

Investigation of dimethyldioxirane as a bleaching reagent for kraft pulp

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ABSTRACT: *The bleaching efficiency of dimethyldioxirane was explored for softwood kraft pulps. Preliminary studies demonstrated that kraft pulps could be delignified with dimethyldioxirane. Initial bleaching studies employed dimethyldioxirane prepared by distillation or in-situ from peroxymonosulfate, acetone, water, and sodium bicarbonate. Further studies established that the bleaching reagents could be premixed and added to pulp to afford a comparable bleaching result.*

KEYWORDS: *Acetone, bleaching, kraft pulps, peroxides, sodium bicarbonate.*

In response to recent changes in public policy, the paper industry is examining a variety of nonchlorine-based bleaching procedures. Although no one reagent has been found to have all of the bleaching advantages of chlorine, significant advances have been achieved employing oxygen-based bleaching procedures (1). The use of oxygen, ozone, and hydrogen peroxide have all been successfully incorporated into multistage bleaching sequences (2), and research is continuing to develop alternative oxygen-based bleaching procedures.

A variety of organic and inorganic peroxides have been examined with respect to their bleaching efficiency. Several recent papers by Springer (3, 4) have demonstrated that caroic acid (peroxymonosulfate) can be employed as a bleaching and/or delignification

reagent for kraft pulp. The relative ease of preparing this reagent *in situ* or the application of commercial sources of caroic acid as a triple salt of $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (monopersulfate compound) further enhances the utility of this inorganic peroxide for bleaching. The research efforts of Hammann *et al.* have illustrated that caroic acid supports the bleaching effects of oxygen, ozone, and peroxide in a four-stage bleaching sequence of softwood kraft and ASAM pulps (5). Under optimized conditions, caroic acid was shown to react as an efficient delignifying and brightening agent without overly affecting the physical properties of the pulp.

A review of the chemical literature indicates that peroxymonosulfate can oxidize a wide variety of compounds (6), although most frequently this re-

agent is employed in the presence of a ketone. The research efforts of Montgomery (7) and Edwards (8) have demonstrated that certain ketones can catalyze the oxidative reactions of peroxymonosulfate through the intermediacy of dialkyldioxiranes (see Fig. 1). In the presence of an oxidizable substrate (X), the dioxirane intermediate then becomes the effective oxidant. Recent studies have shown that these cyclic peroxides display impressive reactivity and efficient oxidizing capabilities (9, 10). In light of these results and the potential applicability of caroic acid and/or monopersulfate compound for bleaching kraft pulps, we have initiated a research program directed at evaluating the use of dimethyldioxirane (DMD) as a novel bleaching reagent. This paper describes our initial results of bleaching softwood kraft pulps with dimethyldioxirane, generated from an aqueous solution of acetone, sodium bicarbonate, and monopersulfate compound.

Results and discussion

Initial research efforts were focused on determining the intrinsic bleaching properties of DMD without competing bleaching reactions from the monopersulfate compound. DMD in acetone was readily prepared by adding the monopersulfate compound to an aqueous acetone solution of sodium bicarbonate and vacuum distilling the DMD (10). A 5% charge of DMD in acetone was then applied to softwood kraft pulp with an initial kappa value of 39.5. After stirring the pulp mixture

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(3% consistency, 1:1 acetone/water) for 1 1/2 h at room temperature, the pulp was washed with water, and a kappa value of 12.5 was determined for the bleached pulp. Subsequent caustic extraction removed minor amounts of lignin yielding a final kappa value of 11.9.

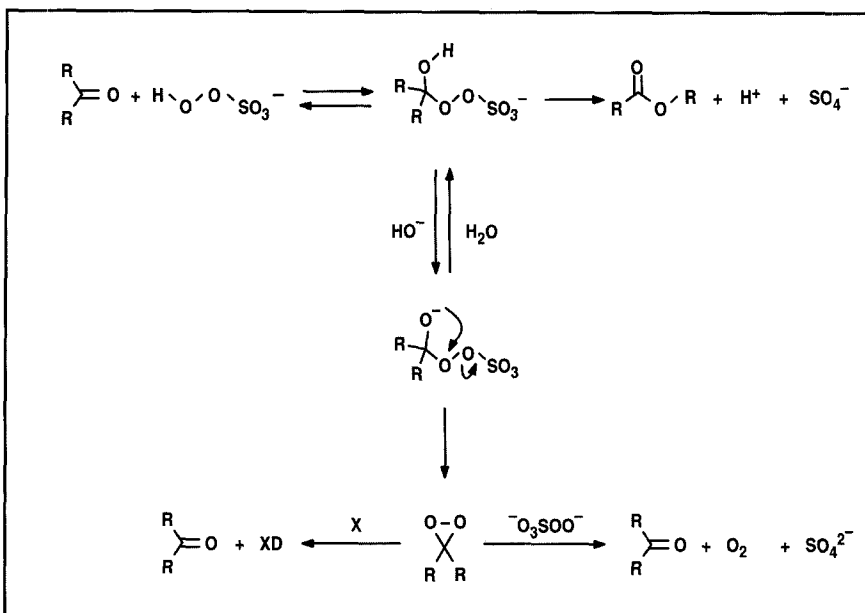
The 66% drop in lignin content indicated that DMD is an exceptionally reactive peroxide with unique bleaching properties. To further explore the potential applicability of this reagent for bleaching chemical pulps, we examined alternative procedures for generating DMD. Initially the bleaching efficiency of *in-situ* generated DMD was examined by employing an aqueous acetone/sodium bicarbonate/monopersulfate compound solution and two different softwood kraft pulp samples. The extent of delignification for two kraft pulps was examined at several charge levels, employing a 2:1 volume acetone-to-water ratio. **Table I** summarizes the experimental results.

