Studies on bleaching of rice straw pulp

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SUMMARY

This paper deals with the study of bleaching characteristics of rice straw pulps of different $KMnO_4$ number. The pulping was carried out using different alkali concentration (6 to 12% NaOH) Three bleaching sequences viz. H. H., C. H. and C. E. H were tried to obtain desired brightness. The results show that pulp of high $KMnO_4$ number could not be bleached satisfactorily by H.H. sequence even after applying high percentage of chlorine charge. However, bleaching with other two sequences i.e. C.H. and C.E.H. has given pulp of desired brightness $77 \pm 2\%$. Pulps of lower $KMnO_4$ number could be bleached by H.H. and C H. sequences satisfactorily. But the chlorine requirement with H. H sequence was on higher side compared to C H. sequence to attain the same brightness. No significant difference was observed in the strength properties of pulp bleached with different sequences.

The growing shortage of conventional materials for paper making, particularly in the raw countries of Asia and Africa, paper industries are switching over to other fibrous raw materials. Mills based on straw as their chief raw material are coming up very fast. Now seeing the pattern of development of paper industries it becomes very much essential to carry out extensive work on these raw materials for proper and effective utilization.

Comparatively not much work has been reported on the straw pulping. Arnovsky et al[1,2,3] pioneered the straw pulping concentrating mainly on wheat straw. Ernst et al[4] reported bleaching of rice straw pulp obtained by kraft and soda processes. Sadawarte et al[5] selected a cooking temperature of 140°C for pressure pulping of rice straw with 10% soda and tried two bleaching sequences H.H. and C.E.H.H. They reported that higher brightness could be obtained by using C.E.H.H. sequence.

Jeyasingam[6] reported bleaching of rice straw pulp obtained at higher cooking temperature El Taraboulsi etal[7] studied the bleaching of rice straw pulp of $KMnO_4$ No. 8.8 and 7.2 using C.E.H., C.E.H.H., C.E./H., C.C.E.H., C E D., C.C.E.D. etc. bleaching sequences.

Inspite of all these well documented work there is need for a systematic study in the various aspects of straw pulping and bleaching. In the present study the bleaching characteristics of rice straw pulps of different $KMnO_4$ numbers are evaluated. Three bleaching sequences H.H., C.H. and C.E.H. which are commonly used for these types of raw materials are tried. At the same time, impact of bleaching on physical strength properties on pulp handsheets is also evaluated.

OBSERVATIONS AND DISCUSSION

1. It can be observed from Table-I that rice straw has high ash and low lignin content. Holocellulose content is on higher side but low molecular weight carbohydrates are very high as shown by 1.0% NaOH solubility.

2. The soda pulping with 6, 8, 10 and 12% NaOH has given well cooked pulp, which did not need any further mechanical treatment for defibration. The pulp yield and $KMnO_4$ number reduced with increasing chemical.

3. It can be seen from Table-III that even with the varying charge of chlorine in Hypo I stage almost all the chlorine was consumed in C-1 and C-2 pulps while in other two, certain amount of residual chlorine was left at high dose of chlorine. In Hypo

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TABLE—I. PROXIMATE CHEMICAL ANALYSIS

Sl. No.	Particulars*	Results%
1.	Moisture	6.67
2.	Ash	15.0
3.	Cold water solubility	11.0
4.	Hot water solubility	13.5
5.	1.0% NaOH solubility	44.3
6.	Alcohol-Benzene solubility	5.9
7.	Holocellulose**	70.1
8.	Lignin**	10.0

*Results are expressed on O.D. raw material basis.
**Corrected for ash

TABLE—II. PULPING DATA OF RICE STRAW

Particulars		C-1	C-2	C-3	C-4
Moisture	%	10.0	10.0	10.0	10.0
Cooking chemical as NaOH on O.D. RM	%	6.0	8.0	10.0	12.0
Bath Ratio		1:4	1:4	1:4	1:4
Cooking schedule					
50 to 140°C	hrs	1.0	1.0	1.0	1.0
At 140°C	hrs	1.5	1.5	1.5	1.5
Unblenched pulp yield	%	59.4	58.4	56.6	54.5
$KMnO_4$ No. (40 ml)		12.1	10.4	7.8	5.5
Black liquor	pH	—	9.6	10.1	10.6
Free alkali	gpl	Nil	0.6	1.6	3.0

II stage where constant amount of hypo was added except C—4, more residual chlorine was left, indicating a maximum limit of hypo consumption under the given conditions. C-1 and C-2 could not attain the desired brightness even with very high chlorine charge i.e. 10%, while C-3 and C-4 could reach to the desired level of brightness.

