Issues Related To Bleaching Of Wheat Straw Pulp

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ABSTRACT

The use of wheat straw as potential fiber source for making pulp and paper is well established. India, and China are main countries where wheat straw fiber add substantial part of production of pulp. The nature of wheat straw fiber support its use as paper making fiber. In India, there are vast varieties of raw materials which are utilized for making pulp and paper. Still the sustainable supply of raw material always remains a matter of cocern along with the other problems of pulp and paper production. This segment also share the major cost of whole process.

Agroresidues as wheat straw, rice straw and bagasse are the annually renewable fibers which has consistent supply. Bagasse being better fiber source than straw for pulp and paper was always a good alternative during the past years, but its use as fuel in power generation by sugar manufacturers has created problem in its consistent supply.

The straw, a renewable fiber, available in abundance and has no threat as such for its supply being the major food crop to feed large population in northern India. Its use as paper making raw material is well established. Due to its open structure the handling is difficult but cooking to low kappa number is less energy and chemical incentive than wood or bamboo. The bleaching of straw remains concern in terms of achieving high brightness. In the present communication the issues related to bleaching of wheat straw, problems in ODL efficiency, presence of dirt content, brightness ceiling, are discussed along with a **new pretreatment option for unbleached pulp kappa number reduction.**

Introduction

India is the second largest wheat producer country in the world after China and accounts for about 12% to the global wheat production. Nearly 80 million tons of wheat is produced in the country. Uttar Pradesh with a share of 33.7% is the major contributor, followed by Punjab (21%), Haryana (13%) and Madhya Pradesh (9.6%). There are 150 paper mills based on agro residues in the country using bagasse & straws as major raw materials in proportion of pulp and paper. These mills use 50% bagasse and 50% wheat/rice straw and other annual grasses & contribute to about 22% of the total production which is 2.2 million tons/ annum. (Nearly 2.5 tons (O.D) of bagasse or 2.3 tons (O.D) of wheat straw are needed to produce one ton of paper.) (1)

Along with wheat an equivalent amount of straw is produced. Thus the total production of wheat straw in the country is around 80 million tons/annum. All the wheat straw is not fully recovered by the farmers e.g., in case of combine harvester more than 25% straw is left in the field as it cuts the plant from a certain height. The left over wheat straw is burnt in the field causing air pollution.

More than 75% of wheat straw collected from fields is utilised as cattle feed. Major states where paper mills use wheat straw as fibrous raw material for paper making are Uttar Pradesh, Punjab and Uttrakhand. Kashipur and Muzaffarnagar have cluster of small paper mills which consume more than 0.6 million tons of wheat straw. The following table shows the gross & net availability of various non-wood raw materials in India.

Availability of Agro based raw materials (million tons/annum)

S. No.	Particulars	Bagasse	Wheat Straw	Rice Straw	Jute/ Kenaf	Total
1	Gross Availability	53.0	115	58.0	3.0	242.9
2	Net Availability	5.2	2.6	16.0	0.5	21.8

India has abundant resources of various nonwood fibers. Diminishing availability of hardwood and increasing prices, have forced major pulp producers to switch over to agro based raw materials like bagasse, wheat straw, rice straw etc. Their contribution is 30-35% of paper production in India. These nonwood fibers are structurally open, loose, annual and renewable in nature and also contains low lignin levels. Therefore straight soda pulping is usually the preferred delignification process for these fibers. (1)

Maximizing the capital effectiveness of pulp and paper operations while maintaining environmental compliance is one of the highest priorities for the industry. A logical way to achieve this goal is improve the ability of our pulping and bleaching operations to deliver high strength, better delignification, and higher pulp yield without introducing further capital costs.

Bleaching of wheat straw pulp in Indian agrobased paper mills are either using CEpH/ CEpHH sequence or following DEpD sequence. The brightness gain in first case is 82-84% and around 85% ISO in later stage respectively. The higher bleachability for achieving higher brightness depends on post digester pulp treatment. Oxygen delignification is an attractive technology to complement pulping operations because of its ability to effectively reduce the kappa number while

maintaining pulp strength, reduction in shives, and address to environmental regulations. It has a prominent place in pulping and bleaching operations worldwide. The oxygen based delignification of nonwood annual fibers has reached its recognition in industry in many developing countries. The same is yet to gain importance in Indian scenario. The main restraints are probably the non availability of optimum process conditions for diverse nature of Indian species.

