Upgrading of Cellulose Pulps II-Removal of Lignin*

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This work deals with the feasibility of upgrading the highyield bamboo pulp by methods leading to maximum removal of lignin. Treatment with chlorine based chemicals with varying process parameters like time, temperature, consistency and concentration of chemicals were studied so as to remove maximum of lignin. It was seen that, out of the total chlorine demand, if major part of it is applied in chlorination stage, it leads to better deligni fication. Chlorine dioxide treatment leads to selective delignification with better yield than that of second hypochlorite treatment. The work has suggested that even if paper grade pulp from easily accessible sources is available, it can be conveniently delignified to obtain an upgraded, cellulose pulp without appreciable degradation.

Introduction

In view of the global shortage of petrochemicals based products it is apparent that cellulose based products like rayon and cellulose plastics will have good demand. This will require refined grades of pulp for which there is a great shortage All existing dissolving grade pulp plants are processing specific raw materials with certain set methods leading to a pulp fulfilling their own requirement. There is practically a void in the availability of ready dissolving grade pulp. With the knowledge that sufficient technical know-how is available in the country to process cellulosic raw materials to get paper grade pulps, if attempt is made to upgrade this typc of pulp by maximum removal of noncellulosics, a major step towards self sufficiency in refined grade pulps can be visualised.

During the last decade lot of work[1-2] has been done for obtaining cellulose pulp from agricultural residues and other raw materials. However, the problem which remains unsolved is that how the residual lignin, hemicelluloses, and ash should be removed from the pulp with minimum of degradation. Delignification by chlorine based reagents appeared worth trying. Elemental chlorine and hypochlorite ion both degrade lignin without too drastic action on the carbohydrate fraction of pulp and are therefore used. The standard delignificati on procedure consits of three main stages. The first one is the acidic chlorination that degrades most of the residual lignin, to be followed by alkali extraction by which the alkali soluble lignin products are removed, and the third is hypochlorite treatment which leads to further delignification and destroys the residual chromophoric groups.

Karnik[3] has developed the process to delignify unbleached bamboo pulp. Pande[4] did chlorination studies on pre-hydrolysed bamboo kraft pulp. His conclusion that highly condensed and inaccessible lighin in kraft pulp poses a serious problem, is worth noting. The present work deals with the upgrading of paper grade bamboo pulp, with particular reference to lignin removal, by the use of chlorine based chemicals.

EXPERIMENTAL

Raw Material

The raw material for the present investigation was bamboo pulp obtained from a paper mill in South India. According to the information supplied, the pulp was obtained by kraft cooking process in the high-yield pulping range. The pulp was stored over saturated sodium chloride solution and samples were withdrawn from the stock when required.

Analysis of pulp

Until otherwise indicated, the

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TAPPI methods were used for analysis. Analysis of pulp is given in Table 1. The results in this table and all subsequent tables are based on oven dry pulp. Chlorine consumption (demand) of the pulp was found out according to SCAN–C 29: 1972[5]. The average value found was 5.4 g. Cl_2 per 100 g. O. D. pulp. This chlorine demand was applied in chlorination and hypochlorite stages in two ratios i.e. 60 : 40 and 80:20 respectively.

(A) Chlorination

The pulp sample (8-10g) was weighed accurately, transferred in a 500 ml flask and suspended in water, chlorine water of known strength was put into the pulp suspension, volume was adjusted so that required amount of chlorine was put into the suspension. Time, consistency, and temperature were varied. Stirring was frequently done. After the treatment, the pulp was thorougly washed and air dried. Residual chlorine[6], yield and permanganate number were found out. The results are tabulated in Table 2.

(B) Alkali Extraction

The chlorinated pulp was subjected to sodium hydroxide extraction, in which temperature and time of extraction were varied. The concentration of alkali was such that the pH of the suspension was between 9–10. A few experiments, by varying consistency was found to be satisfactory to work with. After the treatment the pulp was thoroughly

TABLE 1. Analysis of Raw Material (Pulp)

Sl.No.	Title	Composition of Pulp (per cent)
1.	α–Cellulose	69.5
2.	β–Cellulose	14.7
6.	γ–Cellulose	3.2
4.	Hollo cellulose	93.5
5.	Hot water solubles	3.8
6.	Ash	2.0
7.	Pentosans	19.0
8.	Alcohol-benzene solubles	1.0
9.	Lignin	6.6
10.	Permanganate number	16.1
11.	7.14 per cent alkali solubles	5.9
12.	10.0 per cent alkali solubles	17.9
13.	Copper Number	0.9

TABLE 2. Chlorination of pulp with time, Consistency, and Temperature as Variables

Permanganate No. of Pulp=16.1
Chlorine Demand=5.4 g Cl_2 per 100 g O. D. pulp
Chlorine Added =3.2 per cent
pH =2.5 to 3

