OPTIMIZATION OF ECF BLEACHING AND REFINING OF KRAFT PULPING FROM OLIVE TREE PRUNING

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The aim of the present work was to find an optimum kraft pulping process for olive tree pruning (OTP) in order to produce a bleachable grade pulp of Kappa number about 17. The kraft pulp produced under optimized conditions showed a viscosity of 31.5 mPa.s and good physical, mechanical, and optical properties, which are acceptable for paper grade production. The strength and optical properties were measured on pulps unrefined and refined in a PFI mill with up to 2000 revolutions before and after bleaching. The OTP pulp was bleached to 90% ISO brightness (kappa < 1); however the process demanded a long sequence of stages, OD(EP)D(EP)D, and a higher than usual total chemical dosage (24.78 kg/odt pulp). Overall, OTP is suggested as an interesting raw material for cellulosic pulp production because its properties are comparable to those of other agricultural residues currently used in the paper industry.

Keywords: Kraft pulping; Olea europaea; Agricultural wastes; Refining, ECF bleaching

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INTRODUCTION

Pulp production in Europe amounts to 36.9 million tons per year, which represents 21.6% of the world's production; the production of paper and cardboard accounts for 25.3% of the total with 88.7 million tons. Considering just Spain, the production of paper and cardboard has increased by 4.97% between 2005 and 2010 (ASPAPEL).

This increase in production must be accompanied by advances in technologies that are environmental friendly, such as alternative raw materials compared to the conventional feedstocks, and improvements in the processes of cooking and bleaching of cellulose pulps. In the past, the pulp and paper industry has been identified as being a main source of pollution due to an increase in color, organic load, and toxicity of the effluents generated by the industry (López *et al.* 2001, 2003; Bayer *et al.* 1999; Calvo *et al.* 2007). In this sense, the search for non-wood raw materials, fast-growing plants, or agricultural residues has received more attention in recent years in the paper industry (Ye *et al.* 2005; Leminen *et al.* 1996). Among these, agricultural residues are produced in greater abundance; however, to date, their use is less than 40%. In the future, their use may be of interest to the paper industry (Hu 2008; Hou *et al.* 2011).

Olive Tree Prunings (OTP) are presented as one of the most abundant agricultural residues in the Mediterranean region of the European Union (EU) with a harvested area of 4.8 million hectares; this type of woody crop is one of the few in Spain that has increased its area by 0.3% in 2010 (FAO; MARM).

Taking into account that the current production data in the EU is estimated at 13.5 million tons, of which 7.9 are produced in Spain, the use of OTP can be proposed as a renewable biomass of interest for cellulose pulp and chemical reagents production

(Gominho *et al.* 2001). Currently these residues are burned in the field, with consequent environmental problems, such as the risk of fire or mineral-ization of the organic soil layer. Biannually, one hectare of dry pruned olives can produce three tons of residual biomass, and the generation of 2500 kg of olive tree pruning residues per hectare can be estimated. Recovery of these residues produces an important valorization because they do not have a specific application (AGENER).

The kraft process is one of the more widely used cooking processes in chemical pulping (Man Vu *et al.* 2004) with a satisfactory delignification, high yield, and high viscosity of the cellulose component for pulp production. The woody nature of the olive tree prunings makes this raw material suitable for kraft pulping processes.

In this paper, the kraft process was used to cook OTP. The cooking and bleaching conditions of the process were optimized in order to assure the brightness of the kraft pulp. These bleaching stages were carried out with an elemental chlorine free (ECF) bleaching sequence.

ECF bleaching for chemical pulp production has increased drastically in recent decades, offering many environmental benefits in comparison to traditional methods, because the residual chlorine content in the organic substances of the bleaching effluxents has a composition similar to that found in the environment – naturally degradable and non-persistent (Svenson *et al.* 2006; Solomon 1996; Calvo *et al.* 2007; Torres *et al.* 2004).

The main objective of this work was to design an ECF bleaching sequence for kraft pulp from olive tree prunings, in order to determine an optimal sequence, taking into account the consumption of chemical reagents and the brightness degree achieved.

