Per-oxy Alkaline Extraction of Wheat Straw Soda and Soda AQ Pulp

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The goal of cleaner production in pulp and paper industry can be achieved by adopting technological developments. When appropriate. environmental management procedures and clean technologies are applied to pulp and papermaking operations, the environmental impact of the pulp and paper industry is low and industry can be regarded as well adapted to the requirements of a sustainable society. It may not always be possible to incorporate the state of the art technologies into the existing process lines due to very many reasons, viz. cost of the technology, capital investment and compatibility of the technology with the materials used in the process. Keeping the indigenous users in view, some of the ideas were tried, especially in the area of reduction of residual lignin in pulp prior to bleaching process. This is achieved by solublizing and extraction of the part of the residual lignin in the alkaline medium. Any significant reduction of residual lignin in the unbleached pulp has positive impact on the bleaching process. Post digester delignification is a process by which use of chlorine and chlorine based bleach chemicals can substantially be reduced. Laboratory pulping studies of wheat straw with additive Aq followed by peroxy alkaline extraction indicated significant reduction of pulp kappa. Initial pulp kappa of 22 (without Aq) could be reduced to 15 with addition of 0.03% of Aq. Soda-Aq pulp kappa could further be reduced up to 8 by using peroxy extraction process.

INTRODUCTION

The pulp and paper industry has too often been the subject of environmental controversies in Asia. In Asian countries it is segregated into three categories. At one end are the world class mill with advanced technology which are competitive globally. The second category mills are the medium scale units those are generally 10-20 years old with inferior production quality and difficult to be competitive globally but fulfil the domestic and regional market needs. The third category is the small mills in India, China and other countries that use non-wood raw materials. These small and medium size mills have outdated technology and equipment, and are relatively inefficient, and end up with environment problems. (1)

The use of agriculture based raw materials for paper production has been increasing with time, specifically in Asian countries due to depletion of forest based raw materials. China is the third largest manufacturer of paper and paperboard, utilizes more than 50% non-wood pulp in its paper industry. In India there are over 400 mills producing 4.5 millions tonnes of paper. About

Estimated Availability of Non Wood Fibres World wide (1999) (2)

	Bagasse	Wheat Straw	Rice Straw
World Wide Availability (million BDMT)	1,022	600	360
Total world wide paper making pulp capacity (mil.met.tons)	3238	1,0961	

33% of the total production come from the agro residue based mills. Most of these agro based mills are in medium or small scale sector. (1)

Figures in the above table indicate that the availability as well as pulp making capacity of straws is increasing, and straw pulping in today's context is thrust area of research and development.

The world wide technological developments have made paper making a state of art cleaner production, especially for large paper mills. Some of the new technologies are

- Organosolve pulping (Organocell, alcell, ASAM etc.)
- Peroxyacid pulping (Milox process etc.)
- Enzyme pulping
- Extended delignification (Oxygen- alkali digestion, RDH, Superbatch etc.)
- Additive pulping (Aq pulping, MSS Aq pulping etc.)

The first three technologies, i.e. organosolve pulping, peroxyacid pulping, enzyme pulping are in developing stage. Extended delignification (Oxygen- alkali (digestion, RDH, Superbatch etc.), though very encouraging in terms of energy conservation and pollution load generation, but it requires significant huge investment for its implementation.

Literature reveals that there are other options also available for kappa reduction, in digester by additive pulping (3,4), post digester alkaline leaching (5,6) etc. Additive pulping, though is not very widely applied by manufacturers but has potential from both environment and economics point of view. It has been observed that AQ pulping is affective in terms of kappa reduction, rejects minimization and yield improvement.

Brown stock washing that is responsible for the efficiency of further bleaching process has been studied repeatedly, but the efficiency of the process has limitations since the pH of the stock being washed is reduced during the process. This aspect was examined by Favis and co-workers (7) and inferred that fibre swelling enhances diffusion of degraded lignin. Further studies on the influence of pH by Grignon & Scallan (8) and Hagstrom- Nasi and co-workers (9) on fibre swelling indicates that higher pH helps in swelling of the fibres thereby enhancing the rate of diffusion of lignin from fibres. The studies on post digester alkaline leaching of soft wood pulp reveals that it can reduce pulp kappa from 30-40%.

The present work on alkaline extraction with hydrogen peroxide of soda and soda AQ pulp of wheat straw reveals optimization of various parameters for extraction, so that the maximum advantage of this process for the improvement in bleachability can be obtained.

EXPERIMENTAL

- **Raw Materials Preparation**

Wheat straw was locally collected in chopped form and used in laboratory studies. It was kept in polythene bags for attaining uniform moisture. Moisture content of this sample was determined as per the standard procedure and pulping experiments were carried out.

