Use of perborate in the bleaching of ethanolamine pulp from olive wood

E. Ramos*, M.J. de la Torre and J.C. Gutiérrez
Ingeniería Química, Universidad Pablo de Olavide, Ctra. Utrera km 1, 41013 Sevilla, Spain.

Uso del perborato en el blanqueo de pastas celulósicas de madera de olivo obtenidas con etanolamina

Ús del perborat en el blanqueig de pastes cel·lulòsiques de fusta d'olivera obtingudes amb etanolamina

Recibido: 11 de enero de 2016; revisado: 4 de marzo de 2016; aceptado: 7 de marzo de 2016

RESUMEN

En este trabajo se estudia la influencia de la concentración de perborato (2,5 a 5,5%), temperatura (60 a 80 ºC) y tiempo (60 a 180 minutos) sobre las características de las pastas blanqueadas (rendimiento, índice Kappa, viscosidad, blancura y relación viscosidad/Kappa), el consumo de reactivos (porcentaje en peso de reactivo consumido por pasta seca) y propiedades físicas de las hojas formadas (índice de desgarro, índice de estallido, alargamiento y longitud de ruptura). Se utiliza en este estudio pastas de olivo obtenidas mediante el proceso etanolamina-sosa-antraquinona.
Para establecer las ecuaciones que relacionan las características de las pastas con las variables del proceso se utiliza un diseño factorial central compuesto centrado en las caras, lo que permite obtener las condiciones óptimas de operación. Las ecuaciones obtenidas, que relacionan las variables dependientes con las de operación, reproducen los resultados experimentales con errores menores del 10%.
Las condiciones de operación más aconsejables se corresponden con una temperatura baja (80 ºC) y con valores elevados de tiempo (180 min.) y concentración de perborato (5,5%). Considerando que en el mejor de los casos se obtiene una blancura de 63%, operando bajo las condiciones más enérgicas, se concluye que este proceso no debe realizarse para blanqueos en una sola etapa.

Palabras clave: Blanqueo; residuos agrícolas; olivo; TCF; perborato de sodio.

SUMMARY

In this work, we studied the influence of the bleacher concentration (2.5-5.5%), temperature (60-80 ºC) and time (60-180 min) on the reagent (perborate) consumption by dry pulp, various properties of the bleached pulp (yield, kappa number, brightness and viscosity/kappa number ratio), and some physical properties of paper sheets obtained from it (tear index, burst index, stretch and breaking length). The pulp was previously obtained by ethanolamine-soda-anthraquinone cooking of olive wood.
A face-centred composite factor design was used to derive equations relating the pulp properties to the operational variables with a view to identifying the optimum operating conditions. The equations thus obtained reproduced the experimental results with errors less than 10% in all cases. The most suitable operating conditions were found to be a low temperature (60 ºC), a long time (180 min) and a high perborate concentration (5,5%). Because the pulp brightness achieved never exceeded 63% -not even under the most drastic conditions-, the process should not be used with one-step bleaching sequences.

Key words: Bleaching; agricultural residues; olive; TCF; sodium perborate.

RESUM

En aquest treball s'estudia la influència de la concentració de perborat (2,5-5,5%), temperatura (60 a 80ºC) i temps (60-180 minuts) sobre les característiques de les pastes blanquejades (rendiment, índex Kappa , viscositat, blancor i relació viscositat / Kappa), el consum de reactius (percentatge en pes de reactiu consumit per pasta seca) i propietats físiques de les fulles formades (índex d'esquinçament, índex d'esclat, allargament i longitud de ruptura). S'utilitza en aquest estudi pastes d'olivera obtingudes mitjançant el procés etanolamina-sosa-antraquinona.
Per establir les equacions que relacionen les característiques de les pastes amb les variables del procés s'utilitza un disseny factorial central compost centrat en les cares, el que permet obtenir les condicions òptimes d'operació. Les equacions obtingudes, que relacionen les variables dependents amb les d'operació, reprodueixen els resultats experimentals amb errors menors del 10%.
Les condicions d'operació més aconsellables es corresponen amb una temperatura baixa (80ºC) i amb valors elevats de temps (180 min.) i concentració de perborat (5,5%). Atès que en el millor dels casos s'obté una blancor del 63%, operant sota les condicions més enèrgiques, es conclou que aquest procés no ha de realitzar-se per blanquejos en una sola etapa.

