

SHORT TCF SEQUENCES IN THE BLEACHING OF *EUCALYPTUS* *CAMALDULENSIS* PULP. A COMPARATIVE STUDY

JUHA FISKARI,* MIIKKA SVELA,** KYÖSTI RUUTTUNEN,** VILLE ALI-REKOLA,**
PETRI KILPELÄINEN*** and HERBERT SIXTA**

*Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki,
A.I. Virtasen Aukio 1, FIN-00560 Helsinki, Finland

**Department of Forest Products Technology, School of Chemical Technology,
Aalto University, FIN-02015 Espoo, Finland

***Finnish Forest Research Institute (METLA), P.O. Box 18, FIN-01301 Vantaa, Finland

✉ Corresponding author: Juha Fiskari, juhnis@live.com

Received December 18, 2013

This research was undertaken to evaluate the bleaching response of *Eucalyptus camaldulensis* in different Totally Chlorine Free (TCF) bleaching sequences. The goal was to compare bleaching sequences, which include a peroxy acid stage – either peracetic acid (Paa) or Caro's acid (Caa) –, to simple hydrogen peroxide bleaching.

The *E. camaldulensis* kraft pulp sample was obtained from a South Asian pulp mill. Its kappa number was 11 and viscosity 1020 mL/g, respectively.

According to the results, peracetic acid and Caro's acid proved to be potential additional alternatives for hydrogen peroxide alone. Both of these bleaching agents can be used between oxygen delignification and the final hydrogen peroxide stage for improved brightness stability, as well as reduced hydrogen peroxide consumption. Moreover, they can be used in a bleaching sequence without any major capital investment.

Keywords: *Eucalyptus camaldulensis*, TCF bleaching, hydrogen peroxide, Caro's acid, peracetic acid

INTRODUCTION

Due to environmental and/or marketing reasons, some mills producing eucalyptus kraft pulp may have to choose totally chlorine free (TCF) bleaching technology in their bleaching sequence, which in its simplest form consists of a chelation stage (Q) followed by a single hydrogen peroxide stage (P), which is then the only actual bleaching stage. The practical limit for a H₂O₂ charge in a single P stage is about 2.5% on pulp – or 25 kg/ADt.¹ However, the charge can be substantially higher, especially in bleaching operations with more than one P stage. Operational problems, such as disturbances in a chelation stage prior to hydrogen peroxide bleaching, can significantly increase the chemical consumption due to rapid decomposition of hydrogen peroxide.² Nevertheless, bleaching with hydrogen peroxide alone is known to be a more expensive way to bleach pulp to full brightness – typically 85-88% ISO for TCF hardwood pulp – than an elemental chlorine free (ECF) sequence.³

Moreover, TCF bleaching of kraft pulp with hydrogen peroxide alone leads to a relatively high residual lignin concentration, which in turn may lead to undesired brightness reversion. Generally, however, a final P stage leads to relatively good brightness stability in TCF sequences, even when the pulp has a high residual lignin content.¹ In addition, hydrogen peroxide-based kraft pulp bleaching requires a relatively low cooking kappa number, as well as high kappa number reduction in oxygen delignification, both of which may lead to a lower pulp quality and decreased yield.² These issues are even more pronounced when the feedstock consists of *E. camaldulensis*, which is known to have unusually high lignin content.⁴

Peroxy acids, such as peroxymonosulfuric acid (Caro's acid) and peracetic acid, can be introduced in a pulp bleaching sequence as a Caa or a Paa stage, respectively. They have higher oxidation potential than hydrogen peroxide, and they are capable of selectively oxidizing lignin.⁵

According to a previous study,⁶ peroxy acids can increase the TCF pulp brightness threshold by 3–4 brightness points when applied at the beginning of a TCF bleaching sequence. According to a study by Jääskeläinen *et al.*,⁷ pulp treatment with peroxy compounds at pH higher than 3.0 did not significantly affect pulp viscosity, while at pH below 3.0, the viscosity decrease became significant, which was caused by acid hydrolysis.