The bleaching efficiency of *in-situ* generated DMD was evaluated through a series of control experiments which employed monopersulfate compound/sodium bicarbonate/water as the bleaching system. For these latter experiments, the bleached pulp was washed with water, followed by an acetone wash, and a final water wash. The results of the control experiments and the *in-situ* generated DMD bleaching/caustic extraction experiments are summarized in **Fig. 2** and **Table I**.

A comparison of the water-based bleaching reactions versus the aqueous acetone reactions demonstrates that the latter system is more efficient at removing lignin. The fact that these differences remain after washing the control bleached pulps with acetone suggests that the differences in kappa values were not solely due to solubility differences in oxidized lignin. Our results are consistent with a recent patent application filed by Lee Chung Li (11), which employed monopersulfate compound and an acetone/water slurry to bleach softwood kraft pulps.

The changes in viscosity for bleaching the 39.5 kappa softwood kraft pulp

1. General reaction mechanism for peroxymonosulfate and ketones



I. Effects of monopersulfate compound treatment on the delignification of a softwood kraft pulp^a

Charge, % ^a	Kappa number ^b				
	Initial	Water ^c		Water/acetone ^d	
		Bleached ^e	Extracted ^g	Bleached ^e	Extracted ^g
145	39.5	27.7	26.2	16.3	10.1
72	39.5	31.6	30.1	17.8	10.8
30	39.5	32.3	30.5	26.6	21.3
15	39.5	—	—	28.5	23.9
3	39.5	38.1	36.6	35.5	34.7
16	27.6	23.4	21.0	16.9	14.0
8	27.6	26.2	24.0	20.9	19.0

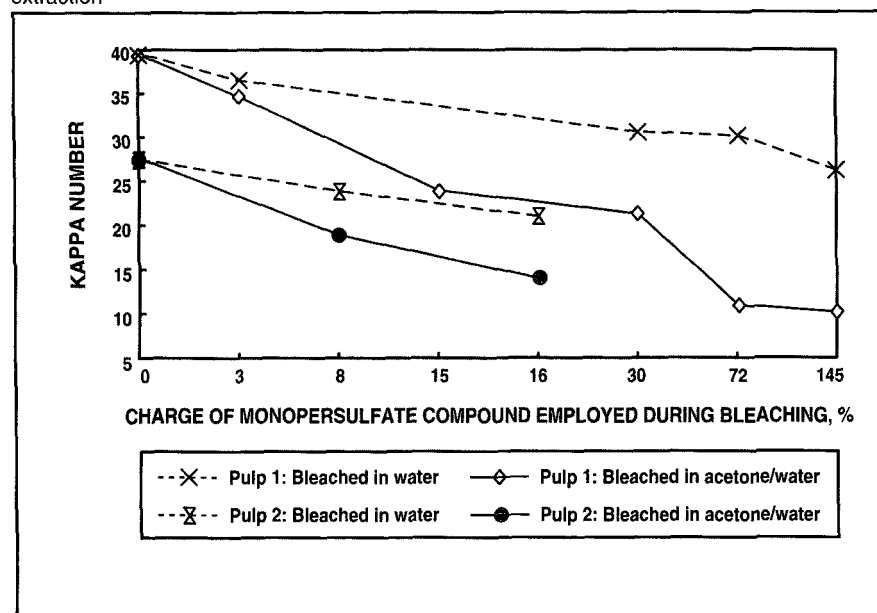
^aAll bleaching reactions employed equal weight equivalents of monopersulfate compound and NaHCO₃; the high-kappa pulp experiments employed 7.50 g of dry weight pulp, and the low-kappa pulp experiment employed 12.00 g dry weight pulp; ^bKappa values were determined following TAPPI procedures (12); ^cBleaching reactions employing only water (300 mL) as a solvent; ^dBleaching reactions employing a 2:1 mixture of acetone/water (300 mL) as a solvent; ^echarge of monopersulfate was based on percent dry pulp; ^fKappa value after bleaching; ^gKappa value of pulp after bleaching and extracting with 1.5% NaOH solution.

II. Effects of monopersulfate compound treatment on the viscosity of a 39.5 kappa softwood kraft pulp 38.7 cp pulp^a

Charge, %	Viscosity ^b , cp				
	Starting	Water ^c		Water/acetone ^c	
		Bleached ^e	Extracted ^f	Bleached ^e	Extracted ^f
30	38.7	32.3	26.7	25.1	26.8
15	38.7	--	--	29.2	28.4

^aFor full experimental detail, see Table I; ^bViscosity values were determined following TAPPI procedures (13); ^cBleaching reactions employing only water; ^dBleaching reactions using a 2:1 mixture of acetone/water; ^eKappa value after bleaching; ^fKappa value of pulp after bleaching and extracting with 1.5% NaOH solution.

