BLEACHING OF SOFTWOOD KRAFT PULP WITH OXYGEN AND PEROXIDE

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The bleaching of spruce kraft pulp with oxygen and peroxide according to the (OP)-Q-(EOP)-P sequence is investigated. Pulp brightness and properties highly depend on unbleached pulp Kappa number and on the residual lignin content after the EOP stage. At the same time, the final P stage conditions strongly influence the bleaching results. In order to achieve satisfactory pulp brightness, it is necessary to split the chemical charge in the P stage, so that the peroxide is added in two or three consecutive steps. The successive addition of peroxide significantly improves pulp brightness in the P stage.

Keywords: pulp bleaching, oxygen, hydrogen peroxide

INTRODUCTION

Oxygen and peroxide are widely used today in pulp bleaching, in elementally chlorine free (ECF) and totally chlorine free (TCF) sequences. Over the last decades, oxygen delignification has been the most important way of lignin removal before the subsequent pulp bleaching. At present, there are many variants of oxygen delignification intended to eliminate the lignin on a large scale with minor cellulose degradation.[1] One-stage oxygen delignification was first developed, allowing the decrease of the lignin content with 35-50%.[2] Later, the researchers' attention was focused on two-stage technologies, allowing the reduction of the lignin content by 60-70%.[2] An example is represented by the OxyTrac process, which contributes to high delignification, ≈70% for softwood pulp, with good selectivity.[3] Also, it was found that a small addition of peroxide, besides oxygen, determines enhanced lignin removal.[4]

The chief benefits of oxygen delignification are related to its favorable effects on the environmental parameters of the bleaching plant. In addition, this process allows a substantial reduction of water consumption in the pulp mill and the recovery of chemicals from wastewater flows.[5,6] The use of oxygen is rational for eliminating chlorine-based compounds from bleaching sequences. In this situation, bleaching with peroxide and ozone must be performed. Ozone is well-known for its high oxidation potential and good selectivity under appropriate conditions,[7] but this reagent needs to be manufactured in the pulp mill and it is expensive. In addition, the implementation of ozone bleaching and delignification requires supplementary capital costs.[6]

Hydrogen peroxide is less reactive than ozone. This reagent must be purchased from producers and does not require important modifications of the bleaching plant. Peroxide is easier to manipulate and in many pulp mills there is necessary experience regarding peroxide bleaching.

In this context, oxygen and peroxide show the highest potential from the point of view of the benefits related to pulp bleaching. Therefore, it is important to estimate if the softwood kraft pulp can be bleached with oxygen and peroxide, which are the results and the reagent consumption, as well. The aim of the paper is to determine the oxygen and peroxide bleaching conditions of spruce kraft pulp.

EXPERIMENTAL

Bleaching experiments were performed in the laboratory, using industrial spruce kraft pulp from SOMES-Dej pulp mill, Romania.

The unbleached pulp kappa number was 24.6 and intrinsic viscosity – 1050 dm^3/kg. Oxygen delignification (single- and two-stages) was carried out in a rotating stainless steel autoclave at 0.5 MPa oxygen pressure, 10% pulp consistency, 60 and 90 minutes respectively, at 105 °C.

Oxygen-peroxide delignification was performed in the same manner, using a peroxide charge of 10 kg/t of pulp and 0.2 MPa oxygen pressure. The Q-stage was carried out with 3 kg/t EDTA at 6% consistency, 120 minutes at 60 °C. The initial pH of the Q-stage was 5.5 (H_2SO_4). The EOP stage was carried out with oxygen (0.2 MPa), peroxide (2-10 kg/t), and retention time 120 minutes at 70 °C. The final peroxide stage was performed with 10, 30 and 50 kg/t H_2O_2, 30-360 minutes at 80 °C. D stage was performed using 10 kg/t ClO_2 at 10% consistency, 70 °C and 180 min. The content of transitional metals in the investigated pulps has not been determined. The conditions of the bleaching stages are summarized in Table 1. The pulps were analyzed to determine kappa number (ISO 302:2004), viscosity (ISO 5351:2010) and brightness (ISO 2470-1:2009).

