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Increase in brightness ceiling of agro residue pulps in cost effective manner specifically for wheat straw

Submitted to

Indian Agro & Recycled Paper Mills Association

by

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Particulars of the Project

1.	Project No.	:	ACIRD/IARPMA/0214-24/159
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3.	a. Project Team (ACIRD)	:	N. K. Bhardwaj (PI) Sandeep Tripathi (Co-PI) Ankush Gupta Deepak Kumar Izhar Alam Nipun Dogra Nirmal Sharma O. P. Mishra R. Vardhan
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4.	Sponsoring Agency	:	Indian Agro & Recycled Paper Mills Association
5.	Implementing Agency		Avantha Centre for Industrial Research and Development Central Pulp and Paper Research Institute
6.	Participating Agencies	:	Shreyans Industries Ltd. (Unit: Shree Rishabh Papers, Banah, Punjab)
7.	Date of Start	:	February 2014
8.	Duration of the Project	:	24 +12 months

Contents

Nomenclature

AA	:	Active alkali
AQ	:	Anthraquinone
COD	:	Chemical oxygen demand
CREP	:	Corporate responsibility for environmental protection
ECF	:	Elemental chlorine free
EDTA	:	Ethylene diamine tetra acetic acid
HEDP	:	Hydroxy ethylidene diphosphonic acid
IARPMA	:	Indian Agro & Recycled Paper Mills Association
ODL	:	Oxygen delignification
PAA	:	Per acetic acid
PC	:	Post colour
RAA	:	Residual active alkali
°SR	:	Schopper Riegler
TAED	:	Tetra acetyl ethylene diamine
TCF	:	Total chlorine free
TDS	:	Total dissolved solids
TS	:	Total solids
TSS	:	Total suspended solids

1. EXECUTIVE SUMMARY

Indian Agro & Recycled Paper Mills Association (IARPMA) sponsored this project to carryout research on Indian agro based raw materials specifically on wheat straw to bleach them to a brightness level of +85% ISO in cost effective manner. Financial support for this project was granted by CESS Committee, Development Council for Pulp, Paper and Allied Industry, Department of Industrial Policy & Promotion, Ministry of Commerce & Industry, Govt. of India. Objectives of the project were:

- To find out reasons behind low brightness development in agro pulps
- To study the effect of different bleaching chemicals and modern bleaching processes on agro pulps
- To suggest best process for bleaching of agro pulps to bleach +85% brightness
- Demonstration of results in the plant scale

Under this project the lab scale studies were carried out at Avantha Centre for Industrial Research and Development (ACIRD), Yamunanagar. Results of the laboratory scale studies revealed that:

- With the pre-bleaching acid treatment of pulp, final brightness of pulp achieved was 86.5% (Gain in brightness by 1.6-2.0 units).
- With the post-bleaching acid treatment of pulp or in-situ acid treatment of pulp, final brightness of pulp achieved was 86.0% (Gain in brightness by 1.2-1.5 units).
- Hydrogen peroxide (H_2O_2) pre-treatment of unbleached wheat straw pulp improved final bleached pulp brightness by 1.7-2.1 units with substantial reduction in chlorine based bleaching chemicals and pollutants generated during bleaching.
- With the replacement of 20% Cl_2 with ClO_2 in chlorination stage of bleaching, final brightness of pulp achieved was 86.3% (Gain in brightness by 1.5-1.8 units).
- With the addition of last peroxide stage in bleaching sequence, final brightness of pulp achieved was 87.4% (Gain in brightness by 2.6-2.9 units).

- With the enzymatic pre-bleaching treatment of pulp, final brightness of pulp achieved was 85.2% (Gain in brightness by 0.7-1.0 unit).
- Use of hydrogen peroxide activator in E_{OP} stage of bleaching sequence improved the final bleached pulp brightness by 1.1 units and whiteness by 1.5 units while using similar bleaching chemicals.

In a meeting conducted by IARPMA at Shreyans Papers Limited on July 5, 2016, it was decided to carry out lab study on two selected processes using mill pulp prior to conducting plant trial on any one of the process

- Hydrogen peroxide pre-bleaching treatment of pulp:
- Use of hydrogen peroxide activator in E_{OP} stage of bleaching

Plant scale study carried out with the addition of hydrogen peroxide stabilizer in E_{OP} stage at Shreyans Paper Mills Ltd. (Unit: Shree Rishabh Papers, Banah, Punjab) resulted in the following:

- Average final pulp brightness improved by 1.1 units to 83.6% from a control of 82.5%. During the trial a few values also crossed the brightness ceiling of 85%, whereas during control run none of the value obtained was above 85% brightness.
- During trial average final pulp whiteness obtained was 69.9 indicating the whiteness improvement by 3.2 units.
- Similarly with the addition of hydrogen peroxide stabilizer in E_{OP} stage, average final pulp yellowness reduced to 7.6 indicating the reduction in yellowness of 1.1 point.
- As expected viscosity of final bleached pulp was improved marginally to 5.6 cP compared to 5.2 cP obtained during control.
- Physical strength properties of pulp, specifically tear index and breaking length, obtained before and during trial period were comparable.
- There was marginal improvement in the morphological properties, specifically fiber length and coarseness of the pulp with the use of hydrogen peroxide stabilizer in E_{OP} stage of bleaching.

2. INTRODUCTION

Production of pulp and paper in India is divided in three segments i.e. wood based, agro residue based and recycled fiber based paper mills. Recycled fiber based paper mills are producing low cost papers of relatively inferior quality as compared to wood and agro residue based mills. On the other hand agro residue based mills are also producing low cost papers of relatively inferior quality as compared to wood based mills.

One of the main reasons behind low quality paper of agro residue based mills is low brightness of pulp. Agro residue pulps, except bagasse are very difficult to bleach to a brightness level of +85% ISO. Agro residue based mills are looking for processes which will be able to produce pulp of +85% ISO brightness.

Indian Agro & Recycled Paper Mills Association (IARPMA) has sponsored this project to carryout research on Indian agro based raw materials specifically on wheat straw to bleach them to a brightness level of +85% ISO in cost effective manner.

Financial support for this project was granted by CESS Committee, Development Council for Pulp, Paper and Allied Industry, Department of Industrial Policy & Promotion, Ministry of Commerce & Industry, Govt. of India.

Under this project the lab scale studies on mixed agro pulp and wheat straw were conducted at Avantha Centre for industrial Research and Development (ACIRD), Yamunanagar on following areas:

- Find out reasons behind low brightness development in wheat straw pulp
- Effect of different treatments to the raw material on pulp brightness
- Effect of using different additives and modifications during pulping
- Effect of different pre and post bleaching treatments, modifications during bleaching to increase brightness ceiling

Validation studies on selected processes for bleaching of agro pulps were conducted at Central Pulp & paper Research Institute (CPPRI), Saharanpur.

Pre-plant trial studies using mill pulp and the bleaching conditions were carried out at ACIRD and CPPRI.

Based on the encouraging lab scale results obtained at Avantha Centre for Industrial Research & Development (ACIRD) using (i) hydrogen peroxide pre-bleaching treatment of pulp and (ii) hydrogen peroxide activator (DSOST) in E_{OP} stage of bleaching, it was proposed to explore the suitability of any one processes on plant scale.

Plant scale trial using hydrogen peroxide activator in E_{OP} stage of bleaching for improving brightness and whiteness was carried out at Shreyans Industries Ltd. (Unit: Shree Rishabh Papers) at Banah, Nawanshahr, Punjab.

3. LITERATURE REVIEW

Agro residues have been utilized by pulp and paper industry since long. Bleaching of agro residue pulp is comparatively tough than the bleaching of wood based pulps. Even use of oxygen alone could not be able to improve brightness ceiling of the straw pulps due to the formation of oxygen radicals made from reaction of transition metals present in the pulp and oxygen (Pasi et al., 2002). Several studies have been carried out on total chlorine free (TCF) bleaching of wheat straw pulp using ozone and xylanase enzyme. Studies showed suitability of these processes on wheat straw pulp to limited extent. None of the study concluded in production of +85% brightness of final bleached pulp produced from wheat straw pulp (Roncero et al., 2003; Singh et al., 2011). Different conventional sequences and elemental chlorine free (ECF) short sequence bleaching have been studied comparatively. Chlorine dioxide based bleaching sequence was found the best in term of brightness development for wheat straw pulp (Ghose, 2005). Few studies have been conducted recently to enhance the brightness of wheat straw by eliminating chromophoric compounds responsible for limiting the brightness development, use of peroxide bleach booster chemicals and enzymes (Pan et al., 2005; Liu et al., 2010; Zheng et al., 2012).

The TCF bleaching of pulp using potassium permanganate in intermediate bleaching stage between oxygen and peroxide was explored by Chen 1999. They worked out OMnP bleaching sequence for soda-AQ pulp and illustrated that chelation prior to peroxide treatment is helpful to increase brightness to 80 % ISO (Chen et al., 1999). Using four different TCF bleaching sequences wheat straw pulp was reported to be bleached up to a whiteness level 80-83% (Wang et al., 2003). Another study carried out by pulping wheat straw at low lignin content followed by bleaching with the TCF bleaching sequences AQ(PN)P and QZEYP achieved brightness greater than 80%. Authors also reported better viscosity of bleached pulp and improved brightness stability compared to chlorinated bleached pulp using CEH sequence (Cao et al., 2005). Oxidative-reductive-oxidative bleaching sequence for wheat straw kraft pulp was reported to achieve higher brightness with more selectivity in terms of lignin removal and less cellulose degradation (Tong et al., 2006). Brightness values of greater than

80 % ISO using O/Q/OP sequence for wheat straw soda cooked pulp were achieved by hydrogen peroxide treatment in alkaline media with different chemical additives. The addition of 2.0 % sodium silicate was reported to be quite effective for both to reduce the peroxide bleach consumption and to achieve the brightness of 80 % ISO (Hedjazi et al., 2007). The TCF bleaching of soda-AQ wheat straw pulp using O_PQPo sequence was reported to achieve bleached pulp brightness of 80.2 % ISO while using chelation and peroxide treatment (Niu et al., 2007).

Different conventional sequences and ECF short sequence bleaching have been studied for comparison. None of the TCF bleaching sequence reported brightness greater than 80% from wheat straw pulp. Chlorine dioxide based bleaching sequence was found the best in terms of brightness development for wheat straw pulp (Ghose, 2005). The ECF bleaching sequence was reported to achieve improved brightness for bleaching the wheat straw pulp applying 3% chlorine dioxide (2% in D_0 stage and 1% in D_1 stage) in $D_0E_PD_1$ bleaching sequence (Ahmad et.al 2014). Few studies have been conducted recently to enhance the brightness of wheat straw pulp by eliminating chromophoric compounds responsible for limiting the brightness development, use of peroxide bleach booster chemicals and enzymes (Pan et al., 2005; Liu et al., 2010; Zheng et al., 2012).

For enhancing the brightness of different raw material pulps several novel chemicals and process modifications are being studied by various researchers in laboratory as well as plant scale level. Use of enzyme in pre bleaching stage, acid pre treatment followed by alkaline extraction, tetra acetyl ethylene diamine (TAED), per acetic acid (PAA), hydrogen peroxide stabilizer have shown the potential to increase brightness of pulp to some extent.

Tetra acetyl ethylene diamine (TAED)

Hydrogen peroxide is a very effective bleaching chemical due to its high oxidation potential. It reduces the demand of other bleaching chemicals specifically chlorine dioxide and helps to boost the final brightness. Addition of an activator to the peroxide stage increases its efficiency further. Addition of TAED to peroxide stage generates a more powerful oxidative peracetic acid.

Hydrogen peroxide and water react with TAED to form consecutively tri-acetyl ethylene diamine and di-acetyl ethylene diamine with the release of two molecules of peracetic acid or acetic acid (Turner et al., 2004; Davies and Deary, 1991; Suchy and Argyropoulos, 2002). The compounds with O- or N-bounded acetyl groups have potential to react with the strongly nucleophilic hydroperoxy anion to yield peroxyacetic acid (Hofmann 1992). Peracetic acid and peroxyacetic acids are stronger bleaching agents than hydrogen peroxide due to higher redox potential (Hauthal et al., 1990). Mill trial with Potlatch Corporation, Lewiston, Idaho, USA, evaluated the industrial application of peracetic acid generated by reacting TAED and peroxide. Significant reduction of total chlorine dioxide consumption was achieved (Turner et al., 2004). Several plant scale trials were taken with per acetic acid but it is still not being used commercially due to high cost of manufacturing and handling hazards (Dence and Reeve 1996; Sidharth et al., 2010). These obstacles can be overcome with use of TAED with H_2O_2 due to in-situ generation of peroxyacids. It -was also reported that with the use of TAED some specific properties of the paper viz. brightness and bulk also got improved (Hsieh et al., 2006). Presently TAED is widely used in detergent and textile industry. It is odorless, colorless, storage stable solid and safe to handle. Reaction products of TAED are non toxic. It is biodegradable and generates ammonia, water, carbon dioxide and nitrate and does not generate ethylene diamine (Tompsett 1994). H_2O_2 / TAED bleaching system was also found more effective to decrease the carbonyl group content than H_2O_2 alone and resulted in higher brightness and whiteness of final bleached pulp (Young Raymond 1998, Zhao et al., 2010)

At ACIRD detailed studies were carried out using TAED during oxygen delignification (ODL) stage, after ODL and during oxidative extraction stages to improve the brightness and whiteness of mixed hardwood bamboo pulp. Study concluded that with the use of TAED along with H_2O_2 in ODL stage one could improve brightness of final bleached pulp by 1.5-1.7% and CIE whiteness by 1.8-1.9 points compared to control. Use of TAED along with H_2O_2 after ODL stage resulted in improved final bleached pulp brightness by 1.9-2.1% and CIE whiteness by 2.2-2.4 points compared to control. Use of TAED in E_{OP} stage also improved final pulp brightness and whiteness by 1.1-1.8% and 1.8-2.0 units, respectively. With the use of TAED in E_{OP} stage, chlorine dioxide dosage in D_1 stage was reduced by 3.0 kg/TP with comparable brightness and improved whiteness of the pulp (Sharma et al., 2013).

Per acetic acid (PAA)

Per acetic acid (PAA) has been evaluated as a delignification or bleaching agent for chemical pulp and textile since early 1950's (Hatch 1993). Bailey and Dence published a research paper describing the use of PAA for both delignification and brightening of chemical pulp (Bailey 1966). Liebergott has reported use of peroxy acids in different stages of pulping and multistage bleaching process for chemical pulps (Liebergott 1994). The brightness and whiteness of fully bleached kraft pulps were efficiently increased with 1-2 kg PAA/tonne pulp. Brightness reversion of bleached pulps as such and during beating was also prevented by use of PAA. Use of PAA in bleaching stages or in the storage tower for bleached pulp increases pulp brightness and bleaching selectivity. The optical properties of fibres are improved and pulp brightness is stabilized when PAA is used in stock preparation or post bleaching (Jakara et al., 1999). In spite of their known delignifying and oxidizing power, poor stability and high chemical cost have been considered as a major disadvantage for their potential use in prebleaching or bleaching applications (Ricketts 1997).

At ACIRD studies were carried out to improve the optical properties of final bleached paper grade and dissolving grade hardwood pulps by treatment with PAA. Study concluded that treatment of bleached mill pulps with PAA at a dose level of 0.5-1.0 kg/TP at ambient temperature and normal plant pulp pH increases the final pulp brightness by 1.0 to 1.5 points and whiteness by 2.0 to 3.5 points. Yellowness and the post colour (PC) number are also reduced and pulp viscosity is not affected. Treatment time of 2-3 hours is found to be sufficient. Improvement in brightness and whiteness is sustained when PAA treated pulp is used for the production of high brightness paper (+96% ISO). The brightness increases by 0.7 and 1.0 points and CIE whiteness increases by 1.6 and 2.2 points when the dissolving grade pulp is treated with PAA at a dose level of 0.5 and 1.0 kg/TP, respectively at ambient temperature for 3 hours. Addition of PAA at a dose level of 0.5-1.0kg/TP in E_{OP} and dioxide stage does not result in much improvement in final brightness and whiteness. About 1.0 and 3.0 kg of

ClO_2 can be replaced by treatment with PAA at a dose level of 1.0 and 1.5 kg/TP, respectively. Use of PAA in D stage can partially replace ClO_2 where ClO_2 is a limitation (Tripathi et al., 2007).

