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OXYGEN DELIGNIFICATION OF WHEAT STRAW

Mittal K.C.,Head- Pulp & Chemical recovery,
Upadhyaya J.S.,Senior Instructor (P&P),
Gupta S.C. and Chawla R.K.,
B.E. (P&P) Final Yr.students
INSTITUTE OF PAPER TECHNOLOGY,
SAHARANPUR, U.P.

Abstract:

A study has been undertaken to assess the suitability of wheat straw to be pulped by means of alkali-oxygen single stage and multistage cooking process. The effect of few cooking variables, such as oxygen presence, alkali charge, type of alkali on yield and Kappa number, brightness, color reversion and strength properties have been evaluated.

The pulps have also been bleached in CEH and HEH sequences and properties like brightness, post color no, and strength properties of the pulps have been evaluated.

The results conclude that single stage alkali-oxygen pulping is better than two stage delignification for wheat straw, which is due to porous and bulkier raw material having lower lignin content compared to wood/bamboo.

1.0 Introduction:

Oxygen was first employed in the pulp mill as a bleaching agent primarily to reduce the volume of effluent and its toxicity from the bleach plant after a patent issued in 1867. The original process involved a treatment of alkaline pulp slurry with air at atmospheric pressure but due to poor solubility of oxygen in water, high oxygen pressure and extremely good mixing equipment was needed.

In the middle of 1950's, the Sovient Researchers Nikitin and Akim et. al. started investigations for the possibilities of unsing molecular oxygen in the presence of alkali for bleaching and refining of dissolving pulps at high pressures upto 15 Bar and high consistencies. Statisfactory dissolving pulps were obtained with required alpha cellulose and viscosity but paper grade pulp could not be produced due to attack of oxygen on cellulose. Later a group of French Scientists, Robert and his associates in 1963 discovered the inorganic compounds, of which magnesium, carbonate proved to be the best, have such an effect that the formation of intermediate compounds could be inhibited and thus strength properties of pulp could be maintained during oxygen bleaching. This work led to the development of Alkali oxygen bleaching process and M/s. South African Pulp and Paper Industry Commercialised the process in 1970 at Enstra, South Africa.

Later oxygen was proposed as a pulping agent in a multistage soda oxygen process in which wood chips are partially cooked with NaOH, defibrated mechanically and finally delignified with alkali-oxygen. Soda-oxygen pulping appears to remove lignin from the outer and inner parts of the fiber cell wall before removing it from the middle lamella. the draw-back to its use is the low solubility in cooking liquor. This causes serious problems of mass transfer in a heterogeneous chemical process such as wood cooking. Even applying very high oxygen pressure, useful mass transfer of the delignifying agent (molecular oxygen) into the fiber walls, where the reaction should take place, is difficult to obtain in cooking of wood/bamboo. In case of wheat straw, as for other annual plants, but unlike that of wood, the above problem is much less important, since the plant structure permits much easier diffusion and penetration of the delignifying agent (molecular oxygen) into the reactive zones of the fibre wall.

Environmental consideration are having a substantial influence on the development of technology for existing plants and new installations in the pulp and paper industry. At the same time, raw material and processing cost are on the increase. These problems have promoted much interest in search for novel sulfur free pulping process which could offer the desired higher pulp yield and its qualities and are less polluting then the conventional kraft process. Among the various approaches investigated during the past two decades, the two stage and single stage oxygen pulping system seems to offer the most promising alternative to the existing kraft process in terms of yield and pulp quality.

2.0 Results and Discussions:

Studies on Soda delignification of wheat straw have been carried out in the presence of molecular oxygen. The research work has been planned to study.

1. Effect of Cooking variables of on yield and degree of delignification,
2. Bleching characteristics of Soda Oxygen Pulps and
3. Effect of Oxygen on Pulp properties.