Table 1
Conditions for spruce pulp bleaching with oxygen and peroxide*

Bleaching stage	Chemical charge (kg/t)	NaOH charge (kg/t)	Temperature (°C)	Retention time (minutes)
Oxygen	0.5 MPA	18	105	60-90
Chelation	EDTA, 3 kg/t	H_2SO_4, pH 5.5	60	120
Oxidative alkali	Oxygen 0.2 MPa			
extraction	Peroxide 2-10	18	70	120
Peroxide	5-50	20-30	80	30-180
Chlorine dioxide	10	-	70	180

*Consistency: Q-stage 6%; O-, EOP- and P-stages 10%

Table 2
Oxygen delignification stages of spruce kraft pulp

Sequence*	Kappa number	Lignin content reduction, %	Pulp brightness, % ISO	Pulp viscosity, dm^3/kg
O	13.5	45	44.2	940
(OP)	11.5	53.2	50.1	910
O-O	9.5	61	55.0	870
O-(OP)	7.5	70	68.0	830

*Incoming pulp: kappa number 24.6; viscosity 1050 dm^3/kg; Peroxide in (OP): 10 kg/t

RESULTS AND DISCUSSION

The first trials were performed in order to determine the influence of different oxygen delignification methods on lignin removal from unbleached pulp. The results presented in Table 2 show that the delignification degree depends on the number of oxygen stages and on the addition of peroxide.

Thus, single-stage delignification reduces the lignin content by approximately 45% (in the O-stage), and the addition of 10 kg/t peroxide (OP-stage) increases the delignification up to 53%, as well as pulp brightness.

Two-stage oxygen delignification strongly increases the quantity of dissolved lignin, which in the O-(OP) sequence reaches the superior limit of approximately 70% of the initial lignin content. At the same time, pulp brightness increases up to 68%, which represents a high level for this stage of bleaching. Pulp viscosity decreases according to the lignin removal, and as shown in Table 2, the value of this parameter stays above the limit that determines pulp degradation.

After oxygen delignification, the pulps were treated in a Q-stage in order to improve the performance of peroxide bleaching. The addition of 3 kg/t EDTA, at 60 °C, 120 minutes, followed by pulp washing determines a brightness increase of 1.5-2 units in all experiments. After the Q-stage, the pulps were treated in an usual oxidative alkali extraction stage (EOP); the results are presented in Table 3. The performance of the EOP-stage enhances with the increase of peroxide addition, as presented in Figure 1.

The brightness values depend on the pulp treatment before the EOP-stage, and it is obvious that in the last series of experiments (series 4, Figure 1), the highest brightness is obtained (80%

ISO with 10 kg/t peroxide in the EOP-stage). Consequently, the O-(OP)-Q-EOP sequence allows obtaining semibleached pulp with high brightness. The chemical consumption is presented in Figure 2. Based on this prebleaching sequence, final bleaching can be performed either with ClO_2 (ECF sequence), or peroxide (TCF sequence). When using ClO_2, the final pulp brightness depends on the chemical addition, and it is easy to obtain values ranging between 84-86% ISO, as shown in Figure 3.

Table 3
Influence of EOP stage on pulp kappa number and brightness

Prebleaching sequence*	Kappa number		Brightness (% ISO)	
	After Q-stage	After EOP-stage	After Q-stage	After EOP stage
O-Q-(EOP)	13.5	7.5	46.0	60.0
(OP)-Q-(EOP)	11.5	6.8	52.1	66.5
O-O-Q-(EOP)	9.5	5.5	56.8	71.8
O-(OP)-Q-EOP	7.5	3.8	68.8	74.0

*Peroxide in EOP: 4 kg/t

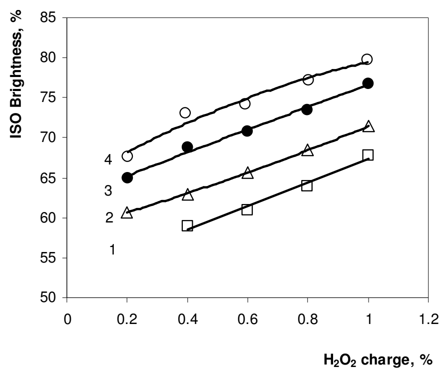

Figure 1: Influence of peroxide addition in EOP-stage on pulp brightness: 1 – O-Q-(EOP); 2 – (OP)-Q-(EOP); 3 – O-O-Q-(EOP); 4 – O-(OP)-Q-(EOP)

