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Kraft Bagasse Pulp Delignification with Dimethyldioxirane

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ABSTRACT

Dimethyldioxirane (DMD), which is a source of active oxygen, is effective agent that can be used in chemical pulp bleaching. In this study, delignification of kraft bagasse pulp has been carried out by using DMD. The effect of the applied charge of DMD (as active oxygen) and pH of the delignification medium were studied. The optimum conditions of the applied DMD charge and pH of the delignification reaction were achieved at pH range from 8~9, 2% of DMD (as active oxygen) and the rest of delignification reaction conditions were 25℃, 60 min, and 12% pulp consistency. The development of brightness per unit kappa number removal (Δ Brightness/ Δ Kappa number) has highest value at the optimum condition.

The study showed that the reactivity of kraft bagasse pulp could be enhanced to wards alkaline hydrogen peroxide bleaching by pulp treatment with DMD.

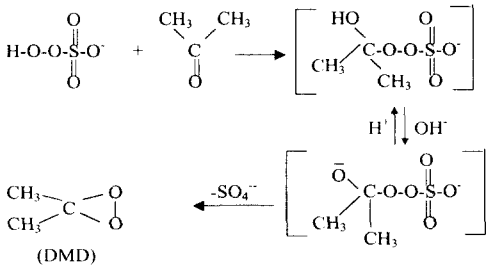
1. Introduction

Concerns regarding the environmental effects of chlorinated organic compounds formed as by-products during pulp bleaching created a demand in the pulp market for "totally chlorine-free" pulps, i.e., pulps produced without the use of chlorine or chlorine compounds. Persulphuric acid or Caro' s acid and its caroate anions have features that are attractive for kraft pulp bleaching[1-2]: 1) Caro' s acid is more efficient solubilizer of lignin than is H_2O_2, 2) it is marginally more expensive than H_2O_2, because H_2SO_4 is the only reactant needed to generate it from H_2O_2, and[3] the sulphate anions in the resulting bleaching effluent can be recycled to the kraft recovery system. The formation reactions for Caro' s acid and caroate anions are summarized in the following equations:

$$x\ H_2SO_4+H_2O_2 \rightleftarrows H_2SO_5+(x-1)\ H_2SO_4+H_2O$$
$$H_2SO_5+H_2O \rightleftarrows HSO_5^-+H_3O^+$$

Recently a cyclic peroxide, namely; dimethyldioxirane (DMD), which possesses a relatively high oxidation potential, has been described as being selective reagent for use in the pulp bleaching.[3-5]

DMD has been proposed for bleaching purposes since its application gave comparable results to other oxidative agents as part of bleaching sequences.[6] DMD formation is summarized as follows:



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DMD is capable of transferring an oxygen atom to a variety of donor compounds yielding an oxidized product. Work with lignin-like model compounds[7] has showed that DMD electrophilically attacks the aromatic rings of both etherified and non-etherified structures. This is a significant advantage of this reagent, over other bleaching agents such as chlorine dioxide, oxygen, or hydrogen peroxide which act solely on structures passessing free phenolic hydroxyls.[8]

It is an object of the present study to provide a process for bleaching kraft bagasse pulp that avoids the use of chlorine-containing bleaching agents. In this study, the delignification of kraft bagasse pulp with DMD was examined, together with the effect of pH on delignification and reduction of degree of polymerization.

2. Experimental

2.1 Material

Kraft bagasse pulp of kappa number 17.30, DP 950 and brightness 39.50. The pulp was delivered from Edfu Mill-Egypt.

2.2 Methods

Treatment of kraft bagasse pulp with dimethyldioxirane (DMD):

Dimethyldioxirane was generated by the in-situ method.[9] The method comprises exposing the pulp at pH 6.0 to 10.0 to a mixture of persufuric acid and acetone. The charge of dimethyldioxirane as active oxygen (AO) was calculated as one oxygen atom per HSO_5^- anione. Persulfuric acid was prepared and analyzed according to Greenspan and Mackellar.[10]