2.1 Effect of Cooking Variables on Yield and Delignification:

The effect on Pulp yield and delignification caused by the following variables has been examined:

1. Presence of Oxygen,
2. Type of Alkali,
3. Alkali charge and cooking technique.

2.1.1 Presence of Oxygen:

Cooks with caustic soda (12% as Na2O) and Alkali-Oxygen were carried out at temperatures, 160°C and 130°C respectively. The results are given in the Table-II & III.

The figures in the Table-II show that under otherwise equivalent cooking conditions (except cooking temperature) oxygen has a considerable effect on delignification. Soda oxygen cooking at 130°C results in a Kappa No. -21.0 which is almost the same for soda pulp obtained at 160°C. But the unbleached pulp yield is higher for soda oxygen cooked pulp. the higher yield is either to more selective delignification or more likely to repreciptation of dissolved matter on the fiber as a consequence of the lower final pH value (about 8 compared to 10) which results from oxygen cooking. The positive effect of oxygen is more evident when the alkalinity is due to sodium carbonate or bicarbonate.

2.1.2. Type of Alkali:

The type of Alkali used in Oxygen cooking is of great importance. The Table-III shows the results of alkali oxygen cooks where the alkaline agent is either caustic soda or sodium carbonate or sodium bi-carbonate, while other cooking conditions being maintained equal.

As for delignification, caustic soda gave the best results while bicarbonate has least effect. At 130°C and 2 hours cooking time, the Kappa No. obtained from cooking of wheat straw with caustic soda, sodium carbonate and sodium bi-carbonate were 21.0, 39.0 and 52.0 respectively.

As regards the effects on pulp yields, the results obtained do not permit comparison at equal delignification. However, the substitution of carbonate for caustic soda or bicarbonate for carbonate, resulted in higher yields attributable to lower delignification, thus with no effect on delignification selectivity. On the contrary, marked differences can be observed as regards delignification rate. Caustic soda will give fastest cooks while bicarbonate the slowest ones.

2.1.3 Alkali Charge and Cooking Technique:

The effect of alkali charge on delignification has been studied in two stage cooking of wheat straw. In first stage, wheat straw was cooked with 8% NaOH as Na2O in the absence of oxygen and the resultant pulp was cooked with varying amount of caustic soda in the presence of oxygen. The wheat straw was also cooked with equivalent total amount of caustic soda in one stage under similar cooking conditions used in first stage. The results are given in the Table-IV.

The results indicate that the wheat straw cooked with total 10% and 12% NaOH as Na2O results unbleached pulps of Kappa No. of 31.0 and 16.0 respectively. The unbleached pulp yields were accordingly 46.5% and 42.5%. These results of two stage soda-oxygen cooking if compared with the single stage soda oxygen cooking with same amount of caustic soda (results given in Table-III) indicate that bleachable grade, unbleached pulp with higher yield of about 13% can be obtained. Further, the Kappa No. of unbleached pulp also indicates that single stage soda oxygen cooked pulp will be better in view of strength properties.

2.2 Bleaching Characteristics of Soda Oxygen Pulps:

The effect of oxygen on bleaching characteristics of unbleached pulps and brightness reversion of corresponding bleached pulps have been studied. The bleaching was carried out in a three stage CEH and HEH sequences. the results are given in Table-V.

The results given in the Table-V indicate that alkali and alkali oxygen cooked pulps have almost the same bleachability but the brightness reversion is lower in case of latter pulps. the two stage alkali oxygen cooked pulps were found to have higher post colour number as compared to single alkali oxygen cooked pulps. these results also conclude that alkali oxygen cooking of wheat straw, if made in a single stage, with sodium carbonate bleachability is higher and the increment of delignification due to oxygen is superior to that obtained in caustic soda cooking whereas the brightness reversion is lower indicating lower degradation of carbohydrates. In addition there will be a reducting in pollution due to low toxicity of bleach plant effeluent.