EXPERIMENTAL

Characterization of Raw Material

OTP collected from the southeast of the province of Córdoba (Spain) were used. These residues were separated manually, removing the leaves and the fractions of wood with a diameter greater than 1 cm. When the size of the sample was homogenized, it was stored in polyethylene bags to achieve constant moisture, determined by means of the following standard analytical procedures:

Table 1. Standard Analytical Procedures

Oven dry quantity	TAPPI 664 cm-97
Sample preparation	TAPPI T 257 cm-85
Hot water soluble compounds	TAPPI T 207 cm-08
Acetone extractives	TAPPI T 280 wd-06
Length of fiber	TAPPI T 233cm-06
Total extractives	TAPPI T 204 om-88
Contents of insoluble lignin in acid	TAPPI T 222 om-98
Acid-soluble lignin	Goldschmid 1971
Constant moisture	TAPPI T 264 cm-97

An aliquot of the sample (homogenized and with constant moisture) was subject-ted to quantitative acid hydrolysis with 5 mL of 72% sulfuric acid; and later, posthydrolysis was performed with 4% sulfuric acid at 121°C and 2 atm for 60 minutes to ensure complete conversion of oligomers to monomers (Garrote *et al.* 2003). The solid residue from acid hydrolysis was recovered by filtration and considered as Klason lignin. The monomers and acetic acid contained in the liquid phase were determined by high performance liquid chromatography (HPLC) to quantify sugar contents (glucose, xylose, arabinose) and acetyl groups. Chromatographic analysis was performed using a refractive index detector and an Aminex HPX-87 H column, eluting with 0.01 M H_2SO_4 at a flow rate of 0.6 mL/min.

The analysis of carbohydrates (Wallis *et al.* 1996), uronic acid contents (Sundberg *et al.* 1996), the siringyl/guaiacyl ratio by liquid chromatography after oxidation with nitrobenzene (Lin and Dence 1992), and acetyl-group analysis (Solar *et al.* 1987) were determined.

Kraft Pulping Process

The kraft cooking process was performed in an electrically heated rotary digester, Regmed, with four vessels, each of them containing a reactor having a capacity of two liters. The time and temperature were controlled through a computer. All the cooking processes were made to produce pulp with a kappa number of about 17; this parameter was reached while maintaining the following variables constant: sulfidity: 30%; liquid/solid ratio: 4/1; maximum temperature: 165°C; time to maximum temperature: 70 min; time at maximum temperature: 60 min.

The kraft cooking process was optimized by varying the active alkali concentration to achieve an appropriate relation between yield and Kappa number. The pulp was separated from the liquor and disintegrated for 10 minutes at 2000 rpm without rupture of the fibers. A sufficient quantity of pulp is produced to determine the yield of the cooking process, TAPPI T 257-02, Kappa number, TAPPI T 236 om-06, and viscosity, TAPPI T 230-om 04. The residual alkali was assessed according to TAPPI T 625 wd-99.

ECF Bleaching

An elemental chlorine free sequence (ECF) composed of OD(EP)D(EP)D stages was used to bleach the kraft pulp in order to achieve a brightness of about 90% ISO. General oxygen delignification and bleaching conditions are listed in Tables 2 and 3.

Table 2. General Oxygen Delignification and Bleaching Conditions for Olive Tree Prunings (*Olea europaea*)

OD(EP)D(EP)D	Consistency (%)	Temperature, °C	Time, min	Kappa factor (KF)	Final pH
O	10	100	60	-	10.6
D_1	10	80	120	0.24	-
(EP)	10	80	90	-	8.12
D_2 (1)	10	80	120	-	5.2
D_2 (2)	10	80	120	-	5
D_2 (3)	10	80	120	-	5.1
(EP)	10	70	60	-	11
D_3 (1)	10	80	120	-	4.8
D_3 (2)	10	80	120	-	5
D_3 (3)	10	80	120	-	5.2

The following standard analytical procedures were used for the characterization of the resulting bleached pulp: Kappa number, TAPPI T 236 om-06; viscosity, TAPPI T 230 om-04; forming handsheets for reflectance testing, TAPPI T 272 sp-08; diffuse brightness of pulp, TAPPI T 525 om-06; brightness stability, TAPPI T 260 wd-98 (4h; 105,8º; 0% HR); and hexenuronic acid contents, TAPPI T 282 pm-07. The indirect analysis of TOC allowed for the evaluation of the total yield of the bleached pulp as described by Longue Júnior *et al.* (2005).

