Approach Towards Ultra High Brightness (90+ISO) with Low Impact on the Environment

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ABSTRACT: The recent trend in the Indian market being towards pulps of high brightness (85-90% ISO), the pulp and paper industry is ultimately forced to choose multistage bleaching sequences to reach the target. The revised environmental regulations on paper mill effluents with regard to chlorinated organics has imposed a restriction in the usage of chlorine and chlorine containing compounds. Under these circumstances, bleaching to very high brightness with acceptable effluent quality is really a challenging task for the Indian paper industry. This paper highlights the usage of Elemental chlorine free (ECF) bleaching sequences that can easily be retrofitted in the existing bleaching systems of kraft hardwood and bagasse, to achieve 90% ISO with decrease in the chlorinated organics.

KEY WORDS: Chlorine free bleaching, AOX, High brightness, Peroxide bleaching, Oxygen delignification, Sequesteration, short bleaching sequence.

INTRODUCTION

New products are primarily developed to meet the specific requirements of the customers. Growing competition in the present day market has forced the Pulp and Paper industry, to go for pulps of very high brightness levels (85 to 90% ISO). Invariably, the new products developed are of very high brightness and cleanliness, with multistage bleaching sequences involving huge amounts of chlorine and chlorine containing compounds such as hypochlorite and chlorine di oxide. Use of excessive amounts of such compounds, ultimately results in the formation of chlorinated organics in the bleach plant effluent. Elemental chlorine is the major contributor for the production of chlorinated organics (1). The chlorinated organics are also measured as Adsorbable Organic Halogens (AOX) which comprises of EOX (Extractable Organic Halogens), EPOX (Extractable Persistent Organic Halogens) and POX (Purgable Organic Halogens). These organic halogens are primarily chlorinated phenols, chlorinated resin acids and chloroform. Among these, the two major chlorinated compounds: Tetrachloro Dibenzo Dioxin (TCDD) and Tetrachloro Dibenzo Furan (TCDF) (Fig 1) are the most toxic compounds even at ppt levels to the aquatic environment (2).

The formation of chlorinated organics in the bleach plant effluent is mainly because of the substitution reactions that occur during the chlorination of the

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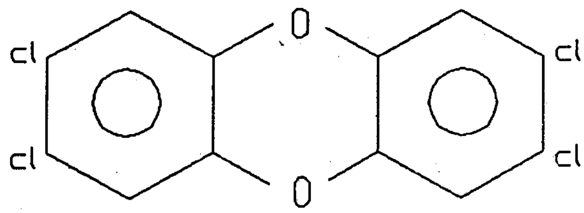
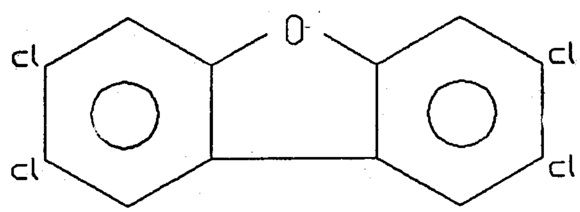
FIG:1



2,3,7,8 Tetrachloro di benzodioxin



2,3,7,8 Tetrachloro di benzofuran

residual lignin, remaining after the pulping process. The substitution reactions are a function of the amount of chlorine applied to the pulp (1). Therefore the following are in practice to reduce the usage of chlorine and in turn chlorinated organics generation.

1. Maintaining lower Kappa factor,
2. Achieving lower unbleached pulp Kappa number,
3. Substitution of chlorine di oxide for chlorine,

Since the contribution of chlorine is significant for AOX generation, total elimination of molecular chlorine in bleaching considerably reduces these toxic substances in the effluent. On the other hand, chlorine is the most versatile bleaching agent because of its effectiveness and relatively low cost. So, bleaching of pulps without molecular chlorine to high brightness levels 90% ISO, presents a formidable challenge to the paper industry.

Elemental chlorine free bleaching gains a special significance in view of the imposition or more stringent governmental regulations with respect to chlorinated organics. The discharge limits for TOCl, which is a synonymous term to AOX, has been included in the recent revised specifications for effluents emanating from pulp and paper mills in India.

