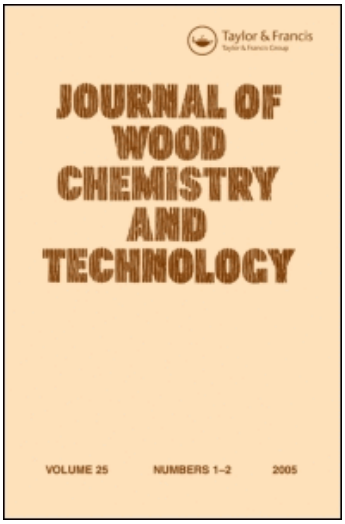

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TCF BLEACHING OF KRAFT PULPS WITH LACCASE AND XYLANASE

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ABSTRACT

The paper shows the results of hydrogen peroxide and ozone bleaching with the use of laccase-mediator-system (LMS) and a combination of laccase and xylanase. The TCF bleaching of birch and pine kraft pulps before as well as after oxygen delignification is particularly effective in the following bleaching sequences: LQPZP, LZQPP and ZLQPP. The pretreatment of pulp with xylanase increases the laccase access to lignin.

INTRODUCTION

A typical pulp obtained by the kraft method contains about 3–5% of residual lignin the removal constitutes the main aim of the bleaching process. Despite the fact that pulp of which fibres have a more developed capillary system than fibres in wood, removal of the residual lignin is made difficult due to its modification during pulping. Many studies including those carried out at the Institute of Papermaking and Printing have confirmed that the use of enzymes, from both hydrolase and oxidoreductase groups, accelerates the delignification process taking place in the subsequent

bleaching with oxygen agents.[1–28] Call was the first who has used laccase in the presence of 1-hydroxybenzotriazole (HBT) for bleaching kraft pulps.[1,2] Since then, various research groups have been focusing their attention on laccase-mediator-system.[3–7] The first paper to examine the interaction between laccase and xylanase was Kristiina Poppius-Levlin, Wei Wang, Marjatta Ranua, Marja-Leena Niku-Paavola, Liisa Viikari.[8] In the research works on the use of enzymes in chemical pulps bleaching it has been proved that the enzymatic treatment allows a reduction in chemical requirement in TCF bleaching.[9–14,23,28] The results of the ESR measurements have confirmed the radical character of the kraft pulp lignin oxidised with laccase. It has been found that, in enzymatic treatment of kraft pulp with laccase in the presence of HBT the highest radical concentration was found at the point of the lowest kappa number.[27,28]

RESULTS AND DISCUSSION

The bleaching of **birch and pine pulps without oxygen delignification**, performed according to various bleaching sequences resulted in a product with a brightness of 70–85% ISO and a kappa number of 8.0–5.0.[23,28] Considering the increase in brightness of birch and pine pulps over the control, the best bleaching sequences with laccase were No. 1–3 and 7–9 (Table 1). The highest brightness was obtained for the sample bleached according to the sequences No. 3 and 9. This brightness (82.3% ISO for birch pulp and 81.9% ISO for pine pulp) was due to the use of laccase and the introduction of the Z stage between two pulp bleaching stages with hydrogen peroxide as well as the use of the chelating agent just before the peroxide stage.

Beneficial effects are due to the introduction of ozone in the first bleaching stage followed by laccase addition. For instance, in the case of birch pulp bleached according to the sequence No. 2 compared to No. 1 (Table 1), there was obtained not only a higher brightness increase by 1.3% ISO in relation to the sequence in which laccase was used before the treatment with ozone, but also a further decreases in kappa number by 0.5 unit. The use of ozone at the beginning of bleaching probably activated lignin increasing its susceptibility to degradation under the influence of laccase.

In the bleaching sequences with laccase and xylanase No. 4–6, the highest increase in brightness, by about 3.6% ISO, in relation to the reference sample and the highest decrease in kappa number by about 0.8–1.2 unit compared to the reference sample were obtained in the scheme No. 5 (Table 1). The pretreatment of pulp with xylanase has freed the fibre surface from some xylan which inhibited the laccase access to lignin and allowed better pulp bleaching with oxygen bleaching species.

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Table 1. Results of the Bleaching of Birch and Pine Kraft Pulp Without Oxygen Delignification