Hydrogen peroxide stabilizer

Various technologies and bleaching chemicals viz. oxygen, ozone and hydrogen peroxide are being used by the paper mills to improve optical properties of pulp. The use of hydrogen peroxide and oxygen in the extraction stage are well known technologies (Walsh, 1991; Sjodin, 1994 and Roy, 1995). The function of alkaline extraction is to remove soluble lignin which has been oxidized in previous bleaching stages and reactivate residual lignin for the following oxidative stage. After pulp oxidation with chlorine dioxide, a significant fraction of lignin remains in the pulp because of lignin's limited solubility at acidic pH. Therefore the extraction stage is useful after an oxidation stage for better dissolution of alkali. There is always scope for increasing the efficiency of the extraction stage. Some hydrogen peroxide activators are used to increase the efficiency of peroxide, but with their use bleaching costs increase significantly. The alkaline extraction stage requires careful observation and control of various parameters. By increasing the efficiency of alkaline extraction, pulp with better final brightness or reduced consumption of other bleaching chemicals can be produced. In addition, pulp with high brightness stability can be produced with a low level of chlorinated compounds discharged to effluent. To push the efficiency of peroxide bleaching further, high temperature peroxide bleaching is applied. Efficiency of peroxide bleaching can be improved by accelerating the reactions of peroxide with pulp by increasing the temperature (Clarke and Clarke, 1999). At high temperature decomposition of H_2O_2 may occur; the decomposition reactions are initiated by metal ions that enter with furnish and water used in the process. Decomposition reactions due to metal ions can be minimized by implementing an efficient metal removal treatment. However, thermally induced decomposition of peroxide occurring at temperatures greater than 110°C cannot be avoided. As the temperature is raised beyond the range of 110-120°C, the peroxide becomes unstable and decomposes spontaneously (Rajan, 1998). To improve oxidative alkaline extraction performance of hardwood and softwood kraft pulps, efficacy of sodium carbonate–sodium hydroxide mixtures and oxidized white liquor was explored during multistage bleaching (Parthasarathy, 1997). Earlier studies conducted on plant scale showed a reduction in chlorine dioxide usage by 8-10% with the use of bleaching enhancement additives while maintaining final target brightness and pulp strength, when used in elemental chlorine free (ECF) sequences (Brogdon, 2004). To enhance the efficacy of the oxidative extraction stage, different process variables and chemicals were studied and it was concluded that the use of hydrogen peroxide in the extraction stage is a must for its cost effectiveness (Levis, 2009).

Currently, mills are using a higher dosage of hydrogen peroxide to improve their pulp quality, reduce pollution load and reduce chlorine dioxide consumption as the price of chlorate has gone up tremendously. The application of hydrogen peroxide stabilizers is more relevant for pulp and paper mills using higher dosages of hydrogen peroxide. Hydrogen peroxide is the most widely used oxidative bleaching agent in the pulp and paper industry. Its environmental impacts are also minimal as it decomposes to form oxygen and water. There are two main reactions in hydrogen peroxide bleaching. The first leads to a brightness increase while the second reaction leads to hydrogen peroxide decomposition (Anderson and Amini, 1996). The principal reactive species in peroxide bleaching is the perhydroxyl ion (HOO-) formed by addition of alkali to hydrogen peroxide. The perhydroxyl anion is a strong nucleophile intermediate and under alkaline conditions is mainly responsible for the oxidation of chromophores in lignin (Dence and Reeve, 1996). The hydroxyl radical and superoxide radical are also generated during the reaction. The hydroxyl radical is an exceptionally strong electrophile and oxidant, capable of reacting with both lignin and carbohydrates. The superoxide radical is a strong nucleophile. Delignification with hydrogen peroxide is the result of the action of the hydroxyl radical, the hydroperoxy radical and the superoxide radicals (Reeves et al., 1995 and Suss et al., 1996).

Lab scale and plant scale studies were carried out at ACIRD to improve the extraction stage efficiency by optimizing treatment conditions, chemical dosage, using hydrogen peroxide stabilizer on mixed hardwood pulp. Study showed following benefits in lab as well as plant scale:

Lab scale studies

- With the modification in the extraction stage conditions final bleached pulp brightness improved by 1.3-3.4 units and whiteness improved by 2.5-3.6 units.
- Use of hydrogen peroxide stabiliser in the extraction stage of pulp bleaching improved pulp brightness by 0.6-1.0 units and whiteness by 1.3-1.4 units.
- While using hydrogen peroxide stabiliser in the extraction stage of bleaching of rayon grade pulp, there is potential for saving of 1.0 kg hydrogen peroxide per tonne of the pulp to achieve the similar final pulp brightness. With the use of same dose of H_2O_2, the brightness and whiteness of final bleached pulp were improved by 0.6 and 1.4 units, respectively.

Plant scale studies

- During the plant scale trial, using hydrogen peroxide stabiliser in E_{OP} stage of bleaching, the brightness variation was reduced substantially, compared to control run as only 6.0% values of final pulp brightness were found below 89% brightness compared to the 27.1% of the same during control run.
- With the use of hydrogen peroxide stabiliser, final pulp brightness and whiteness were improved by 0.7 and 1.3 points, respectively, with improvement in brightness stability of pulp.

Acid treatment followed by alkaline peroxide treatment

The paper Industry in India went through technological changes to increase productivity, improve product quality and meet CREP (Corporate responsibility for environmental protection) norms. But the changes are not as fast as they need to be especially in pulping and bleaching area. Most of the mills are still using conventional batch digester for cooking of raw material, and hence production of a low unbleached pulp kappa number (<15) is not viable. This affects negatively on unbleached pulp yield and strength. Post digester treatment by any method reduces, bleach chemical demand substantially. The bleaching of unbleached pulp of low kappa number results in better bleachability and low effluent load. Some of the large paper mills have adopted oxygen pretreatment technology, but for most of the mills especially agro based mills it is not economical due to various reasons (Tarranikov and Demasher, 2005; Marcelo and Landim, 2005; Hong et al., 2006).

The acid pretreatment of unbleached pulp is discussed in literature for the minimization of soda carryover and better bleaching point of view, but in some recent studies, the elimination of hexanuronic acid (HexA) by acid pretreatment and reduction of bleach chemical demand is discussed. (Henricson, 1997). The unsaturated sugars derived from hemicelluloses undergo alkaline degradation during pulping and form glucuronic acids, also called hexanuronic acids. These compounds readily consume bleaching reagents such as chlorine, chlorine dioxide, ozone, and hydrogen peroxide (Henricson, 1997; Vuorinen et al., 1999).

Analysis of hardwood data indicates that HexA contribute approximately 20-60% of total kappa number for the kraft pulp (Henricson, 1997).

HexA can be eliminated by acid pretreatment in certain conditions, which can reduce bleach chemical requirement of pulp. ECF bleaching studies of birch kraft pulp suggested that an acid hydrolysis stage prior to Do stage could lead to a 50% reduction in bleaching cost. The advantages of acid pretreatment are triple fold (Bajpai et al., 2005; Tenkanen et al., 1999; Vuorinen et al., 1999, Allen and Douek, 1980).

Elimination of hexanuronic acid by converting them into 2- Furoic acid and 5-carboxy-2- furaldehyde, removal of metal ions and pitch content results in low bleach chemical demand, better bleaching response and enhanced brightness ceiling effect (Henricson 1997, Bajpai et al., 2005).

Laboratory scale study was carried out at CPPRI with acid pretreatment followed by alkaline peroxide extraction of pulp (AALP) of indigenous non-wood raw materials viz bagasse, wheat straw and bamboo. Study concluded that the AALP pretreatment of unbleached pulp of non wood raw materials resulted in quite appreciable drop (30-42%) in kappa number of pulps. The maximum drop in kappa number was observed with bagasse (42%) followed by wheat straw (36%) and bamboo (30%) pulps. This was accompanied by simultaneous gain in brightness of up to 10 units. In addition, the drop in the pulp strength is negligible. It was further observed that the bleaching response of such pulps was better than the oxygen treated pulps and it was possible to achieve higher final pulp brightness. The removal of undesirable metal ions likes iron, calcium, and magnesium, from the pulps was equally significant in acid leaching step. The above studies indicated that the acid followed by alkali and peroxide treatment of pulps from wheat straw, bagasse and bamboo could be a viable route for reducing unbleached kappa number for small mills using these raw materials and achieving high final pulp brightness and could be seen as substitute for oxygen delignification step (Lal et al., 2006).

Pre-bleaching enzyme treatment

Studies carried out on enzyme pre-treatment of pulp showed potential to improve bleachability of pulp. Studies conducted using crude enzymes (containing xylanase and cellulase) during pre-treatment on bleaching of unbleached wheat straw pulp resulted in increase in brightness by about 3% compared to the control under identical bleaching conditions (Jian Zhao et al. 2006). Enzyme and hot water treatment of wheat straw was studied to improve the brightness of the wheat straw pulp (J. Zhao *et. al*., 2004 and S. Mustajoki *et.al.* 2010). Enzymatic treatment with xylanase or cellulase can also improve the stability of brightness of wheat straw pulp (Chen et al., 1990). Bio-bleaching using laccase-mediator enzyme system followed by peroxide treatment increased bleachability of pulp, reduced the consumption of bleaching chemicals and the load of effluents on environment with a negligible loss of pulp strength. Application of enzyme and ozone in a multistage XOAZRP sequence was studied to bleach the wheat straw pulp (Han et al., 2002). Pretreatment of wheat straw pulp using cellulase-free xylanase produced from Bacillus stearothermophilus resulted in 4.75% and 22.31% increase in brightness and whiteness, respectively. Further chlorine dioxide and alkaline bleaching sequences ($C_DED_1D_2$) resulted in 1.76% and 3.63% increase in brightness and whiteness, respectively (Garg et al., 2011).

Treatment of raw material

Wheat straw pre-treated with Ceriporiopsis subvermispora (C.S.) and Phlebia subserialis (P.S.) prior to soda-AQ pulping showed that both fungal pretreatments enhanced delignification and carbohydrate degradation. P.S. pretreatment increased the brightness and decreased the kappa number (Fatehi, et. al 2009). Authors prepared organocell organosolv straw pulp and developed six different bleaching sequences to bleach the pulp. Introduction of an enzymatic stage that was included as intermediate stage increased the effectiveness of final bleaching stage. Authors reported that ligninase and chelation, both treatments, have potential to increase the bleaching capabilities of peroxide (Pekarovicova et al., 1994). Authors also worked with non wood (wheat straw) material by treating the raw material with mildly acidic liquor containing a mixture of formic and acetic acids, and chelating agents in a low temperature, un-pressurized alkaline peroxide bleaching of pulp and achieved the final pulp brightness about 80% with the yield over 50% (Johansson et al., 2000).

4. OBJECTIVES

- To find out reasons behind low brightness development in agro pulps
- To study the effect of different bleaching chemicals and modern bleaching processes on agro pulps
- To suggest best process for bleaching of agro pulps to bleach +85% brightness
- Demonstration of results in the plant scale

5. MATERIALS AND METHODS

5.1. Experimental

Collection of raw material and pulp samples

For the study wheat straw and unbleached pulp samples were collected from agro based paper mills situated in Punjab and Himachal Pradesh. Different chemicals and enzyme samples were procured from chemical suppliers.

Raw material preparation

Wheat straw samples collected from different places were manually depithed and wet cleaned in laboratory simulating the mill conditions followed to clean the wheat straw and other agro raw materials. Cleaned and washed wheat straw was air dried to a moisture level of 15-20%, mixed thoroughly and kept in polythene bag to attain uniform moisture. Moisture content was determined as per standard procedures prior to pulping experiments. Wheat straw samples were analyzed for proximate analysis after grinding in Wiley mill and screening on 40 mesh sieve.

Pulping

Pulping experiments were performed in autoclave digester consisting six bombs of 2.5 l capacity, rotating in an electrically heated air/polyethylene glycol bath. The pulping conditions like time, temperature, bath ratio and were varied to get targeted kappa number pulp.

Bleaching

Oxygen delignification of pulp was carried out in ODL rector (electrically heated pressurized vessel having high sheer mixing facility during the treatment). Other bleaching experiments were performed simulating mill conditions to achieve higher brightness.

Effluent

Filtrate generated from each stages of bleaching was mixed in respective proportion and analysed for different properties.

***Analytical* techniques**

Following standard test methods were followed to analyze different properties of pulp, black liquor and effluent generated during bleaching:

Test	Test method followed
Brightness	Tappi T 525
Cellulose	Updegroff (1969)
Chemical oxygen demand (COD)	IS: 3025 (Part 58)
CIE whiteness	Tappi T 560
Handsheet preparation	Tappi T 205
Hemicelluloses	Deschatelets (1986)
Kappa number	Tappi T 236
Klason lignin	Tappi T 222
Moisture	Tappi T 264
1% NaOH solubility	Tappi T 212
PFI Refining	Tappi T 248
pH	IS: 3025 (Part 11)
Silica	Tappi T 244
Solvent extractives	Tappi T 204
Total dissolve solids	IS: 3025 (Part 16)
Total suspended solids	IS: 3025 (Part 17)
Viscosity	Tappi T 230

5.2. Facilities of ACIRD used


Pulping digesters


Oxygen bleaching reactor

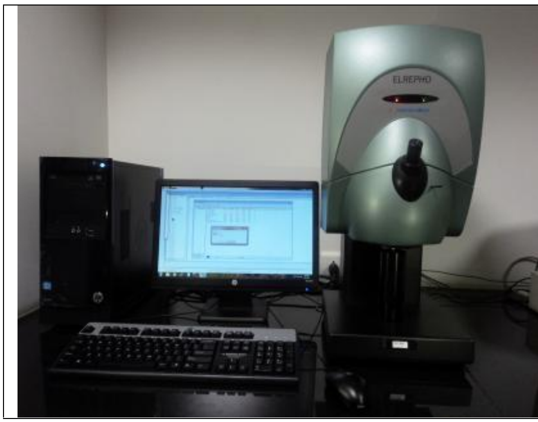
Unbleached pulp analysis


Unbleached and bleached pulp testing lab

AOX analyzer

Image analyzer

Fibre tester



Brightness tester

Papermaking and paper testing lab

6. RESULTS AND DISCUSSIONS

Based on the literature review following pathway was selected to increase brightness ceiling of agro residue pulps in cost effective manner specifically for wheat straw.

Finding out the reasons behind low brightness development

- Effect of hexenuroninc acids
- Effect of metal ions
- Presence of nonfibrous material

Raw material Upgradation

- Effect of washing of wheat straw
- Effect of additives

Modifications during pulping

- Effect of kappa number
- Effect of pulping additives

Modifications during bleaching

- Pre-bleaching treatments of pulp
- During bleaching improvements
- Post-bleaching treatments of pulp

Validation studies on selected process at CPPRI

Pre-plant trial studies at ACIRD

Pre-plant trial studies at CPPRI

Demonstration of results in the plant scale

Studies carried out and results obtained under each segments discussed above are described in detail in the forthcoming sections/chapters of the report.

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Reasons behind low brightness development

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6.1. Reasons behind low brightness development

Based on the literature available on bleaching response of wheat straw pulp different ailments responsible for low brightness development for wheat straw pulp were evaluated.

6.1.1. Effect of hexenuroninc acids (HexA)

Hexenuronic acid (HexA) is formed as a side product during alkaline pulping. The native raw material does not contain any HexA. Some 4-O-methylglucuronic acid groups present in xylan are known to be converted into the corresponding unsaturated acids (HexA) by ß-elimination of methanol during alkaline cooking of wood. Presence of HexA in the pulp results in increased consumption of permanganate in kappa number measurement and thus gives erroneous information about the amount of residual lignin in the pulp. It is considered to cause increased consumption of bleaching chemicals, decrease in brightness, greater brightness reversion and poorer metal removal.

HexA content in different raw materials was analysed. Results showed that wheat straw has second highest HexA content among the raw materials evaluated at ACIRD. Presence of higher amount of HexA content in wheat straw pulp may be the main reason for lower development of brightness during bleaching. Detailed results of HexA content in different raw material pulp are given in Table 6.1.1.

Table 6.1.1: HexA content in different raw material pulps

Raw material	HexA (µmol/g)
Eucalyptus	37.0
Wheat straw	12.7
Rice Straw	10.4
Bagasse	6.2

To determine the effect of pulping conditions on HexA content, wheat straw was cooked using different active alkali (AA) dosage. HexA content in wheat straw pulps of different kappa number wwas determined. Results showed that HexA content increased with the reduction of kappa number of the pulp. Hexenuronic acid content in different kappa number pulps of wheat straw is shown in Figure 6.1.1.

