in the case of hemp (5.6%).

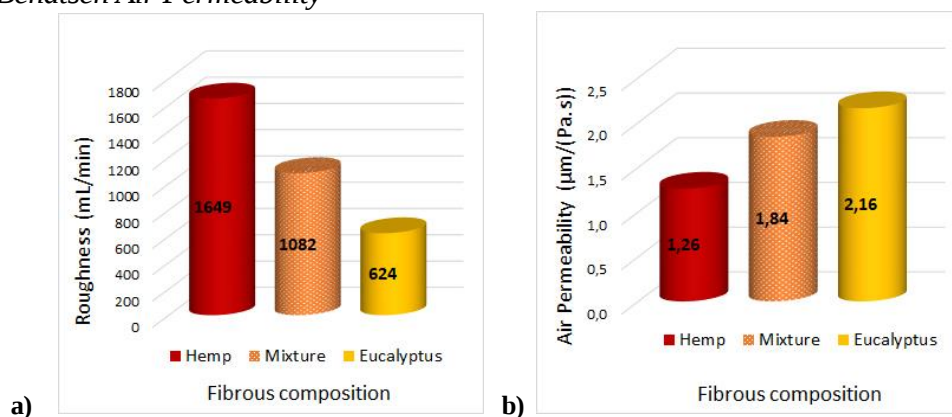
Properties of Paper Samples

As expected, due to the different fibre morphology, refining aptitude of the different pulps was quite distinct, as one can observe through Schopper-Riegler freeness values ($^{\circ}$ SR) in Figure 3.

Figure 3. Refining Curves - Pulps Beatability

The beating process of unbleached hemp pulp presented satisfactory results compared with those obtained with the eucalyptus pulp (Figure 3), namely, easier refining, requiring a shorter residence time in the equipment to achieve the same beating degree, as already referred by other authors (Correia et al. 2003). This occurrence is possibly attributed to the high number of hemicelluloses present and to the smaller length of short core hemp fibres in comparison with eucalyptus fibres. This experimental observation finds some similarities in the research literature (Malachowska et al. 2015, Danielewicz and Surma-Ślusarska 2017). Nevertheless, the hemp pulp presented much worse drainage than eucalyptus pulp in the laboratory papermaking process, pointing to a higher fibrillation of the former, fact also documented in the literature (Danielewicz and Surma-Ślusarska 2017).

In this study, handsheets with diverse compositions exhibit distinctive results as shown in the following figures. Figure 4 presents the structural properties results – Bendtsen roughness and air permeability.

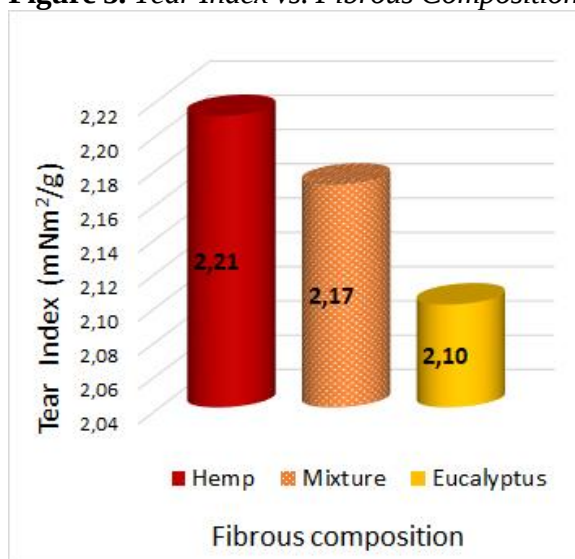
Figure 4. Structural Properties vs. Fibrous Composition a) Bendtsen Roughness b) Bendtsen Air Permeability