Table 3. Chemical Reagents Used in General Oxygen Delignification and Bleaching Conditions for Olive Tree Prunings (*Olea europaea*)

OD(EP)D(EP)D	NaOH (%)	H_2SO_4 (%)	$MgSO_4$ (%)	O_2 (bar)	ClO_2, as Cl_2 (%)	H_2O_2 (%)
O	2	-	0,15	500	-	-
D_1	-	3.5	-	-	2.59	-
(EP)	1.2	-	0.15	-	-	0.5
D_2 (1)	-	1.6	-	-	1.5	-
D_2 (2)	-	1.2	-	-	2.0	-
D_2 (3)	-	0.8	-	-	2.5	-
(EP)	0.5	-	0.5	-	-	0.2
D_3 (1)	-	1.6	-	-	2.0	-
D_3 (2)	-	1.2	-	-	2.5	-
D_3 (3)	-	0.8	-	-	3.0	-

Data oven dry pulp.

Bleached Pulp Refining

Kraft pulp and bleached pulp were refined in a PFI mill to zero, 500, 1000, and 2000 revolutions. Handsheets were made in an ENJO-F-39.71 sheet former, TAPPI T 205 sp-02 (Forming handsheets for physical tests of pulp) which were stored in an air-conditioned environment with a constant moisture of 50% ± 2% and a temperature of 23 ºC ± 1 ºC in order to obtain grammage, TAPPI T 220 sp-01 (Physical testing of pulp handsheets); tensile index, TAPPI T 494 om-01 (Tensile breaking properties of paper and paperboard); burst index, TAPPI T 403 om-02 (Bursting strength of paper); tear index, TAPPI 414 om- 04 (Internal tearing resistance of paper); Schopper-Riegler degree (ISO 5267/1; Pulps-Determination of drainability-Part 1: Schopper Riegler degree); and ISO brightness, TAPPI T 525 om-06 (Diffuse brightness of paper, paperboard, and pulp).

RESULTS AND DISCUSSION

Characterization of Olive Tree Pruning (OTP)

Table 4 shows the results obtained in the chemical characterization compared to other raw materials, for example two species of eucalyptus (*Eucalyptus globulus* and *Eucalyptus urograndis*), which were included as a reference species or other agricultural residues (vine shoots, sunflower stalks, or cotton stalks) reported by other authors.

Table 4. Chemical Characterization of Several Agricultural Residues and Different Species of Eucalyptus

Raw Materials	Hemicelluloses (%)	Cellulose (%)	Klason Lignin (%)	Ash (%)	Extractives (%)
Eucalyptus globulus	25.83	46.30	22.90	0.40	2.09
Eucalyptus urograndis	20.10	47.90	29.60	0.30	0.87
Olive tree pruning	25.80	35.67	19.71	1.36	10.36
Sunflower stalks	29.66	42.10	13.44	7.90	4.07
Cotton stalks	14.38	58.48	21.45	2.17	1.42
Wheat straw	36.48	39.72	17.28	6.49	4.01
Vine shoots	26.00	41.14	20.27	3.49	4.87

Source of information: Rodríguez *et al.* 2008

The data show that the cellulose content was slightly lower in agricultural residues than the reference species of eucalyptus. The ash contents of OTP were found to be lower than those found for other agricultural residues. The extractives content of OTP was very high, this value being comparable to certain species such as *Leucaena leucocephala* (Honduras) with a value equal to 6.05%, *Arundo donax* with a value of 7.30, or *Sorghum stalks* with a value equal to 7.99% (Rodríguez *et al.*, 2008).

The Klason lignin content of OTP was lower than the species of eucalyptus and other agricultural residues. However, the siringyl/guaiacyl ratio (S/G) was higher for *E. urograndis* (2.9) than for the OTP (2.0).

