

Laboratory study on bleaching softwood kraft pulp by a totally chlorine-free process including the novel ozone bleaching

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THE USE OF CHLORINE-CONTAINING chemicals in pulp bleaching leads to the formation and subsequent discharge of organochlorine compounds, which are collectively called adsorbable organic halides (AOX). Chlorine dioxide bleaching generates much less AOX than chlorine bleaching. Therefore, the pulp and paper industry is replacing more chlorine by chlorine dioxide in its bleach plants.

There is no firm evidence that the effluents from chlorine dioxide bleaching are harmful, particularly after they have been subjected to the secondary treatment (1). However, due to a general suspicion about the toxicity of these organochlorine compounds, there is a growing market for totally chlorine-free (TCF) bleached pulp, especially in Germany.

Production of TCF fully bleached pulp from hardwood kraft and softwood sulfite has become a reality; however, it is still a challenge to produce TCF fully bleached softwood kraft pulp. One of the main reasons is because softwood kraft pulp usually contains more lignin and therefore is more difficult to bleach. Therefore, incorporation of ozone bleaching in a TCF bleaching process may be necessary to reach a full brightness, i.e., ISO brightness of more than 88% for softwood kraft pulp (2, 3).

Ozone, a strong oxidizing agent, is known to be a very efficient delignification chemical. If it is used in a

conventional manner, severe carbohydrate degradation is unavoidable, especially at an ozone charge of more than 1%. Even at ozone charges between 0.5 and 1%, recent literature (4, 5) shows that a loss of 10–15% of the physical properties is typical for kraft softwood pulp bleached by ozone-based TCF bleaching compared to those of the same pulp bleached by chlorine-containing bleaching due to the severe carbohydrate degradation.

Recently, it was found (6) that ozone bleaching of softwood kraft pulp (kappa no. of about 30), impregnated with a solution of dioxane–water that is acidified to a pH of about 2, can significantly improve the ozone-to-lignin carbohydrate selectivity. Laboratory results showed that a semibleached pulp of kappa no. 4 and viscosity of 26–28 mPa·s can be obtained when an unbleached kraft pulp (kappa no. 30 and viscosity of 33 mPa·s) was subjected to this novel ozone bleaching technique at an ozone consumption of about 2% and high consistency, followed by a standard E(O) stage. In this paper, production of fully bleached softwood kraft pulp from this novel ozone semibleached pulp, by using hydrogen peroxide–based brightening chemicals, is discussed.

EXPERIMENTAL

The novel ozone bleaching was performed at room temperature either in modified Rotovap equipment or a specially designed rotation vessel. The fluffed unbleached chemical

ABSTRACT

Conventional softwood kraft pulp with a kappa number of about 30 was bleached in the laboratory by a totally chlorine-free (TCF) bleaching process based on a novel ozone bleaching technology developed earlier. Neither oxygen nor extended delignifications were included. The delignification stage was carried out with the ZE(O) sequence. It was found that the presence of 1,4-dioxane in the impregnation liquor during ozone bleaching significantly improves the lignin-to-carbohydrate selectivity. The ozone delignification was performed by charging 2% ozone to a high-consistency pulp impregnated with an aqueous and acidified (pH = 2) solution of 70% dioxane. The kappa number and viscosity of the ZE(O) pulp were about 4.0 and 26.5 mPa·s, respectively.

It was shown that a one-stage peracetic acid or dimethyl dioxirane (DMD) treatment increased the brightness to a maximum of about 82% ISO. When hydrogen peroxide was used for brightening at a temperature of less than 90°C, the brightness was also limited to the low 80s. However, full brightness (i.e., >88% ISO) can be achieved when the final peroxide bleaching is carried out at higher temperature and pressurized conditions at a charge as low as 2.0%. A ZE(O)QPPa sequence resulted in the production of fully bleached pulp with a brightness above 88% ISO and a viscosity similar to that of conventional chlorine-bleached pulp, thus representing a promising TCF bleaching sequence. A comparison of its physical properties with those of a DEDED-bleached pulp is also given.

Application:

A laboratory study showed that ozone-based TCF bleaching sequences can produce fully bleached softwood kraft pulp with strength and optical properties similar to those of chlorine dioxide-bleached pulp.

