REUSE OF ULTRAFILTRATION PERMEATE AS A PRELIMINARY STEP IN THE PULP AND PAPER PRODUCTION

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Permeate is a part of the stream generated in the ultrafiltration process. This stream could be utilized due to its composition in low molecular compounds. In this work, different combinations have been used to study the use of ultrafiltration permeate as a preliminary step in the pulp and paper production. The results showed that the use of ultrafiltration permeate, obtained from the black liquor of olive tree pruning fractionation, as cooking liquor instead of the preliminary step is an excellent option, with yields of 35.6% and physical properties of paper sheets similar to those obtained by the use of green traditional liquor (0.599 kN/g burst index and 1.076 mNm^2/g tear index).

Keywords: ultrafiltration permeate, pulp production, black liquor, olive tree prunings

INTRODUCTION

The olive tree is a food crop that has to be pruned twice a year to improve productivity and provide a correct growth of the tree and fruits.[1]The agricultural importance of the olive lies in obtaining oil from the fruit and/or in the sale of the fruit (olives). The olive tree prunings have no economic importance and therefore are considered as waste. However, these prunings area natural resource that has consumed nutrients and water, and in the majority of cases are burned or used as agricultural amendment without even trying to evaluate them.[2]

In 2010, world production in the olive sector amounted to 20.632.686 tonnes, in a cultivated area of 9.532.923 hectares. Spain is the leading producer with 2.092.800 hectares, followed by Tunisia with 1.645.100 hectares, Italy with 1.190.800 hectares, Greece with 834.200 hectares and Turkey, with 826.199 hectares. In the 2009/10 campaign, Spanish production was 46.3% of world production. Taking into account that one hectare of dry pruned olives can produce 3 tons of leftover biomass every two years, the generation of 2500 kg of olive tree pruning residues per hectare can be estimated.[3-4]

The soda process is the most ancient and simple of all processes of pulping that are known, and can be used to treat both softwood and hardwood species, as well as different alternative raw materials. It has been proven that the rate and selectivity of the delignification process could be improved by adding small amounts of certain organic compounds that act as catalysts; some compounds used for this purpose are anthraquinone, hydrazine, hydroxylamine, etc.[5]

The membrane separation has gained considerable interest in the last years, due to its implementation in various fields, such as food, chemical, biological, and pharmaceutical industries.[6]Membrane processes have been used in pulp and paper mills since the late 1960s, and the majority of applications have been aimed at the treatment of bleach plant effluent and fractionation of spent sulphite liquor.[7]

With the use of membrane technology, two streams are generated: permeate and retentate,[8] the retentate stream is recirculated to the feed tank and the permeate stream is collected separately. Membrane technology permits to concentrate the organic matter as lignin in the retentate and its further recovery. The application of the ultrafiltration technology in the process of lignin recovery presents important benefits, such as the possibility of liquor withdrawal at any position, without adjustment of the pH or temperature, the possibility to control the molecular mass of the lignin fraction by the membrane cut-off and limits the expenditure of energy.[7,9] Lignin recovery from the retentate could be used in different applications due to the diversity of functional groups present. Lignin could be applied as dispersant in blends,[10] as emulsifier,[11]chelating agent[11]or adsorbent agent[12]and could be generate a large amount of chemical reagents due to its aromatic composition.[13]

Whereas, the permeate stream will contain the low-molecular compounds. This permeate could present a different utility of recovering compounds dissolved in this stream. In this work, the permeate stream generated in the ultrafiltration process of black liquor from the fractionation of olive tree pruning has been reused as a preliminary cooking step in the pulp and paper production.

The aim of this work is to use the ultrafiltration permeate in an olive tree pruning soda pulping process and compare the results obtained with those achieved by olive tree pruning soda pulping process using green liquor.

EXPERIMENTAL

Raw material characterization

Olive tree (*Olea europaea*) pruning residue was supplied by "Agricultural Cooperative San Fco of Asís", Montefrío, Granada, Spain. After a manual separation to remove small branches and leaves, the shoots were air-dried to constant moisture content and placed in plastic bags for storage until used. In this work, a wood chip size of 30 x 3 mm was used.

Chemical analysis of the raw material was carried out according to the following procedures: moisture (Tappi T11m-59), cellulose (Tappi T9m-54), lignin (Tappi T222), ethanol-benzene extractives (Tappi T6m-59), ash (Tappi T15m-58).

Pulping of the raw material

The raw material was pulped in a stainless steel digester, provided by Metrotec S.A., with 15 L capacity, able to work up to 20 atmospheres of pressure. Once obtained, the pulps were washed immediately with water at room temperature to remove the reagent and avoid lignin re-precipitation. Later, the pulps were fiberized in a disintegrator at 1200 rpm for 30 minutes with a 10% consistency. The pulp was then beaten in a Sprout-Bauer refiner, operating at 0.5% pulp consistency, by using a disk spacing of 0.1mm, and the fiberized material passed through a Sommerville screen model K134 to remove uncooked particles. Finally, water was eliminated through centrifugation and the pulps were dried at room temperature until a humidity of 90%-92% was reached.