Paraules clau: Blanqueig, residus agrícoles, olivera, TCF, perborat de sodi

*Corresponding author: eramgom@upo.es, Tel.: +34 954 977 349

INTRODUCTION

The sustained increase in the use of wood as a papermaking raw material for more than a century has led to its annual consumption reaching levels similar to those of petroleum. In fact, paper production has grown in recent decades gradually (3% of average), specifically from 390 to 400 tonnes in 2008-2012. The increase in production is mainly due to increment in the Asia-Pacific region (16%) that counteracts declines in Europe and North America (10% and 15% respectively) in the same period [1].

The dramatic increase in the consumption of wood, which accounts for 90-95% of all raw materials used to manufacture paper, has resulted in a growing shortage of raw materials for this purpose and led to massive soil deforestation and its associated environmental problems. This has promoted extensive search for alternative raw materials in recent years.

Olive pruning residues are highly abundant in Spain – particularly in the southern region of Andalusia, which accounts for more than 60% of the 2 million ton produced in the country each year [2]. These residues lack a specific use, so they are usually burnt on site, which raises problems such as atmospheric pollution or the risk of fire.

Previous studies on the characteristics of these residues (specifically, on their suitability for making cellulose pulp) have shown that the potential of olive wood for this purpose lies in between that of other agricultural residues (*e.g.* wheat straw, sunflower, sorghum and cotton stalks) and pine and eucalyptus wood [3].

The cooking of raw materials for the production of pulp generates large amounts of highly polluting wastewater (particularly in conventional sulphite- and sulphate-based processes). One solution to this problem is using an organic solvent to separate wood fibres from lignin.

A variety of solvents [particularly alcohols [4,5] and organic acids of low molecular weight [6]] have been tested for this purpose. The resulting acidifying or delignifying effect damages cellulose fibres to some extent and ultimately detracts from the quality of the resulting paper. This could be avoided by using solvents such as ethanolamine in an alkaline medium. In fact, this reagent has provided pulp from coniferous and leafy wood [7,8] and non-wood plant raw materials [9,10,11,12,13,14,15,16] the properties of which are on a par with those of kraft pulp and in higher yields. In addition, ethanolamine has been tested as a additive in alkaline pulping processes [17,18].

Pulp bleaching sequences involving chlorine or a chlorinated reagent produce highly polluting wastewater. This has promoted research into alternative, elemental chlorine-free (ECF) and totally chlorine-free (TCF) sequences. Because the latter remain largely impractical, it might be interesting to conduct deeper research into the bleaching of cellulose pulp with non-chlorinated reagents such as sodium perborate [19,20,21].

In fact, sodium perborate has been used as a bleacher for kraft pulp for more than 20 years and proved more efficient than hydrogen peroxide in terms of optical and physical properties of the bleached pulp. Sodium perborate has been used with thermomechanical pulp from coniferous [22] and eucalyptus wood [23], and also with recycled pulp [24]. Unsurprisingly, its low cost and little toxicity have raised much interest in it as a bleacher for paper pulp [25].

The chemical structure of perborate involves peroxo bonds between boron atoms in a tetrahedral arrangement. In water, it decomposes into hydrogen peroxide, and sodium and boron hydroxides [26]. Because the actual bleacher is hydrogen peroxide released by the reagent, the reaction conditions must be suited to it.

In this work, we developed empirical models to describe the perborate bleaching of ethanolamine pulp from olive wood. To this end, we used a faced-centred factor design to relate pulp properties to the independent variables of the process with a view to establishing the optimum operating conditions.