Pulping

Wheat straw was pulped using soda process as well as soda-Aq process. Optimization experiments were carried out for soda-Aq process in a series digester consisting of six bombs each of 2.5 ltr capacity, rotating in an electrically heated polyethylene glycol bath. Washing of the pulp was carried out with cold water. After thorough washing, the pulps were screened in laboratory 'Serla' screen using mesh with 0.25mm slot width. Pulp yield and kappa numbers of the unbleached pulps were determined as per the standard procedure (10).

Cooking Conditions

Raw material in each bomb	:	200g
Bath ratio	:	1:5
Cooking temp. °C	:	165
Cooking time, min.	:	90

Cooking schedule

Ambient to 100°C	:	30 min.
100°C to 165°C	:	100 min.
At 165°C	:	90 min.

- **Per-oxy-alkaline extraction of pulps**

Extraction of soda and soda-AQ pulp with sodium hydroxide as well as with sodium hydroxide together with hydrogen peroxide was carried out at different temperatures viz. 65° C and 85°C for one hour duration. The treated pulps were again washed to remove the extracted residual lignin and subjected for conventional CEH bleaching together with the control soda and soda-Aq pulp of wheat straw.

- **Per-oxy-extraction conditions**

Reaction temp.	:	65°C and 85 °C
Reaction time	:	60 min.
Consistency	:	8 %

- **Bleaching**

Extracted pulps together with the control pulps after washing were bleached by CEH sequence to around + 80% ISO brightness level under the normal bleaching conditions. Different stages of CEH bleaching were optimized and finally the pulps were bleached by using optimum bleach chemical.

Bleaching conditions

- **Effluent Characteristics**

Effluent characteristics mainly AOX of CEH bleach effluent of control, sodium hydroxide extracted and sodium hydroxide together with hydrogen peroxide extracted pulps of wheat straw were determined as per the standard test method (11).

	Cl_2 stage	Extraction stage	Hypo stage
Consistency (%)	3.0	8.0	8.0
Reaction time (min)	30	60	120
Reaction temp (°C)	Amb	60	40

Table 1 : Soda and Soda-Aq pulping of wheat straw

Particulars	1	2	3	4	5	6	7	8
Cooking chemical as Soda,%	16	16	16	16	16	16	16	16
Anthraquinone, %	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07
Unscreened pulp yield, %	50.8	50.9	51.2	51.3	51.3	51.5	51.6	51.6
Screened rejects, %	0.55	0.52	0.5	0.45	0.44	0.4	0.4	0.4
Kappa number	22.8	18.1	15.7	14.9	14.7	14.8	14.9	14.7
Black liquor analysis:								
a) pH	9.5	9.2	9.0	8.8	8.8	8.9	9.1	9.0
b) RAA, gpl	1.67	1.55	1.40	1.24	1.43	0.99	1.24	1.05
c) Total solids, %	11.4	10.9	10.7	10.5	10.2	9.85	10.6	9,73

Table 2 : Alkaline extraction of soda and soda-Aq unbleached pulp of wheat straw with and without the use of hydrogen peroxide.

Particulars	Soda pulp		Soda-Aq pulp	
	E	Ep	E	Ep
Initial kappa no.	22.8	22.8	14.9	14.9
Caustic, %	2	2	2	2
Consistency, %	8	8	8	8
Peroxide, %	-	0.5	-	0.5
Reaction temp., °C	85	85	85	85
Reaction time, min.	60	60	60	60
Final kappa no.	16. 7	14.3`	10.7	8.1
Kappa reduction, %	26.7	37.3	27.7	45.2
Shrinkage, %	3.0	3.8	2.9	3.7

E -Alkaline extraction (2% Soda); Ep -Alkaline peroxide extraction (2% Soda, 0.5% H_2O_2) .

Table 3 : Optimization of CEH bleaching of different pulps of wheat straw.

Particulars	Soda Control	Soda Extraction (Ep)	Soda-Aq Control	Soda-Aq Extraction (Ep)
Unbleached pulp Kappa number	22.8	14.3	14.9	8.1
Brightness % ISO	32.4	39.3	33.3	45.1
Viscosity cm^3/g	744.5	799.8	761.3	975.2
Chlorination stage:-				
Chlorine added as available Cl_2 %	4.9	3.2	3.0	1.8
Consumed%	4.64	3.0	2.8	1.6
Extraction stage:-				
Soda added %	2.0	2.0	2.0	2.0
Hypo stage:-				
Hypo added as available Cl_2 %	1 2 3	1 2 3	1 2 3	1 2 3
Hypoconsume,%	0.96 1.93 2.54	0.86 1.58 2.5	0.92 1.7 2.5	0.86 1.54 2.3
Brightness, % ISO	78.3 82..5 83.1	81.2 83.0 82.7	72.7 80.281.2	76.6 81.4 81.9

Table 4 : Large scale CEH bleaching of different pulps of wheat straw.

