Improvement of etareed (Ochlandra Travancorica) thermomechanical pulp through chemical modification

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SUMMARY

Etareed (Ochlandra travancorica) gives very good chemical pulp, however its thermomechanical pulp (TMP) exhibits low strength properties. Modification of this high yield pulp with oxidising agents like ozone and acidic sodium chlorite under mild conditions results in significant improvement of strength properties without appreciable yield loss. Optical properties are also affected. Investigation of ultrathin sheets by infra-ed spectrophotometry indicate reduction of aromaticity with simultaneous increase in the carbonyl content due to chemical modification of lignin and carbohydrates. The increased intensity of carbonyl absorption bands seems to be due to formation of carboxyl groups during oxidation, which increases the intermolecular bonding, resulting in improved fibre flexibility and hydrophilicity of lignin. Modification of lignin is also indicated by the increased amount of acid soluble lignin fraction in oxidised pulp.

Introduction

The ever increasing cost of paper production, due to shortage of raw materials, expensive chemicals and various other factors, is attracting the attention of paper technologists & scientists allover towards high yield pulps which could substantially relieve the pressure on fast depleting resources of pulp wood. Softwoods have long been used for the production of mechanical pulp, however the low strength, partly due to appreciable amount of residual lignin required blending of chemical pulp in varying amounts to impart requisite properties to the paper. In recent studies high yield pulp from softwoods have been modified by oxidative treatments to improve strength properties remarkably

The objective of the present work was to investigate the effect of oxidation on thermomechanical pulp properties of etareed which has been found to be very good raw material for chemical pulp[1], but its TMP exhibits low strength.

LITERATURE

Rothenberg etal[2] reported chemical modification of mechanical pulps considerably improved strength properties. Increase in sheet bonding by ozonization was observed by Goring etal [3,4] Liebergott[5] and Soteland etal[6] also showed that ozonization increased the strength of groundwood pulp. Backorik[7] modified high yield pulps with oxidising reagents like peracetic acid and sodium chlorite for improving strength. Soteland[8] noted that ozonization of softwood mechanical pulps reduced the brightness by 2 to 4 units where as hardwood pulps on the contrary showed a considerable increase. Pilot Plant trials for ozone treatment of mechanical pulps, and runability tests of ozonised furnishes on a full scale paper machine in Norway during 1975-76 were found to be quite encouraging. The tearing strength of the ozonized furnish was remarkably good and lesser linting problems during printing were encountered.

Results and Discussion

There was insignificant loss in the yield of ozonized Pulp however it went down to 92 and 86 percent after first and second chlorite treatment. Along with the removal of lignin there was increase in acid soluble lignin fraction, which indicated its chemical modification Table 1.

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TABLE—1. CHEMICAL ANALYSIS OF UNTREATED & TREATED PULPS

Treatment	Yield %	Klason lignin %	Acid Soluble %	Total lignin	Carboxyl content m. mole/100 g o. d. pulp
Untreated	100.0	20.9	1.8	22.7	3.4
Acid sodium chlorite o.1 mole/100 g o. d. pulp 1×90 min.	92.0	16.8	2.7	19.5	—
Acid sodium chlorite 2×90 min.	86.0	13.1	3.4	16.5	15.0
Ozone (0.8% on o.d. pulp)	99.7	20.2	2.5	22.7	6.6

Amount of carboxyl groups increased from 3.4 m. mole/100 g of pulp in untreated to 15 and 6.6 m. mole/100 g in case of chlorite and ozone treated pulps. Infra-red spectra of ultra thin handsheets of sodium chlorite treated pulp Fig 1 indicates the increase in carbonyl groups as the absorption band near 1710 cm^{-1} has become stronger. The aromatic skeltal bands between 1600 cm^{-1} and 1400 cm^{-1} have also substantially decreased which may be due to cleavage of aromatic nuclii Fig. 2, leading to increased number of carbonyl groups. The slight shift in 1600 cm^{-1} absorption band towards higher wave number also indicates the formation of conjugated double bonds due to oxidation of lignin. In the infrared spectra of ozonized pulp Fig 3, there is indication of increased intensity of absorption band due to carbonyl groups but not that pronounced as in case of chlorite treated pulp.