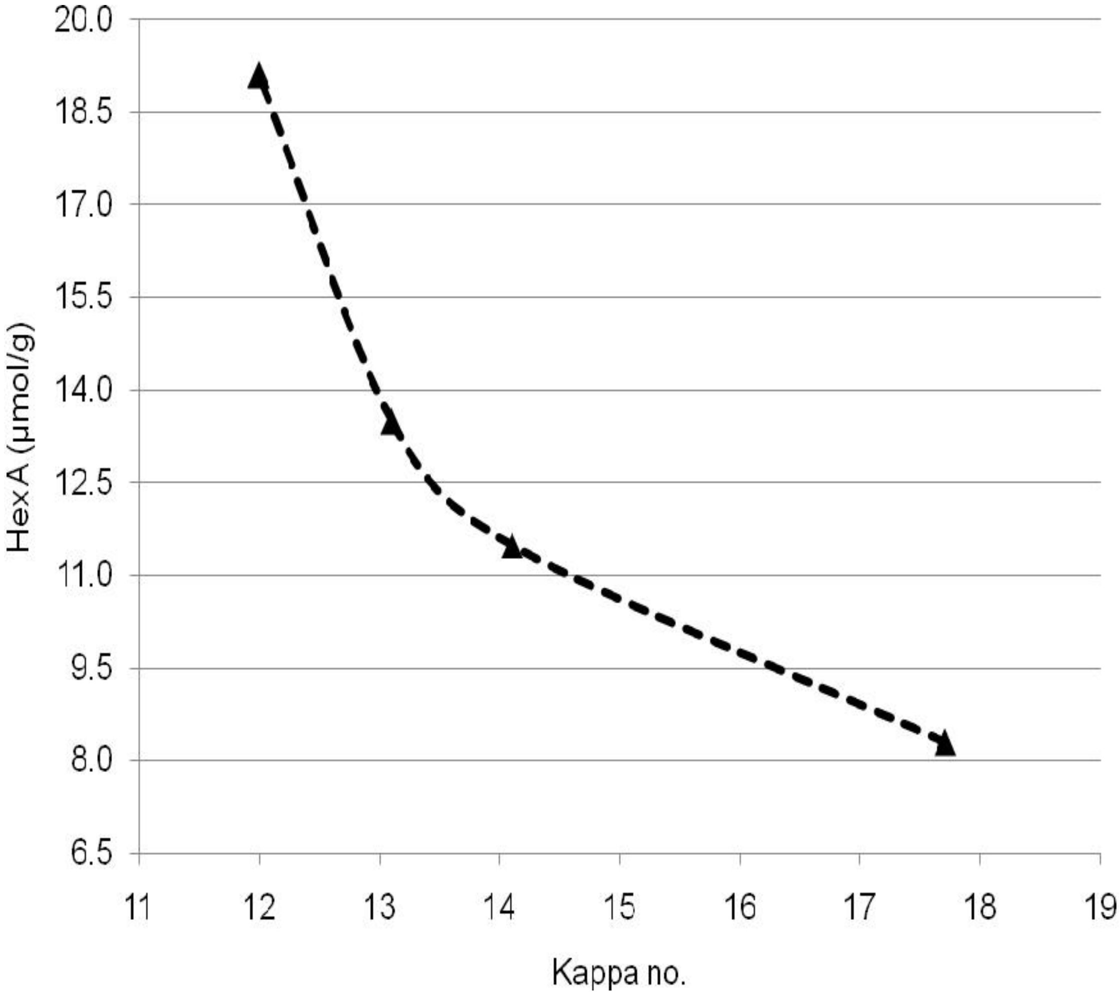

Figure 6.1.1: Hexenuronic acid content in different kappa number pulps

Treatment of wheat straw pulp with hot acid was found most efficient for the removal of hexenuronic acid. Results showed that 70-76% of HexA were removed through an acid pre treatment of unbleached wheat straw pulp having different kappa number. Results of the acid treatment of wheat straw pulps and their effect on removal of HexA are given in Table 6.1.2.

Table 6.1.2: Effect of kappa number and pre-bleaching acid treatment on HexA content in wheat straw pulp

Particulars	Set-1	Set-2	Set-3	Set-4
Unbleached pulp				
Kappa no.	17.7	14.1	13.1	12.0
HexA (μmol/g)	8.3	11.5	13.5	19.1
Acid treatment *(Time - 2h, Temperature - 90 °C, pH - 2)*				
Kappa no. (Eliminating contribution of HexA)	17.2	13.6	12.1	10.6
HexA after acid treatment (μmol/g)	2.1	3.5	3.5	4.6
Decrease in HexA (μmol/g)	6.2	8.0	10.0	14.5
Decrease in Kappa no.	0.5	0.5	1.0	1.40

Effect of HexA content on bleached pulp brightness

Acid pre-treated and untreated unbleached wheat straw pulp of kappa number 15.4 was bleached using $D_0E_{OP}D$ sequence to find out the impact of HexA content on final bleached pulp brightness. Result showed that wheat straw pulp having HexA content 12.0 μmol/g was bleached to a brightness level of 83.6% ISO only whereas pulp containing HexA content 5.0 μmol/g bleached to a brightness level of 85.6% ISO. Detailed results of bleaching of pulps are given in Table 6.1.3.

Table 6.1.3: Effect of HexA content in pulp on bleaching

Particulars	Control	Acid pre-treated
Kappa no.	15.4	14.5
HexA content (μmol/g)	12.0	5.0
D_0 stage *(Consistency - 5%, Time - 45 min, Temperature - 55°C)*		
ClO_2 added (%)	1.46	1.39
End pH	2.3	2.2
Residual ClO_2 (ppm)	29.7	35.1
E_{OP} stage *(Consistency - 10.0%, Time - 120 min, Temperature - 80°C, H_2O_2 - 0.5%)*		
NaOH added (%)	2.3	2.2
End pH	10.40	10.23
E_{OP} pulp brightness (% ISO)	76.5	78.0
E_{OP} pulp kappa number	1.9	1.8
D Stage *(Consistency - 10%, Time - 180 min, Temperature - 75°C)*		
ClO_2 added (%)	0.5	0.5
End pH	3.64	3.41
Brightness (% ISO)	83.6	85.6
CIE Whiteness	73.9	75.8
PC number	0.63	0.43
Viscosity (cP)	11.9	11.4

6.1.2. Effect of metal ions

Presence of higher amount of metal ions in the wheat straw pulp is another reason behind lower brightness development of pulp during bleaching. Wheat straw pulp has 2 to 4 times higher values of metal ions specifically manganese, iron and magnesium compared to eucalyptus pulp. Values of the different metal ions in wheat straw pulp and eucalyptus pulp are given in Table 6.1.4.

Table 6.1.4: Metal ions in wheat straw and eucalyptus

Metals	Value in unbleached pulp (ppm)	
	Wheat straw	Eucalyptus
Copper (Cu)	4.6	4.3
Manganese (Mn)	44.5	11.2
Zinc (Zn)	52.3	--
Iron (Fe)	204	37.9
Magnesium (Mg)	2,140	688
Calcium (Ca)	6,135	6503

6.1.3. Presence of non-fibrous material

Presence of higher amount of non fibrous raw material such as ash, silica and parenchyma tissues in wheat straw pulp makes the pulp very difficult to bleach to higher level of brightness. Wheat straw pulp taken for the study had average fiber length of 0.827 mm and average fiber width 19.1 µm. Though the average fiber length of wheat straw looked comparable to a few hardwood pulps but distribution of wheat straw fibers was more toward shorter fibers, mainly parenchyma cells and epidermal cells. Distribution of wheat straw fibers according to length is shown in Figure 6.1.2 and according to width in Figure 6.1.3.

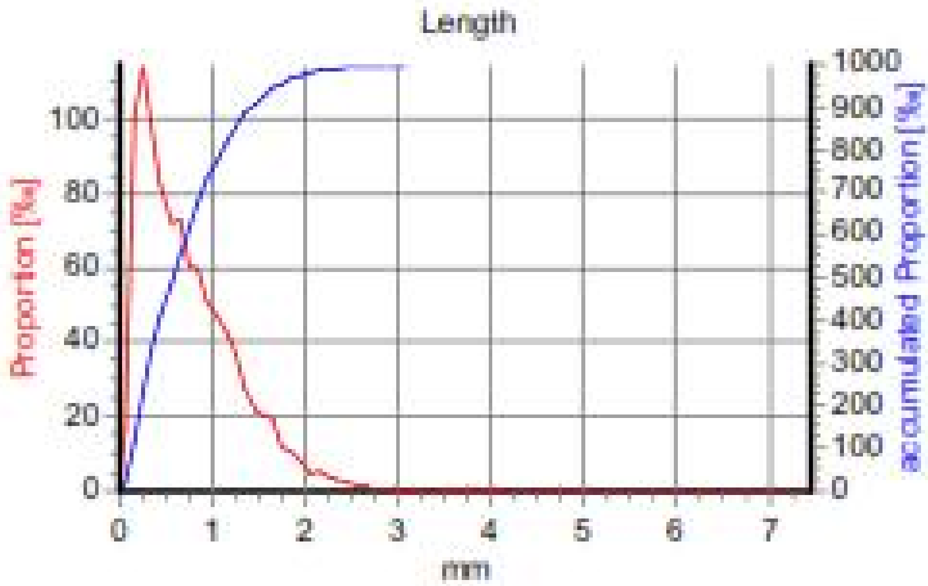

Figure 6.1.2: Length wise distribution of wheat straw fibers in pulp

Figure 6.1.3: Width wise distribution of wheat straw fibers in pulp

Results of the studies carried out on elimination/reduction of these factors through different processes and their effect on final pulp brightness is given in next sections of the report.

Raw material upgradation

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6.2. Raw material Upgradation

6.2.1. Proximate chemical analysis

Proximate chemical analysis of wheat straw collected from agro based paper mills situated in Punjab, Himachal Pradesh and purchased from nearby areas of Yamuna Nagar, Haryana was carried out. There was marginal difference in the cellulose, hemicelluloses and lignin content in wheat straw collected from different locations. Detailed results of proximate chemical analysis of wheat straw collected from different places are given in Table 6.2.1.

Table 6.2.1: Proximate chemical analysis of wheat straw

Parameters	Results		
	Punjab	Haryana	Himachal Pradesh
Acetone extractives (%)	2.1	2.4	2.3
Water soluble extractives (%)	9.2	10.3	10.2
Total extractives (%)	11.3	12.7	12.5
1% NaOH solubility (%)	34.2	33.6	33.7
Hemi cellulose (%)	38.9	37.9	37.5
Cellulose (%)	43.4	44.5	45.1
Lignin (%)	16.4	15.7	15.4
Ash (%)	7.9	8.8	8.2
Acid insolubles (%)	6.3	6.5	6.3
Silica content (%)	6.1	6.4	6.2

6.2.2. Effect of washing of the wheat straw

Washing of wheat straw substantially removes the non-fibrous material present in wheat straw. Washing of the straw removed the iron content by 73% and inorganic impurities by 56% from as such wheat straw. Detailed results are given in Table 6.2.2. Trend of removal of undesired materials from wheat straw by dry depithing and wet cleaning is shown in Figure 6.2.1.

Table 6.2.2: Effect of raw material cleaning on different impurities

Parameters	As such	Dry depithed	Wet cleaned
Ash (%)	12.3	11.7	7.9
Silica (%)	6.5	6.3	6.1
Calcium (ppm)	4500	4080	3750
Iron (ppm)	260	240	150

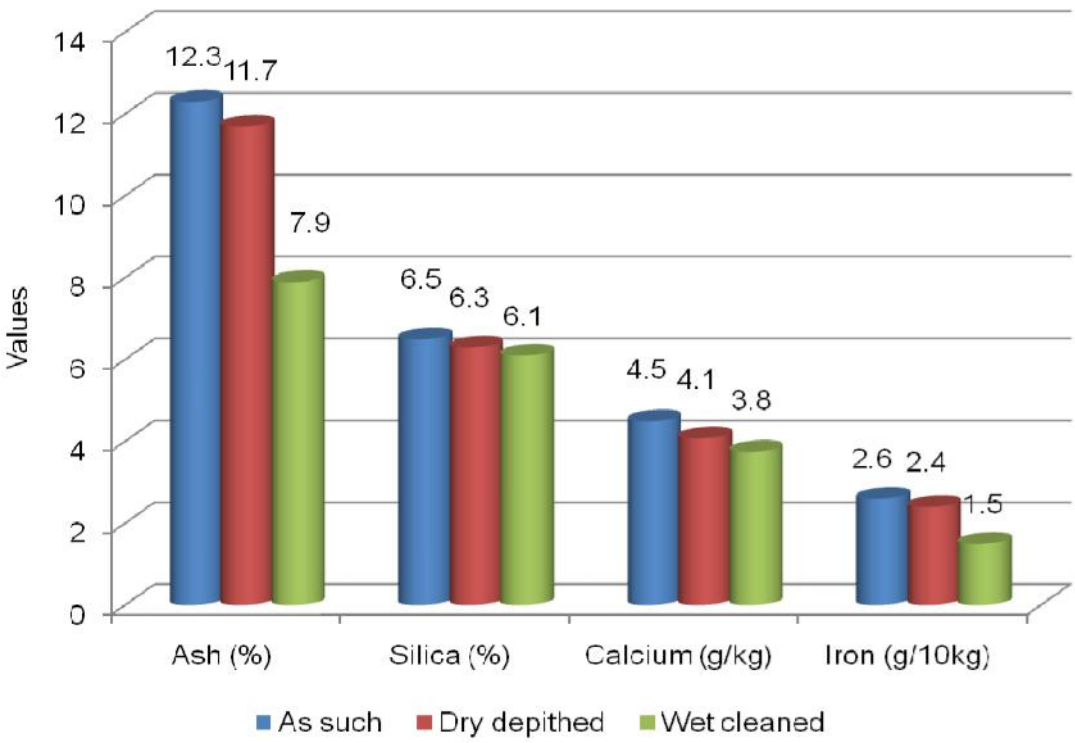

Figure 6.2.1: Effect of dry depithing and wet cleaning on removal of impurities

As such and wet cleaned wheat straw was cooked to produce about 10 kappa number unbleached pulp and bleached using $D_0E_{OP}D$ sequence to evaluate effect of raw material cleaning on brightness ceiling. Detailed results of soda pulping of as such and wet cleaned wheat straw are given in Table 6.2.3.

Table 6.2.3: Effect of raw material cleaning on pulping

Particulars	Set-1	Set-2	Set-3	Set-4
	As such		Wet cleaned	
Pulping conditions				
AA as NaOH (%)	16.0			
Anthraquinone (%)	0.05			
Bath ratio	1:4			
Temperature (ºC)	166			
Cooking time (min)	30			
Pulp properties				
Screened pulp yield (%)	51.2	51.4	51.6	51.8
Rejects (%)	0.14	0.12	0.16	0.18
Kappa no.	10.3	10.8	9.3	9.7
Black liquor properties				
pH	11.3	11.3	11.2	11.1
Free alkali (g/l)	2.9	2.8	3.4	3.3
Black liquor solids, w/w (%)	11.2	11.3	10.7	10.8

By maintaining all the standard bleaching conditions, unbleached pulp produced from as such wheat straw pulp was bleached to a brightness level of 83-84.1% ISO. Results of the bleaching of unbleached pulp produced from as such wheat straw are given in Table 6.2.4.

Table 6.2.4: Results of bleaching of pulp produced from as such wheat straw

Parameters	Results		
Kappa Number	10.5		
D_0 Stage *(Consistency -5%, Temperature - 55°C, Time - 45 min - 0.25)*			
ClO_2 added (%)	1.0		
Residual Cl_2 (ppm)	10.8		
End pH	2.5		
E_{OP} Stage *(Consistency -10%, Temperature - 80 °C, Time - 90 min)*			
NaOH added (%)	1.36		
H_2O_2 added (%)	0.5		
Final pH	10.3		
Residual H_2O_2 (ppm)	20		
Kappa Number	1.7		
Brightness (% ISO)	77.6		
D Stage *(Consistency -10%, Temperature - 80 °C, Time - 180 min)*			
ClO_2 added (%)	0.4	0.6	0.8
Final pH	3.5	3.6	3.8
Residual ClO_2 (ppm)	10.8	27	59.4
Brightness (% ISO)	83.0	83.6	84.1

Unbleached pulp produced from wet cleaned wheat straw was bleached to higher brightness level of 84.8-86.3% ISO compared to the pulp produced from as such wheat straw pulp. This may be due to the removal of non-fibrous material from the wheat straw. Results of the bleaching of unbleached pulp produced from wet cleaned wheat straw are given in Table 6.2.5.