So achieving high brightness, while abiding the governmental regulations, is the chief objective of this work. Studies have been oriented towards achieving high brightness of 90+ISO, with bleaching sequences without involving molecular chlorine. Bleaching agents like oxygen, peroxide, enzymes, hypochlorite, and chlorine di oxide, have been utilised judicially, to achieve the target brightness with minimum number of stages. The sequences discussed are easily retrofittable in the existing bleach plants and require no major modifications. The number of stages involved are very less and low generation of chlorinated organics can be expected in the effluent.

EXPERIMENTAL

Pulps

Unbleached screened hardwood kraft pulp and unbleached screened bagasse kraft pulp were collected from the plant. The pulps were washed thoroughly over 250 mesh, and thickened in a hydro extractor and shredded to uniform consistency. The unbleached pulp characteristics are given in Table 1.

Table-1.

Initial Pulp characteristics

Pulp	Kappa Number	Brightness % ISO	Viscosity cP s
Bagasse Unbleached Pulp	9.4	50.4	30.8
Bagasse Oxygen delignified pulp	3.8	65.2	28.1
Hardwood Unbleached pulp	16.2	25.9	9.4
Hardwood oxygen delignified pulp	7.1	47.9	8.4

Bleaching

Bleaching of pulps were carried out in the laboratory with 20g (o.d.) pulp for exploratory tests and 200g (o.d.) pulp for optimised sequences. Conditions maintained during various bleaching sequences are given in Table 2.

Oxygen delignification was performed in laboratory programmable digester, under the conditions given

Table-2.

General Bleaching conditions

Parameter	Oxygen O	OP	Acid Peroxide AP	Oxidative Extraction EP	Peroxide P	chelation Q	Hypo chlorite H	Chlorine di oxide D	Enzyme X
Consistency, %	8.0	8.0	10	8.0	8.0	3.5	8.0	8.0	8.0
Temperature, °C	120	100	85	60	90	85	40	70	50
Reaction Time, min	30	60	60	60	240	30	120	180	120
Sodium hydroxide, %	2.0	2.0	-	var.	var.	-	var.	-	-
pH	10-12	10-12	5	10-12	10-11	5	9.5-10.0	3.5-4.0	4.5
Oxygen Pressure. MPa	0.5	0.5	-	-	-	-	-	-	-

EDTA in 'Q' Stage 0.2%
Q stage is always preceded by acidwash at 5 pH

in Table 2. Magnesium carbonate was mixed with the pulp before adding the alkali. In the peroxide reinforced oxygen stage, (OP) peroxide was also mixed with the pulp after alkali addition. Oxidative extraction, peroxide bleaching, chlorine di-oxide bleaching and hypochlorite bleaching were performed in polythene bags. Oxidative extraction (EP) with peroxide in the extraction stage was performed by adding the required hydrogen peroxide with the alkali. Acid peroxide (AP), delignification was carried out as per the conditions in Table 2 with 500 ppm of sodium molybdate as catalyst. Alkaline peroxide (P) bleaching was preceded by acid wash and chelation step (Q). The pulps were acidified with dilute sulphuric acid to pH 5.0, at 3.5% consistency and then dewatered. The pulp was subsequently treated with 0.2% EDTA under the conditions given for Q stage followed by dewatering. Subsequently the pulp was subjected to alkaline peroxide bleaching.

Hypochlorite bleaching and chlorine di oxide bleaching were carried out under the conditions mentioned and the desired pH was maintained throughout the bleaching period by addition of buffer. The pulps, after bleaching, were washed with demineralised water equivalent to 20 times the od weight of the pulp. Pulp evaluation was carried out as per Tappi standards. Kappa number, brightness pads and handsheets for pulp evaluation, were done as per Tappi standards. Brightness Post colour number and other optical properties were determined using Elrepho.

RESULTS AND DISCUSSION

As the primary objective of chlorine free bleaching is to achieve very high brightness without molecular chlorine, it was felt that the incoming kappa of the unbleached pulp should be reduced. Generally, chlorine free bleaching sequences, either ECF or TCF, are commenced with low kappa of unbleached pulp. This is attained either by oxygen delignification, or by modern pulping technologies like Rapid Displacement Heating (RDH), Modified Continuous Cooking (MCC), Extended Modified Continuous Cooking (EMCC) (3).