Analysing Figure 4a, one can observe that eucalyptus pulp handsheets reveal a roughness almost three times lesser than hemp handsheets. The mixture provided,

as expected, an intermediate value, fact attributed to the fibre's length and the homogeneity of this biometric parameter. Hemp pulp handsheets disclose a high roughness due to the strong difference between the lengths of bast fibres and short fibres (core). The bast fibres commit the paper formation and the ensuing smoothness, as one can perceive from the results presented by the paper obtained with the blend pulp. In Figure 4b, it is possible to check higher air permeability on eucalyptus pulp handsheets results. This property, such as roughness, varies also with the fibre bonding arrangement, being expected a higher permeability in the hemp pulp handsheets. This is not the case, probably due to the presence of high amount of short core fibres that fill the fibrous structure and reduce the pores that connect both sides of handsheets which were responsible for the air passage. The blend pulp handsheets have an intermediate air permeability, but nearer to the results of the eucalyptus pulp handsheets, considering the abundance of short core fibres of hemp with a length of about half of the average length of eucalyptus fibres (Foelkel and Zvinakevicius, 1980).

Paper strength is accountable for significant gains in runnability during printing and packaging processes therefore it is increasingly important to enhance mechanical paper properties. Among the strength properties, tearing resistance of hemp pulp handsheets outstands; tear index is superior to the others, as shown in Figure 5.

Figure 5. Tear Index vs. Fibrous Composition



The influence of bast fibres length induces the highest tear index, and for the same reason, the blend pulp handsheets present an intermediate value of this property, slightly closer to the result obtained with the hemp pulp handsheets, revealing the importance of fibre length.

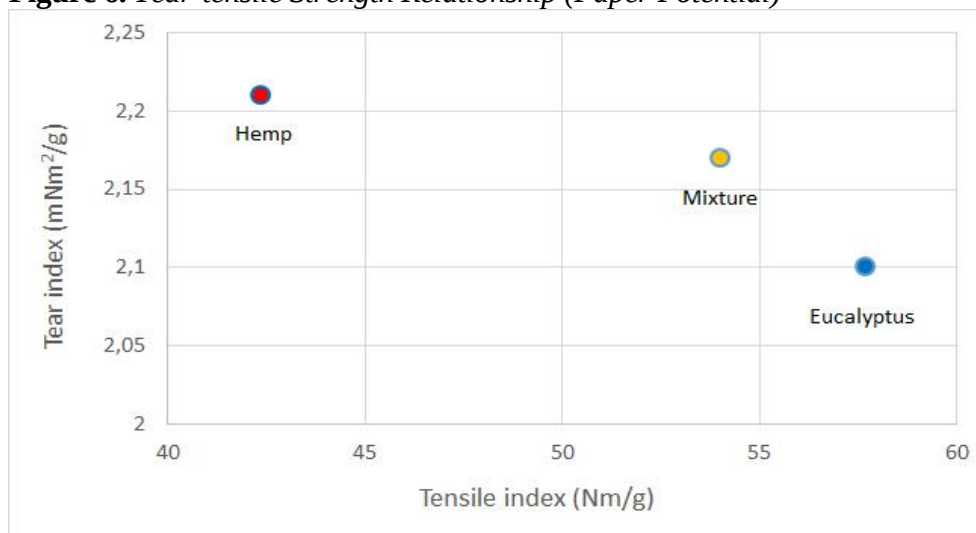
On the other hand, tensile strength of hemp handsheets (tensile index 42.4 N.m/g) is lower than the eucalyptus handsheets strength (tensile index 57.7 N.m/g) that is also mentioned in other studies about non-woody fibres (Karlsson et al. 2007, Danielewicz and Surma-Ślusarska 2017). The mixture handsheets showed

an intermediate tensile index (54.0 N.m/g), even though more approximate to the eucalyptus pulp value, which can possibly be explained by its fibrous constitution: a minor amount of bast fibres and a huger amount of eucalyptus and core small fibres (~17% of fibres with very high length and ~83% of fibres with an identical shorter length).

The relationship between handsheets' tear and tensile indexes is used as a parameter to assess the pulp and paper strength potential (Danielewicz and Surma-Ślusarska 2017). The hemp handsheets showed the highest tear index while eucalyptus handsheets revealed the highest tensile index, as shown in Figure 6.