2.3 Effect of Oxygen Cooking on Pulp Properties:

As wheat straw has proved to be more suitable for Alkali Oxygen cooking, it is interesting to evaluate the effect of oxygen on Pulp properties. The Table-VI shows the paper properties of wheat straw unbleached and bleached pulps obtained by caustic soda/carbonate oxygen cooking. The results indicate that under controlled conditions the degradation of carbohydrates can be avoided.

3.0 Conclusion:

Expriments have concluded that presence of Oxygen in alkaline cooking of wheat straw results in a better delignification of wheat straw. Oxygen is specially effective when alkaline agent used has in itself the poor delignification power (Na2CO3) or NaHCO3). Pulp yield is not affected by the presence of oxygen. As for the cooking variables, it is found that.

-- Type of alkali used plays a major role in delignification.

-- The alkali charge is important for both delignification and yield.

-- In the case of caustic soda, low temperature, short cooking time and higher alkali concentration are required as compared to sodium carbonate.

-- The presence of Oxygen in caustic soda cooking of wheat straw normally may give rise to a significant decrease in pulp strength which can be due to carbohydrate deploymerisation by oxygen in alkaline medium but our results do not show such impairment of pulp strength.

The discrepancy of behaviour between caustic soda and carbonate can be explained the fact that in the presence of carbonate, oxygen has the possibility of displaying its delignification potential to a larger extent than in the presence of caustic soda.

4.0 Experimental:

(A) Proximate Analysis of Wheat Straw:

A sample of wheat straw was allowed to reach the equilibrium moisture in the atmosphere. It was ground and screened through 80 mesh. The material retained on 80 mesh was taken for analysis. Proximate analysis of wheat straw was carried out as per TAPPI standards. The analysis of wheat straw are given below:

TABLE - I

Sl No.	Chemical and Fiber Properties	
1.	Total Ash	4.5%
2.	Silica and silicates	2.5%
3.	Alcohol-benzene Solubility	5.3%
4.	Solubility in 1% hot Naoh	40.2%
5	Hot water solubility	10.4%
6.	Cold Water Solubility	7.6%
7.	Holo Cellulose	74.1%
8.	Alpha Cellulose	39.1%
9.	Lignin	19.5%
10.	Pentosans	24.5%

(B) Soda Pulping of Wheat Straw :

Caustic soda cooking of wheat straw was carried out using 8%, 10%, 12%, alkali as Na2O under following cooking

(1) Cooking Conditions :

Amount of NaoH as Na2O (on O.D.Raw Material) %	: 8,10,12
Maximum Temperature	: 160°C
Bath Ratio	: 1:5
Time to Maximum Temperature (160°C)	: 60 mts.
Time at Maximum Temp.	: 120 mts.
Total cooking time	: 180 mts.

The cook was carried out in electrically heat tumbling digester. At the end of the cook the pressure was rapidly reduced to zero and the cooked material was discharged. Defibration was accomplised in a laboratory low consistency refiner. Care was taken to avoid fiber cutting as much as possible. The refined pulps were washed and analysed for Kappa number and yield. Results are tabulated in Table-IV.

(C) S0da Oxygen Single Stage Pulping :

The process used consists of an alkaline cook in the presence of oxygen, under pressure in the digester. The cook was carried out in the same digester mentioned above.

Oxygen was passed through a non-return valve connected to the vent valve of the digester after attaining the temperature. Alkali oxygen cooking of wheat straw was carried out using 12% NaoH, Na2Co3 and NaHCO3 as Na2O,. The cooking conditions are given below :

Chemicals applied as Na2O %	: 12% NaOH/ : Na2Co3/NaHCO3
Bath Ratio	: 1:5
Maximum Temp. °C	: 130°
Time to Max. Temperature Min.	: 60
Oxygen presence used	**: 5 Kg./cm²**
Oxygen passed Min	: 120 min.
MgCo3 added	: 0.5

The temperature of the digester was raised to 130°C within 60 mts. Then O2 was passed for 120 mts. and the pressure was maintained at 5 kgs/cm². After cooking, pressure was reduced to zero rapidly. The pulp was discharged, refined in the laboratory refined in the laboratory refiener, washed and analysed for kappa number and yield. Results are tabulated in Table-III.

