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Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

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R. Yáñez^a; J. L. Alonso^a; J. C. Parajó^a

^a Chemical Engineering Department, Faculty of Science, University of Vigo (Campus Ourense), Ourense, Spain

Online publication date: 06 March 2003

To cite this Article Yáñez, R. , Alonso, J. L. and Parajó, J. C.(2003) 'Totally Chlorine Free Bleaching of Organosolv Pulps', *Journal of Wood Chemistry and Technology*, 23: 2, 161 – 178

To link to this Article: DOI: 10.1081/WCT-120021923

URL: <http://dx.doi.org/10.1081/WCT-120021923>

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY

Vol. 23, No. 2, pp. 161–178, 2003

Totally Chlorine Free Bleaching of Organosolv Pulps

R. Yáñez, J. L. Alonso,* and J. C. Parajó

Chemical Engineering Department, Faculty of Science,
University of Vigo (Campus Ourense),
Ourense, Spain

ABSTRACT

*Populus tremula** *tremuloides* wood samples were processed in acetic acid–water–HCl media (Acetosolv pulping) and then subjected to totally chlorine free (TCF) bleaching sequences in order to obtain dissolving grade pulps. Several bleaching sequences (ZQP₁P₂, EOQP₁P₂, EOPaaQP₁P₂, and EOZQP₁P₂) were assayed for this purpose. The best results corresponded to an EOZQP₁P₂ sequence, which led to pulps suitable for the manufacture of viscose and cellulose nitrate.

Key Words: TCF; Bleaching; Organosolv pulps; Aspen; Acetosolv pulps; Dissolving pulps.

*Correspondence: Dr. José L. Alonso, Assistant Profesor of Chemical Engineering, Chemical Engineering Department, Faculty of Science, University of Vigo (Campus Ourense), As Lagoas, 32004, Ourense, Spain; Fax: +34 988 38 70 01; E-mail: xluis@uvigo.es.



INTRODUCTION

The world's leading pulping method is the kraft process, which utilizes Na_2S and NaOH as the pulping chemicals and which produces pulps of good quality from a variety of raw materials within a wide range of quality specifications. The main drawbacks of this process are the resistance of the pulps to bleaching and the utilization of sulfur-containing chemicals, which can cause odoriferous emissions.^[1-3]

Organosolv pulping, based on the utilization of organic solvents as pulping agents, provides an interesting alternative to the current commercial technologies. The Acetosolv process (based on the utilization of HCl-catalyzed acetic acid media) has received attention because of its ability to cause extensive removal of both lignin and hemicelluloses under mild conditions, with no significant cellulose degradation. This technology has been successfully assayed on a variety of lignocellulosic materials such as hardwoods and softwoods^[4-7] and has shown a number of favorable features. For example, acetic acid is a process-derived product (generated by hydrolysis of acetyl groups), hemicelluloses are partially converted into marketable chemicals (sugars or furfural, depending on the severity of the pulping conditions), and the solubilized lignin fragments are sulfur-free and can be recovered by precipitation upon water addition.^[8]

The ability of this technology to effect extensive delignification and hemicellulose removal raises the possibility of developing a process for making pulps which can be used to manufacture cellulose derivatives such as carboxymethylcellulose, cellophane, viscose, or cellulose acetate. The suitability of a given pulp for the manufacture of cellulose derivatives depends on a number of quality parameters, which must reach target values dependent on the desired end product. For example, the manufacture of cellulose acetate requires low contents of xylan (<3%) and mannan (<2%)^[9-12] and intrinsic viscosities above 500 mL/g^[13], whereas hemicellulose contents as high as 7% with viscosities in the range 500–600 mL/g are acceptable for the manufacture of viscose or cellulose nitrate.^[9]

Bleaching the pulps to reach the quality needed for a given application requires sequential treatments with a variety of chemicals (with the possible participation of enzymes) in order to remove the residual hemicelluloses and lignin as well as other chromophores. Traditional bleaching technologies involve the utilization of chlorinated chemicals, which can lead to the formation of environmentally hazardous chlorine-containing compounds. This situation has fostered the development of totally chlorine free (TCF) bleaching sequences that employ environmentally friendly chemicals (such as ozone, hydrogen peroxide, peracids, and oxygen) to achieve the expected quality standards.^[10,13]



This work deals with the development of TCF bleaching sequences suitable for the manufacture of high quality pulps from Acetosolv-delignified aspen wood.