In the Indian context, where the principal raw materials are hardwoods and bagasse, having comparatively lower lignin content than softwoods, conventional kraft pulping itself yields low kappa pulps (10 for bagasse and 20 for hardwoods), without suffering loss in pulp strength and/ or yield. Technologies like RDH and MCC require major changes in the process design. Alternately our strategy was to use oxygen delignification, which has proved itself to be a versatile delignifying step, to lower the unbleached pulp kappa number. Among the oxidative steps available for delignification, viz P, EO, EOP, O, Oxygen is the most efficient with respect to kappa number reduction, economically, without significant loss in pulp yield or strength.

Oxygen delignification

Optimum conditions for oxygen delignification were determined using the Plackett and Burman design of experiments (4). Based on those experiments, following linear equation was arrived at for kraft hardwood and bagasse pulps.

Bagasse pulp

Kappa number: 5.4 -0.6 (alkali% - 2.0) - 0.05 (temp.-110) - 0.02 (time-37.5)

Hardwood pulp

Kappa number: 7.35 - 0.020 (time-37.5) - 0.036 (temp.-110) - 0.345 (alkali - 4.0) - 0.053 (pres.-6.5)

The incoming Kappa of the unbleached pulp entering oxygen delignification is usually maintained on the higher side to exploit the advantages of higher yield and strength (5). But the lower kappa numbers are preferred for bagasse due to the following reasons:

1. At higher kappa numbers, bagasse gives a pulp of poor cleanliness with higher amount of shives, which are not desirable for ECF bleaching to high brightness.
2. Lower the unbleached pulp kappa number, better will be the ease of bleachability with ECF sequence particularly in the case of hardwoods, which has a poorer bleaching response in comparison to bagasse.

Oxygen is not a specific delignifying agent. It has very low selectivity in comparison to chlorine (6). Hence preserving the cellulose from degradation is of paramount value and is accomplished by addition of magnesium compounds. Hence it is the usual practice to add magnesium carbonate or magnesium sulphate and restrict the kappa reduction to 50% to minimise loss in strength and yield. The Plackett and Burman design of experiments for oxygen delignification were carried out in optimising various parameters like temperature, alkali time, oxygen pressure, and consistency. The results achieved with the above experiments (Table 1) show a 50-55% reduction in kappa number over the unbleached pulp. A brightness of 65% ISO for bagasse pulp and 48% ISO for hardwood pulp, were obtained.

Optimisation of further bleaching stages

The oxygen delignified pulps were subjected to various bleaching sequences which result in 90% ISO brightness. It has been our experience that bagasse pulps are easily bleachable than hardwood pulps and have excellent response to bleaching even with very little amount of bleach chemicals. In the regular CEH bleaching of bagasse pulps, the kappa number of the pulp after chlorination and extraction reaches a value as low as 2-2.5 and even 0.5% hypochlorite is sufficient to attain 82-83% brightness.

Sequences for Bagasse pulps

The oxygen delignified bagasse pulp (Kappa 3.8) was treated with 0.5% calcium hypochlorite, followed by a final chlorine di oxide brightening stage $O\text{-}H_{0.5}\text{-}D_1$. Contrary to our expectations, the brightness obtained (Table 3) was only 86% ISO. For effective chlorine di oxide brightening, the incoming kappa number of the pulp entering the chlorine di oxide stage should be less than 2.0, Increasing the hypochlorite charge from 0.5 to 1.0% in the O-H-D sequence was sufficient to reach the target of 90% ISO. Hence, this simple short sequence was sufficient for attaining high brightness, and this can be easily retrofitted. The attainment of 90% ISO even with short three stage sequence stands testimony for the excellent bleaching response of bagasse pulps.

Table-3

Optimisation of ECF Sequences for 90% ISO

Sequence	Brightness %ISO
Bagasse pulp	
O	65.6
$O\text{-}H_{0.5}\text{-}D_1$	85.9
$O\text{-}H_1\text{-}D_1$	89.7
OP_2	76.8
$OP_2\text{-}H_{0.5}\text{-}D_1$	86.9
$OP_2\text{-}H_1\text{-}D_1$	90.4
Q/OP_2	80.9
$Q/OP_2\text{-}H_{0.5}\text{-}D_1$	88.9
$Q/OP_2\text{-}H_1\text{-}D_1$	90.8
$Q/P_2\text{-}H_1\text{-}D_1$	87.4
$Q/P_2\text{-}H_2\text{-}D_1$	90.1