4. Optimization of chlorine charge has been done by varying the chlorine charge in chlorination stage and basing on the residual chlorine and $KMnO_4$ number of alkali extracted pulp and chlorinated pulp respectively, where optimum chlorlination stage was added.

It can be observed from tables that higher the $KMnO_4$ number pulp required higher chlorine for attaining the desired brightness. The pH in chlorination decrases with increasing chlorine charge, at the same time lowering of unbleached pulp $KMnO_4$ number increased the pH in chlorination stage. The elimination of extraction stage (C-1, C-2) by using C H. sequence increases the chlorine consumption compared to C.E.H. sequence to attain the same brightness. C.E.H. sequence was not tried with C-3 and C-4 pulps as their $KMnO_4$ number was comparatively low and required low percentage of chlorine in chlorination stage.

5. The bleaching of pulps under optimized conditions was done for C-1 and C-2 using C.E.H. and C.H. sequences and for C-3 and C-4 using H.H. and C H. sequences (Table-VIII A & B). If we compare C.E.H. and C.H. sequences (C-1, C-2) the chlorine requirement in case of C.E.H. sequence was quite lower but the shrinkage was on higher side. The viscosity of C E.H. pulp was on higher side and P.C. number on lower side, compared to C.H. sequence. Comparing the H.H. and C.H. sequence (C-3, C-4) chlorine requirement by H.H. sequence is much higher than C.H sequence. Shrinkage and P.C. number were on higher side while pulp viscosity was on lower side. Now if we compare C.H. sequence for all the four pulps, as usual chlorine requirement increases with increasing $KMnO_4$ number, at the same time P.C. number and pulp shrinkage during bleaching follow the similar trend.

6. It can be seen from Table-IX that bulk is on higher side for pulps of C-1 bleached with C.E.H. and C.H. sequences than all other pulps which have nearly the same bulk. By comparing the bleached pulps of C-1 — C-4 using C.H. sequence, no definite conclusion could be made on strength properties, however they have shown an increasing trend (with decreasing $KMnO_4$ number of unbleached pulp, i.e. the properties of C-4 bleached pulp are ons higher side than others If we compare propertiet of C.E H. and C.H. bleached pulps (C-1, C-2) no. much difference is observed. However, C.E.Hs bleached pulps have comparatively higher properties since they require lower chlorine during bleaching which has not adversely affected the pulp as compared to C.H. sequence. where higher chlorine was required.

In case C-3 & C-4 bleached pulp properties, pulps bleached with H.H. sequence have given lower strength properties compared to C.H sequence.

EXPERIMENTAL

The rice straw sample was collected locally from Koraput region. After atmospheric conditioning it was manually chopped for further studies.

Proximate Chemical Analysis

The straw sample was powdered in laboratory grinder and taken for proximate chemical analysis. The analysis was carried out using ISI/TAPPI Standard methods. The results are recorded in Table-I.