I.R. SPECTRA OF ULTRA THIN HANDSHEETS OF ETA REED THERMOMECHANICAL PULP
1_ UNTREATED PULP
2_ SODIUM CHLORITE TREATED PULP

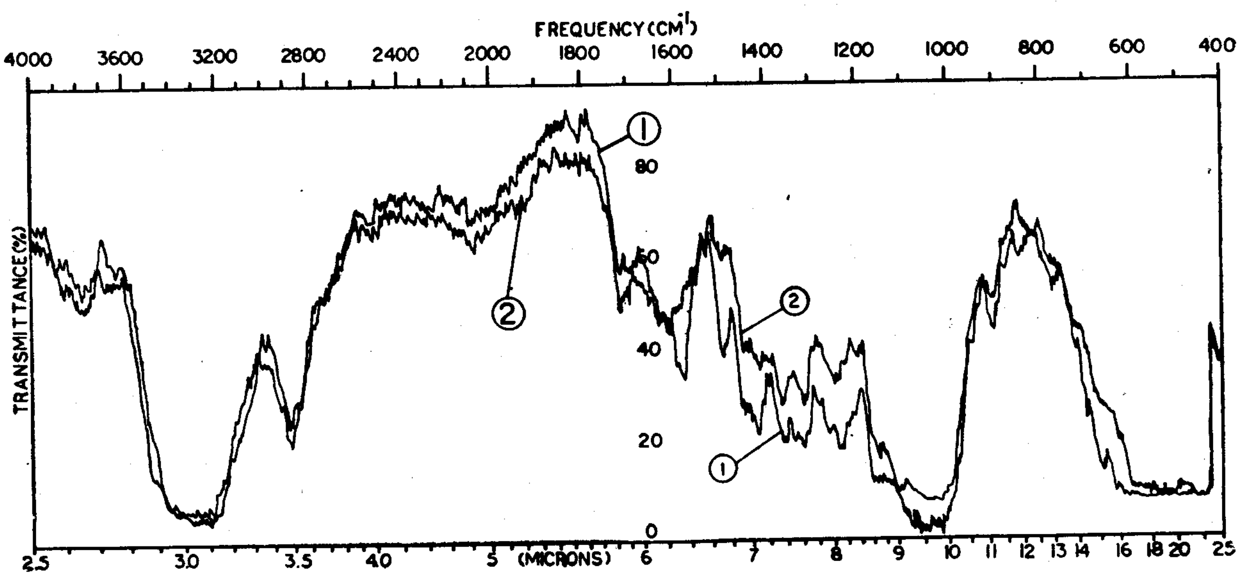
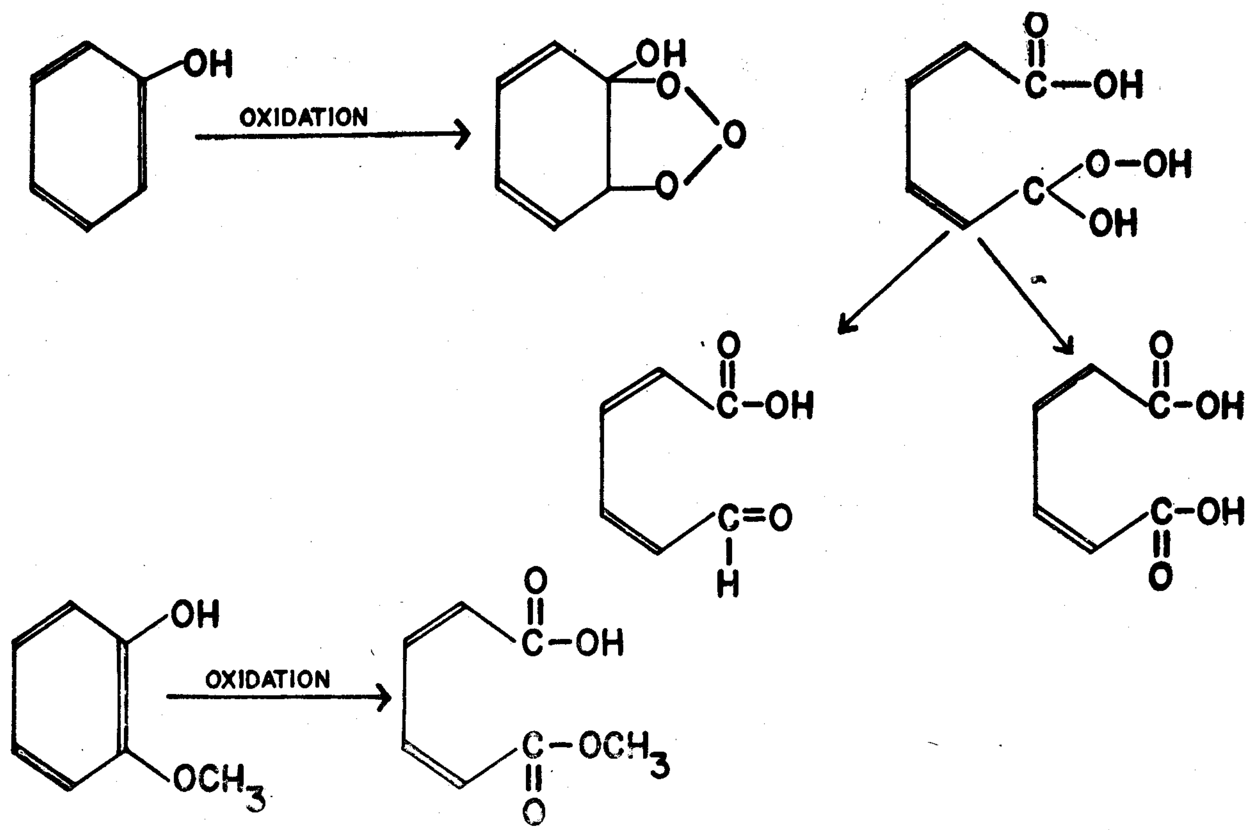