No.	Bleaching Sequence	Kappa Number[1]	ΔKn	Brightness[2] (% ISO)	ΔB (% ISO)
		Birch			
1	$BZQP_1P_2$	6.8		77.5	
	$LZQP_1P_2$	6.3	−0.5	80.0	+2.5
2	$ZBQP_1P_2$	6.8		77.5	
	$ZLQP_1P_2$	5.8	−1.0	81.3	+3.8
3	BQP_1ZP_2	6.2		78.9	
	LQP_1ZP_2	5.2	−1.0	82.3	+3.4
4	$BXQP_1P_2$	7.3		75.6	
	$LXQP_1P_2$	6.5	−0.8	78.2	+2.6
5	$XBQP_1P_2$	7.3		75.6	
	$XLQP_1P_2$	6.1	−1.2	79.2	+3.6
6	$(B+X)QP_1P_2$	7.6		75.5	
	$(L+X)QP_1P_2$	6.8	−0.8	77.5	+2.0
		Pine			
7	$BZQP_1P_2$	7.0		75.2	
	$LZQP_1P_2$	6.5	−0.5	78.1	+2.9
8	$ZBQP_1P_2$	7.0		75.2	
	$ZLQP_1P_2$	6.0	−1.0	79.0	+3.8
9	BQP_1ZP_2	6.3		78.3	
	LQP_1ZP_2	5.5	−0.8	81.9	+3.6
10	$BXQP_1P_2$	7.5		74.0	
	$LXQP_1P_2$	6.8	−0.7	77.0	+3.0
11	$XBQP_1P_2$	7.2		74.1	
	$XLQP_1P_2$	6.5	−0.7	78.0	+3.9
12	$(B+X)QP_1P_2$	7.5		73.9	
	$(L+X)QP_1P_2$	7.0	−0.5	76.0	+2.1

Z – ozone dose was 0,3% o.d. pulp; *B* – buffer.
[1]The standard deviation of kappa measurements was 0.1.
[2]The standard deviation of brightness measurements was 0.3.

In bleaching of **birch and pine pulps after oxygen delignification**, it was found that the action of ozone in the sequences No. 1, 7 and No. 2, 8 (Table 2) was more effective before the enzymatic treatment, which was associated with a higher decrease of kappa number and a higher increase in pulp brightness 1.1–1.3% ISO in relation to the sequence in which ozone was used after the treatment with laccase.

Table 2. Results of the Bleaching of Birch and Pine Kraft Pulp After Oxygen Delignification

No.	Bleaching Sequence	Kappa Number[1]	ΔKn	Brightness[2] (% ISO)	ΔB (% ISO)
		Birch			
1	$BZQP_1P_2$	3.2		84.8	
	$LZQP_1P_2$	2.3	−0.9	87.1	+2.3
2	$ZBQP_1P_2$	3.0		84.9	
	$ZLQP_1P_2$	1.6	−1.4	88.2	+3.3
3	BQP_1ZP_2	2.3		86.6	
	LQP_1ZP_2	1.0	−1.3	89.0	+2.4
4	$BXQP_1P_2$	3.6		83.1	
	$LXQP_1P_2$	3.2	−0.4	84.8	+1.7
5	$XBQP_1P_2$	3.6		83.1	
	$XLQP_1P_2$	2.6	−1.0	85.8	+2.7
6	$(B+X)QP_1P_2$	3.6		83.0	
	$(L+X)QP_1P_2$	3.4	−0.2	85.0	+2.0
		Pine			
7	$BZQP_1P_2$	2.3		84.1	
	$LZQP_1P_2$	1.6	−0.7	86.2	+2.1
8	$ZBQP_1P_2$	2.4		84.2	
	$ZLQP_1P_2$	1.3	−1.1	87.5	+3.3
9	BQP_1ZP_2	2.3		86.0	
	LQP_1ZP_2	1.0	−1.3	88.9	+2.9
10	$BXQP_1P_2$	3.6		83.1	
	$LXQP_1P_2$	3.1	−0.5	85.2	+2.1
11	$XBQP_1P_2$	3.6		83.1	
	$XLQP_1P_2$	2.5	−1.1	86.2	+3.1
12	$(B+X)QP_1P_2$	3.6		82.5	
	$(L+X)QP_1P_2$	3.2	−0.4	84.2	+1.7

Z – ozone dose was 0,3% o.d. pulp; B – buffer.
[1]The standard deviation of kappa measurements was 0.1.
[2]The standard deviation of brightness measurements was 0.3.

Considering the place of stage Z in the bleaching sequences No. 1, 7 and No. 3, 9; e.g. for birch pulp after the oxygen delignification, it is seen that better results were obtained in the sequence No. 3 (Table 2). The ozone treatment of pulp after a single stage of hydrogen peroxide bleaching and before the next one resulted in a considerable increase in pulp brightness up to 89% ISO, i.e. by about 2% ISO, more than in the case of the sequence

No. 1. The effect is therefore similar as in the case of pulps before oxygen delignification (Tables 1 and 2).

The amount of the ozone used has an important effect on the pulp viscosity. Acidic ozone treatment removes Mg ions from the bleached pulp, making it more susceptible to carbohydrate degradation which has a negative effect on the pulp strength properties. From our studies concerning the bleaching process with enzymes it follows, that a slight decrease in the pulp strength properties and viscosity was observed when ozone was used in a quantity of 0.75% o.d. pulp (Table 3).

EXPERIMENTAL

Pulp Samples

Kraft pulps from domestic pulp mills were used for the examinations. Their characteristics are given in Table 4.

