COMPARATIVE STUDY OF *OLEA EUROPEA* AND *EUCALYPTUS UROGRANDIS* KRAFT PULPS

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The aim of the present work was to find an optimum Kraft pulping of olive tree prunings to obtain pulp with a Kappa number of about 17, in order to compare its properties with those of *Eucalyptus urograndis*. The sulfidity used was of 30%, the liquid/solid ratio was 4:1 and the effective alkali applied was 20%. The maximum cooking temperature was of 165 °C with a heating rate of 70 minutes and a working time of 60 minutes (after reaching the temperature). The produced pulps were subjected to chemical and morphological analysis and to PFI mill refining. Then, handsheets were formed in order to carry out physical-mechanical and optical tests.
The hemicelluloses content of these agricultural residues is higher than that presented by *E. urograndis*, which makes olive tree prunings interesting for a secondary industry. The values of the analyzed properties of olive tree prunings are not higher than those found for *E. urograndis*, and in some cases they are very close. Also, some values found for olive tree prunings are higher than those of *E. urograndis*, such as the values of opacity, which makes Kraft olive pulp appropriate for printing and reading paper.

Keywords: Kraft pulping, *Olea europea*, *Eucalyptus urograndis*, agricultural wastes

INTRODUCTION

In 2009, the world production of paper and paperboard was 376.8 million tons, the European Union (EU) being the second largest producer with 102.4 million tons (27.2%), behind Asia, which produces about 160.9 million tons (42.2%).[1]

Even so, the annual production of paper pulp in the EU is not enough to meet the current demand, because member countries are densely populated and they present a forest land shortage.[2] The use of fast-growing species, such as tagasaste, leucaena, paulownia;[3-5] agricultural residues, such as olive and orange tree prunings or several cereal straws, such as wheat or rice;[6-8] and the use of recycled materials have been investigated for some time.[9]

Agricultural residues are an important alternative to woody plants for various reasons, such as:

- Economic raw material for paper industry (harvesting and transport costs);
- High levels of production of these wastes;
- Heterogeneity of waste and consequently, heterogeneity of cellulosic fibers with a wide application on paper and cardboard;
- Elimination of a waste that causes pollution and pest problems;
- Valorization of a residue, which is sometimes burned *in situ* for its maximum optimization;
- An increase in the profitability of farms.

Olive tree prunings are an important agricultural waste in the EU, which produces 13.6 million tons from a cultivated area of 480 thousand hectares. Their abundance in the Mediterranean region should be emphasized: Spain is the first producer, with a harvested area of 2.5 million hectares (Has), followed by Tunisia with 1.5 million Has, Italy with 1.19 million Has and, at a greater distance, Turkey with 730000 Has and Greece with 650000 Has. Taking into account that one hectare of dry pruned olives can produce 3 tons of residual biomass every two years,[10] a generation of 2500 kg of olive tree pruning residues per hectare can be estimated.[11]

For this reason, olive tree prunings are presented as an alternative raw material to woody ones, suitable for the production of cellulose pulps. The Kraft process is one of the most widely used cooking processes in chemical pulping. In this type of process, the raw material is treated with an alkaline solution consisting of sodium hydroxide and sodium sulphite at high temperatures (between 150 °C and 170 °C) to dissolve the lignin in a high percentage. Hence, the fibers of the raw material are mainly composed of cellulose and hemicelluloses; thus, a satisfactory delignification, high yield, and high viscosity is provided.[12-15] The woody nature of olive tree prunings does not make this raw material suitable for other pulping processes.

The aim of this paper was to compare the Kraft pulp of olive tree prunings with that of forest raw materials from the genus *Eucalyptus*, specifically *Eucalyptus urograndis* hybrid species (*Eucalyptus grandis x Eucalyptus urophylla*), which presents a high productivity and excellent fiber quality features.[16] For this reason, in this work Kraft pulping of olive tree prunings was used for comparing olive tree pruning Kraft pulp with *E. urograndis* Kraft pulp, with a Kappa number of ±17. The required effective alkali charge to achieve the Kappa number, viscosity, residual alkali, chemical composition and physical-mechanical and optical properties of both unbleached pulps were analyzed in this work.