Process variables	STAGE				
	Q	P	Pa	DMD	(PO)
Consistency, %	2	10	10	10	20
Time, min	30	120, 240	60	60	120
Temp., °C	50	80, 90	60	25	105
O ₂ pressure, psi	-	-	-	-	70
Chemicals, %	DTPA: 0.6 H ₂ SO ₄ to acidify pulp	NaOH: 2.5 H ₂ O ₂ : 1–3 MgSO ₄ : 0.1 DTPA: 0.2	Pa: 1.0–3.0 Initial pH of 7 by NaHCO ₃	Active oxygen: 0.5–1.5 pH: 7.0–7.5 by NaHCO ₃	NaOH: 2.5 H ₂ O ₂ : 1–3 MgSO ₄ : 0.1

I. Conditions in the bleaching stages

pulp at approximately 40% consistency is contacted with a 3.83% (by weight) ozone in air mixture at a flow rate of 1.0 L/min. Dioxane solution (70%) acidified by H₂SO₄ to pH 2 was used as the impregnation liquor during the ozone bleaching; the ozone charge was 2%. It was found that the vast majority of ozone (over 95%) was consumed during the course of the reaction. The oxidative extraction stage, E(O), was performed in a specially designed bomb (7). The process conditions were as follows:

- Sodium hydroxide charge: 2.0%
- Oxygen pressure: 205 kPa
- Pulp consistency: 10%
- Temperature: 70°C
- Time: 1 hour.

The ZE(O) delignified pulp has the following properties:

- Brightness: 55.0–60.5% ISO
- Kappa no.: 4.3–5.8
- Viscosity: 26.0–28.6 mPa·s.

DMD bleaching was carried out by mixing the pulp slurry with the appropriate ratio of acetone and water and then adding sodium bicarbonate for pH control. Oxone (2KHSO₅·KHSO₄·K₂SO₄) was then added to the pulp slurry. The bleaching was performed at 25°C for 1 hour in a plastic bag. Occasional kneading was provided.

The chelation stage (Q) with diethylenetriamine pentaacetic acid (DTPA) was carried out at 50°C and 2% pulp consistency for 30 min. The pulp was acidified to pH 5 by the addition of H₂SO₄ before 0.6% DTPA was charged. The pulp was washed thoroughly after the Q stage. The conventional hydrogen peroxide stage (P) was done in a sealed polyethylene bag at 10% consistency and 90°C for 4 hours. The ranges of chemical charges (H₂O₂, NaOH, DTPA, and MgSO₄) are listed in Table I. After the P stage, the pulp slurry was washed thoroughly with distilled water.

The (PO) stage was performed under oxygen pressure and in a specially designed stainless steel bomb with an internal Teflon liner so that the pulp sample could not directly contact the metal surface. An oil bath was used to thermostat the bomb reactor at the desired value. The chemical charges and other operating parameters are listed in Table I. After the (PO) stage, the bleached pulp was washed thoroughly with distilled water and made into handsheets for further analysis.

In peracetic acid bleaching (Pa) experiments, the pulp sample was weighed into a polyethylene bag mixed with a sufficient quantity of NaHCO₃ and water to provide the initial pH and the required consistency. The appropriate amount of 30% peracetic acid was then added

and rapidly mixed with the pulp. The chemical charges and other operating conditions are listed in Table I. After the Pa stage, the pulp slurry was thoroughly washed with cold distilled water and made into handsheets for further analysis.

Viscosity and kappa tests were performed according to TAPPI T 230 om-89 and T 236 cm-85, respectively. The brightness and the strength properties were measured in accordance with the CPPA standard methods.

RESULTS AND DISCUSSION

Hydrogen peroxide bleaching

Hydrogen peroxide is an effective brightening chemical and has been applied to bleach mechanical pulp for a long time. Recently, due to the pressure to decrease the use of chlorine-containing bleaching chemicals in bleach plants, hydrogen peroxide has been accepted as a brightening chemical for chemical pulps.

The management of metal ions is very important for an efficient peroxide stage. For example, van Lierop *et al.* (8) reported that, to obtain optimum results from alkaline peroxide bleaching, a chelating stage, namely the Q stage, is unavoidable. They also suggested to position the Q stage just before the hydrogen peroxide bleaching. Therefore, a DTPA chelating stage was performed on the ZE(O)-treated pulp. The Q stage was carried out by adding 0.6% (on

Peracetic acid charge, % on pulp	Brightness, % ISO	Pulp viscosity, mPa-s
1	72.2	20.0
2	76.0	19.4
3	79.2	17.9

II. Development of pulp properties during peracetic acid treatment of the ZE(O) pulp

DMD charge, % as active oxygen	Brightness, % ISO	Pulp viscosity, mPa-s
0.5	74.1	24.2
1.0	77.1	20.0
1.5	78.2	19.8

III. Development of pulp properties during the DMD treatment of the ZE(O) pulp

an o.d. pulp basis) of DTPA to a 2%-consistency pulp suspension to give more uniform pH conditions (8). The detailed experimental conditions are listed in Table I.