Caro's acid can be introduced to the bleaching process as a salt of Caro's acid, Oxone®.⁸ Otherwise, on-site production of Caro's acid requires a simple reactor. Necessary chemicals are sulfuric acid and hydrogen peroxide. Peracetic acid can be delivered as a distilled or equilibrium solution by a supplier, where available. However, in the long run, a process with a distillation plant is a better approach for low-cost peracetic acid.⁹

A South Asian kraft pulp mill produces paper grade pulp with conventional batch cooking and two-stage oxygen delignification. Currently, the mill's practice is to bleach oxygen-delignified pulp with a single very long P stage that has a hydrogen peroxide consumption of up to 60 kg/ADt. Prior to the hydrogen peroxide bleaching, the pulp is chelated with ethylenediamine-tetraacetic acid (EDTA) in a Q stage. To improve the bleaching performance, the Q stage could easily be converted into a combination of chelation and acidic bleaching. This offers an opportunity to use new chemicals in the existing bleach plant without any major capital costs.

This paper describes a laboratory study on *E. camaldulensis* pulp to compare alternative TCF bleaching sequences to the existing QP sequence. The additional bleaching chemicals investigated are peracetic acid and Caro's acid, as they could be charged to the existing Q stage without any major modifications or additional equipment. The results demonstrate a decrease in the overall chemical consumption, as well as an improvement in pulp quality.

EXPERIMENTAL

Materials

Industrial eucalyptus (*E. camaldulensis*) brown stock pulp was supplied by a South Asian kraft pulp mill. The mill had cooked the pulp with a conventional batch cooking system to a kappa number of about 20, followed by a two-stage oxygen delignification. The kappa number of the pulp sample was about 11 and its viscosity was of 1020 mL/g. Peracetic acid was supplied by Kemira as an equilibrium solution. A triple salt of peroxymonosulfate, Oxone®, was used instead

of Caro's acid in the Caa stage. Other chemicals used in this research were of analytical grade.

Bleaching experiments

Each bleaching sequence was performed at 10% consistency in polyethylene bags, which were kept in a water bath. Pulp samples were preheated and known amounts of chemicals were added to the dilution water, which was also preheated. The pulp and chemicals were thoroughly mixed by hand, which was repeated a few times to ensure their reaction with the pulp. After each bleaching stage, the pulp samples were washed four times with cold de-ionized water and finally centrifuged to a consistency of approximately 30%. All chemical charges were calculated based on oven dry (OD) pulp.

The chemical charges and conditions in the QP stage were suggested by the South Asian mill. The chelation was performed adding 0.05% EDTA at 50 °C and pH 5.7 over a 30 minute reaction time. The temperature in the P stage was 70 °C, and the reaction time was 360 minutes.

The chemical charges and conditions in the Caa and Paa stages were based on our previous experience on laboratory bleaching. In the Caa stage, sulfuric acid was added to decrease pH to 3.7. In the Paa stage, the filtrate pH was 3.6. Both Caa and Paa bleaching stages were carried out at 80 °C for 90 minutes. The bleaching chemical charges of all three sequences are presented in Table 1. To compare the charges of different bleaching chemicals with one accounting system, the total bleaching charge in each sequence is expressed as oxidation equivalents (OXE).

Analyses

Finnish Forest Research Institute (METLA) analyzed pulp samples for their metals content with an Inductively Coupled Plasma – Emission Spectroscopy (ICP-OES) analysis. The device used in the analysis was Thermo Scientific iCap 6000 series.

Kappa numbers were determined by SCAN 1:00 and viscosities by SCAN-CM 15:99. ISO brightness was measured by SCAN-CM 11:95 and SCAN-P 3:93, where the methods are for the preparation of laboratory sheets and ISO brightness determination, respectively. The brightness reversion measurements were performed according to TAPPI method UM 200. After 4 hours of oven drying at 105 °C, the samples were measured according to SCAN-P 3:93.

RESULTS AND DISCUSSION

Table 2 presents ICP-OES metal analysis results before and after chelation. “Before Q” denotes the mill pulp as such (from post-oxygen washer), and “After Q” is the same mill pulp after being subjected to laboratory chelation with EDTA.