Particulars	Soda Control	Soda Extracted	Soda-Aq Control	Soda-Aq Extracted
Unbleached pulp Kappa number	22.8	14.3	14.9	8.1
Brightness % ISO	32.4	39.3	33.3	45.1
Viscosity cm^3/g	744.5	799.8	761.3	975.2
Chlorination stage:-				
Chlorine added as available Cl_2 %	4.9	3.2	3.0	1.8
Extraction stage:-				
Soda added %	2.0	2.0	2.0	2.0
Hypo stage:-				
Hypo added as available Cl_2 %	2.0	2.0	2.0	2.0
Brightness %ISO	82.3	83.1	80.2	81.9
Post color number	2.63	2.44	2.72	2.59
Viscosity cm3/g	475	431	455	407
COD, mg/l	648	423	496	330
BOD, mg/l	225	209	205	158
AOX, kg/t	5.4	4.0	3.8	1.5
Color,pcu	800	512	615	109

Table 5 : Physical strength properties of unbleached pulps of soda control, soda extracted, soda-Aq control and soda-Aq extracted.

Pulp Type	PFI	Freeness	Apparent Density	Burst Index	Tensile Index	Tear Index	Fold Kohler Molin	Porosity Bendtsen
Unbleached	rev	ml,CSF	g/cm^3	$Kpam^2/g$	Nm/g	MNm^2/g	log	ml/min
SODA	0	440	0.74	3.75	62.0	5.50	1.65	185
Control	500	245	0.89	5.05	82.5	4.45	1.85	15
SODA	0	375	0.80	3.90	65.0	5.95	1.65	140
Extracted	500	245	0.84	4.90	81.5	4.90	1.81	20
SODA-Aq	0	400	0.74	3.70	69.0	5.00	1.75	110
Control	500	215	0.84	4.15	76.0	4.80	1.90	25
SODA-Aq	0	390	0.72	3.30	57.0	5.20	1.79	70
Extracted	500	65	0.75	4.50	77.0	5.00	2.22	10

Table 6 : Physical strength properties of bleached pulps of soda control, soda extracted, soda-Aq control and soda-Aq extracted.

Pulp Type Unbleached	PFI rev	Freeness ml,CSF	Apparent Density g/ cm³	Burst Index Kpam²/g	Tensile Index Nm/g	Tear Fold Index MNm²/g	Porosity Kohler Molin log	Bendtsen ml/min
SODA	0	370	0.73	3.70	68.0	5.00	1.60	60
Control	500	220	0.75	4.25	73.5	4.70	1.72	20
SODA	0	400	0.67	3.50	69.0	4.70	1.57	60
Extracted	500	210	0.68	4.10	70.0	4.60	1.57	20
SODA-Aq	0	380	0.80	3.30	59.0	4.40	1.28	90
Control	500	135	0.82	4.60	77.0	4.25	1.77	5
SODA-Aq	0	375	0.75	3.45	68.0	4.10	0.95	80
Extracted	500	200	0.76	3.75	70.0	3.90	1.73	10

- **Pulp Viscosity**

Different pulps before and after extraction as well as after CEH bleaching were analyzed for viscosity as per the standard procedure (12).

- **Bleached pulp Brightness & Post color number**

Pulps brightness before and after extraction and post color number of finally CEH bleached pulps was determined as per procedure.

RESULTS AND DISCUSSION

a. The results of Aq optimization are shown in table - 1. The soda-Aq pulping studies were carried out using 16 % soda and varying doses of Aq (0.01 to 0.07%). It was found that addition of 0.03% anthraquinone is found to be sufficient to reduce kappa from 22.8 (without Aq) to 14.9 (with 0.03% Aq). There was no further reduction in kappa no. by increasing Aq dose up to 0.07%. The unscreened pulp yield was improved from 50.8% (without Aq) to 51.3% (with 0.03% Aq), so there is a marginal gain of 0.5% in unscreened yield.

b. The results of alkaline extraction with and without peroxide are furnished in table-2. It was found that the addition of 0.5 % of peroxide in alkaline extraction of soda pulp resulted in substantial drop in pulp kappa no. Soda pulp with initial kappa 22.8 was reduced to 16.7 by addition of 2% of caustic. Whereas addition of 0.5% peroxide along with 2% caustic the kappa was reduced from 22.8 to 14.3. In case of soda-Aq pulp, the initial kappa 14.9 was reduced to 10.7 by addition of 2% of caustic. Addition of 0.5% peroxide along with 2% caustic resulted in reduction of kappa from 14.8 to 8.1.

