

Dimethyldioxirane as a nonchlorine agent for chemical pulp bleaching

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ABSTRACT: *Dimethyldioxirane has demonstrated superb selectivity and reactivity in pulp bleaching. It can completely replace chlorine/chlorine dioxide in the chlorination stage, and it bleaches both hardwood and softwood kraft pulps.*

KEYWORDS: *Chemical treatment, kraft pulps, multistage process, oxygen bleaching, Populus, Tsuga.*

Concerns about the formation of chlorinated organic compounds when using chlorine-containing agents in chemical pulp bleaching have hastened the search for selective nonchlorine-containing bleaching agents. Several well known nonchlorine-containing oxidants, i.e., molecular oxygen, hydrogen peroxide, peracids, and ozone, have been considered as potential candidates for the replacement of elemental chlorine or chlorine dioxide. Unfortunately, oxygen delignification cannot exceed a 50% delignification because of its limited selectivity (1), and hydrogen peroxide is not an effective delignifying agent either under alkaline (2) or acidic conditions (3). Peracetic acid delignification causes a severe penalty in pulp viscosity (4). Ozone exhibits poor bleaching selectivity and low generation efficiency. Since ozone is a very aggressive oxidant and reacts very fast with pulp, improved equipment con-

cepts will be required to allow a homogeneous bleaching effect (5, 6). Recently, a great deal of effort has been focused on monoper-oxy-sulfuric acid pulp delignification with encouraging results (7-9).

Paprican's recent effort in the search for a new selective nonchlorine-containing bleaching agent has included a new class of oxidants termed dioxiranes (10, 11). The chemistry of dioxirane was indisputably characterized after the first isolation and identification of dimethyldioxirane (DMD) by Murray *et al.* (12).

Bleaching with isolated activated oxygen

A joint project was undertaken by Paprican and the University of Missouri, St. Louis, to bleach pulp with dimethyldioxirane, termed activated oxygen (AO), and prepared according to Murray's method (12). The results

were extremely promising in selectivity and effectiveness of chemical pulp delignification (13). These were later confirmed by Ragauskas' findings (14). Aspen pulp (kappa no. 16.4) was treated with activated oxygen at 0.55% active oxygen charge on od pulp, designated as A in a bleaching sequence at 14.2% pulp consistency for 1 h. This one-stage treatment decreased the kappa number to 3.4, a 79% delignification, as shown in Table I. The chlorine dioxide bleaching stage (0.8% ClO₂ charge by weight on oven-dried pulp) following A stage produced a pulp of 86.8% ISO brightness. This A-bleached aspen pulp had a far superior zero-span tensile strength (17.0 km) to that of the same pulp delignified by oxygen to a level of 67% (10.6 km). It should also be noted that the pulp bleached by an AD sequence had a comparable zero-span tensile strength to those of the unbleached pulp and the pulp fully bleached via a conventional bleaching sequence, (C+D)ED.

In a further trial, aspen pulp was treated with activated oxygen (0.55% AO on od pulp) at 7.6% pulp consistency for 1 h. The resulting pulp of 5.3 kappa (68% delignification) displayed a 2.0% yield loss based on the unbleached pulp. When the aspen pulp was oxygen-delignified to 5.4 kappa, it suffered a 7.3% yield loss. This result confirmed the selective nature of activated oxygen.

As a result, activated oxygen is indisputably a promising candidate for selective delignifying agent for chemical pulps. However, the chemical yield of activated oxygen in isolated form

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based on the charge of monoperoxy-sulfate is extremely low, less than 1%, according to the published method. The use of isolated activated oxygen via this method would not be practical for an industrial application. Therefore a method of in-situ generation of activated oxygen in the pulp slurry was tested (15).

Bleaching with *in-situ* generated activated oxygen

Bleaching with *in-situ* generated activated oxygen was carried out by mixing the pulp slurry with an appropriate amount of acetone in water solution for 10 min and then adding an appropriate amount of sodium bicarbonate (NaHCO_3) for pH control (7.0–7.5). Monoperoxy-sulfate (the active component of Oxone) was then added to the resulting pulp slurry at 25°C with only initial kneading. The reaction of acetone with monoperoxy-sulfate at nearly neutral pH generated activated oxygen *in situ*, which subsequently bleached the pulp.

A mill hemlock kraft pulp (kappa 31.5) was treated with activated oxygen generated *in situ* using 0.9% AO charge, which resulted in a 34.6% kappa number reduction, as listed in Table II. The following caustic extraction condition further reduced the kappa number by 21.9%. Activated oxygen reacts with residual kraft lignin in a way similar to elemental chlorine/chlorine dioxide. After A treatment, the residual lignin was further solubilized in a subsequent caustic extraction stage. The AE-bleached pulp has a comparable viscosity to the same hemlock kraft pulp bleached by a (C+D)E sequence to the same degree of delignification (57% kappa reduction), as shown in Table II. The viscosity preservation by activated oxygen bleaching is superior to that by molecular oxygen delignification.