Sequence	Brightness %ISO
Hardwood pulp	
O	47.9
O-Q/P_2-H_2-D_1	87.6
O-Q/P_2-H_2-D_2	90.4
O-AP_1-E-H_2-D_1	86.0
O-$AP_{0.5}$-$EP_{0.5}$-H_2-D_1	89.3
O-$AP_{0.5}$-$EP_{6.?}$-H_2-D_2	90.3
O-X-$EP_{0.5}$-H_2-D_2	90.9
O-X-$AP_{0.5}$-$EP_{0.5}$-H_2-D_2	91.8
O-Q/OP_2-AP_1-H_2-D_1	88.9
O-Q/OP_2-AP_1-H_2-D_2	90.0

Since the response of bagasse pulp to E C F bleaching was found to be good, further sequences without oxygen delignification were thought of. The selection of other bleaching agents depend upon the availability and selectivity. The use of bleaching agents like ozone is not applicable at present in the Indian context.

Peroxide bleaching

Hydrogen peroxide is chosen as the alternative to oxygen. The advantage of hydrogen peroxide is its good selectivity whereas, it has the disadvantage of low reactivity (6). Also it is highly susceptible to decomposition by metal ions like copper, manganese and iron. Various options are available for improving the reactivity and stability of hydrogen peroxide (7). Methods available for increasing the reactivity include enhancing temperature, increasing reaction time and increasing oxidation potential with compounds like nitrilamine. Stability of peroxide can be improved by removing metal ions by acid wash, chelation with a sequestering agent like EDTA, DTPA. Substantial improvement in brightness has been obtained by resorting to such stabilisation and activation steps (8). Our studies showed that including the reaction temperature from 60° C to 90° C and the reaction time from 2 hours to 4 hours, including an acid wash and chelation step resulted in a 8 to 12 points additional gain, for the same peroxide charge. While bleaching with the same amount of peroxide at 60° C for 2 hours gave a final brightness of 68% ISO, bleaching with the same amount of peroxide at 90° C for 4 hours preceded by an acid wash and chelation step (Q), yielded a brightness of 76% ISO for bagasse pulp (Data not shown). The acid wash followed by chelation dramatically improved the peroxide residuals, which may be attributed to the fact that metal ions deactivating peroxide have been taken care of well.

Based on these grounds, the unbleached bagasse pulp was bleached with 2% hydrogen peroxide, under the specified conditions. The peroxide bleached pulp subsequently reached 90% ISO with hypochlorite and chlorine di oxide stages. But the hypochlorite charge had to be increased from 1.0% to 2.0% to reach the target brightness. As mentioned earlier, hydrogen peroxide has lower delignifying ability in comparison to oxygen (9), and this has to be compensated by additional dosage of hypochlorite. So the short Q/P_2-H_2-D_1 sequence could also reach 90% ISO in case of bagasse. No doubt, bleaching with the O-H_1-D_1 sequence is cheaper in comparison to Q/P_2-H_2-D_1, but considering retrofittability, peroxide stage takes an edge over oxygen with lesser capital investment. The chelation step (Q) improves the brightness gain by 3-4 points. This gain is significant in case of TCF sequences, where every single point gain in high brightness range is important. Whereas in the ECF sequences, the final brightening stages are taken care of by powerful oxidising agents like hypochlorite and chlorine di oxide, and the gain of 3-4 point due to chelation, may not be carried over to the final stage. This was substantiated by our studies (Table 3) that, OP stage without chelation gave 76.8% ISO brightness while OP stage with chelation (Q/OP_2) gave 80.9% ISO, for bagasse pulp. But subsequent bleaching with hypochlorite and chlorine di oxide resulted in same utlimate brightness of 90% ISO.

Sequences for hardwood pulp

The hardwood pulps owing to their higher kappa number, has necessarily to be oxygen delignified to lower the initial kappa number. Lowering the hardwood pulp kappa to the level of unbleached bagasse pulp, with oxygen, was thought of. Similar bleaching sequences, as in the case of bagasse were tried to attain the 90% ISO brightness. The hardwood pulp after oxygen delignification, had a kappa number of 7.1 and brightness of 48.7% ISO. (Table 2).