2. Delignification of softwood kraft pulp by monopersulfate compound followed by caustic extraction



III. Effects of varying premixing conditions for an 8% charge of monopersulfate compound^a delignifying a 27.6 kappa softwood kraft pulp

Premixture solvent Volume, mL	Premixture Acetone: water	Premixing time, min	Kappa number	
			Bleached ^b	Extract ^c
160	3.0:1.0	5.0	21.7	20.5
80	3.0:1.0	5.0	21.8	20.2
80	3.0:1.0	15.0	24.0	23.5
80	No acetone	5.0	24.4	23.1
80	1.0:1.0	5.0	24.1	20.8
80	1.0:1.8	5.0	25.3	23.9
80	1.0:3.0	5.0	23.9	21.2
80	1.0:7.0	5.0	24.0	21.4
80	1.0:7.0	15.0	23.9	23.3
20	1.0:1.0	5.0	25.1	23.3

^aBleaching reagent was premixed for a fixed period of time and was then added to an aqueous slurry of pulp, (12 g dry pulp, 2% consistency) and stirred for 1 h; ^bKappa value after bleaching; ^cKappa value of pulp after bleaching and extracting with 1.5% NaOH solution; ^dRatio of acetone to water is volume:volume.

with monopersulfate compound are summarized in **Table II**. These data also indicate that the use of acetone is advantageous with respect to changes in viscosity during bleaching. The experimental results summarized in Table I and II are suggestive of an enhanced bleaching effect due to the *in situ* generation of DMD, although the possible contribution of solvent effects on the peroxy monosulfate oxidation reactions could not be precluded.

To address these issues and to develop a bleaching system with greater potential for practical application we focused our research efforts on developing an experimental procedure which minimized the acetone component. The bleaching of softwood kraft pulp was therefore investigated employing an aqueous pulp slurry and a premixed solution of the bleaching reagents. The bleaching mixture employed an 8% charge of monopersulfate

compound and varying amounts of acetone and water. After vigorously stirring the bleaching solution for a fixed time period, it was then added to the pulp slurry. The resulting mixture was stirred for 1 h at room temperature and after washing was analyzed for lignin. The bleached pulp was then extracted with an aqueous 1.5% NaOH solution, at room temperature. The kappa values for the bleached and extracted pulps are summarized in **Table III**. The results of these studies demonstrate that the bleaching response is sensitive to the premixing conditions and that small amounts of acetone enhance the overall delignification process. The premixing time was also shown to influence the extent of delignification, and based upon current experimental data, the optimal time is approximately 5 min.

The increased delignification in the presence of acetone is attributed to the formation of the DMD and its enhanced bleaching efficiency. A comparison of the bleaching results using the most efficient premixing conditions (Table III, second entry) versus using an acetone/water solution (Table I, last entry) indicates that the final kappa values are comparable after caustic extraction. These results suggest that there is no need to employ acetone as a co-solvent during bleaching. Instead, by employing the premixing conditions developed in this paper, it is possible to get an effective bleaching response with significantly less acetone.

Conclusions

The bleaching of softwood kraft pulps with monopersulfate compound can be improved significantly when employing small amounts of acetone. Based upon the results of our research efforts, the increased delignification of the pulps when monopersulfate compound and acetone is employed is attributed to the *in situ* generation of DMD, which was shown to be an efficient bleaching reagent. Preliminary bleaching studies have shown that *in situ* generation of DMD can be

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achieved prior to addition to the pulp. By employing this procedure, there is no need to use an aqueous acetone slurry of pulp to enhance the bleach capabilities of peroxymonosulfate. These results suggest that the use of DMD generated from monopersulfate compound or alternative chemical procedures could be of potential use for bleaching kraft pulps in an oxygen-based bleaching sequence.

Experimental

Material

Acetone, sodium bicarbonate, and monopersulfate compound (trade name, Oxone) were commercially purchased and used without further purification. Bleaching studies employed two different industrial, never-dried, southern pine kraft pulp samples which

had starting kappa values of 39.5 and 27.6.

General bleaching procedure

All bleaching experiments employing DMD were executed following standard laboratory procedures for handling peroxides (14). Bleaching experiments were performed in an open beaker for 1 h (7.5 g dry weight of pulp) with stirring at room temperature. The bleached pulp was then filtered and washed. The wash cycle employed either three water rinses (500 mL) or water (500 mL) followed by acetone (500 mL) followed by a third water wash (500 mL). The latter treatment was employed only if no acetone was used during the bleaching reaction. The resulting pulp was then analyzed for residual lignin content.

Bleached pulp (4 g dry weight of pulp) was then extracted with an aqueous 1.5% NaOH solution at room temperature, for 3/4 h (300 mL) and then washed with water (3 x 500 mL). A sample of this pulp was then analyzed for lignin content. □

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