Critical to activated oxygen bleaching is the charge of acetone which influences the amount of DMD formed under the *in situ* bleaching conditions. For example, the hemlock kraft pulp

I. Kappa number, zero-span tensile and brightness of aspen kraft pulp bleached with DMD or molecular oxygen or by conventional bleaching

Bleach sequence	Chemical charges, % od pulp	Kappa number	Degree of delig., %	Zero-span tensile, km	Brightness, % ISO
Unbleached	—	16.4	—	16.3	40.6
AD	A:0.55% AO	3.4	79	17.0	59.4
	D:0.8% ClO_2	—	—	17.4	86.8
O	O_2 :100 psig :2.0% NaOH	5.4	67	10.6	70.7
(C ₅₀ +D ₅₀)ED	C+D:3.3% Cl_2	—	—	—	—
	E:2.0% NaOH	—	—	—	—
	D:1.0% ClO_2	—	—	18.4	89.9

II. Kappa number and viscosity of hemlock kraft pulps bleached by in-situ-generated activated oxygen, oxygen delignification and a conventional (C+D)E sequence.

Bleach sequence	Chemical charges, % od pulp	Kappa number	Degree of delig., %	Viscosity, mPa·s
Unbleached	—	31.5	—	33.5
AE	A ^a :0.9% AO	20.6	35.0	28.3
	E:3.0% NaOH	13.7	57	26.0
AEP	A ^b :2.7% AO	—	—	—
	E:3.3% NaOH	5.4	82.9	21.0
	P ^c :4.0% H_2O_2 :2.5% NaOH	4.0	87.3	21.0
O	O_2 :100 psig :1.8% NaOH	22.1	30	23.2
(C+D)E	C+D:3.0% Cl_2	—	—	—
	E:2.0% NaOH	13.6	57	28.5

^a A stage was carried out using 16% acetone charge at 25°C for 30 min.

^b A stage was carried out using 32% acetone charge at 25°C for 30 min.

^c Peroxide stage was carried out at 60°C and 14% pulp consistency for 60 min with 3.0% sodium silicate and 0.5% MgSO_4 .

was delignified to a kappa of 13.7 units after the AE stages using 0.9% AO and 16% acetone charges at the A stage, while the same pulp was delignified to a kappa of 17.2 units under the same conditions except that 4% of acetone charge was used instead of 16%.

The hemlock kraft pulp can also be delignified by the AE sequence at 2.7% AO charge to a kappa number as low as 5.4 (82.9% kappa reduction) while

maintaining the bleached pulp viscosity as high as 21.0 mPa·s. This AE-bleached pulp was further brightened by a peroxide brightening stage to 71% ISO without further loss of viscosity.

The AE-bleached pulp of 5.4 kappa was subsequently bleached by a DED sequence to a 90.9% ISO brightness. A complete replacement of elemental chlorine with activated oxygen in chemical pulp bleaching to high market pulp brightness was achieved. The

III. Optical and strength properties of pulps produced by AEDED, (C+D)EDED and, O(C+D)EDED sequences.

Bleach sequence	Chemical charges	Tear ind., mN·m ² /g	Tens.ind., N·m/g	Burst ind., kPa·m ² /g	Zero-span tens., km	Bulk, cm ³ /g	Bright., % ISO
AEDED	A:2.7% AO E:3.2% NaOH D:1.0% ClO ₂ E:1.0% NaOH	19	32.2	2.4	14.2	2.01	90.9
(C+D)EDED	D:1.0% ClO ₂ C+D:6.0% Cl ₂ E:3.6% NaOH D:1.0% ClO ₂ E:1.0% NaOH						
O(C+D)DED	D:1.0% ClO ₂ O ₂ :100 psig :1.8% NaOH C+D:4.8% Cl ₂ E:2.9% NaOH D:1.0% ClO ₂ E:1.0% NaOH D:1.0% ClO ₂	18	33.2	2.5	15.1	2.06	90.1
		19	29.5	2.2	14.0	1.97	91.8

IV. Kappa number and viscosity of hemlock kraft pulps bleached via AE and OAE sequences.

Bleach sequence	Chemical charges, % of pulp	Kappa number	Degree of delig., %	Viscosity, mPa·s
Unbleached	—	31.5	—	33.5
OAE	O ₂ :100 psig :1.8% NaOH	22.1	30.0	23.2
	A:0.9% AO	12.6	60.0	21.0
	E:2.0% NaOH	8.0	75.0	19.0

strengths of the pulp produced via AEDED are identical to those of pulps bleached by conventional processes such as (C+D)EDED and O(C+D)EDED, as illustrated in **Table III**.