Fig. 1



A SIMPLE MECHANISM FOR OXIDATION OF PHENOLS FIG.NO.2

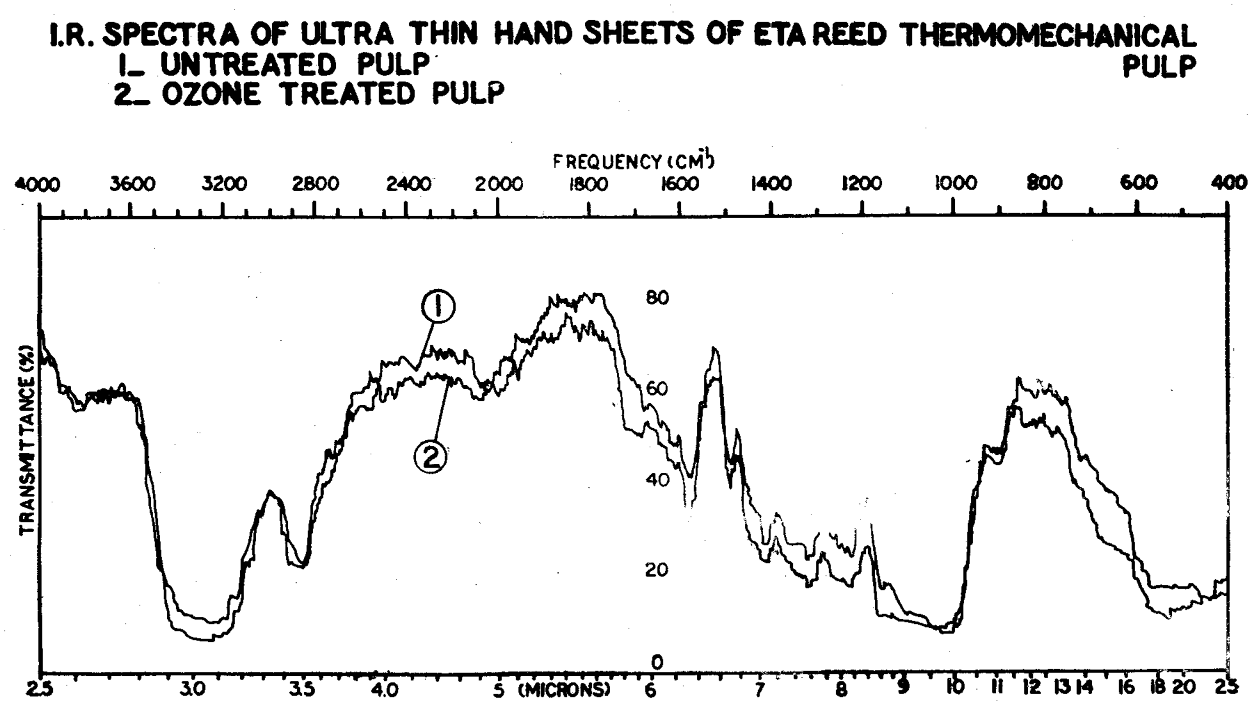


Fig. 3

Stength properties

Sodium chlorite treatment of the whole pulp substantially improved tensile, burst and tear. The apparent density increased from 0.36 to 0.46 g/cm³. Ozone treatment of pulp also improved strength but to a lesser extent as compared to sodium chlorite, Table 2. Hence the chemically modified thermomechanical pulp of etareed has developed comparable strength properties.