Enzymes

A xylanase preparation, *Ecopulp TX-100S* (Primalco), of bacterial origin showing its optimal activity in neutral medium and a laccase preparation separated from *Cerrena unicolor* fungi, showing its optimal activity at pH = 5.8 (McIlvaine buffer) were used for the experiments. The xylanase activity was determined by the DNS method, using birch xylan (Sigma)[29] as substrate, and the laccase activity was measured by the method proposed by Leonowicz.[30]

Xylanase Treatment

Pulp samples were placed in plastic bags and immersed in a water bath. The treatment conditions were as follows: enzyme dose 2U X/g o.d. pulp, pulp concentration 10%, time 60 min, temperature 49–50°C, pH = 6.8 (phosphate buffer). The contents of bags were periodically mixed (every 10 min) by hand kneading. Once the enzymatic process was completed, the enzyme was deactivated by immersing the pulp in boiling water for 5 min. Reference pulp samples (without enzyme) were treated in the same way with phosphate buffer.

Table 3. Effect of the Quantity of Ozone on the Birch and Pine Kraft Pulps (After Oxygen Delignification) Bleaching with Oxygen Agents in the Sequence LQP_1ZP_2

Type of Pulp	Ozone Quantity (% o.d. Pulp)	Ozone Consum.[1] (%)	Yield[2] (%)	Brightness[3] (% ISO)	Viscosity (dm^3/kg)	DP*[4]	Breaking Length[5] (km)	Tear Factor[6] ($mN\,m^2$/g)	Burst Factor[7] ($kPa\,m^2$/g)
Birch	0.30	89	97.8	89.0	590	839	7.8	8.9	5.5
	0.50	88	95.5	91.0	573	812	7.7	8.7	5.4
	0.75	88	93.3	92.2	531	747	7.4	8.6	5.2
Pine	0.30	90	97.9	88.9	478	665	7.9	8.6	5.9
	0.50	91	95.3	91.3	454	628	7.8	8.6	5.8
	0.75	90	92.9	92.5	412	564	7.5	8.3	5.5

*Degree of polymerisation.
The standard deviation of:
[1]ozone consumption measurements was 0.01.
[2]yield measurements was 0.2.
[3]brightness measurements was 0.3.
[4]DP measurements was 2.1.
[5]breaking length measurements was 0.03.
[6]tear factor measurements was 0.1.
[7]burst factor measurements was 0.05.

Table 4. Characteristics of the Kraft Pulps Under Investigation

Pulp No.	Types of Pulp	Kappa Number	Viscosity (dm^3/kg)	Brightness (% ISO)
	Birch			
1	Before oxygen delignification	21.7	925	36.3
2	After oxygen delignification	12.7	842	48.9
	Pine			
3	Before oxygen delignification	34.8	949	28.5
4	After oxygen delignification	22.5	849	34.2

Laccase Treatment

The process was carried out in a Biostat B bioreactor of B. Braun, modified accordingly to run the process under increased oxygen pressure. The optimal conditions for the laccase treatment were as follows: enzyme dose 1000 UL/g of birch pulp and 2000 UL/g of pine pulp, temperature 50°C, time of treatment 2 h, oxygen pressure 0.1 MPa, pulp concentration 10%, pH = 5.8. A pulp sample was mixed with the reactants and placed in the reactor to which oxygen was then continuously added. Once the process was completed, the treated pulp was removed and rinsed with distilled water.

Bleaching Process

Pulps before and after the oxygen delignification (O) were bleached with hydrogen peroxide and ozone according to the following schemes: LQPZP, ZLQPP, LZQPP, LXQPP, XLQPP, (L + X)QPP, where: X – xylanase, L – laccase, P – hydrogen peroxide, Z – ozone, Q – chelating agent. The bleaching of pulps with hydrogen peroxide (P) was carried out by placing the pulp samples in plastic bags and immersing them in a water bath. The conditions of bleaching are given in Table 5.

Ozone (*Z*) for the bleaching of kraft pulps was generated in a Labo76 generator of the French firm Trailigaz with a maximum capacity of 8 g O_3/h. The ozone dose was 0.3–0.75% o.d pulp at a concentration of 25–30% and temperature 20°C, pH 2.5–3.0. The unreacted ozone was determined by iodometry and the results obtained were used to calculate its real consumption.

Table 5. Conditions of Pulp Bleaching with Hydrogen Peroxide

Bleaching Variant	Pulp Concentration (%)	(%) o.d. Pulp				Time (min)	Temp. (°C)
		H_2O_2	NaOH	Na_2SiO_3	$MgSO_4$		
P_1	10	1	1	–	0.2	60	70
P_2	10	1	1.5	3	0.2	60	80

Characteristics of Pulps

Kappa number, yield, viscosity and strength properties were determined according to the known methods.[31,32] The pulp brightness was determined according to ISO Standard No. 3688.[32]

CONCLUSIONS

The TCF bleaching of birch and pine kraft pulps before as well as after oxygen delignification is particularly effective in the following bleaching sequences: LQP_1ZP_2, $LZQP_1P_2$ and $ZLQP_1P_2$. The use of ozone at the beginning of bleaching is more effective than its introduction just after the laccase treatment as ozone activates lignin increasing its susceptibility to the action of this enzyme. The bleaching of pulps with ozone according to the scheme where ozone is used between two peroxide stages is the most beneficial process due to the pulp brightness increase. The pretreatment of pulp with xylanase increases the laccase access to lignin.

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