Kraft bagasse pulp was mixed with 3.0 times its weight of acetone (stage would have to be channeled to recovery system for acetone). Different DMD charges (as active oxygen) were applied on the treated pulp with acetone. The DMD doses were ranged from 0.5 to 2.5% (AO based on o.d. pulp) at different pH from 6 to 10 for 60 min at 25°C and 12% consistency. The buffer is sodium bicarbonate. The active oxygen (AO) consumption was determined as follows:

$$\text{AO consumption, \%} = \frac{AW - bV \times W/C - W \times 10^4}{AW}$$

A = AO applied (as % o.d pulp)
W = weight of o.d. pulp
b = 0.016 (for 0.01 mol/L thiosulphate)
v = thiosulphate titre (mL)
C = Pulp consistency (12% = 0.12)

-Hydrogen peroxide bleaching: The pulp was treated with 2%H_2O_2 (on o.d. pulp) at 70°C, pH = 11 for 60 min and 10% pulp consistency.

-Pulp tests:

Kappa number SCAN-C 1:77
Degree of polymerization (DP)[11]
Brightness: Tappi standard method T 216 wd-27
Breaking length: Tappi standard method T 404 om-87
Tear factor: Tappi standard method T 414 om-88

3. Results and Discussions

3.1 Kraft bagasse pulp delignification by using DMD

Kraft bagasse pulp was delignified with dimethyldioxirane (DMD) using applied charge from 0.5 to 2.5% active oxygen (based on o.d. pulp) at different values of pH of reaction medium. The rest delignifying conditions (Time, 60 min; temperature, 25°C and

Table 1. Effect of applied DMD dose (as active oxygen) and pH on the properties of kraft bagasse pulp

DMD (% AO on o.d. pulp) Added	Consumed	pH	Yield, %	Kappa number	Bright. % ISO	DP
Unbleached kraft bagasse pulp				17.30	39.50	950
1.50	1.25	6.00	95.75	10.20	42.98	890
1.50	1.30	7.00	96.20	6.55	53.79	907
1.50	1.46	8.00	96.85	4.60	69.50	915
1.50	1.47	9.00	96.55	3.61	67.50	883
1.50	1.23	10.00	96.43	4.87	61.55	875
0.50	0.50	8.00	97.20	6.75	49.85	935
1.00	1.00	8.00	97.15	5.10	62.07	922
1.50	1.46	8.00	96.85	4.60	69.50	915
2.00	1.93	8.00	95.30	3.56	73.25	895
2.50	1.94	8.00	95.10	1.93	73.60	882

The rest delignificatioin conditions : Time 60 min.
Temp. 25℃.
Consistency 12%.

consistency, 12%) were kept constant, Table 1. As can be seen, the delignification achieved was measured in terms of kappa number. At fixed charge of DMD (1.5% active oxygen on pulp), the reduction of kappa number of the pulp was essentially dependent upon the pH values of the delignification medium. The optimum pH values, at which highest degree of delignificant, were ranged from 8 to 9. After this pH range, pH = 10, raising of kappa number was noted. Thus, highest selectivity of DMD delignification of the pulp was manifested through the range of pH from 8 to 9. The degree of polymerization (DP) was affected by pH as shown in Table 1. The lowest degradation effect (highest DP) was achieved at pH = 8. Therefore, the delignification with DMD is more selective at pH = 8. At pH equals to 8, increasing of the applied dose of DMD resulted in significant decrese of kappa number of the produced pulps with slightly decreasing of degree of polymerization. Thus, delignification with DMD could result pulp characterized by high degree of delignification and low DP degradation.

The development of brightness per unit kappa removed (Δ Brightness/ Δ kappa) is considered on important feature of the delignification process at different conditions.

Fig. 1 shows the effect of pH on the development of brightness per unit kappa removed during the pulp delignification with DMD. As shown in Fig. 1, (Δ Brightness/ Δ kappa) increases with increasing of pH values from 6 to 8. After pH equals to B, decreasing of (Δ Brightness/ Δ kappa) was observed. As shown in Fig. 2, (Δ Brightness/ Δ kappa) passes through a maxima at 2% applied dose of DMD (as active oxygen). There , optimum value of (Δ Brightness/ Δ kappa) could be achieved at pH equal to 8 and 2% applied dose of DMD.