Similar results were reported earlier by Li and Macleod (6), where kappa no reduction at 100°C was 31-40% at different concentration of alkali, and in present studies we have obtained drop of 26.7% to 45.2% in our experiments on wheat straw at various conditions as shown below in table 2.

c. Optimization of bleaching conditions is given in table 3. The four pulps viz. soda control (kappa 22.8), peroxy extracted soda (kappa 14.5), soda-Aq control (kappa 14.8), and peroxy extracted soda-Aq (kappa 8.1), pulps were bleached using CEH sequence to get 80% ISO brightness level. The chlorine demand for these pulps was 4.9 %,3.0%, 2.8% and 1.6% respectively. There was substantial reduction in chlorine demand of peroxy extracted pulp in comparison to untreated soda control and soda- Aq control pulp. Hypo requirement for four pulps was almost similar i.e. 2% to achieve brightness level around +80 % ISO.

d. The result of large scale CEH bleaching of four pulps viz. soda control, per-oxy extracted soda, soda-Aq control, and per-oxy extracted soda Aq pulp are furnished in table-4. The final brightness of the four pulps was 82.3, 83.1, 80.2 and 81.9% ISO respectively by using 2% hypochlorite dose. Moreover, the viscosity of four pulps is 475, 431, 455 and 407 cm^3/g respectively. Pre-bleaching extraction with alkaline peroxide has marginally reduced the viscosity of the pulps.

Bleached pulp effluents of these pulps were analyzed for different characteristics as COD, BOD, AOX and color. The results indicate that there is substantial improvement in the effluent quality when the unbleached pulps are pre-treated with alkaline peroxide. This is primarily due to the reduction in kappa in the alkaline peroxide extraction process prior to bleaching (Table.4).

e. The results of physical strength properties of unbleached and bleached four pulps are furnished in table-5 and 6 respectively. Soda control and per-oxy extracted soda pulp required 500 rev to get 245 csf. While by applying same refining treatment on soda- Aq and soda-Aq per-oxy extracted pulp freeness obtained was 215 and 165 ml, csf. Strength properties of bleached pulp (table-6) reveals that freeness of pulps was similar after treating them at uniform degree of PFI revolutions i.e. 500 rev. Strength properties of four bleached pulps viz. soda control, per-oxy extracted soda, soda-Aq control, and per-oxy extracted soda-AQ were similar, but different for the tensile index which is affected by the pre-treatment of unbleached pulps with alkaline peroxide.

CONCLUSIONS

Laboratory experiments on addition peroxide to the alkaline extraction of wheat straw soda and soda AQ pulp has shown enhanced the lignin removal from the pulp there by reducing the pulp kappa. This process has significant influence on the effluent quality.

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REFERENCES

1. Cleaner Production at Pulp and Paper Mills: A guidance Manual by UNEP- NIEM-1997.
2. Atchison, Joseph E., "Tables for paper on update on global use of non wood plant fibres and some prospects for their greater use in the united states" , TAPPI North American Non Wood Fibre Symposium, 1998.
3. Sood,Y.V.,and Kapoor,S.K "Modified soda pulping of wheat straw (Triticum volgare)", IPPTA 21(1), (1984).
4. Zhinan, Feng and Raimo, J.Alen,"Soda-AQ pulping of wheat straw" , Appita 54 (2), (2001).
5. K.Ala-Kaila and I Reilama, "Stepwise delignification response in an industrial two stage oxygen alkali delignification process", Pulp and Paper Canada, 102 (6), (2001).
6. LI,J.,Macleod, J.M.," Alkaline leaching of kraft pulps for lignin removal", J.Pulp Paper Sci,19(2),(1993)
7. Favis,B.D. and Goring,D.A.I.," A moderl for the leaching of lignin macromolecules from pulp fibres",J.Pulp Paper Sci.,10(5),(1984)
8. Grignon. J.. and Scallan, A.M.,"Effect of pH and neutral salts upon the swelling of cellulose gels",J.Applied Polymer Sci.,25, (1980)
9. Hagstrom Nasi, C.,Jarvinen,R.,Sundquist,J. and Moilanen, K.M., "Determination and characterization of the leachable lignin from unbleached kraft pulp", Int. Symp. Wood & Pulping Chem.. Poster Session. Paris (1987).
10. TAPPI Standard Method No T226-OS-76.
11. Per Koch, Christensen, "Pulp bleaching manual", Department of chemical engineering, the Norwegian institute of technology, Norway.
12. SCAN Standard method - SCAN-C 15 : 62.