MATERIAL AND METHODS

Raw material

The raw material used to obtain cellulosic pulps was olive prunings from Granada province, Spain. The pulping solvent used, ethanolamine 99% PS (Solvents, reagents and intermediates to be used in organic synthesis), were supplied by PANREAC and the bleaching solvent used, sodium perborate tetrahydrate, were supplied by MERCK

Characterization of the raw material and cellulose pulp

The components of the raw material were characterized in accordance with TAPPI 204 [27] (ethanol-benzene extractables), TAPPI 211 [27] (ash), the method of Wise et al. [28] (holocellulose), TAPPI 203 os-61 [27] (α-cellulose) and TAPPI 222 om-98 [27] (lignin).

The breaking length, stretch, burst index and tear index of the paper sheets were determined in accordance with UNE 57-054, UNE 57-028, UNE 57-033 and UNE 57-058 [29], respectively; and the degree of refining, kappa number, brightness and viscosity of the pulp in accordance with UNE 57-025, TAPPI 236, UNE 57-062 and UNE 57-039, respectively. Finally, the amount of unreacted perborate was quantified iodometrically.

Pulping process

The raw material was cooked in a 15 L tank wrapped in a jacket consisting of electrical heating wires. The whole ensemble, which was heated as required, was connected via a rotary axle to a control unit including a motor actuating the reactor and the required instruments for measurement and control of the pressure and temperature. The set-up also included a safety valve for the reactor and a conventional vent valve.

The reactor was fed with wood chips about 2 cm in size. The solid/liquid ratio used was 4:1, and ethanolamine, soda and anthraquinone were supplied in the amounts required to obtain a proportion of 70, 1 and 0.5% by dry pulp, respectively. Then, the mass was cooked at 185 ºC for 30 min.

After cooking, the reactor contents were filtered and the solid obtained washed with water and then processed in a defiberizer for uncooked material, a Sprout-Waldron disc refiner, a fibre-uncooked material separator and water, prior to air-drying.

The resulting pulp (yield 43.88%) exhibited a degree of refining of 23.5 ºSR, a kappa number of 38, a viscosity of 796 mL/g, a brightness of 33.60% and a breaking length of 2067 m.

Bleaching process

The pulp was supplied with the bleaching reagents and placed in heat-proof transparent bags that were immersed in a thermostated bath. All pulp samples had the same consistency (10%) and pH (10.5), and were supplied with identical amounts of magnesium sulphate (0.2%) and DTPA (0.5%). Tests were conducted at different, fixed perborate concentrations, using variable bleaching temperatures and times in each.

Experimental design

The face-centred factor design used [30] required performing 15 experiments for the three operational variables (*viz.* perborate concentration, temperature and time). The values of the independent variables were normalized to others from -1 to 1 (Table 1) by using the following expression:

$$X_n = 2\,\frac{X - \bar{X}}{X_{max} - X_{min}} \qquad 1$$

where X, $\bar{X}$, X_{max} and X_{min} are the absolute, mean, maximum and minimum value, respectively, of the independent variable concerned.

Experimental data were fitted to the following second-order polynomial model by using the statistical software BMDP:

$$Z = a_0 + \sum_{i=1}^{3} b_i X_{ni} + \sum_{i=1}^{3} c_i X_{ni}^2 + \sum_{\substack{i=1\\j=1}}^{3} d_{ij} X_{ni} X_{nj} \quad (i < j) \qquad 2$$

where Z denotes the response or dependent variable concerned [*viz.* yield (YI), kappa number (KN), viscosity (VI), brightness (BR), degree of refining (SR), proportion of perborate used by dry weight (PBP), tear index (TI), burst index (BI), stretch (ST), breaking length (BL) or viscosity/kappa number ratio (VKR)]; X_n is the normalized value of the independent variable in question (*viz.* X_{PB}, X_T and X_t for the normalized perborate concentration, temperature and time, respectively); and a_0, b_i, c_i and d_{ij} are unknown characteristic constants that were calculated from the experimental results. The polynomial was simplified by deleting the negligible terms previously identified using the stepwise method [20].