(D) Soda Oxygen Two Stage Pulping :

Already cooked high Kappa No. Pulps (8% as Na2O cooks) were taken for O2 delignification in the tumbling digester. The pulps were bleached with oxygen of 5 kg/cm² pressure at 10% consistency.

The conditions are given below :

Consistency of the pulp %	: 10
Caustic applied %	: 2.0, 4.0
MgCo3 added %	: 0.5
Time to temp. (130°C)	: 30 mts.
Oxygen pressure used	: 5 kg/cm²
Oxygen passed Min	: 60

O2 unbleached pulps were washed and analysed for kappa number. Results are tabulated in Table-V.

(E) Bleaching of Pulps :

All the above mentioned pulps were bleached by CEH and HEH sequences. Amount of chlorine was added according to the Kappa number of the pulps. The conditions of each stage are given below :

1. CEH Bleaching of pulps:

(i) (C) Stage:

Amount of Cl2	: 50% of total chlorine d demand.
Consistency of pulp	: 3%
Reaction Temp.	: Ambient
pH	: Below 2.0%
Retention time	: 40 mts.

(ii) (E) Stage:

Amount of alkali added	: 2.0%
Consistency of pulp	: 10%
pH	: 11.0
Temperature	: 60°C
Retention Time	: 60 mins.

iii) (H) Stage

	1 2
	: **CEH HEH**
Amount of Cl2 added	: 50%, 70%, 30%
Buffer(NaOH)	: As required.
Consistency of pulp	: 8.0%
Temperature	: 40°C
pH	: 10.0
Retention Time	: 120 mins.

After the completion of CEH/HEH sequences the pulps were analysed for brightness and P.C.No. Results are tabulated in Table-V.

The unbleached and bleached pulps were beaten in PFI mill under standard contiditons upto 40°SR. Hand sheets were prepared on British Sheet Former and its strength properties were determined. Results are tabulated in Table-VI.

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TABLE - II

EFFECT OF OXYGEN ON DELIGNIFIFCATION

CONSTANT COOKING CONDITIONS :

1. Bath ratio — 1:5
2. Time to Max.Cooking Temp. — 60mts.

Sl. No.	Particulars	Units	1	2
1.	Cooking chemicals used	%	NaOH	NaOH
2.	Amount of cooking chemical used as Na2O	%	12.0	12.0
3.	Maximum cooking temp.	^0C	160	130
4.	Amount of MgCo3 used	%	--	0.5
5.	Oxygen Pressure at cooking temp.	kg./cm²	--	5.0
6.	Time at max. cooking temp.	Mins.	120	120
7.	Unscreened Pulp Yield	%	46.0	55.0
8.	Kappa No.	-	20.0	21.0
9.	pH of spent liquor	-	10.0	8.0

TABLE - III

EFFECT OF TYPE OF ALKALI ON ALKALI OXYGEN COOKING

sl. No.	particulars	Units	1	2	3
1.	Cooking chemicals used.		NaOH	NaHCO3	Na2CO3
2.	Amount of cooking chemicals used as Na2O	%	12	12	12
3.	Bath ratio		1:5	1:5	1:5
4.	Maximum cooking temp.	°C	130	130	130
5.	Time to max. temperature.	mins	60	60	60
6.	Time at max. temperature	"	120	120	120
7.	Amount of MgCO3 used	%	0.5	0.5	0.5
8.	Oxygen Pressure at cooking temp.	kg/cm^2	5.0	5.0	5.0
9.	Unbleached and unscreened pulp yield	%	55.0	66.5	63.0
10.	Kappa No.		21.0	52.0	39.0
11.	pH of spent liquor		8.0	8.0	8.0