Table 6.2.5: Bleaching of pulp produced from wet cleaned wheat straw

Parameters	Results		
Kappa Number	9.5		
D_0 Stage *(Consistency -5%, Temperature - 55°C, Time - 45 min)*			
ClO_2 added (%)	0.9		
Residual Cl_2 (ppm)	10.8		
End pH	2.3		
E_{OP} Stage *(Consistency -10%, Temperature- 80 °C, Time - 90 min)*			
NaOH added (%)	1.2		
H_2O_2 added (%)	0.5		
Final pH	10.2		
Residual H_2O_2 (ppm)	12.2		
Kappa Number	1.5		
Brightness (% ISO)	78.3		
D Stage *(Consistency -10%, Temperature - 80 °C, Time - 180 min)*			
ClO_2 added (%)	0.4	0.6	0.8
Final pH	3.6	3.8	3.7
Residual ClO_2 (ppm)	16.2	37.8	48.6
Brightness (% ISO)	84.8 (+1.8)	85.7 (+2.1)	86.3 (+2.2)

Physical strength properties of the bleached pulp obtained from as such, dry depithed and wet cleaned wheat straw were determined. Tear and tensile indices were marginally improved in the pulp produced from wet cleaned wheat straw compared to pulps produced from as such and dry depithed wheat straw. Detailed results of physical strength properties are given in Table 6.2.6.

Table 6.2.6: Effect of raw material cleaning on strength

Parameters	Results		
	Control	Dry Depithed	Wet Cleaned
Brightness (% ISO)	83.2	83.8	85.7
°SR	29	28	28
Grammage (g/m^2)	61.0	61.2	60.1
Bulk (cc/g)	1.33	1.32	1.31
Tensile index (Nm/g)	46.7	49.1	50.9
Burst index (kN/g)	4.1	4.1	4.0
Tear index (mNm^2/g)	5.7	5.8	6.2
Roughness (ml/min)	83	70	66

Effect of using machine back water during washing of wheat straw

Generally paper mills are utilizing their machine back water (b/w) in wheat straw wet cleaning system; therefore effect of b/w washing having different total dissolved solid (TDS) and total suspended solids (TSS) on pulping properties were studied. Results showed that while using higher TDS and TSS back water for washing of wheat straw, kappa number of pulp increased and free alkali in black liquor reduced. Detail results of pulping of wheat straw washed using different TDS and TSS back waters are given in Table 6.2.7.

Table 6.2.7: Pulping results of wheat straw washed with different TDS and TSS

Particulars	Set-1	Set-2	Set-3	Set-4
TDS in wash water (g/l)	5000	4000	3000	2000
TSS in wash water (g/l)	1000	800	600	400
Pulping condition *(Bath ratio - 1:4, Temperature - 166ºC, Time - 30 min, AA - 15%, AQ - 0.05%)*				
Screened pulp yield (%)	52.2	52.6	52.8	53.1
Rejects (%)	1.7	1.5	1.4	1.2
Kappa no.	11.6	11.2	10.7	10.2
pH	11.1	11.3	11.4	11.5
Free alkali (g/l)	2.3	2.7	3.3	3.6
Black liquor solids, w/w (%)	11.6	11.2	11.1	11.0

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Modifications during pulping

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6.3. Modifications during pulping

There is limited scope for improvement in brightness of final bleached pulp through modifications in pulping except reduction in kappa number which may cause yield loss and use of pulping additives to reduce metal ions during pulping. Different chelating agents were used to see the effect of using them on metal ion content in unbleached pulp. Ethylene diamine tetra acetic acid (EDTA) and Hydroxy ethylidene diphosphonic acid (HEDP) removed a few metal ions during pulping to some extent but their impact on final brightness could not be established. Metal ion content in unbleached pulp obtained after using chelating agents in pulping is given in Table 6.3.1.

Table 6.3.1: Removal of metal ions by using EDTA and HEDP in pulping

Metals	Value in unbleached pulp (ppm)		
	Control	EDTA	HEDP
Copper (Cu)	4.6	1.6	1.2
Manganese (Mn)	44.5	42	42
Zinc (Zn)	52.3	38	36
Iron (Fe)	204	95	126
Magnesium (Mg)	2,140	1920	1843
Calcium (Ca)	6,135	--	--

Efficacy of different oxidative and reductive pulping additives reported in literature to reduce kappa number of pulp was evaluated for wheat straw. Results showed that anthraquinone (AQ) is the best in terms of reduction in kappa number for wheat straw among different additives used in study. Detailed results of pulping of wheat straw using different pulping additive on properties of pulp are given in Table 6.3.2.

Table 6.3.2: Pulping of wheat straw using different additives

Parameters	Control	$NaBH_4$	AQ	AQD
Pulping conditions				
AA dose (%)	15			
Additive dose (%)	-	0.05	0.05	0.1
Temperature (°C)	166			
Cooking time (min)	20			
Pulp properties				
Unscreened yield (%)	58.2	59.4	59.9	59.6
Rejects (%)	1.7	1.7	0.7	0.8
Kappa no.	19.1	19.3	15.2	16.6
Brightness (%ISO)	34.6	35.1	35.9	35.3
Viscosity (cP)	13.0	14.6	15.8	15.4
Black liquor properties				
Free alkali as NaOH(g/l)	4.5	4.2	3.8	4.0
Black liquor solids (%)	14.3	14.0	12.9	13.3

Unbleached pulps produced using sodium borohydride ($NaBH_4$), anthraquinone (AQ) and derivatised anthraquinone (AQD) were bleached using conventional $CE_{OP}HH$ bleaching sequence using desired amount of bleaching conditions. Chlorine dose was used by applying 0.26 kappa factor in the chlorination stage for all the four pulps. Similarly 0.6% hydrogen peroxide in E_{OP} stage, 1.5% calcium hypo chlorite in H_1 stage and 0.5% calcium hypo chlorite in H_2 stage of bleaching were used for all the pulps. There was marginal improvement in the final bleached pulp brightness in the pulps produced using pulping additives compared to control. None of the pulps achieved the targeted brightness level of +85% ISO. Detailed results of bleaching the pulps are given in Table 6.3.3.

Table 6.3.3: Bleaching of pulps produced with pulping additives

Parameters	Control	$NaBH_4$	AQ	AQD
Kappa number	19.1	19.3	15.2	16.6
C Stage *(Consistency – 2.5%, Temperature – 40°C, Time – 45 min)*				
Cl_2 added (%)	4.97	5.02	3.95	4.32
Final pH	2.4	2.3	2.4	2.4
E_{OP} Stage *(Consistency – 10%, Temperature – 80°C, Time – 120 min)*				
NaOH added (%)	2.73	2.76	2.17	2.38
H_2O_2 added (%)	0.6	0.6	0.6	0.6
Final pH	10.4	10.2	9.7	10.2
Kappa number	1.0	0.9	0.9	0.9
Brightness (% ISO)	73.8	73.2	74.4	74.6

Parameters	Control	$NaBH_4$	AQ	AQD
H_1 Stage *(Consistency – 10%, Temperature – 40^oC, Time –120 min)*				
Hypo added (%)	1.5	1.5	1.5	1.5
Final pH	7.5	7.8	8.0	8.0
Brightness (%ISO)	82.5	83.5	83.1	83.6
H_2 Stage *(Consistency –10%, Temperature - 40^oC, Time – 120 min)*				
Hypo added (%)	0.5	0.5	0.5	0.5
Final pH	7.0	7.1	7.0	7.0
Brightness (%ISO)	83.2	84.0	83.7	84.1

Modifications during bleaching

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6.4. Modifications during bleaching

To improve the final pulp brightness different pre-bleaching treatments, during bleaching modifications and post-bleaching treatments were studied based on the benefits reported in the literature and some novel treatments of wheat straw pulp also carried out.

6.4.1 Pre-bleaching treatments of pulp

Different pre-bleaching treatments like enzymatic treatment of pulp using commercially available xylanase enzyme, chelating agents, chelating agent along with hydrogen peroxide, acid pre treatment of pulp were explored on wheat straw pulp.

Enzymatic pre-bleaching treatment

Efficacy of different commercially available enzymes was compared and bleaching experiments were carried out using best available xylanase enzyme having xylanase activity 10,300 IU/g prior to bleaching after optimizing enzyme treatment conditions. Control and enzyme treated pulps were bleached by $CE_{OP}HH$ and $DE_{OP}D$ bleaching sequences. The optical, physical strength properties of pulp and properties of effluent generated during bleaching of pulps were evaluated. Results showed that final pulp brightness was marginally improved with the use of enzyme in pre-bleaching stage while using similar bleaching chemicals in different stages of bleaching. There was no noticeable difference in the physical strength properties and properties of the effluent generated during bleaching after enzymatic treatment of pulp compared to control pulp.

Detailed results of bleaching of wheat straw pulp using $CE_{OP}HH$ and $DE_{OP}D$ sequence are given in Table 6.4.1 and Table 6.4.2, respectively. Detailed results of physical strength properties of pulps bleached using $CE_{OP}HH$ and $DE_{OP}D$ sequence are given in Table 6.4.3 and Table 6.4.4, respectively. Detailed results of properties of effluent generated during bleaching of pulps using $CE_{OP}HH$ and $DE_{OP}D$ sequence are given in Table 6.4.5 and Table 6.4.6, respectively.

Table 6.4.1: Bleaching of control and enzyme pre-treated pulps with $CE_{OP}HH$ sequence

Particulars	Control	Enzyme
Kappa number	14.7	
Enzyme treatment *(Consistency - 8.0%, Temperature - 65°C, Time - 1 h)*		
Enzyme added (g/T)	-	150
C Stage *(Consistency – 2.5%, Temperature - 40°C, Time - 45 min., KF-0.26)*		
Chlorine added (%)	3.82	3.82
End pH	2.3	2.3
E_{OP} Stage *(H_2O_2-0.7%, Consistency - 10%, Temperature - 75°C, Time - 120 min.)*		
NaOH added (%)	2.3	2.3
End pH	10.0	10.1
Brightness (% ISO)	75.9	77.2
Kappa number	1.2	1.0
H_1 Stage *(Consistency - 10%, Temperature - 40°C, Time - 120 min.)*		
Hypo added (%)	0.5	0.5
End pH	8.7	8.7
Brightness (% ISO)	82.6	82.4
H_2 Stage *(Consistency - 10%, Temperature - 40°C, Time - 120 min.)*		
Hypo added (%)	0.25	0.25
End pH	7.6	7.5
Residual hypo (ppm)	35.5	49.7
H_2 Brightness (% ISO)	84.8	85.2
Viscosity (cP)	9.3	8.9

Table 6.4.2: Bleaching of control and enzyme pre-treated pulps with $DE_{OP}D$ sequence

Particulars	Control	Enzyme
Kappa number	14.7	14.7
Enzyme pre - treatment *(Consistency - 8.0%, Temperature - 65°C, Time - 1 h)*		
Enzyme added (g/T)	-	150
D_0 stage *(Consistency - 5%, Time - 45 min, Temperature-55°C)*		
ClO_2 added (%)	1.4	1.4
End pH	2.26	2.34
E_{OP} stage *(Consistency - 10.0%, Time - 120 min, Temperature - 80°C, H_2O_2- 0. 5%)*		
NaOH added (%)	2.1	2.1
End pH	10.4	10.3
Brightness (% ISO)	75.8	76.8
Kappa number	1.4	1.0
D Stage *(Consistency - 10%, Temperature - 75°C, Time - 180 min.)*		
ClO_2 added (%)	0.6	0.6
End pH	3.9	3.7
Brightness (% ISO)	84.5	85.3
Viscosity (cP)	13.9	13.7

Table 6.4.3: Physical strength properties of control and enzyme pre-treated pulps bleached with $CE_{OP}HH$ sequence

Particulars	Control		Enzyme	
No. of revolutions	0	100	0	100
^{o}SR	28.5	37	28.0	36
Grammage (g/m^2)	61.4	61.7	61.5	61.3
Bulk (cc/g)	1.46	1.40	1.45	1.36
Tensile index (Nm/g)	43.9	53.3	44.1	52.8
Burst index ($kN.m^2/g$)	2.80	3.60	2.76	3.60
Tear index (mNm^2/g)	6.21	5.33	6.10	5.26

Table 6.4.4: Physical strength properties of control and enzyme pre-treated pulps bleached with $DE_{OP}D$ sequence

Particulars	Control		Enzyme	
No. of revolutions	0	100	0	100
^{o}SR	32	40.5	32.5	40
Grammage (g/m^2)	60.6	61.2	61.7	61.2
Bulk (cc/g)	1.44	1.34	1.46	1.38
Tensile index (Nm/g)	49.2	56.7	49.4	56.9
Burst index (kN/g)	4.2	4.8	4.1	4.71
Tear index (mNm^2/g)	7.57	6.74	7.50	6.75

Table 6.4.5: Properties of the effluent generated during bleaching of control and enzyme pre-treated pulps with $CE_{OP}HH$ sequence

Particulars	Control	Enzyme
pH	2.64	2.67
Total solids (%)	0.45	0.44
Colour (PCU)	753	677
COD (kg/t)	110	98

Table 6.4.6: Properties of the effluent generated during bleaching of control and enzyme pre-treated pulps with $DE_{OP}D$ sequence

Particulars	Control	Enzyme
pH	3.3	3.3
Total solids (%)	0.37	0.37
Colour (PCU)	384	329
COD (kg/t)	81	80

Pre-bleaching acid treatment

Acid pre treatment of wheat straw pulp was given at 2.0 pH, 80 °C temperature, 10% consistency for 60 minute using sulfuric acid to maintain the pH. Results showed that acid pre treatment of pulp reduced the copper, manganese, zinc, iron and magnesium content in pulp by 61%, 28%, 77%, 68% and 57%, respectively. Detailed results of effect of acid treatment on different metal ion are given in Table 6.4.7.

Table 6.4.7: Metal ions in the pulp before and after acid treatment

Metals	Value in unbleached pulp (ppm)	
	Control	Acid treated
Copper (Cu)	4.6	1.8
Manganese (Mn)	44.5	32.2
Zinc (Zn)	52.3	12.2
Iron (Fe)	204	65
Magnesium (Mg)	2,140	916
Calcium (Ca)	6,135	--

Control and acid pre treated pulps were bleached using $CE_{OP}HH$ and $CE_{OP}D$ bleaching sequences. Results showed that acid treatment of pulp prior to bleaching of pulp with $CE_{OP}HH$ and $CE_{OP}D$ improved final pulp brightness by 1.6 units and 2.0 units, respectively. Detailed results of bleaching of control and acid pre-treated pulps with $CE_{OP}HH$ sequence are given in Table 6.4.8. Detailed results of bleaching of control and acid pre-treated pulps with $DE_{OP}D$ sequence are given in Table 6.4.9.

Table 6.4.8: Bleaching of control and acid pre-treated pulps with $CE_{OP}HH$ sequence

Particulars	Control	Acid treated
Kappa number	14.7	
C Stage *(Consistency – 2.5%, Temperature - 40°C, Time - 45 min)*		
Chlorine added (%)	3.82	3.82
End pH	2.3	2.1
E_{OP} Stage *(H_2O_2-0.7%, Cy - 10%, Temperature - 75°C, Time - 120 min.)*		
NaOH added (%)	2.3	2.3
End pH	10.0	10.0
Brightness (% ISO)	75.9	77.2
Kappa number	1.2	1.0
H_1 Stage *(Consistency - 10%, Temperature - 40°C, Time - 120 min.)*		
Hypo added (%)	0.5	0.5
End pH	8.7	8.5
Brightness (% ISO)	82.6	84.5
H_2 Stage *(Consistency - 10%, Temperature - 40°C, Time - 120 min.)*		
Hypo added (%)	0.25	0.25
End pH	7.6	7.5
Brightness (% ISO)	84.8	86.4 (+1.6)
Viscosity (cP)	9.3	9.2

Table 6.4.9: Bleaching of control and acid pre-treated pulps with $DE_{OP}D$ sequence

Particulars	Control	Acid treated
Kappa number	14.7	14.7
D_0 stage *(Consistency - 5%, Time - 45 min, Temperature - 55°C)*		
ClO_2 added (%)	1.4	1.4
End pH	2.3	2.2
E_{OP} stage *(Consistency - 10.0%, Time - 120 min, Temperature - 80°C, H_2O_2- 0. 5%)*		
NaOH added (%)	2.1	2.1
End pH	10.4	10.2
Brightness (% ISO)	75.8	77.7
Kappa number	1.4	0.9
D Stage *(Consistency - 10%, Temperature - 75°C, Time - 180 min.)*		
ClO_2 added (%)	0.6	0.6
End pH	3.9	3.8
Brightness (% ISO)	84.5	86.5 (+2.0)
Viscosity (cP)	13.9	13.7

Pre-bleaching EDTA-Peroxide treatment

Efficacy of hydrogen peroxide along with EDTA was evaluated to enhance final pulp brightness. Peroxide treatment of pulp showed comparable results in terms of reduction in kappa number and bleachability of pulp compared to oxygen delignification (ODL) of pulp. Detailed results of oxygen delignification, peroxide pre-treatment followed by bleaching of pulps with $CE_{OP}HH$ sequence are given in Table 6.4.10. Results of oxygen delignification, peroxide pre-treatment followed by bleaching of pulps with $DE_{OP}D$ sequence are given in Table 6.4.11.