EXPERIMENTAL

Raw material

Olive tree (*Olea europaea*) pruning residue was supplied by "Agricultural Cooperative San Fco of Asís", Montefrío, Granada, Spain. Two fractions were obtained through screening and manual separation. The main fraction consisted of stems with a diameter above 1 cm, and the residual fraction consisted of small stems (below 1 cm) and leaves. These fractions were air-dried to constant moisture content and placed in plastic bags for storage until used. In this work, the main fraction was utilized, with a wood chip size of 30 x 3 mm.

Morphological analysis and basic density

The chips were disaggregated and washed according to the technical standard LCP 02pp-97 of the Pulp and Paper Laboratory of the Federal University of Viçosa, Brazil. A solution of acetic acid and nitric acid in the ratio of 5:1 was used for six hours and the samples were colored in Astra blue, under stirring for ten minutes. A small amount of the suspension for the preparation of handsheets was taken to be observed on an image analyzer, where only one hundred of fibers from each sample were measured. The length, width and diameter of lumen were determined by measuring the size of the fibers by miscroscopy. The cell wall thickness of the fiber was mathematically determined as a half of the difference between fiber length and the diameter of lumen.

The number per gram of fibrous material, coarseness, and fines content in the pulp were also determined in a Galai CIS-100 equipment, in which a fibrous suspension flow took place at a constant speed. A laser beam came into contact with a quartz cuvette, allowing the images to be captured by a video camera and analyzed by a *Wshape* © software, suitable for the analysis of fibrous material. The results were interpreted by the software and transferred to Excel for data processing.

The relation between the dry weight and the saturated volume of the chips (basic density) was determined by TAPPI T 258 om-94.

Chemical analysis

Olive tree prunings were milled in a Willey mill following the TAPPI standards for sampling and preparation of wood for chemical analysis, TAPPI T 257 cm-85 (2000) and TAPPI T264 om-88, respectively. Subsequently, the assessment of total extractives (TAPPI T 204 om-88), acid insoluble lignin (TAPPI T 222 om-98), acid soluble Klason lignin,[17] carbohydrate analysis,[18] uronic acids content,[19] the ratio of Siringyl/Guaiacyl groups by liquid chromatography after oxidation with nitrobenzene,[20] and the acetyl groups analysis[21] were carried out.

Kraft pulping

The concentrations of the reagents were expressed as sodium hydroxide based on absolutely dry wood. Pulpings were carried out in a Regmed rotatory digester, with four individual digesters with a capacity of two liters each, electrically heated and equipped with a thermometer and a pressure gauge, making possible four pulpings simultaneously. The time and temperature of the pulping were monitored by an electronic controller coupled to a computer, with a temperature sensor (PT100) kept in direct contact with the raw material and the white liquor.

The sulfidity used was 30%, the liquid/solid ratio was 4:1 and the percentage of active alkali was the one resulting in a pulp with a Kappa number of ±17. Four preliminary pulpings were carried out in order to obtain a delignification curve related to the effective alkali applied. The maximum cooking temperature was of 165 °C, with a heating rate of 70 minutes and a time of working of 60 minutes (after reaching the temperature).

After cooking the raw material, the pulp was discharged into a pulp washer fitted with a 150 mm stainless steel mesh and washed with water. The disaggregation of the fibers was performed in a hydrapulper laboratory of 25 liter capacity. Later, the cellulose was treated on a Voith scrubber plate with slits of 0.2 mm. Then, it was dried with a centrifuge and stored in polyethylene bags.

Next, handsheets were formed according to TAPPI T218 sp-97, for the subsequent determination of Kappa number (TAPPI T236 om-99) and viscosity (TAPPI T 230 om-99). The black liquor pH was also determined according to TAPPI standards T625 cm-85 and TAPPI T 625 cm-85.

Kraft pulp refining

The produced pulps were subjected to PFI mill refining, according to TAPPI T 248 sp-00 (2000), varying the speed from 0 to 2000 rpm and studying the development of the refining curve.