Table 1: *Absolute and normalized values of the operational variables used in the bleaching of ethanolamine pulp from olive wood.*

E	PB (%)	T (ºC)	t (min)	X_{PB}	X_T	X_t
1	4,0	70	120	0	0	0
2	5,5	80	180	1	1	1
3	2,5	80	180	-1	1	1
4	5,5	80	60	1	1	-1
5	2,5	80	60	-1	1	-1
5	5,5	60	180	1	-1	1
7	2,5	60	180	-1	-1	1
8	5,5	60	60	1	-1	-1
9	2,5	60	60	-1	-1	-1
10	4,0	80	120	0	1	0
11	4,0	60	120	0	-1	0
12	4,0	70	180	0	0	1
13	4,0	70	60	0	0	-1
14	5,5	70	120	1	0	0
15	2,5	70	120	-1	0	0

E: experiment number; PB, T y t: absolute values of perborate concentration (%), temperature (ºC) and bleaching time (min); X_{PB}, X_T y X_t: normalizad values of perborate concentration, temperature and bleaching time.

RESULTS AND DISCUSSION

The olive prunings used contained: 10.4% ethanol-benzene extractables, 61.5% holocellulose, 35.7% α-cellulose and 19.7% lignin.

Table 2*: Experimental values of the dependent variables in the bleaching of pulp obtained with the experimental design used.*

E	YI (%)	KN	VI (mL/g)	BR (%)	SR	PBP (%)	TI (mN·m²/g)	BI (KN/g)	ST (%)	BL (m)
1	97,34	28,41	821,6	57,1	19,00	3,86	0,87	0,99	1,30	1466,7
2	92,69	23,85	766,4	62,7	19,00	5,44	0,81	0,96	1,17	1476,1
3	96,57	28,31	785,7	55,2	17,50	2,50	0,87	0,89	1,16	1354,2
4	97,49	29,29	815,5	58,6	18,50	5,06	0,80	0,95	1,23	1550,5
5	98,50	31,04	831,3	54,2	17,75	2,43	0,86	0,93	1,22	1511,5
6	96,73	28,38	825,9	59,1	20,00	5,13	0,83	0,93	1,37	1555,6
7	97,06	29,41	807,3	53,1	19,50	2,50	0,89	0,89	1,31	1551,8
8	98,05	29,94	828,0	55,0	18,25	4,69	0,79	0,87	1,28	1406,9
9	99,08	31,95	840,0	52,4	16,50	2,44	0,83	0,89	1,21	1362,3
10	97,17	26,49	809,3	59,2	17,75	3,94	0,91	1,00	1,33	1535,2
11	98,28	28,50	830,7	55,6	18,25	3,84	0,88	0,98	1,42	1692,1
12	96,17	27,26	802,0	58,6	17,00	3,98	0,83	0,95	1,39	1562,7
13	98,80	30,11	822,9	54,6	16,00	3,77	0,91	0,96	1,28	1494,8
14	95,14	26,19	817,1	59,6	17,50	5,16	0,79	0,94	1,29	1474,4
15	97,89	29,32	837,1	54,7	16,00	2,49	0,93	0,89	1,04	1287,8

YI: yield; KN: kappa number; VI: viscosity; BR: brightness; SR: degree of refining; PBP: percent weight of perborate used by dry pulp; TI: tear index; BI: burst index; ST: stretch and BL: breaking length

Table 2 shows the experimental results for the dependent variables of the bleaching process, namely: pulp yield, kappa number, viscosity, brightness, degree of refining, weight percent of perborate used by dry pulp, tear index, burst index, stretch and breaking length.

The influence of the independent variables involved in the bleaching process (*viz.* the perborate concentration, temperature and time) on the properties of the resulting pulp and paper sheets, and on bleacher consumption, was determined in a multiple regression analysis of the three operational variables listed in Table 1 as independent variables, such variables squared and their binary interactions, all using the experimental values of the dependent variables listed in Table 2.