Table 1
Chemical charges (as % on OD pulp) in the P stages of the investigated bleaching sequences

Bleaching sequence	Oxone®, %	Paa, %	H ₂ O ₂ , %	NaOH, %	MgSO ₄ , %	OXE/ODt
QP	—	—	6.0	2.0	0.05	3528
QCaaP	0.6	—	3.0	1.5	0.05	1843
QPaaP	—	0.6	2.5	1.5	0.05	1628

Table 2
Measured ion concentrations (mg/kg) and ash content (%) in pulp, before and after chelation

	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	P	Zn	Ash (%)
Before Q	27.9	2170	5.51	98.5	96.7	1400	2.21	6400	0.345	202	3.47	4.6
After Q	20.1	1690	0.65	77.6	21.9	874	0.94	174	0.335	29.6	1.44	0.9

Table 3
Kappa number, kappa no. reduction, viscosity, and brightness results after bleaching

Bleaching sequence	Kappa no. before P stage	Final kappa no.	Total kappa no. reduction	Viscosity, mL/g	Brightness, % ISO
QP	10.3	8.8	1.5	908	84.0
QCaaP	8.2	7.4	2.9	853	83.4
QPaaP	6.0	5.1	5.2	841	83.8

As Table 2 reveals, the original pulp sample was not well washed. Its high sodium content is the result of significant wash loss as alkali (NaOH). Its ash content was therefore also high, and especially so when compared to the Q stage pulp, which had been washed thoroughly. The relatively low degree of calcium removal could be explained by the fact that part of the calcium was present as precipitates, such as calcium oxalate, which has very low solubility and is therefore difficult to remove by chelation.^{10,11} Fortunately, manganese contents in the pulp samples were very low. Chelation with EDTA had further reduced the Mn concentration by almost 60%. Much of the magnesium was also removed, as expected,¹¹ although Mg concentrations were very high in both samples. These factors resulted in very high Mg/Mn molar ratios; after chelation, the ratio was about 2100. This significantly exceeds the Mg/Mn molar ratio necessary to stabilize hydrogen peroxide against decomposition reactions. Moreover, very high magnesium concentrations can slow down delignification and brightening by hydrogen peroxide.² The removal of iron was not very effective, while copper was removed quite well. According to a previous study by Granholm *et al.*,¹² the removal of iron from oxygen-delignified hardwood pulp is very challenging, apparently due to iron(III)

precipitates, and the EDTA charge should be at least 0.1% for the maximal iron removal. The high iron concentration in the mill pulp sample is known to originate from the water supply of the mill.

After the bleaching experiments, the pulp samples were characterized for kappa number, viscosity and brightness (Table 3).

As can be seen from the data presented in Table 3, the implementation of both Caa and Paa stages prior to the P stages resulted in substantially lower final kappa numbers, as compared to the QP sequence. As expected, the Paa stage was significantly more effective in delignification than the Caa stage. This can be explained by the fact that Paa has twice the relative oxidizing power of Oxone®, 26.30 OXE/kg and 13.14 OXE/kg, respectively. At the same time, the resulting viscosities of the QCaaP and QPaaP sequences were only some 50-60 units lower, when compared to the viscosity after the QP sequence. However, the viscosity after the QPaaP sequence was only slightly lower than that after the QCaaP sequence. In all, this was a clear indication of the good delignification selectivity of peracetic acid, which has also been demonstrated by Kumar *et al.*¹³ However, both QPaaP and QCaaP yielded acceptable viscosities, which suggests that they did not cause any major

damage to the pulp, which was also described by Brasileiro *et al.*¹⁴ in their previous studies. The hydrogen peroxide charge after the Paa stage could be reduced to 2.5%, while the QCaaP sequence required 3.0% of H₂O₂ in the final P stage. All investigated sequences reached approximately the same ISO brightness. Therefore, the hydrogen peroxide savings for QCaaP and QPaaP were of 3.5% and 3.0%, respectively. This is many times more than the chemical cost of the 0.6% charge of Paa or Caa (Oxone®).