The analysed mixture seems to exhibit an interesting behaviour, denoting a high tearing resistance while keeping a good tensile strength. This fact indicates that hemp plant fibres can be blended with eucalyptus fibres improving the mechanical performance of final paper, namely for packaging products.

Figure 6. Tear-tensile Strength Relationship (Paper Potential)



Conclusions

The whole stem of national industrial hemp presents cellulose content above 50% and high lignin content (similar of *Eucalyptus globulus* lignin content). Bast and core fibres have very different lengths, but similar widths.

In the kraft cooking process, hemp needed a larger liquid-to-wood ratio and presented greater difficulty of delignification than eucalyptus. Hemp and eucalyptus pulping have similar yields and produce pulps with identical cellulose polymerization degrees, but the kappa number of the unbleached pulp reveals that cooking is more extensive and selective in the case of eucalyptus.

Eucalyptus and hemp pulps, after being subjected to the same bleaching steps, exhibit identical ISO brightness, but hemp revealed a greater suitability for bleaching. Both bleached pulps viscosities are similar, nevertheless, hemp pulp reveals less degradation during the bleaching process.

When compared with a eucalyptus pulp, hemp pulp displays a better

beatability due to the presence of short core fibres and shows a higher tearing resistance justified by the presence of bast fibres.

In short, it seems that the hemp plant used integrally presents a good paper potential highlighting namely the bleachability, the beatability and the tearing resistance of unbleached pulps. The mixture of hemp and eucalyptus fibres (50:50) also reveals a good paper potential, exhibiting simultaneously very good tear and tensile strengths.

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References

- Aitken Y, Cadel F, Voillot C (1988) *Constituants fibreux des pâtes, papiers et cartons - pratique de l'analyse*. (Fibrous constituents of pulp, paper and cardboard - practice of analysis). Grenoble, France: Centre Technique du Papier et École Française de Papeterie et des Industries Graphiques.
- Amaducci S, Scordia D, Liu FH, Zhang Q, Guo H, Testa G, Cosentino SL (2015) Key cultivation techniques for hemp in Europe and China. *Industrial Crops and Products* 68(Jun): 2-16.
- Barberà L, Pèlach MA, Pérez I, Puig J, Mutjé P (2011) Upgrading of hemp core for papermaking purposes by means of organosolv process. *Industrial Crops and Products* 34(1): 865-872.
- Boulloc P, Allegret S, Arnauld L (2013) *Hemp industrial production and uses*. Wollingford, UK: CABI Publishing, 328.
- Cardoso GV, Foelkel CEB, Frizzo SMB, Rosa CAB, Assis TF, Oliveira P (2011) Efeito do teor de lignina da madeira de *Eucalyptus globulus* Labill no desempenho da polpação kraft. (Effect of lignin content of *Eucalyptus globulus* Labill wood on kraft pulping performance). *Ciência Florestal* 21(1): 133-147.
- Correia F, Roy DN, Goel K (1998) Pulping of Canadian industrial hemp (*Cannabis sativa* L.): presents some findings of using non-wood sources. *Pulp and Paper Canada - Ontario*- 99(9): 39-41.
- Correia F, Roy DN, Goel K (2001) Chemistry and delignification kinetics of Canadian industrial hemp (*Cannabis sativa* L.). *Journal of Wood Chemistry and Technology* 21(2): 97-111.
- Correia F, Roy DN, Chute W (2003) Hemp chemical pulp: a reinforcing fibre for hardwood kraft pulps. *Pulp and Paper Canada -Ontario*- 104(5): 51-53.
- Danielewicz D, Surma-Ślusarska B (2010) Processing of industrial hemp into papermaking pulps intended for bleaching. *Fibers & Textiles in Eastern Europe* 18(6): 110-115.
- Danielewicz D, Surma-Ślusarska B (2017) Properties and fibre characterisation of bleached hemp, birch and pine pulps: a comparison. *Cellulose* 24(11): 5173-5186.
- Danielewicz D, Surma-Ślusarska B, Kmiotek M, Dybka-Stępien K (2018) Susceptibility of selected non-wood fibrous raw materials for processing into unbleached and