Only those terms with a Snedecor *F*-value greater than 4 and a Student *t*-value greater than 2 were considered to be statistically significant. Also, all 95% confidence intervals for the coefficients of each variable or constant parameter in the models excluded zero.

The equations thus obtained to relate the dependent variables to the pulp and paper properties, and bleacher consumption, were as follows:

$$YI = 97{,}13 - 0{,}90\,X_{PB} - 0{,}68\,X_T - 1{,}27\,X_t \quad [3]$$

$$KN = 27{,}78 - 1{,}24\,X_{PB} - 0{,}92\,X_T - 1{,}513\,X_t + 1{,}17\,X_t^2 - 0{,}51\,X_T\,X_t \quad [4]$$

$$VI = 823{,}2 - 4{,}9\,X_{PB} - 12{,}4\,X_T - 15{,}0\,X_t - 10{,}7\,X_t^2 - 5{,}2X_{PB}\,X_T - 7{,}5\,X_T\,X_t \quad [5]$$

$$BR = 57{,}2 + 2{,}5\,X_{PB} + 1{,}5\,X_T + 1{,}4\,X_t - 0{,}9\,X_t^2 + 0{,}4\,X_{PB}\,X_T + 0{,}8\,X_{PB}\,X_t \quad [6]$$

$$SR = 17{,}1 + 0{,}6\,X_{PB} + 0{,}6\,X_t + 1{,}2\,X_T^2 - 0{,}57\,X_T\,X_t \quad [7]$$

$$PBP = 3{,}88 + 1{,}31\,X_{PB} + 0{,}08\,X_T + 0{,}12\,X_t - 0{,}09\,X_{PB}^2 + 0{,}09\,X_{PB}\,X_T + 0{,}09\,X_{PB}\,X_t \quad [8]$$

$$TI = 0{,}88 - 0{,}04\,X_{PB} - 0{,}04\,X_{PB}^2 \quad [9]$$

$$BI = 0{,}98 + 0{,}02\,X_{PB} + 0{,}02\,X_T - 0{,}06\,X_{PB}^2 + 0{,}01\,X_{PB}\,X_t \quad [10]$$

$$ST = 1{,}32 + 0{,}04\,X_{PB} - 0{,}05\,X_T - 0{,}14\,X_{PB}^2 + 0{,}07\,X_T^2 + 0{,}04\,X_T\,X_t \quad [11]$$

$$BL = 1511{,}6 + 39{,}6\,X_{PB} - 135{,}9\,X_{PB}^2 + 96{,}7\,X_T^2 - 71{,}2\,X_T\,X_t \quad [12]$$

$$VKR = 29{,}67 + 1{,}11\,X_{PB} + 0{,}54\,X_T + X_t - 1{,}5\,X_t^2 \quad [13]$$

where YI denotes yield, KN kappa number, VI viscosity, BR brightness, SR degree of refining, PBP the percent weight of perborate used by dry pulp, TI tear index, BI burst index, ST stretch, BL breaking length and VKR the viscosity/kappa number ratio; and X_{PB}, X_T and X_t are the normalized perborate concentration, temperature and time, respectively.

Table 3 lists the Snedecor *F*-values and the largest *p* and multiple-*r* obtained from the previous equations. The estimates provides by such equations reproduced the experimental results with errors less that 5% for the yield, kappa number, viscosity, brightness, weight percentage of perborate used by dry pulp, burst index, breaking length and viscosity/kappa number ratio; and with errors of 5-10% for the degree of refining, burst index and stretch. The values of the operational variables leading to the best values for the dependent variables were identified by using non-linear multiple programming [31] as implemented by More and Toraldo [32]. Table 4 shows the optimum values of the dependent variables and those of the independent variables required to obtain them. Figures 1 and 2 illustrate the results for the viscosity and brightness as plots of their variation with temperature and time at a constant, high perborate concentration. Because the pulp brightness achieved never exceeded 63%, the process should not be used with one-step bleaching sequences.