Optical properties

There was improvement in brightness in case of chlorite treatments only from 40.8 to 42.7 to 55.9 percent ISO after first and second treatment respectively Table 2.

TABLE—2. PROPERTIES OF ETAREED TMP PULPS TREATED WITH SODIUM CHLORITE AND OZONE

Pulp	Yield %	Apparent dansity (g/cm³)	Burst index (kPa.m²/g)	Tensile index (N.m/g)	Tear index (mN.m²/g)	Fold log.	Bright-ness (% ISO)	Sp. Scatt. Co-eff. (m²/kg)	P.C. No.
Untreated	100.0	0.36	0.40	15.0	4.30	0.48	40.8	40.7	Nil
Acid sodium chlorite 1×90 min.	92 0	0,39	1.20	26.0	5.95	0.95	42.7	33.1	—
Acid sodium chlorite 2×90 min.	86.0	0.46	2.40	39.0	7.10	1.67	55.9	28.2	1.7
Ozone treated	99.6	0.39	1.00	23.0	4.80	0.70	40.3	39.0	Nil
TMP, commercial softwood[9]	—	—	1.15-2.50	25 0-40.0	6.70-11.20	—	—	—	—

The increase in burst and tensile are obvious as they increase linearly with density so long as there is no radical change in the fibre dimensions. The tear index which normally shows inverse relationship with density also increased in this case. The improvement is probably due to change in bonding potential of fibres after oxidative treatment. In untreated pulp sheets the bonded area is smaller which permits lesser number of fibres to participate in tear rupture where as in treated pulp sheets the tear stress is distributed over greater number of fibres due to improved bonding of sheet matrix. Relatively larger increase in tear after second chlorite treatment may be due to lignin removal in addition to chemical modification because in case of ozonization during which yiled loss was negligible there was only marginal increase in tear index. Short span tensile test Table 3 shows that after oxidative treatments the fibre length index (FLI) is not affected which indicates that the treatments do not degrade the fines present in untreated pulp. There is definite increase in bonding index (BI) which is due to increase in flexibility and bonding capability of fibres. Contrary to normal expectation the fibre strength index (FSI) also increased, which is likely to be due to incrcased compactness of fibres in sheet matrix caused by improvement in flexibility of fibre segments. For comparison tensile, burst and tear index values of a commercial (imported) softwood thermomechanical pulp[9] are also included in Table 2 which shows that the chemically modified thermomechanical pulp of etareed has developed comparable strength properties.

TABLE -3. SHORT SPAN TENSILE ANALYSIS RESULTS OF ETAREED TMP PULPS

Pulp	FSI (km)	FLI (mm)	BI (%)
Untreated	6.2	0.17	66
Acid sodium chlorite 1×90 min.	6.6	0.17	76
Acid sodium chlorite 2×90 min.	7.8	0.18	85
Ozone treated	6.6	0.17	72

Scattering coefficient decreased as expected due to increased compactness. Marginal brightness reversion was observed in only the pulp after two chlorite treatments which may be due to modification of lignin and cellulose side chains.

Scanning Electron Microscopic examination

The SEM photomicrograph of untreated pulp sheet Fig. 4 shows rigid fibre segments with little confirmability to one another. The handsheets of treated pulps are more compact as fibre segments are well conformed to each other due to improved fl xibility Fig. 5, 6.