Consistency (percent)	Time of chlorination in Minutes	$KMnO_4$ No at 28°C	$KMnO_4$ No at 40°C	Yield per cent at 28°C	Yield per cent at 40°C	Residual Chlorine per cent at 28°C	Residual Chlorine per cent at 40°C
2.0	15.0	15.3	15.8	98.0	95.0	0.90	0.47
2.0	30.0	13.8	13.9	94 0	94.0	0.80	0.26
2.0	60.0	10.3	9.7	93.0	92.5	0.19	0.12
3.0	15.0	13.0	12.2	95.0	93.7	0.67	0.44
3.0	30.0	11.2	10.0	92.2	93.0	0.37	0.20
3.0	60.0	9.7	9.5	91.0	90,0	0.04	0.06
3.0	90.0	9 5	–	79.5	–	0.03	—
5.0	15.0	11.7	10.3	97.0	94.0	0.24	0.24
5.0	30.0	11.1	10.4	95.0	92.5	0.17	0.03
5.0	60.0	9.0	8.7	74.0	88.0	0.03	0.01

washed, air dried, and the yield was found out. The lignin content of the pulp extracted under best suited conditions was estimated. The average results are recorded in Table 3. Under the same conditions, the alkali extration stage was repeated when 80 percent of total chlorine demand was given in chlorination stage, the pH was maintained around 10. Approximately 2.5 percent (pulp basis) of alkali was added. The results are summerised in Table 5.

(C) Hypochlorite Treatment

Pulp after alkali extraction was transferred to 500 ml flask, and 40 percent of total chlorine demand was given at this stage. pH of the mixture was kept between 10-11 and 5 percent consistency was maintained. Temperature and time of treatment were varied. Pulp was thoroughly washed and air dried. Residual chlorine content[6], yield, and lignin content of pulp was determined as recorded in Table 4. Results for hypochlorite treatment, which are recorded in Table 5, were found out by giving 20 percent of total chlorine demand in hypochlorite stage under the conditions found above.

(D) Second Hypochlorite Treatment

The pulp obtained from first hypochlorite treatment was given second hypochlorite treatment by adding 1.1 percent (pulp basis) active chlorine at 40°C for two hours, the consistency being 5.0

TABLE 3. Alkali Extraction with Temperature and Time as Variables

Temperature °C	Time Minutes	Yield per cent based on chlorinated pulp	Lignin per cent based on original pulp
30	60	80.5	—
60	60	79.6	—
75	30	80.5	—
	60	78.1	—
	75	77.7	2.78
	90	77.6	—
90	60	78.0	—

TABLE 4. Hypochlorite Treatment with Temperature and time as Variables

(Total chlorine demand is divided in the ratio of 60:40 in chlorination and hypochlorite treatment)

Temp. °C	Time mins	Yield p. c. based on E.P.*	p. c. Residual Cl_2 Content	p. c. α–cellulose	Lignin per cent based on O P.**
40	60	93.5	0.07	88.5	—
	120	90.9	nil	92.5	1.39
	180	90.5	nil	92.8	—
60	120	90.5	0.01	—	—

* E. P. alkali extracted pulp

** O. P. original pulp.

TABLE 5. Effect of Increased Chlorine in Chlorination

(Total chlorine demand is divided in the ratio of 80.20 in chlorination and hypochlorite treatment)

Treatment	Yield p.c. based on O.P.	Residual Cl_2 content p.c.	Lignin per cent based on O. P.
Chlorination	76.0	0.08	—
Alkali extraction	68.4	—	—
Hypochlorite treatment	64.6	nil	70.8

percent. The pulp suspension was continuously stirred. Pulp was washed and air dried. Complete analysis of the pulp was done and results are recorded in Table 6.

(E) Delignification with Sodium Chlorite and Acetic Acid

(Chlorine Dioxide Treatment)

The yield during second hypochlorite treatment was very poor and the lignin content of the pulp was rather high, so it was decided to give chlorine dioxide treatment to first hypochlorite treated pulp. Chlorine dioxide content of solution was analysed[7] and required amount of it was added to pulp samples. Conditions[8] of the treatment are pH 3.2 to 3.8, temperature 80°C, time 3 hours and consistency 5.0 percent, Pulp suspension was occasionally stirred. Pulp was thoroughly washed, air dried and analysed. The results are included in Table 6.

Characterization of Pulp Samples

Original pulp, second hypochlorite treated, and chlorine dioxide treated pulps were characterized by viscometry and copper number estimation, U-tube viscometers were used and Iron-Sodium Tartrate complex (FeTNa complex) was employed as a solvent for pulp components. Results are given in Table 6.