Table 3: *Statistical parameters obtained for equations 3-13.*

Dependent variable	Statistical parameters		
	Snedecor's F	P <	R mult.
YI (%)	13,84	0,026	0,889
KN	21,91	0,069	0,961
VI (mL/g)	16,23	0,075	0,961
BR (%)	102,77	0,027	0,994
SR	6,24	0,064	0,845
PBP (%)	2542,94	0,0010	0,9997
TI (mN·m²/g)	9,94	0,033	0,790
BI (KN/g)	13,74	0,068	0,920
ST (%)	7,08	0,079	0,893
BL (m)	9,58	0,045	0,891
VKR	15,15	0,042	0,926

The data of Table 4 and 5, and Figs. 1 and 2 -and similar others-, allowed us to predict whether specific changes in the operational conditions would substantially alter the results for the dependent variables (Table 5). This allowed the operating conditions required to obtain acceptable levels of the different dependent variables to be identified. Table 6 illustrates the most suitable conditions for this purpose. As can be seen, using high levels of all operational variables can be expected to provide pulp of maximum brightness. However, such conditions will detract from other physical properties of the pulp, which will be 3-20% worse than their respective best values; also, as expected, the yield will be minimal and the perborate consumption per gram of pulp maximal.

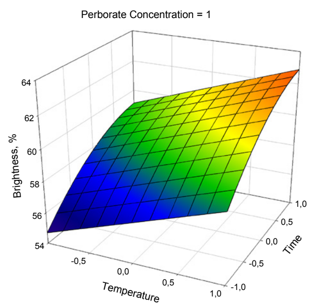

Figure 1: *Variation of brightness with the temperature and time at a high perborate concentration.*

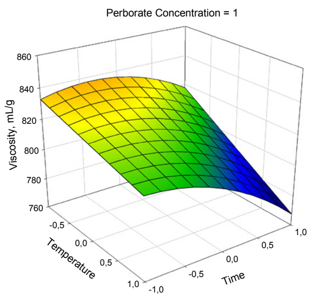

Figure 2: *Variation of viscosity with the temperature and time at a high perborate concentration.*

Table 4: *Values of the operational variables in the bleaching required to obtain the optimum values of the dependent variables.*

Dependent variable	Optimum value of dependent variable	Normalized values of the independent variables leading to optimum variables of dependent variables		
		X_{PB}	X_T	X_t
YI (%)	99,98	-1	-1	-1
KN	24,75	1	1	0,86
VI (ml/g)	837,2	1	-1	-0,35
BR (%)	62,9	1	1	1
SR	20,07	1	-1	1
PBP (%)	2,44	-1	1	-1
TI (mN·m²/g)	0,89	-0,5		
BI (KN/g)	1,00	0,25	1	1
ST (%)	1,48	0,14	-1	1
BL (m)	1682,4	0,14	-1	1
VKR	31,49	1	1	0,33

Table 5: *Relative effects (percent) of each independent variable on the mean variation of each dependent variable in the bleaching, resulting from variations in each independent variable over the range -1 to +1 (normalized values).*

Dependent variable	Independent variables		
	Perborate concentration	Temperature	Time
YI (%)	1,80%	1,36%	2,54%
KN	10,02%	10,98%	16,41%
VI (ml/g)	0,07%	3,58%	2,33%
BR (%)	11,76%	6,04%	7,00%
SR	5,98%	9,16%	11,66%
PBP (%)	107,38%	0,82%	2,46%
TI (mN·m²/g)	10,11%	0,00%	0,00%
BI (KN/g)	9,34%	3,99%	0,50%
ST (%)	12,33%	12,74%	5,39%
BL (m)	10,60%	10,76%	8,46%
VKR	7,05%	3,43%	8,47%

Table 6: *Values of the dependent variables for the bleached pulp and resulting paper sheets (and deviations from the optimum levels) obtained under the conditions stated.*