TABLE—III. OPTIMIZATION OF 'HH' SEQUENCE

PARTICULARS		C-1 ($KMnO_4$ No. 12.1)				C-2 ($KMnO_4$ No. 10.4)				C-3 ($KMnO_4$ No. 7.9)				C-4 ($KMnO_4$ No. 5.5)				
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	5
HYPO I STAGE																		
Cl_2 added	%	4.0	5.0	6.0	7.0	4.0	5.0	6.0	7.0	4.0	5.0	6.0	7.0	3.0	4.0	4.0	5.0	6.0
Cl_2 consumed	%	3.98	4.92	5.55	6.40	4.0	4.90	5.80	6.80	3.90	4.72	5.57	6.44	2.83	3.69	3.69	4.24	4.76
Final pH		6.4	6.2	6.1	6.0	6.9	6.8	6.6	6.3	7.1	7.0	6.8	6.7	7.8	7.5	7.6	7.4	7.4
HYPO II STAGE																		
Cl_2 added	%	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	1.0	1.0	3.0	3.0	3.0
Cl_2 consumed	%	1.80	1.67	1.66	1.60	2.70	2.62	2.68	2.68	2.29	2.26	2.25	2.21	0.83	0.8	1.81	2 12	1.89
Final pH		7.2	7.2	7.4	7.3	7.0	6.9	7.0	6.6	7.2	7.1	7.0	7.0	7.6	7.7	7.6	7.3	7.3
Brightness (Elrepho)	%	67.4	67.7	70.4	72.0	69.7	70.0	72.0	72.5	73.4	76.0	77.3	78.0	73.5	75.0	77.3	77.2	78.9

TABLE—IV. OPTIMIZATION OF 'CEH' AND 'CH' SEQUENCE
Unbleached Pulp $KMnO_4$ No 12.1 (C-1)

Particulars		1	2	3	4	5	6
CHLORINATION							
Cl_2 added	%	2.0	3.0	4.0	5.0	6.0	7.0
Cl_2 consumed	%	1.98	2.96	3.81	4.40	4.65	5.44
Final pH		2.6	2.3	2.1	1.9	1.8	1.7
ALKALI EXTRACTION							
NaOH added	%	0.6	0.8	1.0	1 3	1.5	1.7
Final pH		9.0	9.1	9.3	9.5	9.8	9.9
$KMnO_4$ No. (A.E. pulp)		6.3	4.6	3.6	2.9	2.4	2.4

N.B. :—4.5% Cl_2 is taken as optimum dose.

OPTIMIZATION OF 'H' STAGE OF 'C.E.H.' SEQUENCE

HYPO STAGE							
Cl_2 added	%	0.5	1.0	1.5	2.0	2.5	3.0
Cl_2 consumed	%	0.50	0.95	1.27	1.64	2.15	2.60
Final pH		7.1	7.2	7.4	7.3	7.1	7.4
Brightness (Elrepho)	%	71.3	76.8	78.3	79.3	80.4	80 8

OPTIMIZATION OF 'H' STAGE OF 'C.H.' SEQUENCE

HYPO STAGE							
Cl_2 added	%	1.0	1.5	2.0	2.5	3.0	3.5
Cl_2 consumed	%	1.00	1.48	1.94	2.36	2.80	3.20
Final pH		5.3	5.4	5.3	5.6	5.5	5.8
Brightness (Elrepho)	%	62.4	68.7	72.0	74.1	77.7	80.3

TABLE - V. OPTIMIZATION OF 'C.E.H.' AND 'C.H.' SEQUENCES
Unbleached pulp $KMnO_4$ No. 10.4 (C-2)

Particulars		1	2	3	4	5
CHLORINATION						
Cl_2 added	%	2.0	3.0	4.0	5.0	6.0
Cl_2 consumed	%	2.00	2.89	3.60	3.90	4.50
Final		3.7	2.7	2.4	2.1	2.0
ALKALI EXTRACTION						
NaOH added	%	0.6	0.8	1.0	1.3	1.5
Final pH		8.7	9.2	9·3	9.6	9.6
$KMnO_4$ No. (A.E. pulp)		5.9	4.5	3.6	3.2	3.0

N.B. :—4.0% Cl_2 is taken as optimum dose.