Therefore it is an imperative necessity to capitalize the advantage of oxygen delignification in Indian medium sized agro based mills. Though oxygen delignification before bleaching is yet to be practiced in Indian Mills at large scale, the same has already been started in the extraction stage of bleaching as reinforcing delignification agents.

To make oxygen delignification technology more viable, two stage oxygen delignification technology comes in practice, which is well established for wood based mills now.. The impact of two stage oxygen delignification technology on pulp yield, kappa number reduction , impact on viscosity etc. is also compared with single stage oxygen delignification (2-8)

In the present communications factors which affects bleachability of wheat straw pulp are discussed. The two stage ODL for mix agro residual raw materials followed by ECF bleaching is presented here. The findings of a new and efficient pretreatment technique for pulp kappa number reduction is also the part of this paper.

Result and Discussion

1. Low lignin content and low kappa number

Agro based raw materials generally have low lignin content than wood. The lower lignin content results in a more easily pulped material, with low h factor and chemical demand. The unbleached pulp kappa number is also lower than wood. The continuous pandya type digester results even lower pulp kappa number i.e 12-15. The open structured raw material has a more accessible cell wall structure that is why penetration of pulping chemicals in straw proceeds more readily. The results of chemical analysis of wheat straw and bagasse are depicted in table 1.

Pulping of raw material

Table 1
Proximate chemical analysis of Wheat straw, Bagasse and Sarkanda

Properties	Unit	Wheat straw (UP)	Wheat straw (Punjab)	Bagasse
Ash	%	8.1	5.7	5.7
Cold water solubility	%	11.1	5.4	6.4
Hot water solubility	%	16.7	9.6	12.2
N/10 NaOH solubility	%	41.8	36.1	38.2
Alcohol benzene solubility	%	6.0	2.8	4.1
Acid insoluble Lignin	%	15.7	19.9	19.7
Holocellulose	%	66.6	74.0	70.0

The results of pulping experiments are given in table 2. The unbleached pulp kappa number 12-15 can be achieved with substantial strength i.e intrinsic viscosity.

Table 2.
Unbleached pulp characteristics wheat straw and bagasse

Parameters	Wheat straw	Wheat straw	Bagasse
Cooking process	Soda AQ	Soda AQ	kraft
Cooking chemical NaOH /Na_2O %	16	15	15
Unbleached pulp kappa	12	15	17
Unbleached pulp brightness, %	35	33	36
Unbleached pulp viscosity cm^3/g	920	863	1020

2. Presence of high silica content

The major disadvantage of straws is presence of higher silica content. The wet cleaning of wheat straw removes substantial part of adhered silica. The Ash content in wheat straw is 4-8% and silica 4-6% which get dissolved in spent liquor when straw goes through alkaline pulping. It creates severe operating problems in soda recovery. Now a days a number of straw based Indian Pulp and Paper Mills are practicing non conventional recovery for silica rich black liquor of straw. The chemical recovered in the form of sodium carbonate is further utilized by various industries.

3. Cleanliness of pulp

Table 3
The distribution as per mass percent

	Percent
Internodes	68.5
Leaves sheathes	20.3
Leaves blades	5.5
Nodes and fines	4.2
Grains and Debris	1.5

The structure of wheat straw plant contains internodes, leaves-sheaths, leaves blades, nodes and fines grain and debris(3,4). The distribution as per mass percent is depicted in table given below.(2)

The inter nodes has higher lignin content than other parts, while silica content is higher in leaves. The node portion of straw has stronger fiber bundles and differ in pulping and bleach chemical demand. After washings these unbleached part reflects as dirt size varying 0.1-0.3 mm^2. (2-5). The nodes are responsible for shives and dirt content in wheat straw pulp. The harvesting technique of wheat straw also has impact on straw quality.