Table 6.4.10: Hydrogen peroxide pre-treatment of pulp (Alternative to ODL) followed by bleaching using $CE_{OP}HH$ sequence

Particulars	Control	ODL	Peroxide treated
Peroxide treatment *(Peroxide – 1.5%, Consistency - 10%, Temperature - 80°C, Time - 2 h, EDTA – 0.2%)* ODL *(Oxygen – 1.6%, Consistency - 10%, Temperature - 90°C, Time – 90 min)*			
Kappa Number	14.3	9.2	10.3
Brightness (% ISO)	40.3	48.3	54.2
Viscosity (cP)	14.1	12.3	12.2
Properties of $CE_{OP}HH$ bleached pulp			
Cl_2 /NaOH used (%)	4.9 /2.6	3.6 /1.7	3.7 /1.8
Brightness (% ISO)	84.9	85.9	86.6
CIE (Whiteness)	76.1	76.9	77.8
Viscosity (cP)	10.2	10.0	9.9
Properties of the Effluent generated during bleaching			
Color (kg/t)	47.7	32.8	29.8
COD (kg/t)	61.7	42.5	47.4
AOX (kg/t)	2.5	1.7	1.8

Table 6.4.11: Hydrogen peroxide pre-treatment of pulp (Alternative to ODL) followed by bleaching using $D_0E_{OP}D$ sequence

Particulars	Control	ODL	Peroxide treated
Peroxide treatment *(Peroxide – 1.5%, Consistency - 10%, Temperature - 80°C, Time - 2 h, EDTA – 0.2%)* ODL *(Oxygen – 1.6%, Consistency - 10%, Temperature - 90°C, Time – 90 min)*			
Kappa Number	14.3	9.2	10.3
Brightness (% ISO)	40.3	48.3	54.2
Viscosity (cP)	14.1	12.3	12.2
Properties of $D_0E_{OP}D$ bleached pulp			
ClO_2 /NaOH used (%)	2.27 /2.3	1.69 /1.6	1.66 /1.7
Brightness (% ISO)	84.6	85.6	86.7
CIE (Whiteness)	75.1	76.7	77.9
Viscosity (cP)	12.1	11.9	11.7
Properties of the Effluent generated during bleaching			
Color (kg/t)	20.1	16.2	14.7
COD (kg/t)	44.5	27.4	29.6
AOX (kg/t)	0.66	0.39	0.43

6.4.2 Modifications during bleaching

Comparison of different bleaching sequences

Different bleaching sequences like $CE_{OP}HH$, $C_DE_{OP}HH$, $C_DE_{OP}HD$, $C_DE_{OP}DD$, $D_0E_{OP}D$ and $D_0E_{OP}DP$ were studied to compare their efficacy to produce higher brightness pulp. Highest brightness 87.4% was achieved with bleaching sequence $D_0E_{OP}D$ followed by 86.9% with $C_DE_{OP}HD$ and $C_DE_{OP}DD$ sequences, 86.3% with $C_DE_{OP}HH$ sequence, 84.8% with $CE_{OP}HH$ sequence, 84.5% with $D_0E_{OP}D$ bleaching sequence. The data on final pulp brightness achieved with different bleaching sequences is shown in Figure 6.4.1.

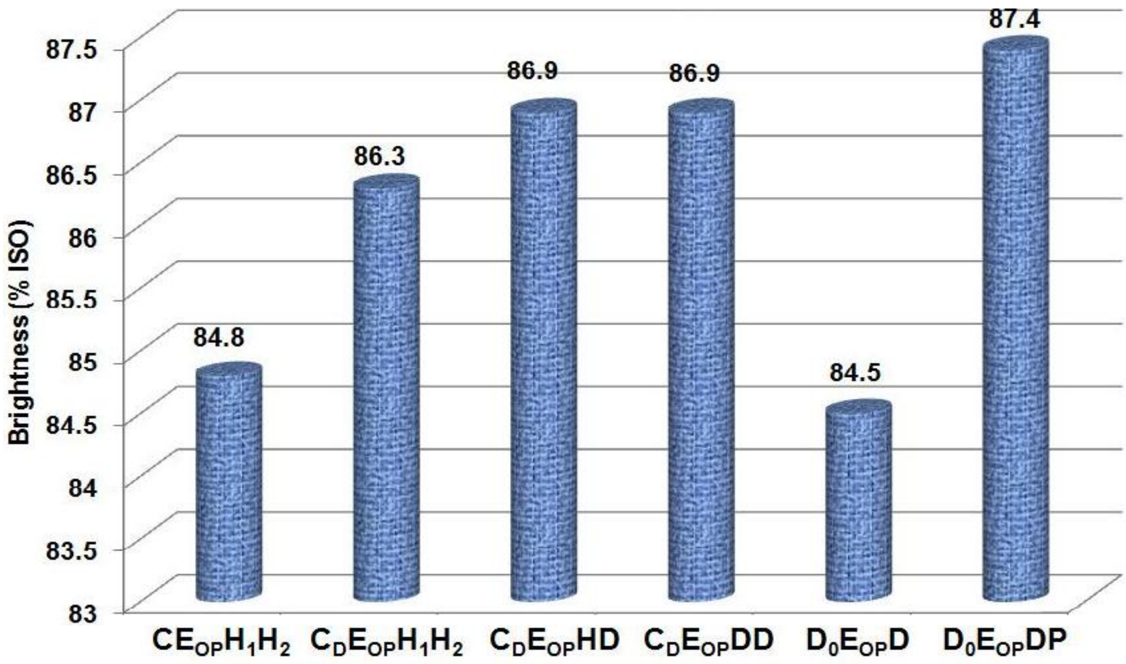

Figure 6.4.1: Final pulp brightness achieved by using different bleaching sequences

Hydrogen peroxide activator in E_{OP} stage of bleaching

Efficacy of commercially available hydrogen peroxide activator was evaluated in E_{OP} stage of bleaching for development of brightness in different stages of bleaching. Results showed that with the use of hydrogen peroxide activator either bleaching chemicals could be reduced to produce pulp of similar brightness or final bleached pulp brightness could be improved using similar bleaching chemicals compared to control. Detailed results of bleaching of pulp with and without hydrogen peroxide activator are given in Table 6.4.12.

Table 6.4.12: Bleaching of pulp with and without hydrogen peroxide activator

Parameters	Control	With activator	
		Same bleaching chemicals	Reduced bleaching chemicals
Kappa Number	12.9		
C stage *(Consistency - 3.0%, Temperature - 35°C, Time - 45 Min.)*			
E_{OP} stage *(Cy - 10.0%, Temperature - 70°C, Time - 120 Min, O_2 - 0.6%)*			
Activator dose (g/TP)	0	100	
H_2O_2/NaOH added (%)	0.5/2.2	0.5/2.2	0.4/2.05
Residual H_2O_2 (ppm)	10.2	6.8	3.4
Kappa No.	1.1	0.9	1.0
Brightness (% ISO)	76.8	78.3	77.9
H_1 stage *(Cy - 10.0%, Hypo - 0.80%, Temperature - 45°C, Time - 120 Min.)*			
Activator dose (g/TP)	0	50	
Brightness (% ISO)	83.6	84.2	83.8
H_2 stage *(Cy - 10.0%, Hypo - 0.3%, Temperature - 45°C, Time - 120 Min)*			
Brightness (% ISO)	84.2	85.1 (+0.9)	84.8
Whiteness (CIE)	75.8	77.1 (+1.3)	76.1
PC number	2.63	2.21 (-0.42)	2.21
Viscosity (cP)	10.6	11.3 (+0.7)	12.0

6.4.3. Post-Bleaching treatment of pulp

Post bleaching acid treatment

Pulps bleached using $CE_{OP}HH$ and $D_0E_{OP}D$ sequences were treated with acid in similar fashion as pre-bleaching acid treatment. Results showed that final bleached pulp brightness can be enhanced by 1.8 - 2.1 units with an acid treatment of bleached pulp. Detailed results of post bleaching acid treatment of pulp are given in Table 6.4.13.

Table 6.4.13: Post bleaching acid treatment of wheat straw pulp

Particulars	Results	
Bleaching sequence	$CE_{OP}HH$	$D_0E_{OP}D$
Final bleached pulp brightness (% ISO)	84.8	84.5
PC number	2.17	1.23
Acid treatment *(Consistency -10%, Temperature- 80 °C, Time – 60 min, 2 pH)*		
Brightness of pulp after acid treatment (% ISO)	86.6	86.6
Increase in brightness (Units)	1.8	*2.1*
PC number	1.41	*1.24*

Post bleaching per acetic acid treatment

Pulps bleached using $CE_{OP}HH$ and $D_0E_{OP}D$ sequences were treated with per acetic acid (PAA) to assess their potential for enhancing the final pulp brightness. Commercially available PAA having about 35% purity was applied on final bleached pulp at a dose of 1.0%. With the use of PAA final bleached pulp brightness was improved by 1.5 - 1.8 units. Detailed results of post bleaching PAA treatment of pulp are given in Table 6.4.14.

Table 6.4.14: Post bleaching PAA treatment of wheat straw pulp

Particulars	Results	
Bleaching sequence	$CE_{OP}HH$	$D_0E_{OP}D$
Final bleached pulp brightness (% ISO)	84.8	84.5
PC number	2.17	1.23
PAA treatment *(Consistency -10%, Temperature- 50 °C, Time – 30 min, 5.0 pH)*		
Brightness of pulp after PAA treatment (% ISO)	86.3	86.3
Increase in brightness (Units)	1.5	*1.8*

Summary of the brightness achieved by applying different processes during the study are given in Table 6.4.15

Table 6.4.15: Brightness achieved by different processes studied

Process	Brightness achieved (% ISO)	Brightness gain (Unit)
Pre-bleaching acid treatment	86.5	1.6 - 2.0
Post-bleaching acid treatment	86.6	1.8 - 2.1
In-situ acid treatment of pulp	86.0	1.2 - 1.5
H_2O_2 pre-treatment of pulp	86.7	1.9 - 2.2
Replacing 20% Cl_2 with ClO_2	86.3	1.5 - 1.8
Addition of last peroxide stage	87.4	2.6 - 2.9
Enzyme pre-treatment	85.2	0.7-1.0
Hydrogen peroxide activator	85.1	0.9-1.1

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Validation studies on selected processes at CPPRI

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6.5. Validation studies on selected processes at CPPRI

Role of CPPRI under the scope of project activities

The scope of CPPRI pertaining to the project was validation of the findings of lab scale studies carried out at ACIRD by running the experiments under similar conditions or based on the studies carried out earlier related to bleaching of wheat straw pulp.

WORK CARRIED OUT

Preparation/collection of agro-residue pulp (wheat straw)

Wheat straw mill pulp normally available in the form of mixed pulp with bagasse or sarkanda was available. Wheat straw and bagasse mixed unbleached pulp was collected from Naini tissues, Kashipur.

Unbleached wheat straw pulp of desired kappa number was also prepared in laboratory.

Pretreatment of pulp simulating with the conditions according to ACIRD conditions

The pretreatment experiments of unbleached pulp was carried out as per conditions provided by ACIRD as given below

- Effect of hot water washing of wheat straw followed by pulping and $D_0E_{OP}D$ bleaching
- Effect of acid pretreatment followed by $D_0E_{OP}D$ bleaching
- Effect of hydrogen peroxide pretreatment and comparison with oxygen pretreatment

RESULTS AND DISCUSSIONS

Unbleached pulp characteristic

Unbleached wheat straw pulp was prepared in CPPRI laboratory. The unbleached pulp had following characteristics

Parameters	CPPRI	ACIRD
Unbleached pulp kappa number	11	10.5
Unbleached pulp brightness,%	32	
Unbleached pulp viscosity, cP	16	

Table 6.5.1: Unbleached pulp prepared after Hot water (HW) washing of wheat straw

Parameters	CPPRI		ACIRD	
	As such	HW washed	As such	HW washed
Unbleached pulp kappa number	11	9.5	10.5	9.5
Drop in kappa number, unit		1.5		1.0
Unbleached pulp brightness, % ISO	32	35		
$D_0E_{OP}D$ Bleaching				
$D_0E_{OP}D$ pulp brightness, % ISO	83.8	86.5	84.1	86.3
Gain in brightness, units		2.7		2.2

Table 6.5.2: Effect of acid pretreatment on final bleached pulp brightness

Particulars	Brightness achieved* (% ISO)	
	ACIRD	CPPRI
Pre bleaching acid treatment *(Consistency -10%, Temperature- 80 °C, Time – 60 min, 2 pH)*		
Control	84.8	85
Acid (H_2SO_4) treated	86.4 *(+1.6)*	86.5 (+1.5)

*Bleaching sequence followed was $CE_{OP}H_1H_2$.

Table 6.5.3: Hydrogen peroxide pre-treatment of pulp (Alternative to ODL) followed by bleaching using $D_0E_{OP}D$ sequence

Particulars	ACIRD			CPPRI		
	Control	ODL	Peroxide treated	Control	ODL	Peroxide treated
Kappa Number	14.3	9.2	10.3	13.0	6.0	7.0
Brightness (% ISO)	40.3	48.3	54.2	35	48	52
Viscosity (cP)	14.1	12.3	12.2	16	12	11.5
$D_0E_{OP}D$ Bleaching						
Brightness (% ISO)	84.6	85.6	86.7	84.0	85.0	86.8
CIE (Whiteness)	75.1	76.7	77.9	--	--	--
Viscosity (cP)	12.1	11.9	11.7	11.0	10.8	10.5
Properties of the Effluent generated during bleaching						
Color (kg/t)	20.1	--	14.7			
COD (kg/t)	44.5	--	29.6			
AOX (kg/t)	0.66	--	0.43			

Peroxide treatment *(Peroxide – 1.5%, Consistency - 10%, Temperature - 80°C, Time - 2 h, EDTA – 0.2%)*

ODL *(Oxygen – 1.6%, Consistency - 10%, Temperature - 90°C, Time – 90 min)*

OBSERVATIONS

Wheat straw pulp with unbleached kappa number 11-15 is prepared, which on bleaching results in brightness below 85(% ISO). A number of factors are involved in brightness ceiling effect in wheat straw bleaching which are:

- Cleanliness of raw material
- Presence of high hexenuronic acid
- Presence of metal ions
- Generation of fines and poor post digester washing

Once addressed these problems by effective washing of wheat straw or unbleached pulp pretreatment, it is possible to increase brightness ceiling and it is possible to bleach wheat straw pulp as high as 86-87% ISO brightness as compared to unwashed and untreated pulp bleaching where it is 83-84 % ISO.

A number of experiments were conducted at CPPRI during the project period. In order to validate the results of ACIRD finding on project, some experiments replicating with ACIRD conditions were conducted on wheat straw pulp produced in CPPRI laboratory.

It is observed that

1. Hot water washing of wheat straw helps in unbleached pulp kappa number reduction by 1-1.5 point which results in gain of final bleached pulp brightness by 1-1.5 point as compared to control (table 1).
2. Similarly acid pre treatment also helps in improving the final bleached pulp brightness by 1-2 point (table 2).
3. The effect of hydrogen peroxide pretreatment as replacement of capital intensive ODL technology is also studied by ACIRD and similar observation also made by CPPRI. Hydrogen peroxide is as effective as oxygen pretreatment in terms of reduction of kappa number and same is also helpful in improving the final brightness of bleached pulp after $D_0E_{OP}D$ sequence (table 3).
4. In addition, studies on mill pulp (wheat straw bagasse mixed pulp) collected from agro based mill were also carried out and it was observed that there is no markable difference in results of both pulp samples.

RECOMMENDATIONS

Experiments on combined effect of hot water washed wheat straw followed by pulping and hot acid treatment should also be worked out. It is possible to increase the ceiling of brightness 3-4 point as comparison to control sample.

The findings are based on replication of experiments multi times both by ACIRD and CPPRI and the same can be scaled up to mill scale.

Pre-plant trial studies at ACIRD

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6.6. Pre-plant trial studies at ACIRD

In a meeting conducted by IARPMA at Shreyans Papers Limited on July 5, 2016, salient findings of the project were presented. In the meeting, it was decided to carry out lab study on two selected processes using mill pulp prior to conducting plant trial at Shreyans Paper Mills Ltd.

(i) ***Hydrogen peroxide pre-bleaching treatment of pulp:*** Hydrogen peroxide pre-treatment of unbleached wheat straw pulp improved final bleached pulp brightness by 1.7 - 2.1 units with substantial reduction in chlorine based bleaching chemicals and pollutants generated during bleaching.