OPTIMIZATION OF 'H' STAGE OF 'C.E.H.' SEQUENCE

HYPO STAGE						
Cl_2 added	%	0.5	1.0	1.5	2.0	2.5
Cl_2 consumed	%	0 50	0.96	1.35	1.76	2.1
Final pH		7.7	7.4	7.4	7.3	7.1
Brightness (Elrepho)	%	73.3	78.3	80.1	81.2	82.0

OPTIMIZATION OF 'H' STAGE OF 'C.H.' SEQUENCE

HYPO STAGE						
Cl_2 added	%	2.0	2.5	3.0	3.5	4.0
Cl_2 consumed	%	1.92	2.26	2.76	3.13	3.51
Final pH		5.2	5.6	5.5	5.8	6.0
Brightness (Elrepho)	%	75.3	76.5	78.7	79.8	79.5

TABLE—VI

OPTIMIZATION OF 'C.H.' SEQUENCE
Unbleached Pulp $KMnO_4$ No. 7.8 (C–3)

Particulars		1	2	3	4
CHLORINATION					
Cl_2 added	%	1.0	2.0	3.0	4.0
Cl_2 consumed	%	1.00	1.92	2.50	3.00
Final pH		5.8	5.1	3.0	2.4
ALKALI EXTRACTION					
NaOH added	%	0.5	0.6	0.8	1.0
Final pH		9.4	9.2	9.4	9.4
$KMnO_4$ No. (A.E. Pulp)		4.8	3.4	2.4	2.0

N.B.—2.0% Cl_2 is taken as optimum dose.

OPTIMIZATION OF 'H' STAGE

HYPO STAGE					
Cl_2 added	%	1.0	2.0	2.5	3.0
Cl_2 consumed	%	1.00	1.86	2.22	2.57
Final pH		6.9	6.8	6.8	6.8
Brightness(Elrepho)	%	69.2	74.0	77.5	78.7

TABLE—VII

OPTIMIZATION OF 'C.H.' SEQUENCE
Unbleached Pulp $KMnO_4$ No. 5.5 (C—4)

Particulars		1	2	3	4
CHLORINATION					
Cl_2 added	%	0.5	1.0	1.5	2.0
Cl_2 consumed.	%	0.50	1.00	1.46	1.83
Final pH		6.4	6.3	6.0	5.3
ALKALI EXTRACTION					
HYPO STAGE					
NaOH added	%	0.4	0.5	0.5	0.6
Final pH		9.1	9.5	9.2	9.4
$KMnO_4$ No. (A.E. Pulp)		4.9	4.1	2.9	1.9

N.E.—1.5% Cl_2 is taken as optimum dose.

OPTIMIZATION OF 'H' STAGE

HYPO STAGE					
Cl_2 added	%	1.5	2.0	2.5	3.0
Cl_2 consumed	%	1.40	1.73	2.10	2.60
Final pH		6.9	6.9	7.0	7.0
Brightness (Elrepho)	%	72.0	73.1	76.2	77.0

TABLE—VIII (A)

BLEACHING WITH 'C.E H ' AND 'C.H.' SEQUENCES UNDER OPTIMUM CONDITIONS

Particulars		C—1 ($KMnO_4$ No. 12.1) 'C.E.H '	'C.H.'	C—2 ($KMnO_4$ No. 10.4) 'C.E.H.'	'C.H.'
CHLORINATION					
Cl_2 added	%	4.5	4.5	4.0	4.0
Cl_2 consumed	%	4.18	4.18	3.60	3.60
Final pH		2.2	2.2	2.4	2.4
ALKALI EXTRACTION					
NaOH added	%	1.2	—	1.2	—
Final pH		9.4	—	9.5	—
HYPO STAGE					
Cl_2 added	%	1.0	3.0	1.0	3.0
Cl_2 consumed	%	0.94	2.82	0.88	2.64
Final pH		7.3	5.5	7.7	6.3
Total Cl_2 added	%	5.5	7.5	5.0	7.0
Total Cl_2 consumed	%	5.12	7.00	4.48	6.24
Brightness (Elrepho)	%	77.1	77.0	79.1	78.0
Shrinkage	%	20.00	16.00	17.32	14.72
P.C. No.		5.10	8.10	3.47	6.42
Viscosity cp (CED)		6.2	5,1	5.0	4.7
Alpha cellulose in Pulp	%	80.3	77.8	80.1	78.5

TABLE—VIII (B)