The operating conditions used in this study were as follows: 175 ºC temperature with 15% soda and 1% anthraquinone (both over dry matter), a liquid/solid ratio of 8, during 120 minutes (after reaching the working temperature). Figure 1 shows the work scheme.

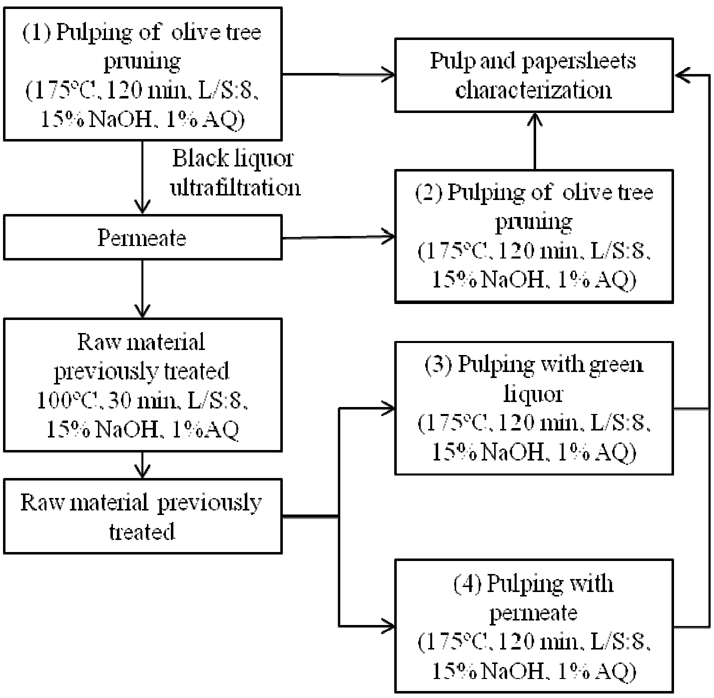

Figure 1: Work scheme

Characterization of pulps and paper sheets

Pulps and papers obtained from different pulping processes were characterized according to the following standard methods: yield (gravimetrically), viscosity (Tappi T230om-94), Kappa number (Tappi T236cm-85), lignin (Tappi T222), breaking length (Tappi T494om-96), burst index (Tappi T403om-97), tear index (Tappi T414om-98) and brightness (Tappi T525om-92).

Ultrafiltration process and permeate characterization

The black liquor obtained in the fractionation process was processed in a Pall Membralox XLab5 pilot unit, equipped with a 3L 326 stainless steel tank with water jacket for temperature control, a recirculation pump and a set of tubular membranes supplied by IBMEM – Industrial Biotech Membranes (Frankfurt, Germany). The membrane used (15 KDa) was made of ceramic material (TiO_2), tubular and multichannel type, with an external and hydraulic diameter of 10 and 2 mm, respectively, and a surface of 110 cm^2. The black liquor solution was filtered, and a permeate fraction of 15 KDa and a retentatefraction greater than 15 KDa were obtained.

The different obtained fractions (permeate and retentate) were characterized as to their pH, density, inorganic matter (IM), organic matter (OM) and total dissolved solids (TDS) contents and lignin content (LC). TDS analysis was carried out following the procedure of the NRL LAP-012. The inorganic matter was achieved by a similar method to ash content analysis (Tappi T211). Lignin content was gravimetrically determined following an internal procedure.

RESULTS AND DISCUSSION

Raw material characterization

The values obtained for olive tree pruning characterization were: holocellulose 69.2%, lignin 19.5%, extractives 9.0% and ash 1.2%.

Ultrafiltration process

The physico-chemical properties of different fractions obtained are shown in Table 1. Rough black liquor has been characterized and the results have been included for comparison.

No significant differences in the inorganic matter content of the analyzed liquid samples were detected. This fact was observed by Jönsson *et al.*,[14] who found that the retention of the main inorganic elements (sodium, potassium and sulphur) during the ultrafiltration process of kraft cooking liquor was almost zero, regardless of the membrane cut-off, due to their small size. Whereas, TDS and OM contents of the alkaline fractions increased in the ultrafiltration resulting liquid fractions.

However, the most important data could be observed regarding the lignin content, which is extremely low in the permeate fraction, and this is the reason to study other alternatives for using the permeate stream differently from trying to recover the lignin.

Table 1
Physico-chemical characterization of different ultrafiltration resulting liquid fractions

Fraction	pH	Density (kg/m^3)	TDS[a] (%)	IM[b] (g/mL)	OM[b] (g/mL)	LC[c] (g/mL)
Rough liquor	13.4	1.043	0.1088	0.0854	0.0233	0.0062
Permeate (<15 KDa)	13.1	1.061	0.1218	0.0822	0.0396	0.0016
Retentate (>15 KDa)	12.9	1.058	0.1232	0.0906	0.0326	0.0139

[a] Total dissolved solids
[b] Inorganic and organic matter referred to TDS content
[c] Lignin content referred to OM content

Characterization of pulps and paper sheets

Table 2 shows the results obtained for the different pulping processes.