(ii) ***Use of hydrogen peroxide activator in E_{OP} stage of bleaching:*** Use of suitable hydrogen peroxide activators improved the final bleached pulp brightness by 1.1 units and whiteness by 1.5 units while using similar bleaching chemicals.

Hydrogen peroxide pre-bleaching treatment of pulp

Table 6.6.1: Results of pre-bleaching treatments on mill unbleached pulp

Particulars	Results			
Unbleached mill pulp properties				
Kappa number	15.0			
Brightness (% ISO)	38.1			
Viscosity (cP)	10.1			
Pre-Treatment	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20*
Pre-treatment (***ODL:*** *Temperature - 90°C, NaOH - 1.8%, Time - 60 min. Oxygen 1.5%;* ***Peroxide with EDTA:*** *Temperature - 80°C, H_2O_2 - 1.5%, NaOH - 0.3%, Time - 120 min., EDTA - 0.2%;* ***Peroxide with Bleach S-20:*** *Temperature - 80°C, H_2O_2 - 1.5%, Time - 120 min., Bleach S-20 - 0.7%)*				

Pre-Treatment	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20*
Properties of filtrate generated after pre-treatment				
Volume of filtrate (m^3)	--	--	9	9
pH	--	--	9.1	9.1
COD (mg/l)	--	--	4570	4780
Colour (kg/t)	--	--	5100	5070
Total solids (%)	--	--	0.63	0.66
Properties of pulp after pre-treatment				
End pH	--	10.5	9.0	9.1
Kappa number	15.0	10.4	10.6	9.0
Brightness (% ISO)	38.1	47.8	49.1	48.9
Viscosity (cP)	10.1	7.8	8.0	8.0
Kappa reduction (%)	0.0	30.7	29.3	40.0

*collected from the mill.

Table 6.6.2: Bleaching of the pulps using $CE_{OP}HH$ sequence

Particulars	Results			
	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20
Kappa number	15.0	10.4	10.6	9.0
C stage *(Consistency - 2.5%, Time - 45 min, Temperature - 35°C,)*				
End pH	2.4	2.6	2.5	2.5
Residual Cl_2 (ppm)	23	28	25	28
E_{OP} stage *(Consistency - 10%, Time - 60 min, Temperature - 70°C, H_2O_2 - 0.6%, O_2 - 3.5 kg/cm^2)*				
Final pH	10.8	10.7	10.8	10.8
Residual H_2O_2 (ppm)	38	34	28	34
Brightness (%ISO)	74.3	77.6	77.5	76.5
Kappa no	1.6	1.4	1.4	1.4
H_1 stage *(Cy - 10%, Time - 120 min, Temperature - 40°C,* Hypo - 1.5 %*)*				
Final pH	7.8	7.6	7.6	7.6
Residual hypo (ppm)	375	401	398	529
Brightness (%ISO)	84.5	86	85.6	85.7

Particulars	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20
H_2 stage *(Cy - 10%, Time - 120 min, Temperature - 40°C,* Hypo - 0.5 %*)*				
Final pH	6.9	6.8	6.8	6.8
Residual hypo (ppm)	107	121	110	128
Brightness (%ISO)	85.2	86.6	86.5	86.4
CIE whiteness	76.1	78.8	78.5	78.3
ASTM yellowness	5.24	4.5	4.61	4.68
Viscosity (cP)	4.6	4.4	4.6	4.5

Table 6.6.3: Properties of the effluent generated during bleaching of pulps

Particulars	Results			
	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20
Volume of filtrate (m^3/t)	66	66	66	66
pH	3.6	4.1	3.6	3.6
COD (mg/l)	1440	760	860	840
Colour (mg/l)	1270	330	355	394
AOX (mg/l)	53	32	35	30

Table 6.6.4: Physical strength properties of bleached pulps after pre-treatments

Particulars	Results			
	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20
No. of revolutions	100	100	100	100
°SR	34.5	35.0	34.0	34.0
Grammage (g/m^2)	61.3	61	61.3	61.1
Tensile index (Nm/g)	42.02	43.9	45.59	47.06
Burst index (kN/g)	3.24	3.17	3.32	3.35
Tear index (mNm^2/g)	5	4.8	5.25	5.31
Double fold (no.)	28	23	39	36

Hydrogen peroxide activator in E_{OP} stage of bleaching

Table 6.6.5: Bleaching of mill pulp using hydrogen peroxide activators 'A' & 'Bleach S-20' in E_{OP} stage

Parameters	Control	Activator-'A'#	Bleach S-20*
		Same bleaching chemicals	Reduced bleaching chemicals
Kappa Number	15.0		
C stage *(Consistency - 2.5%, Temperature - 35°C, Time - 45 Min.)*			
End pH	2.2		
Residual Cl_2 (%)	29.7		
E_{OP} stage *(Consistency - 10.0%, Time - 90 Min)*			
Activator (g/TP)	0	250	7000
Temperature (°C)	70		60
Oxygen (kg/cm²)	3.5		0
NaOH added (%)	2.5		2.0
H_2O_2 added (%)	0.6		0.45
End pH	10.8	10.9	10.0
Brightness (% ISO)	74.8	76.7	76.9
Kappa No.	1.6	1.5	1.4
H_1 stage *(Cy - 10%, Time - 120 min, Temperature - 40°C,* Hypo - 1.5 %*)*			
End pH	7.8	7.7	7.7
Brightness (% ISO)	84.7	85.4	85.3

Parameters	Control	Activator-'A'#	Bleach S-20*
		Same bleaching chemicals	Reduced bleaching chemicals
H_2 stage *(Consistency - 10%, Time - 120 min, Temperature - 40°C,* Hypo - 0.5%*)*			
End pH	7.2	7.2	7.1
Residual Cl_2 (ppm)	95	102	110
Brightness (% ISO)	85.3	86.2	85.8
Whiteness (CIE)	76.4	77.5	76.8
PC number	2.0	1.8	1.9
Viscosity (cP)	4.7	4.9	4.7

#Activator selected during ACIRD lab study. *collected from the mill.

SALIENT FINDINGS

Results obtained with the use of unbleached pulp collected from mill were similar to those obtained with lab produced pulp.

(i) ***Hydrogen peroxide pre treatment:*** Hydrogen peroxide pre-treatment of unbleached mill pulp improved final bleached pulp brightness and whiteness by about 1.3 and 2.4 units, respectively with substantial reduction in chlorine based bleaching chemicals and pollutants generated during bleaching.

(ii) ***Hydrogen peroxide activator in E_{OP} stage of bleaching:*** Use of hydrogen peroxide activator 'A' in E_{OP} stage of bleaching improved final bleached pulp brightness and whiteness by 0.9 and 1.1 units, respectively while using similar bleaching chemicals.

Efficacy of hydrogen peroxide activator (DSOST/277/45-16) in E_{OP} stage of pulp bleaching (Studies carried out on mill pulp collected from agro based pulp and paper mill situated in Punjab)

Table 6.6.6: Efficacy of DSOST/277/45-16 in E_{OP} stage of bleaching

Parameters	Results			
Kappa Number	12.6			
C stage *(Consistency – 2.5%, Temperature - 35°C, Time - 45 Min.)*				
Cl_2 added (%)	3.4			
End pH				
Residual Cl_2 (%)				
E_{OP} stage *(Consistency - 10.0%, Temperature - 70°C, Time - 90 Min, NaOH - 2.1%, H_2O_2 - 0.7%, O_2 - 0.5%)*				
Activator dose (g/TP)	0	100	150	200
End pH	10.4	10.5	10.4	10.4
Kappa No.	1.5	1.5	1.4	1.4
Brightness (% ISO)	76.4	77.2 (+0.8)	77.8 (+1.4)	78.0 (+1.6)
H_1 stage *(Consistency - 10.0%, Temperature - 40°C, Time - 120 Min, hypo - 1.0%)*				
End pH	7.9	8.0	7.9	7.9
Brightness (% ISO)	85.2	86.8 (+1.6)	87.0 (+1.8)	87.3 (+2.1)
H_2 stage *(Consistency - 10.0%, Temperature - 40°C, Time - 120 Min, Hypo - 0.3%)*				
End pH	7.1	7.1	7.0	7.0
Brightness (% ISO)	85.9	86.9 (+1.0)	87.6 (+1.7)	88.0 (+2.1)
Whiteness (CIE)	77.4	79.5 (+2.1)	80.1 (+2.7)	80.8 (+3.4)
Viscosity (cP)	4.5	4.6	4.8	4.6

Pre-plant trial studies at CPPRI

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6.7. Pre-plant trial studies at CPPRI

Validation of work carried out by ACIRD on unbleached pulp of Shreyans Paper Mills Ltd:

Progress review meeting was held at Shreyans Paper Mills Ltd on July 5, 2016 which was attended by CPPRI, ACIRD and IARPMA officials on Cess project "Increase in brightness ceiling of agro residue pulps in cost effective manner specifically for wheat straw"

During course of discussion on studies conducted by ACIRD, committee members advised that findings of the study should be validated by CPPRI before commencing the mill scale trial at Shreyans Paper Mills Ltd., Ahemedgarh, Punjab.

The unbleached pulp sample collected from Shreyans Paper Mills Ltd. was pretreated with

1. Oxygen pretreatment
2. Peroxide pretreatment
3. Peroxide pretreatment with Bleach S-20
   The control and pretreated pulp than subjected to $CE_{OP}HH$ bleaching.
4. Physical properties evaluation of pretreated pulp and effluent analysis for pH, COD, color and AOX was also carried out.

Table 6.7.1: Result of different pre treatment conditions conducted by CPPRI and ACIRD

Chemical used for treatment	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20*
NaOH added,%		1.8	0.3	
Peroxide added,%			1.5	1.7
EDTA added, %			0.2	-
Bleach S-20 added, %				0.7

Improvement in brightness w.r.t. control, CPPRI study ACIRD study	37.2 38.1	46.8 (25.8%) 47.8 (25.4%)	47.4 (27.4%) 49.1 (28.8%)	53.0 (42.5%) 48.9 (28.3%)
Kappa reduction (%) CPPRI study ACIRD study	 0.0 0.0	 35.5 30.7	 31.6 29.3	 40.7 40.0

Table 6.7.2: Result of $CE_{OP}HH$ bleaching stage of pretreated pulp and as such pulp using Activator "A" and Bleach S-20*conducted by CPPRI and ACIRD

Chemical used for treatment	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20*	Activator "A" Same bleaching chemical	Bleach S-20* Reduced bleaching chemicals
Chlorine added in C-stage,%	3.88	2.5	2.65	2.3	3.88	3..88
NaOH added in E stage, %	1.5	1.5	1.5	1.5	1.5	1.5
Oxygen added, kg/cm^2	3.5	3.5	3.5	3.5	3.5	0
Activator A added, g/TP in E_{OP} stage	-	-	-	-	250	

Bleach S-20* added g/TP in E_{OP} stage	-	-	-	-	-	7000
NaoH added in E_{OP} stage, %	-	-	-	-	2.5	2.0
H_2O_2 added in E_{OP} stage, %	0.6	0.6	0.6	0.6	0.6	0.45
Total hypo added in H_1 and H_2 stage,%	2.0	2.0	2.0	2.0	2.0	2.0
Final pulp brightness (%ISO) CPPRI study	85.2	86.2 (1.0 point)	86.4 (1.2 point)	86.2 (1.0 point)	86.1 (0.9 point)	86.2 (1.0 point)
ACIRD study	85.2	86.6 (1.4 point)	86.5 (1.3 point)	86.4 (1.2 point)	86.2 (1.0 point)	85.8 (0.6 point)
Bleached pulp viscosity (cP), CPPRI study	4.4	4.4	4.5	4.5	5.0	4.8
ACIRD study	4.6	4.4	4.6	4.5	4.9	4.7

Table 6.7.3: Result of bleach effluent analysis conducted by CPPRI and ACIRD

Particulars	Control	ODL	Peroxide Pre-treatment with EDTA	Peroxide Pre-treatment with Bleach S-20*
pH				
CPPRI study	3.4	4.6	3.5	3.8
ACIRD study	3.6	4.1	3.6	3.6
COD (mg/l)				
CPPRI study	1560	1482	1359	2264
ACIRD study	1440	760	860	840
Colour (mg/l)				
CPPRI study	2800	3008	2184	2608
ACIRD study	1270	330	355	394
AOX (mg/l)				
CPPRI study	*	*	*	*
ACIRD study	53	32	35	30

Observations

1. The study conducted on unbleached pulp collected from Shreyans Paper Mills.
2. The experiments were carried out using the pretreatment & bleaching sequences similar to the conditions employed by ACIRD.
3. The reductionsin kappa number measured are 35.5%, 31.6% and 40.7% in ODL, peroxide pretreatment with EDTA and peroxide pretreatment with bleach S-20respectively.
4. The results with respect to kappa number reduction are comparable with results of ACIRD.
5. The results of pretreatment of unbleached pulpwith peroxide pretreatment+ EDTA and peroxide pretreatment+bleach S-20on pulp brightness & pulp viscosity are more or less similar and also comparable with the results obtained after ODL. The similar findings were also observed by ACIRD.
6. Similarly the response of hydrogen based peroxide Activator “A” & bleach S-20 for improvement of final pulp brightness & pulp viscosity was also carried out. The result indicate that the both chemicals are effective in improving the pulp brightness but increase the chlorine demand (1.58%) in comparison to result obtained on pulp pretreatment with peroxide pretreatment+bleach S-20. While the results of CPPRI & ACIRD are more or less comparable towards the response of above mentioned combination of chemicals for improving the pulp brightness and its properties.

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Demonstration of results in the plant scale

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6.8. Demonstration of results in the plant scale

Background

Based on the encouraging lab scale results obtained at Avantha Centre for Industrial Research & Development (ACIRD) using (i) hydrogen peroxide pre-bleaching treatment of pulp and (ii) hydrogen peroxide activator (DSOST) in E_{OP} stage of bleaching, it was proposed to explore the suitability of any one or both the processes on plant scale at Shreyans Industries Ltd. (Unit: Shree Rishabh Papers) at Banah, Nawanshahr (Punjab). Suitability of both the processes for improving brightness and whiteness was also validated at Central Pulp & Paper Research Institute (CPPRI) prior to plant scale trial.