In spite of the lower kappa number of the hardwood pulp after oxygen delignification, in comparison to bagasse unbleached pulp, subsequent Q/P_2-H_2-D_1

bleaching sequence with the same amount of chemicals as applied for bagasse pulp, could not yield a brightness of 90% ISO, which clearly indicates the poorer response of the hardwood pulps to ECF bleaching. Hence the final chlorine di oxide charge was increased to 2% to achieve 90% ISO. (Table 3).

As a further step towards achieving high brightness, reducing the kappa number of the oxygen delignified pulp to still lower levels, was thought of. The efforts towards further kappa number reduction included acidic peroxide (AP), peroxide reinforced oxygen (OP), and peroxide reinforced oxidative extraction (EP), and enzyme pretreatment (X).

Acidic peroxide stage (AP)

Molybdenum catalysed acidic peroxide delignification of kraft pulps has been reported to be effective in removing phenols by oxidation to Ortho and Para quinones (10). The phenolic biphenyl structures, present in the kraft residual lignin, are unreactive to oxygen, while they are oxidised by acidic peroxide. The acidic peroxide treatment, which is only a pretreatment stage, to active the lignin, is usually followed by an extraction stage to dissolve the oxidised lignin. Hence the oxygen delignified hardwood pulp, was treated with acidic peroxide followed by peroxide reinforced oxidative extraction. This was subsequently bleached with hypochlorite and chlorine di oxide (Table 3) 90% ISO could be obtained with lesser amount of peroxide in comparison to the O-Q/P$_2$-H$_2$-D$_2$ sequence. It may be noted that the total peroxide charged in the AP and EP stages put together was 1.0% only. So with a reduced peroxide charge in comparison to O-Q/P$_2$-H$_2$-D$_2$ sequence, 90% ISO could be achieved by molybdenum catalysed acidic peroxide stage, with the sequence O-AP$_{0.5}$-EP-$_{0.5}$-H$_2$-D$_2$.

Enzyme treatment

Xylanase, a hemicellulolytic enzyme, has been commercially successful, as a potential pretreatment step, enhancing bleachability of pulps with reduced bleach chemicals (11). The exact mechanism of the enzyme treatment is that, it induces the cleavage of the residual lignin and the redeposited hemicellulose during pulping, which otherwise creates difficulty in lignin removal during bleaching (12).

Xylanase enzyme pretreatment was tried out as an alternative for the Acidic peroxide stage, in the sequence O-AP$_{0.5}$-EP-$_{0.5}$-H$_2$-D$_2$. The Oxygen delignified hardwood pulp was subjected to xylanase enzyme pretreatment under the prescribed conditions in Table 2. Subsequently, the pulp was extracted with alkali reinforced with hydrogen peroxide. The pulp after extraction and subsequent hypochlorite, and chlorine di oxide stages, reached 90% ISO with O-X-EP-$_{0.5}$-H$_2$-D$_2$ sequence. The enzyme pretreatment thus could replace the acidic peroxide delignification in the O-AP-EP-H-D sequence (Table 3). Also, introduction of enzyme pretreatment in O-AP$_{0.5}$-EP-$_{0.5}$-H$_2$-D$_2$ sequence, after oxygen delignification could give additional gain of 2 points resulting a brightness of 91.4% ISO.

Multistage oxygen delignification

Restricting the kappa number reduction to a maximum of 50% has been the standard practice, in oxygen delignification systems. So when more than 50% reductions are required, multistage oxygen delignification may be resorted to (6), Whereas oxygen has certain limitations in removing all types of lignin. Some of the groups are resistant to oxygen delignification. Hence, in our studies with multistage delignification, the second oxygen stage was peroxide reinforced to improve the efficiency. The temperature was restricted to 100° C to avoid peroxide decomposition. A chelation step could enhance the OP stage pulp brightness from 62 to 70% ISO. But the kappa number reduction was only from 7.2 to 6.5. This naturally necessitated an acidic peroxide stage even after the second stage oxygen, to reach the target of 90% ISO, with hypochlorite and chlorine di oxide in the subsequent stages.

While many such options were tried for hardwood, with respect to reducing the kappa number, the final bleaching had to be necessarily, 2% hypochlorite followed by 2% chlorine di oxide to achieve 90% ISO (Table 3).