The ZE(O)Q pulp was further bleached with a hydrogen peroxide stage at 90°C and 10% pulp consistency for 4 hours. A small amount of magnesium sulfate (0.1% on o.d. pulp) was added to minimize the hydrogen peroxide decomposition (9). About 0.2% DTPA was also added in the hydrogen peroxide bleach liquor in the P stage, because it was reported (8) that the presence of DTPA in the bleach liquor offered some brightness gain.

When 3.0% hydrogen peroxide was charged, of which 2.1% was consumed, the ZE(O)QP pulp brightness reached 84% ISO, while its viscosity remained at 18.0 mPa-s. Since a further increase in hydrogen peroxide is not considered economical in practice, no attempt was made to reach a higher brightness by further increasing the hydrogen peroxide charge.

Peracetic acid bleaching

In the 1960s, Bailey and Dence (10) published a paper describing the use of peracetic acid for both brightening and delignifying pulp. Recently, driven by TCF pulp bleaching, peracetic acid has resurfaced as one of

the alternative chemicals for bleaching chemical pulp. Hill *et al.* (11) examined the effects of time, temperature, pH, and peracetic acid charge on the delignification and selectivity, and reported that peracetic acid is a good delignification agent. The cost of peracetic acid, once perceived as too expensive for commercial use in bleach plants, has been reduced significantly by distillation technology (11). Therefore, peracetic acid was included in this study as one of the brightening chemicals.

The optimum operating condition of a peracetic acid brightening has been reported (10). pH was considered to be the most important parameter, and the optimum pH is at neutral range, while a temperature of 50–80°C is suitable for minimizing carbohydrate degradation.

Therefore, in this study, the initial pH was chosen at about 7, which gave a final pH of greater than 5. Other conditions were a temperature of 60°C, a pulp consistency of 10%, and a reaction time of 1 hour. The peracetic acid charge varied at 1, 2, and 3%. No chelating stage was performed prior to the Pa stage.

The brightness and viscosity of the bleached pulps are shown in Table II. We can conclude that peracetic acid has a bleaching power comparable to that of hydrogen per-

oxide. Note that the viscosity of peracetic acid-bleached pulp in each case still remains above 18 mPa-s, indicating that the carbohydrate degradation is comparable to that during hydrogen peroxide bleaching.

DMD as the brightening stage

Recently, Lee *et al.* (12) have identified a new oxidative bleaching agent, dimethyl dioxirane (DMD) as one of the alternative nonchlorine bleaching chemicals. It was claimed (12) that DMD reacts with residual lignin in a similar mechanism as chlorine, and it can effectively delignify conventional softwood kraft pulps. It was found (12) that a DMD charge of 3.0% (as active oxygen) was required to decrease the kappa number from 31.5 to 5.7 after the DMD and extraction stages. Application of DMD in the final brightening stage was reported by McDonough *et al.* (13).

The experimental conditions in this study were based on those reported in the delignification stage (12). The pH was controlled at 7.0–7.5 by adding sodium bicarbonate. The ratio of acetone to water was 70:30 (by weight). Other conditions are listed in Table I. The DMD charge (as active oxygen) varied at 0.5, 1.0, and 1.5%. The brightness and viscosity of the bleached pulp are shown in Table III. With a 0.5% DMD charge, the pulp brightness reached 74.1% ISO and attained a viscosity of 24.2 mPa-s. When 1.5% DMD was charged, the pulp brightness increased to 78.2% ISO, and the viscosity remained at 19.8 mPa-s.

The results indicate that the DMD is a much more selective bleaching chemical than hydrogen peroxide. However, it appears to be difficult to reach a full brightness, i.e., a brightness of more than 88% ISO, in a single stage of the DMD treatment.

KEYWORDS

Brightness, chlorine free bleaching, hydrogen peroxide, kraft pulps, multi-stage process, ozone bleaching, pre-treatment, softwood pulps.

Sequential bleaching with DMD and peracetic acid

From the results obtained in previous sections, it is clear that neither a single DMD nor a peracetic acid stage can bleach the ZE(O) pulp to high brightness. However, the results showed that both DMD and peracetic acid are selective in reacting with residual lignin. This led to the idea that a combination of DMD and peracetic acid stages might give positive results.