The objective of the trial was to demonstrate best process obtained in lab scale study to enhance brightness of pulp in cost effective manner. The details on the trial are given below:

Trial date and time: November 24, 2016 to November 29, 2016

Biochemical used: DS-OST (Supplied by M/s ProKlean Technologies Ltd., Chennai)

Dosage used: 150 g/TP (24.11.2016, 2:30 pm to 25.11.2016, 10:00 am), 19.5 h

200 g/TP (25.11.2016, 10:00 am to 26.11.2016, 10:00 am), 24 h

150+50 g/TP (26.11.2016, 10:00 am to 29.11.2016, 10:00 am), 72 h

Place of addition: At chlorine washer repulper conveyer (E_{OP} stage inlet)

Dosing: As such biochemical added using peristaltic pump along with E_{OP} filtrate

Quantity used: 100 kg (Supplied as free sample by the manufacturer)

Observations:

- Before conducting the trial average final pulp brightness, whiteness and yellowness were 82.5%, 66.7 and 8.7, respectively.
- With the addition of hydrogen peroxide activator in E_{OP} stage, average final pulp brightness improved to 83.6% indicating the brightness improvement of 1.1 points. During the trial a few values also crossed the ceiling of 85%, whereas during control run none of the value was obtained above 85% brightness. Occurrence of higher (≥83.5 <85.0) brightness values was improved to 60.6% from 24.2% obtained during control run. (Please refer Table 6.8.1 and Figure 6.8.1).
- During trial average final pulp whiteness obtained was 69.9 indicating the whiteness improvement by 3.2 units. Occurrence of higher (≥70.0) whiteness index values was improved to 51.5% from 27.3% obtained during control run. (Please refer Table 6.8.2 and Figure 6.8.2).
- Similarly with the addition of hydrogen peroxide activator in E_{OP} stage, average final pulp yellowness reduced to 7.6 indicating the reduction in yellowness of 1.1 point. Occurrence of lower (<8.0) yellowness values was improved to 63.6% from 30.3% obtained during control run. (Please refer Table 6.8.3 and Figure 6.8.3).
- As expected viscosity of final bleached pulp was improved marginally to 5.6 cP compared to 5.2 cP obtained during control. (Please refer Figure 6.8.4).
- Physical strength properties of pulp, specifically tear index and breaking length were obtained comparable before and during trial period. (Please refer Figure 6.8.5 and Figure 6.8.6).
- There was marginal improvement in the morphological properties, specifically fiber length and coarseness of the pulp with the use of hydrogen peroxide activator in E_{OP} stage of bleaching. (Please refer Annexure 1)

Table 6.8.1: Number of occurrence in final pulp brightness slabs

Brightness slab	Pre-trial	During trial
≥85.0	0 (0%)	3 (4.5%)
≥83.5 <85.0	8 (24.2%)	40 (60.6%)
≥82.5 <83.5	10 (30.3%)	12 (18.2%)
≥80 <82.5	14 (42.5%)	11 (16.7%)
<80	1 (3.0%)	0 (0%)

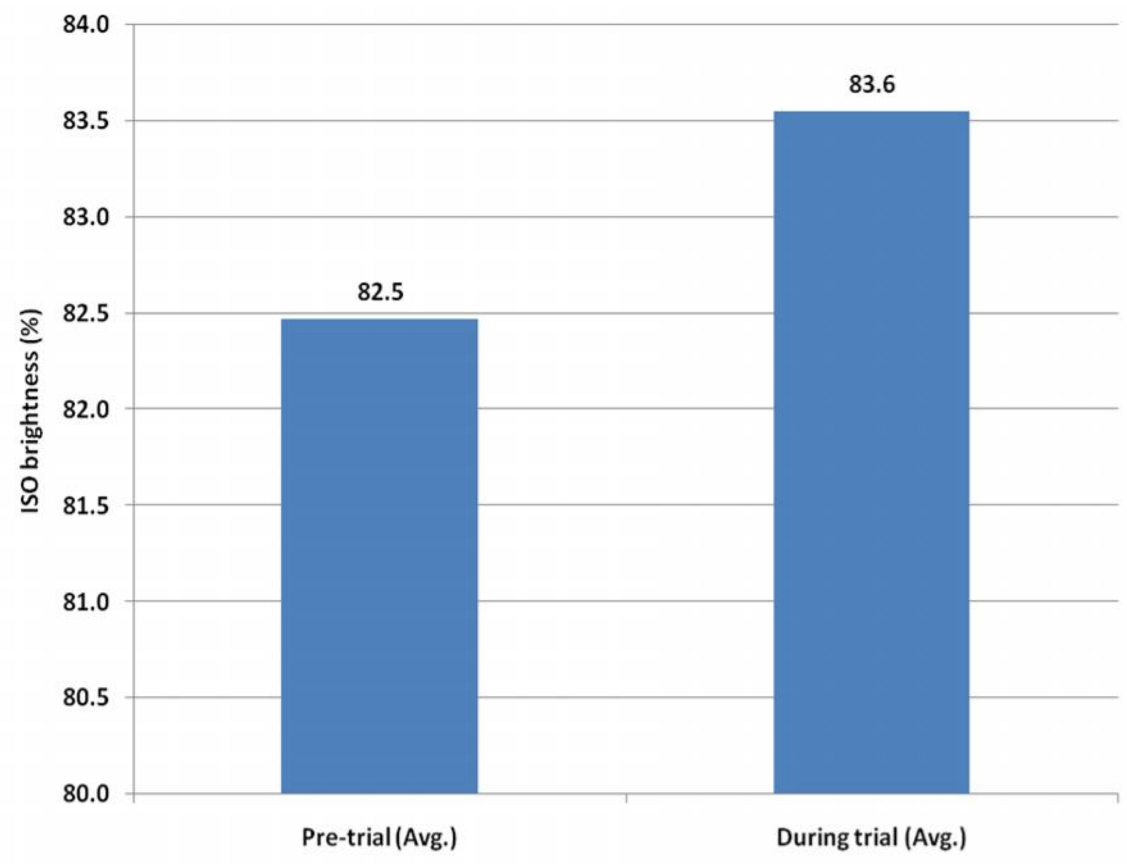


Figure 6.8.1: Effect of hydrogen peroxide activator on average final pulp brightness

Table 6.8.2: Number of occurrence in final pulp whiteness slabs

Whiteness slab	Pre-trial	During trial
≥75	0 (0%)	3 (4.5%)
≥74 <75.0	0 (0%)	4 (6.1%)
≥70 <74	9 (27.3%)	27 (40.9%)
≥65 <70	13 (39.4%)	25 (37.9%)
≥60 <65	8 (24.2%)	7 (10.6%)
<60	3 (9.1%)	0 (0%)

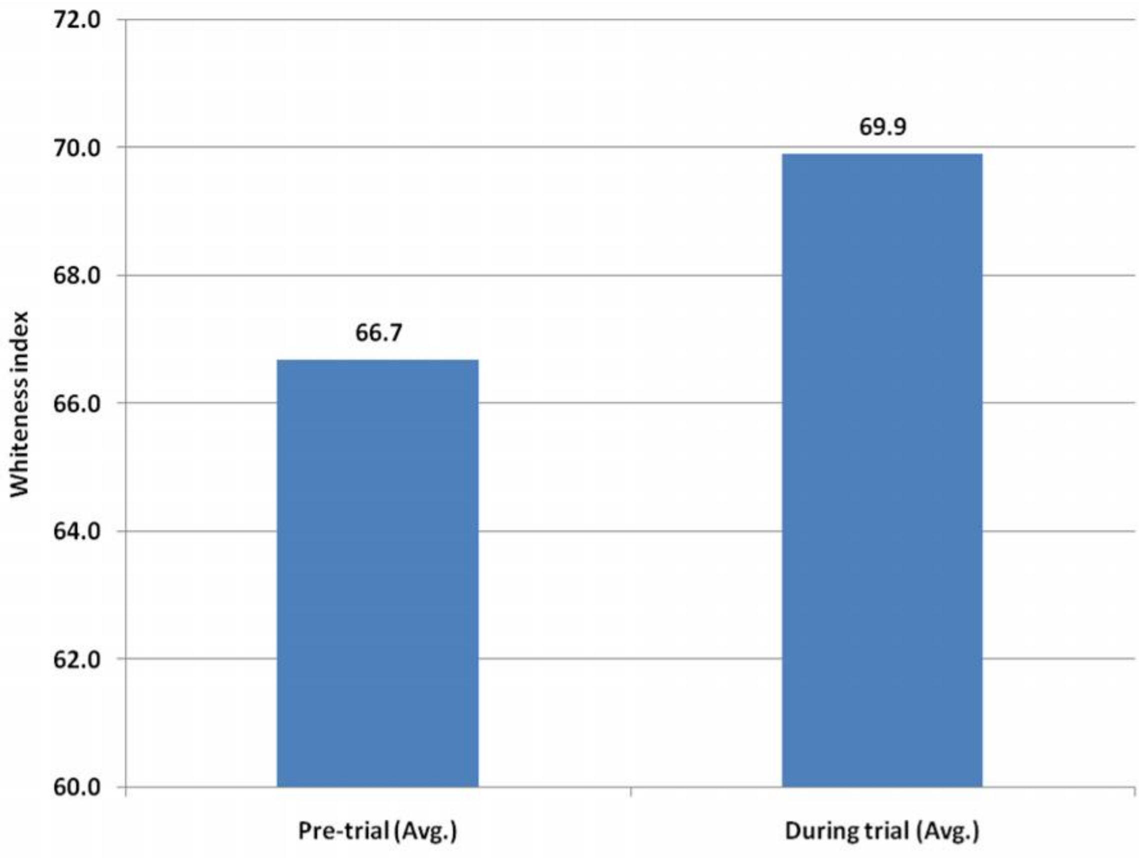


Figure 6.8.2: Effect of hydrogen peroxide activator on average final pulp whiteness

Table 6.8.3: Number of occurrence in final pulp yellowness slabs

Yellowness slab	Pre-trial	During trial
<6	0 (0%)	7 (10.6%)
≥6.0 <8.0	10 (30.3%)	35 (53.0%)
≥8.0 <10.0	16 (48.5%)	21 (31.8%)
>10	7 (21.2%)	3 (4.5%)

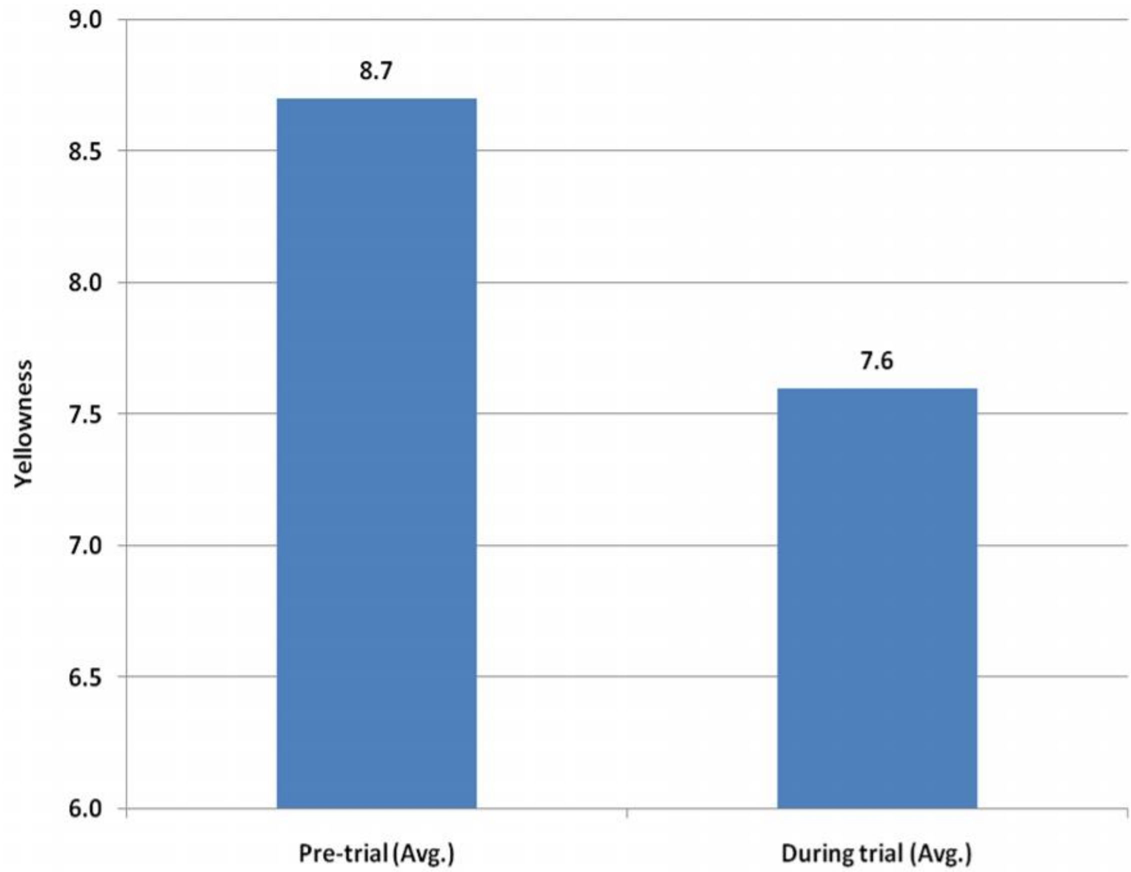


Figure 6.8.3: Effect of hydrogen peroxide activator on average final pulp yellowness

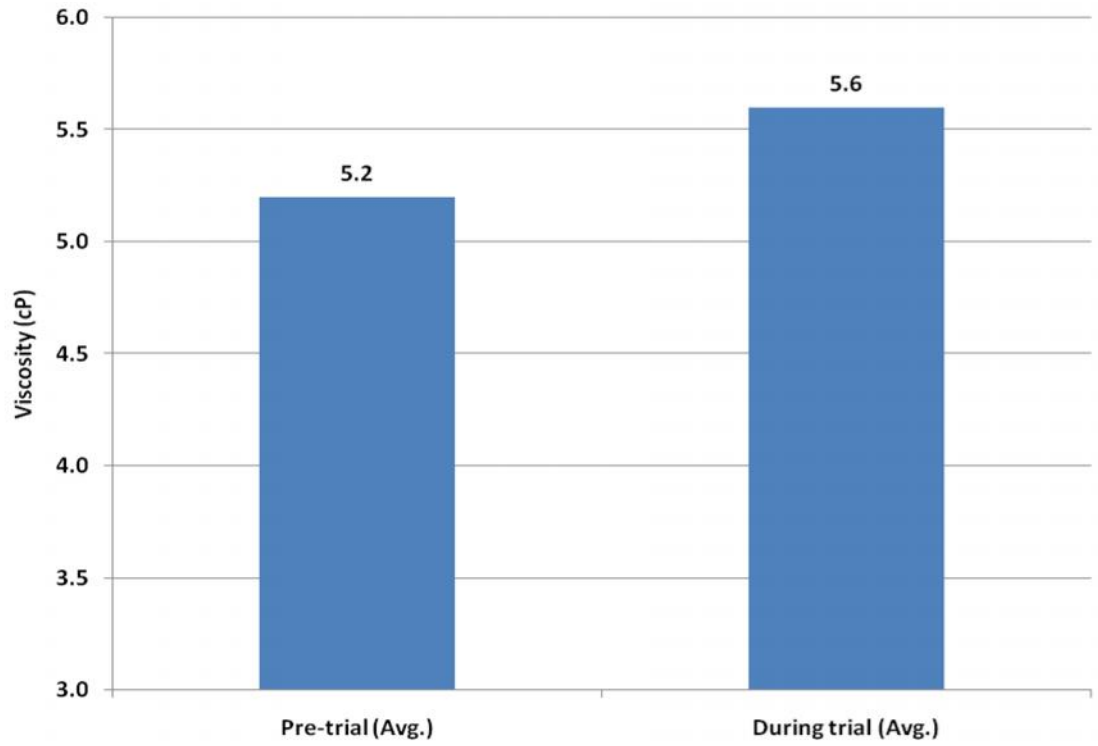


Figure 6.8.4: Effect of hydrogen peroxide activator on final pulp viscosity

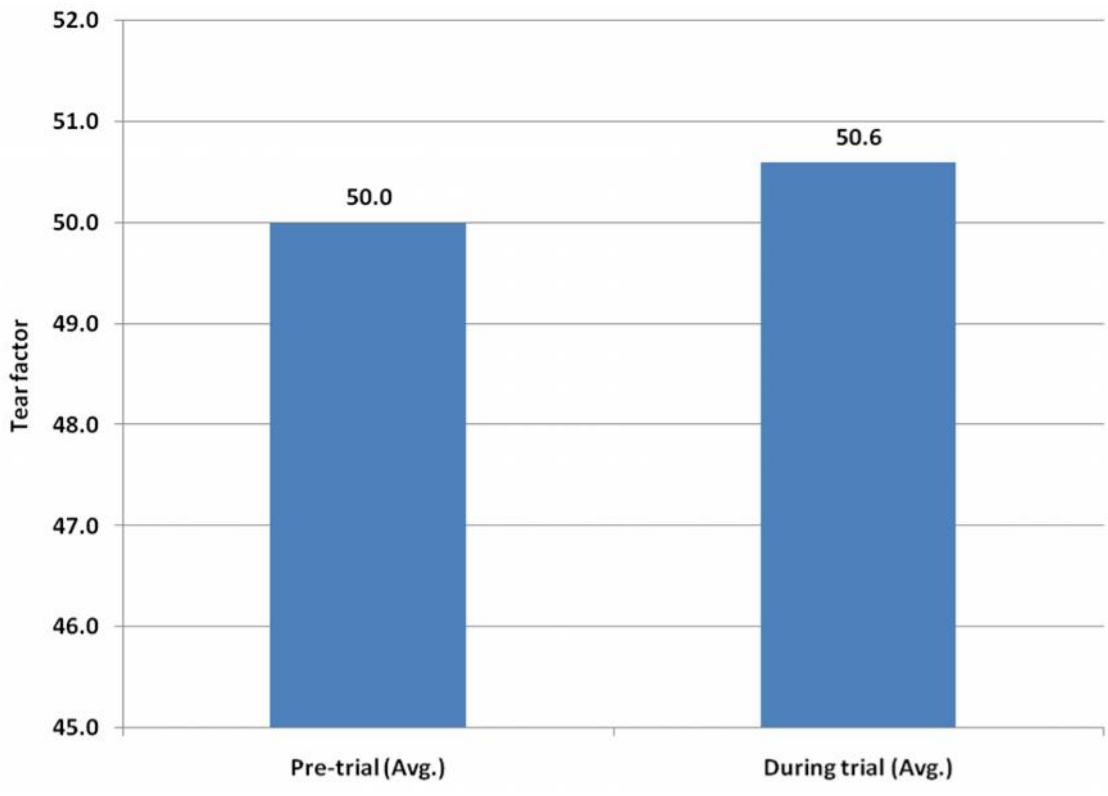


Figure 6.8.5: Effect of hydrogen peroxide activator on tear factor of bleached pulp