Dependent variable	Operating conditions: high perborate concentration (1), high temperature (1) and long time (1)		Operating conditions: low temperature (-1), low perborate concentration (-0,72) and long time (0,95)	
	Value of the dependent variable	Deviation from the optimum value, %	Value of the dependent variable	Deviation from the optimum value, %
YI (%)	94,28	5,7	97,25	2,73
KN	24,77	0,09	29,70	20
VI (ml/g)	767,5	8,3	818,6	2,22
BR (%)	62,9	0	54,2	13,9
SR	18,93	5,68	18,98	5,43
PBP (%)	5,48	124,59	2,93	19,97
TI ($mN·m^2/g$)	0,8	10,11	0,89	0,22
BI (KN/g)	0,97	3,36	0,91	9,57
ST (%)	1,12	19,08	1,38	7,16
BL (m)	1440,8	14,36	1577	6,27
VKR	30,82	2,12	27,93	11,31

If our objective is to obtain pulp with good physical properties, the values of the operational variables must be: 4, 21% of perborate concentration, 60 °C and 180 minutes, getting the optimum values for breaking length and stretch, also will provide an excellent tear index and burst index, differing only 1,84 and 4,06% from their optimum levels.

On the other hand, using a high perborate concentration (5,5%) at a low temperature (60 ºC) for a long time (180 min) will provide an acceptable level for all dependent variables. Will be obtained the optimum value for degree of refining (20,07º) and an excellent viscosity (817,7 mg/L) which depart by only 2,33% from their optimum value. The remaining variables are less deviate from 12% of their optimum values, with the exception of the percent weight of perborate used by dry pulp.

ACKNOWLEDGEMENTS

This work was conducted within the framework of research project CTM2007-66793-C03-02, which is cofunded by Spain's DGICyT.

REFERENCES

1. FAO Yearbook of Forest Products 2012. http://www.fao.org/docrep/019/i3732m/i3732m.pdf
2. Jiménez, L., Navarro, E., Pérez, I., Maestre, F., 1997. Disponibilidad, Almacenamiento y Caracterización de Residuos Agrícolas para la Fabricación de Pastas Celulósicas para Papel. Investigación y Técnica del Papel. 131, 130-152.
3. Pérez, I., 1998. "Fabricación de papel a partir de madera de olivo". Tesis doctoral. Departamento de Ingeniería Química. Universidad de Córdoba.
4. Gilarranz, M.A., Oliet, M., Rodríguez, F., Tijero, J., 1998. Etanol-Water Pulping. Cooking Variables Optimization. Canadian J. Chemical Engineering. 76 (2), 253-260.
5. López, F., Pérez, A., García, J.C., Feria, M.J., García, M.M., Fernández, M., 2011. Cellulosic pulp from Leucaena diversifolia by soda-ethanol pulping process. Chemical Engineering Journal. 166, 22-29.
6. Shukry, N., Elmeadawy, S.A., Nassar, M.A., 1992. Pulping with Organic Acids: 3. Acetic Acid Pulping of Bagasse. Journal Chemistry Technology and Biotechnology. 54 (2) 135-143.
7. Wallis, A.F.A., 1978. Wood pulping with mono- di- and triethanolamine.APPITA. 31 (6), 443-448.
8. Wallis, A.F.A., 1980. Wood pulping with monoethanolamine in pressure vessels. APPITA. 33 (5), 351-355
9. Kubes, G.J., Bolker, H.I., 1978. Sulfur-free delignification. I.Alkaline pulping with monoethanolamine and ethylene diamine. Celulose Chemistry and technology. 12 (5), 621-645.
10. Guha, S.R.D., Sirmokadam, N.N., Goudar, T.R., Dhopeshwar, R., 1987. Pulping of rice straw by pollution-free organosolv process. IPPTA. 24 (1), 24-26.
11. Jiménez, L., Rodríguez, A., Calero, A.M., Eugenio, M.E., 2004. Use of ethanolamine–soda–water mixtures for pulping olive wood trimmings. IChemE: Chemical Engineering Research and Desing. 82 (A8), 1037–1042.
12. Jiménez, L., Angulo, V., Caparrós, S., Pérez, A., Ferrer, J.L., 2007a. Neural fuzzy modeling of ethanolamine pulping of vine shoots. Biochemical Engineering Journal. 34, 62–68.
13. Jiménez, L., Rodríguez, A., Serrano, L., Moral, A., 2008. Organosolv ethanolamine pulping of olive wood: Influence of the process variables on the strength properties. Biochemical Engineering Journal. 39, 230–235.
14. Rodríguez, A., Serrano, L., Moral, A., Jiménez, L., 2008. Pulping of rice straw with high-boiling point organosolv solvents. Biochemical Engineering Journal. 42, 243–247.
15. Rodríguez, A., Sánchez, R., Ferrer, A., 2011. Simulatión of Hesperaloe funifera diethanolamine pulping by polynomial and neural fuzzy models. IChemE: Chemical Engineering Research and Desing. 89, 648-656.
16. Barberà, L., Pèlach M.A., Pérez, I., Puig, J., Mutjé, P., 2011. Upgrading of hemp core for papermaking purposes by means of organosolv process. Industrial Crops and Products. 34, 865-872.
17. Obst, J.R., Sanyer, N., 1980. Effect of quinones and amines on the cleavage rate of Beta-O-4 ethers in lignin during akaline pulping. TAPPI Journal. 63 (7), 111-114.
18. Salehi, K., Kordsachia, O., Patt, R., 2014. Comparison of MEA/AQ sods and soda/AQ pulping of wheat and rye straw. Industrial Crops and Products. 52, 603-610.
19. Dence, C.W., Reeve, D.W., 1996. Pulp bleaching. principles and practice. TAPPI Press. Atlanta.
20. Ramos, E., 2003. Blanqueo ECF y TCF de pastas celulósicas de abacá, Tesis doctoral. Universidad de Córdoba.
21. Jiménez, L., Ramos, E., Torre, M.J., Pérez, I., 2007b. Bleaching of abaca (Musa Textilis Nee) soda pulp with sodium perborate. Afinidad. 64 (530), 479-485.
22. Varennes, S., Deneault, C., Partenteau, M.M., 1996. Bleaching of thermomechanical pulp with sodium perborate. TAPPI Journal. 79 (3), 245-250.