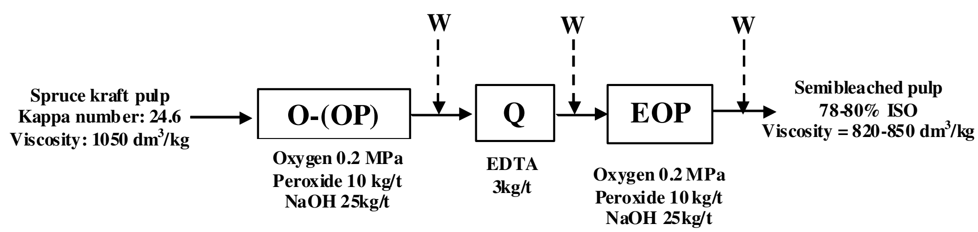

Figure 2: Prebleaching of spruce kraft pulp with oxygen and peroxide (W-interstage pulp washing)

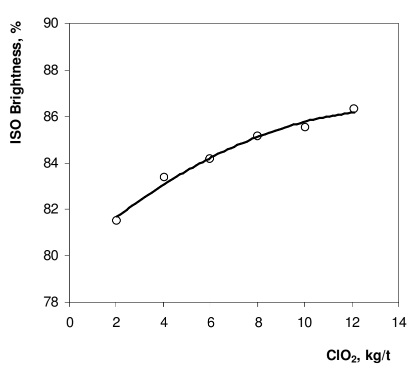

Figure 3: Final bleaching with ClO_2 of O-(OP)-Q-EOP semibleached pulp

If final bleaching is carried out with peroxide, its results will depend on peroxide addition and distribution. Table 4 presents the results obtained for peroxide final bleaching of the pulps prebleached according to the sequences from Table 3. The data in Table 4 indicate that a single peroxide stage is insufficient to reach satisfactory brightness. Even if the most complex bleaching sequence is used, O-(OP)-Q-EOP-P, with a high addition of peroxide (50 kg/t of pulp), the brightness does not exceed 82-83%. This fact shows that the peroxide is not rationally used, and to improve its efficiency, the addition must be distributed in several steps in order to reach a higher concentration of the reagent for the entire bleaching process.

Table 5 presents, comparatively, the results for final bleaching with peroxide added in a single step (P), and in three consecutive steps (P_1-P_2-P_3), without interstage pulp washing. The peroxide addition was the same in both cases, 50 kg/t of pulp. It is obvious that splitting the peroxide addition determines an important increase in pulp brightness. Moreover, the increase in pulp brightness did not lead to an extra loss of pulp viscosity.

The better results obtained through the distribution of peroxide in three consecutive steps are justified by maintaining a higher peroxide concentration in the slurry, for a longer period, and by increasing the reaction time, as shown in Figure 4.

The results from Figure 4 confirm the fact that spruce kraft pulp can be bleached with oxygen and peroxide to satisfactory brightness. One of the possible bleaching sequences is presented in Figure 5. The bleaching sequence shown in Figure 5 might ensure a rational reuse of the filtrates, as suggested in Figure 6. Fresh water is only used for pulp washing in the Q- and P-stages and the filtrate of the P-stage is reused for pulp washing in the EOP-stages. In the same manner, the filtrate of the EOP-stage is carried into the oxygen delignification stage. The acidic filtrate of the Q-stage is sent to the sewer.

Table 4
Final one-stage peroxide bleaching of the spruce Kraft pulp*

Bleaching sequence	Peroxide charge (kg/t)	Pulp brightness (% ISO)	
		After EOP	Final
O-Q-EOP-P	10	60	63.5
	30		68.0
	50		71.5
O(P)-Q-EOP-P	10	66.5	69.0
	30		72.8
	50		76.0
O-O-Q-(EOP)-P	10	71.8	74.0
	30		77.1
	50		79.8
O-O(P)-Q-(EOP)-P	10	74.0	76.8
	30		79.5
	50		82.5

*4 kg/t peroxide in EOP-stage;
peroxide stage: 10% consistency; 80 °C; retention time 120 min; initial pH 11.5

Table 5
Influence of peroxide distribution on the pulp brightness.

Bleaching sequence	Peroxide addition (kg/t)	Pulp brightness (%)	Pulp viscosity, dm^3/kg
O-O(P)-Q-EOP-P	50	82.5	630
O-O(P)-Q-EOP-(P_1-P_2-P_3)	P_1-30	80.0	750
	P_2-10	83.5	670
	P_3-10	86.5	630