Optimised ECF Sequences

The selected ECF bleaching sequences for attaining 90% ISO for bagasse and hardwood kraft pulps are given in Table 4. The sequences shown are very short involving only 3-4 stages for bagasse and 4-5 stages for hardwood. Further, the stages can easily be retrofitted in the existing bleach plant without major modifications. In case of hardwood, it may be noted that reaching high brightness, with ECF bleaching necessarily requires oxygen delignification. Likewise the potential of peroxide bleaching is significantly increased by resorting to enhanced temperature and time with acid wash chelation step. Since most of our mill bleaching systems have a closed backwater system, with recycling of the filtrates, the chances of increase in metal ion concentration is high and this has to be necessarily taken care of by acid wash/ chelation of the pulp to avoid the unfavourable peroxide decomposition reactions.

The stages discussed in each sequences are specific with respect to their bleaching action and have their own significance in the respective sequence.

Table-4.

Selected Short ECF Bleaching Sequences To achieve 90% ISO

Sequence	Brigthness % ISO	Viscosity cP s	PC Number
Bagasse Pulp			
$O-H_1-D_1$	90.2	19.0	0.20
$OP_2-H_1-D_1$	90.4	18.8	0.17
$Q/OP_1-H_1-D_1$	90.2	18.7	0.10
$Q/OP_2-H_1-D_1$	90.8	18.8	0.10
$Q/P_2-H_2-D_1$	90.1	19.1	0.08
Hardwood pulp			
$O-Q/P_2-H_2-D_2$	90.4	5.9	0.17
$O-AP_{0.5}-EP_{0.5}-H_2-D_2$	90.3	4.6	0.27
$O-X-EP_{0.5}-H_2-D_2$	90.9	5.3	0.21
$O-X-AP_{0.5}-EP_{0.5}-H_2-D_2$	91.4	4.1	0.16
$O-Q/OP_2-AP_1-H_2-D_2$	90.2	6.3	0.29

The sequences discussed yield 90% ISO pulps, with additional advantages over the conventional bleaching sequences involving molecular chlorine. The pulp quality with respect to their strength (Table 5) shows a significant improvement over chlorine containing sequences. The pulp viscosity suffers less degradation and the psot color number is very low (Table 3). Above all the chlorinated organics generation is considerable reduced (Fig. 2,3).

Table-5.

Strength Properties of ECF pulps at 300 ml CSF

Sequence	Tensile Index Nm/g	Tear Index mN.m²/g	Burst Index kPa.m²/g
Bagasse Pulp			
$O-H_1-D_1$	74.9	6.71	4.92
$OP_2-H_1-D_1$	74.0	6.46	4.68
$Q/OP_1-H_1-D_1$	71.4	6.61	4.98
$Q/P_2-H_2-D_1$	67.0	6.59	4.44
Hardwood Pulp			
$O-Q/P_2-H_2-D_2$	54.7	6.67	3.25
$O-AP_{0.5}-EP_{0.5}-H_2-D_2$	58.4	5.98	3.71
$O-X-EP_{0.5}-H_2-D_2$	59.6	6.60	3.56
$O-X-AP_{0.5}-EP_{0.5}-H_2-D_2$	55.6	6.18	3.60
$O-Q/OP_2-AP_1-H_2-D_2$	58.8	6.82	3.60

Chlorinated organics (AOX)

As envisaged, the chlorinated organics generated in the ECF bleaching sequences are considerably reduced. About 70% reduction in AOX has been observed which will no doubt result in considerable reduction of TCDD and TCDF which are toxic to biological systems. AOX was calculated using the empirical formula (13)

$$AOX\ kg/t = 0.1\ [C + 0.2D + 0.6H]$$

C,D and H represent chlorine, chlorine di oxide and hypochlorite respectively, all are expressed as C12 in kg/t.

Figures 2 and 3 show the quantity of AOX generated in the ECF sequences. The chlorine containing sequences to achieve 90% ISO have been included for comparison. As evident, a substantial reduction of AOX (50-70%) is observed. Further the colour and COD are substantially reduced (Data not shown). The ECF bleaching thus proves efficient in attaining 90% ISO for bagasse and hardwood kraft pulps with less number of stages with additional advantages of improved strength and lesser pollutants.