23. García, C., Poveda, P., Villar, J.C., 2000. Blanqueo en una sola etapa de alto rendimiento de Eucaliptus Globulus con perborato sódico. Investigación y Técnica del Papel. 143, 55-65.
24. Leduc, C., Launois, A.M., Chabot, B., Daneault, C., 2003. Use of oxidizing agents in the deinking of old newspapers: activated peroxide, perborate-efficiency and impact on environmental. Progress in Paper Recycling. 12 (4), 10-15.
25. Dimitris, Z.L., Argylopoulos, S., 1998. Maintaining the brightness of mechanical pulps with solid state perborate bleaching. Holzforschung. 52 (3), 319-324.
26. Yuan, Z., Ni, Y., Van Heiningen, A., 1998. A Kinetic Model for Peracetic Acid Brighning of an Ozone Delignified Softwood Kraft Pulp. J. Wood Chem. Tecnol. 18 (1), 83-105.
27. TAPPI Standards, 1997. TAPPI Test Methods. Atlanta
28. Wise, L.E., Murphy, M., D'Adieco, A., 1946. Chlorite Holocellulose, its fractionation and beating on summative wood analysis and on studies on the hemicelluloses. Paper Trade Journal, 122 (2), 35.
29. Normas UNE AEN/CTN 57 Celulosa y Papel ASPAPEL. Asociación Española de Normalizacion y Certificación (AENOR)
30. Montgomery, D.C., 1991. Diseño y análisis de experimentos. Grupo Editorial Iberoamericana. Mexico.
31. Press, W.H., Teukolsky, S.A., Vetterling, W.T., 1992. Flannery, B.B. Numerical recipes in C: The art of scientific computing; Cambridge University Press; Cambridge.
32. More, A., Toraldo, A., 1989. Algorithms for bound constrained quadratic programing problems. Numerische Mathematik. 55, 377-400.