Therefore, two experiments were performed on DMD-treated pulps (1% charge as active oxygen) with a peracetic acid stage. The peracetic acid charges were 1.0 and 1.5%, respectively. Other operating conditions are given in Table I. Both bleached pulps gave about 80% ISO brightness and about 18 mPa·s viscosity. There was residual peracetic acid in both cases after an hour of reaction time. This indicated that the bleaching power of the peracetic acid was not used up; this may account for the similarity obtained in the previous results even though the peracetic acid charges were different.

Thus, additional experiments were carried out with 2% peracetic acid charge, and the reaction was allowed to proceed for 210 min (60 min at 50°C, 45 min at 70°C, and 105 min at 80°C) until all the peracetic acid was consumed. The brightness of the resulting pulp reached 88.2% ISO. However, the pulp viscosity was only 6.9 cp. The severe carbohydrate degradation is possibly due to the formation of harmful radical species from the peracetic acid decomposition at the relatively high

temperature. Further studies on the kinetics of the peracetic acid decomposition are currently being conducted in our laboratory. The present results imply that it is possible to fully bleach the ZE(O)-treated kraft softwood pulp to high brightness. Additional efforts should concentrate on minimizing the carbohydrate degradation. Therefore, alternative bleaching sequences were investigated to reach the brightness while maintaining reasonable pulp viscosity.

QPPa bleaching

In the previous sections, we showed that, when peracetic acid and hydrogen peroxide are applied alone in a single stage to the ZE(O) pulp as the brightening stage, the brightness is limited to about 80% ISO. It is known (14) that α -carbonyl and quinone structures are efficiently removed while α,β -unsaturated double bonds are stable and continuously formed during conventional hydrogen peroxide bleaching. On the other hand, double bonds in residual lignin are very reactive toward peracetic acid (15). The brightness ceiling observed in a conventional single peracetic acid or hydrogen peroxide stage is probably due to the fact that not all the lignin structures are effectively removed if either hydrogen peroxide or peracetic acid bleaching is performed alone. Therefore, one might expect that a higher brightness could be achieved by a combination of hydrogen peroxide and peracetic acid brightening.

The same ZE(O) delignified pulp was subjected to a QPPa process. The hydrogen peroxide and peracetic acid charges were 3.0 and 2.0%, respectively. Other conditions are listed in Table I. During the course of bleaching, 69% of the hydrogen peroxide and 61% of the peracetic acid were consumed. The final brightness of the fully bleached ZE(O)QPPa pulp is 88.2% ISO, while the viscosity remains at 18.0 mPa·s.

We determined the strength properties of this ZE(O)QPPa pulp. Its tear index was 18.2 mN·m²/g at 7 km tensile breaking length. This compares favorably with a tear index of 18.5 mN·m²/g for a DEDED-bleached pulp at the same tensile breaking length. Therefore, it can be concluded that the TCF bleaching process ZE(O)QPPa can produce a fully bleached pulp with comparable physical and optical properties as that bleached by a conventional chlorine-containing process and may represent a promising TCF bleaching sequence for conventional softwood kraft pulps.

Further study of the ZE(O)QPPa sequence, including the optimization in each stage, is currently underway in our laboratory. The results, together with the cost comparison between the TCF sequence and the ECF sequence, will be reported in a later paper.

A ZE(O)PaQP sequence was then evaluated to investigate the importance of positioning the hydrogen peroxide stage and the peracetic acid stage. The conditions were the same as those in the ZE(O)QPPa sequence. The final bleached pulp had a brightness of 88.2% ISO and a viscosity of 12.9 mPa·s. This indicated that the carbohydrate degradation was much more severe in the PaQP sequence than in the QPPa sequence, even though the chromophores were effectively removed in both processes. Since peracetic acid is a very selective bleaching agent while the radical species during hydrogen peroxide bleaching are rather unselective, the present results suggest that the less-selective bleaching agent should be placed in an earlier stage, where relatively more residual lignin is present in the pulp.