BLEACHING WITH 'H.H.' AND 'C.H.' SEQUENCES UNDER OPTIMUM CONDITIONS

Particulars		C—3 ($KMnO_4$ No. 7.8) 'H.H.'	'C.H.'	C—4 ($KMnO_4$ No. 5.5) 'H.H '	'C.H.'
CHLORINATION					
Cl_2 added	%	—	2.00	—	1.50
Cl_2 consumed	%	—	1.92	—	1.43
Final pH		—	5.0	—	5.9
HYPO I STAGE					
Cl_2 added	%	5.0	2.5	4.0	2.5
Cl_2 consumed	%	4.74	2.14	3.60	2.10
Final pH		6.8	6.6	7.4	7.0
HYPO II STAGE					
Cl_2 added	%	3.0	—	3.0	—
Cl_2 consumed	%	2.17	—	2.18	—
Final pH		7.0	—	7.0	—
Total Cl_2 added	%	8.0	4.5	7.0	4.0
Total Cl_2 consumed	%	6.91	4.06	5.78	3.53
Brightness (Elrepho)	%	76.3	77.7	77.0	76.5
Shrinkage	%	12.8	11 8	11.2	10.1
P.C. No.		6.9	5.5	6.0	4.6
Viscosity cp (CED)		4.1	5.7	4.2	6.0
Alpha cellulose in pulp	%	73.3	76.8	69.1	75.5

TABLE IX—PHYSICAL STRENGTH PROPERTIES OF BLEACHED PULPS AT '45°' SR

PARTICULARS		C—1		C—2		C—3		C—4	
		C.E.H.	C H.	C.E.H.	C.H.	H.H.	C.H.	H.H.	C.H.
Bulk	cm^3/g	2.00	1.91	1.67	1.68	1 67	1 68	1.55	1.65
Tear factor		32.0	31.5	29.0	28.5	32.5	35.0	18.0	39.0
Burst factor		24.0	22.0	23.5	20.0	18.5	22.5	14 0	29.0
Breaking length	Kn.	3.90	3 50	5.70	5.00	3.80	4.10	3.30	4.60
Double folds	No.	21	21	7	8	6	20	8	19

Pulping

The pulping experiments were carried out taking 750 g. (O.D.) raw material and using 5 lits. capacity electrically heated rotary digester. The soda charge was varied from 6-12% (on O.D. raw material). The pulps obtained were washed thoroughly and analysed for $KMnO_4$ number. The conditions and results are recorded in Table-II.

Bleaching

All the four pulp samples (C–1 to C-4) obtained at different charge of alkali during pulping, were bleached using H.H., C.H. and C.E.H. sequences.

Optimization of 'H. H.' Sequence

All the four pulp samples were tried with H.H. sequence. Varied amount of chlorine as calcium hypochlorite was added in the first stage of hypo. And in the second stage constant/varied dose of chlorine was added. The chlorine dose at which $77\pm2\%$ pulp brightness was obtained was considered as optimum chlorine charge in hypo first stage. The conditions and results are recorded in Table-III.

In case of C–1 and C-2 pulps, the desired brightness could not be attained, while in other two C-3 and C-4 pulps attained the brightness. Large scale (500 g. O.D.) bleachings were carried out under the optimum conditions for pulps of C-3 and C-4. The results are recorded in Table-VIII B.

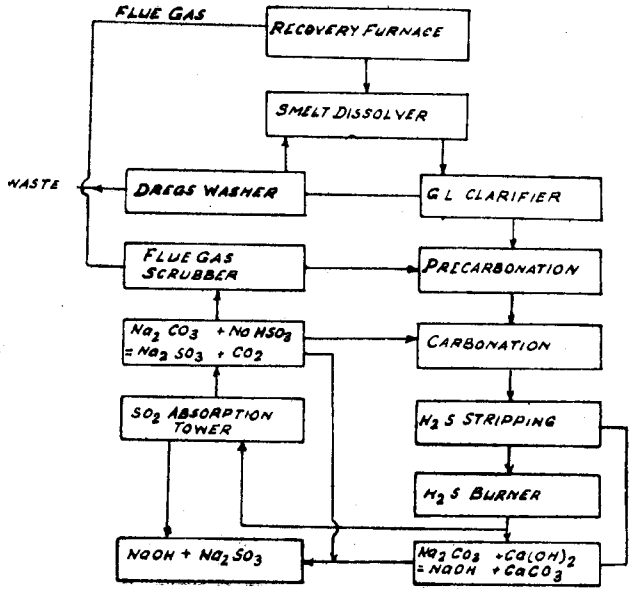
Optimization of C.E.H. and C.H. Sequences