Fig. 2 Chlorinated organics for various bleaching sequences for bagasse

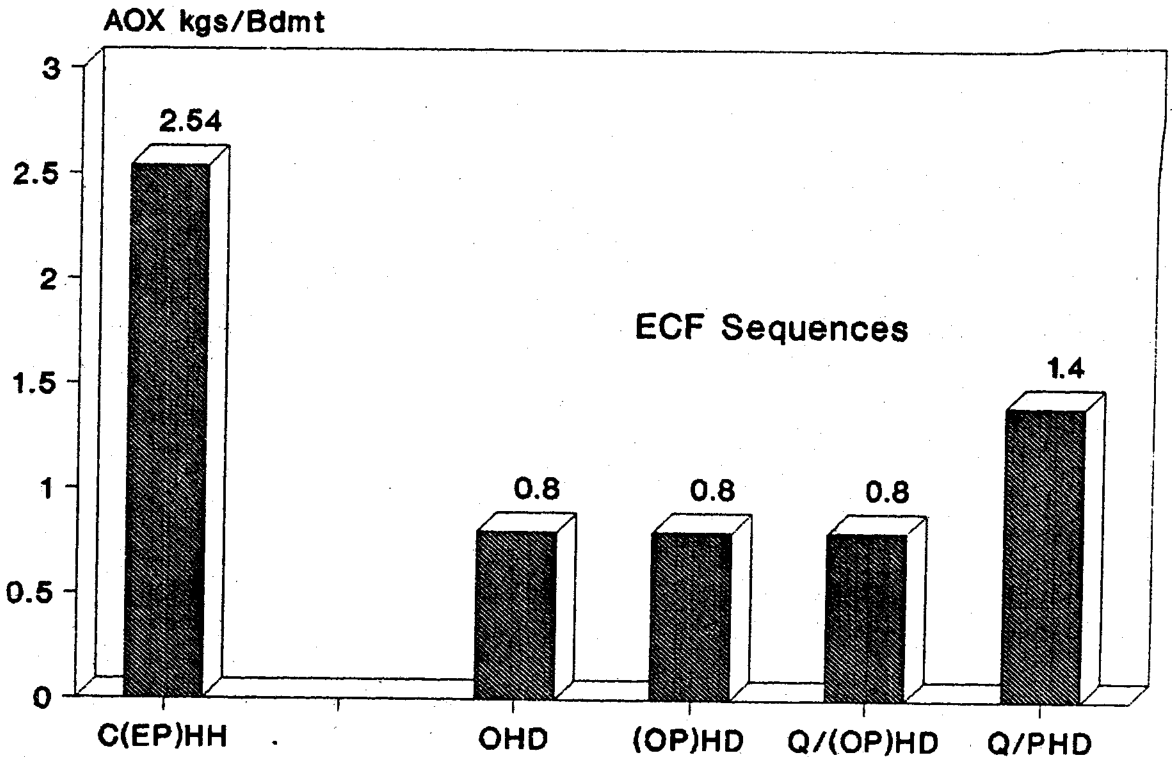
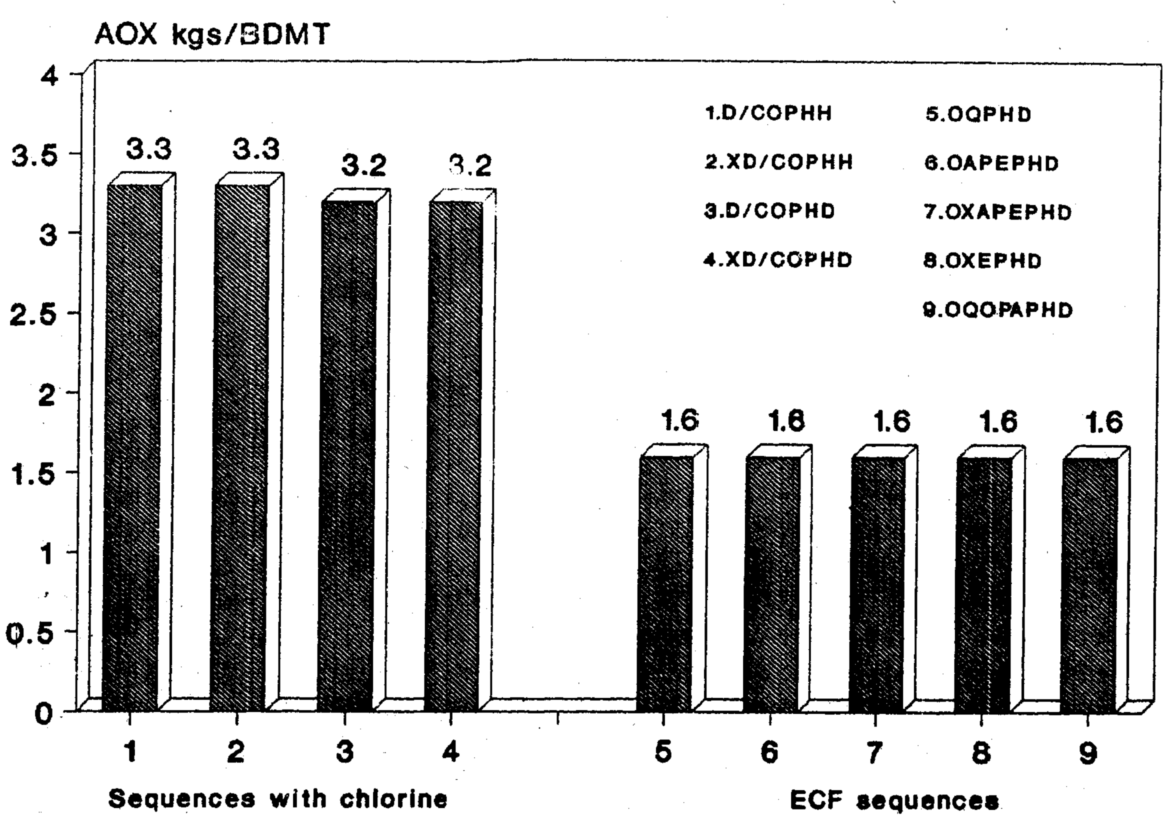