4. Hexenuronic acid

The hexenuronic acid are the intermediate compounds which are formed during bleaching of pulp. The xylose

sugars are main components responsible for formation of hexenuronic acid. Hexenuronic acids contributes in enhancing the pulp kappa number by 2-5 units. The analysis of wheat strw reveals that it has higher pentosan content (20%) than eucalyptus (11%), which is indication of pentose sugar i.e xylose. Hexenuronic acids also cause the brightness ceiling effect to achieve high brightness. Acid pretreatment of pulp before bleaching helps in removal of hexenuronic acid as well as achieving high brightness.(6)

5. Response of Oxygen Delignification (ODL)

The use of ODL technology for wheat straw pulp or mixed agro residue pulp at mill scale is in single digit. In contrast to ODL response at laboratory (~60% kappa number reduction) the same is poor at mill scale around 30% or less). The reasons can be pulp quality i.e poor washing, high carryover to variation in process condition. To make ODL technology more effective in terms of kappa number reduction, yield persevence, the concept of two stages oxygen treatment has come in practice. In two sequential stages of oxygen pretreatment , without interstage washing the unbleached pulp kappa number reduces more than 50% at commercial scale.

ODL response of wheat straw pulp kappa number reduction in single stage ODL at laboratory is ~60% , better than wood. Two stage ODL results in further better kappa number reduction. ODL efficiency of wheat straw pulp is not matched when compared with mill ODL response. At mill scale the ODL efficiency is hardly 30-35%. Many factors are there which affects on ODL efficiency like chemical carry over, low ODL pressure, poor Brown stock washing etc. The results are shown below.

1. Analysis of pulp before oxygen treatment

The pulp initial properties were determined and are given in table 1 below.

2. Pulp characterization after oxygen treatment:

The results of pulp characterization are shown in table 2

Effect of alkali concentration on various parameters:

Addition of alkali during oxygen delignification increases oxygen solubility in aqueous medium and promote delignification. It result in pulp kappa number reduction and simultaneously reduction in pulp yield after oxygen delignification.fig 1, fig 2 and fig 3 .

Table 5
Result of pulp sample (as Such)

S.No.	Parameters	Unit	Result
1.	Brightness	%(ISO)	35.1
2.	Viscosity	cc/gm	847
3.	Kappa Number		12.9
4.	Soda Loss	kg/Ton	15.0
5.	Ash content	%	3.2

Table 6
Oxygen Pretreatment of wheat straw Pulp

S. No.	Parameters	Single stage ODL	Single stage ODL	Single stage ODL	Single stage ODL	Single stage ODL
1.	**Initial Pulp kappa number**	12.9	12.9	12.9	12.9	12.9
2.	**Initial Pulp viscosity**	847	847	847	847	847
3.	**Initial Pulp brightness,% ISO**	35.1	35.1	35.1	35.1	35.1
	Oxygen Pretreatment					
4.	Alkali Charge as NaOH, Kg/ton	10	15	15(10+5)	20 (15+5)	25 (15+10)
5.	Initial pH	10.0	10.0	11.5	11.9	12.4
6.	Kappa Number	9.97	8.5	6.94	6.38	5.92
7.	Reduction in Kappa Number	23.9	34.35	47.0	51.3	54.8
8.	Brightness, % ISO	53.4	54.9	56.2	58.5	60.3
9.	Brightness gain, %	18.4	21.7	24.6	30.4	33.7
10.	Viscosity, cm^3/g	830	830	826	817	807
11.	% Reduction in Viscosity cm^3/g	2.0	2.0	2.5	3.54	4.72
12.	Yield,%	97.2	97.0	96.1	95.8	94.5
13.	Yield Loss ,%	2.8	3.0	3.9	4.2	5.2

6. ECF Bleaching and Brightness ceiling

The straw pulp is known for low brightness during conventional bleaching. CEpHH bleaching of straw pulp i.e. 82-83% ISO. The demand of high brightness >85%ISO can be achieved if bleach plant introducing pulp kappa number could

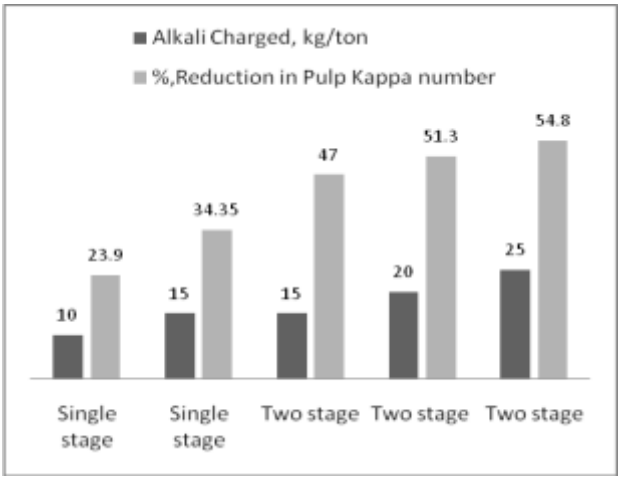

Fig 1. Effect of Alkali Charges on Pulp Kappa Number Reduction During ODL Treatment