- bleached kraft pulps. *Cellulose Chemistry and Technology* 52(3-4): 283-289.
- Danielewicz D, Surma-Ślusarska B (2019a) Bleached kraft pulps from blends of wood and hemp. Part I – demand for alkali, yield of pulps, their fractional composition and fibre properties. *Fibres & Textiles in Eastern Europe* 27(1): 112-117.
- Danielewicz D, Surma-Ślusarska B (2019b) Bleached kraft pulps from blends of wood and hemp. Part II – structural, optical and strength properties of pulps. *Fibres & Textiles in Eastern Europe* 27(2): 111-116.
- Foelkel CEB, Zvinakevicius C (1980) Hardwood pulping in Brazil. *Tappi* 63(3): 39-42.
- Gümüşkaya E, Usta M, Balaban M (2007) Carbohydrate components and crystalline structure of organosolv hemp (*Cannabis sativa* L.) bast fibers pulp. *Bioresour Technology* 98(3): 491-497.
- Hillig KW (2005) Genetic evidence for speciation in *Cannabis* (Cannabaceae). *Genetic Resources and Crop Evolution* 52(2): 161-180.
- Johnson P (1999) Industrial hemp: a critical review of claimed potentials for *Cannabis sativa*. *Tappi* 82(12): 118-128.
- Karlsson H, Beghelli L, Nilsson L, Stolpe L (2007) Abaca as a reinforcement fibre for softwood pulp. *Tappi* 6(10): 25-32.
- Lavoie JM, Beauchet R (2012) Biorefinery of *Cannabis sativa* using one- and two-step steam treatments for the production of high quality fibres. *Industrial Crops and Products* 37(1): 275-283.
- Malachowska E, Przybysz P, Dubowik M, Kucner M, Buzala K (2015) Comparison of papermaking potential of wood and hemp cellulose pulps. *Annals of Warsaw University of Life Sciences - SGGW, Forestry and Wood Technology* 91: 134-137.
- Pahkala K, Pahkala E, Syrjälä H (2008) Northern limits to fiber hemp production in Europe. *Journal of Industrial Hemp* 13(2): 104-116.
- Pinto PC, Evtuguin DV, Pascoal Neto C (2005) Effect of structural features of wood biopolymers on hardwood pulping and bleaching performance. *Industrial and Engineering Chemistry Research* 44(26): 9777-9784.
- Salentijna EMJ, Zhang Q, Amaducci S, Yang M, Trindade LM (2015) New developments in fiber hemp (*Cannabis sativa* L.) breeding. *Industrial Crops and Production* 68(Jun): 32-41.
- Schluttenhofer C, Yuan L (2017) Challenges towards revitalizing hemp: a multifaceted crop. *Trends Plant Science* 22(11): 917-929.
- Smook GA (2016) *Handbook for pulp and paper technologists*. 4th Edition. Atlanta, USA: Tappi Press.
- Stevulova N, Cigasova J, Estokova A, Terpakova E, Geffert A, Kacik F, Singavszka E, Holub M (2014) Properties characterization of chemically modified hemp hurds. *Materials* 7(12): 8131-8150.
- Tutuş A, Çiçekler M, Ozdemir F, Yilmaz U (2014) Evaluation of diospyros kaki grown in Kahra-manmaraş in pulp and paper production. In *Proceedings of the II National Mediterranean Forest and Environment Symposium*. Isparta, Turkey, October 22-24, 2014, 775-784.
- Tutuş A, Karataş B, Çiçekler M (2016) Pulp and paper production from hemp by modified kraft method. In *Proceedings of the 1st IMSEC*. Adana, Turkey, October 26-28, 2016, 982-988.
- Wong A, Chiu C (1995) Pulping and bleaching of hemp (*Cannabis sativa*). In *Proceedings of the Tappi Pulping Conference*. Chicago, USA, October 1-5, 1995, 471-476.