After refining, handsheets were formed with a grammage of 60 g/m^2 in a TAPPI handsheet former and were stored in an air-conditioned environment with a constant moisture of 50% ± 2% and a temperature of 23 °C ± 1 °C, in order to carry out the physical-mechanical and optical tests (LCP technical Standard 03 pp-97).

Characterization of paper sheets

A minimum of 5 replicates were performed for each of the physical-mechanical and optical tests. Thus, weight (TAPPI T 410 om-98), thickness (TAPPI T 411om-97), brightness (TAPPI T 452 om-96), by a Datacolor E2000 equipment, opacity and light scattering coefficient (TAPPI T 519 om- 96), air flow resistance (TAPPI T 460 om-96), burst index (TAPPI T 403 om-97), tear index (TAPPI T 414 om-98), tensile index (TAPPI T 494 om-96), elongation (TAPPI T 494 om-96), apparent specific gravity (TAPPI T 220 sp-96), and apparent specific volume (TAPPI T 220 sp-96)[22] were determined.

The tensile strength test was performed in an Instron equipment model 4204, connected to a computer for data input and output, allowing analysis at an average distance of 100 mm, a speed of test of 25 mm/min and a cell load capacity of 1000 N. This test provides the results of strength at the point of rupture, tensile index, stress and strain at proportional limit (elastic) strain energy (TEA) and specific modulus of elasticity (MOE), simultaneously.

RESULTS AND DISCUSSION

Morphological analysis and basic density

Table 1 shows the results obtained from the analysis of the fibers and the determination of the basic density. Length (0.71 mm), width (13.61 µm) and thickness values (3.75 microns) of the olive tree prunings were between the average values of hardwoods (0.75-1.5 mm; 10-20 µm and 3.2-7.3 µm, respectively).[23] The fiber length and the width of the cell wall are the most studied anatomical parameters because of their influence on the quality of the production of paper pulp. The longest fibers have the best resistance to tearing and the shortest ones are the most appropriate in order to make the sheets of paper; likewise, the fibers with higher thickness result in a higher grade of opacity and softness, required for printing and writing paper and paper "tissue", respectively.[24]

For pulping and paper production, it is desirable that the material has a uniform density, since the rate of impregnation of the chips in the delignification is influenced by the specific mass.[25] Wehr and Barrichello[26] consider that high densities can provide an increased productivity due to a greater alkali charge for a given volume of the digester; but if a high charge of alkali is needed, other authors mention that it would cause high losses in the desirable characteristics for the production of printing and writing paper.[27] The basic density of olive tree is high, which causes a loss of yield and viscosity in the production of cellulosic pulp. However, low densities imply a large specific consumption of wood. This is a disadvantage which olive tree prunings do not show.

Chemical analysis

Table 2 shows the results obtained for chemical characterization. The lignin content of olive tree prunings was lower than that of *E. urograndis* (26.5% viz. 29.6%), similar to the siringyl/guaiacyl ratio (S/G), which was also higher for *E. urograndis* (2.9) compared to the olive tree prunings (2.0). According to Barbosa *et al.*,[28] the rate of delignification is influenced by the structure of lignin, being directly proportional to the S/G ratio, since the siringyl structure of lignin is more reactive and therefore, it is easier to remove during the Kraft pulping process. According to Rodrigues *et al.*,[29] the nature of the lignin ratio (S/G), in terms of delignification rate, consumption of chemical reagents and yield of the cooking process, is more important for the production of pulp than the content of lignin in the wood. Delignification does not depend only on the accessibility to lignin, but also on its reactivity,[30] the last one being influenced by the S/G ratio.[31] Studies by Gomes[32] *et al.* also show that the S/G ratio has a higher influence on the cooking yield than the content of lignin in the wood. Thus, they found a good connection between the S/G ratio and the yield, remarking that the desirable raw material for Kraft pulp production must present a low lignin content, which is associated with a high S/G ratio. The lignin content, as well as the S/G ratio, were found lower for the olive tree prunings than for eucalyptus, which will affect the yield of the process, although it can be compensated by the low price of this feedstock.