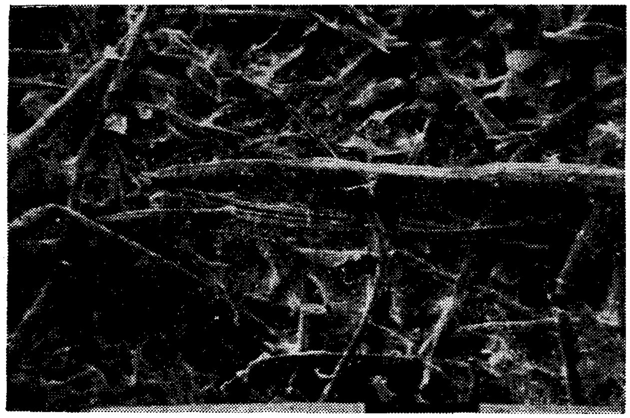


Fig. 4—Untreated Etareed TMP Pulp

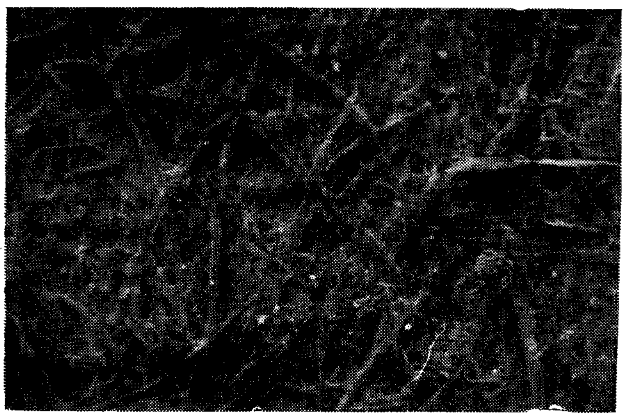


Fig. 5—Ozone Treated Etareed TMP Pulp

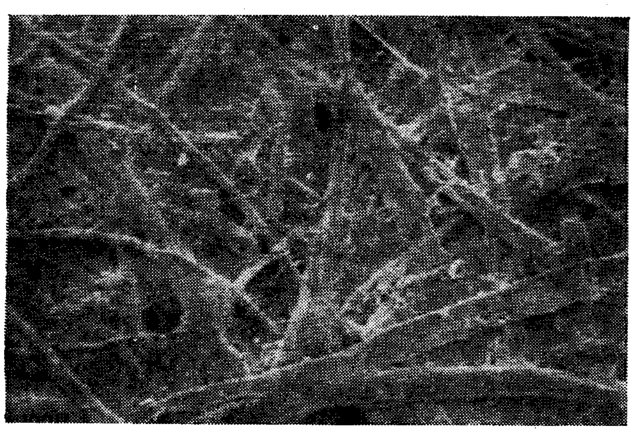


Fig. 6—Sodium Chlorite Treated Etareed TMP Pulp

Conclusions

Treatment of etareed TMP with sodium chlorite and ozone resulted in chemical modification of lignin and cellulose. The total carboxyl content increased by approximately 2 to 4.4 times with simultaneous decrease in aromaticity. Acid soluble lignin fraction also showed increasing trend. The yield loss in case of ozonized pulp was negligible however in case of sodium chlorite treatment, it was more but still the final yield was more than 85 percent. Strength properties improved significantly. Tensile and burst incraesed as much as by 6 and 2.5 times respectively in the extreme cases. Short span tests showed no change in fibre length index indicating negligible fibre damage, whereas fibre strength index and bonding index increased substantially. Sodium chlorite treatment improved brightness however it was unchanged after ozonization. Scattering coefficient decreased due to increased compactness of the sheet.

EXPERIMENTAL

Material

Whole thermomechanical pulp was taken for the investigations. The pulp was produced by two stage refining of overnight water soaked chips in TMP pilot plant (Defibrator) of the institute. The details are given in the paper presented by Kulkarni et al. [10].

Ozonator

Ozone was produced by WELSBACH ozonator type T408 from Ozone Process Div. Philadelphia, Penn. Oxygen was passed through the ozonator at the rate of 20 L/hr. Out coming oxygen was found to have 2 percent ozone.

Treatments

Mild acidic (pH·3) sodium chlorite (80% purity) treatment 0.1 mole/100 g o.d. pulp at 4 percent consistency was given at 70°C. After the reaction period the pulp was filtered and washed with distilled water. The ozone treatment 0.8 percent on o.d. pulp was given at room temp on pulp at 30 percent dry content. The pulp was kept in a glass cylinder (25 cm long, 5 cm dia). A cintered glass disc was fitted on the ozone entrance side to ensure uniform gas distribution.

Analysis

For studying the changes in pulp, ultra thin sheets 10 gsm were prepared and investigated by infrared spectrophotometer, Perkin Elmer 735 according to the procedure given by Polčin et al[11].

Carboxyl groups were determined by dynamic ion exchange method with calcium ions as reported by Sobue and Okubo[12].

Klason lignin was determined as per TAPPI standard T222 OS-74 and acid soluble lignin by U.V. spectrophotometer, Perkin Elmer 402, taking absorptivity value of 110 l g^{-1} cm^{-1} (TAPPI UM 250).

The handsheets were prepared and tested according to ISO standards. Short span tests were carried out for dry and wet handsheets using Pulmac Zero span tester. The tensile tests were performed at the optimum clamping pressure determined by varying the clamping pressure and the pressure at which the maximum breakage load was obtained was taken as optimum. The tests were conducted at different spans. The graph between breaking length and span was plotted and extrapolated to zero span. The parameters-fibre length index, fibre strength index and bonding index were determined as described by Cowan[13].

Optical properties were tested on ziess Elrepho photometer.

SEM photomicrographs of pulp sheets were taken on cambrige Scanning Electronmicroscope.

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