EXPERIMENTAL

Raw Material

Chips of *Populus tremula** *tremuloides* wood were kindly provided by the Federal Research Centre of Forestry and Forest Products, Institute of Wood Chemistry and Chemical Technology of Wood, Hamburg, Germany.

Acetosolv Pulping of Wood

Delignification treatments were carried out under selected conditions reported elsewhere.^[4] Table 1 shows the operational conditions used in pulping, as well as data concerning pulp yield and pulp composition.

Table 1. Operational conditions employed in the acetosolv processing of aspen wood and data concerning pulp yield, pulp composition, and physicochemical characteristics of pulp.

a) Operational conditions	
Temperature (°C)	120
Acetic acid (weight percent of liquor)	80
Reaction time (min)	40
HCl (weight percent of liquor)	0.3
Liquor to wood ratio (g/g)	8.3
b) Experimental data	
Pulp yield (% o.d. basis)	49
Pulp composition	
Cellulose (% o.d. basis)	81.8
Xylan (% o. d. basis)	6.2
Klason lignin (% o.d. basis)	1.5
Acetyl groups (% o.d. basis)	6.0
Intrinsic viscosity (mL/g)	796
Alkaline resistance R10 (%)	79.2
Alkaline resistance R18 (%)	86.5
Brightness (%)	20.0



Bleaching of Pulp

Ozone Treatment (Z Stage) in Acetic Acid or Aqueous Media

The Z stage corresponding to the first step of a ZEQP₁P₂ sequence was carried out in acetic acid medium. The Acetosolv pulp sample was suspended in glacial acetic acid at 5% consistency and the pH was adjusted to 2 by addition of concentrated sulfuric acid. The pulp was filtered to reach 35% consistency, fluffed in a laboratory mill and treated with ozone at room temperature at the charges listed below. The Z stage corresponding to the EOZQPP sequence was carried out in an aqueous medium using a similar procedure in which the pulp was initially suspended in water instead of acetic acid.

Alkaline Extraction (E Stage)

Pulps were treated with NaOH solutions (at 1–9% charges) in sealed polyethylene bags immersed into a shaking bath under a variety of operational conditions (see below). After treatment, the pulps were filtered and washed with distilled water.

Chelation Treatment (Q Stage)

Pulps were mixed with EDTA (at a charge of 0.3 g/100 g of dry pulp) and deionized water to reach 2% consistency. After pH adjustment to 6 with 1 M NaOH and 1 M H₂SO₄, the suspension was kept for 60 min at 60°C in a stirred glass reactor, and then filtered and washed with deionized water.

Alkaline Peroxide Bleaching (P Stage)

Pulps were mixed with MgSO₄ (0.5% pulp basis), NaOH (at 1.5–2.0% charges, see below), H₂O₂ (see below), and deionized water to reach 10% consistency. The pH was adjusted to 11 with 1 M NaOH and 1 M H₂SO₄ and the reaction was carried out at 70°C in sealed polyethylene bags immersed in shaking baths for the desired reaction time (see below).



Organosolv Pulps

165

Oxygen Delignification (O Stage)

Pulps were mixed with 0.5 g $\text{MgSO}_4/100$ g of dry pulp, NaOH (at 1–4% charges, see below), and water to reach 10% pulp consistency and placed into a 4.5 L stainless steel reactor, which was pressurized with oxygen (600 kPa) and kept at 95°C for 60 min.

Peracetic Acid Bleaching (Paa Stage)

Pulps were bleached with commercial peracetic acid (39% weight percent in acetic acid solution) and water at 10% consistency. The peracetic acid concentrations employed are listed below. After pH adjustment (see below), the suspensions were placed into plastic bags and immersed in a water bath at 70°C for 60 min.