The content of glucans (cellulose) in both raw materials exceeded 40% of their chemical composition, followed by xylans, in a higher percentage for olive tree prunings (16.3%) than for *E. urograndis* (10.8%). For the rest of hemicelluloses, the contents were greater for olive tree prunings. The cellulose content is directly related to the yield of pulping, so a high content of hemicelluloses in olive tree prunings had an adverse effect on the yield of the process, because they are easily degradable in the pulping process. However, the high content of hemicelluloses can give promising results in a secondary use in the textile, pharmaceutical and food industries, in terms of sugar production.[33-35] So, in a biorefinery scheme, the raw material can be subjected to treatment stages preceeding pulping, to reach a compromise solution between the solid yield and the sugar production, so as to obtain two streams: a liquid phase rich in hemicellulose-derived products and a solid fraction rich in cellulose and lignin, suitable for subsequent pulping processes.

The uronic acids content was found higher for *E. urograndis* (5.6%) than for *O. europaea* (2.5%). These acids generate hexenuronic acids during Kraft pulping, which, according to Costa *et al*.,[36] affects bleaching in a negative way. During subsequent bleaching processes of cellulosic pulps, the hexenuronic acids consume the chemical reagents, decreasing the effectiveness of pulp bleaching. Thus, olive tree prunings present an advantage, being more stable when bleached.

Kraft pulping

Four pulping tests were carried out for each raw material under study (olive and eucalyptus) to obtain a delignification curve related to the applied effective alkali in order to achieve a kappa number of about 17.

The required effective alkali charge to achieve the same Kappa number was different for the two raw materials studied, being of 16.8% for *E. urograndis* and 20% for olive tree prunings. Taking into account that the Kraft process for the cellulose pulp production has a low selectivity in reactions of lignin elimination, the carbohydrates are significantly degraded during the reactions of delignification. Hence, low viscosities and yields will be obtained in pulps, if a greater alkali charge is required.[37]

Table 3 shows the operational values and the results for Kappa number, viscosity, yield and pH of the residual liquor of the obtained pulps. The pH values obtained were as expected, around 13, in order to avoid the reprecipitation of lignin in the fibers at the end of pulping.

Table 1
Fiber characteristics and basic density of *E. urograndis* and *Olea europaea*

Raw material	Length (mm)	Width (μm)	Diameter of lumen (μm)	Thickness (μm)	Basic density (Kg/m^3)
Eucalyptus urograndis	1.07	20.06	10.59	4.73	499
Olea europaea	0.71	13.61	6.11	3.75	616

Table 2
Chemical analysis of *Olea europaea* and *Eucalyptus urograndis*

Raw material	E, %	L, %	S/G	GL, %	XI, %	GA, %	MA, %	AR, %	AcU, %	AC, %
Eucalyptus urograndis	0.87	29.6	2.9	48.5	10.8	0.9	0.6	0.3	5.6	2.1
Olea europaea	5.06	26.5	2.0	42.9	16.3	1.7	1.8	3.3	2.1	2.5

E: extractives, L: lignin, S/G: siringyl/guaiacil, GL: glucose, XI: xilose, GA: galactose, MA: manose, AR: arabinose, AcU: uronic acids, AC: acetyl groups

Table 3
Results of pulpings for Kraft pulp production

Raw material	EA, %	KN	VI, cP	YI, %	Residual liquor	
					pH	EA, (g/L)
Eucalyptus urograndis	16.8	17.3	42.8	54.1	13	8.4
Olea europaea	20	17.5	30.2	31.4	12.3	3.6

EA: effective alkali, KN: Kappa number, VI: viscosity, YI: yield

Table 4
Dimensions of cellulose fibers

Raw material	Coarseness, (mg/100 m)	Nº fibers/g (million)	Average length (mm)	Average width (µm)	Fines content (%)
Eucalyptus urograndis	7.88	15.20	0.84	29.40	8.57
Olea europaea	5.30	41.97	0.45	33.59	13.31