TABLE - IV

EFFECT OF ALKALI CHARGE ON ALKALI OXYGEN PULPING

Sl. No.	Particulars	Units	1	2	3	4
First Stage						
1.	Cooking chemical (NaoH) used as Na_2O	%	8	8	10	12
2.	Bath ratio		1:5	1:5	1:5	1:5
3.	Time to Maximum cooking temp.	Mins	60	60	60	60
4.	Time at Max. cooking temp.	"	120	120	120	120
5.	Maximum cooking temp.	°C	160	160	160	160
6.	Unscreened Pulp Yield.	%	50.0	50.0	47.0	46.0
7.	Kappa No.		54.0	54.0	23.0	20.0
Second Stage						
1.	Caustic Soda used as Na_2O	%	2.0	4.0	--	--
2.	Consistency of Pulp	%	10.0	10.0	--	--
3.	Amount of $MgCO_3$ used.	%	0.5	0.5	--	--
4.	Maximum cooking temp.	°C	130	130	--	--
5.	Time to maximum cooking temp.	mins.	30	30	--	--
6.	Oxygen pressure at 130°C	kg/cm²	5.0	5.0	--	--

7.	Oxygen passed	mins.	60	60	--	--
8.	Total cooking time.	"	90	90	-	-
9.	Unscreened pulp yield based on O.D. raw material.	%	46.5	42.5	--	--
10.	Kappa No.		31.0	16.0	--	--

TABLE - V

BLEACHING CHARACTERISTICS OF SODA AND SODA OXYGEN PULPS

Sl. No.	Particulars	Units	Soda cooked pulps Table	Two stage alkali oxygen pulps II-1	Table	IV-1	Table	IV-2	Single Stage alkali oxygen pulps Table	III-1	Table	III-3
	Bleach Sequence		CEH	HEH	CEH	HEH	CEH	HEH	CEH	HEH	CEH	EHE
1.	Chlorine consumption in chlorination stage	%	2.3	—	3.57	—	1.73	—	2.3	—	4.49	—
2.	Caustic soda consumption in alkali extraction stage.	%	2.0	-	2.0	-	2.0	—	2.0	—	2.0	—
3.	Chlorine consumption in Hypochlorite stage	%	2.3	3.22	3.57	4.99	1.73	2.42	2.3	3.38	4.49	6.28
4.	Caustic soda consumption in alkali extraction	%	—	2.0		2.0	–	2.0	—	2.0	—	2.0
5.	Chlorine consumption in second hypochlorite stage	%	—	1.38	—	2.14	—	1.03	—	1.45	—	2.69
6.	Brightness	%	75	72	72	68	82	75	78	72	72	68
7.	Post color number.		4.1	5.2	3.5	4.5	5.3	5.3	2.8	3.5	2.4	3.0

TABLE - VI

PROPERTIES OF SODA AND SODA OXYGEN PULPS

Sl No.	Particulars	Soda Cooked pulps Table II-1 Unbleach Pulp	Bleached Pulp CEH	Two stage alkali Table IV-1 HEH		Unbleach Pulp CEH	Bleached Pulp HEH	Oxygen pulps Table IV-2 Unbleached Pulp	Bleach Pulp CEH	Bleach Pulp HEH	Unblea Pulp	Single stagealkali Table III-1 Bleach Pulp CEH	Bleach Pulp HEH	Unbleached Pulp	OxygenPulps Table III-3 Bleached Pulp CEH	Bleached Pulp HEH
1.	Double folds	256	125	315	400	255	205	511	427	332	366	816	837	108	154	330
2.	Burst factor	47	45	42	44	32	46	46	48	53	52	48	47	30	43	46
3.	Tear factor	49	51	65	80	53	87	27	33	73	37	47	43	33	37	40
4.	Breaking length (M)	3400	2300	3000	2500	2000	3400	3800	4500	4100	3600	5300	3300	2600	4000	4100