Analytical Characterization of Pulps

The analytical assays were performed according to the following procedures: moisture, ISO 638:1978 method; quantitative acid hydrolysis, TAPPI T13m method; Klason lignin, gravimetric determination of the insoluble residue coming from above quantitative acid hydrolysis; cellulose (as glucan), by HPLC determination of the glucose contained in hydrolyzates from the TAPPI T13m assay; xylan, by HPLC determination of the xylose contained in hydrolyzates from the TAPPI T13m assay; *kappa* number, ISO 302:1981 method; viscosity, SCAN C15:62 method; alkaline resistances (R10 and R18 tests), ISO 699:1982 method; saponifiable groups (as NaOH equivalent), by KOH–ethanol saponification.

RESULTS AND DISCUSSION

The effect of the operational conditions on the Acetosolv delignification of aspen wood were established in a previous study.^[4] The pulp to be used in bleaching was obtained under conditions leading to a minimum lignin content. Table 1 summarizes the operational conditions employed in pulping as well as experimental data concerning pulp yield, pulp composition, and physicochemical characteristics of the pulp. The most remarkable feature of this pulp was its relatively high content of acetyl groups, generated by esterification of cellulose with acetic acid. Similar behavior has been reported in related studies dealing with organic



acid-based processes.^[13–15] In order to meet the target values for quality parameters, acetyl group removal had to be accomplished during the alkaline stages included in bleaching.

In the same way, the unbleached pulp had a xylan content of 6.8% that had to be decreased. Considering the intrinsic viscosity of the unbleached pulp (800 mL/g) and the minimum desirable viscosity of a fully bleached pulp (in the vicinity of 500 mL/g), it can be seen that a narrow range of viscosity loss in the bleaching sequence is allowed. Because of this, the pulp is hardly suitable for manufacturing cellulose derivatives requiring very high purity (such as cellulose acetate), and the present research is oriented towards the production of a bleached pulp useful for dissolving pulp applications that need lower quality standards (for example, viscose or cellulose nitrate).

Development of a ZEQP₁P₂ Bleaching Sequence

Ozone treatments in acetic acid media (Z stage) were used to remove the residual lignin. With this procedure, interstage washing with water is avoided, and the delignification is improved by the higher ozone solubility in acetic acid relative to aqueous media. Experimental work was carried out under conditions of temperature, pH, and consistency selected from literature data (see the methods section for operational conditions). The ozone charge was an operational variable within the range of 2–5 kg/metric ton o.d. pulp. Table 2 shows the corresponding experimental data. The residual lignin content decreased steadily with the ozone charge, whereas minor effects were observed on the amount of cellulose, xylan, and acetyl groups. In agreement with related literature data,^[1,14] significant viscosity losses (about 150 mL/g) were observed in all the experiments, a finding that can be ascribed to the decrease in the polymerization degree of cellulose chains by oxidative degradation reactions. However, the cellulose degradation could be lower than suggested by the viscosity data, because the carbonyl groups generated during the ozone treatments may cause additional depolymerization of cellulose chains during the viscosity determinations (which are carried out in alkaline media and in the presence of cupriethylenediamine).^[16] On the basis of the experimental results shown in Table 2, the conditions of experiment Z3 were selected for further experimentation.

Alkaline treatments of the pulps (E stage) cause removal of acetyl groups (which would be of interest only for the manufacture of cellulose acetate) as well as further delignification. A set of 16 experiments with incomplete factorial structure was carried out at 12.5% consistency to



Organosolv Pulps

167

Table 2. Ozone charges employed in ozone treatments in acetic acid media and properties of pulps obtained in experiments.

Exper. code	Ozone charge (kg/metric ton)	Cellul. (%)	Xylan (%)	Acetyl groups (%)	Klason lignin (%)	Intrinsic visc. (mL/g)	Alk. resist. R10 (%)	Alk. resist. R18 (%)
Z1	2	88.2	5.7	6.7	1.4	642	84.7	88.5
Z2	3	88.5	5.6	6.7	1.0	626	85.5	89.3
Z3	4	89.0	5.4	6.7	0.7	666	86.1	90.3
Z4	5	87.6	5.8	6.9	0.5	574	85.7	88.9



assess the effects of temperature (in the range 50–90°C), reaction time (in the range 60–120 min), and alkali concentration (in the range 1–5 g/100 g o.d. pulp) on pulp yield, pulp composition, and physicochemical properties of pulp (see Table 3). All the experiments led to pulps with Klason lignin contents in the range 0.3–1.6%, and brightnesses in the range 40–59.9% ISO. The extent of acetyl group removal increased with the alkali charge, but incomplete removal of acetyl groups was observed even in the experiments carried out with the highest alkali loading. The effects on the residual xylan were of minor importance (a finding in agreement with results reported in the literature by Saake et al.^[14]), where the reduction in viscosity depended on the operational conditions and the alkaline resistances increased owing to the removal of acetyl groups.