Fig 3. Chlorinated organics for various bleaching sequences for hardwood



CONCLUSIONS

1. It is possible to bleach bagasse and hardwood pulps to 90% ISO using ECF sequences, without using ozone.
2. The bleaching response of bagasse is excellent towards ECF bleaching.
3. The sequences discussed for high brightness, are considerably short.
4. Oxygen delignification is a preferred necessary step in hardwood ECF sequence to make it feasible.
5. The ECF bleaching yields a pulp of better strength and viscosity than the chlorine containing sequences.
6. Considerable reduction in AOX generation is observed thereby taking the TCDD and TCDF to below detectable levels.
7. The sequences discussed are easily retrofittable in existing bleach plant for hardwood and bagasse without major modifications.

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REFERENCES

1. Mounteer, A.H., Colodette, J.L. Campos, A.S., Gomide, J. L., in International Pulp bleaching conference 1991, P. 83.
2. Kirk O Neal., Keane, S., Zielinski, R., Jennings, P., Halloran P., Schween G., Morcock B., and Rabert, B., in the effect of Dioxins and Furans - U.S. Environmental Protection Agency, EPA 560/ 5-90-013 1993.
3. Andrews., Chang, H.M., Jameel, H., in International pulp bleaching conference, 1991. P.51.
4. Plackett, R.L. Burman, J.P., Biometrika 33:305 (1946).
5. Prasad, D.Y., Gnanasekaran, A., Mohan Rao, N.R., Tappi Journal Aug 1994.
6. McDonough, T.J., in 1991 Bleach plant operations short course. Tappi, Atlanta G.A., U.S.A. P.58.
7. Liebergott, N., Van lierop, B., and Fleming, B.I., in PPC 94:11 (1993) P.35.
8. Earl, P. Nyugen, X.T., in Non-Chlorine bleaching conference 1993, South Carolina, U.S.A., P.40.
9. Liebergott, N., Van Lierop, B., and Fleming. B.I., in PPC 94:10 (1993) P.45.
10. Kubelka, V., Francis, R.C., and Dence, C.W., in JPPS vol. 18 (3), 1992 P.51.
11. Tolan, J.S., in Non-chlorine bleaching conference, 1993 South Carolina, U.S.A. P. 40.
12. Paice, M.G., Gurnagul, N., Page, D.H., Jursek, L., 78th Annual meeting CPPA, 1992.
13. Lewko, L. Van Donkelaar, A., in Paper vol. 19:11(91). P.31.
14. Claudio, E., Silva jr. D.A., in International Pulp Bleaching conference, 1991.