Pulps that show better yield values were obtained using ultrafiltered and rectified black liquor. This could be explained by the black liquor having lignin in its composition and therefore less lignin was removed from the raw material. The Klason lignin values of the pulps were 6.32, 11.08, 11.16 and 12% for pulps 1, 2, 3 and 4, respectively (Fig. 2).

The Kappa number is higher in the pulp obtained using ultrafiltered and rectified black liquor, which agrees with having higher content of lignin. The brightness is lower for the pulps obtained using the permeate of the black liquor.

For both Kappa number and brightness values, pulps 3 and 4 show better values (lower for Kappa number and higher for brightness), compared to the values obtained for pulps 1 and 2, both not treated with the permeate (Fig. 3).

Table 2
Chemical and physical characterization of pulps and paper sheets obtained with soda process

Pulp / Properties	1 (175 ºC, 120 min, 15% NaOH, 1% AQ, L/S:8)	2 (175 ºC, 120 min, 15% NaOH, 1% AQ, L/S:8)	3 (175 ºC, 120 min, 15% NaOH, 1% AQ, L/S:8)	4 (175 ºC, 120 min, 15% NaOH, 1% AQ, L/S:8)
Yield,%	31.6	35.6	52.1 (18.4)*	58.7 (20.7)*
Kappa number	24.1	36.3	16.9	18.1
Viscosity, mL/g	764	759.4	561.4	580.8
Beating degree, ºSR	28	12	18	19
Tensile index, Nm/g	11.95	10.28	10.66	9.76
Burst index, kN/g	0.589	0.599	0.441	0.475
Tear index, mNm^2/g	1.078	1.076	0.939	0.881
ISO Brightness, %	25.7	22.5	33.0	31.8

1→ green liquor; 2→ black liquor ultrafiltrate; 3 → green liquor after pretreatment with ultrafiltrate liquor (100ºC, 30 min, 15% NaOH, 1%AQ, L/S:8); 4 → black liquor ultrafiltrate after pretreatment with ultrafiltrate liquor (100ºC, 30 min, 15% NaOH, 1%AQ, L/S:8)
* effective yield after previous treatment

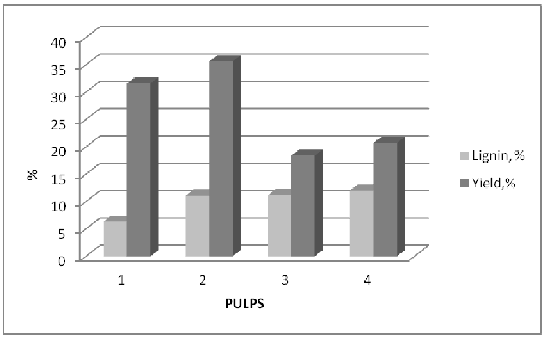

Figure 2: Yield and lignin content

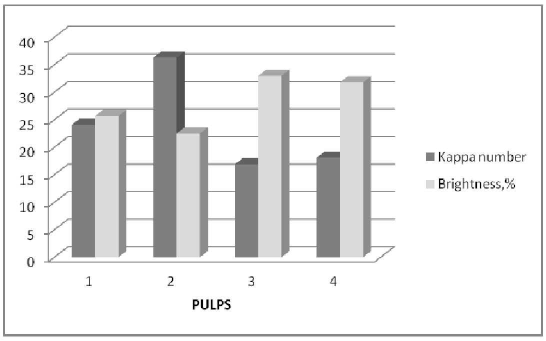

Figure 3: Kappa number and brightness

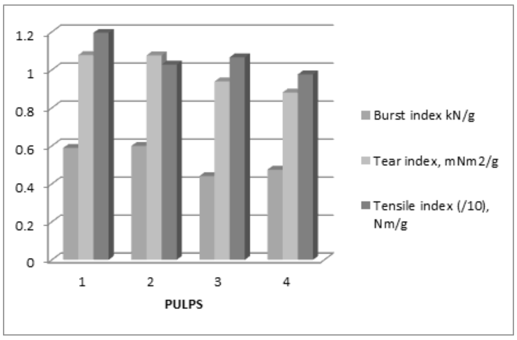

Figure 4: Properties of paper sheets

The physical properties of the paper sheets made with the pulps obtained showed similar values (Fig. 4), although for the pulp obtained using the permeate of the black liquor, the values of tensile, burst and tear indexes decreased slightly with respect to the values obtained with green liquor (pulping 1).

CONCLUSION

Comparing the results obtained in the pulping of the olive tree pruning after a previous step of impregnation with permeate, it could be concluded that this stage does not provide significant advantages to justify it. Thus, the viscosity and yield diminish significantly, while brightness values increase slightly. The values of physical properties suffer only little variation.

With the results obtained using green liquor and permeate in the pulping processes, it could be concluded that it is possible to use the ultrafiltered black liquor in the pulping process, adding the necessary active alkali.

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