Characterization of unrefined Kraft pulp handsheets

The physical-mechanical and optical properties of pulp are expressed in terms of tensile index, since this index is one of the most important properties in the production of several types of papers.[38] The dimensions of the fibers of the unrefined Kraft pulp (Table 4) were determined with the automatic Galai-CIS-100 equipment – the Galai technique quantifies a large number of fibers, pieces of fibers and fines which reduce the length measurement of all fibers. A decrease in the individual weight of each fiber causes a high number of fibers per gram of pulp, since they undergo some alterations in the process of pulp and paper making. According to Foelkel,[39] the presence of fines has a drastic effect on the drainage of the handsheets, concluding that the increase in drainage resistance (°SR) of the pulp is directly related to the increase of the fines generated from the treatments carried out on pulps.

The percentage of fines is very important in the uses of a pulp, as it increases the possibility of bonds among the fibers. Therefore, a pulp without fines has a low ability to form bonds and a lower physical and mechanical resistance. An excess of fines causes problems of drainage, drying and pressing in paper machines. An increase in the density of the final handsheets causes a growth in the porosity and in the specific surface area of the fiber.[40]

Olive tree pruning Kraft pulp refining

Refining causes surface delaminations, which favor the appearance of new contact surfaces. Thereby, the ability to form hydrogen bonds is increased and thus, the tensile index.[41] The intensity in the refining causes a high compression of the fibers and a decrease of the pores or the empty interfibrillar spaces, making the flow of water more difficult and therefore, reducing the drainability of the pulp[42]. The refining assessment is not always easy, since a large increase in the degree of refining (°SR) is desirable in some cases, but sometimes it requires a slight improvement. However, a good resistance is important in both cases. Thus, the assessment should be based on the properties that are important in each specific case, depending on the quality of the paper that is required to obtain.

The increment in the refining intensity causes some damage to the structure of the fibers, such as a decrease in average length and width, increasing, consequently, the fines content in the pulp. Thus, the values of the physical-mechanical properties of the paper sheets first reach a maximum value and then they begin to decrease due to the excessive mechanical damage caused by this treatment to the fiber surface.

Figure 1 shows that the required energy consumption to achieve a similar tensile index value (60 N.m/g) is analogous in the two pulps considered.

Schopper-Riegler degree

Figure 2 shows that Schopper-Riegler degree was greater for the olive tree prunings (60 °SR) than for *E. urograndis* (30 °SR) for the same tensile index.

Tear index

Figure 3 shows that the tear index of the handsheets made from Kraft olive pulp is lower than the tear index for the eucalyptus. The tear index values reached by olive pulps, corresponding to a tensile index of 40 N.m/g, were of about 5 mN.m^2/g, similar to those presented by a mechanical pulp used in newsprint.

Burst index

The evolution of the burst index with the increase of the refining was similar for both pulps (Figure 4). The burst index values presented by the handsheets made from Kraft olive pulp, corresponding to a tensile index value of 50 N.m/g, were of about 2 kPa.m^2/g, being similar to those presented by press-type mechanical pulps.

Opacity and light scattering coefficient

Opacity is a property that is related to the amount of light transmitted through the paper. Thus, a perfectly opaque paper is the one that does not visibly allow light to pass through it. The opacity of a sheet of paper depends on: the amount of filler, the degree of bleaching, the coating material, the weight and the thickness of the paper. Therefore, the opacity is an essential property for printing and writing paper.

Refining tends to decrease the opacity and light scattering coefficient. According to Queiroz,[43] this decrease can be explained by the increase in the compression of the structure of the handsheets, which reduces the number of fiber-air interfaces. Gomide *et al.*[24] show that the opacity can be improved by using pulps with a high number of fibers per gram, since they have an increased number of optical surfaces for light scattering in the structure of the paper.