The chlorine charge in chlorination stage was optimized by varying the chlorine dose and then alkali extraction was carried out. The $KMnO_4$ number of alkali extracted pulp was determined. Based on the residual chlorine and alkali extracted pulp $KMnO_4$ number, the optimized dose of chlorine was fixed. The optimization of 'H' stage of C.E.H. pulp was done by taking alkali extracted pulps (with optimum chlorinc) and by varying the hypochlorite charge. The chlorine charge which has given brightness of $77\pm2\%$ was taken as optimum. Since unbleached pulps C-3 and C-4 have comparatively low $KMnO_4$ number and satisfactorily bleached with 'H.H.' and C.H. sequences C.E.H. bleaching was not tried.

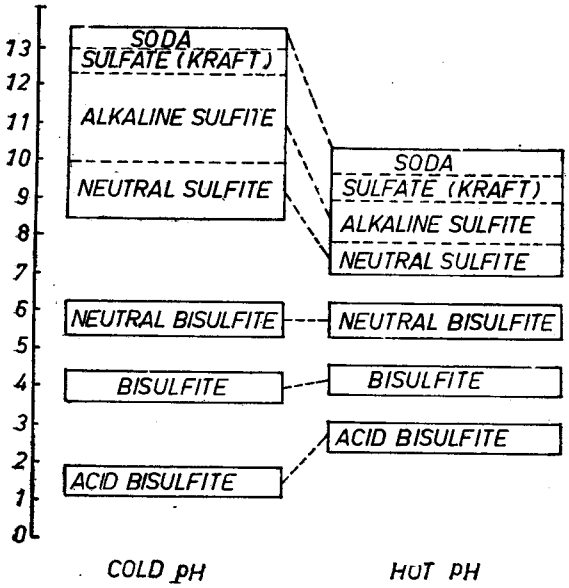
Optimization of 'H' stage of C.H. sequence was done similar to 'H' stage of C.E.H. sequence but in this set chlorinated pulp was taken instead of alkali extracted pulp.

The conditions and the results of these optimization experments for all the four pulps are recorded in Table IV to VII.

The large scale bleaching for pulps using C.H. sequence for C-1 to C-4 pulp samples and using C.E.H. sequence for C-1 and C-2 pulp samples wlere carried out and results are recorded in Table VII A and VIII B.



THE POSITION OF VARIOUS PULPING PROCESSES ON THE PH SCALE



The following constant conditions were maintained during bleaching experiments :

	Temperature °C	Consistency %	Retention Time hrs.
Chlorination	Ambient	3.0	0.5
Alkali extraction	50	5.0	1.0
Hypo I and II stages	40	5.0	2.0

Physical Strength Properties

The bleached pulps obtained under optimum conditions of bleaching were beaten separately in laboratory valley beater to different freeness levels and standard hand sheets (60 ± 1 gsm) were made on British Hand-sheet making machine. After conditioning, the sheets were tested for physical strength properties. The strength properties data at 45° S.R. were taken out by interpolation and recorded in Table-IX.

CONCLUSIONS

1. Pulping of rice straw with higher alkali charge gives low yield and $KMnO_4$ number. In the absence of recovery system, the cooking conditions should be adjusted according to the further pulp processing facilities.
2. The bleaching studies reveal that in order to obtain the bleachable grades from pulps of high $KMnO_4$ number, C.H./C.E.H. sequence has to be incorporated, since H.H. sequence is not capable of giving the desired brightness even with using high chlorine charge.
3. The pulps of lower $KMnO_4$ number could be bleached by H.H. and C.H. sequences to give $77\pm2\%$ brightness but the total chlorine requirement was higher with H.H. sequence compared to C.H. sequence.
4. No significant difference was observed in the strength properties of pulps bleached with different sequences.

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