The sugar contents of OTP were higher than that of *Eucalyptus urograndis*. The content of glucans for both raw materials was higher than the 40% of its chemical constitution, followed by xylans (16.3% versus 10.8%); araban contents of 3.3% versus 0.3%; manan contents of 1.8% versus 0.6%, and galactan contents of 1.7% versus 0.9%. A high content of hemicelluloses can be interesting for a secondary use in the textile, pharmaceutical, and food industries, in terms of sugar production.

The uronic acid contents of the OTP were lower (2.1%) than *Eucalyptus urograndis* (5.6%); these acids generate hexenuronic acids during kraft pulping (Costa *et al.*, 2001), which negatively affect bleaching.

At the end, the basic density for OTP was equal to 616 kg/m^3. Ferreira *et al.* (2006) mention that a high density would cause high losses in the desirable characteristics for the production of printing and writing paper. However, low densities imply a large specific consumption of wood. This is a disadvantage that OTP does not show.

Kraft Pulp Process and Refining

An effective alkali concentration between 18% and 24% was used in order to achieve an optimum yield value, where a Kappa number of about 17 and a moderate consumption of reagents were obtained to carry out a delignification curve.

Table 5. Characterization of Several Kraft Pulps from *Olea europaea*

Effective Alkali, %	18.0	20.0	22.0	24.0
Kappa number	20.7	16.8	15.0	13.5
Total yield (%)	30.3	30.0	29.7	28.6
Screened yield (%)	29.2	29.7	29.3	28.5
Rejects (%)	1.1	0.3	0.4	0.1
pH residual liquor	11.9	12.3	12.6	12.7
Residual effective alkali, g/L	0.8	3.7	6.9	10.5

The results in Table 5 show that with the increase of the effective alkali charge, the Kappa number decreased considerably, causing a decrease in the yield of the process. The increase in the effective alkali concentration of 18 to 20% caused an increase in the screened yield (from 29.2 to 29.7%) due to the transformation of a part of the uncooked material to screened yield. The uncooked material with an effective alkali concentration equal to 18% (1.1%) dropped to 0.3% with 20% effective alkali, and there was an increase in the pH of the residual liquor, which is an indicator of an increase in the amount of unreacted chemical reagent during the process. Thus, it can be concluded that the kraft process is suitable for OTP. The process was performed with a concentration of effective alkali equal to 20% (equivalent to alkali active: 23.5%), achieving a total yield of 32% with a Kappa number of 16.8.

The pulp obtained after the kraft process, with a concentration of 23.5% active alkali, showed a Kappa number of 16.8, a viscosity of 31.52 mPa·s, a value of brightness of 33.02% ISO, and a content of hexenuronic acids of 48.8 mmol/kg.

Subsequently, the pulp was subjected to a refining study, where a certain number of revolutions in the PFI mill were applied to the kraft pulp to achieve a given Schopper-Riegler degree (°SR), evaluating the changes in the physical-mechanical properties of the handsheets formed from refined pulp.

The kraft pulp from OTP was subjected to a refining between 0 and 2000 revolutions, where it was observed that the resistance to drainage increased with the extent of refining, improving the properties of paper handsheets, as shown in Table 6.

Table 6. Variation in the Drainability and the Physical Properties of the Unbleached Kraft Pulp as a Function of the Increase in Beating

PFI revolutions (rpm)	0	500	1000	2000
°SR	20	34	43	58
Energy consumption (W.h)	0	6	11	24
Tensile index (N.m/g)	20.8±1.96	37.07±2.13	43.6±2.56	58.38±2.31
Burst index (kPa.m^2/g)	0.31±4.04	1.25±5.72	1.92±7.40	2.66±6.57
Tear index (mN.m^2/g)	2.05±7.07	4.49±3.53	5.71±1.53	6.42±4.95

An increase in refining resulted in an improvement in the properties of the paper handsheets, reaching a maximum value, after which a greater increase did not result in an improvement of the properties studied.