Activated oxygen was also successfully applied to oxygen delignified pulp. It should be noted that there is much less viscosity loss during the AE stages than that in oxygen delignification stage, as illustrated in **Table IV**.

Aspen kraft pulps of greater than 85.0% ISO brightness were produced via totally chlorine-free bleaching sequences, such as AEP or OAE. The use of oxygen delignification before the activated oxygen stage reduce substantially the required activated oxygen charge for a given brightness. For instance, a reduction of AO charge from 2.7% to 0.9% was realized by an oxygen delignification (30% kappa reduction) before the A stage, as illustrated

in **Table V**. Viscosity, zero-span tensile and brightness were comparable for both AEP- and OAE-bleached pulps.

Conclusion

A new nonchlorine oxidant, in isolated form or generated *in situ* in the pulp slurry, has demonstrated superb selectivity and reactivity in chemical pulp bleaching. We conclude that activated oxygen is a selective nonchlorine bleaching agent which:

1. Reacts with residual lignin via electrophilic oxidation in a way similar to elemental chlorine/chlorine dioxide and renders the residual lignin soluble in the following caustic extraction
2. Can completely replace chlorine/chlorine dioxide in the chlorination stage
3. Bleaches effectively both hardwood and softwood kraft pulps
4. Results in little yield loss in the activated oxygen stage. **□**

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V. Strength and optical properties of the aspen kraft pulps bleached by AEP and OAEP sequences.

Bleach sequence	Chemical charges	Kappa number	Zero-span tens., km	Viscosity, mPa·s	Brightness, %ISO
Unbleached	—	16.4	16.3	50.5	40.6
AEP	A ^a :2.7% AO	2.3	18.5	34.1	76.8
	E:0.5% NaOH	—	—	—	—
	P ^b :2.0% H ₂ O ₂ :2.5% NaOH	—	16.8	19.2	86.7
OAEP	O ₂ :100 psig :1.0% NaOH	11.5	14.5	43.6	50.1
	A ^c :0.9% AO	3.7	15.7	30.1	71.6
	E:0.5% NaOH	—	—	—	—
	P ^b :2.0% H ₂ O ₂ :2.5% NaOH	—	15.5	18.9	85.4

^a A stage was carried out using 32% acetone charge at 25°C and 13.6 % pulp consistency for 30 min.
^b Peroxide stage was carried out at 60°C and 14% pulp consistency for 100 min with 3.0% sodium silicate and 0.5% MgSO₄.
^c A stage was carried out using 8% acetone charge at 25°C and 13.6% pulp consistency for 30 min.

Literature cited

- Munro, F. C., *Pulp and Paper Can.* 88(7): 34(1987).
- Lachanel, D., *Pulp, Paper and Board* (I. F. Hendry and W.J.H. Hanssens, Eds.), Elsevier Applied Science, London and New York, 1987, p. 33.
- Fossum, G. K. and Haggstrom, S. L., U. S. pat. 4,222,819 (Sept. 16, 1980).
- Rapson, W. H. and Anderson, C. B., *CPPA 1985 International Pulp Bleaching Conference Proceedings*, CPPA, Montreal, p. 227.
- Hammann, R. P. M. and Kordsachia, O., *Holzforchung* 45(Supplement): 87(1991).
- Lindholm, C.-A., *STFI 1991 International Pulp Bleaching Conference Proceedings*, STFI, Stockholm, vol. 2, p. 1.
- Springer, E. L., U. S. pat. 4,756,800 (July 12, 1988).
- Cael, J. J., U. S. pat. 4,404,061(Sept. 13, 1983).
- Meier, J. and Arnold, G., U.S. Pat. 5,091,054 (Feb. 25, 1992).
- Murray, R. W., *Chem. Rev.* 89: 1187(1989).
- Curci, R., *Advances in Oxygenated Processes* (A. L. Baumstark, Ed.), JAI Press Inc., Greenwich, CT., 1990, Vol. 2, p. 1.
- Murray, R. W. and Jeyaraman, R., *J. Org. Chem.* 50: 2847(1985).
- Lee, C.-L., PCT, International publication number, WO 91/12369, Aug. 22, 1991.
- Ragauskas, A.J., *Tappi J.*(76):7(87)1993.
- Lee, C.-L., Murray, R.W. and Hunt, K. PCT, International Publication number, WO 92/13993, Aug. 20, 1992.

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