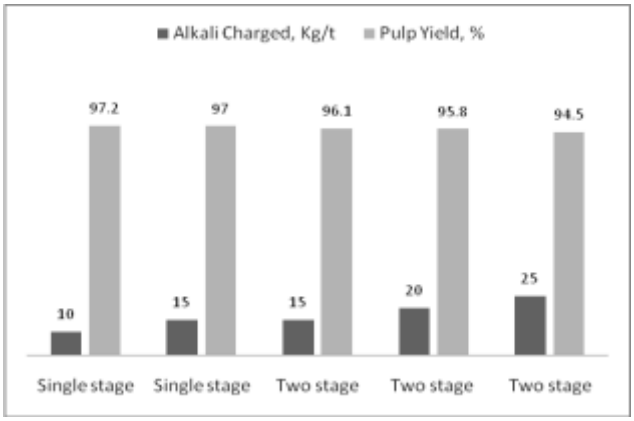

Fig 2. Effect of Alkali Charges on Pulp Yield After ODL Treatment

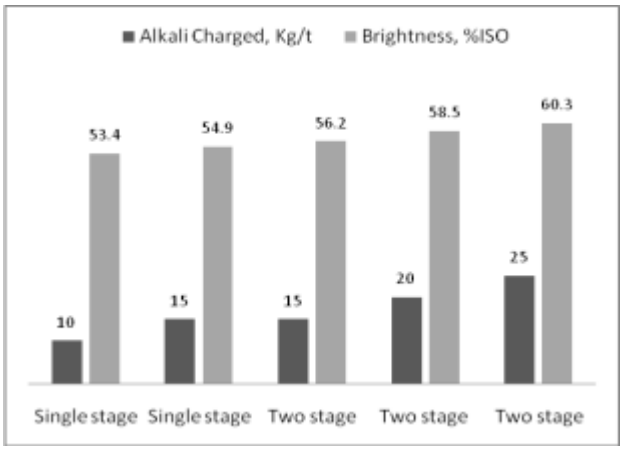

Fig 3. Brightness After ODL Treatment

be reduced substantially around 5-7. This also increase the unbleached pulp brightness which helps in getting higher brightness after DEpD sequence. The acid pretreatment of unbleached pulp inhibit the brightness ceiling effect by removing the hexenuronic acids.

DEpD Bleaching of ODL Pulp

Wheat straw pulp after ODL (oxygen delignification) was subjected to DEpD bleaching. The effect of pulp kappa number reduction has been observed on chlorine dioxide demand as well as final pulp brightness. The results of bleaching are shown in table below.

Physical strength Properties of Bleached Wheat Straw Pulp

Table 8
Physical Strength Properties Of Wheat Straw Unbleached and Oxygen Treated Pulp

	PFI (rev)	Freenes s ml, CSF	Apparent Density g/ cm^3	Burst Index KPam^2/ g	Tensile Index Nm/g	Tear Index mNm^2/ g	Fold Kohler Molin(log)	Porosity Bendtsen (ml/min.)
Unbleached	0	335	0.75	4.70	85.5	4.7	2.28	61.1
	500	**230**	**0.81**	**5.2**	**93**	**4.8**	**2.49**	**12.3**
DEpD Bleached	0	365	0.81	4.5	77.0	4.70	2.55	43.8
	500	**250**	**0.82**	**5.2**	**84.0**	**4.60**	**2.79**	**17.5**
O DEpD Bleached	0	355	0.79	4.20	68.0	4.80	2.45	44.2
	500	**240**	**0.85**	**5.10**	**80.0**	**4.70**	**2.64**	**11.3**

A New alternate technology for kappa number reduction

A new pretreatment method of wheat straw pulp which is substitute of ODL technology has been developed by CPPRI. CPPRI has worked on a new technique of post digester pulp treatment technology. The technology does not require costlier tec hnology set up and can be adopted by some retrofications in fiber line.