TABLE 6. Analysis of Pulps

Title	O. pulp	H_2 pulp		D pulp	
		based on H_2.P	based on O.P	based on D.P	based on O.P
Yield per cent	100.0	87.5*	56.5	97.80*	63.20
α–cellulose p.c.	69.5	88.0	49.7	90.80	57.30
β+γ cellulose p. c.	17.9	—	—	7.80	4.80
Ash per cent	2.0	0.6	0.34	0.11	0.07
Pentosans p. c.	19.0	18.0	10.2	19.40	12.20
Lignin p. c.	6.6	0.75	0.48	0.51	0.32
7.14 p. c. alkali solubles p. c.	5.9	—	—	8.20	5.20
Copper Number	0.9	1.05	—	1.10	—
D. P.	1363	980	—	1084	—

* based on first hypochlorite treated pulp.

H_2.P second hypochlorite treated pulp.

D.P Chlorine dioxide treated pulp.

Discussion

Analysis (Table 1) of the pulp showed that the pulp under investigation is richer in hemicelluloses and lignin, which is expected as it was a high-yield pulp. It does not appear to be degraded as evident from the copper number and degree of polymerization (D.P.).

In chlorination stage, it is noted (Table 2) that as the time of chlorination of pulp is increased beyond 60 minutes, pulp suffers considerable loss of carbohydrates without any appreciable removal of lignin. Three percent consistency is best suited for chlorination reaction. At higher consistencies loss is more, because lot of acid and heat of reaction is generated, which results in degradation of carbohydrates. The temperatures higher than the ambient temperature do not seem to offer any advantage.

It is clear from Tables 4 and 5 that if most (around 80 percent) of the total chlorine to be used for delignification is applied in chlorination stage, the results obtained are better than by applying lesser chlorination stage. The lignin content of final pulp in former case is 0.78 percent, as against 1.39 percent for the latter. A glance at Table 6 shows that the α-cellulose content of the delignified chlorine dioxide treated pulp is more than that of pulp obtained after second hypochlorite treatment. By giving chlorine dioxide treatment to first hypochlorite treated pulp, ash and

lignin are remarkably reduced to a value of 0.07 and 0.32 percent respectively. However, pentosan content is more in chlorine dioxide treated pulp. Copper number is slightly increased, because pulp has undergone oxidative treatments which results in the formation of carbonyl groups. Degree of polymerisation of the second hypochlorite treated pulps is reduced to 980, which shows that there is considerable degradation of cellulose in hypochlorite treatment, affecting the yield which is less (56.5 percent) in comparison to chlorine dioxide treated pulp (63.15 percent). The degree of polymerization of the latter pulp has a higher value of 1084.

The study on delignification processes, with chlorine based chemicals suggests that lignin and ash of a high-yield pulp can be considerably brought down without affecting the D.P. characteristics. However, this is achieved at the cost of low molecular weight α-cellulose fraction, present in the pulp. For pentosans removal some specific treatments have to be given to the pulp. The results obtained have shown that paper grade pulps can be upgraded with respect to lignin by suitable treatments. However, the economics and the scaling up of the process need exhaustive study before making any conclusions with respect to its feasibility on industrial scale.

Conclusions

1. High yield pulps can be upgraded with respect to lignin by suitable treatments with chlorine based chemicals.
2. If most of the total chlorine demand (around 80 percent) is applied in chlorination stage, better delignification of the pulps is obtained.
3. Higher than ambient temperatures do not offer any advantage in chlorination.
4. Final chlorine dioxide stage leads to selective delignification, while preventing the yield losses as compared to a second hypochlorite stage. This stage also results in significant ash removal.
5. Though the treatments result in the loss of α-cellulose fraction, D.P. of the final pulp is not markedly affected.

References :

1. Yadav, R. P., Shekhawat, S. S. and Yayashankar, A.K. Indian Pulp and Paper, *27*:47 (1972)
2. Kamath, N.R. and Sidhanty, A. R. Indian Pulp and Paper, *23*(4):265 (1968)
3. Karnik, M. G. Indian Pulp and Paper, *15*:655 (1961)
4. Pande, G. E. Indian Pulp and Paper, *20* (10) : 599, 601–5 (1966)
5. Anon, Svensk., Papperstidning, *12*:485 (June 1972)
6. Rapson, W. H. 'The Bleaching of Pulp' Mach Printing Company, Easton, Pa, *Tappi* Monograph Series No. 27 (1963)
7. Jangalgi, N. R. 'Chlorine dioxide bleaching of Kraft pulp' Indian Institute of Technology, Bombay, DIIT, Dissertation, 19:(1966)
8. Browning, B. L. 'Methods of Wood Chemistry' Interscience Publishers, N. Y., Vol. II (1967)