A comparative evaluation of the characteristics of pulps obtained in the experiments showed that the best conditions corresponded to experiments E9 and E17 (Table 3a), because of their comparatively low contents of acetyl groups, high brightnesses, good alkali resistances, and acceptable viscosities.

Based on the above findings, additional experiments (see Table 3b) were carried out at the same temperature and for the same reaction time as in experiments E9 and E17, but with higher alkali loadings to achieve increased purification. The experimental results (experiments E23 to E26 of Table 3b) showed that the new operational conditions resulted in increased removal of acetyl groups, higher brightnesses, and better alkaline resistances than the first set of experiments. In the assays of Table 3b, the intrinsic viscosity decreased slightly respect to the previous experiments, a finding already reported for alkaline processing of ozone-treated pulps.^[17–19]

A chelating step (Q stage) was performed before the alkaline peroxide stages in order to remove metal ions able to catalyze the decomposition of hydrogen peroxide to hydroxyl radicals, which react in a non-selective way leading to hydrogen peroxide consumption^[20] and significant cellulose depolymerization.^[21,22] The experimental variables in this stage were fixed as indicated in the methods section, and the resulting pulp was subsequently subjected to two sequential peroxide treatments.

The first peroxide stage (denoted P₁) was studied in a set of eight experiments (denoted P11–P18) in which the three most influential operational variables (NaOH charge, H₂O₂ charge, and reaction time) were assessed at two levels (see Table 4). The ranges for these variables (1.5 or 2 g NaOH/100 g o.d. pulp, 1 or 2 g H₂O₂/100 g o.d. pulp, and 1 or 2 h of treatment) were fixed according to reported results for related experiments^[1,22] and our own experience. In most of the experiments included in Table 4, the Klason lignin contents of the pulps were 0.7.



Organosolv Pulps

169

In comparative terms, the best pulp corresponded to experiment P14, which compares favorably with P15 in terms of viscosity (620 mL/g compared to 593 mL/g), and with the rest of experiments in brightness (80.5% compared to 74.5–79.8%).

In order to reach the final brightness gain, the pulp obtained in experiment P14 was subjected to a second peroxide treatment (denoted P₂) under the same conditions as stage P₁ (1.5 g NaOH/100 g o.d. pulp and 2 g H₂O₂/100 g o.d. pulp for 2 h). With the implementation of the P₂ stage, only minor changes were observed in the chemical composition of pulp, but the viscosity decreased to 590 mL/g and the brightness gain was poor (final brightness, 82.7%). Since additional treatments would lead to pulps with viscosities too low for practical purposes, this stage was considered to be the end of the bleaching sequence, and it was assumed that improvement of the experimental results would require a first stage of a nature which would allow harsher operation in the subsequent bleaching stages. As a summary of the experimental work, Fig. 1 shows the evolution of the main pulp parameters along the bleaching sequence ZEQP₁P₂.

Development of an EOQP₁P₂ Bleaching Sequence

Starting from the unbleached pulp, the alkaline treatment corresponding to the E stage was carried out using 4 g NaOH/100 g pulp (a charge slightly lower than the optimum value determined in the previous section) because the subsequent oxygen treatment to be applied in this case is also carried out in alkaline medium. The E stage was performed at 60°C for 60 min at a consistency 12.5%. The pulp obtained in this assay had a high cellulose content (91.2%) and a typical xylan content (6.2%). The Klason lignin content (1.7%, corresponding to a *kappa* number of 5.8) and the viscosity (792 mL/g) were promising for further bleaching, as well as the ISO brightness (38.3%). The alkaline resistances (R₁₀ = 86.7%, R₁₈ = 92.1%) were lower than expected, a finding that can be explained (at least in part) by the presence of residual acetyl groups (2.3%).