The kraft pulps from OTP required less severe a refining treatment than the pulps studied by other authors from several raw materials such as *Leucaena diversifolia* (Feria *et al.* 2011), eucalyptus kraft pulps (Mutjé *et al.* 2005), or OTP residues obtained by a treatment with soda or sulphite (López *et al.* 2000), to achieve good levels of drainability.

Studies reported by Mutjé *et al.* (2005) showed that for OTP pulps, the resistance to drainability increases with the intensity of the refining, being similar to the °SR for kraft and organosolv pulps from OTP. However, to achieve the same degree of refining in the soda pulping processes, the intensity of refining must be increased to 3500, being lower for the sulfite pulping (López *et al.* 2000).

The obtained data on the properties of paper handsheets from the kraft pulping process in this work were significantly higher than the data obtained by López *et al.* (2000), where the tear index for unrefined pulp using a soda pulping process, was equal to 1.09 mN.m^2/g, for a sulfite pulping process, of 1.51 mN.m^2/g, and for the kraft pulp, this value was equal to 2.05 mN.m^2/g.

For the burst index, the obtained values in the kraft pulp were higher (0.31 kPa.m^2/g) than the corresponding index values from soda pulping (0.23 kPa.m^2/g) or sulfite pulping (0.24 kPa.m^2/g). The revolutions in the case of the soda pulping should be about 7500 to 8500 for a burst index similar to that obtained in the case of the kraft treatment, and greater than 5000 revolutions in the case of sulphite pulping.

The tensile index of refined kraft pulp at 2000 revolutions presented a value higher than those presented by chemical pulp from rice straw (51.8 N.m/g) or wheat straw (41.4 N.m/g) (Yaghoubi *et al.* 2008).

The use of agricultural waste is of great interest for the paper industry; thus, an economic assessment of this type of waste is provided which, until now, has not been commercially exploited. In the case of OTP, it is necessary to refine the pulp to obtain appropriate values for the properties of paper, not being necessary a high extent in the refining to achieve suitable values of physical-mechanical properties of handsheets. As for the optical properties of paper sheets studied, it was seen that the opacity value in the kraft pulp from OTP (99.49%) was higher than the value of the reference species in the paper industry, *Eucalyptus grandis* (96.1 %).

Oxygen Delignification Stage

Oxygen delignification is a standardized technology for the production of bleached pulp. The oxygen stage is affected mainly by the Kappa number and hexenuronic acids content. Therefore, the pulps with a higher Kappa number produce better efficiencies in the delignification with oxygen, as the hexenuronic acids do not react with oxygen. Thus, the elimination of these acids increases the stability of pulp brightness (Vuorinen *et al.* 1999).

Table 7. Results Obtained from Oxygen Delignification Stage Compared to the Unbleached Pulp

Conditions	Brown pulp	Pre-O_2
Kappa number	16.8	10.8
Viscosity, mPa·s	31.52	19.86
pH final	12.3	10.58
Brightness, % ISO	33.02	45.40

Bleaching of Kraft Pulp from OTP

The bleaching sequence was performed on kraft pulp obtained from the cooking processes mentioned above, starting from a Kappa number equal to 16.8. The final aim of the selected sequence was to obtain cellulose pulp with a brightness degree about 90% ISO.

In the D_2 stage, three different concentrations of chemical reagent were used in order to find an optimal value (15, 20, or 25 kg/ClO_2 tons, expressed as Cl_2). Three concentrations of ClO_2 were studied, with a chemical reagent concentration of 20, 25, and 30 kg/ton.

In the D_2 stage, a chemical reagent concentration of 25 kg/ton of ClO_2 was chosen. A concentration of 30 kg/ton of ClO_2 was necessary to achieve a Kappa number of 0.66 and a brightness of 88.9% ISO in the final stage D_3. The brightness reversion was 2.5% ISO, which is indicative of a good quality in the stability of the obtained pulp.

Reagent consumption was almost 100% for all stages, except in the second step (EP), where the consumption of reagents was 84%, which indicates that the chemical reactive load can be reduced.

The HexAs content at the end of the bleaching sequence was very low, which is attributed to the removal/dissolution of the xylan (Loureiro *et al.* 2010).