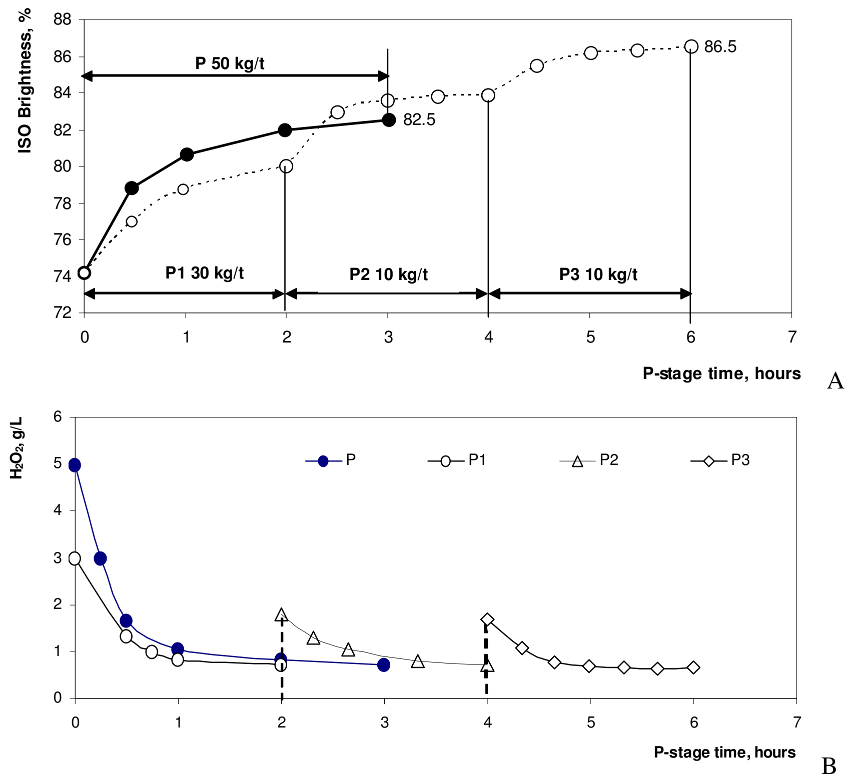

Figure 4: A: Final bleaching with peroxide added in one step (P), and in three consecutive steps (P_1-P_2-P_3); B: Evolution of peroxide concentration during final bleaching with peroxide added in one step and in three consecutive steps

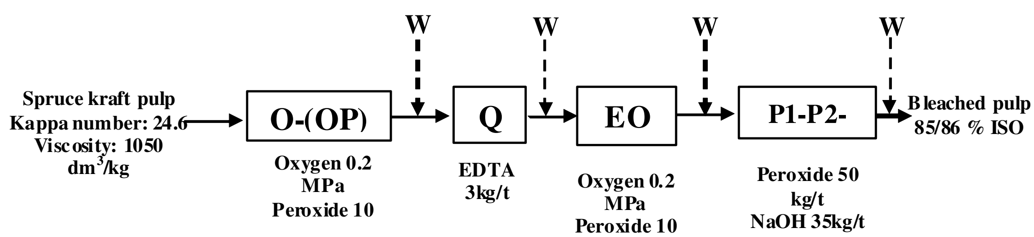

Figure 5: Flowsheet of the bleaching sequence from Table 5

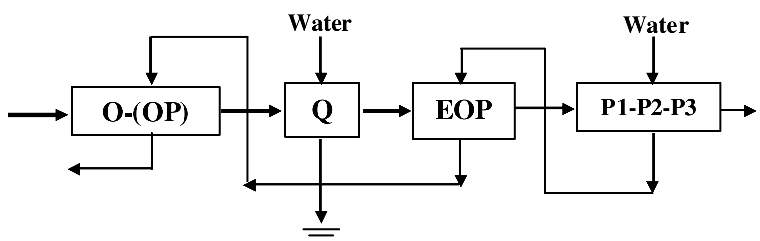

Figure 6: Suggested reuse of filtrates in pulp bleaching with oxygen and peroxide

CONCLUSION

The results presented in this paper prove that spruce kraft pulp can be successfully bleached with oxygen and peroxide. The most important findings are:

- two-stage oxygen delignification with peroxide addition (O-OP) reduces the lignin content in the pulp up to 70%, without significant reduction of pulp viscosity;
- oxidative alkali extraction with oxygen and peroxide (EOP) significantly increases pulp brightness, which reaches 78-80% ISO depending on peroxide addition;
- the best results concerning pulp brightness and peroxide consumption are obtained if the peroxide is distributed in several steps. The brightness increases with 4-5 units in comparison with the case when the peroxide is integrally added at the beginning of the final P bleaching stage.

The sequence O-(OP)-Q-EOP-(P-P-P) is suitable for bleaching spruce kraft pulp to obtain pulp brightness of 85-86% ISO.

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