In the subsequent oxygen treatment (O stage), the effects of the most influential operational variable (the NaOH charge) on the characteristics of pulps were measured in a new set of experiments in which the alkali loading was varied from 1 to 4 kg/kg o.d. pulp. The results (Fig. 2) show that the increased alkali charges resulted in increased brightness and improved R₁₈ alkaline resistances, a fact related to the decreased xylan content of the pulps. The viscosities of the pulps were significantly

**Table 3.** Operational conditions and experimental results concerning the alkaline processing of ozone-treated pulps (pulp consistency = 12.5%).

a) Study of the effects of the main operational variables

Exper. code	T (°C)	Time (min)	Alk. charg. (% o.d. p.)	Pulp yield (%)	Cellulose (%)	Xylan (%)	Acetyl groups (%)	Klason lignin (%)	Intr. visc. (mL/g)	R10 (%)	R18 (%)
E7	50	60	3	100	92.7	6.4	3.1	1.3	594	90.5	90.1
E8	50	90	1	100	90.2	6.3	4.7	1.2	613	87.2	88.6
E9	50	90	5	98.2	92.8	6.5	1.5	0.9	617	91.0	90.1
E10	50	120	3	100	92.1	6.2	2.4	1.3	622	90.1	89.3
E11	70	60	1	100	87.6	6.0	5.5	0.3	574	88.3	87.8
E12	70	60	5	98.0	92.4	6.5	1.9	1.1	610	91.8	91.1
E13	70	90	3	100	91.6	6.5	3.7	1.6	598	89.9	89.6
E14	70	90	3	99.4	91.8	6.4	3.5	1.4	603	88.4	88.9
E15	70	90	3	100	90.9	6.4	3.6	1.4	614	90.6	89.3
E16	70	120	1	100	89.0	6.3	5.0	1.1	605	88.2	87.1
E17	70	120	5	97.0	92.0	6.3	0.9	1.6	626	91.8	92.2
E18	90	60	3	99.6	91.2	6.4	3.6	1.0	616	89.3	89.7
E19	90	90	1	100	88.7	6.2	5.9	1.3	610	88.1	87.6
E20	90	90	5	96.7	92.7	6.2	2.4	1.4	625	91.2	91.5
E21	90	120	3	98.4	90.7	6.3	3.8	0.9	618	89.6	90.4
E22	70	120	3	99.2	90.9	6.4	3.3	1.0	614	90.2	89.6



Organosolv Pulps

171

b) Complementary experiments

Exper. code	T (°C)	Time (min)	Alk. charg. (% o.d. p.)	Pulp yield (%)	Cellulose (%)	Xylan (%)	Acetyl groups (%)	Klason lignin (%)	Intr. visc. (mL/g)	R10 (%)	R18 (%)	Brightness (%)
E23	70	120	7	100	91.1	5.4	0.2	1.2	573	92.8	93.6	64.4
E24	70	120	9	98.1	91.8	5.1	0.2	1.1	585	92.9	93.7	62.6
E25	50	90	7	100	89.5	6.0	0.7	0.9	573	91.5	91.8	65.1
E26	50	90	9	100	91.1	6.1	0.2	1.5	631	91.8	92.4	64.6

**Table 4.** Operational conditions and experimental results concerning the peroxide bleaching stages of the sequence ZEQP₁P₂.

Exper. code	Alkali charge		Time (h)	Pulp yield (%)	Cellulose (%)	Xylan (%)	Acetyl groups (%)	Klason lignin (%)	Intr. viscosity (mL/g)	R10 (%)	R18 (%)	Brightness (%)
	(g/100 g o.d. pulp)	Peroxide charge (g/100 g o.d. pulp)										
P11	1.5	1	1	97.6	86.3	5.3	0.7	0.4	640	90.4	94.5	74.5
P12	2	1	1	100	87.6	5.6	0.8	0.3	625	90.5	94.4	75.8
P13	1.5	2	1	100	85.6	5.5	0.6	0.4	673	89.9	93.5	78.7
P14	1.5	2	2	99.4	84.6	5.5	0.5	0.9	620	90.1	95.4	80.5
P15	2	2	2	99.6	81.7	5.2	0	0.7	593	90.4	95.6	80.9
P16	2	2	1	99.9	84.2	5.4	0	0.6	627	90.4	94.7	77.6
P17	1.5	1	2	99.5	84.1	5.4	0	0.3	623	90.5	94.7	78.3
P18	2	1	2	98.7	84.5	5.4	0	1.2	599	90.9	94.6	79.8