Table 7
DEpD Bleaching of Wheat Straw Pulp

S.No.	Parameters	Single stage ODL	Single stage ODL	Two stage ODL	Two stage ODL	Two stage ODL
1.	Initial Pulp kappa number	13.0	13.0	13.0	13.0	13.0
2.	Pulp kappa number after ODL	9.95	8.3	6.84	6.28	5.90
3.	Chlorination stage factor	0.25	0.25	0.2	0.2	0.2
4.	I stage Chlorine dioxide applied,% as avl chlorine	2.5	2.12	1.4	1.28	1.20
5	Alkali applied as NaOH, %	2.0	2.0	1.5	1.5	1.5
6.	II stage Chlorine Dioxide applied as D,%	0.75	0.75	0.5	0.5	0.5
7.	Brightness % ISO	85.1	85.5	86.5	86.6	86.6
8.	Viscosity after bleaching, cc/g	670	665	675	640	612

The laboratory scale studies on wheat straw pulp were carried out repetitively. The results are shown below in table 5. The study was further scaled up to pilot scale on 350 kg of pulp and finding were even better than laboratory trial.

EXPERIMENTAL

Pulping Experiment:

Optimization of soda/ Kraft pulping chemical requirement to obtain different kappa numbers was carried out with different chemical dosage to attain a desired kappa number.

Experiments were performed in a series digester consisting of six bombs each of 2.5-liter capacity, rotating in an electrically heated polyethylene glycol bath. At the end of the cooking time, the bombs were removed and quenched in the water tank to cool down and the cooked mass from each bomb was taken for washing. Washing was carried out with hot water till the cooked mass was free from spent liquor. After through washing, the unscreened pulp yield was determined and the pulp was screened in laboratory 'Somerville' screens by using mesh of 0.25 mm slot width. Kappa number of the screened pulp was determined as per the TAPPI

S.No	Parameters	Unbleached pulp	ODL	CPT
1	Pulp kappa number	12	7.0	6.0
2	Reduction in kappa number,%	--	41.6	50
3	Pulp Yield,%	--	95	96
4	Pulp brightness% ISO	32	45	55
5	Pulp viscosity, cc/g	920	870	920

ODL- Oxygen delignification
CPT- CPPRI Pretreatment Technology

standard procedure T-236-OS-76.

Determination of pulp kappa number, brightness and viscosity:

As per standard procedures

Oxygen pre-treatment of pulp:

Oxygen treatment of pulp samples was carried out in oxygen reactor. The two stage oxygen treatment of pulp was carried out as per the conditions followed at commercial scale and mentioned below. The two stage treatment was carried out in the same batch, without intermittent washing of the pulp. 100 g of pulp sample was treated with the desired dose of alkali and heated to oxygen treatment temperature i.e 95 ^{o}C. After attaining the temperature oxygen was injected in the reactor to 6 bar pressure.

Stage oxygen treatment was given after completion of first stage.

After completion of treatment time the pressure was released and pulp was collected in muslin cloth. The liquor sample taken out and pulp was washed. The pulp kappa number, brightness, viscosity and yield were determined.

Conclusion

Wheat straw is a potential substitute of wood based raw material.

Wet cleaning of wheat straw helps in dirt/dust removal and it helps in getting clean pulp after bleaching.

Conventional bleaching sequence CEpH/CEpHH has limitation of bleaching of wheat straw pulp to high brightness.

Production of high brightness pulp from wheat straw is also possible by modern bleaching sequences.

The lower kappa number before entering into bleach plant also helps in ECF bleaching to high brightness.

Oxygen treated pulp with lower kappa number shows better bleaching response. Hence two stage ODL treated pulp has better bleaching response than single stage ODL

Brightness of final pulp is also better in case of two stage ODL treated pulp after DEpD bleaching.

The gains in terms of kappa number drop, brightness improvement are better in case of two stage though there is difference in alkali dose too is there, which is high in case of two stage treatment.

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ODL Treatment conditions

S.No.	Condition	Units	Single stage ODL	Two stage ODL	Two stage ODL	Single stage ODL
1	NaOH Charge	Kg/ton	10	18	22	26
2	Oxygen Charge	Kg/ton	18	5+13	5+13	5+13
3	Temperature	^{0}C	90	90+95	90+95	90+95
4	Pressure	Bar	6	6+6	6+6	6+6
5	Time	Min	60	6+60	6+60	6+60
6	Consistency	%	10	10	10	10