The decrease in viscosity from the brown pulp until the last stage of the bleaching sequence was due to the characteristic degradation of the cellulose in the bleaching stages.

Table 8. Results Obtained from ECF Bleaching Sequence

Results	**(O)**	**Bleaching stages**								
		D_1	**(EP)**	**D_2**	**D_2**	**D_2**	**(EP)**	**D_3**	**D_3**	**D_3**
pH final	10.6	-	8.12	5.2	5	5.1	11	4.8	5	5.2
Reagent consumption, %	-	100	92.04	86	86	86	84	100	100	100
Kappa number	10.8	-	4.75				1.81	-	-	0.66
Brightness, % ISO	45.47	71.3	76.9	81.6	81.8	82	80.8	86.5	87.3	88.9
Brightness reversion, % ISO	-	-	-	-	-	-	-	2.3	2.5	2.5
Viscosity, mPa·s	19.86	-	13.71	-	-	10.52	12.29	-	-	13.24

In an ECF bleaching sequence, it is interesting to assess the characteristic parameters in the effluent; among them, the final pH of the sequence of 5.2, the AOX content equal to 8.6 mg/L, the value of color of 77 mg Pt/L, COD with a value of 25.2 kg/ton, BOD equal to 120 mg/L, and finally the yield TOC, which is equal to 595.6 mg/L. These results are relective of a higher yield of the bleaching sequence and therefore a low degradation of the cellulose fibers. The provided data were similar to data from other investigations of bleached kraft pulp in ECF effluent (Calvo *et al.* 2007).

Finally, the obtained pulp with the ECF bleaching sequence was subjected to a refining study, between 0 and 2000 rpm, where a notable decrease in the opacity value from the brown pulp was seen, as it is directly related to the light scattering coefficient of the pulps, which decreases with the extent of the refining, as explained by the increased compression of the structure of the handsheet, which reduces the fiber-air interface number (Gomide *et al.* 2005). For this reason, the value obtained for the bleached pulp was lower than the one obtained for the unbleached pulp.

Table 9. Comparison of Physical-Mechanical Properties of Unbleached Pulp and ECF Bleached Pulp with a Refining Degree of 2000 rpm

Physical-Mechanical Tests (2000 revolutions)	Kraft Pulp	Bleached Pulp
°SR	58	56
Energy consumption	24	24
V.E.A. (cm^3/g)	1.52±1.75	1.39±2.51
T.E.A. (J/m^2)	97.03±1.18	99.63±1.25
Tensile index (N.m/g)	58.38±1.31	49.24±2.31
Tear index (mN.m^2/g)	6.42±2.64	7.19±4.95
Burst index (kPa.m^2/g)	2.66±3.83	2.88±6.57
Opacity (%)	98.34±0.36	77.6±0.37

It can be seen that the physical properties of bleached kraft pulp, without being subjected to refining, had a tear index of 3.01 mN.m^2/g. This value is close to the values reported by other authors (Jiménez *et al.* 1994) for bleached pulp from wheat straw, between 3.93 and 4.59 mN.m^2/g, depending on the bleaching sequence used. However, this does not hold true when comparing the burst index, whose value for bleached pulp from wheat straw is about to 4.64 to 5.76 kPa.m^2/g, being much lower for bleached pulp from OTP (0.57 kPa.m^2/g) or 2.87 kPa.m^2/g, when the pulp is refined with a refining degree of 2000 revolutions.

CONCLUSIONS

1. Kraft pulps were obtained with a Kappa number of 16.8 and a viscosity of 31.52 mPa·s, using a low effective alkali concentration (20%). Moreover, kraft pulp from olive tree prunings (OTP) should be subjected to a low intensity of beating to avoid high resistance to drainage, whereby the energy consumption required in the process is lower than conventional pulps.

2. Kraft pulp from OTP was bleached with an ECF sequence, reaching a value of brightness of about 90% ISO and a Kappa number below one. For this reason and because the OTP is a waste without an economic value, it can be concluded that the unbleached and bleached pulps obtained from OTP can be acceptable for paper grade production.

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