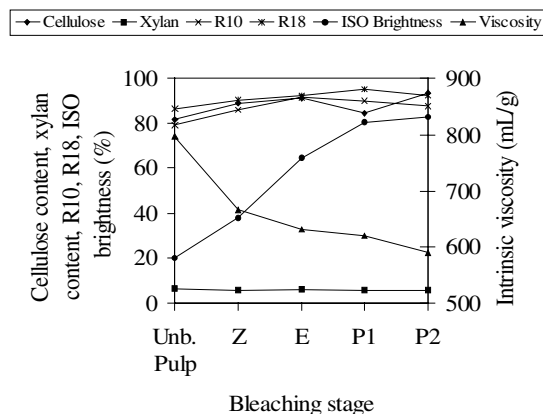


Figure 1. Course of the pulp properties along the bleaching sequence ZEQP₁P₂ (individual stages carried out under the best conditions explored).

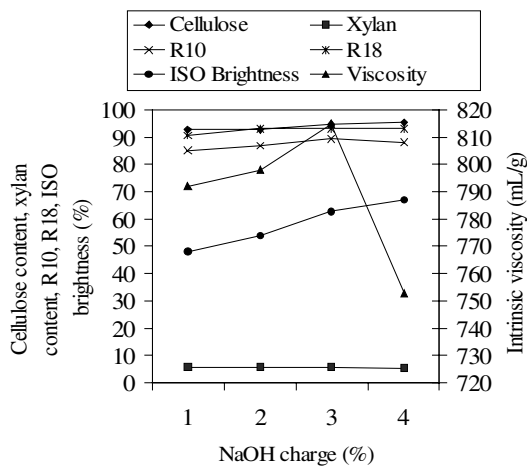


Figure 2. Effect of the NaOH-loading employed in the O stage on the physico-chemical properties of pulps.

affected in the experiment performed under the most severe conditions assayed, in which a viscosity loss of 50 mL/g was determined.

On the basis of the results shown in Fig. 2, the pulp corresponding to the experiment O4 (with favorable brightness and comparatively low xylan content) was selected for further experimentation.



In order to increase the brightness, the selected pulp was subjected to a Q stage and two P stages (P_1 and P_2) under the same conditions employed in the sequence $ZEQP_1P_2$. After this sequence, the final pulp presented 80.2% ISO brightness at 668 mL/g viscosity, with R10 and R18 alkaline resistances of 89.3 and 93.8%, respectively. Even though these results were slightly better than those obtained in the $ZEQP_1P_2$ sequence, with a similar final brightness, the quality specifications were too poor for dissolving-grade pulps, particularly in terms of xylan content and brightness. It can be noted that both parameters can be interdependent: for example, according to literature data, the presence of xylan can prevent the removal of lignin by a number of mechanisms.^[23] Additional experiments (data not shown) carried out with xylanases (Pulpzyme HC, Novo Nordisk Bioindustrial, Madrid, España) under the conditions recommended by the supplier did not succeed, probably because of the structure of samples. Based on these results, a new bleaching sequence (including both alkaline and oxidative acid stages) was assayed.

Development of an $EOPaaQP_1P_2$ Bleaching Sequence

The novelty of this sequence lies in the utilization of a peracetic acid stage (denoted Paa). For this purpose, the unbleached pulp was first treated with NaOH and oxygen under the same conditions employed in the previous sequences, and the peracetic acid treatment was assayed at fixed values of temperature, pulp consistency, and reaction time. Four experiments were performed (see Table 5) at pH 6 or 8 and peracetic acid charges of 0.5 or 1 g/100 g o.d. pulp. Analysis of results showed that the limiting parameter in these kinds of treatments was the viscosity loss

Table 5. Operational conditions and experimental results concerning the peracetic acid stage of the bleaching sequence $EOPaaQP_1P_2$.