As an additional benefit, acidic bleaching chemicals, such as Caro's acid and peracetic acid,

may improve the brightness stability of the bleached pulp. This is shown in Table 4, which lists the brightness reversion results. As Table 4 reveals, the QP sequence had the highest brightness reversion. Both Paa and Caa reinforced bleaching sequences gave better brightness stability than QP, which in this study converted to about one brightness point lower brightness reversion. This is also in good agreement with previous studies.¹⁴ The sequence with peracetic acid gave slightly better brightness stability than that with Caro's acid, which can be explained by differences in final kappa numbers.

Table 4
Brightness reversion measurements (% ISO) and brightness reduction (percentage points)

Bleaching sequence	Brightness reversion, % ISO	Brightness reduction, ppts
Q	63.0	1.9
QP	79.6	4.4
QCaaP	79.7	3.7
QPaaP	80.6	3.2

CONCLUSION

1. Peracetic acid and Caro's acid proved to be efficient alternatives as supplementary TCF bleaching chemicals in hydrogen peroxide-based bleaching. These bleaching agents can be used before the final hydrogen peroxide stage for improved brightness stability without a major decrease in viscosity.

2. The addition of peracetic acid or Caro's acid leads to a significantly lower hydrogen peroxide consumption. In this study, the hydrogen peroxide savings for QCaaP and QPaaP sequences were of 3.5% and 3.0% (35 kg/ODt and 30 kg/ODt), respectively. This easily offsets the chemical cost of the 0.6% (6 kg/ODt) charge of Paa or Caa.

ACKNOWLEDGMENTS: The authors are grateful to Veli-Matti Vuorenalo, Kemira Oyj, for providing the peracetic acid sample.

REFERENCES

- ¹ J. R. Anderson and B. Amini, in "Pulp Bleaching – Principles and Practice", edited by C. W. Dence and D. W. Reeve, TAPPI Press, 1996, pp. 411-442.
- ² J. Fiskari, J. Gullichsen, V. Jokela and K. Ruohoniemi, in *Procs. TAPPI Pulping Conference*, San Francisco, October 19-23, 1997, pp. 1069-1073.
- ³ J. R. Anderson, in *TAPPI Bleach Plant Operations. Short Course Notes*, Atlanta, June 22-26, 1992, pp. 123-133.

⁴ D. Dutt and C. H. Tyagi, *Indian J. Chem. Technol.*, **18**, 145 (2011).

⁵ Y.-Z. Lai, and K. V. Sarkanen, *Tappi J.*, **51**, 449 (1968).

⁶ J. Basta, L. Holtinger, and A. S. Hällström, in *Procs. TAPPI Pulping Conference*, San Diego, November 6-10, 1994, pp. 953-956.

⁷ A.-S. Jääskeläinen, K. Poppius-Levlin, and J. Sundquist, *Pap. Puu*, **82**, 257 (2000).

⁸ D. Stewart, *Cellulose Chem. Technol.*, **34**, 117 (2000).

⁹ N. Nimmerfroth, and H. U. Süß, in *Procs. International Non-Chlorine Bleaching Conference*, Orlando, March 24-28, 1996, pp. 1-12.

¹⁰ T. D. Duong, K. L. Nguyen, and M. Hoang, *J. Colloid Interface Sci.*, **301**, 446 (2006).

¹¹ F. Lundqvist, H. Brelid, A. Saltberg, G. Gellerstedt, and P. Tomani, *Appita J.*, **59**, 493 (2006).

¹² K. Granholm, L. Harju, and A. Ivaska, *BioResources*, **5**, 206 (2010).

¹³ R. Kumar, F. Hu, C. A. Hubbell, A. J. Ragauskas, and C. E. Wyman, *Bioresour. Technol.*, **130**, 372 (2013).

¹⁴ L. B. Brasileiro, J. L. Colodette, D. Pilo-Veloso, and R. C. De Oliveira, *Appita J.*, **55**, 461 (2002).