3.2 Enhancement of kraft bagaase pulp reactivity towards alkaline hydrogen peoxide bleaching

Pure hydrogen peroxide is thought to react, almost exclusively, with the carbonyl structures present in lignins. Its action on

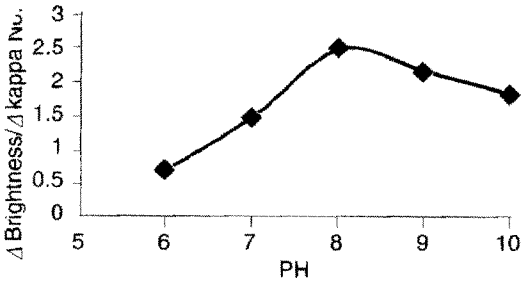

Fig. 1. Effect of pH of applied DMD on the development of brightness per unit kappa removal.

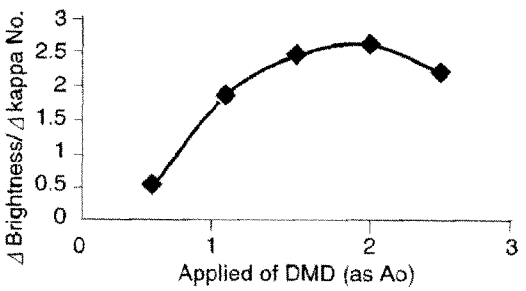

Fig. 2. Effect of applied DMD dose on the development of brightness per unit kappa removal.

residual lignin may not be very significant since small amounts of such species are present.[12] Consequently, hydrogen peroxide is employed toward increasing the pulp brightness at the final bleaching stages rather than for actual delignification purposes. Alternatively, the various modes of decomposition of hydrogen peroxide results in the formation of hydroxyl radicals, oxygen and superoxide ions. There may attack reactive lignin structures, i.e., phenolic units bearing no carbonyl group. The use of alkaline hydrogen peroxide has thus been proposed as a bleaching system for kraft pulps.[12] As shown in Table 2, kraft bagasse, pulp was subjected to 2% alkaline hydrogen peroxide. Low brightness value of the produced pulp has been achieved 61.11% ISO.

The enhancement of krat bagasse pulp reactivity towards alkaline hydrogen peroxide could be carried out by treatment of the pulp with DMD perior to the alkaline peroxide stage, Table 2. As can be seen, the introducing of DMD stage led to increasing of the produced pulp brightness (79.75% ISO) and high degree of delignification (kappa no. = 1.62).

The partition of the applied DMD dose (2% active oxygen) via two stages, as shown Table 2, led to slight decrease in kappa number and increasing of the brightness of the produced pulp. From Table 2, the introduc-

Table 2. Enhancement of the bleachability of kraft bagasse pulp toward alkaline hydrogen peroxide bleaching

Bleaching sequences	Chemical, % on pulp Added	Chemical, % on pulp Consumed	Yield, %	Kappa number	Brightness, % ISO	DP	Breaking length, km	Tear factor
Unbleached kraft bagasse pulp				17.30	39.50	950	5.54	83.60
P (as H_2O_2)	2.00	1.98	95.75	8.54	61.11	915	5.43	80.35
DMD (as active oxygen)	2.00	1.90	95.30	1.65	79.75	880	5.39	77.56
P (as H_2O_2)	2.00	1.92						
DMD (as active oxygen)	1.00	0.98	95.65	1.32	80.83	885	5.40	79.32
DMD (as active oxygen)	1.00	0.96						
P (as H_2O_2)	2.00	1.90						

DMD stages were carried out at 25°C for 60 min at pH = 8 and 12% pulp consistency.

ing of DMD in alkaline hydrogen peroxide bleaching led to non significant decrease in the strength properties (breaking length and tear factor) of the produced pulps.

4. Conclusions

A new class of oxidants (generated active oxygen) used in the bleaching of kraft bagasse pulp has demonstrated good selectivity towards lignin removal. The applied dose of DMD and pH of the delignification media have the principle role in the pulp delignification. pH range from 8 to 9 is much more effective in pulp delignificatioin with slight decreasing of DP than other pH values used. The most selective applied dose of DMD is 2% (as active oxygen). The treatment of kraft begasse pulp with DMD has enhanced the bleachability of the pulp by using alkaline hydrogen peroxide.

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