Exper. code	Peracetic acid charge		Cellulose (%)	Xylan (%)	Klason lignin (%)	Intr. viscosity (mL/g)	Brightness (%)
	(g/100 g o.d. pulp)	pH					
Paa1	1	6	95	5.0	1.2	544	68
Paa2	1	8	96	5.9	0.8	551	65
Paa3	0.5	6	92	5.6	1.2	568	70
Paa4	0.5	8	92	5.6	0.8	580	68



Organosolv Pulps

175

(about 180 mL/g), a fact that can be ascribed to the cellulose degradation caused by the free radicals formed in the decomposition of peracetic acid.^[24] When the selected pulp (experiment Paa3) was subjected to the rest of the bleaching stages (Q, P₁, and P₂) under the same conditions specified above, a pulp with 83% ISO brightness and 686 mL/g viscosity was obtained. These results were better than the ones obtained in the previous cases, but the brightness was still below the target value for dissolving pulps. Considering the benefits obtained when an oxidative stage was coupled with alkaline treatments, the replacement of the peracetic acid step by other oxidative stage (ozone treatment) was considered as a possible strategy for improvement.

Development of an EOZQP₁P₂ Bleaching Sequence

Peracetic acid and ozone are oxidative chemicals employed in TCF bleaching with similar purposes. In this case, the EOZQP₁P₂ sequence is a modification of the EOQP₁P₂ sequence assayed before, in with an intermediate Z stage was inserted. The similarity between the effects reached in ozone and peracetic acid treatments is confirmed in this work by the closely related brightnesses achieved after EO-treatments followed either by one Paa or Z stage. Figure 3 shows the course of the pulp properties along the bleaching sequence. The final results achieved (brightness near

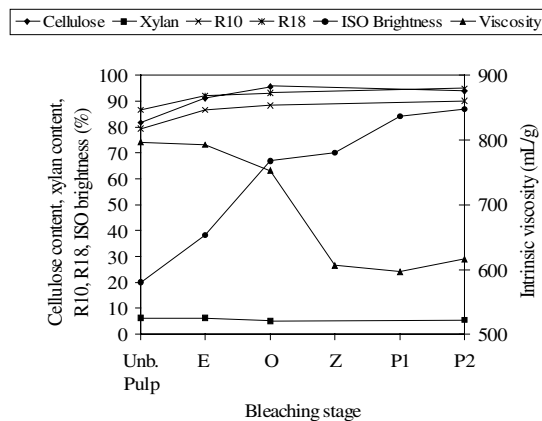


Figure 3. Course of the pulp properties along the bleaching sequence EOZQP₁P₂ (individual stages carried out under the best conditions explored).



90% ISO, intrinsic viscosity above 600 mL/g, R18 alkaline resistance of 95% and 5% residual xylan) meet the requirements to necessary for a substrate for the manufacture of cellulose derivatives such as cellulose nitrate or viscose.

CONCLUSIONS

Selected TCF bleaching sequences have been evaluated for the manufacture of dissolving grade pulps from Acetosolv-delignified aspen. Individual steps of ozone treatments (Z stages, carried out in acetic acid or aqueous media), alkaline extractions (E stages), oxygen delignification (O stages), chelating treatments (Q stages), peracetic acid steps (Paa stages), and alkaline hydrogen peroxide treatments (P stages) have been assayed in four selected bleaching sequences (ZEQP₁P₂, EOQP₁P₂, EOPaaQP₁P₂, and EOZQP₁P₂). The best results were obtained with the last sequence, in which a pulp meeting the target values for manufacture of some cellulose derivatives (such as cellulose nitrate or viscose) was obtained.

ACKNOWLEDGMENTS

The authors are grateful to the “Comisión Interministerial de Ciencia y Tecnología” of the Spanish Ministry of Education for the financial support of this work (in the scope of the Research Project “Development of Processes with Low Environmental Impact for the Manufacture of High-Quality Cellulose Pulps,” reference QUI99-0346).

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**Organosolv Pulps**

177

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