Q(PO) brightening

Recently, Devenyns *et al.* (16, 17) found that, when hydrogen peroxide was used as the final brightening

H ₂ O ₂ charge, % on o.d. pulp	Viscosity, mPa·s	Brightness, % ISO
0	28.6	56.5
1.0	-	86.3
1.5	-	87.5
2.0	15.7	88.0
3.0	15.3	89.2

IV. Bleaching results from the Q(PO) process

stage at high consistency, high temperature (above 100°C), and under oxygen pressure to a well delignified pulp in a (PO) stage, the brightness ceiling is much higher than that achieved in a conventional hydrogen peroxide stage. Also, Colodette *et al.* (18) applied an OQ(PO) sequence to an extended-cooked softwood kraft pulp. Full brightness was achieved; however, the strength properties were somewhat lower. The degradation of carbohydrates was not mentioned in that paper.

It was proposed (16, 17) that the better bleaching results obtained under these conditions were due to the fact that higher consistency and temperature kinetically favor the chemical reactions. However, Colodette *et al.* (18) suggested that other reactive species are formed in (PO) so that more chromophore structures can be removed.

In this project, the (PO) technique was applied to the ZE(O) pulp. A chelating stage (Q) was performed before the (PO) stage to minimize the detrimental effect of transition metal ions. The hydrogen peroxide charge varied at 1.0, 1.5, 2.0, and 3.0%. Other conditions are shown in Table I. The reaction was stopped after 2 hours, and the results are shown in Table IV. The brightness increase was dramatic in the high-consistency, high-temperature hydrogen peroxide stage.

At a hydrogen peroxide charge of as low as 1%, the brightness increased from 56.5 to 86.3% ISO, an increase of almost 30%. With a 2% hydrogen peroxide charge, the

brightness reached 88.0%. We determined the residual hydrogen peroxide at the end of the reaction and found that more than 25% of the hydrogen peroxide charged remained in all cases except at 1% hydrogen peroxide charge. The viscosity loss in the (PO) stage is obvious from Table IV. The present result is in agreement with the finding by Devenyns *et al.* (16) that the (PO) process can bleach a well delignified kraft softwood pulp to a full brightness.

It was previously shown that a QP sequence at a hydrogen peroxide charge of 3% led to a final brightness of about 84% ISO. Compared to the results obtained by the Q(PO) sequence at the same hydrogen peroxide charge, we can conclude that the hydrogen peroxide is consumed more efficiently in the high-consistency, high-temperature hydrogen peroxide stage than in a conventional P stage, i.e., to reach the same brightness, substantially less hydrogen peroxide is required. This represents a significant economic advantage, since hydrogen peroxide is one of the most expensive bleaching chemicals.

CONCLUSION

Bleaching of conventional softwood kraft pulp to full brightness in a TCF process was studied in the laboratory. The prebleaching was carried out with the ZE(O) sequence. It was found that the presence of 1,4-dioxane in the impregnation liquor during ozone bleaching significantly improves the lignin-to-carbohydrate

selectivity. A conventional softwood kraft pulp with a kappa number of about 30 and a viscosity of 33 mPa·s was delignified to a kappa number of about 4–5 and a viscosity of about 26 mPa·s by a ZE(O) sequence with a 2% O₃ charge. Further bleaching of the ZE(O) pulp to a full brightness was studied with hydrogen peroxide, peracetic acid, and dimethyl dioxirane (DMD).

A chelating stage followed by a single, conventional hydrogen peroxide stage cannot produce a fully bleached kraft pulp; neither can a single peracetic acid or DMD stage. However, a QPPa sequence, at a hydrogen peroxide and peracetic acid charge of 3 and 2%, respectively, can successfully produce a fully bleached softwood kraft pulp with a brightness above 88% ISO and strength properties comparable to those of pulp bleached by conventional chlorine-based processes. Also, the Q(PO) process, i.e., a standard chelating stage, followed by a high-consistency, high-temperature hydrogen peroxide stage, can reach a final brightness of greater than 88% ISO. The advantage of Q(PO) over the QP process is that the hydrogen peroxide charge is less and could be as low as 2%, yet the carbohydrate degradation is acceptable.

The significant difference of the present ZE(O)QPPa or ZE(O)Q(PO) sequence over other TCF bleaching processes is that the bleaching process starts with conventional softwood kraft pulp with a kappa number of about 30 without any extended delignification or oxygen delignification stages prior to the bleach plant. This is especially important in North America, where a large fraction of the mills have not installed oxygen or extended delignification technologies to further decrease the lignin content of the pulp entering the bleaching process (5). Also, the carbohydrate degradation during the present TCF

sequences is substantially less than that of other TCF processes as indicated by a much higher viscosity of the fully bleached pulp. The physical properties of the fully bleached pulp treated with the ZE(O)QPPa sequence are the same as those of conventional chlorine-bleached pulps. TJ

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