According to the graphs shown in Figures 5 and 6, olive tree prunings have high opacity and light scattering coefficient. This fact can be explained by the high number of fibers per gram that this raw material presents versus *Eucalyptus urograndis.*

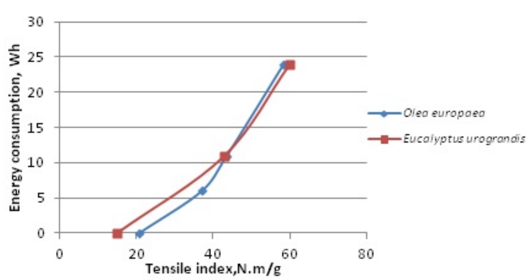

Figure 1: Energy consumption vs tensile index

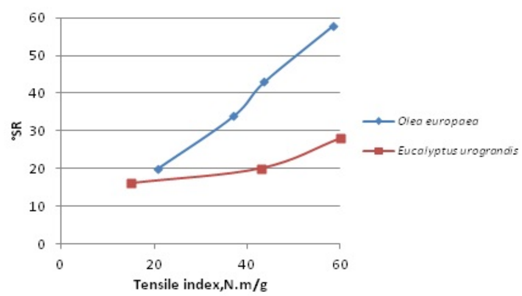

Figure 2: Schopper-Riegler degree vs tensile index

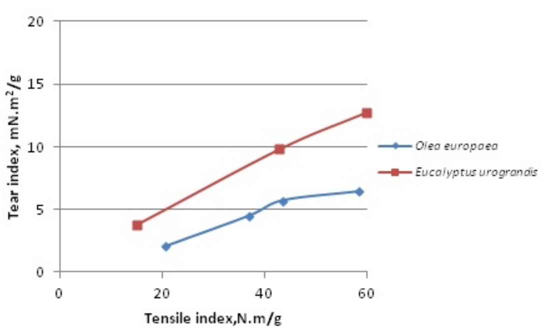

Figure 3: Tear index vs tensile index

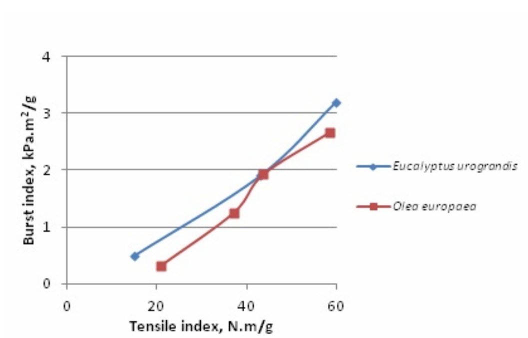

Figure 4: Burst index *vs* tensile index

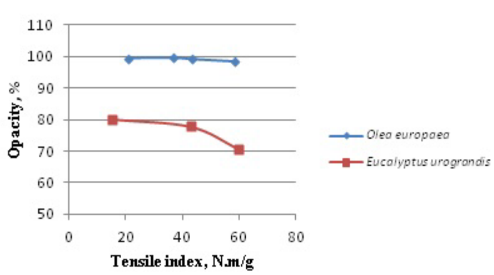

Figure 5: Opacity *vs* tensile index

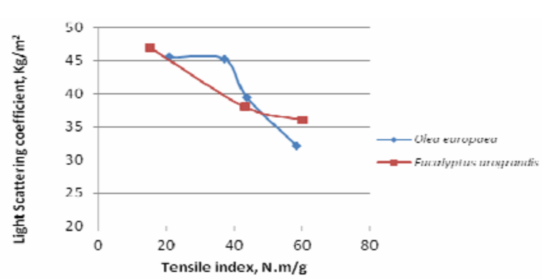

Figure 6: Light scattering coefficient *vs* tensile index

CONCLUSION

Cellulose fibers from olive tree prunings have a lower length than those from *Eucalyptus urograndis*. The hemicelluloses content of this agricultural residue is higher, compared to that of *E. urograndis*, which makes it interesting for a secondary use within the biorefinery concept in food, pharmaceutical and textile industries. The values of the analyzed properties are not higher than those found for *E. urograndis*, and, in some cases, they are very close to them. Furthermore, some values are even higher than those for *E. urograndis*, such as the opacity value. For this reason and because olive tree prunings are an economical raw material for paper industry (considering harvesting and transport costs, mainly), it can be concluded that the pulps obtained from olive tree prunings can be efficiently used as virgin fiber in printed paper for reading.

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