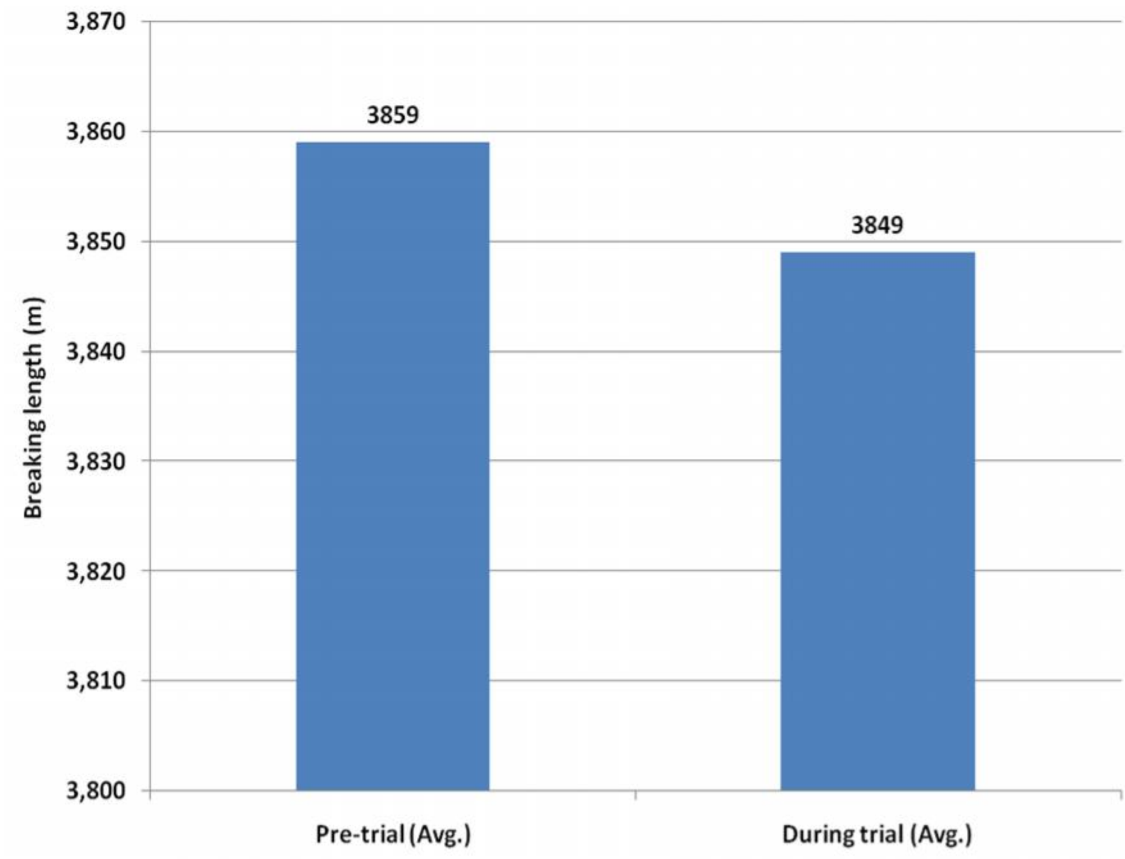


Figure 6.8.6: Effect of hydrogen peroxide activator on breaking length of bleached pulp

Annexure 1

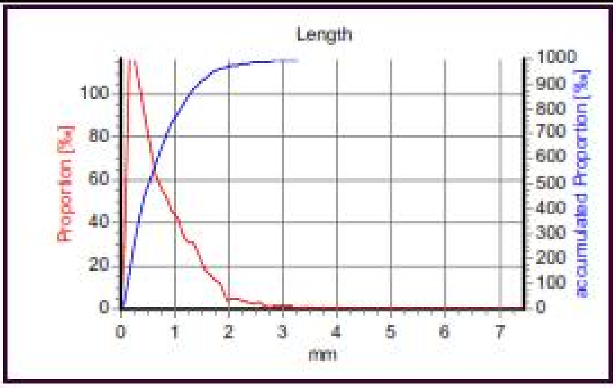
MORPHOLOGICAL PROPERTIES

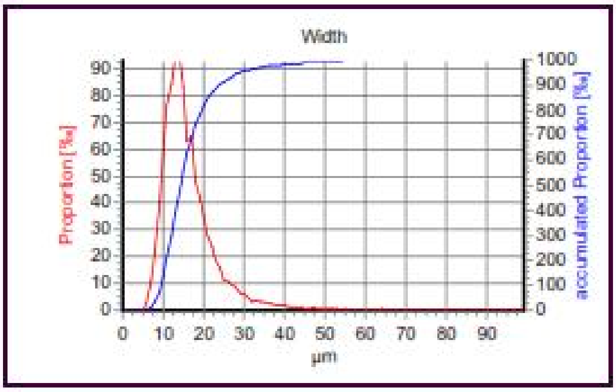
Sample name:	pre trial HW- 2	Number of fibers	11470 (20000)
Sample type:	Default	Number of images	1102
Time:	12-12-2016 14:34:15	Temperature	19.5 °C
Comment			

Length weighted

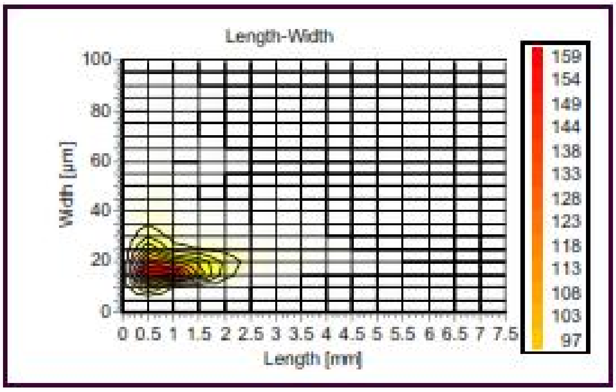
Variable	Value	Difference
Mean length	0.828 mm	0.003 mm
Mean width	17.0 µm	-0.1 µm
Mean shape	88.4 %	0.3 %

Length class	Proportion	Width	Shape
0.2-0.5 mm	0.363	18.3 µm	91.1 %
0.5-1.5 mm	0.523	15.9 µm	87.6 %
1.5-3 mm	0.106	17.5 µm	82.8 %
3-4.5 mm	0.007	20.6 µm	87.6 %
4.5-7.5 mm	0.001	19.5 µm	70.3 %





Variable	Weighting	Value
Length	Length	0.828 mm
Length	Volume	0.781 mm
Length	Arithmetic	0.548 mm
Length	Length-Length	1.226 mm
Width	Length	17.0 µm



Sample name:	pre trial HW- 2	Number of fibers	11470 (20000)
Sample type:	Default	Number of images	1102
Time:	12-12-2016 14:34:15	Temperature	19.5 °C
Comment	-		

Variable	Weighting	Value
Width	Width	21.5 µm
Width	Area	20.1 µm
Width	Volume	25.5 µm
Width	Arithmetic	17.6 µm
Width	Length-Length	16.8 µm
Shape	Length	88.4 %
Shape	Width	89.2 %
Shape	Area	87.9 %
Shape	Length-Length	86.5 %
Fines	Length	16.9 %
Fines	Width	67.3 %
Fines	Area	16.5 %
Fines	Arithmetic	74.4 %
Fines	Length-Length	2.8 %
Number of fibers		11470 (20000)
Number of images		1102

Variable	Weighting	Value
Temperature		19.5 °C
Sample weight		0.100 g
Coarseness adjust		1.000
Coarseness		71.9 µg/m
No. fibers in sample		1738195
Mean kink angle		53.0 °
Number of kinks per mm		0.696 mm-1
Number of large kinks per mm		0.224 mm-1
Number of kinks per fibre		0.557
Number of large kinks per fibre		0.179
Mean kink index		1.796
Mean segment length		0.719 mm
-	-	-
-	-	-
-	-	-
-	-	-

Sample name:	pre trial HW- 2	Number of fibers	11470 (20000)
Sample type:	Default	Number of images	1102
Time:	12-12-2016 14:34:15	Temperature	19.5 °C
Comment			

Variable	Value	Variable	Value
Number of objects measured	482	Number of objects in DB	490
Number of Objects in sample	17778	Number of object images	3732
Objects per 100000 fibers	1023	Mean Object length	0.2589 mm
Object per gram	177776 g-1	Mean Object width	0.1229 mm
Object area/Fibre volume	1.829 mm-1		
Mean Object area	0.0330 mm2		

Proportion area weighted (%)

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	9.6	26.6	13.4
120-150	7.6	14.7	9.4
150-1000	0.5	2.8	15.3

Number of Objects in sample

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	2729	5975	1992
120-150	1955	2766	1033
150-1000	111	369	848

Sample name: During Trial HW-2

Sample type: Default

Time: 13-12-2016 15:28:49

Comment: Plant Trial in Rishabh Paper Mill

Number of fibers 11317 (20058)

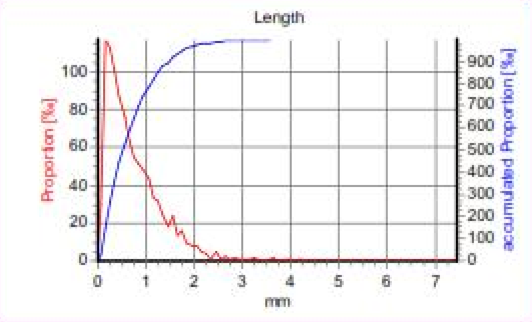
Number of images 1113

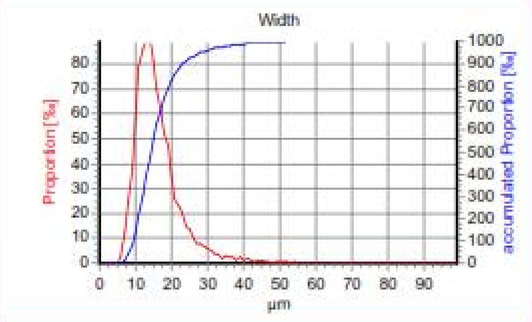
Temperature 24.0 °C

Length weighted

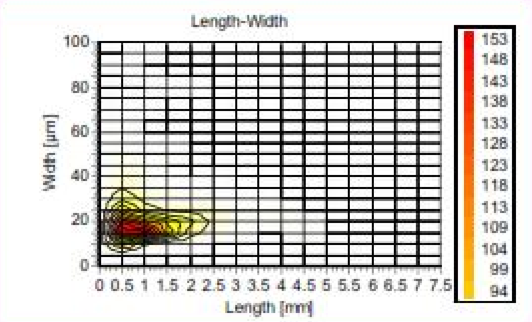
Variable	Value	Difference
Mean length	0.834 mm	0.001 mm
Mean width	16.7 µm	0.2 µm
Mean shape	89.0 %	-0.2 %

Length class	Proportion	Width	Shape
0.2-0.5 mm	0.353	17.7 µm	91.3 %
0.5-1.5 mm	0.522	15.9 µm	88.6 %
1.5-3 mm	0.116	17.5 µm	84.8 %
3-4.5 mm	0.009	18.4 µm	79.4 %
4.5-7.5 mm	0.000	0.0 µm	0.0 %





Variable	Weighting	Value
Length	Length	0.834 mm
Length	Volume	0.798 mm
Length	Arithmetic	0.552 mm
Length	Length-Length	1.232 mm
Width	Length	16.7 µm



Sample name:	During Trial HW-2	Number of fibers	11317 (20058)
Sample type:	Default	Number of images	1113
Time:	13-12-2016 15:28:49	Temperature	24.0 °C
Comment	Plant Trial in Rishabh Paper Mill		

Variable	Weighting	Value
Width	Width	20.6 µm
Width	Area	19.5 µm
Width	Volume	24.5 µm
Width	Arithmetic	17.2 µm
Width	Length-Length	16.6 µm
Shape	Length	89.0 %
Shape	Width	89.6 %
Shape	Area	88.5 %
Shape	Length-Length	87.4 %
Fines	Length	17.3 %
Fines	Width	71.7 %
Fines	Area	17.3 %
Fines	Arithmetic	77.2 %
Fines	Length-Length	2.8 %
Number of fibers		11317 (20058)
Number of images		1113

Variable	Weighting	Value
Temperature		24.0 °C
Sample weight		0.100 g
Coarseness adjust		1.000
Coarseness		73.7 µg/m
No. fibers in sample		1692996
Mean kink angle		50.1 °
Number of kinks per mm		0.599 mm-1
Number of large kinks per mm		0.167 mm-1
Number of kinks per fibre		0.476
Number of large kinks per fibre		0.132
Mean kink index		1.487
Mean segment length		0.755 mm
-	-	-
-	-	-
-	-	-
-	-	-

Sample name:	During Trial HW-2	Number of fibers	11317 (20058)
Sample type:	Default	Number of images	1113
Time:	13-12-2016 15:28:49	Temperature	24.0 °C
Comment	Plant Trial in Rishabh Paper Mill		

Variable	Value	Variable	Value
Number of objects measured	483	Number of objects in DB	485
Number of Objects in sample	17753	Number of object images	3744
Objects per 100000 fibers	1049	Mean Object length	0.2764 mm
Object per gram	177532 g-1	Mean Object width	0.1267 mm
Object area/Fibre volume	2.197 mm-1		
Mean Object area	0.0373 mm2		

Proportion area weighted (%)

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	6.7	24.8	11.4
120-150	5.8	13.9	8.4
150-1000	0.3	4.2	24.5

Number of Objects in sample

Width (µm) \ Length(mm)	0.10-0.20	0.20-0.30	0.30-1.00
100-120	2169	6359	1728
120-150	1691	2830	992
150-1000	74	588	1323

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7. SALIENT FINDINGS

7.1. Findings of laboratory scale studies

Laboratory scale studies carried out on effect of raw material cleaning, modifications in pulping, modifications in bleaching concludes the following:

- With the pre-bleaching acid treatment of pulp final brightness of pulp was achieved by 86.5% (Gain in brightness by 1.6-2.0 units).
- With the post-bleaching acid treatment of pulp or in-situ acid treatment of pulp, final brightness of pulp was achieved by 86.0% (Gain in brightness by 1.2-1.5 units).
- Hydrogen peroxide pre-treatment of unbleached wheat straw pulp improved final bleached pulp brightness by 1.7 - 2.1 units with substantial reduction in chlorine based bleaching chemicals and pollutants generated during bleaching.
- With the H_2O_2 pre-treatment of pulp, final brightness of pulp was achieved by 86.7% (Gain in brightness by 1.9-2.2 units).
- With the Replacing 20% Cl_2 with ClO_2 in chlorination stage of bleaching, final brightness of pulp was achieved by 86.3% (Gain in brightness by 1.5-1.8 units).
- With the addition of last peroxide stage in bleaching sequence, final brightness of pulp was achieved by 87.4% (Gain in brightness by 2.6-2.9 units).
- With the enzymatic pre-bleaching treatment of pulp, final brightness of pulp was achieved by 85.2% (Gain in brightness by 0.7-1.0 unit).
- Use of hydrogen peroxide activator in E_{OP} stage of bleaching sequence improved the final bleached pulp brightness by 1.1 units and whiteness by 1.5 units while using similar bleaching chemicals.

In a meeting conducted by IARPMA at Shreyans Papers Limited on July 5, 2016, it was decided to carry out lab study on two selected processes using mill pulp prior to conducting plant trial on any one of the process at Shreyans Paper Mills Ltd.

- Hydrogen peroxide pre-bleaching treatment of pulp:
- Use of hydrogen peroxide activator in E_{OP} stage of bleaching

7.2. Findings of plant scale studies

Plant scale study carried out on with the addition of hydrogen peroxide stabilizer in E_{OP} stage resulted in the following:

- Average final pulp brightness improved by 1.1 units to 83.6% form initial 82.5%.During the trial a few values were also crossed the ceiling of 85%, whereas during control run none of the value was obtained above 85% brightness.
- During trial average final pulp whiteness obtained was 69.9 indicating the whiteness improvement by 3.2 units.
- Similarly with the addition of hydrogen peroxide stabilizer in E_{OP} stage, average final pulp yellowness reduced to 7.6 indicating the reduction in yellowness of 1.1 point.
- As expected viscosity of final bleached pulp was improved marginally to 5.6 cP compared to 5.2 cP obtained during control.
- Physical strength properties of pulp, specifically tear index and breaking length were obtained comparable before and during trial period.
- There was marginal improvement in the morphological properties, specifically fiber length and coarseness of the pulp with the use of hydrogen peroxide stabilizer in E_{OP} stage of bleaching.

8. ACKNOWLEDGEMENT

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